

Applications, Synthesis and Catalyst Design for Oxygenated Polymers

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If you're not in the state of play,
you can't create anything.

Paula Scher, Graphic Designer

Declaration

The work presented in this thesis was conducted between October 2015 and September 2018 at Imperial College London and the University of Oxford. This is the work of the author unless otherwise stated.

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Abstract

The main focus of this thesis is the synthesis of oxygenated block copolymers. These are attractive materials for a range of applications; however, they are typically associated with time- and labour-intensive synthetic procedures. For this reason, a more efficient one pot combination of two different polymerisation mechanisms, anhydride/epoxide ring-opening copolymerisation (ROCOP) and lactone ring-opening polymerisation (ROP), with a *single* catalytic system was investigated. Three major advances in ‘switch’ catalysis are presented herein: (i) The use of the first chromium salen catalyst, (ii) propylene oxide was accessed as a monomer and (iii) the synthesis of block polyesters from a fully commercial feedstock featuring propylene oxide, phthalic anhydride, (*rac*)-lactide. With these insights, new ‘switch’ catalysts were developed and (potentially) bio-based polycarbonates were tested as future coating materials. An overview is given in Figure 0. 1.

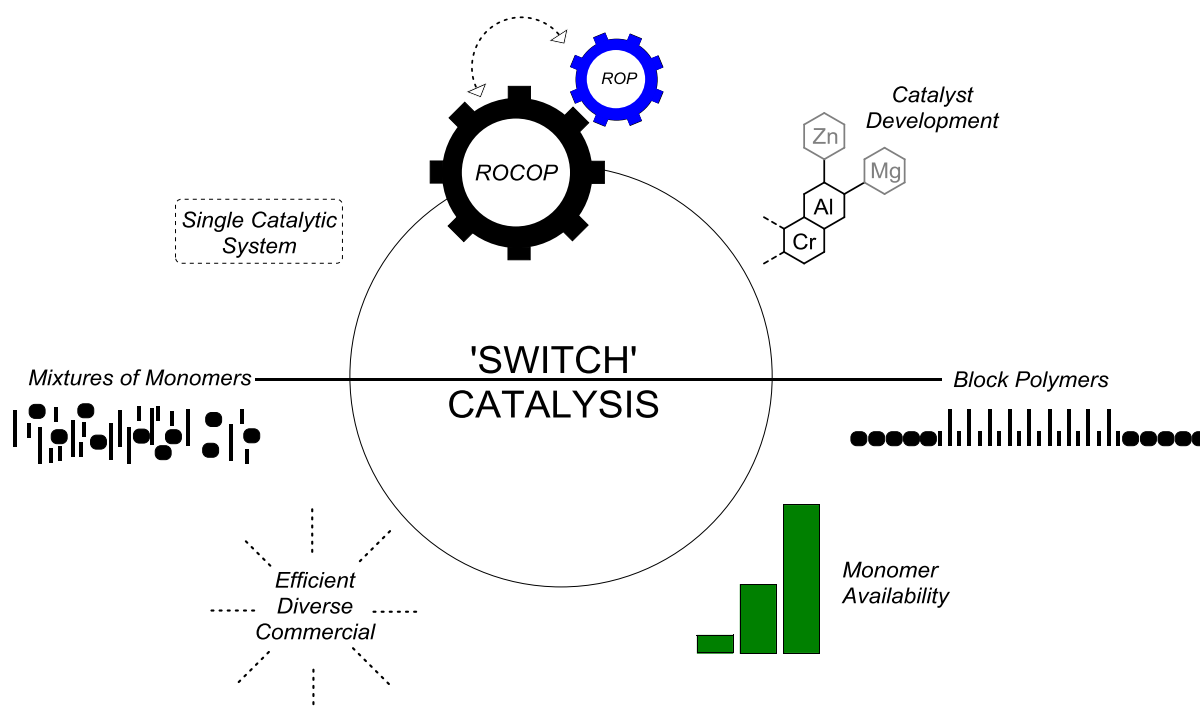


Figure 0. 1 – A brief overview of ‘switch’ catalysis covered in this thesis.

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Abbreviations

A	Anhydride	MeOH	Methanol
AGE	Allyl Glycidyl Ether	min	Minute
Ar	Aryl	M_n	Number Average Molar Mass
ATR	Attenuated Total Reflectance	MP	Melting point
ATRP	Atom Transfer Radical Polymerization	MS	Mass Spectrometry
BDI	β-Diiminate	MW	Molecular Weight (Molar Mass)
BGE	<i>tert</i> -Butyl Glycidyl Ether	N	Degree of Polymerisation
BL	β -Butyrolactone	n	Number of Scans (NMR)
CA	($\pm$)-Camphoric Anhydride	NBA	5-Norbornene-2,3-dicarboxylic Anhydride
cat	Catalyst	^{n} Bu	^{n} Butyl
CHC	Cyclohexene Carbonate	NMR	Nuclear Magnetic Resonance
CHCl ₃	Chloroform	Nu	Nucleophile
CHD	<i>Trans</i> -Cyclohexane-1,2-diol	OAc	Acetate
CHDO	1,4-Cyclohexadiene Oxide	p	Pressure
CHE	Cyclohexene Anhydride	PA	Phthalic Anhydride
χ	Flory-Huggins interaction parameter	PBL	Polybutyrolactone
CHO	Cyclohexene Oxide	PCHC	Poly(Cyclohexene carbonate)
CitrA	Citraconic Anhydride	PCHDC	Poly(Cyclohexadiene carbonate)
CL	ϵ -Caprolactone	PCHNBE	Poly(Cyclohexene norbornene ester)
CMC	Critical Micelle Concentration	PCHPE	Poly(Cyclohexene phthalate)
χN	Segregation Strength	PCL	Poly(Caprolactone)
COSY	Correlated Spectroscopy	PCPC	Poly(Cyclopentane Carbonate)
CTA	Chain Transfer Agent	PDL	Poly(Decalactone)
CuAAC	Copper(I)-Catalyzed Alkyne-Azide Cycloaddition	PEG ₃ -OMe-PO	2-(2,5,8,11)-Tetraoxadodecyloxirane
d	Day	PET	Poly(Ethylene Terephthalate)
<i>D</i>	Diffusion Coefficient	PGE	Phenyl Glycidyl Ether
$\bar{D}$	Dispersity	PLA	Poly(Lactic Acid)
<i>D</i> ₁	Relaxation Delay (NMR)	PLC	Poly(Limonene Carbonate)
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene	PO	Propylene Oxide
DCM	Dichloromethane	PPC	Poly(Propylene Carbonate)
DFT	Density Functional Theory	PPE	Poly(Propylene Phthalic Ester)
DGA	Diglycolic Anhydride	ppm	Parts Per Million
DMAP	4-Dimethylaminopyridine	PPN	Bis(Triphenylphosphine)Imine
DMF	Dimethylformamide	PPO	Poly(Propylene Oxide)
DMTA	Dynamic Mechanical Thermal Analysis	PS	Polystyrene
DOSY	Diffusion Ordered NMR Spectroscopy	PTFE	Polytetrafluoroethylene

DP	Degree of Polymerisation	PU	Polyurethane
DPA	Diphenic Anhydride	<i>r</i>	Rate
DSC	Differential Scanning Calorimetry	RAFT	Reversible Addition Fragmentation chain Transfer
E	Epoxide	RI	Refractive Index
EHGE	2-Ethylhexyl Glycidyl Ether	ROCOP	Ring-Opening Copolymerisation
EHS	Environmental, Health and Safety	ROP	Ring-Opening Polymerisation
EO	Ethylene Oxide	rpm	Revolutions Per Minute
EP	1,3-Epoxypropane	s	Second
Equiv.	Equivalents	SA	Succinic Anhydride
ESI	Electrospray Ionisation	[SalcyCrCl]	N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminochromium(III) chloride
Et	Ethyl	SCRF	Self-Consistent Reaction Field
<i>f_i</i>	Relative Volume Fraction of Block i	SEC	Size-Exclusion Chromatography
g	Gram	SO	Styrene Oxide
GA	Glutaric Anhydride	T	Temperature
GC	Gas-Chromatography	t	Time
GHE	Glycidyl Hexadecyl Ether	T ₁	Spin-Lattice Relaxation (NMR)
GPC	Gel-Permeation Chromatography	^t Bu	<i>Tert</i> -Butyl
h	Hour	TCA	Tricyclic Anhydride
HSQC	Heteronuclear Single Quantum Coherence Spectroscopy	TCE	1,1,2,2-Tetrachloroethane
HT	Head-to-Tail	T _d	Decomposition Temperature
IA	Itaconic Anhydride	TFA	Trifluoroacetate
ICP	Inductively Coupled Plasma	T _g	Glass Transition Temperature
ⁱ Pr	<i>Iso</i> -Propyl	TGA	Thermogravimetric Analysis
IR	Infrared	THF	Tetrahydrofuran
IUPAC	International Union of Pure and Applied Chemistry	THPA	<i>cis</i> -1,2,3,6-Tetrahydrophthalic anhydride
k	Rate Coefficient	TMC	Trimethylene carbonate
<i>k_i</i>	Initiation Rate Constant	TMEDA	N,N,N',N'-Tetramethylethylenediamine
<i>k_{obs}</i>	Observed Rate Constant	TMP-SH	Trimethylolpropane tris(3-mercaptopropionate)
<i>k_p</i>	Propagation Rate Constant	TMS	Trimethylsilane
L	Ligand	ToF	Time of Flight
LA	(<i>rac</i>)-Lactide	TOF	Turnover Frequency
LED	Light-Emitting Diode	Tol	Toluene
L-LA	L-Lactide	TON	Turnover Number
LLDPE	Linear Low Density Polyethylene	TPP	5,10,15,20-Tetraphenylporphyrin
LO	Limonene Oxide	ULDPE	Ultra Low Density Polyethylene
M	mol L⁻¹	UV	Ultraviolet

MA	Maleic Anhydride	vCHO	4-Vinyl-1-Cyclohexene 1,2-Epoxy
MALDI	Matrix-Assisted Laser Desorption/Ionisation	VPO	2-Vinyl Oxirane
mbar	Millibar	W	Watt
mCPBA	Meta-Chloroperoxybenzoic Acid	X	Co-ligand
MDI	4,4'-Methylene Diphenyl Diisocyanate	XRD	X-Ray Diffraction
Me	Methyl	ΔG	Gibbs Energy
Me ₃ MO	2-((2-(2-Methoxyethoxy)ethoxy)-ethoxy)methyl)oxirane		

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Chapter 1

Introduction

‘Switch’ Catalysis and

Post-Functionalisation Modification

1.1. Block Copolymers

A block copolymer consists of constitutionally different polymer chains which are covalently linked together (IUPAC).^[1-3] These materials have transformed several areas of everyday life, from footwear to cosmetics.^[4] What makes block copolymers different from a blend of polymers is the ability to self-assemble on the length scale of a few nanometres to hundreds of nanometres, particularly if thermodynamically incompatible blocks are joined together.^[5] Generally, self-assembly of block copolymers is determined by three parameters: degree of polymerisation (N ; the number of monomers per polymer chain), the Flory-Huggins interaction parameter between blocks (χ) and the relative volume fractions of each block (f_i).^[6] Although self-assembly is a highly complex process and not part of this thesis, the number and complexity of structures for a predicted linear ABC triblock copolymer is astonishing (Figure 1. 1) – these structures can be achieved and changed (only) by adjusting the relative volume fractions of the individual blocks. The range of accessible nanostructures becomes even more diverse if more blocks or different architectures (star, ring, bush, etc.) are considered.

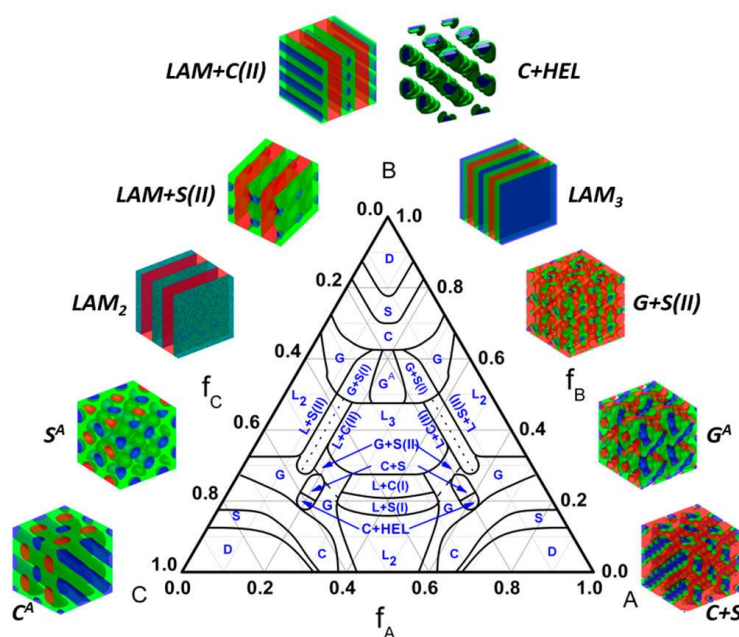


Figure 1. 1 – Simulated morphologies with a linear ABC triblock copolymer ($\chi_{AB}N = \chi_{BC}N = 35$ and $\chi_{CA}N = 15$).^[4] The figure is reprinted (adapted) with permission from *Macromolecules*, **2017**, 50 (1), 3–22. Copyright (2017) American Chemical Society.

Today, block copolymers are mainly used for high volume products, such as thermoplastic elastomers, but this class of materials is highly promising to provide solutions for tomorrows' challenges. This is illustrated in two examples below:

Example 1: Block Copolymers for Lithography

Fabrication of microprocessors is currently limited by the diffraction limitations of photolithography (ca. 30 nm).^[7] Nanopatterning with block copolymers featuring domain sizes < 10 nm may help to overcome these limitations.^[6] Figure 1. 2 illustrates this concept, which relies on preferential etching of one of the blocks after self-assembly on a substrate, which creates a mask (polymer mask). This (etch-resistant) mask is transferred to a silicon wafer and the pattern is formed after further silicon etching (silicon pattern).

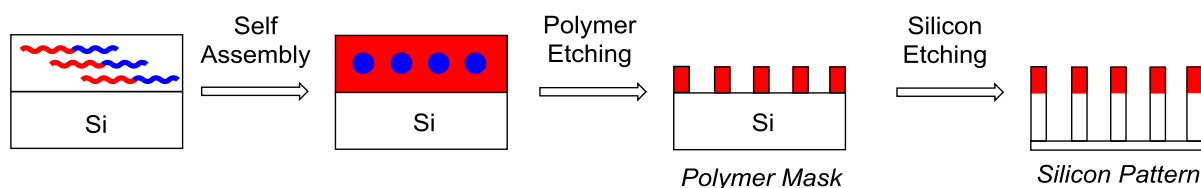


Figure 1. 2 – Systematic illustration of nanopatterning with block copolymers.^[8]

Typically polymers with a high segregation strength χN are used to obtain high contrast (i. e. $\chi N \gg 10.5$) and remarkable silicon patterns below 10 nm have been reported with poly(styrene-*b*-butadiene), poly(styrene-*b*-(methyl methacrylate)) and poly(styrene-*b*-2-vinylpyridine) (Figure 1. 3).^[8-12]

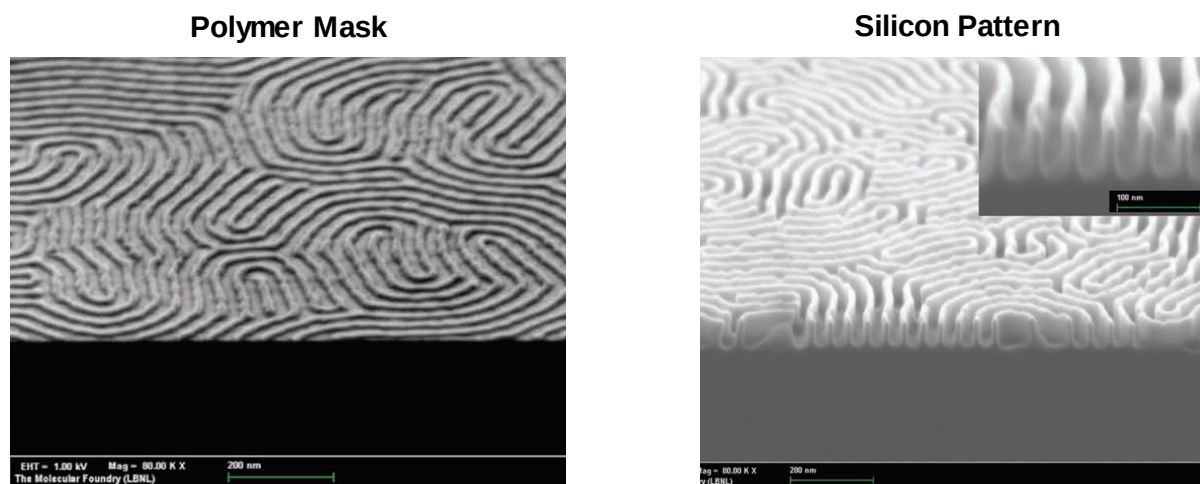


Figure 1. 3 – SEM images reported by Russel and co-workers of thin film surface before (polymer mask, left) and after 15 s of cryo ICP etching (silicon pattern) with poly(styrene-*b*-2-vinylpyridine).^[8] The figure on the right is reprinted (adapted) with permission from *Adv. Mater.* **2012**, 24, 5688-5694. Copyright (2012) John Wiley and Sons.

Example 2: Photonic Polyolefins

Although small domain sizes and low polymer dispersities are key features for applications in lithography, intriguing material properties can be obtained with less well-defined polymers. The effect of these ‘imperfections’ include the increase of domain sizes, which can give rise to photonic materials.^[13] Photonic materials are periodic dielectric materials, which typically contain stacks of materials with different diffractive indices (Figure 1. 4, left).^[14] A range of colours in the visible spectrum were achieved with a copolymer featuring linear low density polyethylene (LLDPE; based on ethylene and 1-octene) as a semicrystalline ‘hard’ block and ultra low density polyethylene (ULDPE) as a soft block (Figure 1. 4, right).^[13]

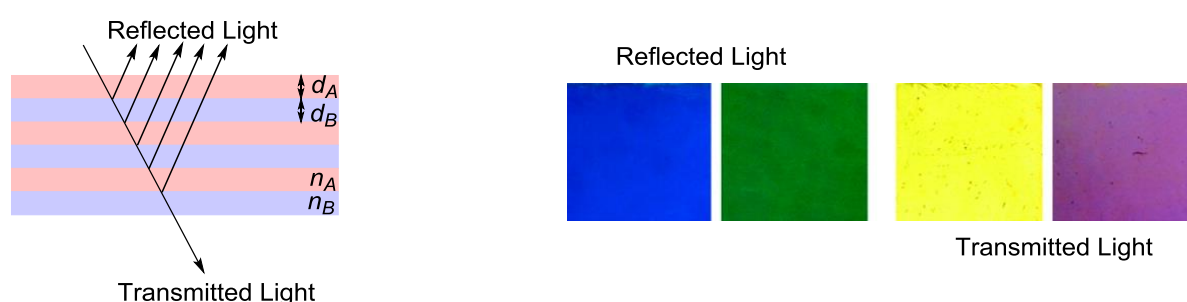


Figure 1. 4 – Illustration of a photonic crystal and reported colours with LLDPE-*b*-ULDPE reported by Weinhold and co-workers.^[13] The figure on the right is reprinted (adapted) with permission from *Macromolecules* **2009**, 42 (11), 3788–3794. Copyright (2009) American Chemical Society.

The wavelength of the reflected light is determined by the refractive index n and the thickness d . In particular, n can be influenced by the crystallinity of polyethylene (through the amount of 1-octene) and d through dispersity as ‘mismatched’ chains act as a swelling agent (Figure 1. 5).

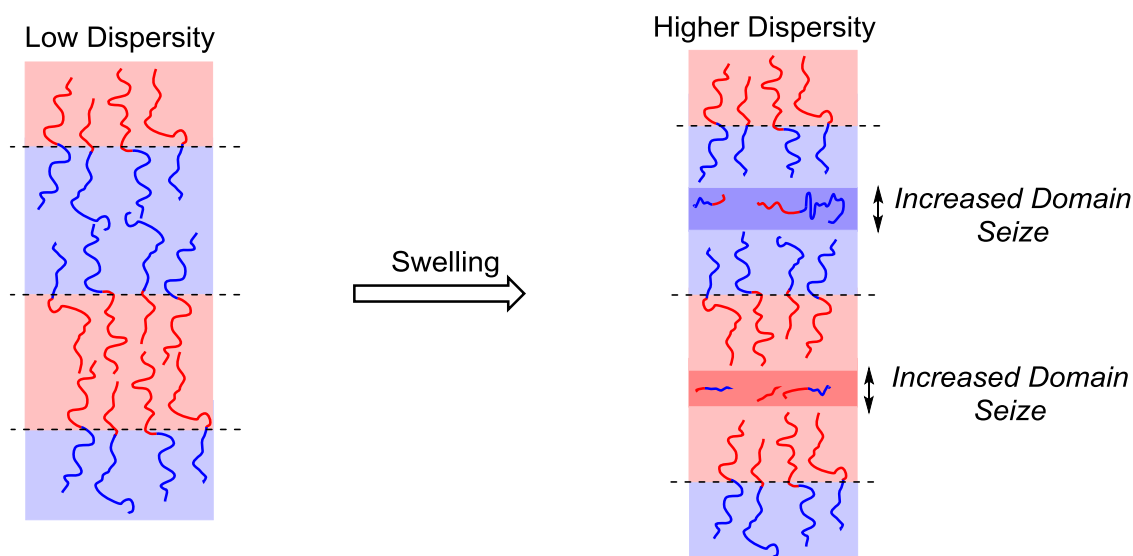


Figure 1. 5 - Schematic representation of ‘swelling’.^[13]

It should be stressed that these are only two out of many examples. A glimpse in the future hints at the use of block copolymers in (i) light-emitting diodes (LEDs), (ii) conducting membranes and (iii) the filtration of fresh water.^[15-18]

Clearly, block copolymers are versatile and promising materials, which makes the controlled and scalable synthesis of these materials an important area of research. To date, several routes have been established for the synthesis of block copolymers, which are summarised in Figure 1. 6.

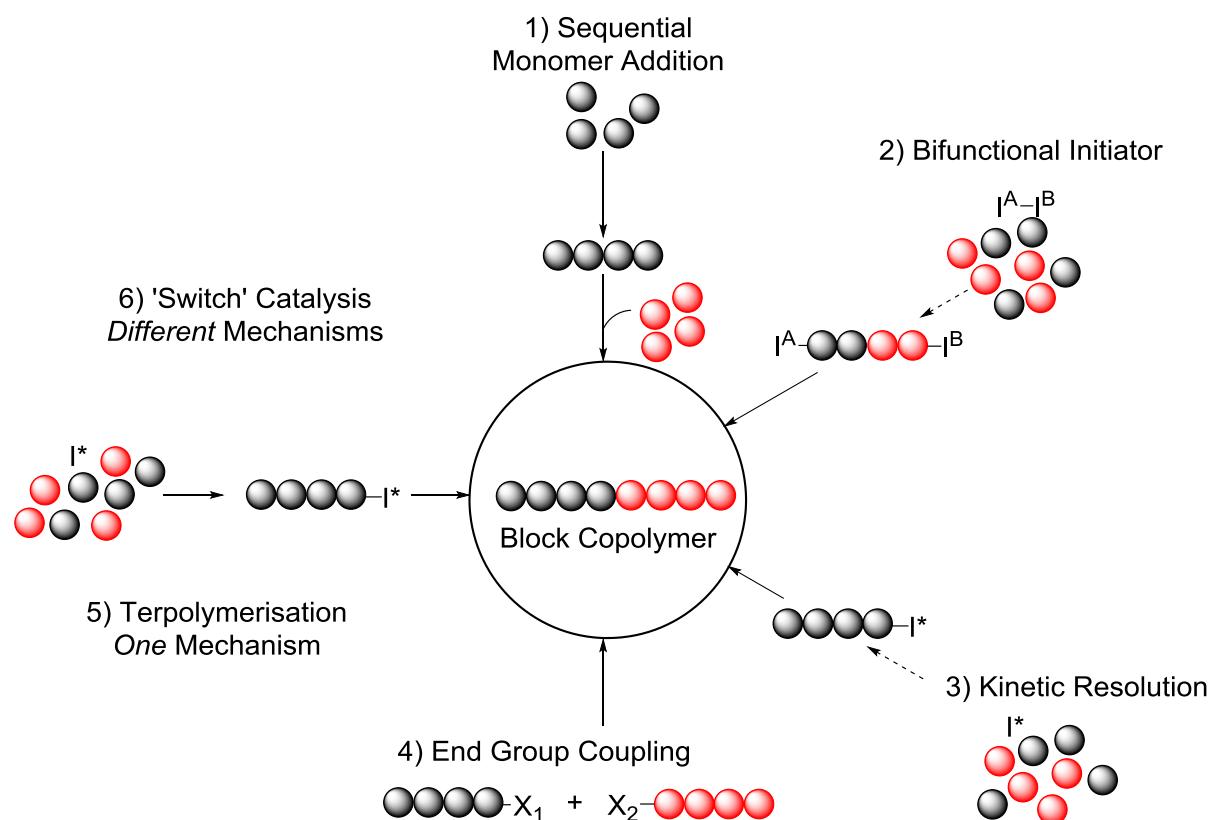


Figure 1. 6 – Routes to block copolymers.^[5]

1. Sequential Monomer Addition

In sequential monomer addition, one monomer is added to a living polymerisation, which forms the first block. Once the monomer is fully consumed, a second monomer is added, without quenching the polymerisation, to generate the second block. This was first illustrated by Szwarc and co-workers in the 1950s and up to 20 blocks have been reported *via* this approach.^[19] Anionic polymerisations of olefins are particularly successful as well as living radical polymerisations of acrylates or methacrylates (ATRP, RAFT) and the ring-opening polymerisation of lactones.^[19-22] Although this approach may allow the formation of high molar mass blocks, sequential monomer addition strategies usually require highly purified

monomers and rigorous anhydrous conditions (anionic polymerisations). In addition, the method is limited to certain classes of monomers and be highly time-dependent: if the monomer is added too early, a tapered copolymer instead of a block copolymer may be formed; if the monomer is added too 'late', side-reactions, such as quenching, cyclisation or chain transfer may occur.

If monomers are mixed together in one pot from the start, whether or not a block copolymer is formed depends upon the relative rates of monomer incorporation ('reactivity ratios').^[23, 24] If reactivity ratios are high, block copolymers are possible. However, more commonly, random or tapered (gradient) copolymers are obtained.^[25, 26]

2. Bifunctional Initiator

A bifunctional initiator contains two initiating groups and allows simultaneous polymerisation of two monomers. Several examples have been reported, from simple diols to the combination of an alkoxyamine (radical initiator) and an alcohol (ROP initiator) or carboxylic acids (epoxide/CO₂ ROCOP initiator, see below) and thiocarbonates (RAFT initiator).^[27-30] Although enabling for specific monomer combinations, the general limitation is the coupling of two orthogonal processes, which typically limits the scope of these reactions. Further, the preparation of such bifunctional initiators is non-trivial.

3. Kinetic resolution

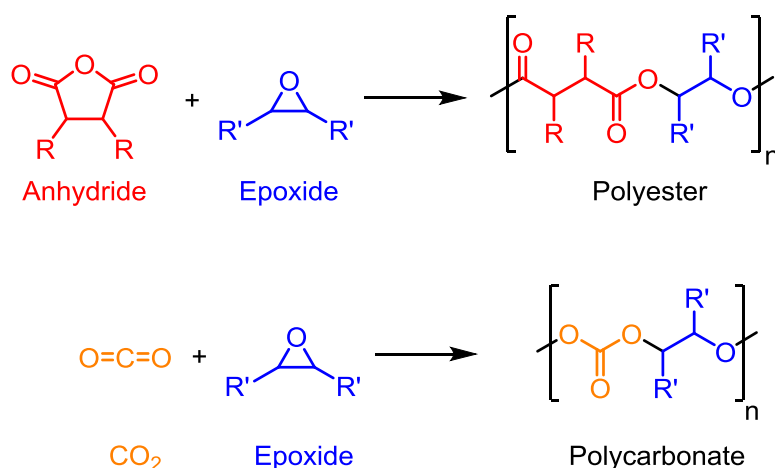
A chiral catalyst can preferentially react with one enantiomer from a racemic mixture. This general principle from asymmetric catalysis can be transferred to polymerisations. One example relevant to polyester chemistry is work by Spassky and co-workers where a binol-derived aluminium alkoxide reacted preferentially with *D*-lactide over *L*-lactide and a stereoblock copolymer was formed.^[31] However, this approach is intrinsically limited and requires highly tailored catalysts.

4. End group coupling

A block copolymer can be formed by coupling of reactive end groups between different polymers. Two examples are the copper-catalysed azid alkyne cycloaddition or the coupling of alcohol-terminated polymers with isocyanates.^[32, 33] Major challenges are the efficient coupling between blocks and the need for quantitative end-capping.

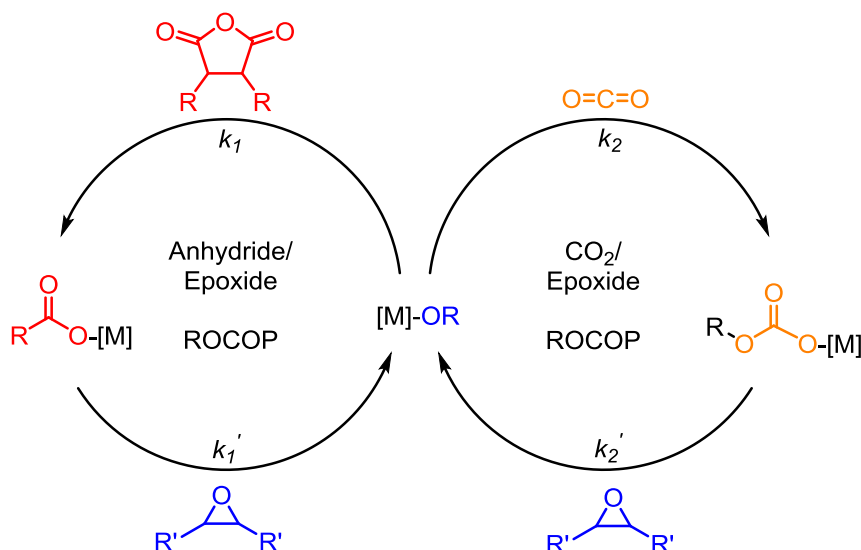
5. Terpolymerisation

In a terpolymerisation, three monomers are polymerised through similar mechanisms.^[34] This one pot-approach is well known and used for the synthesis of oxygenated polymers through the one-pot combination of two ring-opening copolymerisations (ROCOP).^[35] ROCOP is two-step process and for this thesis, two types of ROCOP are relevant, epoxide/anhydride ROCOP and epoxide/ CO_2 ROCOP (Scheme 1. 1).^[36, 37]



Scheme 1. 1 – Anhydride/epoxide ROCOP (top) and CO_2 /epoxide ROCOP (bottom).

Epoxide/anhydride ROCOP proceeds through a metal alkoxide intermediate, which reacts with an anhydride and forms a metal carboxylate species (k_1 in Scheme 1. 2, left). The latter reacts with an epoxide to re-generate the initial metal alkoxide intermediate (k_1') and overall, an ester linkage is formed. In the copolymerisation of epoxides with CO_2 , a metal carbonate species is formed in a first step by nucleophilic attack of the metal alkoxide intermediate at CO_2 (k_2). In a second step, this metal carbonate species reacts with an epoxide to re-generate the initial metal alkoxide (k_2') and a carbonate linkage is formed (Scheme 1. 2, right).^[36-38]



Scheme 1. 2 – Combination of two catalytic ROCOP cycles.^[39]

A recently developed approach to copoly(ester-*b*-carbonates) is the terpolymerisation where three monomers are enchain as the processes share common mechanisms and the same metal alkoxide intermediate. With respect to epoxide/anhydride and epoxide/CO₂ ROCOP, the shared intermediate is a metal alkoxide. This was first thoroughly investigated by Coates and co-workers with cyclohexene oxide (CHO), diglycolic anhydride (DGA) and CO₂.^[39] Instead of a random poly(ester carbonate), two well defined-blocks were obtained using a zinc β -diiminate catalyst. This suggests a kinetic preference for the ring-opening of the anhydride over the incorporation of CO₂ (i. e. $k_1 > k_2$). Interestingly, an overall acceleration was observed for the formation of the second block (polycarbonate) over the first (polyester). This indicates that the rate-determining step of the catalysis is the reaction of the carboxylate or carbonate intermediate with the epoxide and this step is faster for the formation of polycarbonate than polyester (i. e. $k_2' > k_1'$). Similar studies were performed with salen chromium or cobalt catalysts and chromium porphyrin catalysts.^[40-42]

Terpolymerisations are attractive routes to block copolymers and have several advantages over the approaches described in Figure 1. 6 (approaches 1-4), such as intermediary polymers are not isolated and being a one-pot approach from a mixture of monomers, which does not require monomer addition at specific times. It should be noted that this concept relies on kinetic preferences to obtain block copolymers, which may not be given for the combination of two epoxide/CO₂ ROCOPs or two epoxide/anhydride ROCOPs.^[43-46] Nonetheless, the available materials are somewhat limited as typically 'hard' polymers with high glass-transitions temperatures are formed and 'soft' polymers are not readily accessible.^[40, 41, 47, 48] This limitation can be overcome by combining catalytic cycles with different mechanisms, which is the underlying principle of 'switch' catalysis.

1.2. 'Switch' Catalysis

The term 'switch' is frequently used in catalysis and typically involves external stimuli to change between 'on' and 'off' states. Stimuli involve oxidation/reduction, light, changes in coordination geometry, pH value and mechanical stimuli.^[49-56] Herein, the term '*switch*' catalysis is the one-pot combination of two polymerisation mechanisms with a single catalyst, which yields block copolymers; the mechanistic 'switch' is reagent-controlled and occurs once the first monomer has been fully converted.^[57] The main advantages of 'switch' catalysts over the other methods outlined are: (i) it is a one-pot procedure, (ii) only one catalyst is used and (iii) modifications can be achieved easily by changing one of the three components in the feedstock (Figure 1. 7).

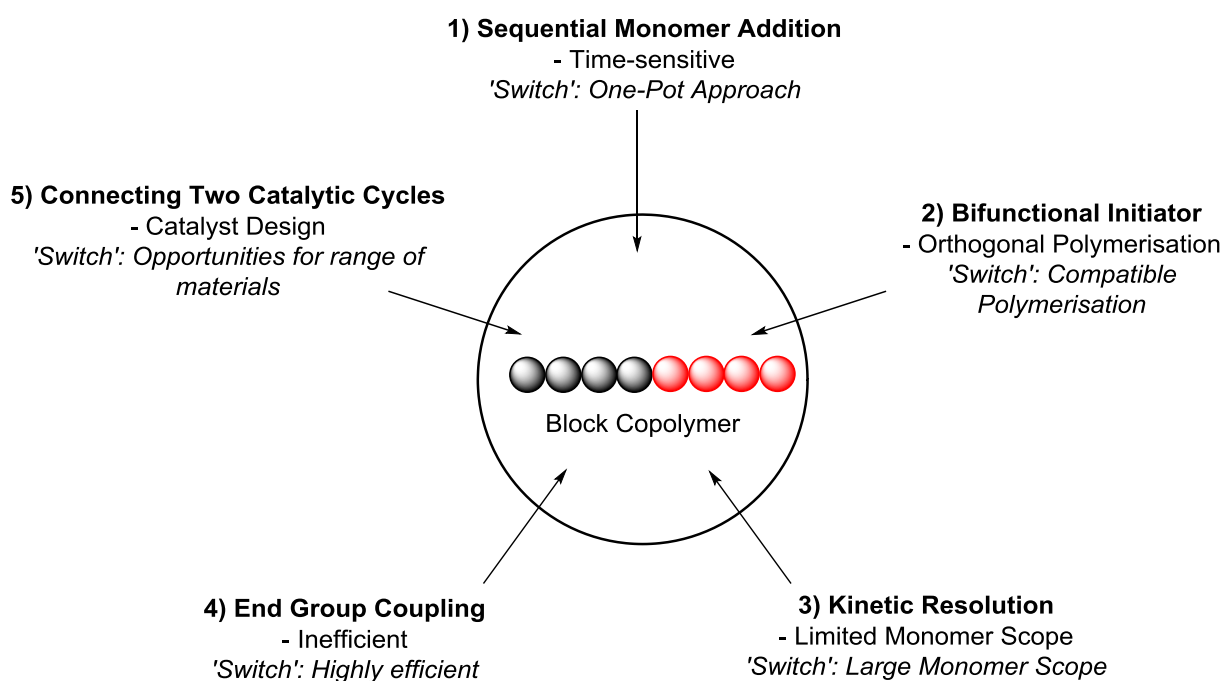
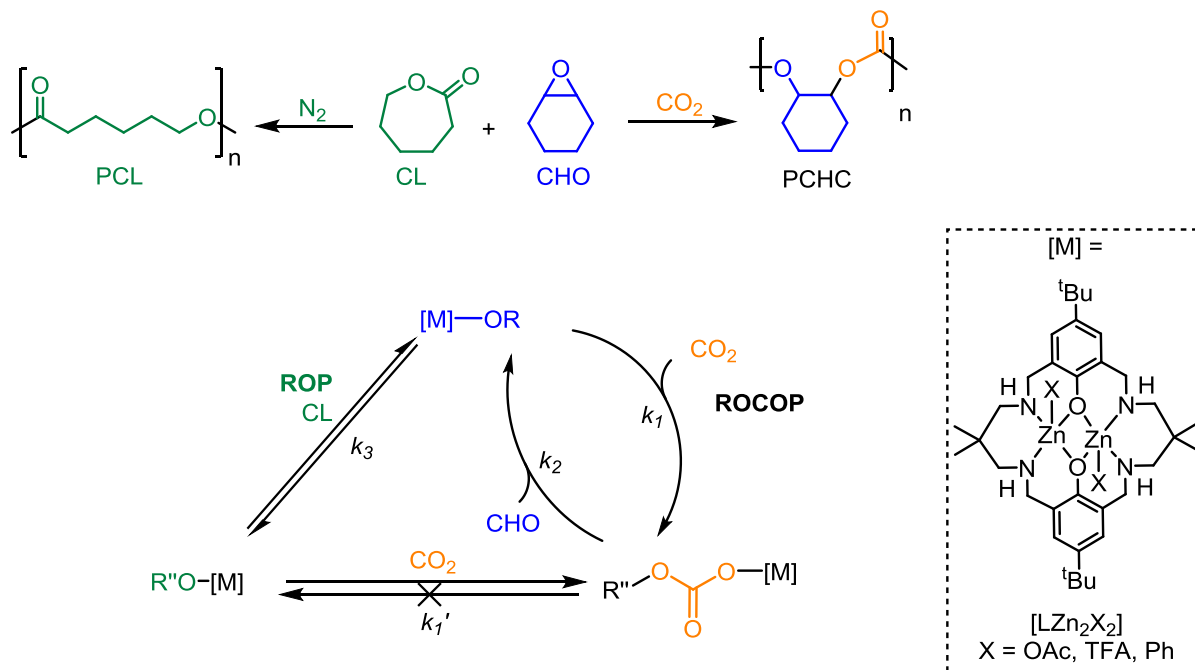


Figure 1. 7 – Benefits of 'switch' catalysis.

This principle was introduced in 2009 by Williams and co-workers with a dinuclear zinc catalyst, which was used to combine epoxide/ CO_2 ROCOP and lactone ROP.^[58] Starting from a mixed feedstock containing ϵ -caprolactone (CL), cyclohexene oxide (CHO) and CO_2 , only CHO/ CO_2 ROCOP was observed and the lactone remained unreacted. The 'switch' occurred once the CO_2 atmosphere was replaced with N_2 and the lactone was rapidly consumed. The observed selectivity suggests that the insertion of CO_2 is the fastest step in the catalysis, followed by the ROP of CL and finally the ring-opening of CHO as the second, rate-determining, step of ROCOP ($k_1 > k_3 \gg k_2$, Scheme 1. 3). It is important to note that CL

ROP was not observed in the presence of CO_2 , which suggested a chemo-selective reaction between the zinc carbonate intermediate and epoxide.



Scheme 1. 3 – ‘Switch’ catalysis with CL, CHO, CO_2 ($k_1 \sim k_1' > k_3 > k_2$).^[58]

With acetate co-ligands, AB copoly(ester-*b*-carbonate)s were obtained.^[58] Upon changing the co-ligand to trifluoroacetate, symmetric ABA copoly(ester-*b*-carbonate-*b*-ester)s were formed, which was attributed to the fast hydrolysis of the trifluoroacetate initiating groups.^[59] Similar architectures were obtained from mixtures of epoxides, anhydrides and lactones with phenyl co-ligands, which were reacted with alcohols *in situ*.^[60]

‘Switch’ catalysis was further studied by DFT for the reaction of zinc alkoxides with different monomers.^[61] In detail, four elementary reactions of the zinc alkoxide with epoxides, anhydrides, CO_2 and CL were studied with respect to (i) the thermodynamic stability of the formed product and (ii) the kinetic barrier (Table 1. 1 and Figure 1. 8). It was concluded that a combination between kinetic and thermodynamic factors explained the observed product selectivity (polyesters from anhydride/epoxide ROCOP and polycarbonates from CO_2 /epoxide ROCOP were formed preferentially over polyesters from ROP): The ring-opening of the anhydride results in the most stable linkage and is associated with a low energy barrier; the insertion of CO_2 forms a stable linkage with a comparable transition state and the ring-opening of CL results in the least stable linkage and is associated with the highest transition state.

Table 1.1 – DFT calculated energy barriers for different polymerisations (ω B97XD/6-31G(d)/SCRF (cpcm, solvent = dichloromethane); all values in kcal mol⁻¹).^[61]

Zn-O bond Monomer	Zn alkoxide	Zn carbonate	Zn carboxylate
CHO	Δ TS = 39.1 Δ Linkage = -16.4	Δ TS = 23.5 Δ Linkage = 0.6	Δ TS = 24.4 Δ Linkage = 2.1
CO ₂	Δ TS = 11.4 Δ Linkage = -5.0	Δ TS = 10.5 ^[a] Δ Linkage = 8.2 ^[a]	Not observed.
PA	Δ TS = 13.3 Δ Linkage = -27.3	Not observed.	Not observed.
CL	Δ TS = 33.6 Δ Linkage = 5.4	Not observed.	Not observed.

^[a] 273.15 K, all other values calculated for 373.15 K.

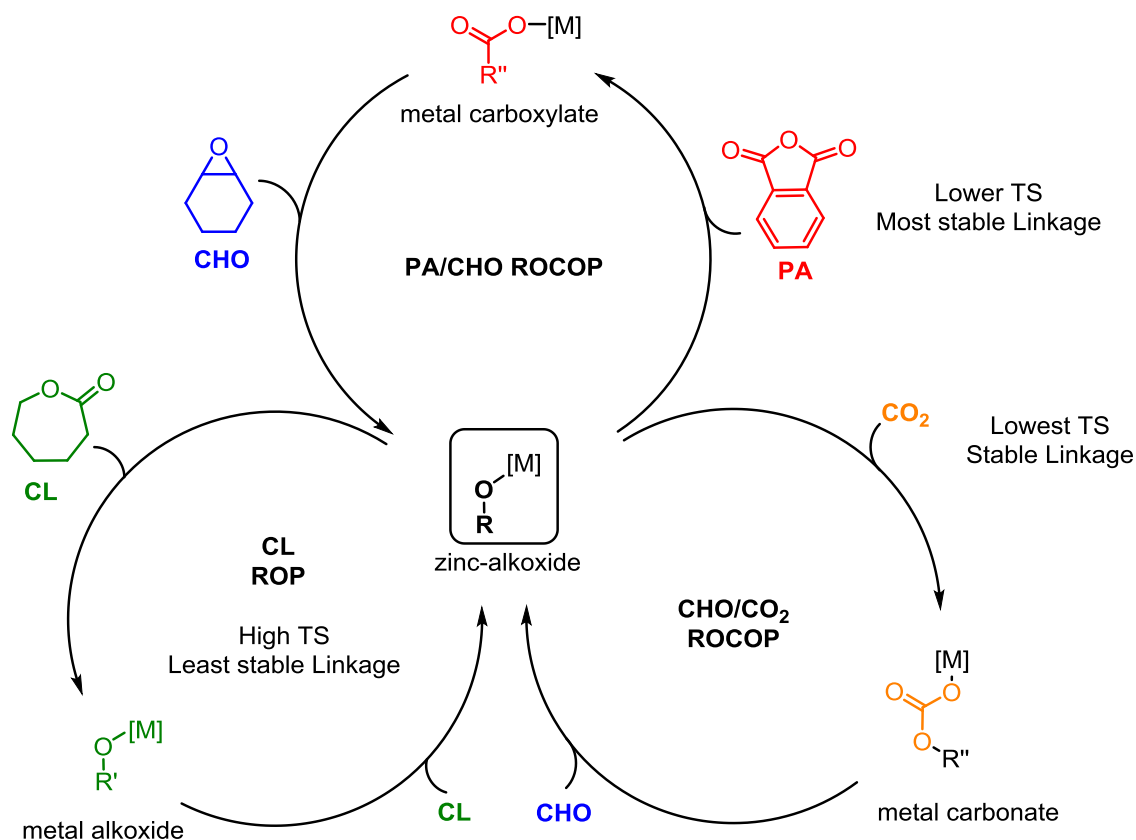
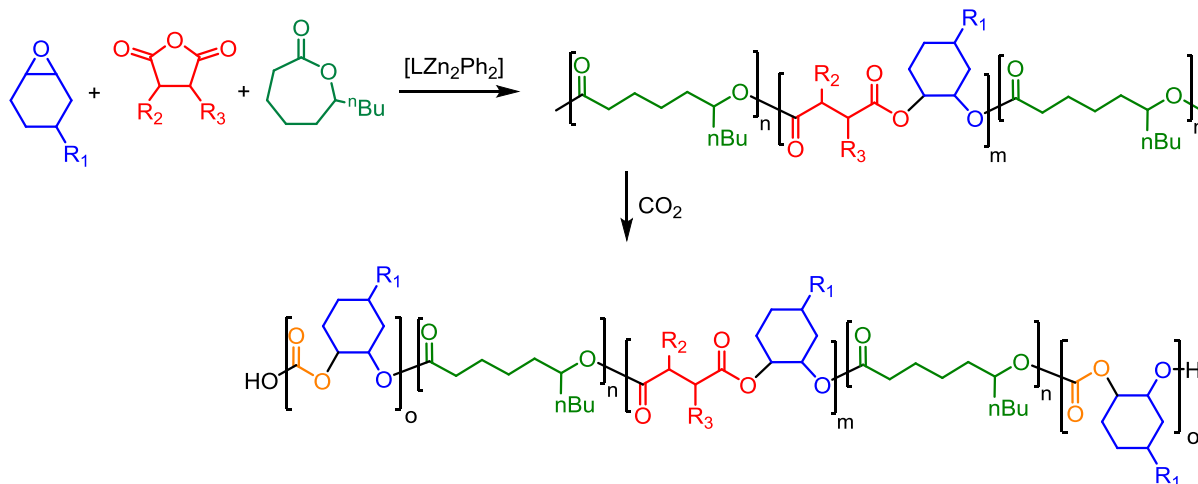
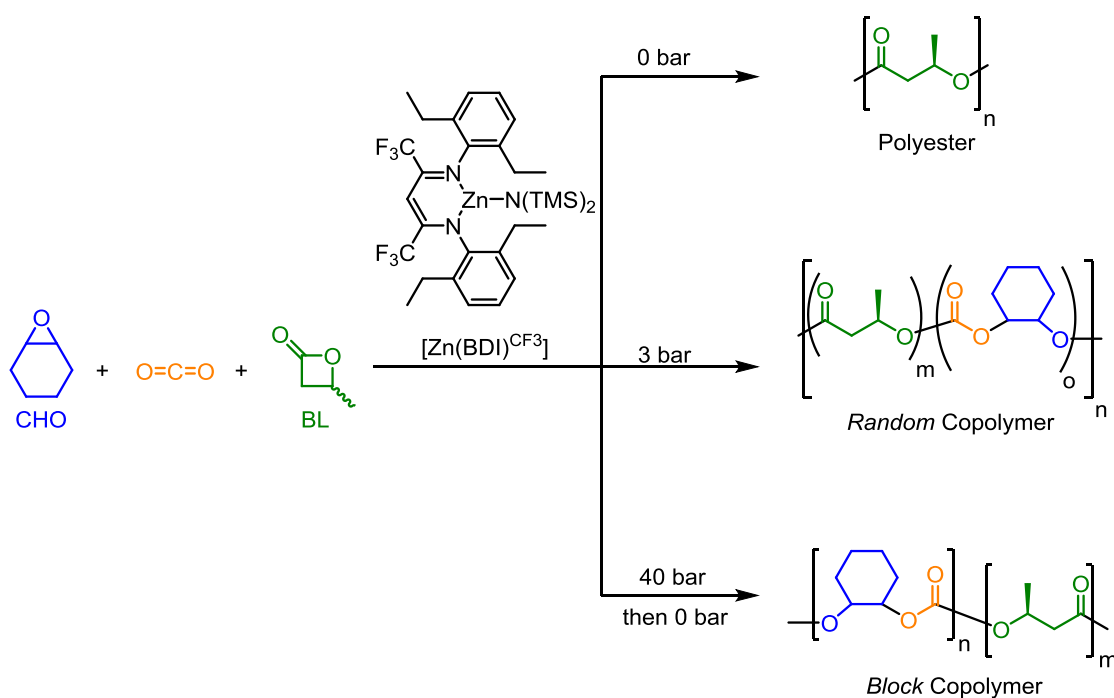


Figure 1.8 – Theoretical evaluation of different polymerisation mechanisms in ‘switch’ catalysis with a dizinc alkoxide.^[61]

Most recently, the predicated formation of block copolymers from a mixture of PA, CHO, DL and CHO was experimentally verified with phenyl co-ligands (Scheme 1. 4).^[62]

Scheme 1. 4 – Synthesis of pentablock copolymers.^[62]

In 2017, the method ‘switch’ catalysis was demonstrated by Rieger and co-worker using β -butyrolactone (BL), CHO and CO₂ and a zinc β -diiminate catalyst (Scheme 1. 5). In this case, the pressure of CO₂ acted as another ‘switching’ agent and three scenarios were found: if no CO₂ was present, only polybutyrolactone (PBL) was formed, if low pressures (three bar) of CO₂ were used, the statistical incorporation of CL, CHO and CO₂ was found and if high pressures (40 bar) were employed, only CHO/CO₂ ROCOP occurred, followed by BL ROP, once the pressure was released. As an aside, high turn-over frequencies (TOF, > 3,000 h⁻¹) alongside high molar masses (> 100,000 g mol⁻¹) and varying degrees of control (1.2 < $\bar{D}$ < 1.8) were reported for this system.^[63]

Scheme 1. 5 – ‘Switch’ catalysis with CHO, CO₂ and BL.^[63]

In summary, 'switch' catalysis is a new one-pot strategy to access block polymers by combining two catalytic cycles with one catalyst. So far, two systems have been reported for 'switch' catalysis: a macrocyclic zinc catalyst (Williams, 2009 – present) and a zinc β -diiminate catalyst (Rieger, 2017).

1.3. Post-Functionalisation Modification

A wide range of polymers can be synthesised through living polymerisations. However, these syntheses are only successful if no reactive groups are present in the monomer that react irreversibly (quench) the initiator/catalyst. For anionic polymerisations, these include functional groups reactive towards deprotonation (alcohols, thiols, amines) or addition (ketone, imines).^[64]

To polymerise these monomers, protecting groups (silyl enole ethers, silyl thioethers, acetals) are introduced before the reaction and are removed afterwards. The choice of the protecting groups is not only dependent on the functionality to be protected but also on the formed polymer, which should not be degraded during deprotection (e.g. acid-catalysed acetal-hydrolysis may be unsuitable for polyesters).^[65-67]

Post-functionalisation modification enables the fine-tuning (tailoring) of polymers for a wide variety of applications. Multiple reactions have been used in the post-functionalisation of polymers, including substitutions and additions; a selection of commonly used reactions is given in Figure 1. 9. Of particular importance for polyesters and polycarbonates are thiol-ene reactions, in which a thiol is added across an alkene with *anti*-Markovnikov selectivity (highlighted in red in Figure 1. 9).^[68-70]

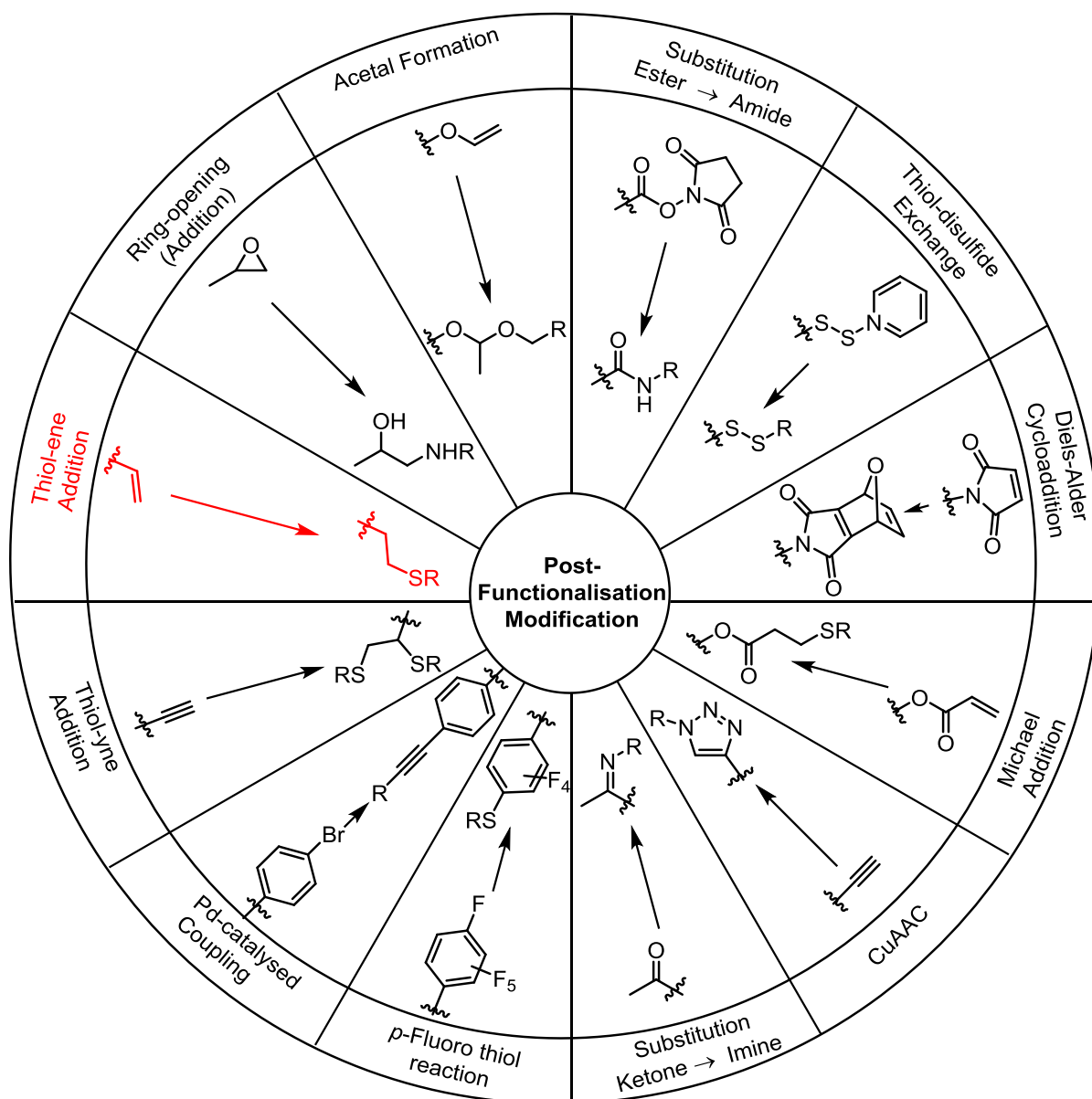
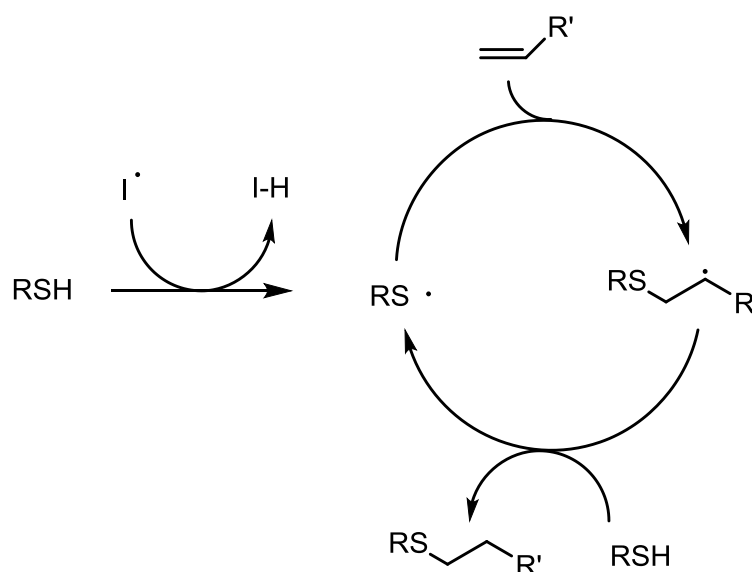


Figure 1. 9 – Selected post-functionalisation modification reactions.^[71]

In thiol-ene reactions, a thiyl-radical is formed from a radical initiator and a thiol is added across an alkene in two steps. First, the thiyl-radical adds to the alkene, generating a carbon-centred radical, when then undergoes chain-transfer with an unreacted thiol to form the coupling product and re-generate the thiyl radical (Scheme 1. 6). Thiol-ene reactions are classified as ‘click’ reactions as they proceed fast (minutes) and without by-products, are stereo- and regiospecific, do not require solvent, are tolerant towards water and oxygen and finally, can be used with a variety of commercial starting materials.^[72, 73]



Scheme 1. 6 - General mechanism of radical thiol-ene reactions.^[72, 73]

Although it has been reported that ‘virtually every alkene’ can be used in thiol-ene reactions, substrates featuring vinyl groups are typically used as internal alkenes have proved to be difficult substrates.^[74] This was attributed to a reversible addition of the thiyl radical to the alkene.^[75, 76] Only a few exceptions have been reported, including limonene, poly(limonene carbonate), poly(cyclohexene carbonate) and strained alkenes, such as norbornene.^[77, 78] Nonetheless, thiol-ene reactions are highly attractive and have been used in this thesis as they allow a straight-forward strategy to modify material properties.

The broad use of thiol-ene reactions with unsaturated polycarbonates has been demonstrated by Greiner and co-workers for poly(limonene carbonate) (PLC). Depending on the substitution of the thiol, antibacterial (R=ammonium salt), hydrophilic (R=polyethylene glycol), water-soluble (R=carboxylate) or rubbery materials (R=aliphatic ester) have been obtained.^[79] Cross-linking of PLC with multifunctional thiols has been investigated by Koning and co-workers and the obtained coating materials showed promising hardness and solvent-resistance.^[80, 81] Beyond PLC, poly(cyclohexadiene carbonate) (PCHDC) and poly(2-vinylloxirane carbonate) have been transformed from water-insoluble into amphiphilic, water-soluble materials^[82, 83] and different terpolymers based CO₂ have been successfully cross-linked to improve their thermal properties.^[84-86]

1.4. Aims and Objectives

The main objective of this thesis is the investigation of 'switch' catalysis. The lead questions include: Is 'switch' catalysis a general concept beyond the two reported zinc catalysts? Can new monomers be used for the synthesis block copolymers featuring blocks other than polycarbonates or polyesters? Is it possible to use commercially relevant monomers? Moreover, applications of unsaturated, potentially bio-based, polycarbonates are investigated after functionalisation *via* thiol-ene reactions. In this section, the key questions target the resulting material properties and differences between polycarbonates featuring internal and terminal alkenes. Finally, new catalysts for 'switch' catalysis are developed and future studies recommended. Key aims and objectives of the individual chapters are outlined in Figure 1. 10.

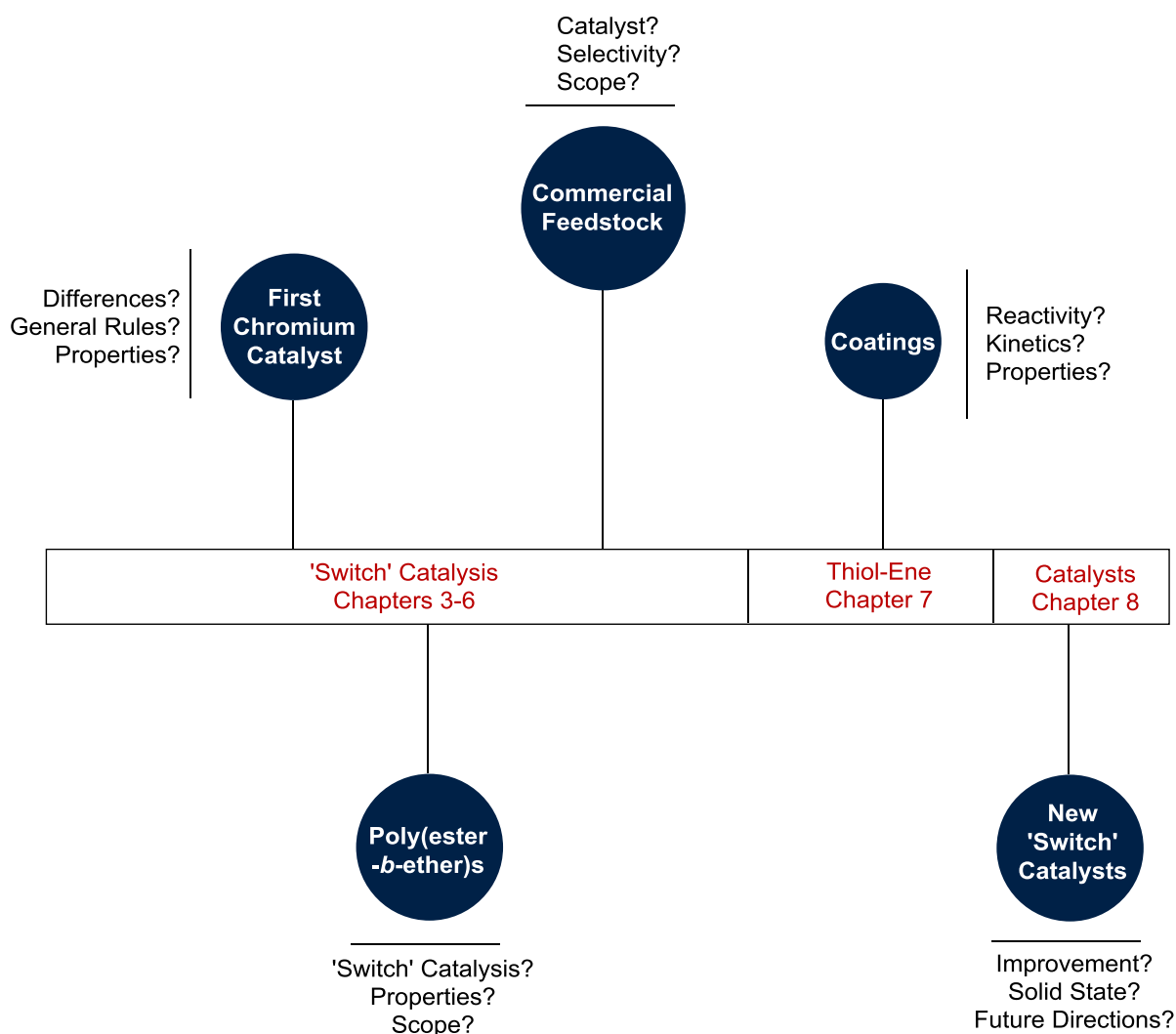


Figure 1. 10 – Aims and objectives covered in this thesis.

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Chapter 2

Methods

A Guide to 'Switch' Catalysis

Publication: T. Stößer, T. T. D. Chen, Y. Zhu and C. K. Williams, *Phil. Trans., R. Soc. A.*, **2017**, 376, 20170066.

2.1. Analysis of ‘Switch’ Catalysis: Part I - Catalysis

The aim in ‘switch’ catalysis is the selective formation of block copolymers from mixed monomer feedstocks, typically containing three or more monomers. The overall analysis contains multiple steps and can be divided into two sections: First, the catalysis is monitored to identify if monomer selectivity is achieved and second, the obtained material is analysed to identify if a block copolymer is formed. Both parts will be discussed individually below.

Starting from a mixed monomer feedstock containing three monomers (epoxide, anhydride and lactone), five scenarios are possible (Figure 2. 1). First, no reaction occurs (A), second, only one or two out of three monomers are polymerised and an incomplete reaction is obtained (B). Third, only partial reaction occurs, as described in B, but the incorporation of two monomers is unselective, i. e. the formation of polyether linkages instead of an alternating polyester is observed. In option D, complete reaction (with respect to anhydride and lactone) is obtained with perfect selectivity for the formation of the alternating AB sequence. In the case of excess epoxide, which is a common condition in anhydride/epoxide copolymerisations, no further epoxide is incorporated apart from the AB sequence and unreacted epoxide is found at the end of the reaction.^[1-4] Finally, full conversion of all reactants may be obtained, including the random incorporation of epoxide. Out of these five scenarios, only one is desirable for ‘switch’ catalysis, the complete and selective reaction (D in Figure 2. 1).

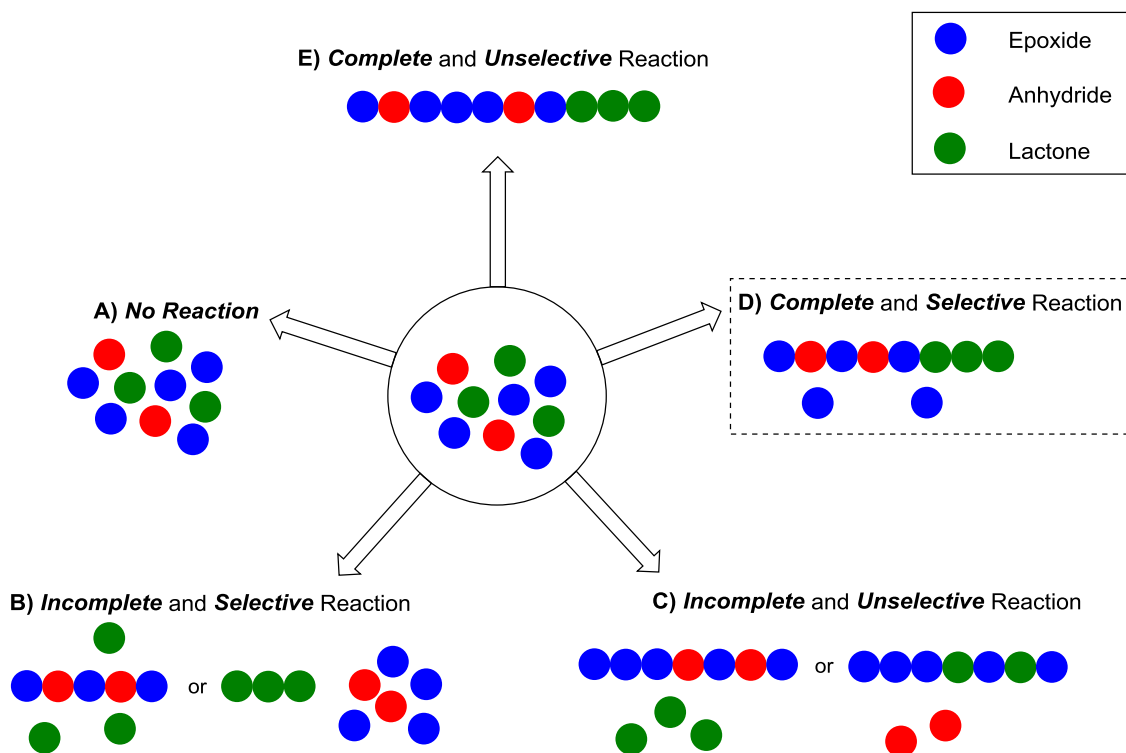


Figure 2. 1 – Polymerisation of a mixed feedstock containing three monomers.

To distinguish between these possibilities, the reaction is monitored either *in situ* or by regular removal of aliquots. The monitored quantity is the conversion or normalised absorption, which is accessible through ^1H NMR or IR spectroscopy, respectively. In the case of NMR spectroscopy, conversions are based on the integral of monomers or polymers relative to an internal standard (mesitylene). The comparison between the integral at the beginning of the reaction ($t = 0$ s) and the integral at a later stage ($t = x$ s) yields the conversion; an idealised plot for the sequential reaction of two monomers is shown in Figure 2. 2.

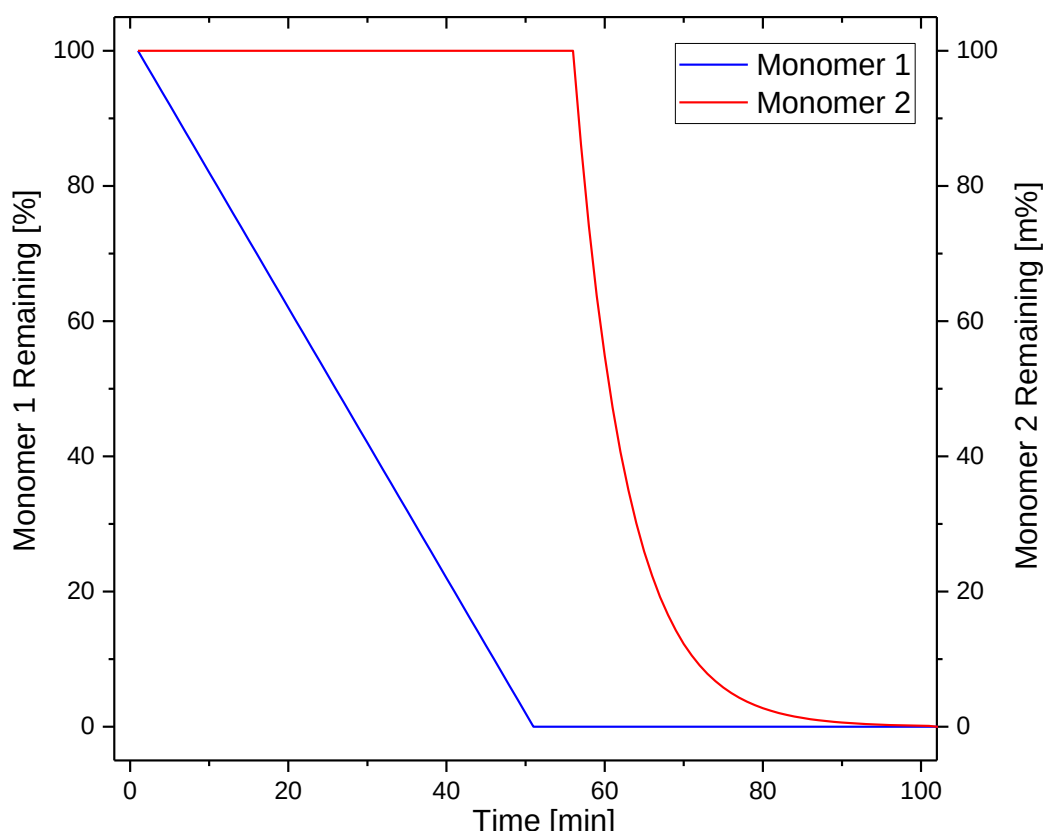


Figure 2. 2 – Idealised plot for the selective polymerisation of monomer 1 (0^{th} order rate law illustrated) followed by monomer 2 (1^{st} order rate law assumed). The conversion is given on the y-axis for a typical plot based on ^1H NMR spectroscopy; with IR spectroscopy, the y-axis would be replaced with (normalised) absorption. Functions used to generate this plot are given in the appendix.

2.2. Analysis of ‘Switch’ Catalysis: Part II - Material

Once the selective reaction of all monomers has been identified, three different products may be formed: the desired block copolymer, a mixture of homopolymers or a transesterified copolymer (Figure 2. 3). The differentiation of these materials is challenging but highly important, which is why a range of analytical techniques should be used.

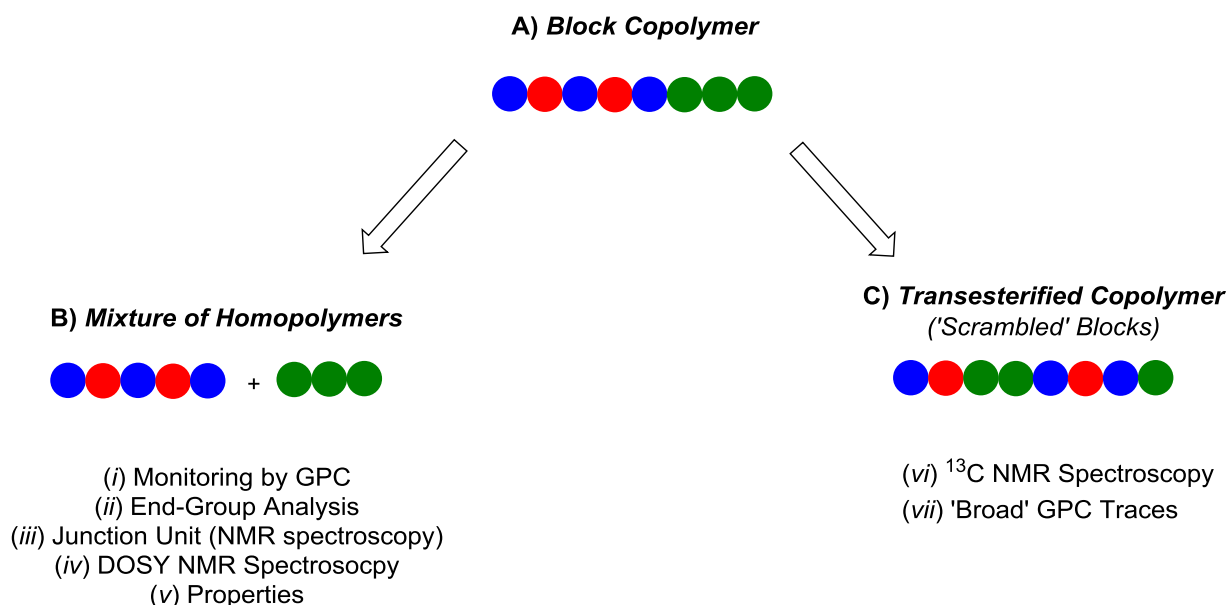


Figure 2. 3 – Possible materials in ‘switch’ catalysis.

Five ways to differentiate between homo- and block copolymers are listed in Figure 2. 3 (B). This includes:

- i. Monitoring by GPC:* If a block copolymer is formed, molar masses are expected to continuously increase throughout the reaction, most importantly after the first block is formed. This is not the case with a mixture of homopolymers, in which case one peak for each block should be obtained and the peak from the first block should not shift in mass while a second peak is formed (Figure 2. 4). This may be combined with UV detectors, if only one of the blocks is UV-active.

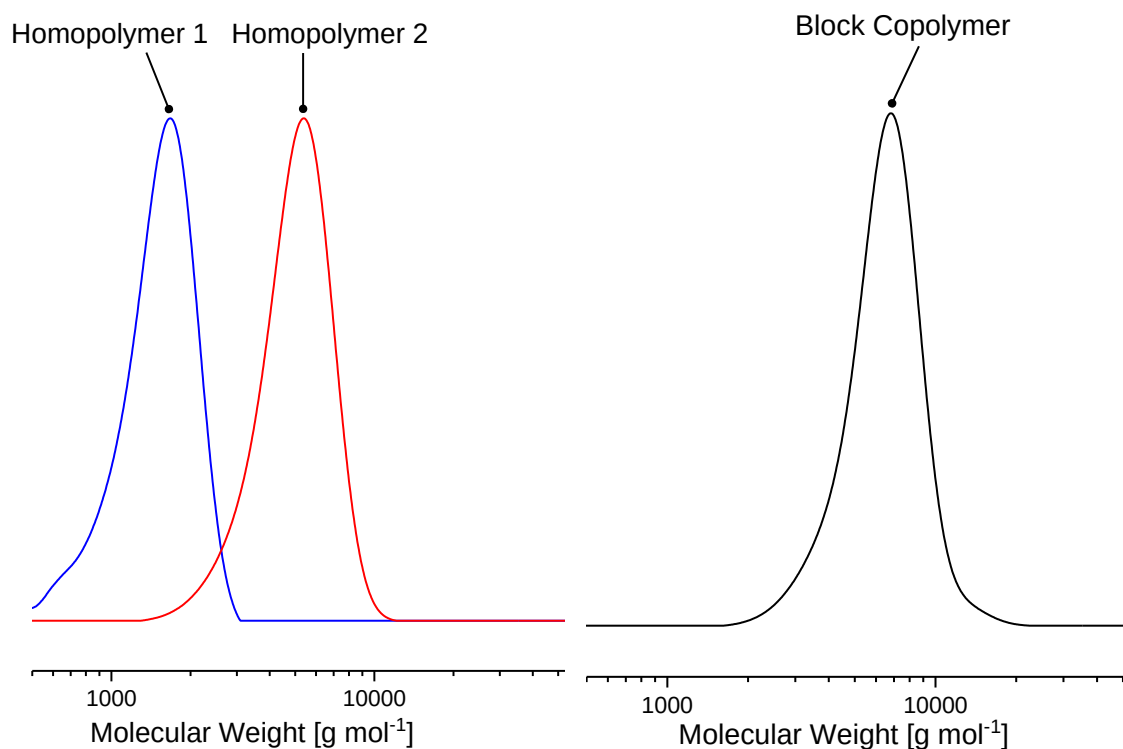


Figure 2. 4 – Comparison between a mixture of homopolymers and a block copolymer (see chapter 4 for details).

- ii. *End-group analysis*: Two different end-groups should be visible for a mixture of homopolymers, whereas only the end-group from the second block is expected for a block copolymer (Figure 2. 5). End-groups may be analysed by ¹H NMR spectroscopy or ³¹P{¹H} NMR spectroscopy after the reaction with a phosphorus reagent reactive towards alcoholysis.^[5] Although the latter is restricted to hydroxyl end groups, this analysis may be helpful as well-defined signals are obtained, which rarely overlay, as opposed to analysis by ¹H NMR spectroscopy.

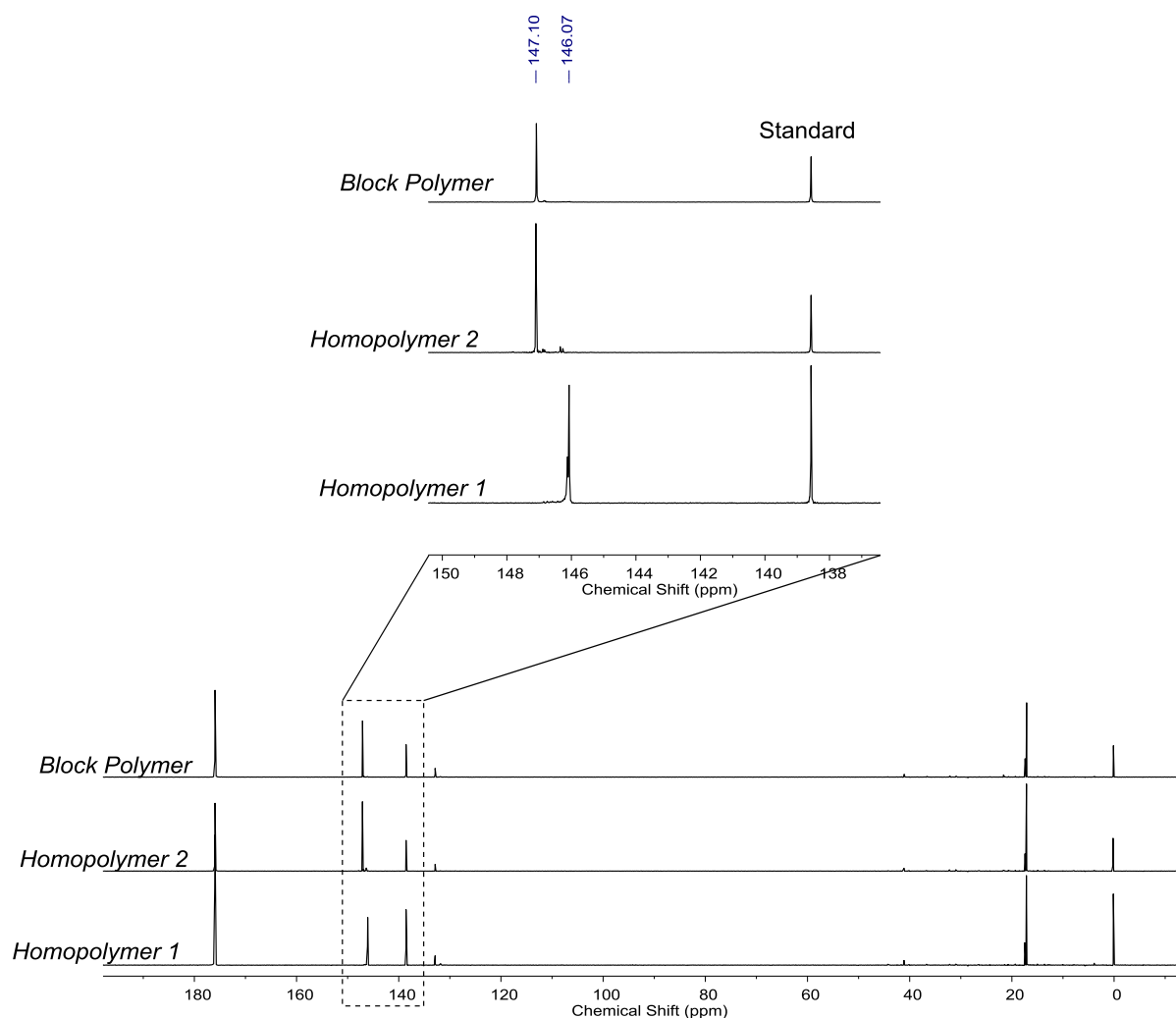


Figure 2. 5 – End group test by $^{31}\text{P}\{^1\text{H}\}$ NMR. In a mixture of homopolymers, two separate signals should be observed (from each of the homopolymers) and for a block copolymer only one end group should be detected (see chapter 4 for details).

- iii. *Junction unit*: If the two blocks are connected to each other, the chemical environment for the point at which one block ends and the next starts is marginally different from the repeating unit. This may be visible as a separate set of signals which can be identified through 2D NMR techniques as this connection to both repeating units is unique for block copolymers.^[6] Although identification of this junction unit is insightful, it should be noted that sharp signals, no overlap and/or rather simple repeating units are necessary to observe these signals.
- iv. *DOSY NMR spectroscopy*: This is a 2D NMR technique with which molecules can be differentiated based on their diffusion coefficient.^[7] For a block copolymer, only one

diffusion coefficient is expected as the polymer diffuses as one particle and both blocks are covalently attached to each other. A mixture of homopolymers, however, diffuses as two different particles and two diffusion coefficients may be observed (Figure 2. 6). Typically, two different coefficients can be observed for a mixture of homopolymers if (i) chemically different polymers are compared (polyester vs. polyether or polycarbonate) and if (ii) molar masses are different. It should be noted that control reactions are highly recommended to validate this technique for similar blocks and to exclude the possibility of similar diffusion coefficients of two homopolymers.

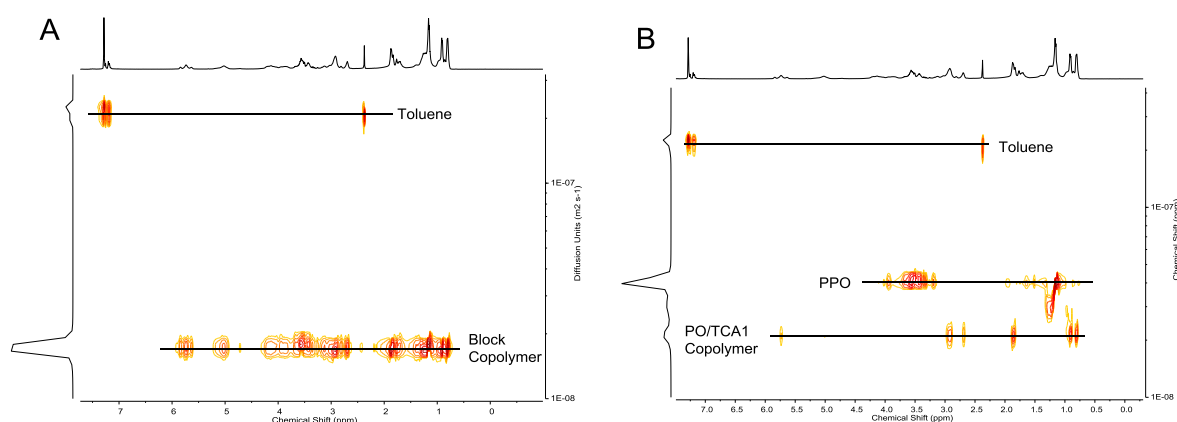


Figure 2. 6 –DOSY NMR spectrum of a block copolymer (A) and a mixture of homopolymers (B) (see chapter 4 for details).

- v. *Properties*: Physical (solubility, appearance), mechanical (strain/stress at break) and thermal properties (glass-transition temperature, decomposition temperature) may vary between mixtures of homopolymers and block copolymers. Typically, these differences are associated to (micro)-phase separation.^[8-11]

If a block copolymer is obtained, the composition of the polymer has to be tested, i.e. if the block architecture is maintained or altered (randomised) at a later stage of the reaction. This may be caused by transesterification and can be investigated by two techniques:

- vi. ¹³C NMR spectroscopy: In the carbonyl-region (160-180 ppm), only two signals, one from each block if symmetric substrates are used, should be observed.¹ This is in contrast to a randomised copolymer for which additional, intermediary signals may be

¹ Junction units and/or end groups may be visible as low-intensity signals.

found. As a control reaction, deliberate transesterification with DBU is recommended.^[12]

- vii. *'Broad' GPC traces:* Transesterification may occur randomly throughout the reaction and polymers with different chain length may be formed. This is visible as a 'broadening effect' (increase in dispersity $\bar{D}$) of GPC traces over time as the distribution of different chain lengths increases over time (Figure 2. 7).

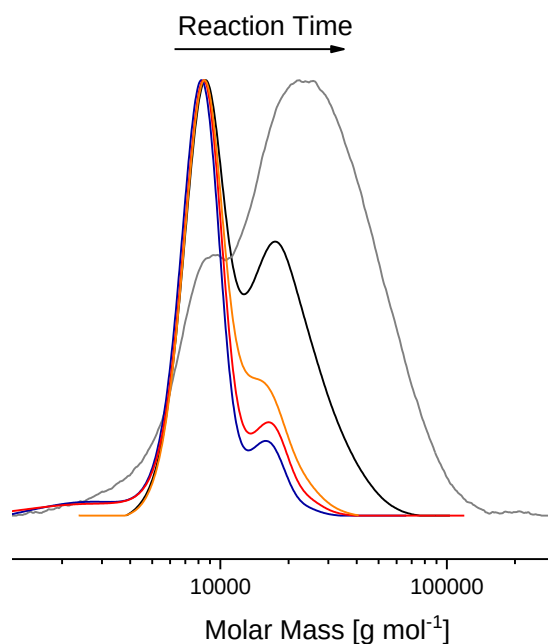


Figure 2. 7 – Indication of transesterification by GPC.

Both techniques ($^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and GPC) are indications of transesterification – however, the extent of transesterification cannot be quantified in general.

On a final note, these guidelines are indicators for block copolymers and discussed for AB diblock copolymers. A direct 'proof' for block copolymers has not been established and the experiments should be adjusted with the materials on hand.

2.3. Overview of Techniques

The main focus of this thesis is 'switch' catalysis (chapters 3-5); material characterisation (chapter 6) and catalyst development (chapter 7) are covered beyond this topic. Overall, multiple techniques were used to answer specific topic-related questions and a brief summary of techniques is provided in Table 2. 1.

Table 2. 1 – Summary of Characterisation Techniques.

Chapter	Technique	Measured Quantity	Measuring Principle	Comments
2-5	NMR Spectroscopy ^[13] Nuclear Magnetic Resonance Spectroscopy (¹ H, ¹³ C, ³¹ P, homonuclear 2D [COSY, TOCSY] and heteronuclear 2D [HSQC, HMBC])	Absorption of electromagnetic radiation by nuclei with non-zero spin in external magnetic field (B ₀)	When B ₀ is applied, degenerated energy levels split (Zeeman splitting). These transitions can be induced by photons and the absorbance of these photons is measured.	1D NMR techniques used for reaction monitoring; 2D NMR techniques for polymer analysis.
	IR Spectroscopy ^[14] Infrared Spectroscopy	Absorption of electromagnetic radiation (infrared region)	Irradiation of sample with specific wavelengths results in molecular vibrations, which is detected as a change in intensity.	Group frequencies (4000-625 cm ⁻¹), typically $\nu_{C=O}$, monitored to distinguish between anhydride, lactone and polyester.
	GPC (SEC) ^[15] Gel-Permeation Chromatography (Size-Exclusion Chromatography)	Absorbance of detector based on refractive index (RI) or UV absorbance.	Macromolecules are separated according to their size by diffusion into cavities (pores) with different volume. Large molecules are eluted first (minimal pore penetration) and small molecules last.	Relative molar masses obtained after calibration against polystyrene standards. Measure for the 'width' of distribution is dispersity $\bar{D}$ (calculated from number- and weight average molar mass, $\bar{D} = M_w/M_n$).
	DSC ^[16] Differential Scanning Calorimetry	Difference in heat flow between sample and reference while heated	Physical transformations (phase transitions) are observed as a change in heat flow between sample and reference	Used for glass-transition temperatures.
	TGA ^[16] Thermogravimetric Analysis	Sample mass over time while heated	Phase transition (vaporisation) and thermal degradation observed as a decrease in mass	Used to determine thermal stability of polymers; value at 95% remaining mass reported (T _{95%}).
	MALDI-ToF ^[17] Matrix-Assisted Laser Desorption/Ionisation with Time-of-Flight Mass Spectrometer	Ions in gas phase	Ionisation through absorption of short laser pulse by matrix (generates plasma). Ions separated after acceleration in electromagnetic field based on their time-of-flight (ToF), which is proportional to their mass-to-charge (m/z) ratio.	Used for end-group determination.

Chapter	Technique	Measured Quantity	Measuring Principle	Comments
6	Raman Spectroscopy ^[18]	Scattered electromagnetic (high intensity) radiation at higher energy than incoming radiation	Inelastic scattering occurs from a higher-energy level of the analysed molecule (Raman scattering)	Used for analysis of vibrational levels of (insoluble) polymer films
	GPC (SEC)	See above.	See above.	See above.
	NMR Spectroscopy			
	DSC			
	TGA			
	DMTA ^[19] Dynamic Mechanical Thermal Analysis	Deformation (amplitude and phase) of sample while applying an oscillating force	Storage modulus E' ('stored energy', describes elastic properties) and loss modulus E'' ('lost energy', viscous properties) calculated from stress (amplitude), strain (force) and phase (δ) as function of time or temperature	E' used to evaluate coatings; δ vs. T plot contains information about glass-transition temperature.
7	XRD ^[20] X-Ray Diffraction	X-Ray diffraction pattern.	X-Rays are diffracted by electrons in crystalline samples and the molecular structure be determined from the electron density distribution	Used to characterise the solid-state structure of complexes.
	NMR	See above.	See above.	See above.
	IR			
	GPC			

2.4. References

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Chapter 3

‘Switch’ Catalysis with [SalcyCrCl]

Part I - Cyclohexene oxide

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3.1. Introduction

'Switch' catalysis is a new approach to prepare block copolymers based on the one-pot combination of two catalytic cycles: ROCOP and ROP. So far, only two complexes, a macrocyclic dizinc and a zinc BDI complex, have been investigated for this approach – although encouraging, the synthesis of these unique catalysts requires multiple steps.^[1-8]

In this chapter, the synthesis of block polyesters is investigated using a commercial chromium salen complex, [SalcyCrCl], and mixtures of epoxides, anhydrides and lactones. A number of fundamental questions are posed to identify if [SalcyCrCl] follows the rules of 'switch' catalysis established for zinc catalysts, such as: what is the selectivity and the product of the polymerisation? Which monomers can be used? What polymer properties result (Figure 3. 1)? The success and the limitations of this catalysis are explored and general guidelines for 'switch' catalysis with metal salen catalysts are developed – a class of catalysts that might enable the wide-spread use of 'switch' catalysis.

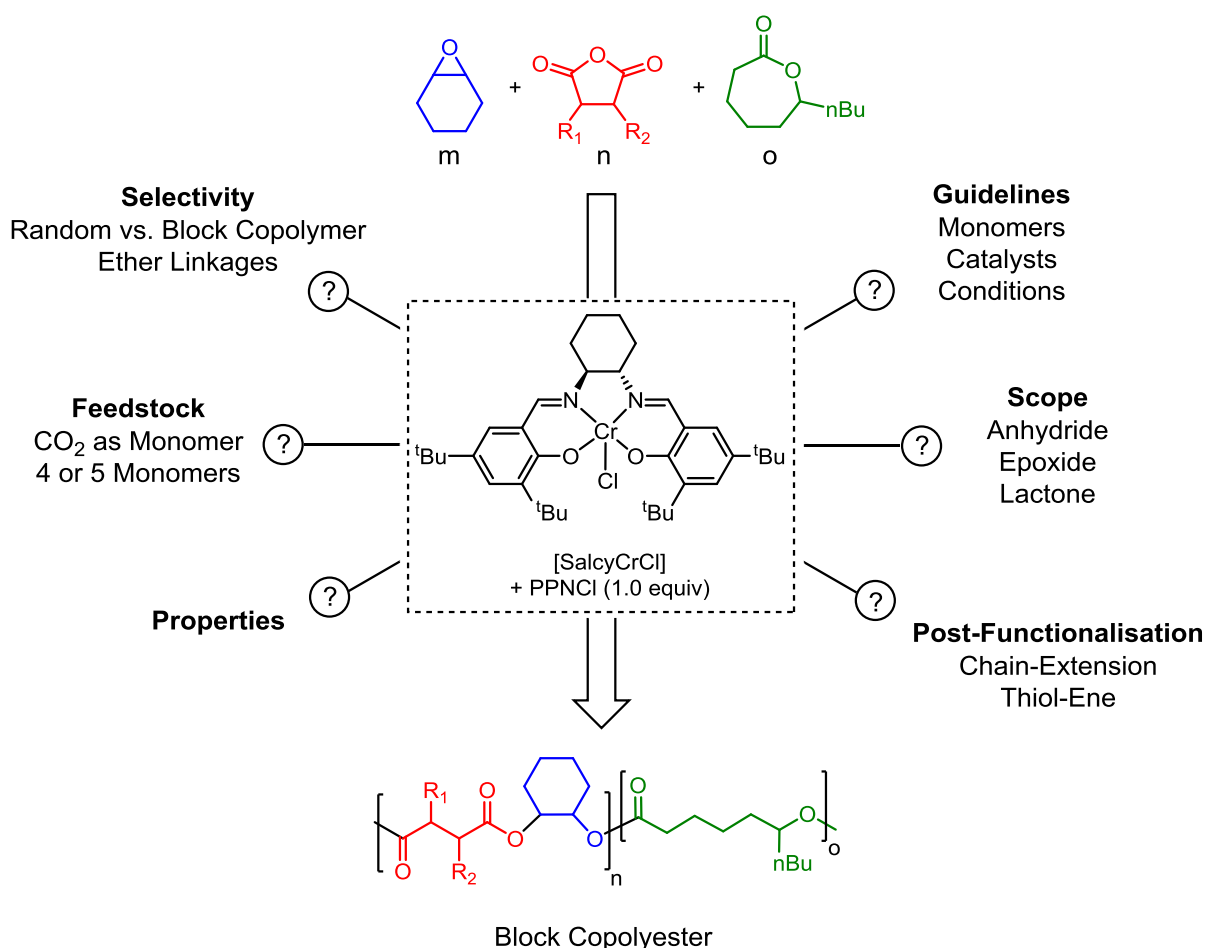
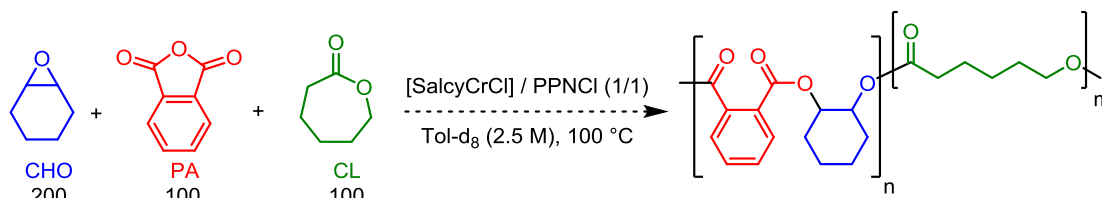


Figure 3. 1 – Lead questions for 'switch' catalysis with [SalcyCrCl] in this chapter.

3.2. One-Pot Polymerisation of Phthalic Anhydride, Cyclohexene Oxide and ϵ -Caprolactone

As a starting point, mixtures containing CHO, PA and CL were investigated (Scheme 3. 1). This choice of monomers was inspired by their recent use in related 'switch' catalysis with zinc catalysts.^[1-5, 8, 9]



Scheme 3. 1 – 'Switch' catalysis with CHO, PA and CL.

To identify if 'switch' catalysis occurs, the general set characterisation outlined in chapter 2 was followed. As a starting point, the reaction was monitored to distinguish between the random incorporation of monomers (not desired) and the selective polymerisation of one (ROP) or two (ROCOP) monomers at a time. The reaction was followed by ^1H NMR spectroscopy and occurred in two stages (Figure 3. 2): First, PA and CHO were consumed within 30 minutes, as observed by the decrease of the resonances attributed to the starting materials ($\delta = 7.9 - 8.1$ [PA] and 3.1 ppm [CHO]) and the increase of the corresponding product signals ($\delta = 7.3 - 7.6$ and 4.9 – 5.2 ppm). This is a strong indication of selective ROCOP of PA and CHO as both monomers were consumed at similar rates and the resulting product signals could be assigned to the alternating polyester. Second, CL was converted into PCL over the next 2.5 hours, as observed by the decrease of the monomer ($\delta = 4.3$ ppm) and increase of the polymer signals ($\delta = 4.2$ ppm). Most importantly, no significant lactone consumption (< 5 %) was detected during ROCOP, which suggests a high selectivity of ROCOP over ROP for this catalysis. Moreover, ROCOP was significantly faster than ROP ($\text{TOF}_{\text{ROCOP}} \sim 200 \text{ h}^{-1}$ vs. $\text{TOF}_{\text{ROP}} \sim 40 \text{ h}^{-1}$) and no polyether linkages were detected at any point of the reaction. The latter is a common side-reaction in ROCOP and could be a competitive reaction to CL ROP. If this polyether formation occurs, it should be observed by ^1H NMR spectroscopy as a broad resonance at 3.3 – 3.6 ppm.^[10]

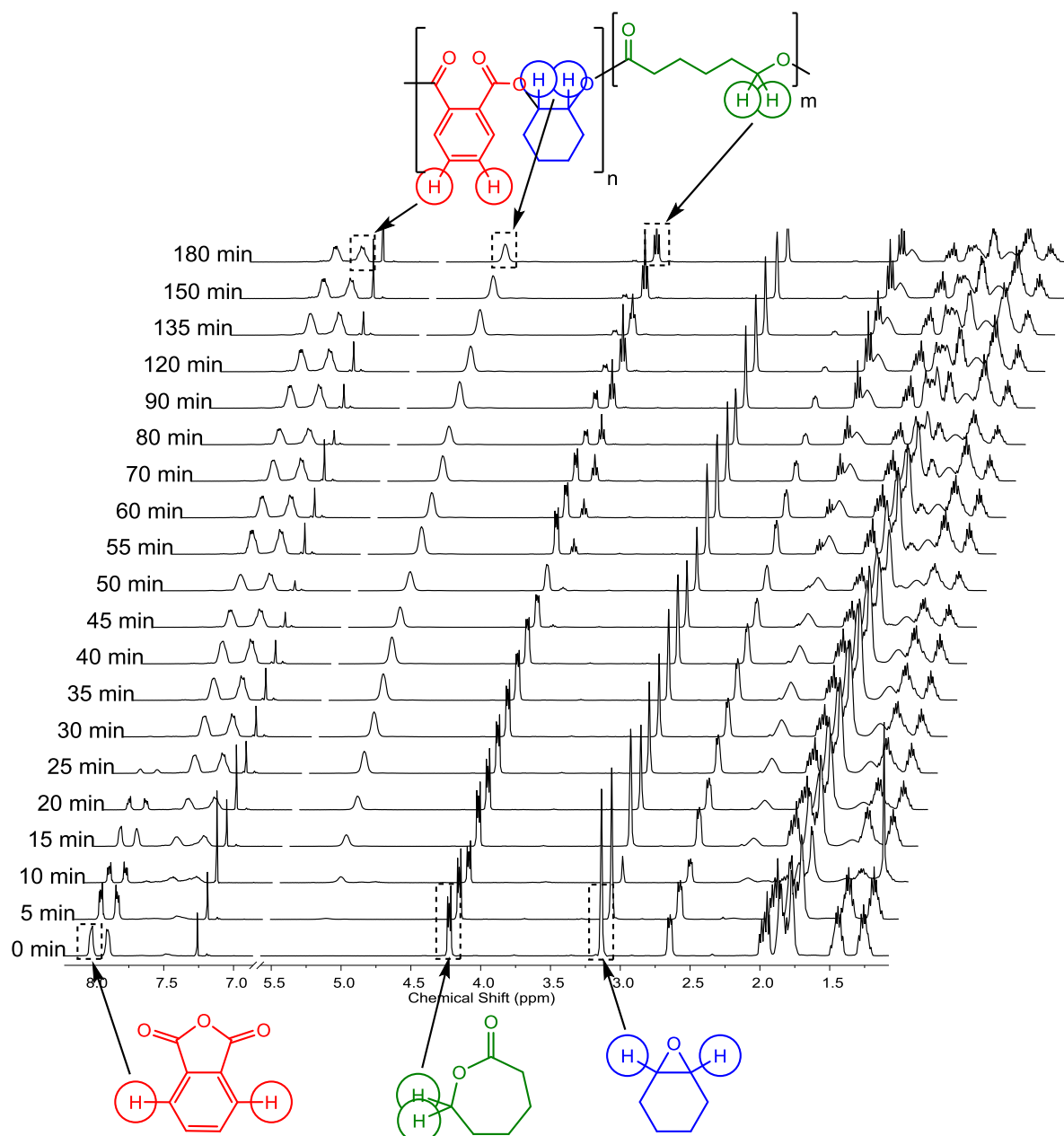


Figure 3. 2 - ^1H NMR spectra of the one-pot polymerisation of PA/CHO/CL at various times.

Next, the formation of poly(cyclohexene phthalate) (PCHPE) and poly(caprolactone) (PCL) were plotted against time (Figure 3. 3). Two trends were clearly visible: the PCHPE formation followed a zeroth order and the PCL formation, a first order trend. This was expected from the general reaction mechanisms for ROCOP and ROP and further kinetic analysis revealed the two observed rate constants, $k_{\text{obs,ROCOP}}^{\text{NMR}} = 5.44 \pm 0.39 \text{ M h}^{-1}$ and $k_{\text{obs,ROP}}^{\text{NMR}} = 1.56 \pm 0.05 \text{ h}^{-1}$ (see appendix).

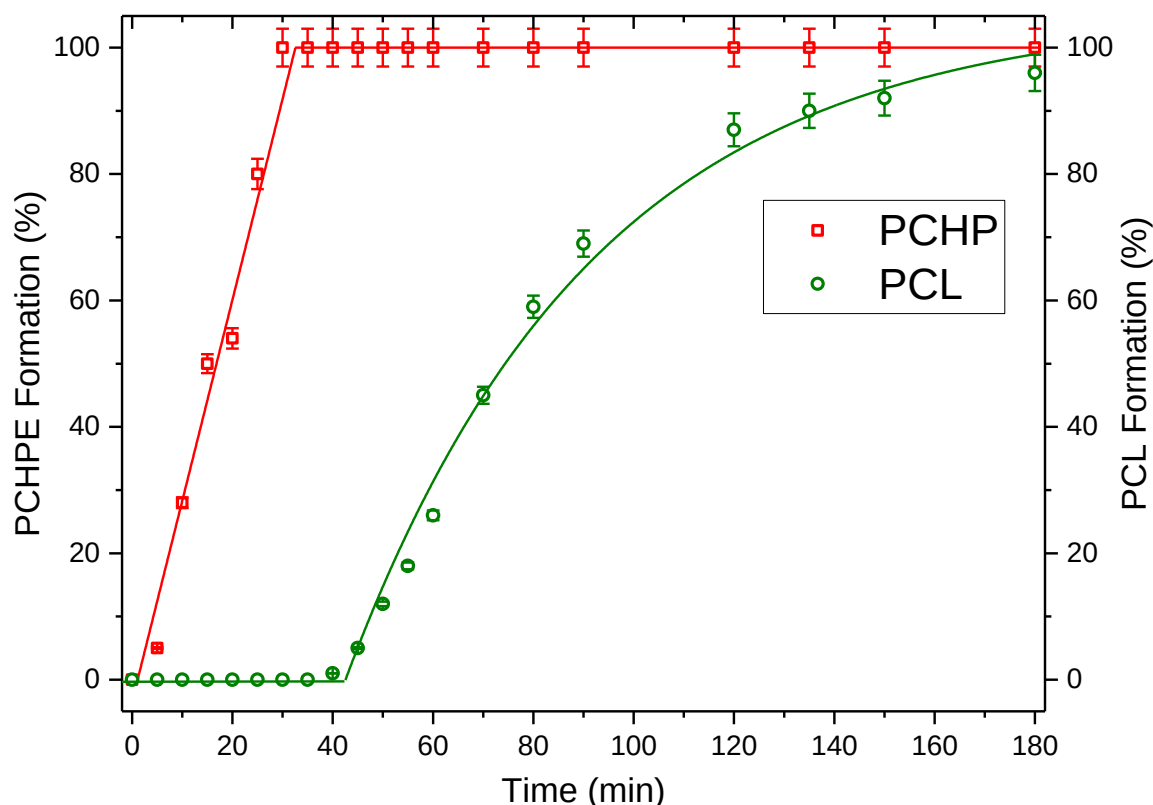


Figure 3. 3 – Conversion vs. time plot for one-pot polymerisation of PA/CHO/CL. An error of $\pm 3\%$ was applied to both plots.

The same reaction was monitored by *in situ* IR spectroscopy with identical conditions (Figure 3. 4). Again, the reaction proceeded in two stages, PA/CHO ROCOP followed by CL ROP. Kinetic analysis revealed comparable rate constants for both techniques, NMR and IR ($k_{obs,ROCOP}^{NMR} = 5.44 \pm 0.39$ vs. $k_{obs,ROCOP}^{IR} = 4.45 \pm 0.02 \text{ M h}^{-1}$ and $k_{obs,ROP}^{NMR} = 1.56 \pm 0.05 \text{ h}^{-1}$ vs. $k_{obs,ROP}^{IR} = 2.90 \pm 0.02 \text{ h}^{-1}$) (see appendix). Small deviations may be ascribed to the quantity of aliquots required for NMR analysis, each of which involved transferring the reaction into the glovebox and which overall results in cooling of the reaction mixture.

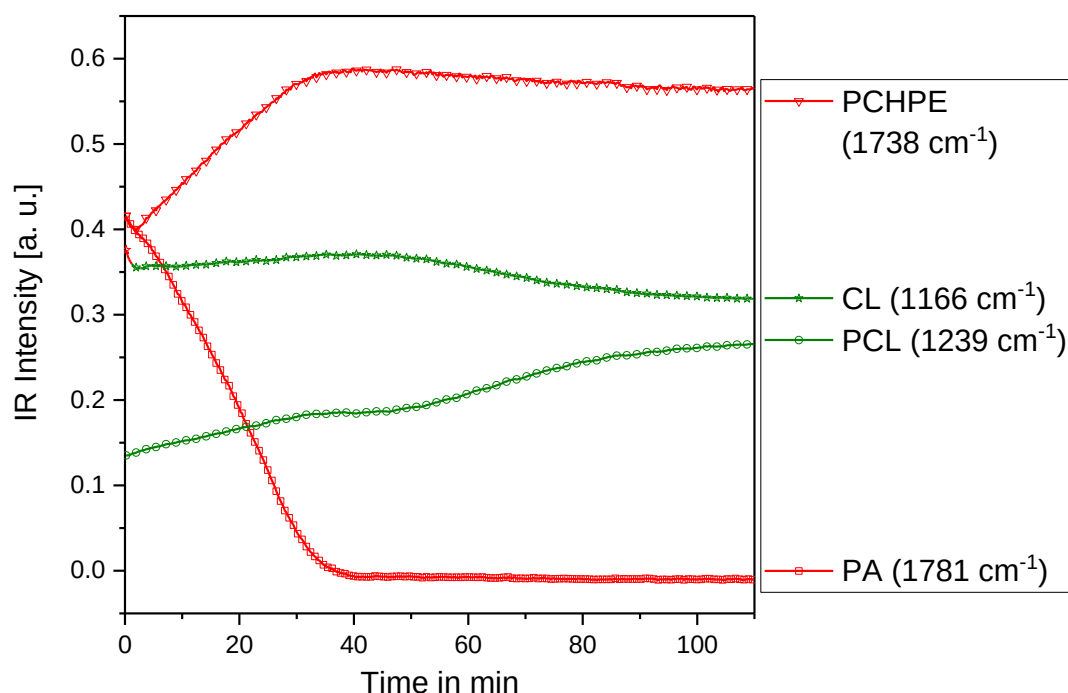


Figure 3. 4 – Monitoring of the one-pot polymerisation of PA/CHO/CL by *in situ* IR spectroscopy (one-point baseline at 1590 cm^{-1} applied).

To identify if a block copolymer or a mixture of homopolymers was formed, the reaction was monitored by GPC (Figure 3. 5). Significant broadening was observed during the ROP of CL and, at the end of the reaction, a high number-average molar mass and dispersity were obtained ($M_n=15,000 \text{ g mol}^{-1}$; $\bar{D}=1.79$). This may be explained by either transesterification ('block scrambling') or slow initiation of CL after ROCOP.

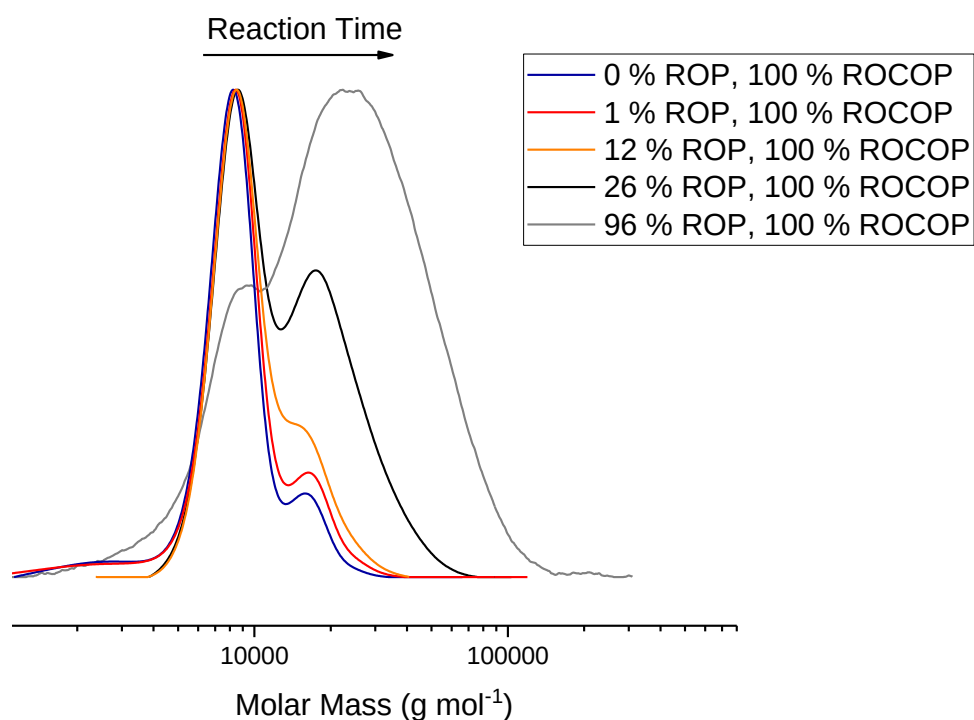


Figure 3. 5 – Monitoring of one-pot polymerisation of PA/CHO/CL by GPC.

Two scenarios are possible for transesterification, transesterification between different blocks or within one of the blocks. To identify which of these side-reactions is dominant, the polymer was analysed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and only signals corresponding to PCHPE and PCL were observed at 173.7 and 166.8 ppm, respectively (Figure 3. 6). No further signals between these resonances were observed as expected from a randomised copolymer.^[8] Consequently, transesterification is proposed to occur only within PCL segments.

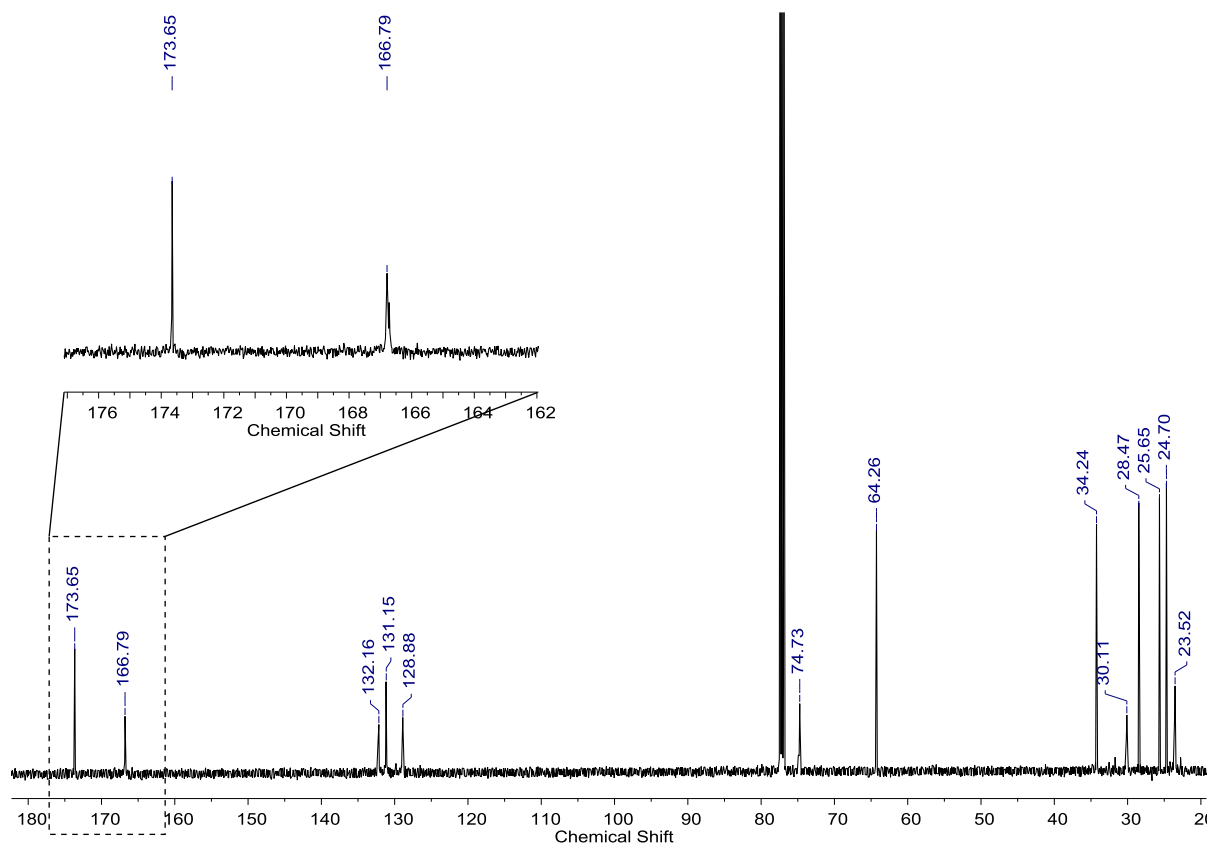


Figure 3. 6 - $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of obtained polyester from the one-pot polymerisation of PA/CHO/CL. The carbonyl region is enlarged.

Finally, slow initiation of ROP may result in further broadening. Whereas a secondary alkoxide should be formed after ROCOP with CHO, a primary alkoxide is the proposed propagating species for CL ROP. The effect of different alcohols on the ROP of CL was recently investigated with dizinc catalyst.^[11] The conclusion of this study was that the initiation rate constant (k_i) for secondary alcohols, such as CHD, was lower than the propagation rate constant (k_p) and a mixture of polymer architectures was obtained. This is a similar scenario as in the attempted 'switch' catalysis and only small differences between k_i and k_p might contribute to the observed broad molar mass distributions.

Although further experiments are necessary to identify the extent of transesterification and/or slow initiation, broad molar mass distributions do not allow for the synthesis of well-defined block copolymers. Sterically demanding substrates, which are inherently less prone to suffer from side-reactions and result in secondary alkoxides as propagating species, were tested next.

3.3. 'Switch' Catalysis with Norbornene Anhydride, Cyclohexene Oxide and ϵ -Decalactone

After transesterification was identified as a side-reaction, NBA, CHO and DL were investigated for 'switch' catalysis (Figure 3. 7).

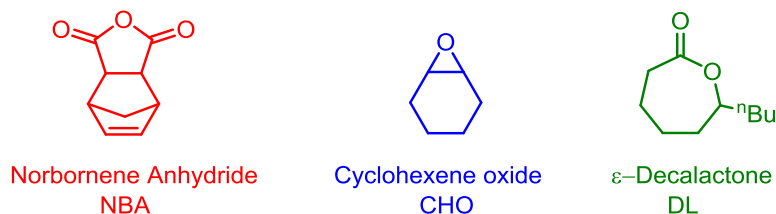
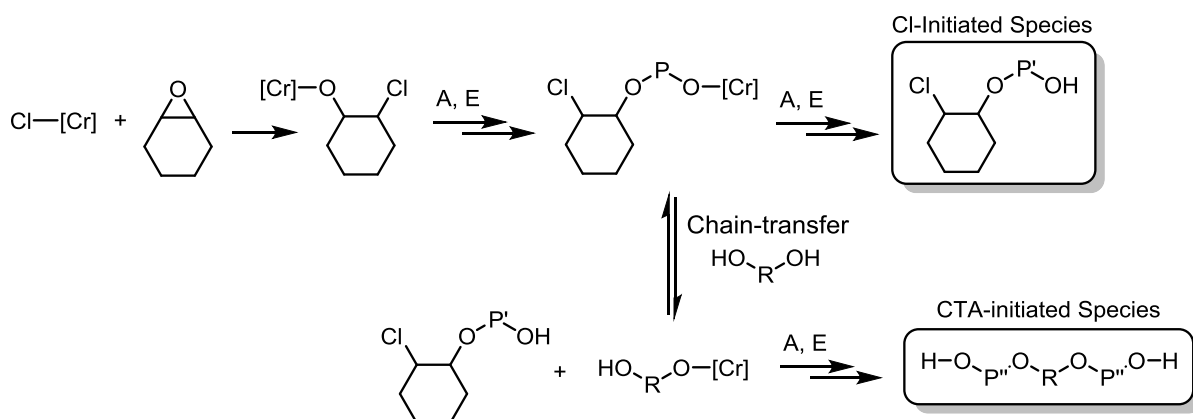


Figure 3. 7 – Structures of NBA, CHO and DL.

First, the activity for ROCOP, ROP and the combination of both processes was tested and high conversions (> 95 %) were achieved after a maximum of three days (see appendix). It should be noted that bimodal molar mass distributions were observed if no CTA was used (Figure 3. 8, left). This may be ascribed to a mixture of chloro-terminated, monofunctional chains (first distribution at lower molar mass) and dihydroxyl-terminated, bifunctional chains (second distribution at higher molar mass). The latter are typically formed through chain-transfer with bifunctional impurities, such as diols or dicarboxylic acids (Scheme 3. 2), which are generated from the reaction of trace amounts of water with the monomers. This is commonly observed for anhydride / epoxide and carbon dioxide / epoxide copolymerisations.^[9, 12-14]



Scheme 3. 2 – Formation of chloro- and dihydroxyl-terminated chains for the ROCOP of anhydrides and epoxides.

Trans-cyclohexene diol (CHD) was added as a bifunctional chain-transfer agent (CTA) to reduce the relative amount of chloro-initiated species. Once 15 equivalents of CHD were added, a monomodal molar mass distribution was obtained and > 95 % of all chains were

CHD-initiated (Figure 3. 8). It should be noted, however, that a small fraction of chloro-initiated species are still present in the mixture but do not have a significant contribution to the obtained molar mass distributions. Nonetheless, these chloride terminated chains are observed by MALDI mass spectrometry (see appendix).

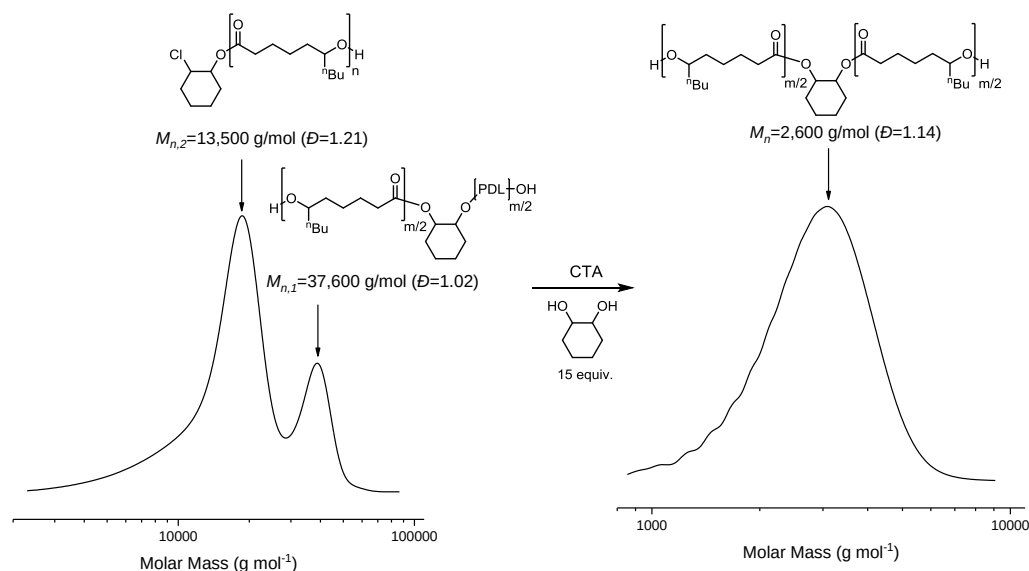


Figure 3. 8 - Effect of chain-transfer agent (CHD) on the homopolymerisation of DL.

To test for 'switch' catalysis, the one-pot polymerisation of NBA, CHO and DL was monitored by regular removal of aliquots, which were analysed by ^1H NMR spectroscopy (integrals determined vs. mesitylene as internal standard; Figure 3. 9). Overall, the reaction can be divided in two stages: First, only anhydride / epoxide ROCOP occurred over 1.5 hours producing poly(cyclohexene norbornene ester) (PCHNBE). This was observed by the decrease of the resonances of the anhydride and epoxide ($\delta = 6.4$ and 3.1 ppm, respectively) and the simultaneous growth of the corresponding polyester signals ($\delta = 4.6 - 4.8$ ppm). Importantly, no significant lactone consumption was observed during this stage ($<3\%$; $\delta = 4.3$ and 1.0 ppm). As a second step, DL was converted into PDL over the course of 36 hours.

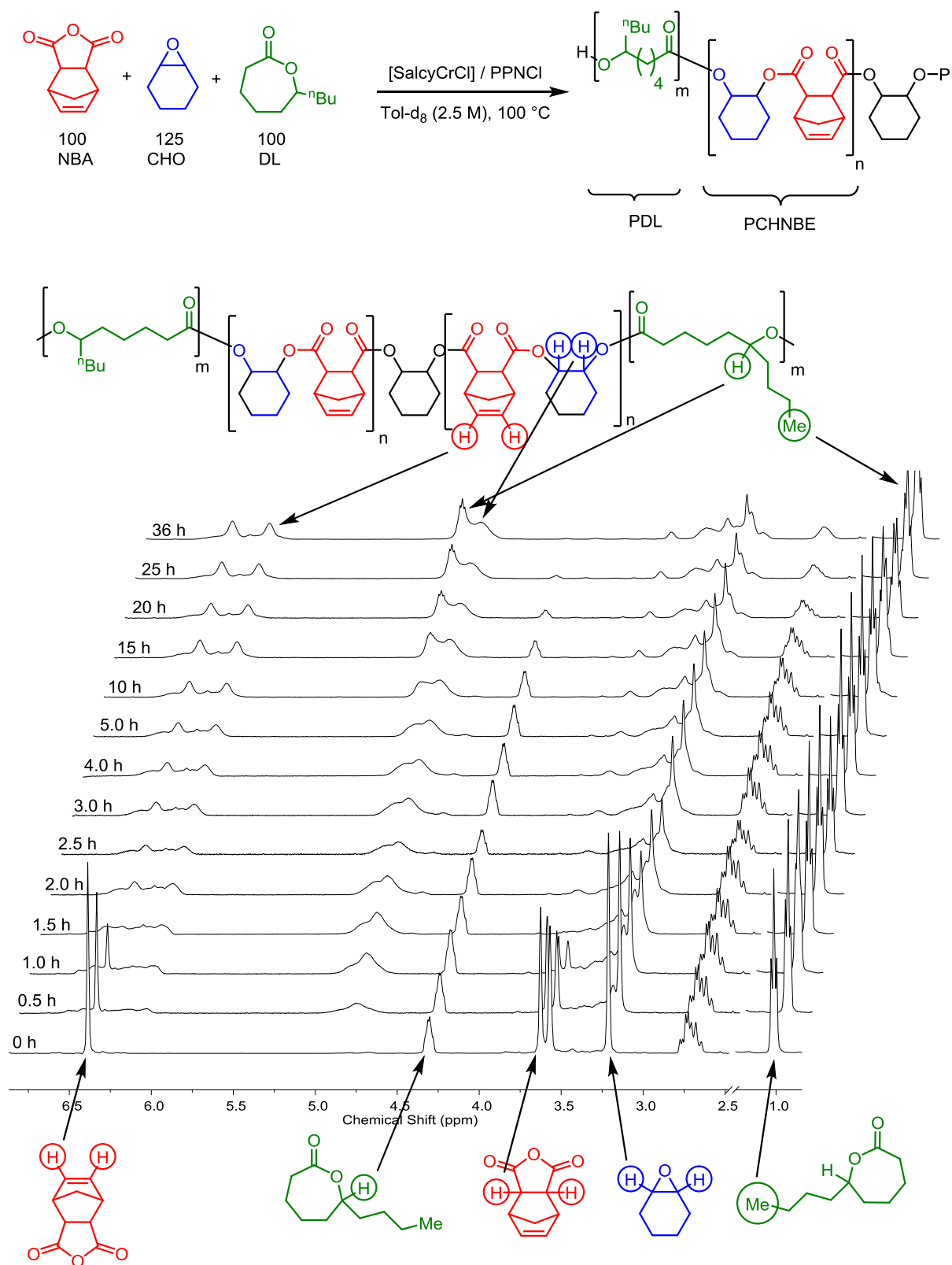


Figure 3. 9 – ^1H NMR spectra at various times of the one-pot polymerisation of CHO, NBA and DL. Reaction conditions: $[\text{SalcyCrCl}]:\text{PPNCI}:\text{CHD}:\text{NBA}:\text{CHO}:\text{DL} = 1:1:10:100:125:100$, Tol-d_8 (2.5 M), 100°C .

The two stages are clearly visible in the conversion vs. time plot and ROCOP was a fast reaction with a TOF $\sim 67 \text{ h}^{-1}$, compared to ROP, where a TOF $\sim 3 \text{ h}^{-1}$ was observed (Figure 3. 10).

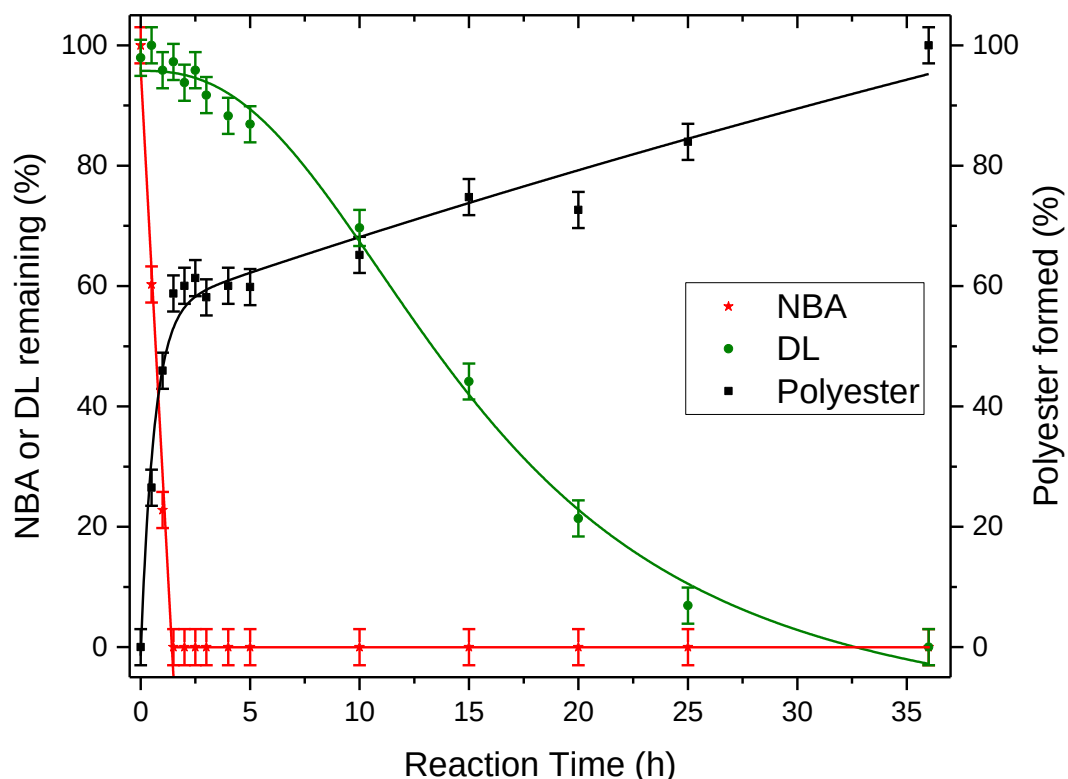


Figure 3. 10 – Conversion vs. time plot for one-pot polymerisation of NBA, CHO and DL. An error of $\pm 3\%$ was applied to all data points.

This data strongly indicated the selective one-pot combination of ROCOP and ROP. However, this could result in a mixture of homopolymers, a block copolymer or a statistical copolymer (*via* transesterification). To analyse the composition of the polymer, aliquots of the reaction were analysed by GPC (Figure 3. 11). A continuous increase in molar mass was observed throughout the reaction, while maintaining narrow, monomodal molar mass distributions ($1.11 < \bar{D} < 1.32$). This is a strong indication for the formation of block copolymers, as opposed to a mixture of homopolymers. In the latter case, the peak after ROCOP (purple in Figure 3. 11) should not increase in mass and be found even at the end of the ROP stage, which was not observed. Most importantly, a significant difference to the previously attempted 'switch' catalysis with PA, CHO and CL was found: Whereas large dispersities were found with CL (Figure 3. 5), low dispersities were now obtained. This suggested that transesterification was successfully suppressed, when DL as a sterically more demanding analogue to CL is used.

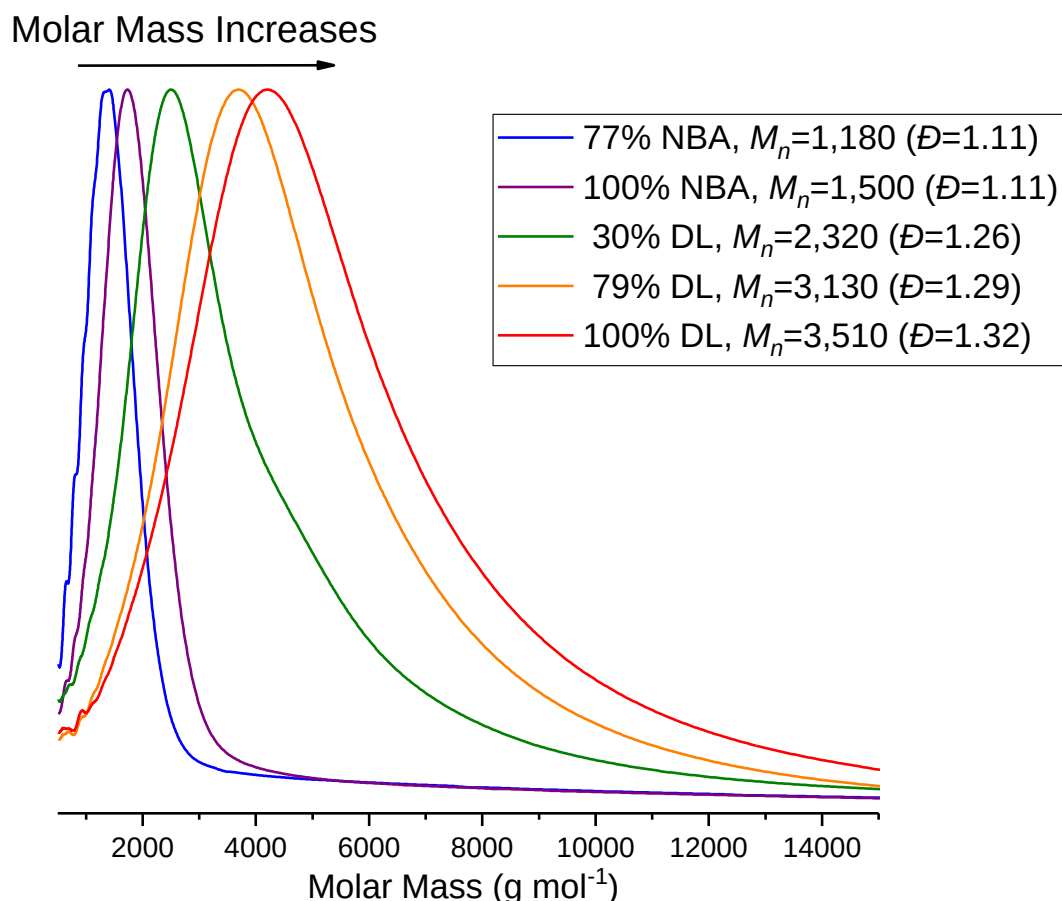
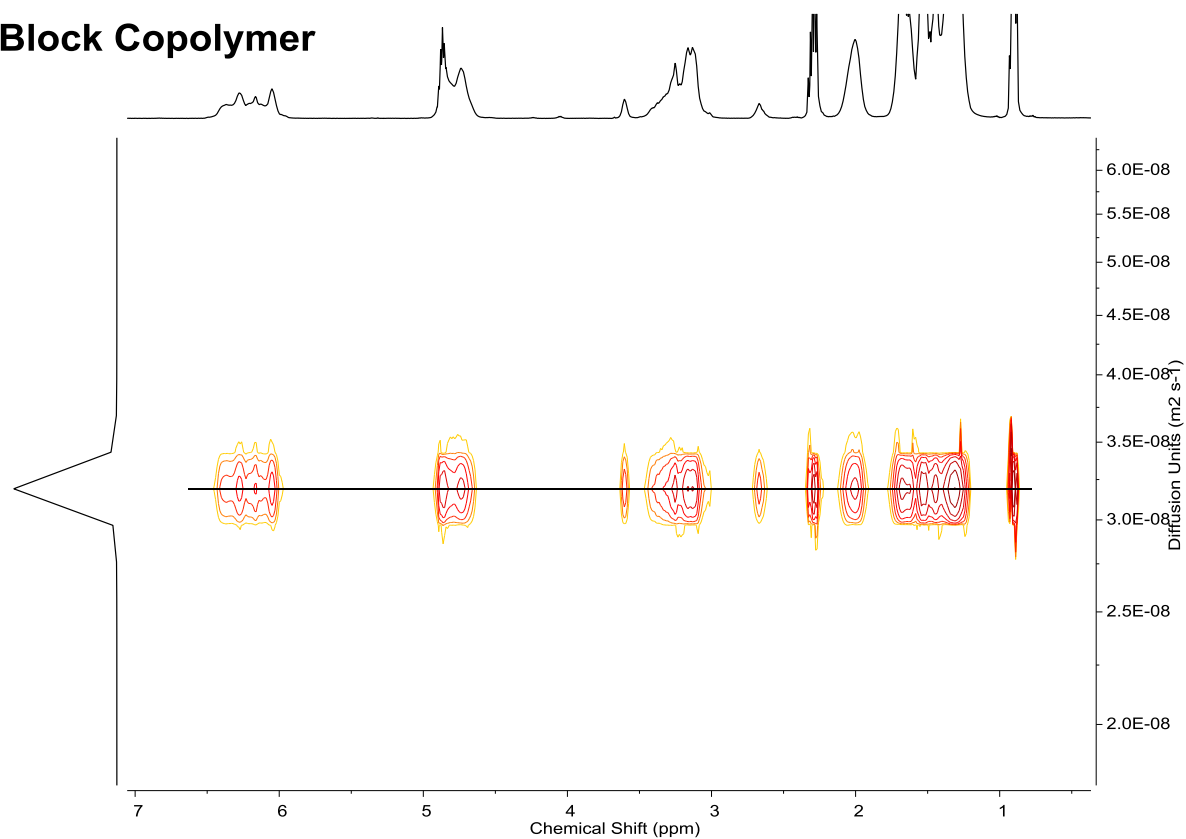


Figure 3. 11 – GPC Traces at different stages of the one-pot polymerisation of NBA, CHO and DL (monomer conversion is given in %).

The polymer was further analysed by DOSY NMR and compared to a blend of homopolymers with similar weights (Figure 3. 12, left). Whereas one diffusion coefficient was observed for the block copolymer (diffusion coefficient $D^{\text{Block}} = 3.10 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$), two different diffusion coefficients were found for the blend ($D^{\text{PCHNBE}} = 2.58 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1} + D^{\text{PDL}} = 2.36 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$). This further confirmed that both blocks were attached to each other, in line with successful 'switch' catalysis.

Block Copolymer



Blend of Homopolymers

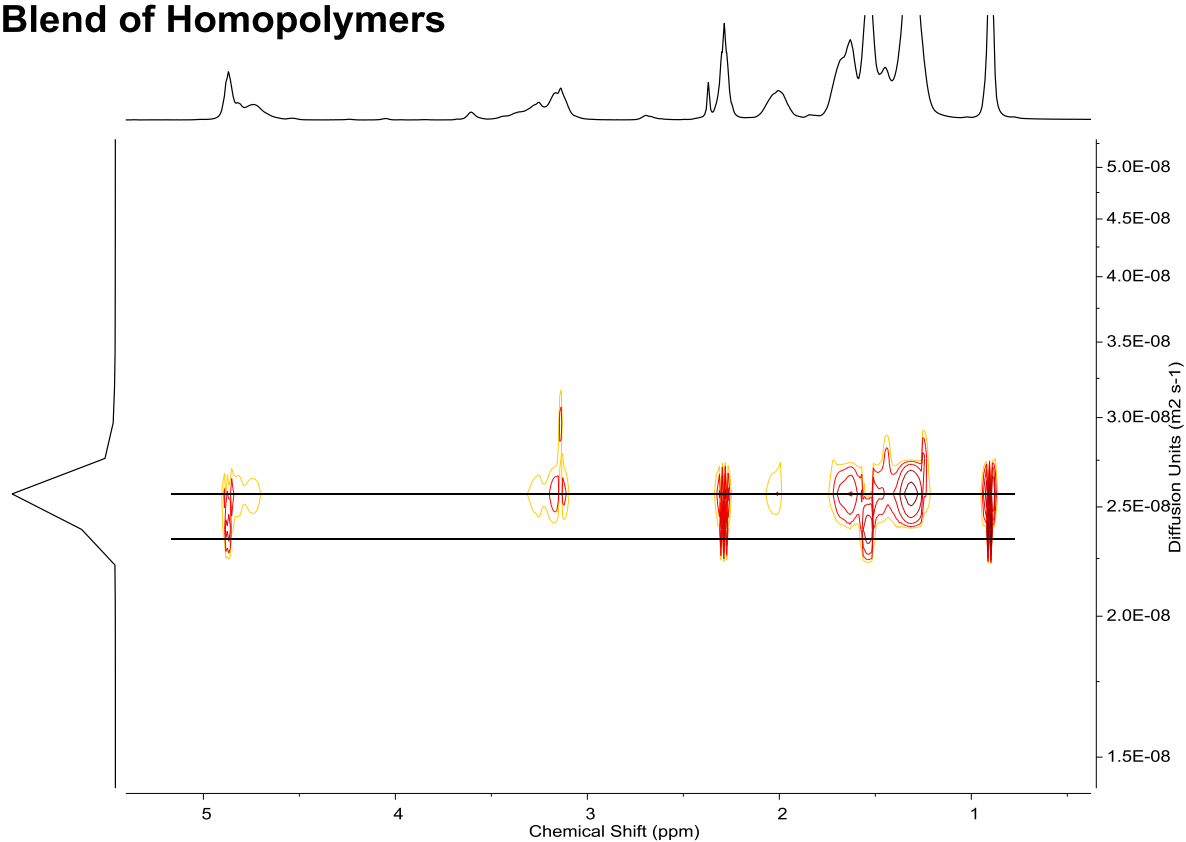


Figure 3. 12 - DOSY NMR of block copolyester (top) and blend of homopolymers (bottom).

The end groups of the obtained polymers were analysed after their reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane, in the presence of bisphenol A as an internal standard (Figure 3. 13). The resulting phosphites were analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and different chemical shifts were found for individually synthesised PCHNBE and PDL after ROCOP and PDL after ROP. For a mixture of homopolymers, both resonances should be detected and in 'switch' catalysis, exclusively PDL-terminated chains should be present. The latter was observed for the proposed block copolyester as only one signal at 147.1 ppm was found. This measurement was repeated with various recycle delays ($D_1 = n \cdot T_1$ with $n = 0.5 - 10$) to account for different relaxation times of the two species and one signal at 147.1 ppm was observed in all cases (see appendix). It should be noted that the polymer does not degrade during this assay, as observed by similar GPC traces before and after analysis (not shown).

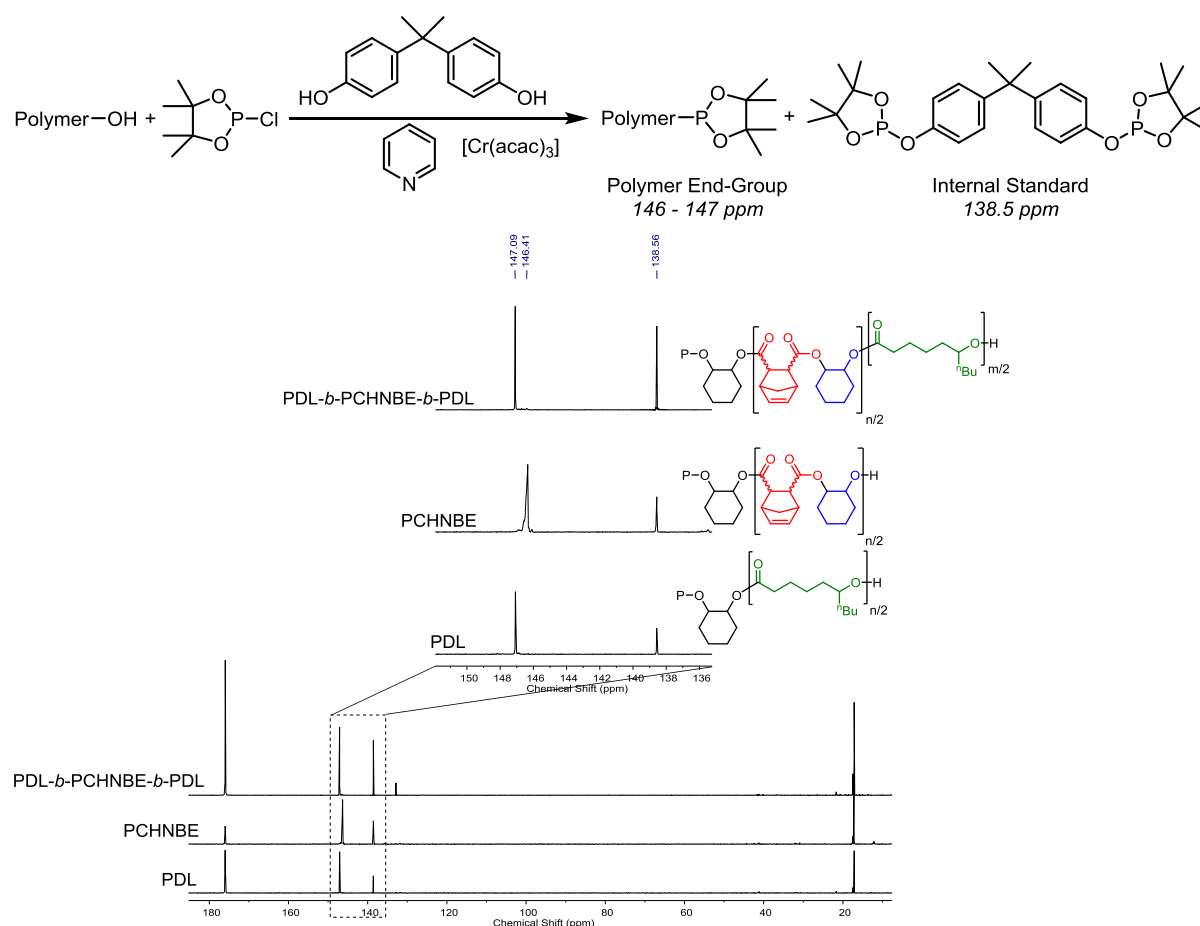


Figure 3. 13 – $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of block copolymer, PCHNBE and PDL after the reaction with 2-chloro-4,4,5,5-tetramethyldioxaphospholane in the presence of bisphenol A as internal standard, pyridine and chromium(III) acetylacetonate. The peaks can be ascribed to the unreacted phosphorus reagent (176 ppm), the phospholane after the reaction with the polymer end group (146-147 ppm), the internal standard (138 ppm) and water (132 ppm).^[15-17]

Moreover, the polyester was isolated by precipitation from hexane and analysed by ^1H and ^{13}C NMR spectroscopy: whereas independently synthesised PCHNBE was insoluble in pentane, PDL of similar chain length is soluble and could not be isolated. This was in contrast to the block copolymer, which was insoluble and PDL signals of similar intensity were observed by ^1H NMR spectroscopy before and after isolation (see appendix). Signals attributed to both blocks were found in the purified polymer by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, i.e. resonances at 173 ppm (PDL) and 172 ppm (PCHNBE, Figure 3. 14 bottom). A number of low-intensity signals were also observed which may be assigned to (partially) epimerised polyester linkages (see next page).

To investigate if transesterification between blocks occurs during the reaction, the polymer was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which deliberately introduces scrambling between blocks.^[8] In this control reaction, further intermediate shifts were observed, suggesting that transesterification is not a dominant side-reaction (Figure 3. 14).

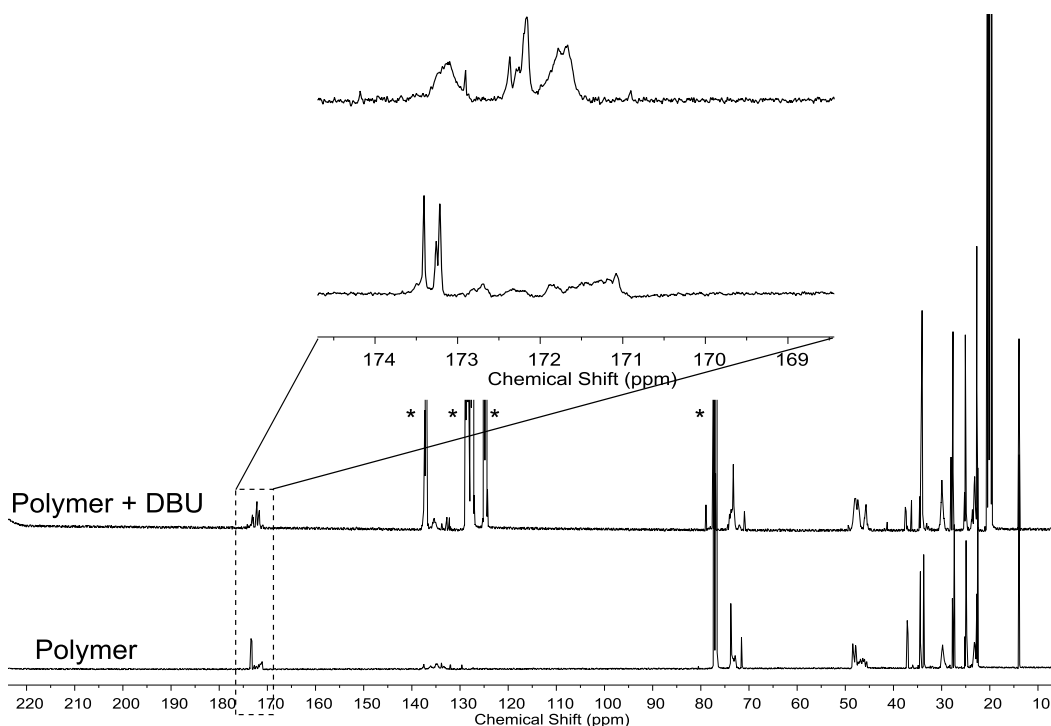


Figure 3. 14 - $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of isolated polymer before (bottom) and after transesterification with DBU (top; carbonyl region extended). Residual solvent signals are marked with *.

To determine the relative stereochemistry of the polyester linkages, the polymer was degraded with lithium aluminium hydride.^[18] Changes in the relative stereochemistry can be attributed to epimerisation caused by basic species and is common for polymerisations with PO, particularly at high conversions.^[19] To examine the extent of this undesired side-reaction, the obtained degradation products were analysed by ^1H NMR spectroscopy. The signals in the alkene region were compared to a control reaction with the unreacted

anhydride (100% *cis* content). The obtained polymer contained 66% *cis* and 34 % *trans* linkages (Figure 3. 15).

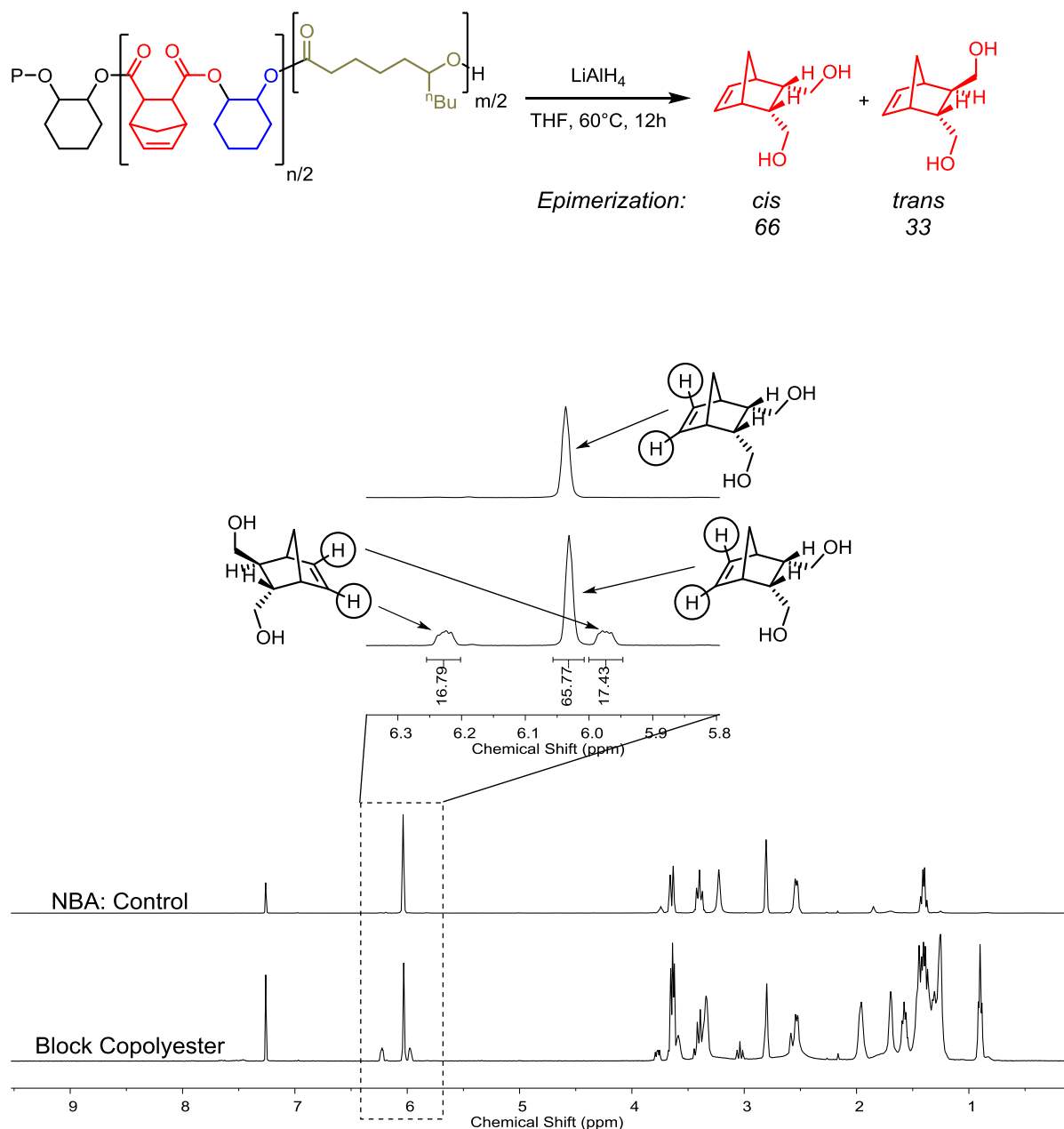


Figure 3. 15 - Degradation products of NBA the produced polymer with LiAlH_4 . The relevant alkene section for the polymer-degradation product is enlarged to determine the *cis:trans* ratio.^[18]

For all reactions, an excess of epoxide was used, which may result in the formation of polyether, particularly over the long reaction times required for DL ROP. The analysis is complicated by similar chemical environments of the chain-transfer agent and the polyether in ^1H NMR spectroscopy ($\delta \sim 3.5$ ppm). For this reason, ^1H NMR spectra of PDL samples synthesised in the presence and the absence of CTA were compared; the polyesters were

synthesised under identical reaction conditions and in the presence of excess epoxide. In the absence of CTA, no significant resonances between $\delta = 3.4$ and 3.8 ppm were found at 98 % conversion and a large amount of unreacted CHO was found at $\delta = 3.1$ ppm. Moreover, the PDL sample containing CTA was analysed by MALDI and only repeating units of $m/z = 170.1$ were found, which further confirmed that no polyether linkages are formed randomly throughout the reaction (see appendix).

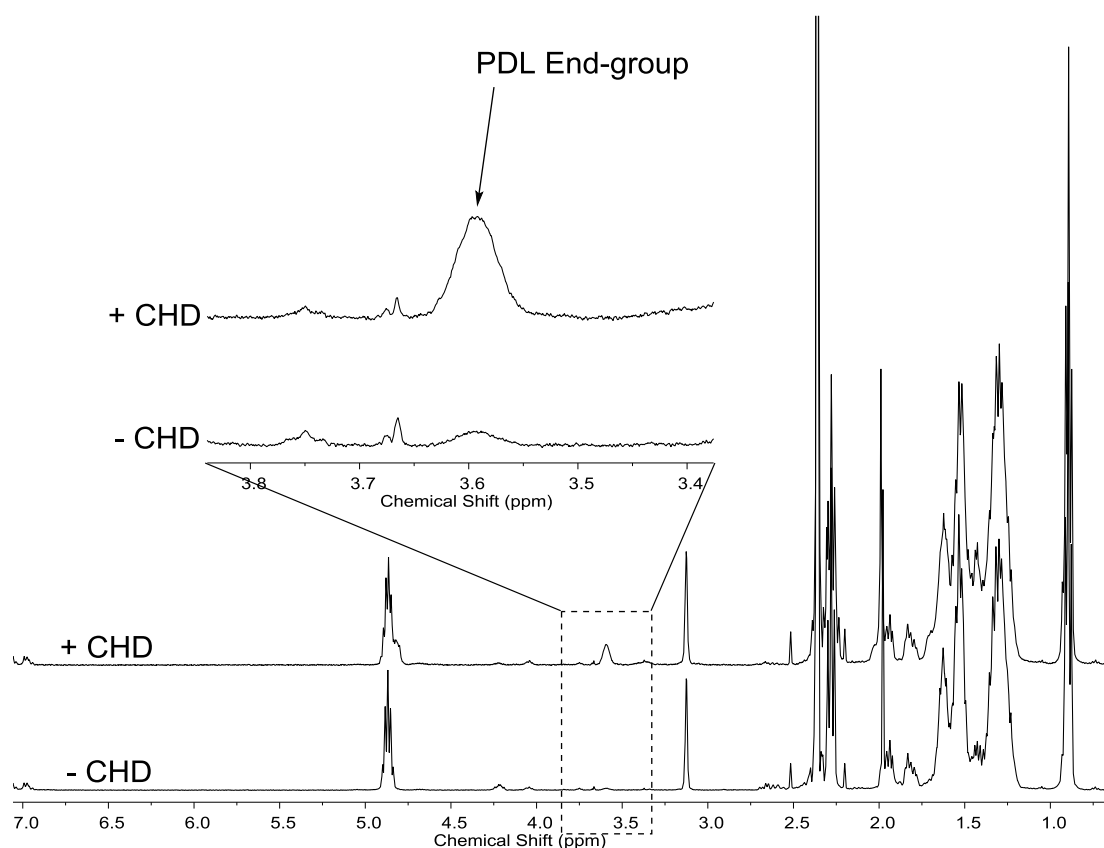


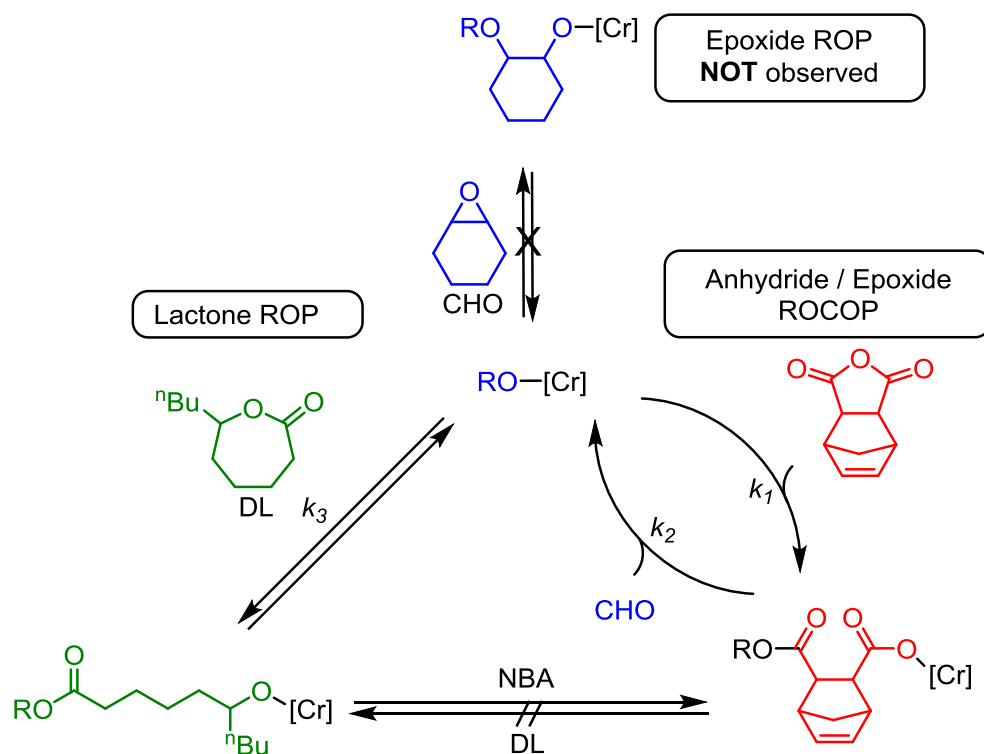
Figure 3. 16 – ^1H NMR spectra of cure reaction mixture of PDL samples synthesised with and without CHD; unreacted CHO can be found at $\delta = 3.1$ ppm.

In summary, all analytical tests confirmed the formation of only one block copolymer structure, PDL-*b*-PCHNBE-*b*-PDL.

3.4. Mechanistic Hypothesis

In this 'switch' catalysis, two different catalytic cycles are combined: anhydride / epoxide ROCOP and lactone ROP. Overall, it is proposed that ROCOP and ROP are connected through a joint chromium alkoxide intermediate (Scheme 3. 3). ROCOP is a two-step process in which an anhydride is attacked first, resulting in a metal carboxylate species (k_1). This intermediate reacts with CHO in a second step, which (re)-generates the initial chromium alkoxide species (k_2). Once ROCOP is completed, ROP of DL occurs (k_3), which proceeds through a metal alkoxide intermediate. It should be noted that the ROP of epoxide forming polyether was not observed.

Similar to reactions with dizinc catalysts, the selectivity is proposed to be a result of differences in rate between ROCOP and ROP as well as a higher barrier to the reaction of the chromium carboxylate with the lactone (or the chromium alkoxide with the epoxide).^[4, 8] Thus, the reaction between the chromium carboxylate intermediate and lactones was hypothesised to be unfeasible.



Scheme 3. 3 - Mechanistic Hypothesis for 'Switch' Catalysis involving NBA, CHO and DL.

To test this hypothesis, a range of experiments were conducted. First, the reactivity of the chromium carboxylate intermediate towards ROP was investigated: preliminary kinetic analyses based on *in situ* IR spectroscopy indicated a zero order in anhydride concentration on the rate of ROCOP (see appendix). This suggests that the ring-opening of CHO was the

rate-limiting step of the reaction and the chromium carboxylate was the resting species of the reaction. To investigate the reactivity of the carboxylate species with lactones, the reaction was performed with an excess of anhydride and lactone relative to the epoxide (DL:NBA:CHO, 200:200:125). The reaction proceeded until the feedstock was deprived of epoxide (~ 60% NBA conversion). At this stage, it was assumed that only the chromium carboxylate was present. The reaction was continued for four days and no significant amounts of PDL were formed, which indicated a high barrier for the ROP of DL for the carboxylate (Figure 3. 17, A). To test if the catalyst was deactivated under these conditions, epoxide (200 equiv.) was re-introduced into the mixture. Full anhydride consumption and high conversions of DL were observed, indicating the formation of a block copolyester (Figure 3. 17, B).

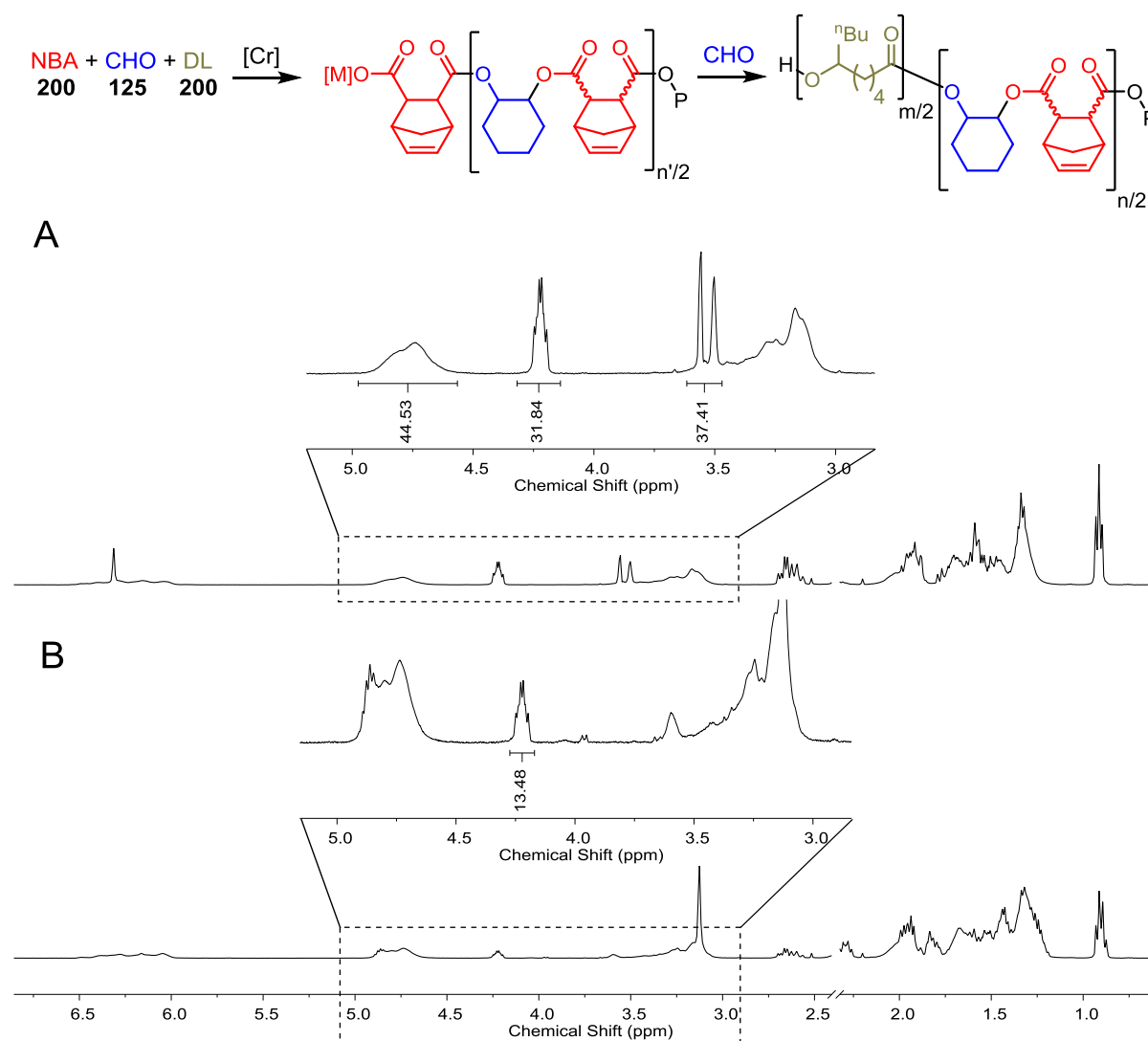


Figure 3. 17 – ^1H NMR Spectra for the polymerisation of NBA/CHO/DL in the excess of NBA (A, first stage) and after the addition of CHO (B, second stage).

The formation of a block copolymer was further confirmed by GPC analysis before and after CHO addition. As expected from a continuous incorporation of monomer, the monomodal peak increased in weight, while maintaining a low dispersity (Figure 3. 18). It should be noted that this hypothesis did not include further species and / or catalyst – cocatalyst equilibria.

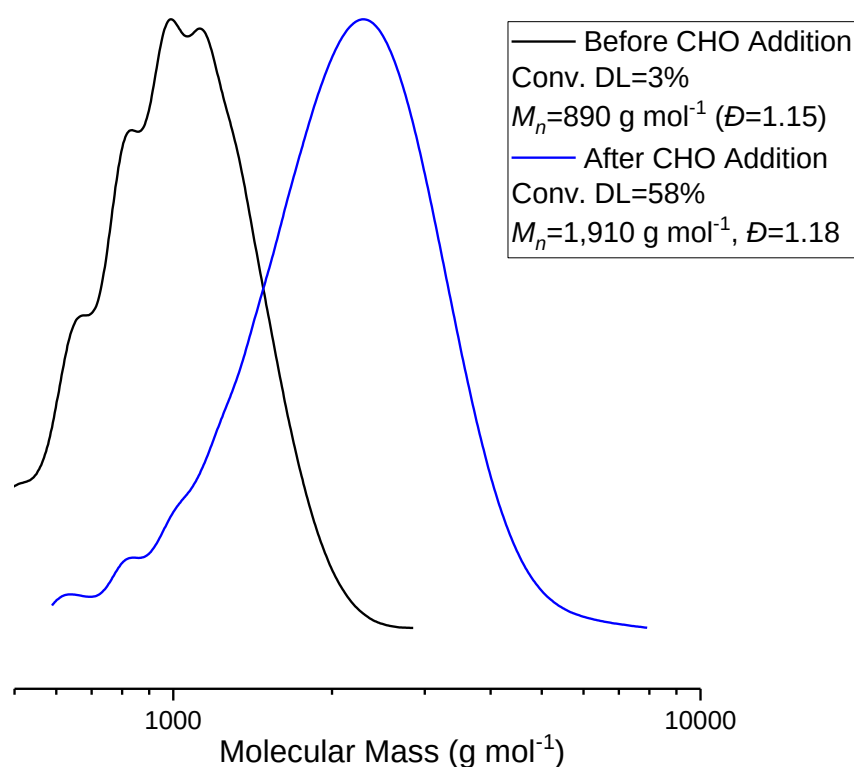


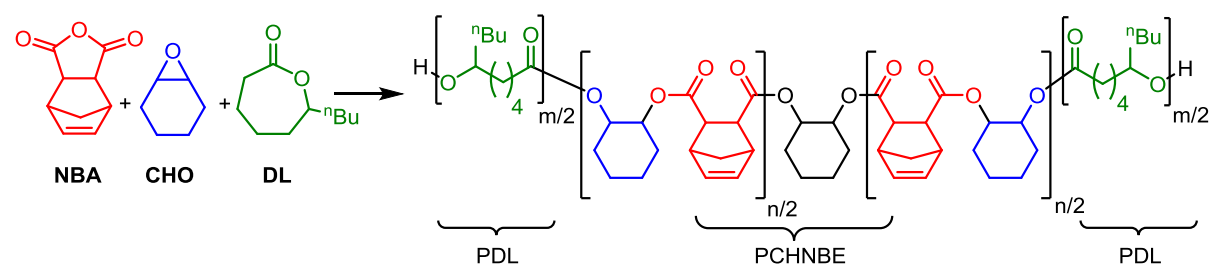
Figure 3. 18 – GPC traces of the polymerisation of NBA/CHO/DL before and after the addition of CHO.

3.5. Thermal Analysis of PDL-*b*-PCHNBE-*b*-PDL

Once the product of 'switch' catalysis was identified, thermal properties of these ABA triblock copolyesters were analysed. The rationale behind choosing this particular set of monomers was, besides introducing steric bulk to minimise side-reactions, the combination of hard and soft blocks to obtain phase-separated materials. Phase separation can be indicated by DSC, in which case two different glass-transition temperatures, corresponding to each block, should be observed.^[7]

Different polyesters ranging from 27 to 96 wt% of PCHNBE were synthesised by changing the relative amounts in the monomer feedstock (Table 3. 1). In most cases, high conversions of both anhydride and lactone (> 95%) were observed. In all cases, monomodal molar mass distributions with M_n values < 5,000 g mol⁻¹ and dispersities $\mathcal{D}$ < 1.3 were obtained. With respect to thermal properties, only one T_g value was observed over a range of compositions, which was indicative of block miscibility.

Table 3. 1 – PDL-*b*-PCHNBE-*b*-PDL copolymers of different compositions.



NBA:CHO:DL ^[a]	Conversion [%] ^[b]		wt% PCHNBE: wt% PDL ^[c]	M_n ($\mathcal{D}$) [g mol ⁻¹] ^[d]	T_g [°C] ^[e]	$T_{g,calc}$ [°C] ^[f]
	NBA	DL				
0:100:800 ^[g]	N. A.	> 95	0	6,670 (1.07)	-54	-54
100:125:400	99	> 95	27:73	4,810 (1.18)	-30	-29
100:125:300	99	> 95	34:66	4,270 (1.19)	-21	-22
100:125:200	99	> 95	44:56	3,340 (1.25)	-4	-11
100:125:100	99	> 95	61:39	2,510 (1.27)	26	11
200:250:100	99	> 95	76:24	2,890 (1.22)	57	33
300:375:100	99	> 95	82:18	3,110 (1.17)	71	43
400:500:100	99	80	89:11	3,260 (1.15)	84	55
500:625:100	99	30	96:4	3,310 (1.13)	111	69
800:1000:0 ^[g]	99	N. A.	100	6,100 (1.18)	77	77

^[a] Molar ratio of starting materials. ^[b] Determined by ¹H NMR spectroscopy (see appendix).

^[c] Weight fractions of polyester blocks calculated from molar ratios in feedstock.

^[d] Determined by GPC, THF, 30 °C, using polystyrene standards (see appendix).

^[e] Determined by DSC measurements from -90 – 160 °C at 10°C min; second or third heating cycle reported. ^[f] Based on Fox Equation with $T_g(\text{PCHNBE})=77^\circ\text{C}$ and $T_g(\text{PDL})=-54^\circ\text{C}$. ^[g] 20 equiv. CTA used.

The observed values were in good agreement with the expected values for miscible blocks based on the Fox equation for polymers with a high content of PDL; in the case of predominantly 'hard' blocks, deviations became more pronounced (values are given in Table 3. 1). This may be result of the low value of the synthesised PCHNBE homopolymer (77 °C) compared to similar polyesters based on CHO (140-150 °C).^[20] These low T_g values may further be ascribed to low molecular weights ($M_n = 5,300 \text{ g mol}^{-1}$ vs. $11,600 \text{ g mol}^{-1}$) and/or a mixture of *cis* and *trans* ester linkages (ca. 50 % vs. 99 %). No indications of crystalline regions were found, which further indicates that the obtained polyesters were amorphous. Nonetheless, T_g values could be tuned over a range of 140 °C, from – 30 °C to 111 °C by varying the relative content of hard (PCHNBE) and soft blocks (PDL).

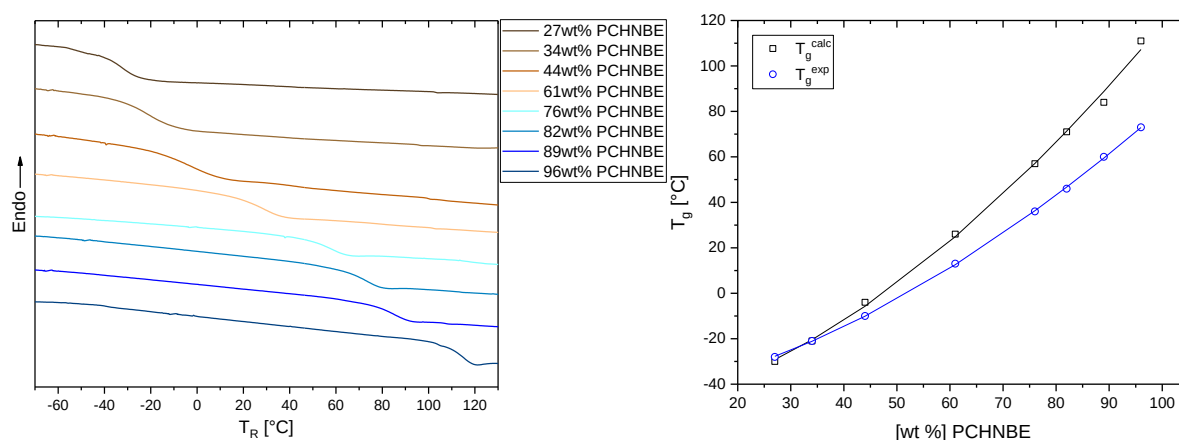


Figure 3. 19 – DSC Thermograms for PDL-*b*-PCHNBE-*b*-PDL with different compositions (left) and comparison with theoretical values (Fox equation for miscible polymers) (right).

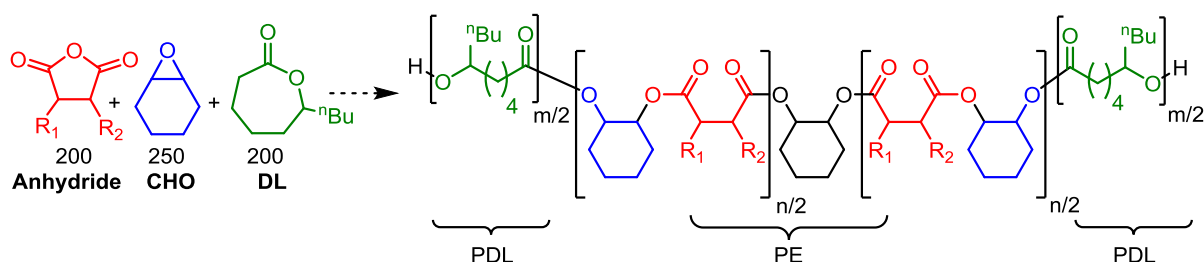
3.6. Scope

3.6.1. Anhydrides

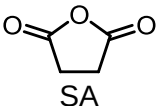
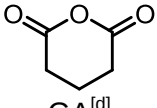
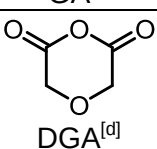
A range of anhydrides was tested for 'switch' catalysis with CHO and DL, including mono-, bi- and tricyclic derivatives (Table 3. 2 - Table 3. 4).

For monocyclic unsaturated substrates (MA, CitrA), partially insoluble materials were obtained. This was likely due to thermal cross-linking during the long reaction times required. Similar complexes, based on Schiff-base ligands with Zn(II) and Co(III), have been reported for the copolymerisation of MA/CHO at 110 °C, but with shorter reaction times of 2.5 hours, as opposed to 3 days. In these literature cases, broad dispersities and polyether formation were also observed at high conversions of the anhydride ($\bar{D} = 1.2 - 1.8$).^[21-23] To avoid cross-linking, the saturated analogue to MA, SA, was tested and did not suffer from this side-reaction. However, low DL incorporation and bimodal molar mass distributions were obtained. Again, the successful copolymerisation of SA/CHO has been reported (with Zn(II) and Al(III) catalysts), but either at lower reaction temperatures or shorter reaction times, and bimodal distributions were typically obtained (when GPC traces were reported).^[24-26] For saturated, six-membered derivatives (GA, DGA), monomodal molar mass distributions and high conversions of DL were found. However, dispersities were broad compared to NBA ($\bar{D} = 1.53$ vs. 1.32), suggesting transesterification. This may be ascribed to insufficient steric bulk and/or long reaction times as similar side-reactions were observed with CL (Figure 3. 4). For this reason, monocyclic substrates were not suitable in this particular 'switch' catalysis.

Table 3. 2 – Scope of 'Switch' catalysis with various anhydrides.^[a]



Anhydride	Conversion [%] ^[b]			M_n ($\bar{D}$) [g mol ⁻¹] ^[c]
	Anhydride	CHO	DL	
 MA	99	73	< 5	N. D. ^[e]
 CitrA	99	82	< 5	2,500 (10.67)

 SA	99	95	< 5	4,190 (1.06) 1,850 (1.09)
 GA ^[d]	99	86	> 90	2,080 (1.31)
 DGA ^[d]	99	95	82	2,960 (1.53)

^[a] Polymerisation Conditions: [SalcyCrCl]:[PPNCl]:[CHD]:[CHO]:[DL]:[Anhydride] = 1:1:15:250:200:200, 100 °C, 2.5 M in toluene, 24-96 h. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, in THF at 30 °C, calibrated using polystyrene standards. ^[d] 20 equivalent of CHD used.

In the case of sterically more hindered bicyclic anhydrides, narrow, monomodal molar mass distributions and high conversions of anhydride and DL (> 95%) were obtained (Table 3. 3). In all cases, perfectly alternating polyesters were found by MALDI and a continuous increase in molar mass throughout the reaction was observed by GPC (see appendix). For PA, the attachment of both blocks could be further confirmed by comparison of RI and UV traces in GPC, as only the polyester from ROCOP contains a chromophore and the UV-active peak increased in mass during ROP (see appendix). Moreover, the ¹³C{¹H} NMR spectrum of the isolated polymer could be compared to recent work on zinc catalysts, as the same block copolymer was synthesised. In this particular case, the authors deliberately subjected the sample to transesterification and peaks at intermediary shifts compared to the resonances of the block copolymer were found (δ = 168.1 and 164.2 ppm from transesterification vs. δ = 172.4 and 166.5 ppm for block copolyester).^[8] Intermediary resonances were absent in the material obtained from 'switch' catalysis with [SalcyCrCl] and similar chemical shifts as reported for the block copolymer were found, which further confirmed that transesterification was not a dominant side-reaction (see appendix). One important difference should be noted when the three bicyclic anhydrides are compared: for PA and THPA, the rate of ROCOP is significantly faster than ROP ($\text{TOF}_{\text{ROCOP}} / \text{TOF}_{\text{ROP}} > 45$), which resulted in the formation of block copolyesters. This is in contrast to CA, where ROCOP was significantly slower and competitive to ROP ($\text{TOF}_{\text{ROCOP}} / \text{TOF}_{\text{ROP}} = 1.4$) and a statistical copolymer is proposed.

Table 3. 3 - Scope of 'switch' catalysis with bicyclic anhydrides.^[a]

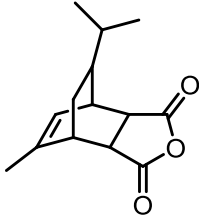
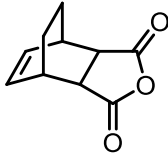
Anhydride	Conversion [%] ^[b]			M_n (Đ) [g mol ⁻¹] ^[c]	TOF _{ROCOP} / TOF _{ROP} ^[d]
	Anhydride	CHO	DL		
 CA	99	80	99	6,700 (1.14)	1.4
 PA	99	76	99	6,200 (1.20)	64
 THPA	99	79	99	4,000 (1.26)	48

^[a] Polymerisation Conditions: [SalcyCrCl]:[PPNCl]:[CHD]:[CHO]:[DL]:[Anhydride] = 1:1:15:250:200:200, 100 °C, 2.5 M in toluene, 24-96 h. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, in THF at 30 °C, calibrated using polystyrene standards.

Finally, well-defined block copolymers were obtained with tricyclic anhydrides (NBA, TCA1, TCA2). Similar to bicyclic anhydrides, high conversions (> 95%), perfectly alternating polyesters from ROCOP and a continuous increase in molar mass were observed. In all cases, ROCOP proceeded ROP and rate differences of up to a factor of 100 were found (TCA2). The polyesters were further isolated from pentane and the composition before and after isolated did not change. Finally, all materials were fully characterised including several 2D NMR techniques.

Table 3. 4 - Scope of 'switch' catalysis with tricyclic anhydrides.^[a]

Anhydride	Conversion [%] ^[b]			M_n (Đ) [g mol ⁻¹] ^[c]	TOF _{ROCOP} / TOF _{ROP} ^[d]
	Anhydride	CHO	DL		
 NBA	99	74	99	3,500 (1.32)	22

 TCA1	99	77	99	6,700 (1.20)	32
 TCA2	99	67	99	5,800 (1.20)	103

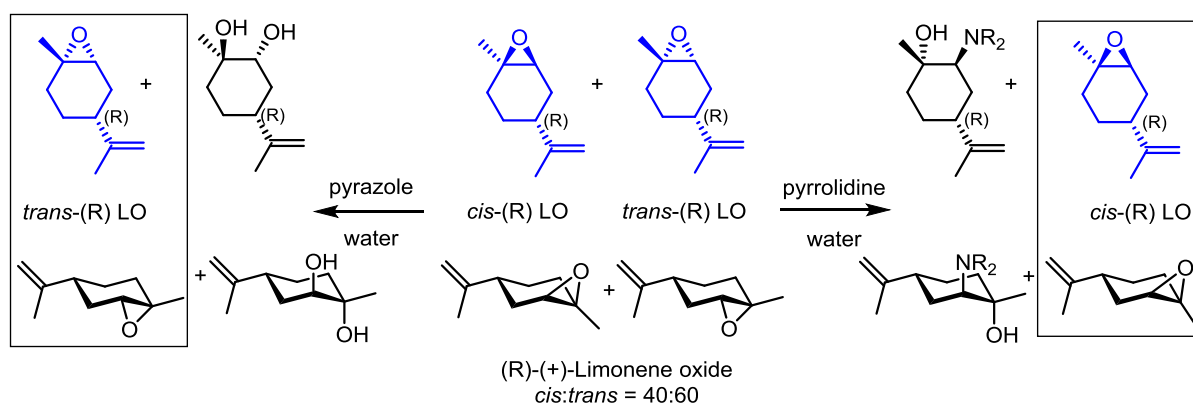
^[a] Polymerisation Conditions: [SalcyCrCl]:[PPNCl]:[CHD]:[CHO]:[DL]:[Anhydride] = 1:1:15:250:200:200, 100 °C, 2.5 M in toluene, 24-96 h. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, in THF at 30 °C, calibrated using polystyrene standards.

To summarise, a range of anhydrides were tested and block copolyesters were obtained with bi- and tricyclic anhydrides. For monocyclic anhydrides, side-reactions dominated, such as cross-linking or transesterification.

3.6.2. Limonene Oxide

The three most common epoxides for ROCOP are cyclohexene oxide (CHO), propylene oxide (PO) and limonene oxide (LO). Although PO is highly attractive for commercial applications due to its low price, it cannot be used under the current reaction conditions due to its low boiling point of 35 °C (vs. the reaction temperature of 100 °C).^[27] LO is more suitable with a higher boiling point of 202 °C.^[28] Herein, 'switch' catalysis was attempted with LO, PA and DL; PA was the anhydride of choice due to (i) a UV-active chromophore, (ii) simplified NMR spectra, and (iii) its successful use with CHO and DL.

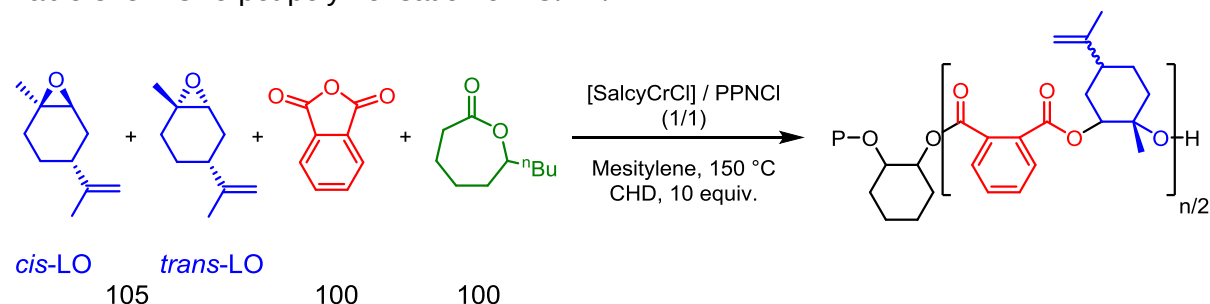
The commercial mixture of LO contains two diastereomers, *cis*- and *trans*-LO. For the copolymerisation with CO₂, only one-isomer can typically be polymerised: an aluminium trisphenolate catalyst reported by Kleij and co-workers can be used for *cis*-LO,^[29] a zinc-BDI catalyst by Coates and co-workers with *trans*-LO.^[30, 31] To investigate the reactivity of [SalcyCrCl] towards the isomers, the commercial mixture was separated by kinetic resolution (Scheme 3. 4) and *cis*- and *trans*- LO were tested individually.

Scheme 3. 4 – Kinetic resolution of commercial limonene oxide.^[32]

With each isomer individually, high conversions and perfectly alternating polyesters were obtained after 20 hours (not shown). Although the copolymerisation of LO/anhydrides is well-known, the reactivity towards the different isomers of LO has generally not been studied.^[26, 33-35] This may be attractive for the synthesis of stereoblock polyesters by kinetic resolution if large differences in rate are obtained. To test this hypothesis and the use of LO for 'switch' catalysis, the one-pot polymerisation of a mixture of *cis/trans*-LO, PA and DL was carefully monitored (Table 3. 5). Two observations could be noted: firstly, ROCOP proceeded rapidly within 2 hours and *cis*-LO was enchainned preferentially, although not exclusively. Consequently, a gradient copolyester, not a stereoblock, is proposed as the product of the reaction. Nonetheless, no polyether was detected and narrow, monomodal molar mass distributions were found at short reaction times (< 4 hours). Secondly, no significant conversion of DL was found after extended reaction times of 16 hours at 150 °C. The latter may be a result of the low reactivity of the tertiary, sterically encumbered alkoxide, which cannot initiate the ROP of DL. This is in line with the unsuccessful use of tertiary and/or sterically hindered alcohols in the ROP of CL with zinc catalysts.^[11] Additionally, slight broadening indicating transesterification was observed at longer reaction times of 16 hours ($\bar{M}_w = 1.22$ [4 h] vs. $\bar{M}_w = 1.34$ [16 h]).

In conclusion, LO can be used for ROCOP but 'switch' catalysis with DL was not observed.

Table 3. 5 – One-pot polymerisation of LO/PA/DL.



Time [h]	Conversion [%] ^[a]		Composition LO [%] ^[a]		Selectivity [%] ^[b]	M_n (Đ) [g mol ⁻¹] ^[c]
	PA	DL	Cis-LO	Trans-LO		
0	0	0	44	56	> 95 %	N. D.
0.5	70	< 5	36	64	> 95 %	1,300 (1.22)
1.0	90	< 5	33	67	> 95 %	1,640 (1.24)
2.0	99	< 5	27	73	> 95 %	2,115 (1.19)
4.0	99	< 5	N. D.	N. D.	> 95 %	2,460 (1.22)
16	99	< 5	N. D.	N. D.	> 95 %	2,130 (1.34)

^[a]Determined by ¹H NMR spectroscopy (PA: 8.02 ppm; LO: 3.00 ppm (*cis*) vs. 3.06 ppm (*trans*); DL: 4.22 ppm) and given in %; ^[b]Only one signal at ca. 3.5 ppm was observed, which was attributed to CHD; ^[c]Determined by GPC (THF, 30 °C, based on PS standards).

3.6.3. Carbon Dioxide and ϵ -Decalactone

Although both anhydride / epoxide and CO₂ / epoxide ROCOP follow similar mechanisms, several differences should be noted: First, back-biting products (cyclic carbonates) are the thermodynamic products of the reaction; second, the reaction proceeds *via* a metal carbonate, as opposed to a metal carboxylate, and third, the observed rates are generally lower than equivalent reactions with anhydrides.^[36]

To test if anhydrides can be replaced with CO₂ in 'switch' catalysis, a series of reactions was carried out: When CO₂, CHO and DL were reacted at 100 °C and 40 bar, the formation of PDL was not observed (Table 3. 6). Instead, the formation of large amounts of *cis*- and *trans*-cyclohexene carbonate was observed (57 and 12%, respectively). This may be a result of long reaction times and high pressures, if the CO₂ insertion in the chromium alkoxide bond is faster than the ROP of DL. It seems likely that lactone ROP might be associated with a high barrier from the chromium carbonate intermediate. To ensure the formation of an alkoxide at the end of ROCOP, the reaction was repeated at 5 bar. Unfortunately, similar results were obtained, DL was not consumed and the high amount of cyclic species persisted. To further reduce the amount of backbiting products, the reaction temperature was lowered to 60 °C while applying 5 bar of pressure. To account for lower rates for ROP at 60 °C (compared to 100 °C), the reaction was performed over the course of seven days. Although the desired linear polycarbonate was obtained as the main product (61 %), no PDL

formation and significant amounts of cyclic carbonates were still observed. This was most likely caused by the long reaction times, at which the putative rates of depolymerisation of PCHC and the DL ROP are competitive.

In summary, CHO/CO₂ ROCOP cannot be coupled with the ROP of DL, presumably due to the low rates of ROP, which are proposed to favour backbiting over ROP.

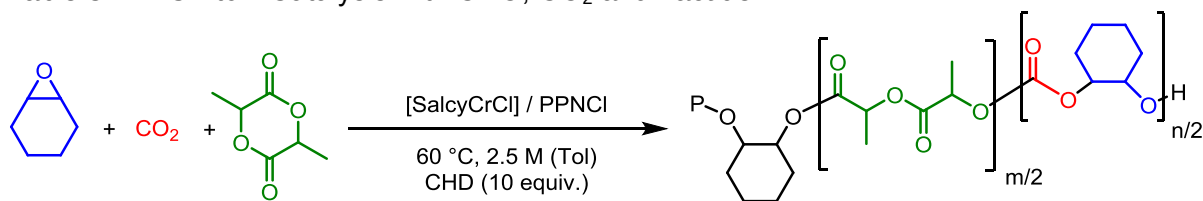
Table 3. 6 - Switch' Catalysis with CHO, CO₂ and DL.

Conditions			Conversion [%] ^[a]		Selectivity [%] ^[b]				<i>M_n</i> (Đ) [g mol ⁻¹] ^[c]
T [°C]	p(CO ₂) [bar]	t [d]	CHO	DL	carbonate vs. ether-linkage	PCHC	<i>Cis</i> -CHC	<i>Trans</i> -CHC	
100	40	3	99	< 5	ca. 95	31	57	12	1,730 (1.31)
100	5	3	79	< 5	ca. 95	14	73	13	840 (1.24)
60	5	7	78	< 5	ca. 95	61	30	9	1,830 (1.33)

^[a]Determined by ¹H NMR spectroscopy (3.10 ppm for CHO, 4.22 ppm for DL) and given in %; ^[b]Determined by ¹H NMR spectroscopy (Polycarbonate (2.08 ppm) vs. Polyether (3.5 -3.7 ppm); H^a (2.08 ppm), H^b (4.00 ppm), H^c (1.89 ppm); ratio obtained by H^x/(H^a+H^b+H^c/2)) and given in %; ^[c]Determined by GPC (THF, 30 °C, based on PS standards).

3.6.4. Carbon Dioxide and Lactide

The monomer for ROP was exchanged from DL to (*rac*)-Lactide (LA) to increase the rate of ROP at 60 °C. Under similar conditions as before, the linear polycarbonate was now formed over cyclic carbonates with high selectivity (ca. 95 %) and high conversions of all reactants (CHO and LA) were observed, alongside with monomodal molar mass distributions (Table 3. 7). To achieve higher molecular weights, the reaction was repeated with a higher monomer loading ([cat]:[co-cat]:[CHD]:[CHO]:[LA] = 1:1:10:1000:600). Although similar conversions and selectivity were obtained, a multimodal GPC trace was detected.

Table 3. 7 - 'Switch' Catalysis with CHO, CO₂ and Lactide.

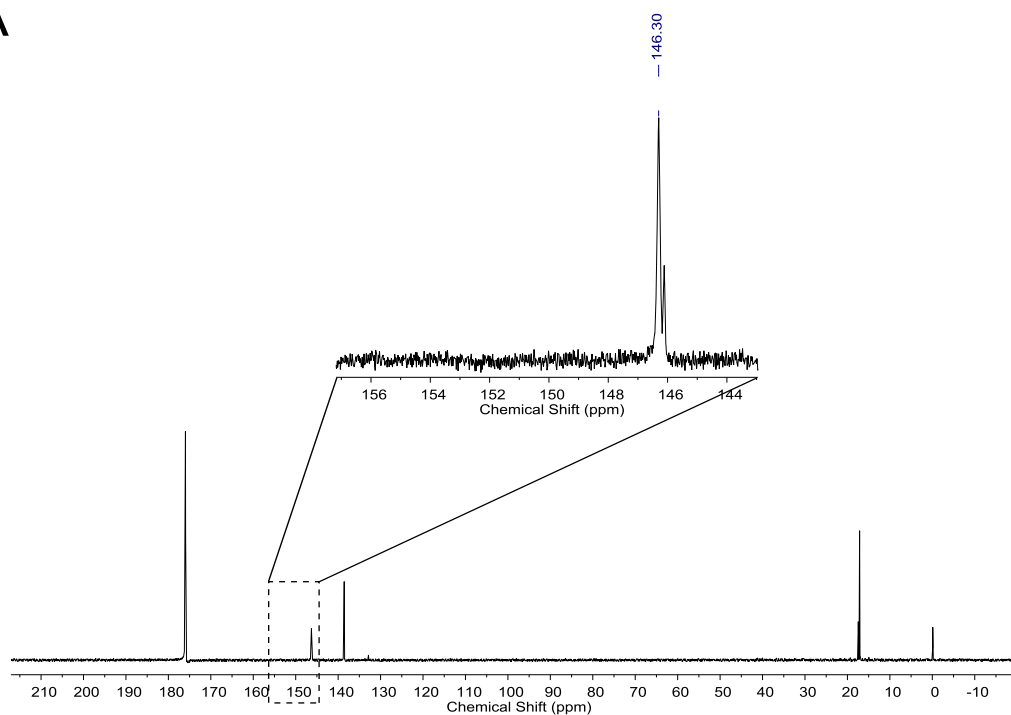
Conditions				Conversion [%] ^[b]		Selectivity [%] ^[b]				<i>M_n</i> (Đ) [g mol ⁻¹] ^[c]
CHO: LA	T [°C]	p(CO ₂) [bar]	t [d]	CHO	LA	carbonate vs. ether- linkage	PCHC	Cis- CHC	Trans- CHC	
250: 200	60	30	1	98	98	> 95	99 %	< 1	1	6,570 (1.35)
1000: 600	60	40	4	98	98	> 95	99 %	< 1	1	20,600 (1.14) 8,000 (1.03) 4,000 (1.04)

^[a]Determined by ¹H NMR spectroscopy (3.10 ppm for CHO, 5.03 ppm for Lactide) and given in %; ^[b]Determined by ¹H NMR spectroscopy (Polycarbonate (2.08 ppm) vs. Polyether (3.5 - 3.7 ppm); H^a (2.08 ppm), H^b (1.89 ppm), H^c (4.00 ppm); ratio obtained by H^x/(H^a+H^b+H^c/2)) and given in %; ^[c]Determined by GPC (THF or CHCl₃, 30 °C, based on PS standards) and given in g mol⁻¹.

To identify if a mixture of homopolymers was responsible for the multimodal GPC trace, the end groups of the polymer were analysed after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane. Two resonances were found at 146.30 and 146.12 ppm with the latter as a low-intensity signal. This peak can be assigned to PCHC end groups and strongly indicates that a copolymer formed as no signals were observed at 147.2 ppm, where PLA end groups are observed (see Chapter 5).^[37] The remaining low-intensity signal may be a consequence of the stereoselective LA ROP. To gain further insight into the polymeric product, the material was analysed by DOSY NMR and only one diffusion coefficient was observed ($D=2.09 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$, Figure 3. 20), which further supports the formation of a block polymer. Analysis by ¹³C{¹H} NMR revealed only signals attributed to the two blocks (169 ppm [PLA] and 154 ppm [PCHC]), indicating that transesterification was not a dominant process. With respect to thermal properties, only one T_g value at 81°C was detected by DSC (see appendix).

Finally, the stereoselectivity of the polymerisation of (*rac*)-Lactide was further investigated by ¹H NMR spectroscopy.

A



B

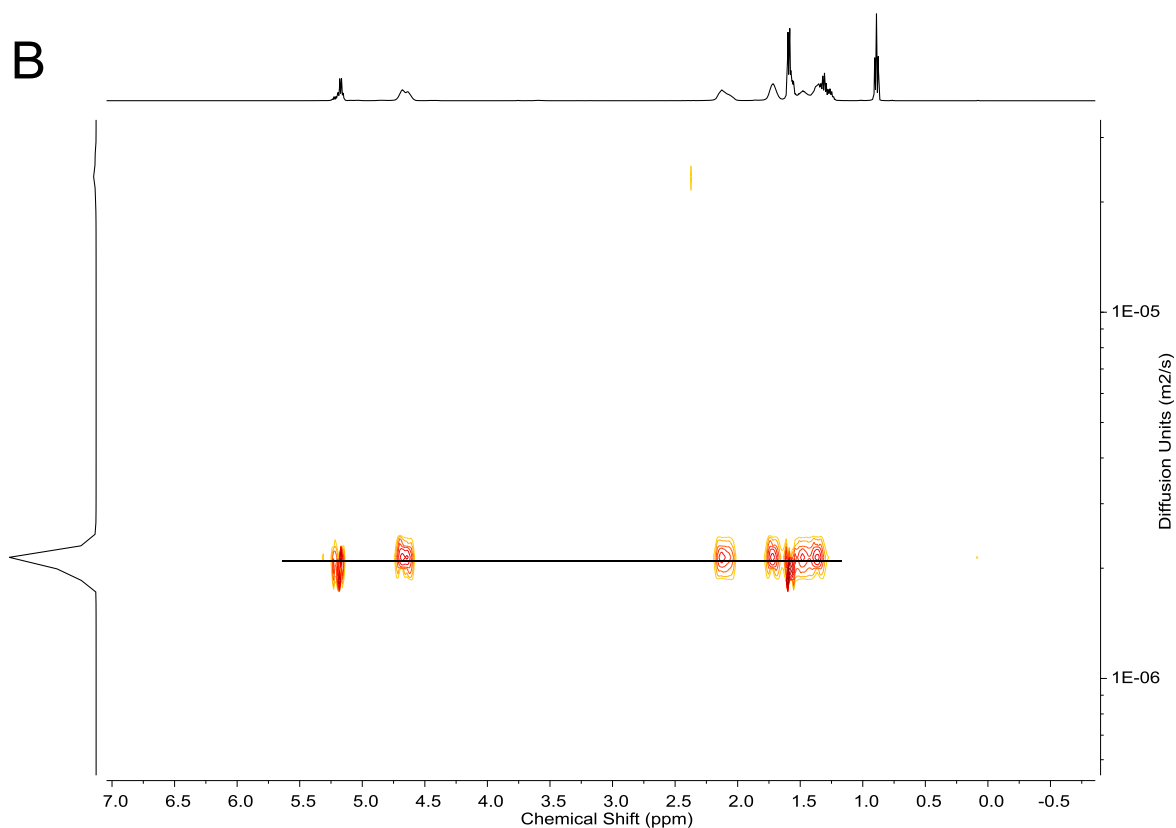


Figure 3. 20 - Top: $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of polymer obtained from CHO, CO_2 and Lactide after the reaction with 2-chloro-4,4,5,5-tetramethyldioxaphospholane (with bisphenol A, $\text{Cr}(\text{acac})_3$ and pyridine). Bottom: DOSY NMR spectrum of the polymer.

Isotactic-enriched PLA was indicated in the ^1H NMR spectrum of crude reaction mixture of the one-pot polymerisation of LA/CHO/ CO_2 as a set of two well-resolved quartets at 5.23 and 5.17 ppm (Figure 3. 20, top). Further analysis by homonuclear decoupled ^1H NMR spectroscopy allowed quantification and isotactic enriched PLA with $P_i = 0.77$ was synthesised (Figure 3. 20, bottom).

Based on these techniques, the formation of a block copolymer is proposed.

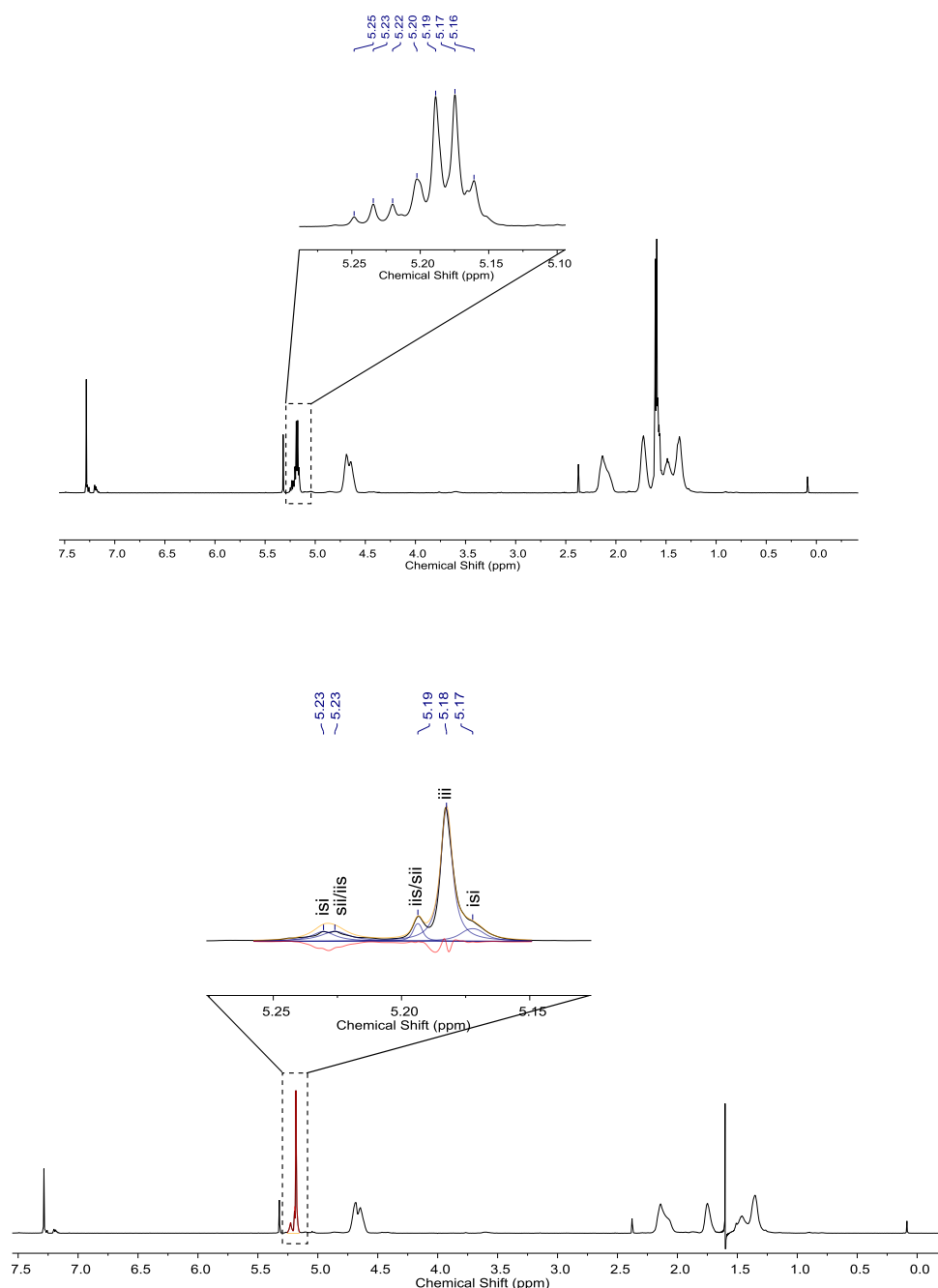
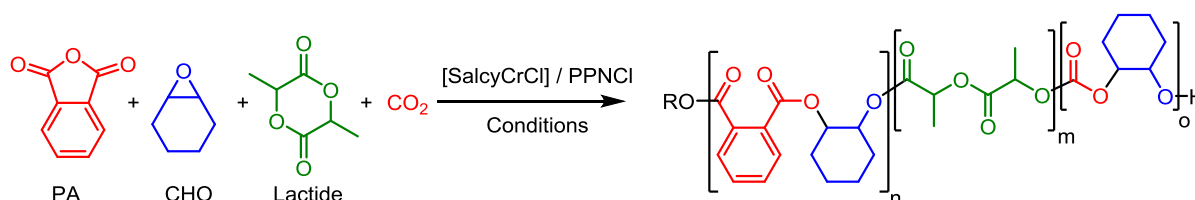


Figure 3. 21 – ^1H NMR Spectra of PCHC-*b*-PLA-*b*-PCHC (A) and homonuclear decoupled ^1H NMR spectra used for determination of P_i value (peaks are shown in navy, sum in orange and residue in red). P_i value based on the Bernoulian statistical model on tetrad level.^[38]

3.6.5. Four Monomers: Carbon dioxide, Cyclohexene Oxide, Phthalic Anhydride and Lactide

Encouraged by these results, the one-pot polymerisation of four monomers, CO₂, CHO, PA and LA was attempted. At 60 °C and 7 days, full conversion of PA, CHO and Lactide was observed with a small amount of *trans*-CHC. The formation of isotactic-enriched PLA was not observed in this case and GPC showed a monomodal molar mass distribution ($M_n = 7,100 \text{ g mol}^{-1}$; $\bar{D} = 1.35$) with little difference between UV and RI traces (appendix). Unfortunately, DOSY was inconclusive and, more importantly, multiple peaks were found after end group analysis by ³¹P{¹H} NMR spectroscopy ($\delta = 149.2, 147.2$ (PLA), 146.2 (PCHC) and 143.7 ppm; see appendix). To avoid reaction times beyond completion, which typically favour side-reactions, the polymerisation repeated at 80 °C and monitored by *in situ* IR.

Table 3. 8 – One-pot polymerisation of PA, CHO, CO₂ and Lactide.^[a]



Conditions				Conversion [%] ^[b]			Selectivity [%] ^[c]				M_n ($\bar{D}$) [g mol ⁻¹] ^[d]
Loading	T [°C]	p(CO ₂) [bar]	t	PA	LA	CHO	PCHC vs. PCHO	PCHC	Cis-CHC	Trans-CHC	
400: 800: 400	60	45	7 d	99	99	99	> 95	84	< 5	12	7,000 (1.35)
430: 1000: 500	80	30	52 h	99	99	69	> 95	77	< 5	23	6,300 (1.35)

^[a]Reaction performed in toluene (5M) in the presence of CHD (10 equiv., entry 1) or benzyl alcohol (10 equiv., entry 2). ^[b]Determined by ¹H NMR spectroscopy (3.10 [CHO], 5.03 [LA], 8.00 ppm [PA]). ^[c]Determined by ¹H NMR spectroscopy (Polycarbonate (2.08 ppm) vs. Polyether (3.5 -3.7 ppm)): For PCHC vs. CHC selectivity: H^a (2.08 ppm), H^b (1.89 ppm), H^c (4.00 ppm). Ratio obtained by H^x/(H^a+H^b+H^c/2)). ^[d]Determined by GPC (THF, 30 °C, based on PS standards).

Analysis by *in situ* IR spectroscopy showed three stages of the reaction, PA/CHO ROCOP followed by LA ROP and finally CO₂/CHO ROCOP (Figure 3. 22). A zeroth order trend in anhydride for PA/CHO ROCOP was observed and a rate constant $k_{obs,PA/CHO-ROCO}^{IR} = 0.133 \pm 0.002 \text{ M h}^{-1}$ was determined. Few data points were obtained to

determine the rate law for Lactide ROP and only an estimate can be provided here with $k_{obs,LA-ROP}^{IR} \geq 950 \text{ h}^{-1}$ (first order in lactide assumed). For CHO/CO₂ ROCOP, a rate constant $k_{obs,CO_2/CHO-ROCO}^{IR} = 7.6 \pm 0.028 \cdot 10^{-3} \text{ h}^{-1}$ ([CHO]_t was calculated from [PCHC]_t and [CO₂] was assumed constant). In terms of TOFs, this is equivalent to $TOF_{LA-ROP} \sim 15,000 \text{ h}^{-1} \gg TOF_{PA/CHO-ROCO} \sim 25 \text{ h}^{-1} > TOF_{CO_2/CHO-ROCO} \sim 10 \text{ h}^{-1}$. Most importantly, the different polymerisation mechanisms occur in sequence and not randomly.

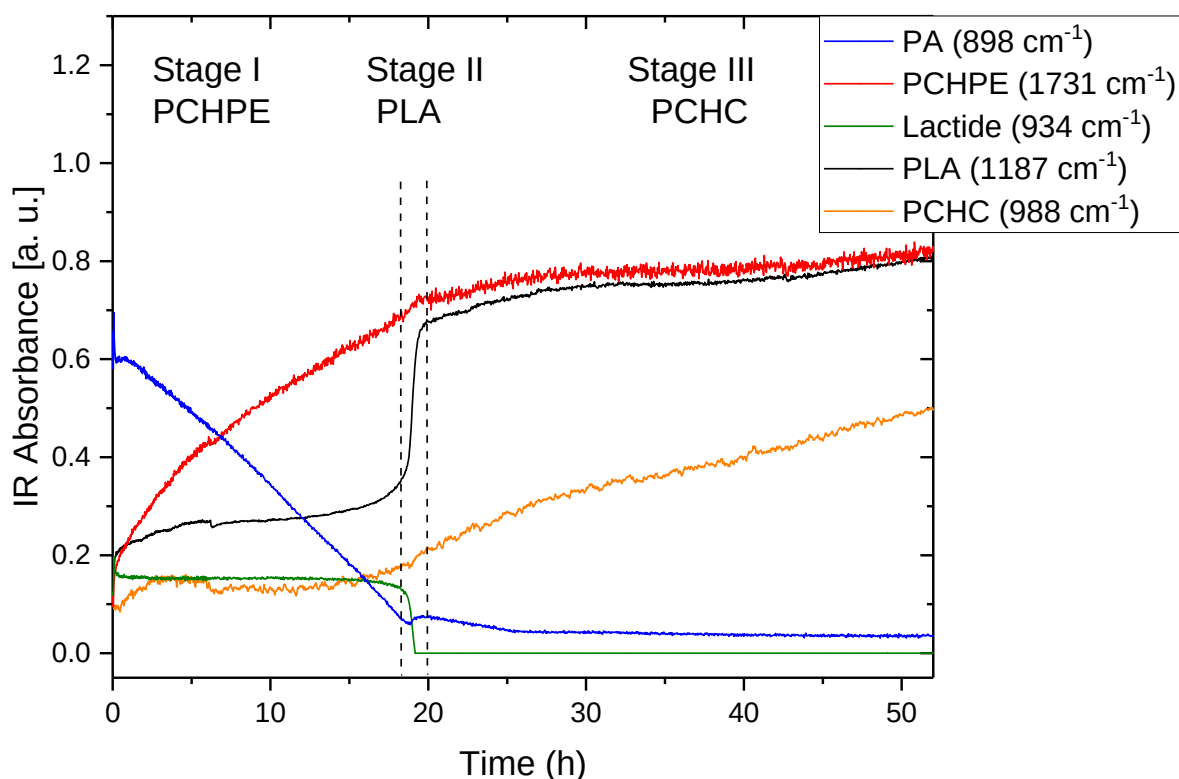


Figure 3. 22 – *In situ* IR plots of one-pot polymerisation of PA, CHO, LA and CO₂.

This *in situ* monitoring of the reaction indicated 'switch' behaviour. Further analysis by GPC revealed a monomodal distribution at low mass ($M_n = 6,300 \text{ g mol}^{-1}$; $\mathcal{D} = 1.35$) and UV and RI traces were similar (Figure 3. 23, top). Although the reaction did not reach completion (conversion CHO = 77%), multiple peaks in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and a small amount of *trans*-CHC was observed (Figure 3. 23, bottom). As this is a complex reaction mixture, more studies are necessary to fully analyse the polymeric product(s).

Three control reactions were performed with these monomers. First, CHO was copolymerised with PA and narrow, monomodal molar mass distributions were obtained ($M_n = 5,800 \text{ g mol}^{-1}$, $\mathcal{D} = 1.13$), as expected from 'switch' catalysis with CHO/NBA/DL. Second, PLA was polymerised in the presence of CHO and broad molar mass distributions were obtained at 60 °C ($M_n = 2,200 \text{ g mol}^{-1}$, $\mathcal{D} = 2.03$). Most notably, the stereoselective ROP of lactide was not observed. Third, significant broadening was observed in the one-pot

polymerisation of CHO, PA and lactide ($M_n = 5,500 \text{ g mol}^{-1}$, $\bar{D} = 1.49$) compared to only ROCOP. This suggests that both transesterification and epimerisation occur during the polymerisation of lactide if an excess of epoxide is present and CO_2 is not applied.

In conclusion, the formation of the expected, linear block copolymers was not found with four monomers (PA, CHO, CO_2 and LA). Nonetheless, *in situ* IR monitoring revealed high rates for the ROP of lactide with turn-over frequencies of $> 15,000 \text{ h}^{-1}$.

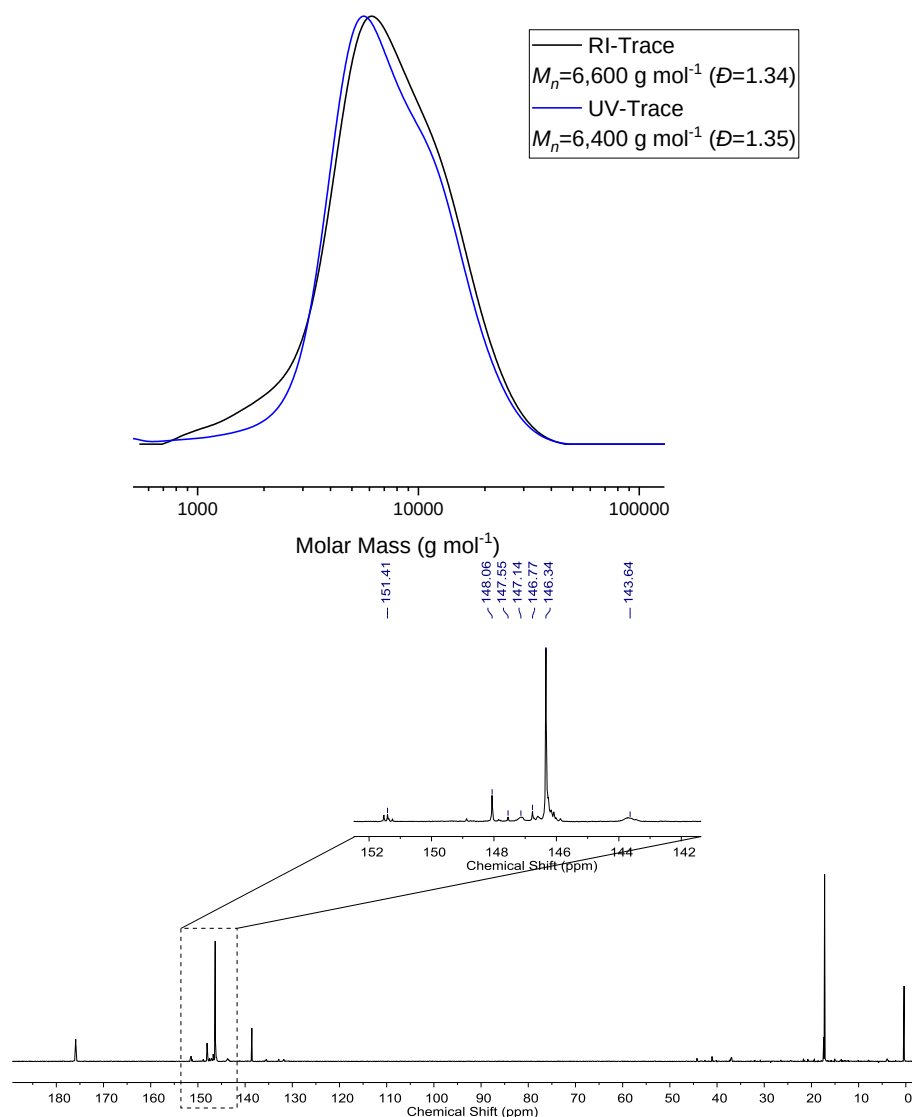


Figure 3. 23 – UV and RI GPC trace of crude mixture obtained from one-pot polymerisation of PA, CHO, CO_2 and Lactide (Table 3. 8, entry 2) and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after the reaction with 2-chloro-4,4,5,5-tetramethyldioxaphospholane (with bisphenol A, $\text{Cr}(\text{acac})_3$ and pyridine) (bottom).

3.7. Post-Functionalisation

Post-functionalisation reactions can be used to tune material properties. This is illustrated in Chapter 6 for thiol-ene reactions with trifunctional thiols and different polymers. In this later example, fully bio-based coating materials were produced – without this post-modification step, the polycarbonates could not be used as coatings. As a proof of concept, two post-functionalisation reactions were conducted with PDL-*b*-PCHNBE-*b*-PDL: First, thiol-ene reactions and second, chain-extension with diisocyanates.

The block copolyester was reacted with two thiols, mercaptoethanol as a hydrophilic and butane thiol as a hydrophobic thiol. In both cases, the alkene functionality was fully converted as indicated by ^1H NMR spectroscopy ($\delta = 5.9$ and 6.5 ppm) (Figure 3. 24) and narrow molar mass distributions before and after the reaction were observed by GPC maintained (Figure 3. 25). Both techniques suggest the successful post-functionalisation of PDL-*b*-PCHNBE-*b*-PDL with thiol-ene reactions.

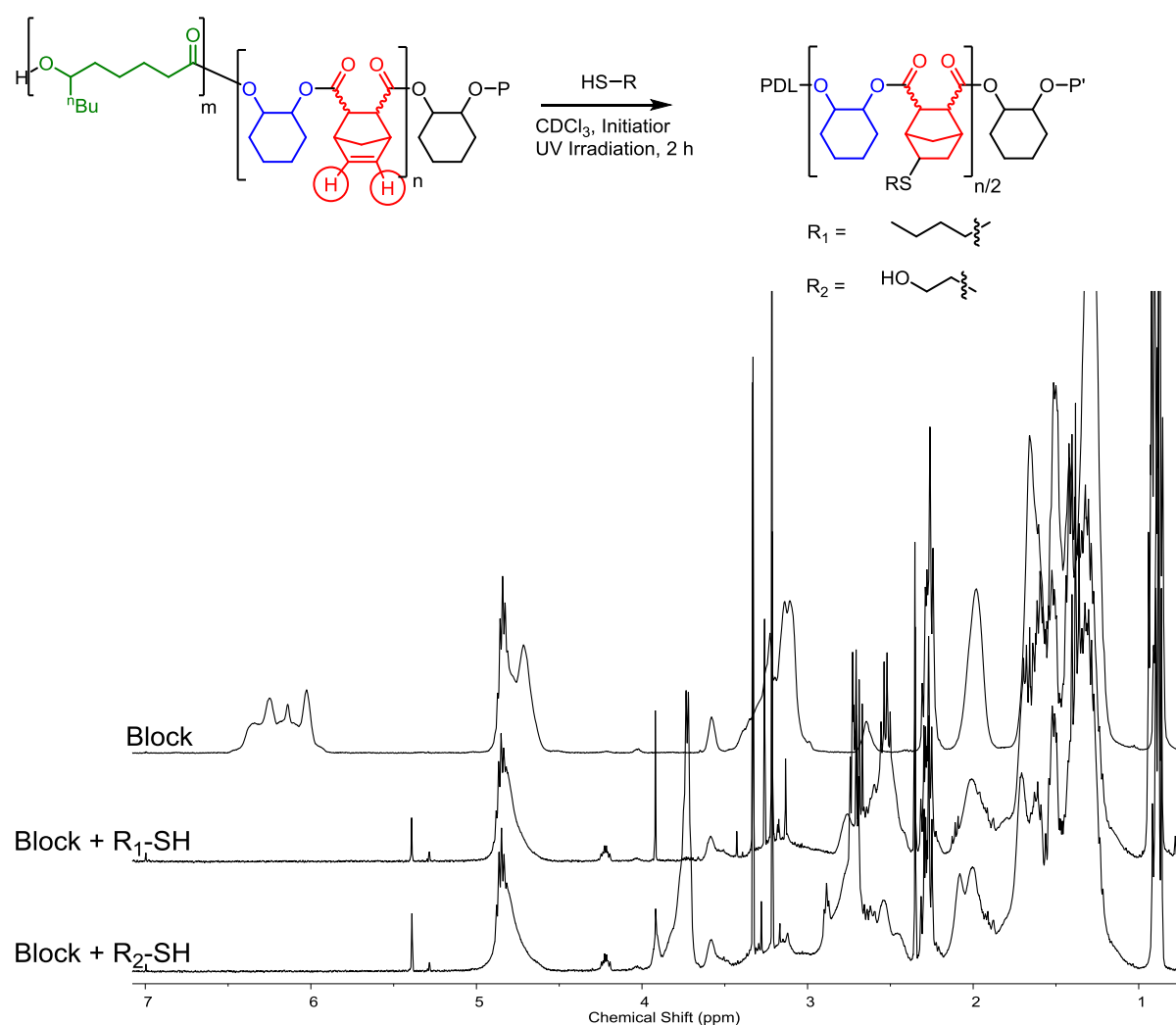


Figure 3. 24 - ^1H NMR spectra before and after thiol-ene reactions.

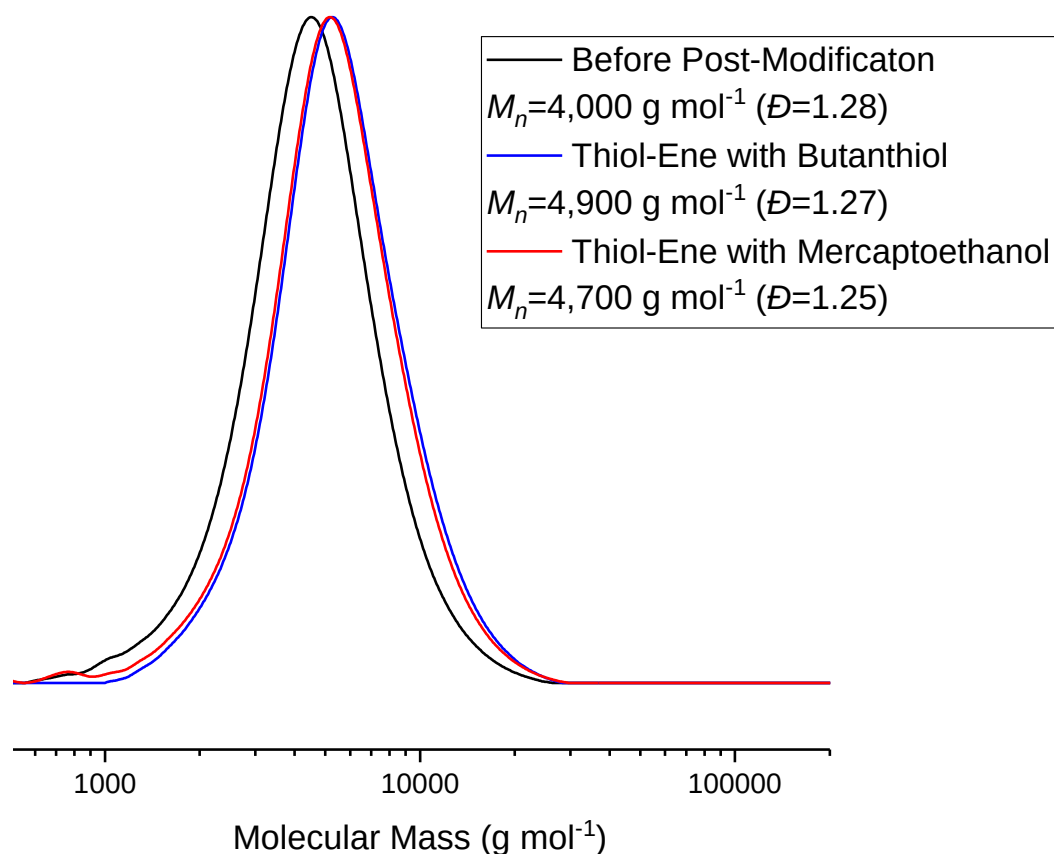


Figure 3. 25 – GPC traces before and after thiol-ene reactions.

Finally, all synthesised polyesters are telechetic materials with hydroxyl end groups. These diols are commonly used in the synthesis of polyurethanes.^[39, 40] To illustrate this potential application, PDL-*b*-PCHNBE-*b*-PDL was chain-extended with 4,4'-methylene diphenyl diisocyanate (MDI). After chain-extension, the molar mass increased from ca. 4 to ca. 70 kg mol^{-1} (Figure 3. 26, left). Moreover, DSC indicated two T_g values at 46 °C and 88 °C, indicating phase separation (Figure 3. 26, right). This is highly encouraging and may be attractive for future thermoplastic elastomers based on multiblock copolyesters.

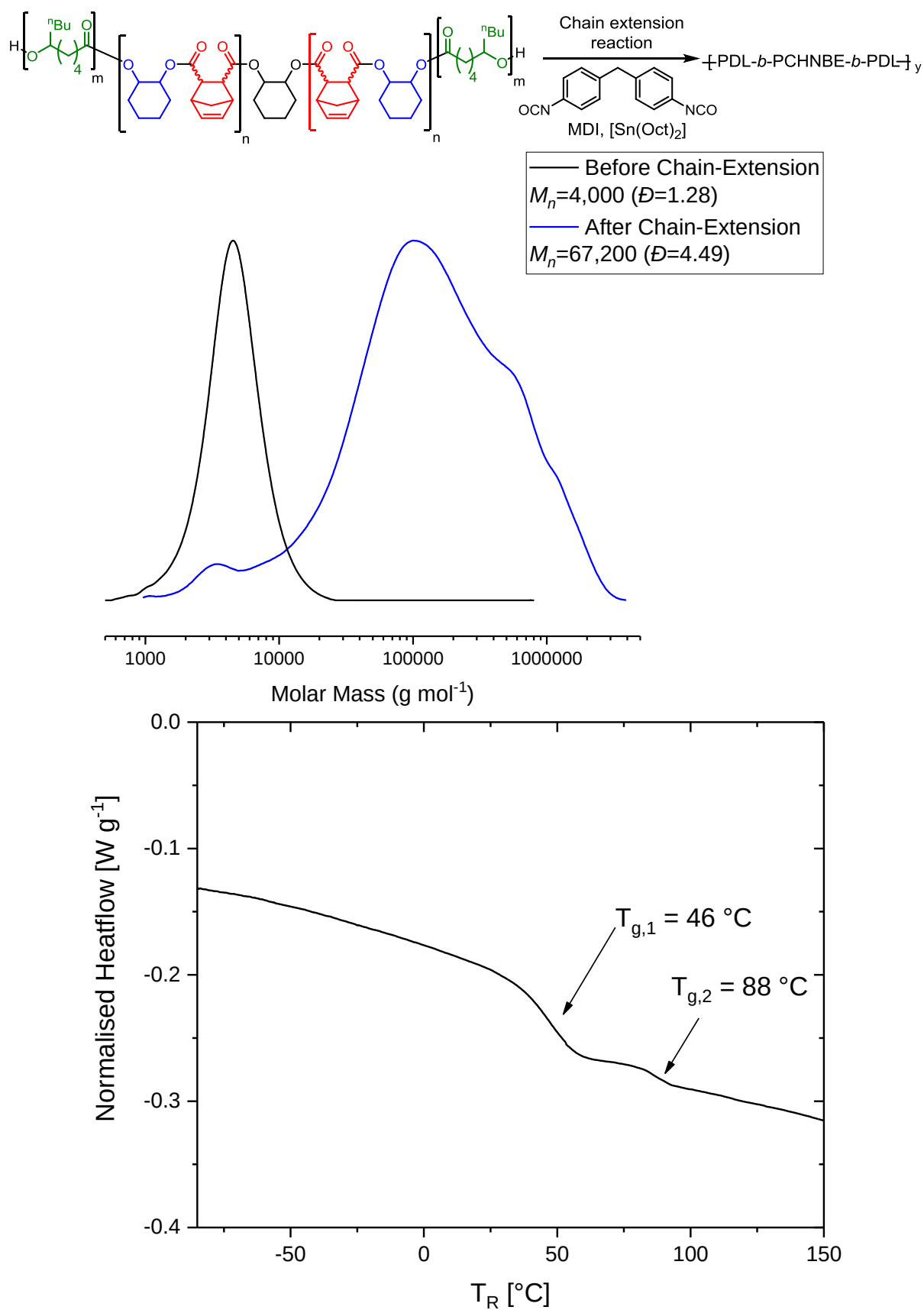


Figure 3. 26 – GPC Chromatogram (left) and DSC thermogram (right, 3rd heating cycle) after chain-extension with MDI.

3.8. Discussion

3.8.1. Phase-Separation

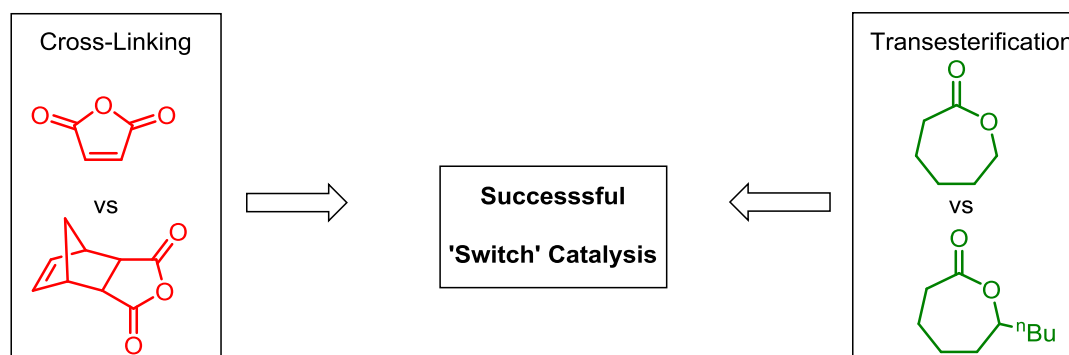
Phase separation of block copolymers can be affected by several parameters, such as architecture, relative volume fractions, the Flory-Huggins interaction parameter (χ) and the degree of polymerisation (N).^[41] In this case, block miscibility was observed for a range of different block compositions, which is likely the result of a low degree of polymerisation. The latter is a consequence of large amounts of chain-transfer agent necessary to control the molar mass distribution (10 – 15 equiv.), which inherently lowers molecular masses. Although phase separation was not observed by DSC initially, two T_g values were observed after chain-extension with MDI, which further substantiates this hypothesis. Similar effects have been observed before, for example with poly(styrene-*b*-isoprene-*b*-styrene): At low molecular weights, one T_g value was observed ($M_n = 11,000 \text{ g mol}^{-1}$, $T_g = 38 \text{ }^\circ\text{C}$) and two T_g values were found at high molecular weights ($M_n = 161,000 \text{ g mol}^{-1}$, $T_{g,1} = -65 \text{ }^\circ\text{C}$, $T_{g,2} = 105 \text{ }^\circ\text{C}$).^[42] This suggests that material with higher weights should be further investigated to achieve phase-separation.

3.8.2. Monomer Scope

Three guidelines for successful 'switch' catalysis with [SalcyCrCl] are proposed based on the substrates investigated in this chapter:

A. Monomers with high steric demand.

Steric demand is a key requirement to suppress transesterification, which results in broadening of molar mass distributions, as seen for CL vs. DL (Scheme 3. 5, right). Moreover, sterically inaccessible substrates are less likely to undergo further side-reactions, such as cross-linking, which was found by comparing MA as a monocyclic unsaturated substrate and NBA, which is a tricyclic derivative (Scheme 3. 5, left).

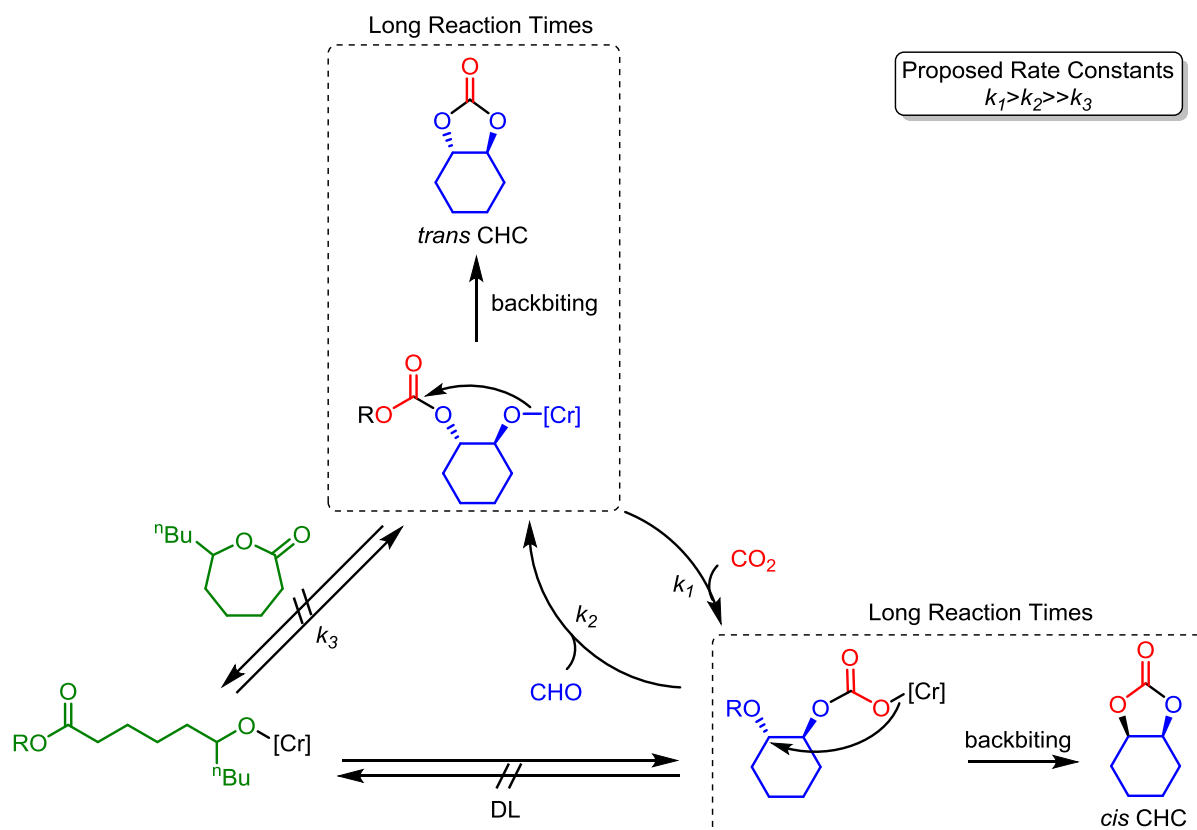


Scheme 3. 5 – Side-reactions in 'switch' catalysis.

B. Suppress backbiting products.

The one-pot polymerisation of CO₂, CHO and DL resulted in the formation of mainly cyclic carbonates. This was most likely caused by long reaction times of several days, during which backbiting occurred, instead of the formation of PDL (i. e. $k_1 > k_2 \gg k_3$ in Scheme 3. 6). As a mixture of *cis*- and *trans*-cyclohexene carbonate was observed, backbiting is proposed from both the chromium alkoxide and the chromium carbonate intermediate (Scheme 3. 6). Here, these cyclisation reactions are faster and/or thermodynamically more favourable than the ROP of DL and therefore, 'switch' catalysis cannot be achieved.

The extent of these side-reactions could be reduced by: (i) lower reaction temperatures, (ii) shorter reaction times (particularly beyond completion) and (iii) faster ROP. The selective formation of PCHC was observed at 60 °C in one day, with only minimal amounts of cyclic carbonates, if coupled with lactide.

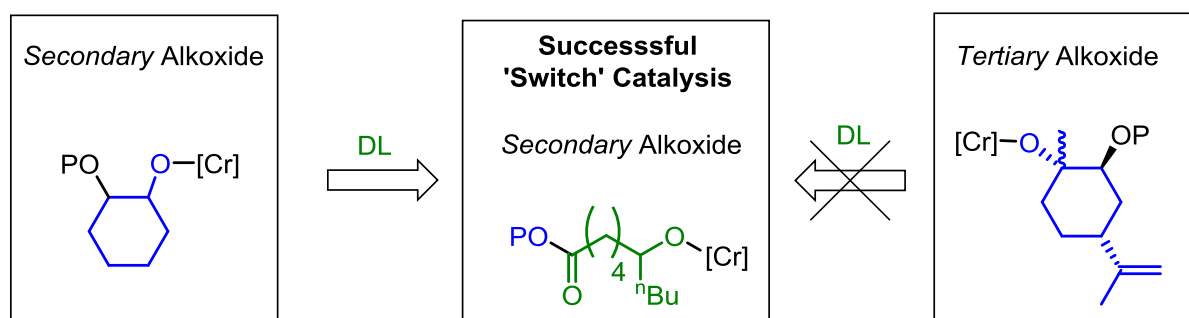


Scheme 3. 6 – One-pot polymerisation of CHO, CO₂ and DL and the proposed formation of backbiting products.

C. Initiating vs. propagating species.

A tertiary alkoxide is proposed as the propagating species for the copolymerisation of LO/PA and no PDL was formed during this attempted 'switch' catalysis. This is likely a consequence of the low reactivity and the high steric bulk of the formed alkoxide at the end of ROCOP

(Scheme 3. 7, right). However, the propagating species for ROP is a secondary alkoxide and therefore large differences in reactivity between secondary and tertiary alkoxides are expected (Scheme 3. 7, left). A different scenario is obtained with CHO, in which a secondary alkoxide is generated. In this case, the reactivity of the two alkoxides for ROCOP and ROP is proposed to be similar and this combination can be used in 'switch' catalysis (Scheme 3. 7, left).



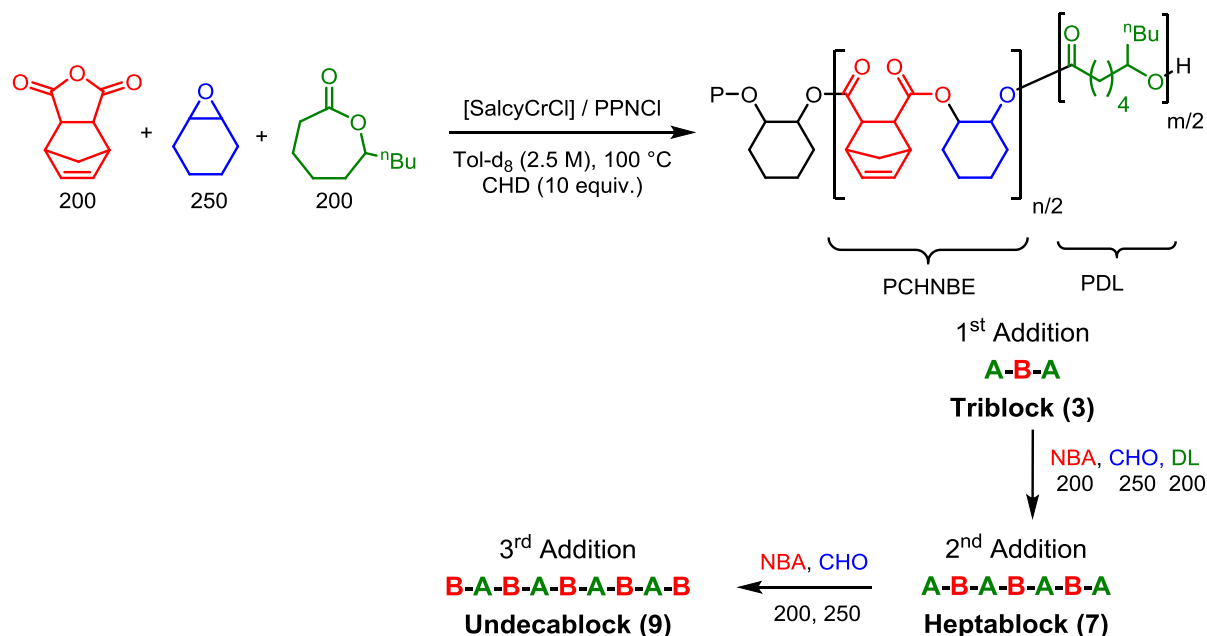
Scheme 3. 7 – Reactivity of proposed chromium alkoxides after ROCOP of LO/PA and CHO/PA towards ring-opening of DL.

In summary, three guidelines are proposed for successful 'switch' catalysis: (i) the use of sterically hindered substrates, (ii) substrates that result in minimal backbiting, and (iii) the appropriate selection of monomers to target similar propagating species for both ROCOP and ROP.

3.8.3. Multiple 'Switching'

To achieve a higher number of blocks, the monomer mixture containing NBA, CHO and DL was added repeatedly to the reaction (Scheme 3. 8). After the first addition, an ABA triblock was formed, as expected from previous results (Table 3. 9, entry 1). Once high conversion (95%) of NBA and DL were obtained, the same monomer mixture was added a second time. Although the anhydride was fully consumed, only partial consumption of DL was observed (38 %), even after prolonged reaction times of eight days (entry 2). Nonetheless, an increase in molar mass was observed and monomodal molar mass distributions were maintained. To test if the catalyst was deactivated, the anhydride/epoxide mixture was added a third time. Surprisingly, the anhydride was fully consumed and the molar mass increased, indicating the formation of an undecablock copolymer (entry 3). It should be noted, however, that an additional shoulder at lower molecular weights was detected, which might be ascribed to the formation of cyclic species.

Overall, 'switch' catalysis can be used to access multiblock copolymers by repeatedly adding monomer mixtures to the reaction. With the present catalyst and monomer selection, heptablock copolymers can be easily achieved; beyond heptablocks, slow reaction times and incomplete conversions of DL were found. This may be a consequence of high viscosities of the reaction mixture after the formation of ABA triblocks.



Scheme 3. 8 – 'Switch' catalysis with multiple monomer additions.

Table 3. 9 – Synthesis of multiblock copolymers.

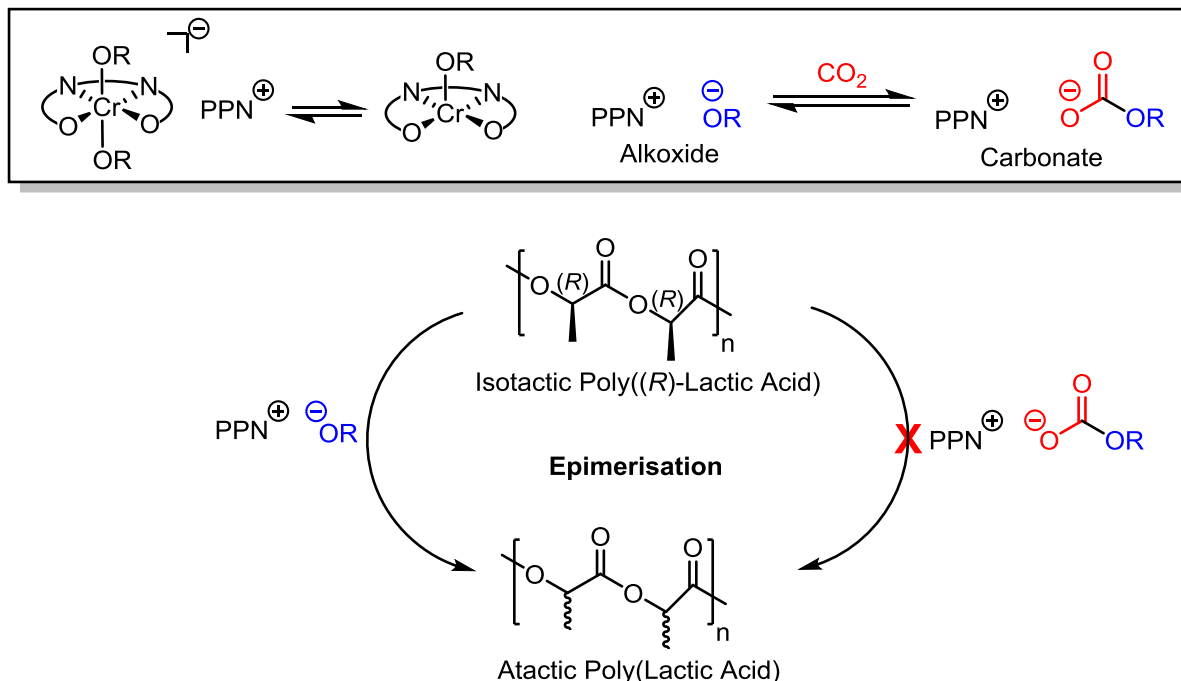
	1 st Addition	2 nd Addition	3 rd Addition
Anhydride Conversion [%] ^[a]	99	99	99
DL Conversion [%] ^[a]	95	38	38
M_n (Đ) [g mol ⁻¹] ^[b]	2,750 (1.21)	4,460 (1.27)	5,540 (1.22) 1,180 (1.13)
Reaction Time [d]	2.5	+ 8	+ 3

^[a]Determined by ¹H NMR spectroscopy (3.60 ppm for NBA, 4.30 ppm for DL); ^[b]Determined by GPC (THF, 30 °C, based on PS standards).

3.8.4. Stereoselectivity

The formation of isotactic enriched PLA was observed in the presence of CO₂; atactic PLA was obtained under nitrogen. This is likely a consequence of epimerisation at the stereogenic center of PLA, which may be caused by the PPN-stabilised alkoxide. In the presence of CO₂, this 'basic' alkoxide (pK_{aH} ~ 16; based on *iso*-propanol)^[43] is converted into a carbonate with slightly decreased basicity (pK_{aH} ~ 10; based on sodium bicarbonate)^[44]

and epimerisation is proposed to be minimised (Scheme 3. 9). Based on this observation, stereoselective polymerisations with a PPNCl as a co-catalyst may be possible in the presence of CO₂ as a 'buffering' agent. A similar effect has recently been found for stereoblock-copolyesters based on NBA/CHO.^[45]



Scheme 3. 9 – Effect of CO₂ on the epimerisation of isotactic PLA.

As an aside, the ROP of lactide was a remarkably fast reaction with a TOF of $\geq 15,000 \text{ h}^{-1}$ and only a few data points were obtained to determine the rate law. For this reason, only an estimate can be provided here with $k_{\text{obs, LA-ROP}}^{\text{IR}} \geq 950 \text{ h}^{-1}$ – nonetheless, this is a highly active catalyst for lactide and 500 equivalents were polymerised in less than two minutes. Although this is only a preliminary value, [SalcyCrCl] is ≥ 10 times more active in solution at 100 °C than Sn(Oct)₂ at 110 °C in neat conditions.

3.9. Summary and Outlook

The synthesis of block copolymers from a mixture of monomers is a challenging task. This is mainly due to a range of side-reactions. In this chapter, the synthesis of ABA triblock copolymers based on anhydrides, cyclohexene oxide and ϵ -decalactone was achieved after careful optimisation of the reaction parameters, most notably the use of sterically hindered substrates and large amounts of chain-transfer agent. The catalysis has been investigated in depth and a general guide for 'switch' catalysis with metal salen catalysts have been developed; further key results are summarised in Figure 3. 27. Overall, this represents the first example of 'switch' catalysis with (i) a commercial catalyst and (ii) a chromium catalyst.

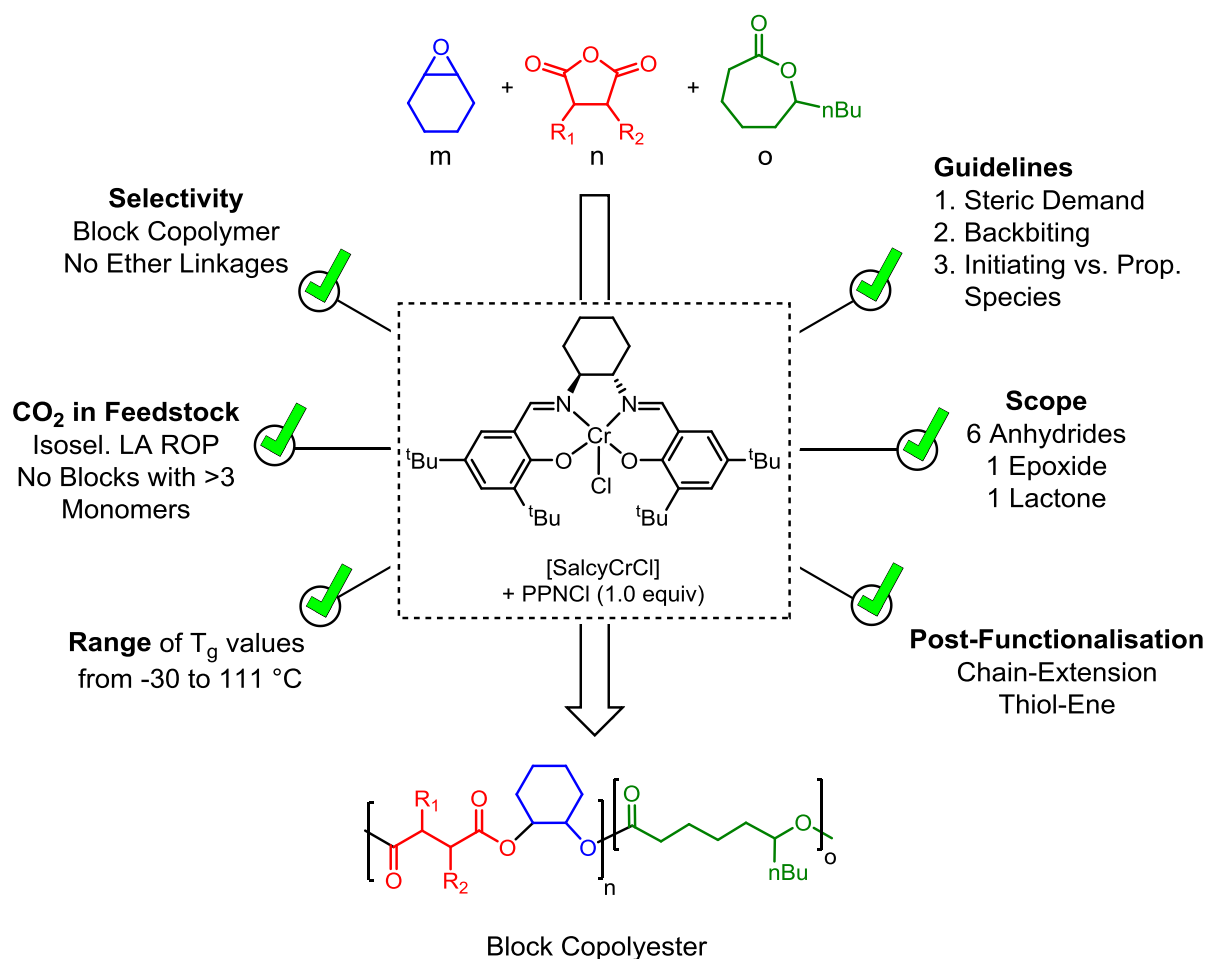


Figure 3. 27 – Main results in 'switch' Catalysis with CHO, anhydrides and DL.

Although these results are highly encouraging, further work in three areas should be considered:

3.9.1. Catalyst

[SalcyCrCl] is a slow catalyst for the ROP of DL and the reaction takes several days to complete, especially at high monomer loading. This is impractical and various changes are possible to enhance the catalytic activity:

i) *Changes in ligand scaffold.* The benefit of electronic and steric tuning of salen catalysts has been demonstrated in various other areas of catalysis.^[46, 47] For ROCOP of CHO/CO₂, an increase in activity by a factor of 90, and in polycarbonate vs. polyether selectivity by a factor of 2, was found by changing the linker group between the imine functionalities from a symmetric *tert*-butyl to an unsymmetric diphenyl derivative (Figure 3. 28, left and middle). Further rate-enhancements were observed for changes on the phenol fragments or the initiating group (Figure 3. 28, right).^[48] Compared to these catalysts, [SalcyCrCl] showed intermediate activity (TOF = 40 h⁻¹) with high selectivity (99%).

Further modification of the backbone might allow CHO/CO₂ ROCOP at 1 atmosphere in the presence of PPNCI (TOF = 100 h⁻¹; 99% carbonate linkages) for unsymmetric salen complexes ('salalen' complex; obtained by methylation of one imine functionality).^[49] This may allow 'switch' catalysis at atmospheric pressure of CO₂, which would be an attractive route to poly(ester-*b*-carbonate)s.

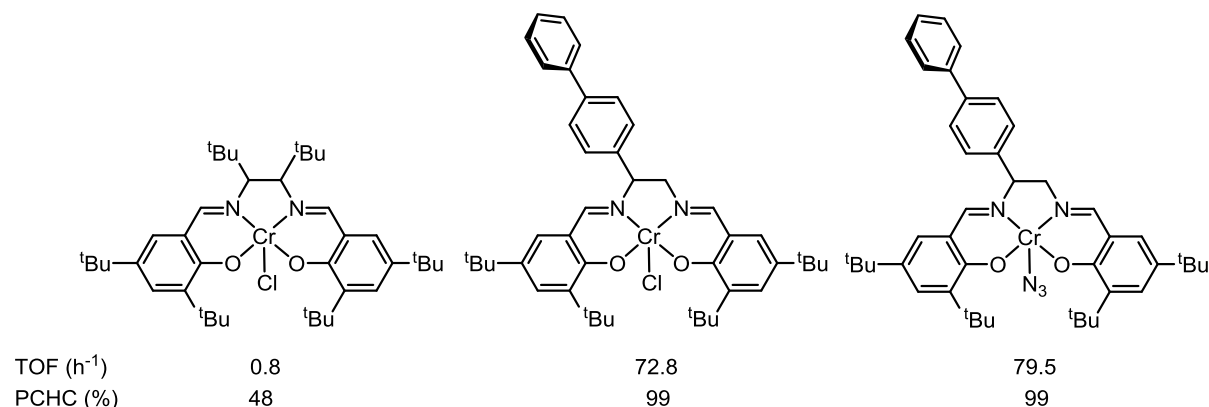


Figure 3. 28 – Different salen complexes and their performance in CHO/CO₂ ROCOP.^[48]

ii) *Incorporation of co-catalyst in the ligand backbone.* The addition of a co-catalyst is essential for the activity of a range of salen catalysts. Although a mechanistic debate is still ongoing, large rate-enhancements (10-20 fold) were found if the co-catalyst is incorporated in the ligand scaffold for the ROCOP of PO / CO₂ (Figure 3. 29, middle and right).^[50, 51] These complexes have not been tested for ROP or 'switch' catalysis, which makes them promising alternatives to [SalcyCrCl].

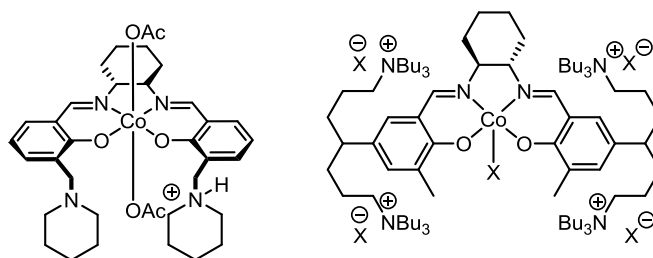


Figure 3. 29 – Bifunctional salen complex with piperidinium moieties (middle) and quaternary ammonium groups (right).^[50, 51]

iii) *Initiating Groups.* In this study, large amounts of CTA were necessary to suppress chloride-initiated polymer chains, which limit molecular weights. Although narrow, monomodal molar mass distributions were obtained, the initiating groups on catalyst and co-catalyst may be optimised.

With respect to the catalyst, more reactive metal species towards alcohols are recommended. This concept has been successfully used with a macrocyclic dizinc catalyst by using a zinc phenyl over a zinc acetate derivative.^[8] It should be noted that organochromium(III) complexes may be more difficult to prepare (Figure 3. 30).^[52, 53] On the other hand, the co-catalyst can be changed easily by salt metathesis reactions. This was demonstrated recently with the new reagent [Ad(PPN)₂] and should be extended to other derivatives. It is worth noting that [Ad(PPN)₂] was used in combination with [Salphen^FAlOTf], and reduces the number of initiating sites and allows access to monomodal mass distributions for polyesters from ROCOP of PO/anhydrides.^[54] A similar strategy may be possible for [SalcyCrCl] for use in 'switch' catalysis (Figure 3. 30).

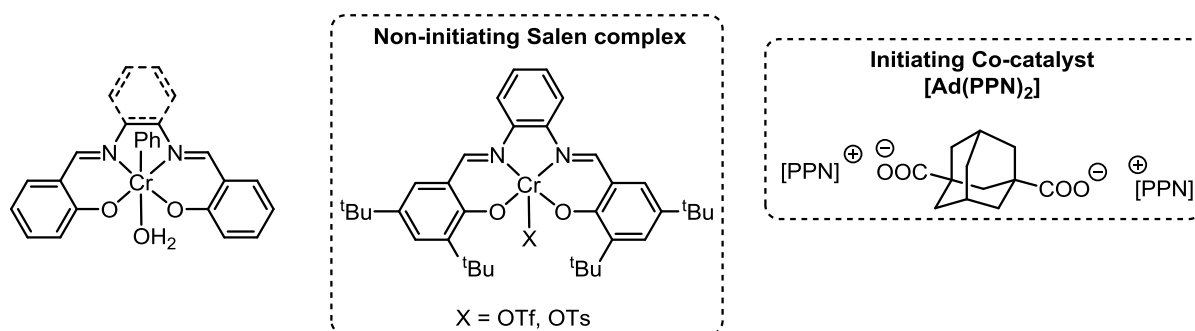


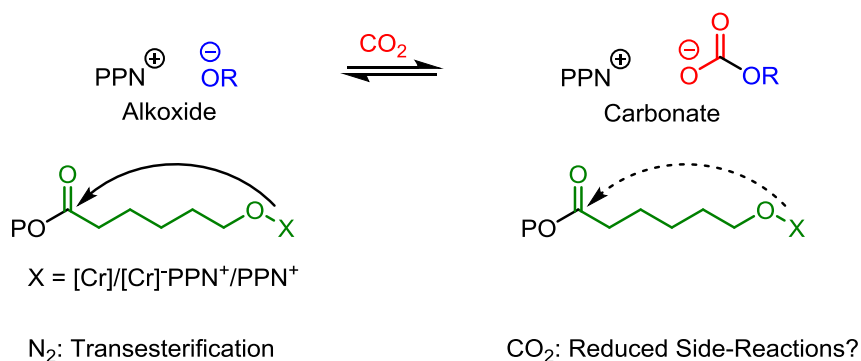
Figure 3. 30 – Arylchromium complex with aqua ligand (left), non-initiating salen complex (middle) and initiating co-catalyst (right).^[52, 54]

iv) *Bimetallic catalysts.* So far, only biszinc complexes have been reported for 'switch' catalysis. In both cases, a co-catalyst was not necessary and molecular weights above 5,000 g mol⁻¹ could be achieved.^[1-4, 8] With respect to chromium, dinuclear, tethered salen

catalysts are highly active for PO ROP with TOFs of ca. 600 h^{-1} .^[55] So far, these complexes have not been tested for ROCOP, and they may be viable candidates for a faster synthesis of block copolymers. This may be combined with changes in the initiating group, as mentioned above, to access high molar mass block copolymers.

3.9.2. Use of Carbon Dioxide to Overcome Side-Reactions

CO_2 had a positive effect on the formation of isotactic PLA, which was ascribed to reduced side-reactions from the PPN-stabilised carbonate (as opposed to the alkoxide). Its use may also have a beneficial effect on CL and other so far difficult monomers in 'switch' catalysis. It should be noted that further insights into these side-reactions, including the nature of the labile/less stable species (neutral chromium alkoxide vs. anionic chromate vs. PPN-stabilised ionic species) are necessary to fully understand the effect of CO_2 .



Scheme 3. 10 – Possible effect of CO_2 on transesterification.

3.9.3. Applications

Based on their molecular masses, these block polyesters may be used in two areas: (i) as coating materials (low weight) or (ii) as thermoplastic elastomers (high weight). The first application requires low melt viscosities for the preparation of the curable mixture and C=C bonds reactive towards radical cross-linking. In this work, the block copolymer PDL-*b*-PCHNBE-*b*-PDL is a promising candidate for coating applications due to its low molar mass ($M_n > 5,000 \text{ g mol}^{-1}$) and internal alkene, which was converted in thiol-ene reactions. For thermoplastic elastomers, high molecular weights are needed, which have been achieved here through chain-extension. Most recently, similar ABA triblock polyesters based on poly(cyclohexene phthalate) (PCHPE) and PDL have been chain-extended with MDI and showed promising properties as TPEs with a high elongation at break ($\epsilon_b > 2450\%$ with 26 wt% of PCHPE).^[7] These materials could also be used as shape-memory materials if the

relative amounts between 'hard' and 'soft' blocks are changed, which further highlights that various material compositions should be tested and compared.

Finally, the T_g value was highly tuneable over a range of ca. 140 °C and dependent on the ratio of PCHNBE and PDL (Figure 3. 31). This may be attractive for applications as plasticisers, where small molecules are generally used. The most prominent example is bisphenol A which is a suspected endocrine disruptor.^[56] Substituting small molecule plasticisers with a polymer may reduce toxicity due to its larger size and have slower leaching.

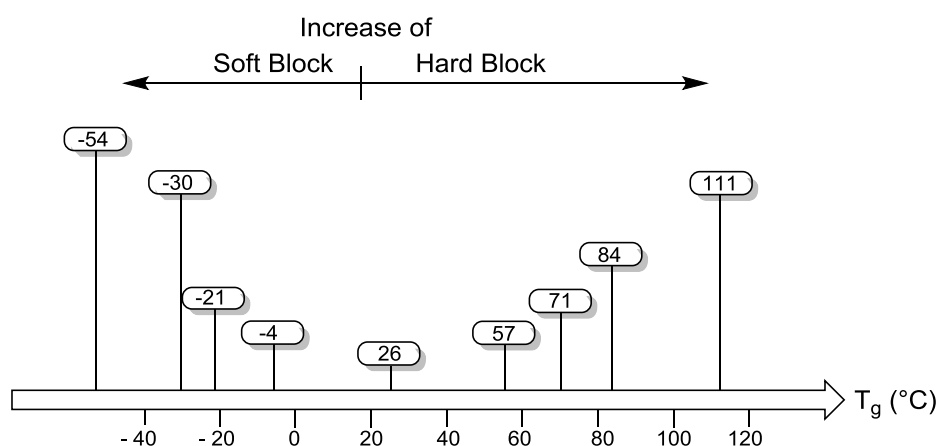
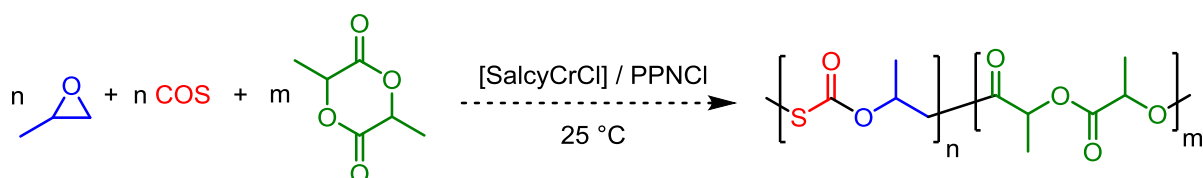


Figure 3. 31 – T_g values of PDL-*b*-PCHNBE-*b*-PDL with various compositions.

3.9.4. Carbonyl Sulfide As a Monomer For 'Switch' catalysis

[SalcyCrCl] is a known, active and selective catalyst for the copolymerisation of COS and epoxides.^[57-59] Poly(thiocarbonate)s have several advantages, such as high chemical resistance, optical and thermal properties.^[60-62] The synthesis and characterisation of block copolymers containing poly(thiocarbonate)s is currently unknown. 'Switch' catalysis may be a unique way to access (multi)-block copolymers in one step. In a first step, the polymerisation of lactide and epoxides with COS is proposed (Scheme 3. 11).



Scheme 3. 11 – Proposed 'switch' catalysis with PO, COS and LA.

By replacing CO_2 with COS, further side-reactions, such as O,S scrambling, need to be considered and the underpinning theory to rationalise 'switch' catalysis should be developed.

Overall, this study represents an important step towards establishing 'Switch' catalysis as an efficient way to synthesise block polymers, which are otherwise only available by labour- and time-consuming, stepwise procedures. The use of a commercial catalyst might facilitate the transition from an 'exotic' synthetic curiosity to an easy-to-use methodology in polymer science and its neighbouring areas.

3.10. References

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Chapter 4

‘Switch’ Catalysis with [SalcyCrCl]

Part II – Propylene Oxide

4.1. Introduction

Due to its low price, propylene oxide (PO) is a highly desirable monomer for commercial applications. However, compared to CHO, PO is challenging to polymerise in a well-controlled manner, a consequence of its asymmetric nature and minimal steric bulk. This facilitates side-reactions such as epimerisation, in which the stereochemistry of the ester-linkage is changed, and transesterification, in which blocks are scrambled or cyclic species are formed.

In this chapter, the synthesis of copoly(ester-*b*-ether)s is studied from PO and anhydrides with [SalcyCrCl]. The rules previously established for 'switch' catalysis are probed and a number of key questions for this catalysis are asked and answered (Figure 4. 1). This includes: how high is the selectivity? Are ether linkages formed throughout the reaction or as a distinct block? Can the feedstock be extended to further monomers? This transformation is the first one-pot transformation to yield poly(ester-*b*-ether)s that (i) uses PO as a monomer, (ii) follows the principle of 'switch' catalysis and (iii) is based on a commercial salen-chromium catalyst.

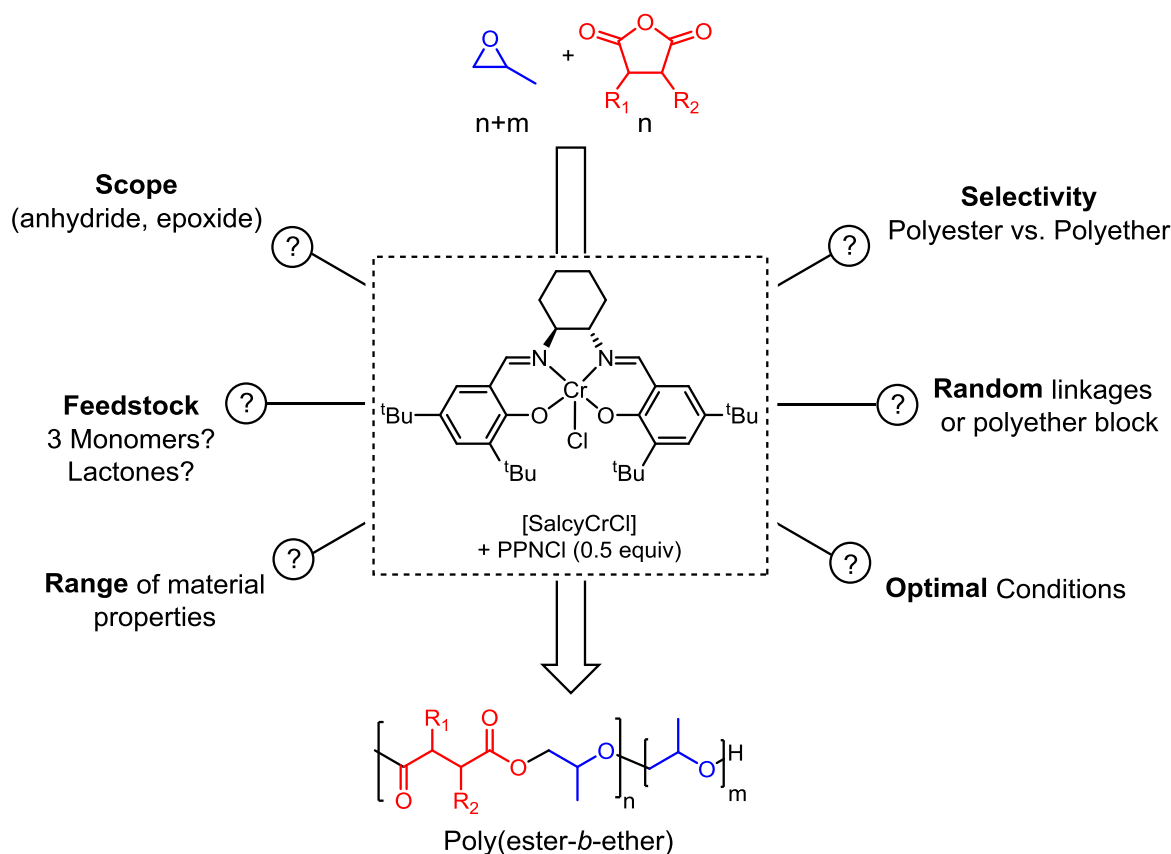
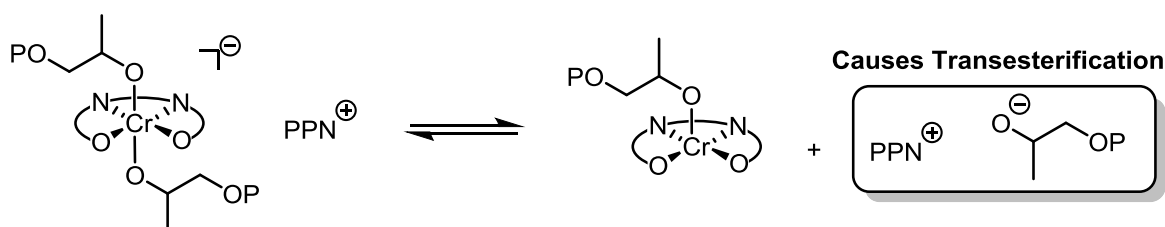


Figure 4. 1 – Overview of 'switch' catalysis with propylene oxide presented in this chapter.

4.2. Synthesis of Block Copolymers

As a starting point, the one-pot polymerisation of PA/PO, using an excess of PO, was investigated. After two days, high conversions of all monomers were observed by ^1H NMR spectroscopy, including the polymerisation of excess PO in poly(propylene oxide) (PPO). Such polyether formation was not observed using CHO. Unexpectedly, aliquot analysis suggested the selective formation of polyester followed by polyether and not a random incorporation of polyether linkages (not shown).

Although encouraging in terms of selectivity, the putative block polymers showed broad molar mass distributions. This may be expected when transesterification occurs. It was hypothesized in the literature that transesterification is caused by free alkoxide terminated chains, stabilised by the co-catalyst counter-cation (Scheme 4. 1).^[1]



Scheme 4. 1 – Proposed species at the end of PO/anhydride ROCOP

To suppress transesterification, the amount of co-catalyst was reduced by using a catalyst:co-catalyst ratio of 2:1. Moreover, the reaction was performed in the presence of excess anhydride to hinder the formation of the alkoxide at the end of the reaction. In this case, significant broadening of GPC traces was still observed (for PO:PA:CHD = 90:100:10, $M_n=920 \text{ g mol}^{-1}$, $\bar{D} = 1.41$). This result indicated that transesterification occurred during ROCOP and not only at the end of the reaction. Coates and co-workers have very recently reported a similar observation, for aluminium catalysts with the same co-catalyst.^[1] However, in their work, transesterification was effectively suppressed if sterically hindered anhydrides were used.

To test if this effect of steric bulk is equally important for the catalyst used herein, [SalcyCrCl], the reaction was repeated using a sterically hindered tricyclic anhydride TCA1 (Figure 4. 2, top). In this case, a significant improvement in molar mass and dispersity was found ($M_n=920 \text{ g mol}^{-1}$, $\bar{D}=1.41$ for PA vs. $M_n=1,800 \text{ g mol}^{-1}$, $\bar{D}=1.14$ for TCA1). After this encouraging result, the one-pot polymerisation of TCA1/PO, in excess PO was revisited and monitored by regular removal of aliquots, which were analysed by ^1H NMR spectroscopy and GPC.

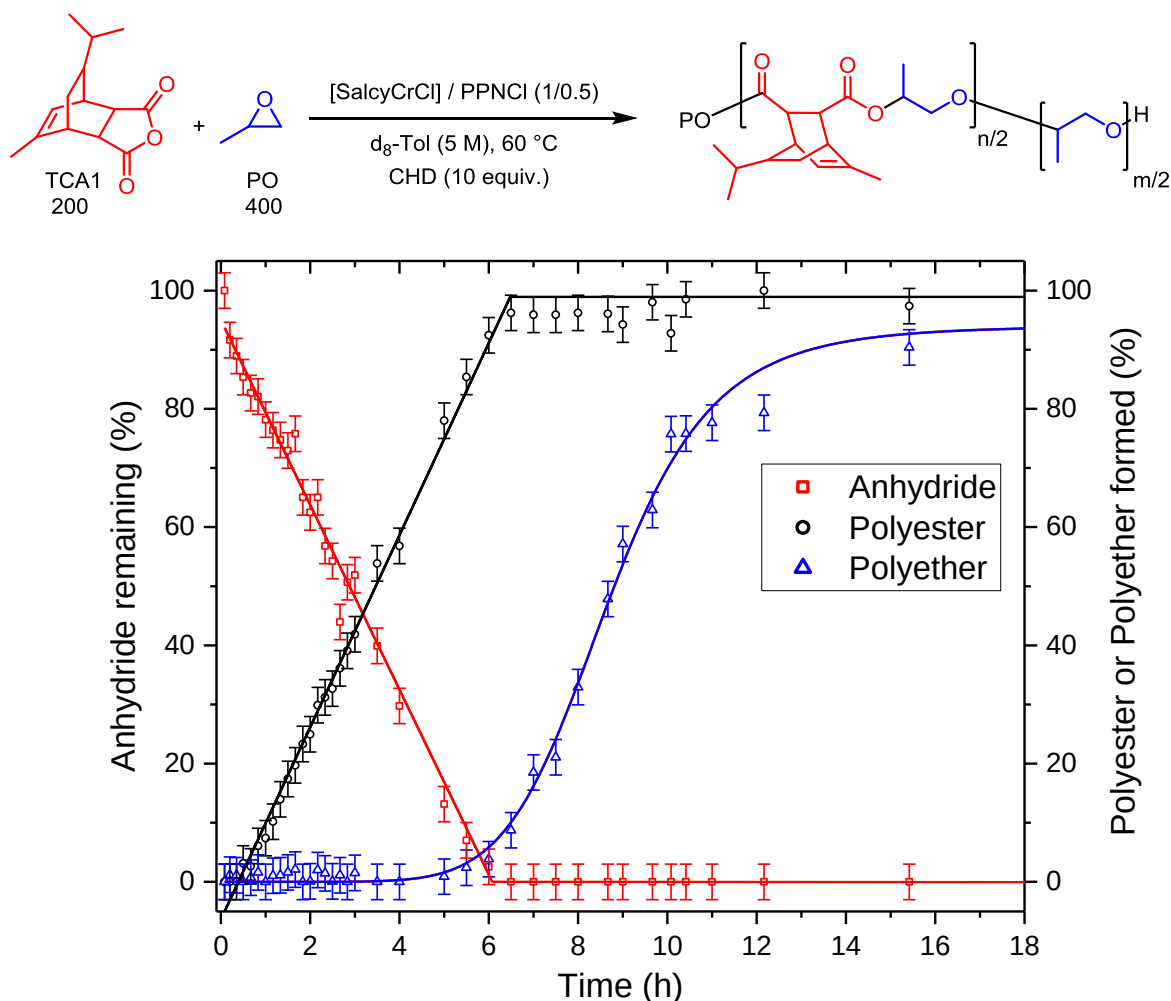


Figure 4. 2 – Normalised polymerisation conversion vs. time plots for one-pot polymerisation of TCA1/PO. Reaction conditions: [SalcyCrCl]/[PPNCI]/[CHD]/TCA1/PO = 1:0.5:10:200:400, Tol-d₈ (5 M), 60 °C. Data was based on integrals from ¹H NMR spectroscopy after normalising against mesitylene as an internal standard. The conversions at the end of the reaction were determined as > 95% for anhydride and polyester and 60% for PPO. An error of ± 3% is applied to all plots.

To investigate the catalysis, multiple ¹H NMR spectra collected during the polymerisation were compiled into a conversion-time plot (Figure 4. 2). Two stages of the reaction were clearly visible: First, ROCOP proceeded until the anhydride is fully consumed and second, excess PO was polymerised. Remarkably, no polyether linkages were detected until the 'switch' point at 6.5 h (> 95% polyester and < 5% polyether formation). This was clearly visible in the individual ¹H NMR spectra before and after 6.5 h as a resonance between 3.72 - 3.29 ppm (Figure 4. 3) and was further confirmed by MALDI-ToF at low conversions, which showed only perfectly alternating polyester chains (see appendix). During ROCOP, a zeroth-order dependence of the rate on the anhydride was observed and further kinetic analysis yielded an observed rate constant of $k_{obs, ROCOP} = 0.78 \pm 0.02 \text{ M}^{-1} \text{ h}^{-1}$ (see appendix). For the homopolymerisation of PO as the

second step, a first-order dependence of the rate on the concentration of PO was observed, after a short initiation time, $k_{obs,ROP} = 0.32 \pm 0.02 \text{ h}^{-1}$ (see appendix). This sigmoidal shape of the conversion-time plots were similar to the previous 'switch' catalysis with CHO/NBA/DL and may be attributed to slower initiation from the polymer chain end.

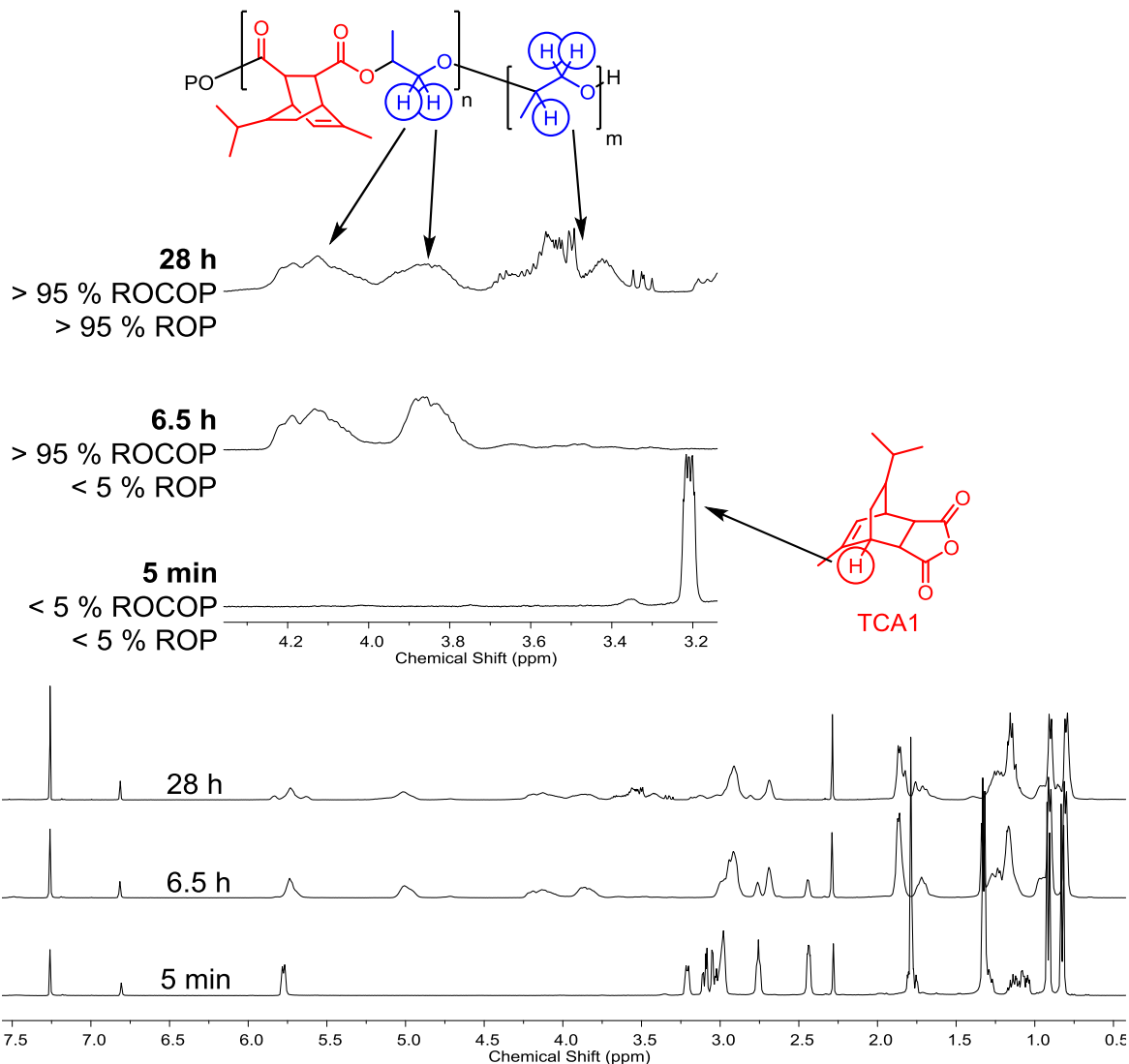


Figure 4.3 - ^1H NMR spectra of one-pot polymerisation of TCA1/PO at different conversions. An overview is given on the left; the relevant polyether region is enlarged on the right. It should be noted that < 5% polyether was formed at the end of ROCOP.

To identify if a block copolymer was formed, the aliquots were analysed by GPC (Figure 4.4). In the case of a mixture of homopolymers, two peaks should be observed, one from each polymer; for a block copolymer only one peak should be detected. Throughout the reaction, monomodal GPC traces were observed that continuously increased in molar mass. The polydispersity should be highlighted as it was still low

($\bar{D}$ =1.13) even after a prolonged reaction time (beyond full monomer conversion). The GPC traces did not change during this time suggesting that side-reactions such as transesterification were successfully suppressed.

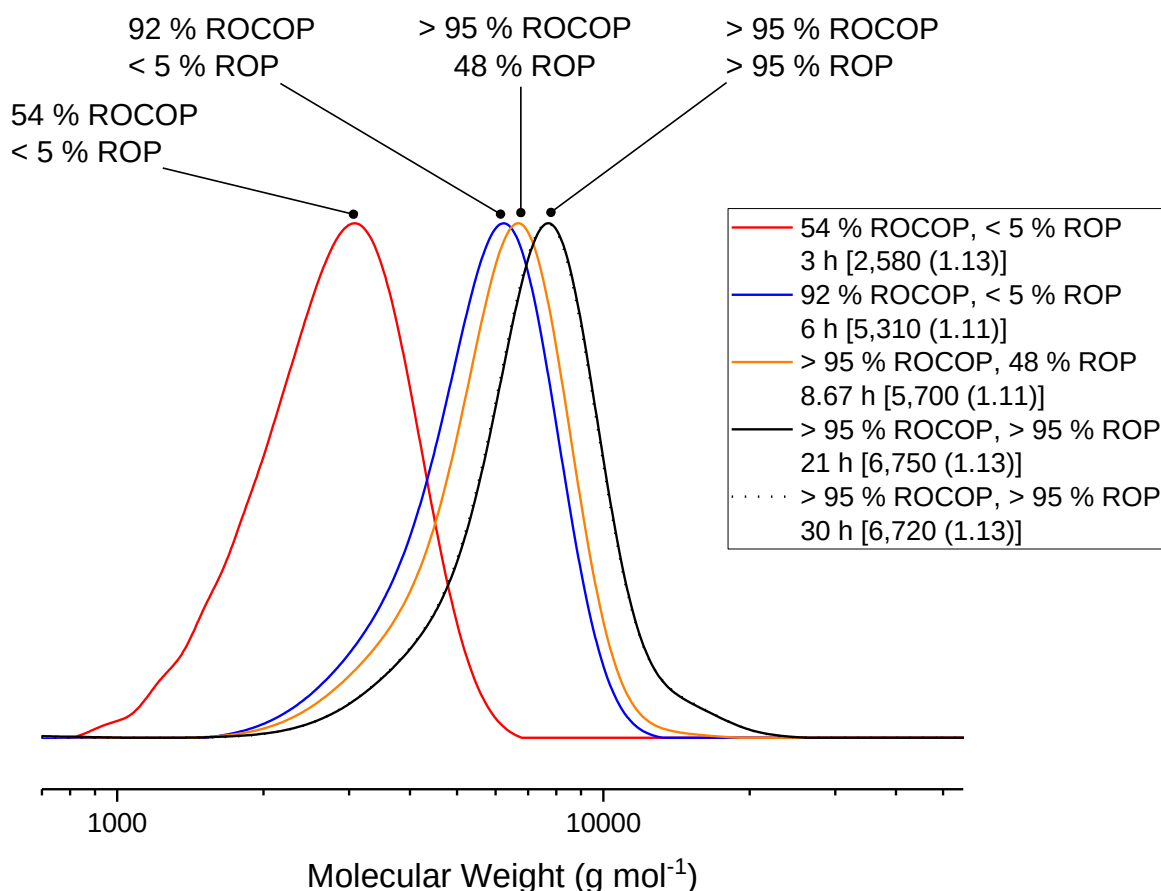


Figure 4. 4 – GPC traces of aliquots for the one-pot polymerisation of TCA1/PO at different stages of the reaction.

To account for the possibility that polyester and polyether have slightly different hydrodynamic radii and a mixture of homopolymers therefore may not be detected easily, all three polymers (PPO, TCA1/PO PE and the block copolymer) were synthesised and analysed. The chromatograms are shown in Figure 4.5 and separate traces for the individual polymers can be observed with only minimal overlap. More specifically, the block copolymer shows a M_n value, which is equivalent to the sum of the homopolymers and in good agreement with the theoretical molar mass.

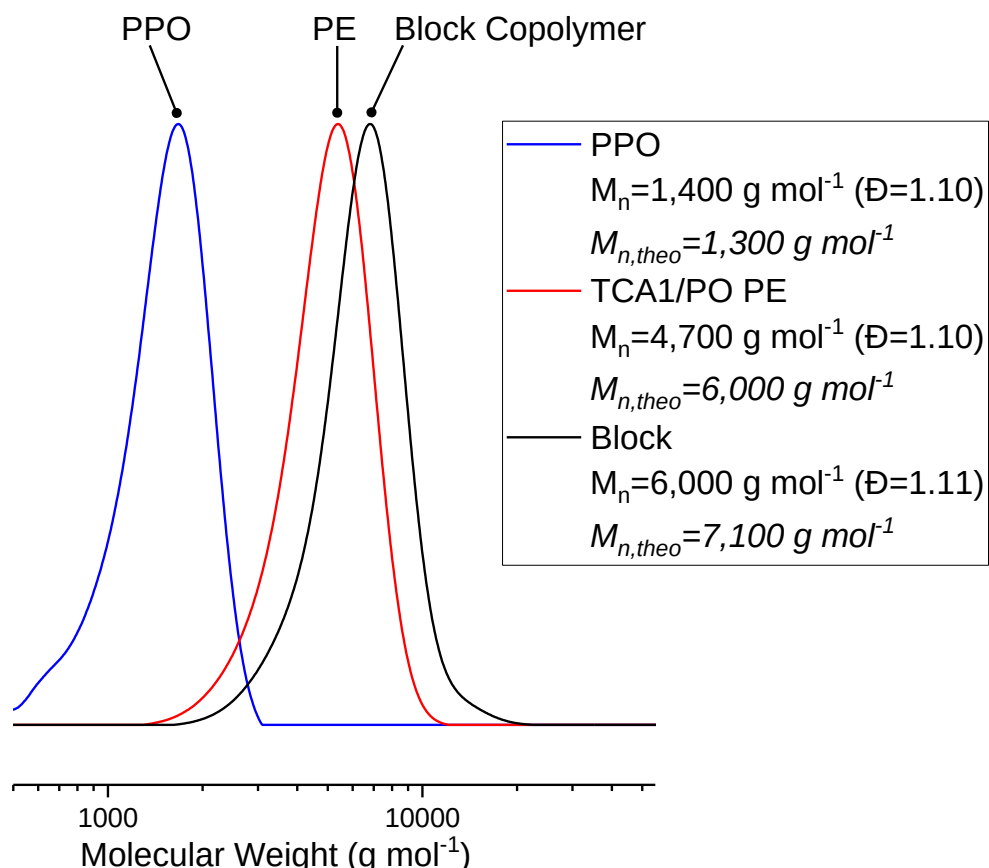


Figure 4.5 – Comparison of GPC traces of PPO, PE and the corresponding block copolymer (DP = 20 in all cases).

This trend of increasing molar masses was not only observed in these 'snapshots' but throughout the entire reaction (Figure 4.6). Furthermore, a correlation between molar mass and time was found: during ROCOP, the molar mass increased linearly with time, as expected from ^1H NMR spectroscopy (anhydride was linearly consumed with time). In contrast, an exponential increase in molar mass with time was observed during ROP, which was again expected from Figure 4.2. It should be noted, that these trends were relative to reaction time, not conversion (in living polymerisations, M_n vs. conversion increases linearly).^[2] Comparatively small changes in molar mass were found during epoxide ROP, most likely due to the lower molar mass of the repeat unit.

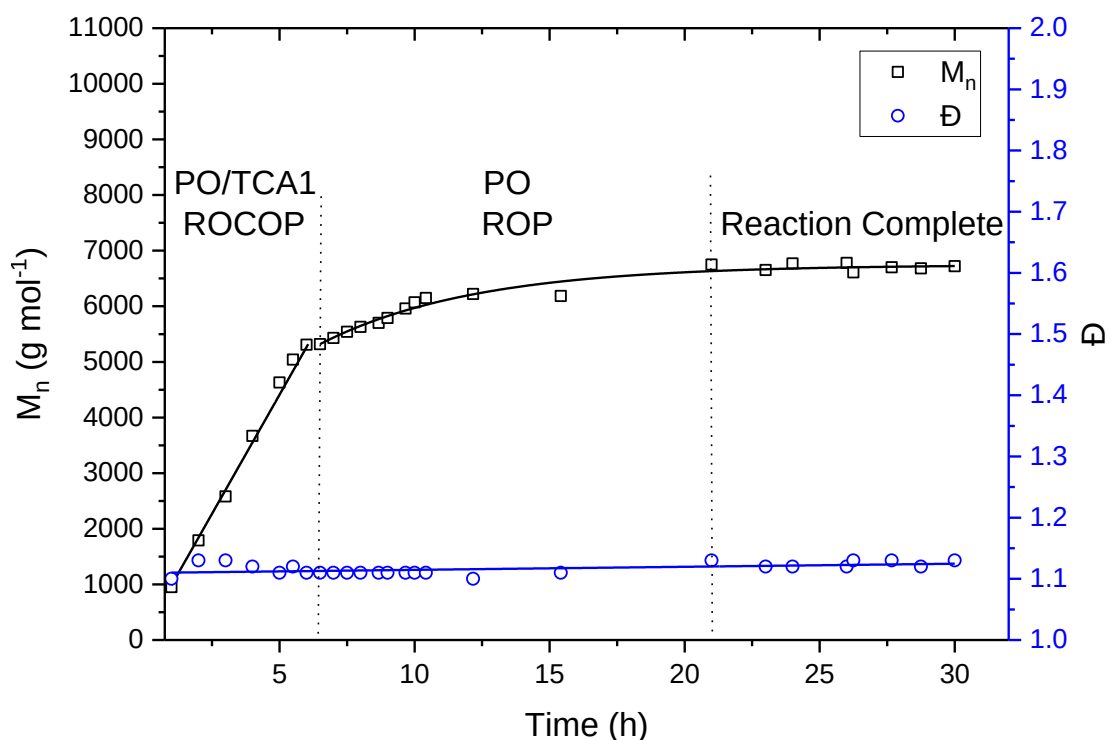


Figure 4. 6 – M_n and $\bar{D}$ values at various stages of the reaction.

Further proof for block copolymer formation was obtained by DOSY NMR spectroscopy (Figure 4. 7). The proposed block copolymer showed one diffusion coefficient ($D^{Block} = 1.70 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$), as expected from covalently attached block segments whereas a mixture of homopolymers, of similar molar masses, exhibited two, clearly separated, coefficients ($D^{ROCOP} = 2.08 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$ and $D^{ROP} = 4.09 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$).

As an aside, the difference in diffusion coefficients for the mixture of homopolymers was significant and the polymers could be easily distinguished from each other. This may be a consequence of the different types and weights of polymers in solution, as similar control experiments for other block polyester were less obvious.

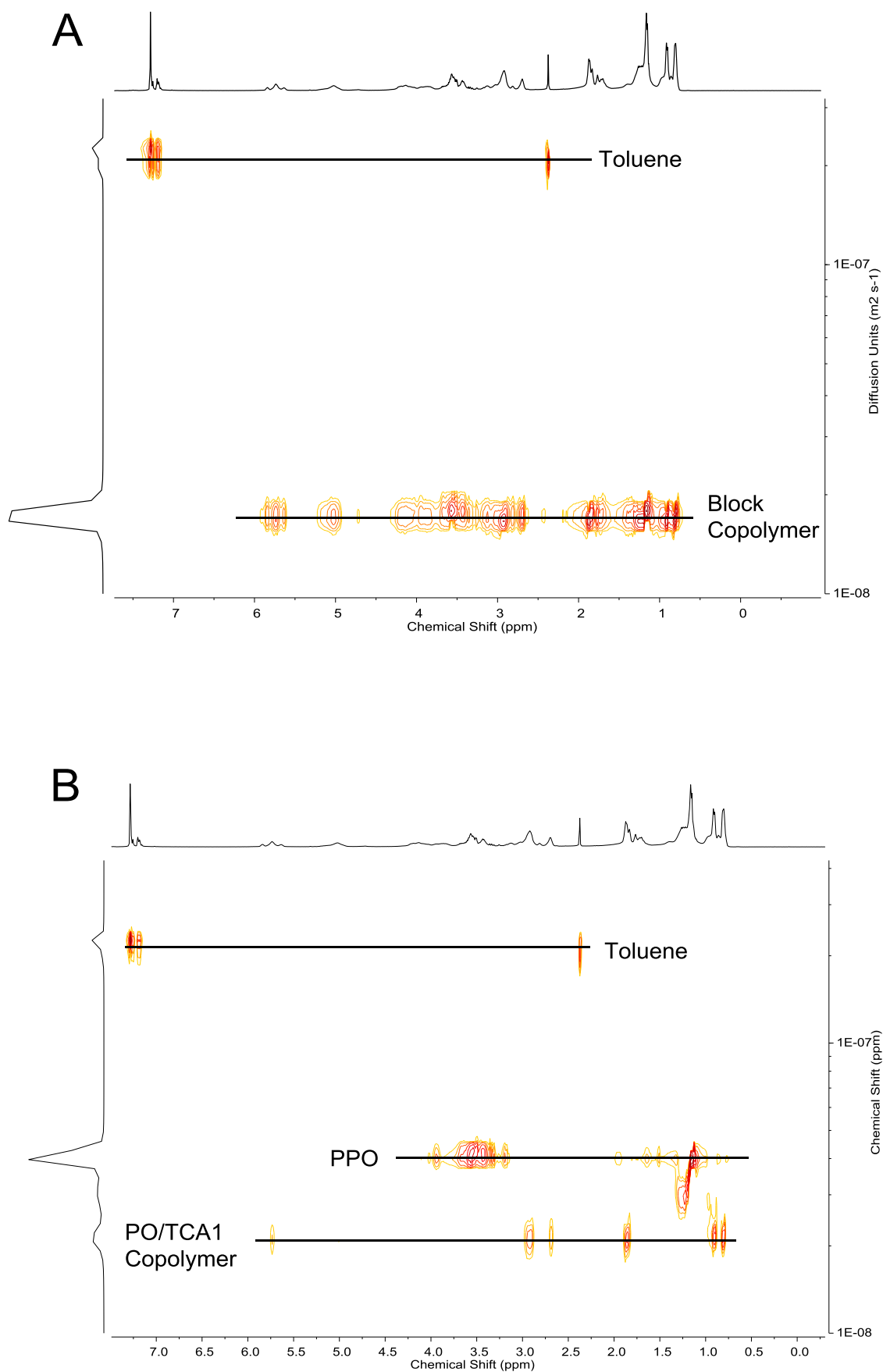


Figure 4. 7 – DOSY NMR spectra of a block copolymer (A) and a mixture of homopolymers (B) of similar molar masses.

Finally, the regio- and stereochemistry of the formed block copolymer was investigated. First, the regioregularity of PPO was analysed by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (Figure 4. 8). Different reports of isotactic PPO showed resonances in the chemical shift region between 73 - 76 ppm.^[3-5] Similar NMR spectra to those reported were obtained suggesting a high degree of regioregularity (HT-linkages). More specifically, a preference for isotactic junction units was found with an **ii** to (**is+si**) to **ss** ratio of 65:29:26. This is a modest degree of stereoselectivity and similar to that observed for aluminium tetraphenylporphyrin chlorid (50:40:10),^[6] but lower than the most *iso*-selective catalysts reported (**is+si** and **ss** are not observed in these cases).^[4, 7-11]

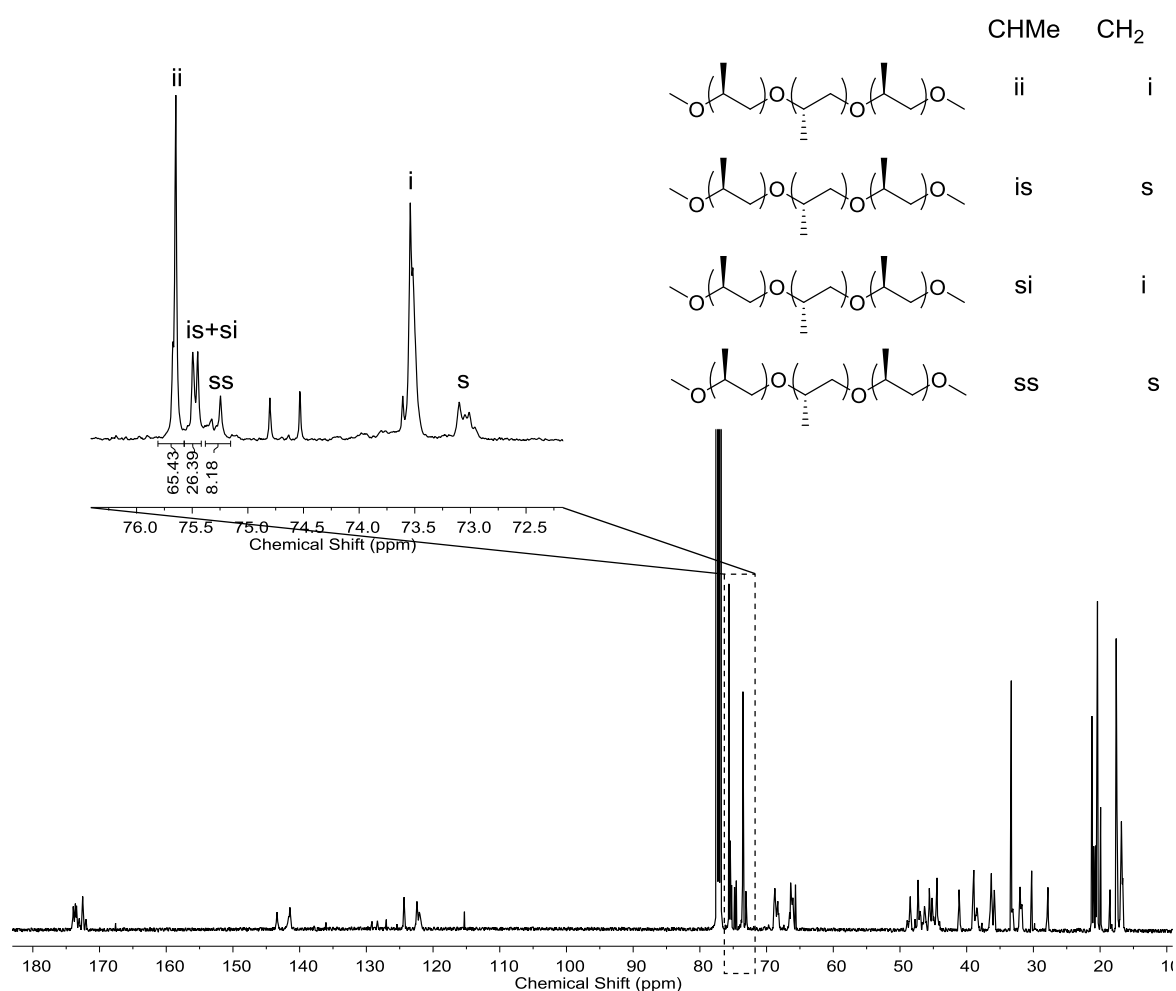


Figure 4. 8 – Extended region of $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum used for the analysis of PPO.^[6]

End groups were further analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, after the reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Figure 4. 9). This provides a further technique to analyse the regioselectivity of the polymerisation as two different chemical

environments should be observed for a regioirregular polymer due to a mixture of primary and secondary alcohol end-groups. Herein, one major signal at 146.05 ppm was found, which was attributed to secondary alcohol end-groups from PPO. A minor signal at 146.11 ppm was further detected and is proposed to be a consequence of the modest stereoselectivity. It is unlikely that this is an indicator for a primary alkoxide, as expected from a regioirregular polymer, due to small differences in chemical shift ($\Delta\delta = 0.06$ ppm). An example for a regio-irregular polymer based on PO is given in Chapter 5 and the two end-groups were found at 145.50 and 147.80 ppm with a difference in shift by 2.30 ppm.

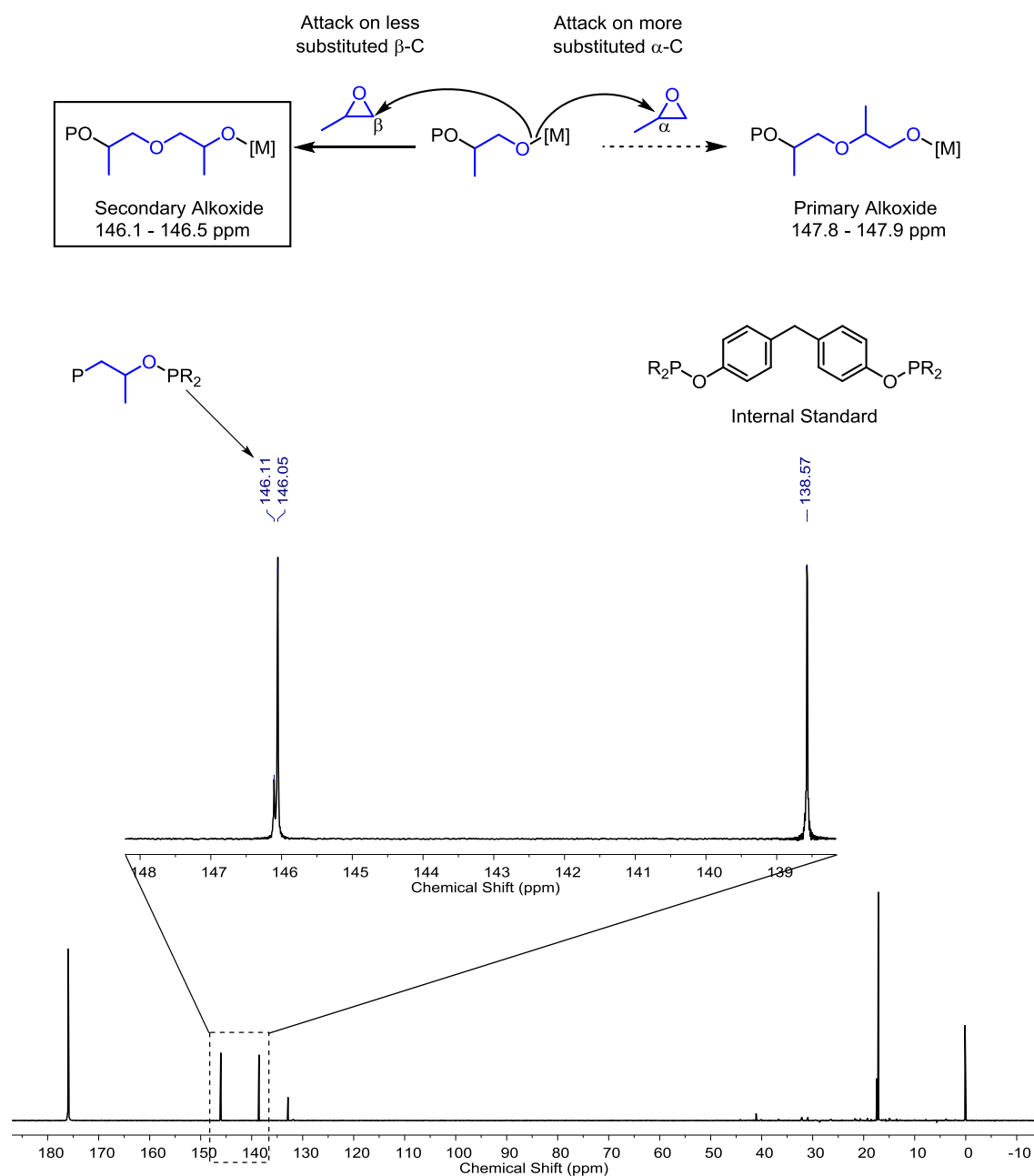


Figure 4. 9 – Formation of different regioisomers for the ring-opening of PO and common chemical shifts for primary and secondary alcohols (top) and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of block copolymer after the reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (bottom).^[12]

To investigate the relative stereochemistry of the ester functionalities in the polyester block, the polymer was degraded by reduction to alcohols with lithium aluminium hydride (Figure 4. 10). Analysis of the reaction products, by ^1H NMR spectroscopy, showed a mixture of *cis*- and *trans*-ester diols (40:60). This suggests slow epimerisation of TAC1 or ester-linkages occurred during the reaction.

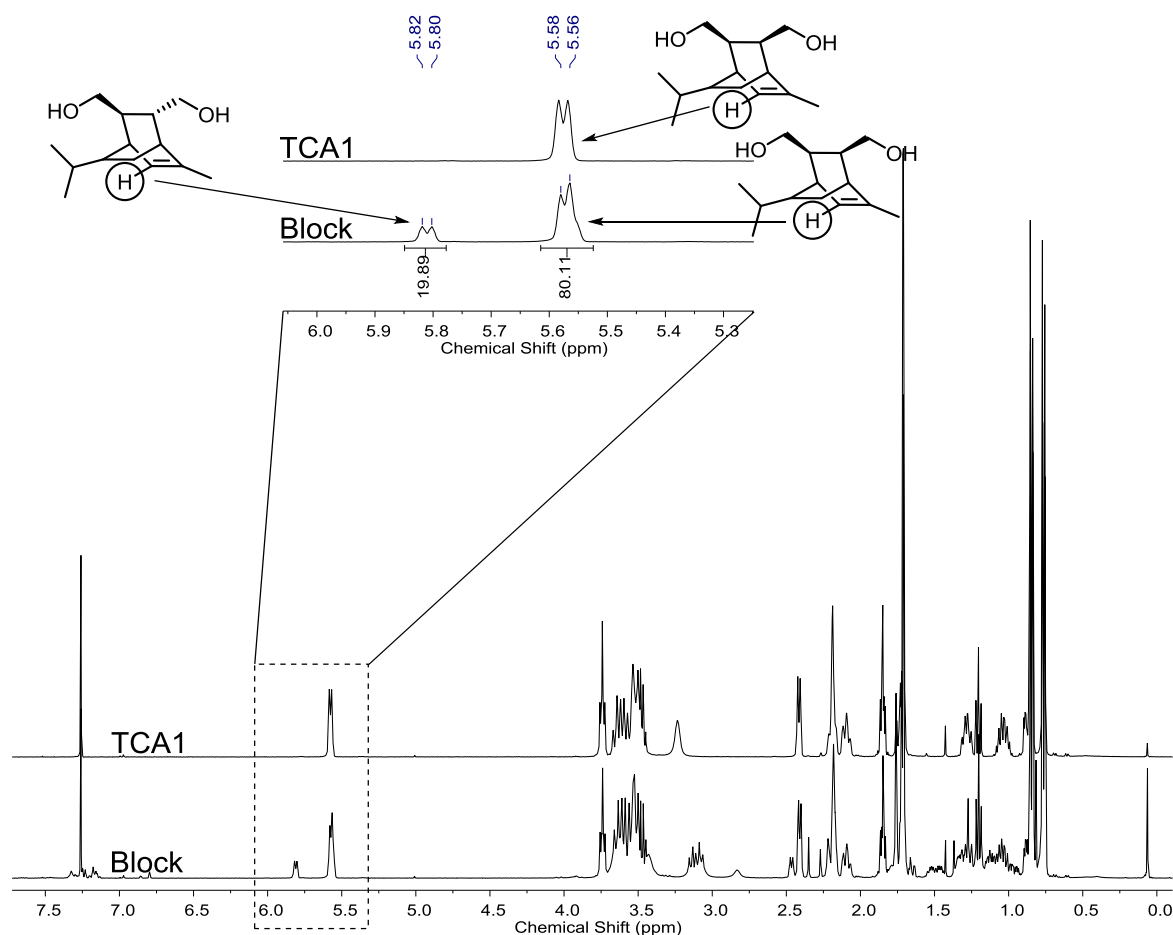


Figure 4. 10 - ^1H NMR spectra of degradation products from TCA1 and the proposed block copolymer obtained from TCA1/PO in CDCl_3 . The ratio of the *cis* and *trans* isomers was determined by integration from the degradation products (*cis:trans* = 20:80).

Finally, the block copolyester was also characterised by a range of 2D NMR techniques, including COSY, HSQC, HMBC and TOCSY. Two observations can be made: firstly, the block copolymer showed the same end group as the corresponding PPO homopolymers and which are quite different to the polyester (Figure 4. 11); secondly, additional signals were observed in the NMR spectra of the block copolymer that were absent in both the polyester and polyether spectra. These are attributed to the junction unit between the two blocks. It should be noted that further analysis of junction units is complicated by the mixture of *cis* and *trans* ester linkages, which may overlay the junction unit signals.

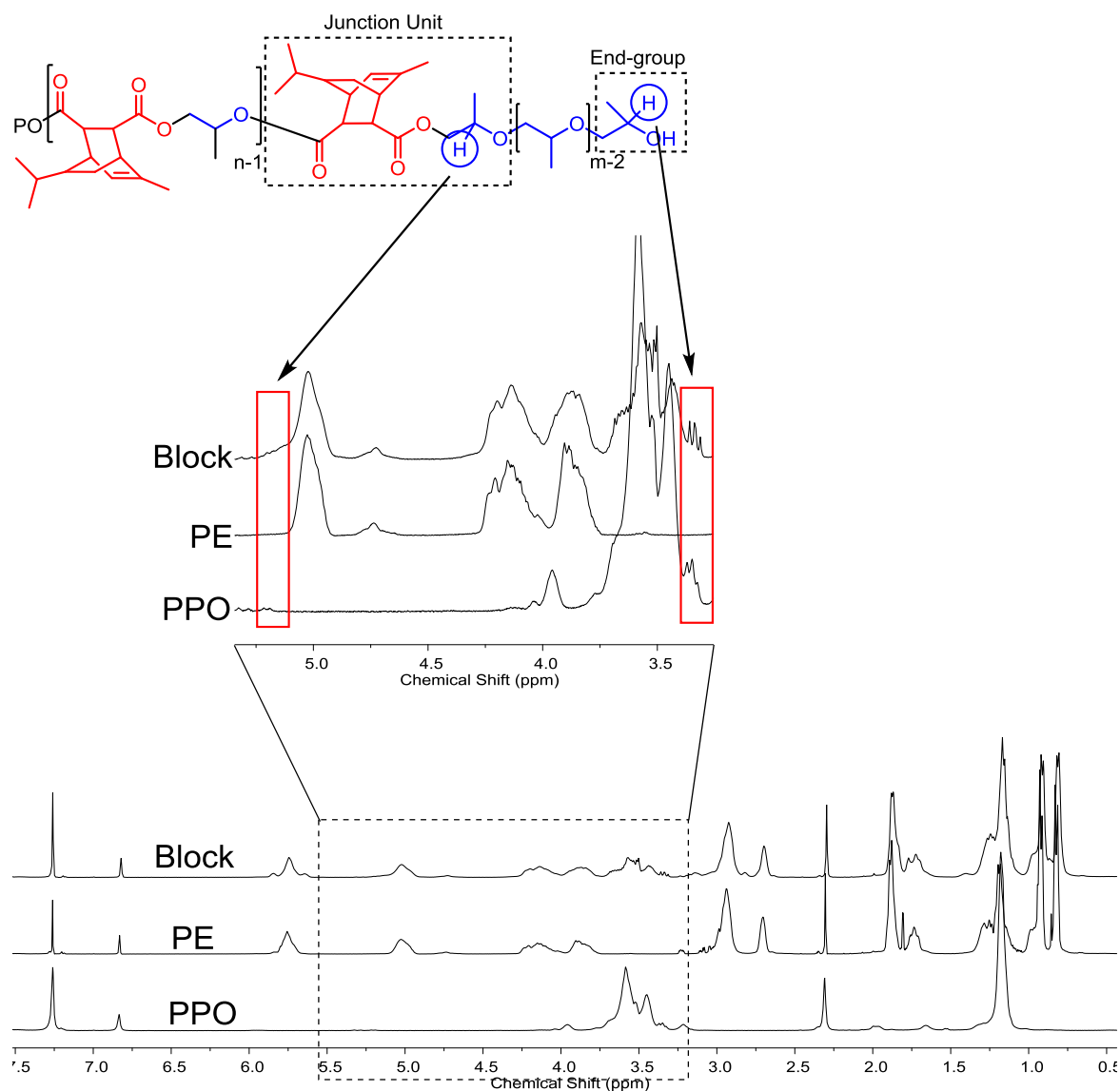
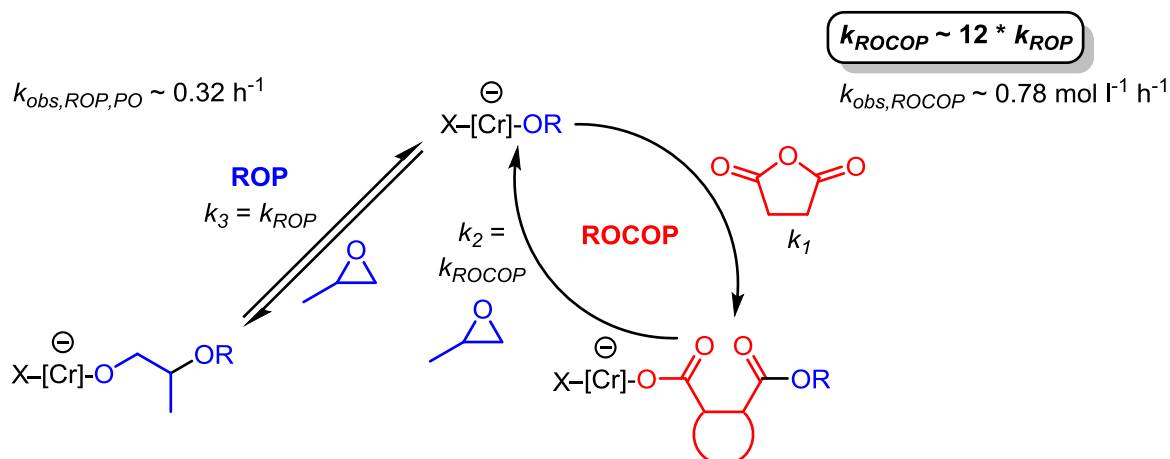


Figure 4. 11 – ^1H NMR spectra of homopolymers (PPO, PE) and the block copolymer.

To test its industrial relevance, the catalysis was investigated at a 25 gram scale of TCA1, in a 100 mL stainless steel reactor. Similar conversions ($> 95\%$ for PO and TCA1) and molar masses ($M_n = 3,700 \text{ g mol}^{-1}$ ($\bar{D}=1.15$)) were achieved in this setup, compared to the small scale reaction. Whilst clearly preliminary in nature, these results highlight the potential to apply the 'switch' method at larger scale and under industrially relevant conditions.

4.3. Mechanistic Hypothesis

The characterisation and analysis clearly indicate that block copoly(ether-*b*-ester-*b*-ether)s were synthesized by 'switch' catalysis. A reaction mechanism is proposed based on the two catalytic cycles, TCA1/PO ROCOP and PO ROP (Scheme 4. 2). Both mechanisms are connected through one common intermediate, a putative hexacoordinate, anionic chromium alkoxide species. ROCOP is a two-step process where the anhydride is ring-opened first, which results in the formation of a chromium carboxylate (k_1). This latter intermediate reacts with PO to (re)generate a chromium alkoxide in a second step (k_2). This cycling between k_1 and k_2 proceeds until the anhydride is fully consumed. At this point, PO ROP occurs, which results in the formation of an alkoxide intermediate (k_3). The order of the rate constants is proposed: $k_1 > k_2 > k_3$ based on the observed monomer selectivity (Figure 4. 2). It should be noted that k_1 cannot be measured directly from the polymerisation kinetics but k_2 can be obtained, as the ring-opening of the epoxide is the rate-determining step of the polymerisation.



Scheme 4. 2 – Proposed reaction mechanism for 'switch' catalysis (with [SalcyCrCl], TCA1 and PO).

The catalytic selectivity is proposed to be determined by the relative rates of reaction of the chromium alkoxide intermediate towards anhydride or epoxide ring-opening, k_1 vs. k_3 , respectively. To determine k_1 , a stoichiometric reaction of the catalyst with TCA1 and PO was monitored by *in situ* IR spectroscopy (Figure 4. 12). First, the catalytic system ([SalcyCrCl]:[PPNCl] = 2:1) was activated by adding one equivalent of PO with respect to the proposed hexacoordinate, anionic chromate species. After twelve minutes, a concentrated solution containing an equivalent of anhydride was added. The absorption at 1779 cm^{-1} ($\nu_{\text{Anhydride+Carboxylate}}$) showed a clear increase in intensity upon addition, followed by a rapid, exponential decay. This was accompanied by an increase in intensity of the band at 1739 cm^{-1} (ν_{Ester}). Second, one equivalent of PO was added to the mixture and a

further, exponential decrease in intensity of the band at 1779 cm^{-1} was observed. As before, the intensity of the band attributed to ester-linkages (ν_{Ester}) increased. Based on these results, k_1 and k_2 were determined as $182.7 \pm 17.6\text{ h}^{-1}$ and $13.6 \pm 0.6\text{ h}^{-1}$, respectively, after fitting the data for a first order rate-law (see appendix). In other words, k_1 is ca. 13 times faster than k_2 . This is in line with a faster ring-opening of the anhydride compared to the epoxide. It may be hypothesized, however, that the reaction conditions differ slightly from the actual catalysis, most notably in concentration (5 M vs. 0.6 M), solvent (toluene vs. chloroform) and temperature ($60\text{ }^{\circ}\text{C}$ vs $50\text{ }^{\circ}\text{C}$), which could explain differences to the expected values.

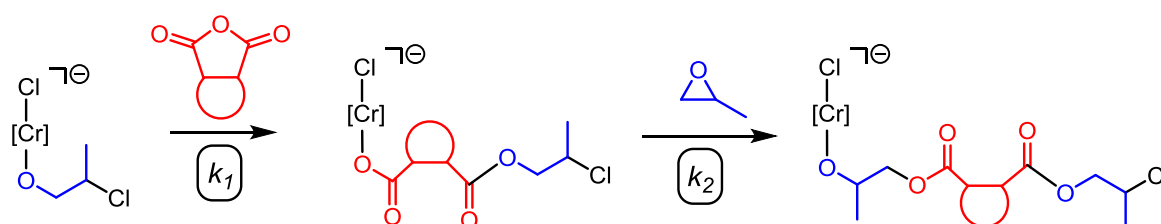
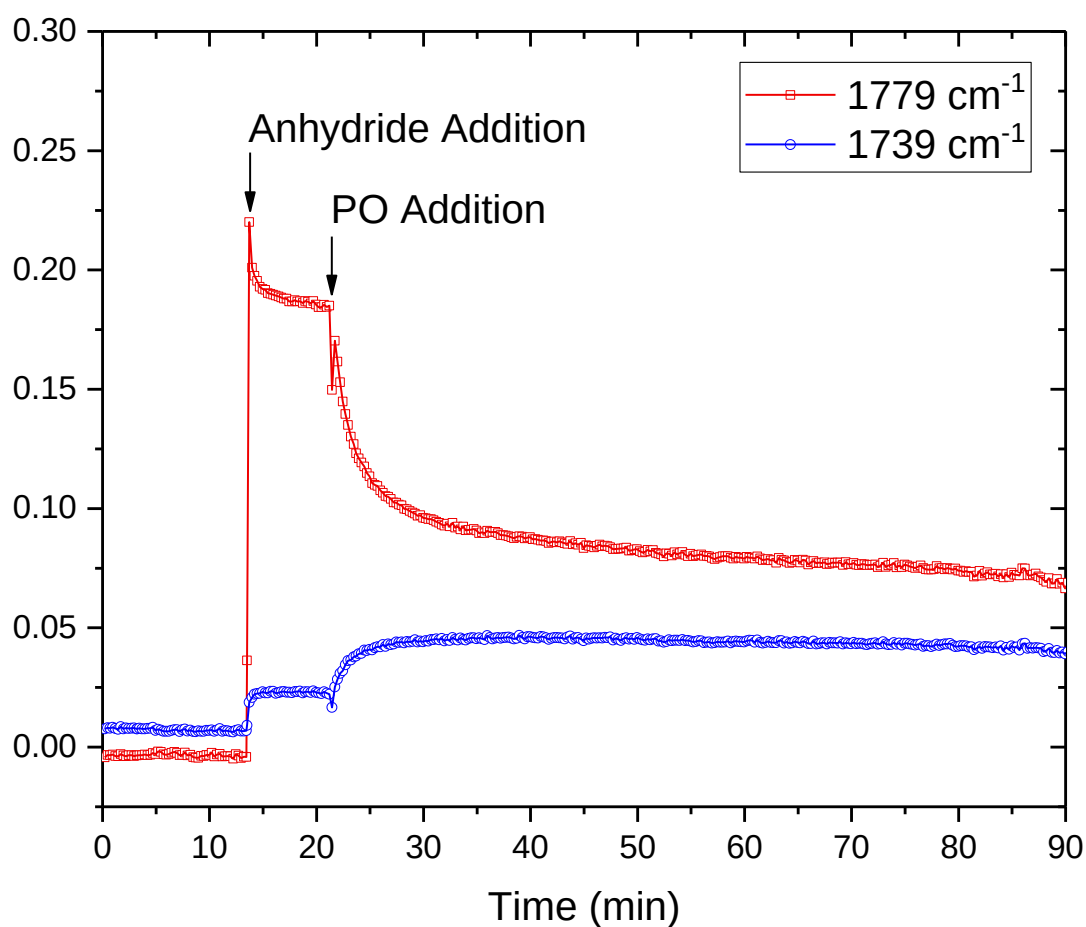


Figure 4. 12 – *In situ* IR monitoring of anhydride and epoxide ring-opening as part of ROCOP.

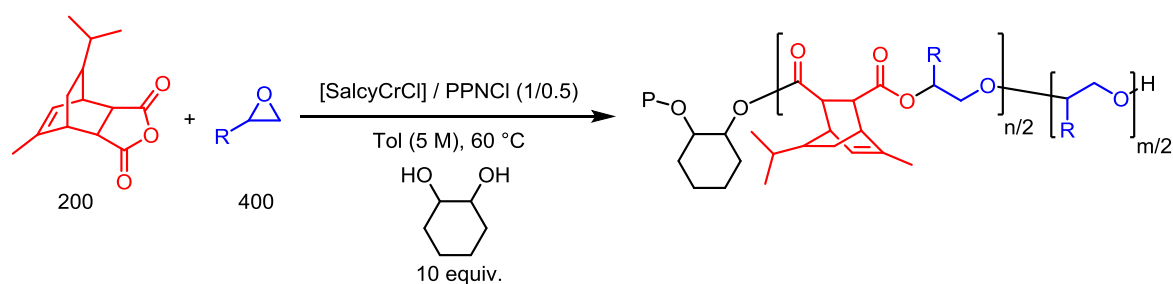
4.4. Substrate Scope

4.4.1. Epoxides

Eight different epoxides were investigated for 'switch' catalysis with TCA1 allowing preparation of eight new poly(ether-*b*-ether-*b*-ether)s (Table 4. 1). In all cases, high conversions of both anhydrides and epoxides were detected and, for the majority of substrates, monomodal GPC traces were obtained. Well-defined block copolymers were synthesised using *tert*-butyl glycidyl ether (BGE), 2-vinyl oxirane (VPO), allyl glycidyl ether (AGE) or 2-ethylhexyl glycidyl ether (EHGE). In these cases, the molar mass of the block copolymer was equivalent to the sum of the corresponding homopolymers (see appendix). For AGE, the material could not be isolated, perhaps due to some cross-linking occurring in air. Similar behaviour was reported for other polyesters prepared from MA/AGE.^[13-14] For BGE, VPO or EHGE, the polymers show one T_g value, with the material from EHGE showing the lowest value at -46°C. In all cases, this DSC data indicates block miscibility at low molar masses. For styrene oxide (SO), a slight decrease in the rate of formation of polyether was found, which may be a result of the high steric demand of the phenyl group directly attached to the epoxide moiety. Nonetheless, a monomodal GPC trace and a high T_g value of 80 °C were obtained. GPC data were bimodal when using phenyl glycidyl ether (PGE), 2-((2-(2-(2-methoxyethoxy)ethoxy)-ethoxy)methyl)oxirane (ME₃MO) or glycidyl hexadecyl ether (GHE). The higher molar mass peak was at ca. twice the molecular mass of the lower peak. This implies a greater amount of monofunctional impurities in the monomer, despite using the same purification procedure for all epoxides (bifunctional impurities would contribute to the main peak initiated from CHD). Unfortunately, the polymer obtained from ME₃MO was highly soluble in organic solvents and could not be isolated (likely a result of the low molecular mass). DSC indicated crystalline domains for GHE (melting point at 22.1 °C), as expected for the linear, aliphatic side chains. As an aside, low-intensity transitions at 95-105 °C were observed by DSC for some samples. This transition was ascribed to residual amounts of the chromium-catalyst (see appendix).

In summary, the substrate scope investigation shows that multiple different epoxides can be used in this catalysis and typically monomodal GPC traces and one T_g value were obtained.

Table 4. 1 – Different epoxide for the one-pot polymerisation with TCA1.



Epoxide	Conversion ^[a]			M_n (Đ) [g mol ⁻¹] ^[b]	T_g [°C] ^[c]
	Epoxide [%]	Anhydride [%]	Time [d]		
 BGE	> 95	99	6	7,900 (1.11)	30 °C
 SO	83	99	6	5,900 (1.15)	80 °C
 PGE	> 95	99	3	9,800 (1.07) + 4,700 (1.04)	39 °C
 ME ₃ MO	> 95	99	6	6,200 (1.11) + 2,900 (1.05)	N. D. [#]
 VPO	> 95	99	3	6,400 (1.14)	26 °C
 AGE	> 95	99	3	8,100 (1.12)	N. D. [*]
 GHE	> 95	99	6	8,800 (1.03) + 4,600 (1.06)	MP: 22.1 °C (-43.2 mJ / mg)
 EHGE	> 95	99	5	7,100 (1.10)	-46 °C

^[a] Determined by ¹H NMR spectroscopy; see appendix for chemical shifts. ^[b] Determined by GPC (THF; 30 °C, PS standards). ^[c] Determined by DSC (3rd heating cycle).

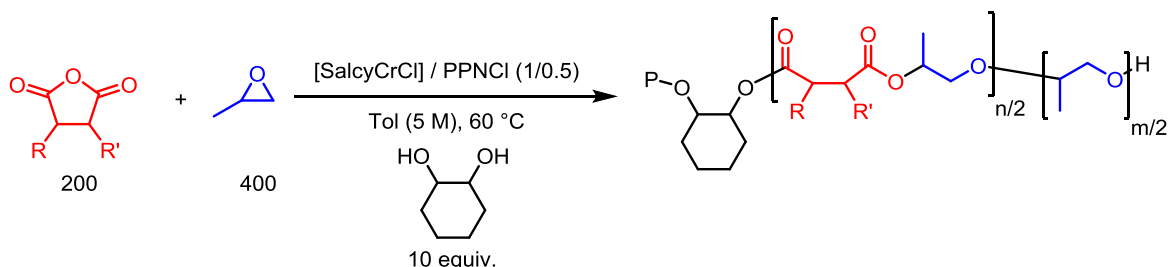
[#] Soluble in pentane (not isolated).

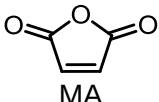
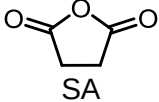
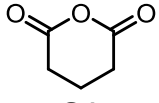
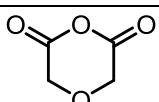
^{*} Insoluble material obtained after isolation.

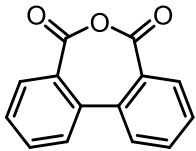
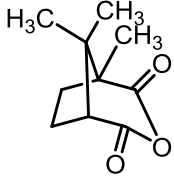
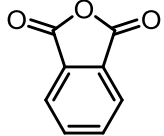
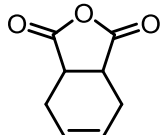
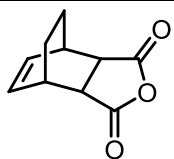
4.4.2. Anhydrides

Next, three classes of anhydrides were tested: mono-, bi- and tricyclic derivatives (Table 4. 2). Although high conversions were obtained in all cases, significant differences in molar mass distributions were found. For monocyclic derivatives (maleic anhydride, succinic anhydride, glutaric anhydride or diglycolic anhydride), broad molar mass distributions were found ($\bar{D} = 1.54 - 3.11$). This is consistent with transesterification occurring more readily due to low steric bulk of the anhydride. One exception to this trend was diphenic anhydride, where a lower dispersity of 1.20 was obtained. This may be ascribed to a comparatively high anhydride steric demand. Bicyclic anhydrides showed lower molar mass dispersities ($\bar{D} = 1.34 - 1.54$). Surprisingly, a further decrease in dispersity to 1.18 was observed with camphoric anhydride. However, in this particular case, ^1H NMR spectroscopy indicated simultaneous formation of polyester and polyether, similar to the copolymerisation with CHO/NBA/DL. This suggests the formation of a random rather than a block copolymer. TCA2 as a representative for a tricyclic anhydride resulted in narrow molar mass distributions.

Table 4. 2 - Different anhydrides for the one-pot polymerisation with PO.



Anhydride	Conversion ^[a]			M_n ($\bar{D}$) [g mol ⁻¹] ^[b]	T_g [°C] ^[c]
	Epoxide [%]	Anhydride [%]	Time [d]		
 MA	67	99	5	5,800 (3.11)	N. D.
 SA	> 95	99	3	5,400 (1.85)	N. D.
 GA	> 95	99	3	1,700 (1.54)	N. D.
 DGA	> 95	99	3	2,100 (2.14)	-11

 DPA	> 95	99	3	5,700 (1.20)	12
 CA	> 95	99	3	6,100 (1.18)	-5
 PA	> 95	99	3	7,800 (1.54)	-27
 THPA	> 95	99	3	5,100 (1.34)	N. D.
 TCA2	> 95	99	3	5,800 (1.19)	N. D.

^[a] Determined by ¹H NMR spectroscopy; see appendix for chemical shifts. ^[b] Determined by GPC (THF; 30 °C, PS standards). ^[c] Determined by DSC (3rd heating cycle).

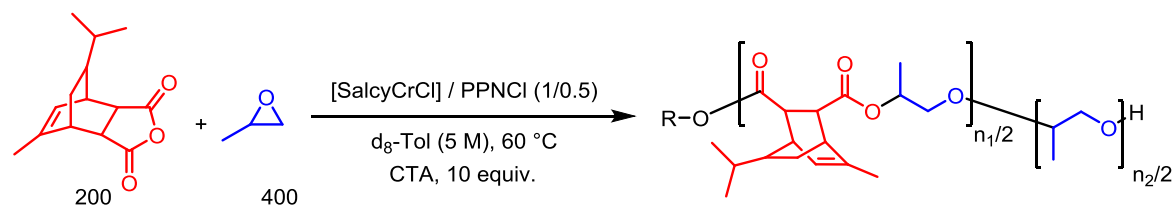
To summarise, a range of different anhydrides can be used in 'switch' catalysis with PO. The successful formation of a well-defined polymer (narrow *D*), however, is only observed for sterically demanding anhydrides, including DPA, PA, THPA and TCA2.

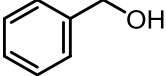
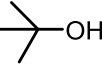
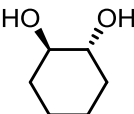
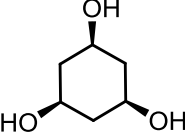
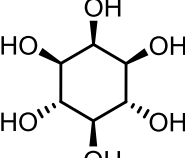
4.4.3. Chain-Transfer Agents

Finally, changes of the type of alcohol chain transfer agent were investigated (Table 4. 3). The selection of CTA had two effects: first, to access monomodal molar mass distributions by reducing chloro-initiation and second, to generate a specific polymer architecture. Until now, a diol (CHD) was used as a bifunctional CTA and the polymer is expected to be initiated on both sides of the alcohol, thereby generating a symmetric ABA triblock (formally, the inner B block would be divided in two parts, which are separated by the CTA, but are considered as one coherent block). Thus, an AB diblock would be

obtained when initiating from a monofunctional alcohol and a star polymer from a trifunctional alcohol.

Table 4. 3 – Range of alcohol CTAs used for 'switch' catalysis with TCA1.



Chain-Transfer Agent	Conversion ^[a]			M_n ($\bar{D}$) [g mol ⁻¹] ^[b]	T_g [°C] ^[c]
	Epoxide [%]	Anhydride [%]	Time [d]		
 Benzyl alcohol	88	99	3	5,900 (1.08)	33 °C
 <i>iso</i> -Propanol	89	99	3	7,000 (1.07)	21 °C
 <i>tert</i> -Butanol	47	99	3	59,000 (1.02) 26,000 (1.09)	61 °C
 <i>trans</i> -1,2-Cyclohexanediol	90	99	3	6,700 (1.12)	41 °C
 <i>cis,cis</i> -1,3,5-Cyclohexanetriol	83	99	3	6,600 (1.14)	42 °C
 Tris(hydroxymethyl)ethane	87	99	3	7,100 (1.11)	34 °C
 <i>myo</i> -Inositol	33	99	3	26,800 (1.09) 10,100 (1.07)	63 °C

^[a] Determined by ¹H NMR spectroscopy; see appendix for chemical shifts. ^[b] Determined by GPC (THF; 30 °C, PS standards). ^[c] Determined by DSC (3rd heating cycle).

Firstly, the influence of the type of the alcohol (primary vs. secondary vs. tertiary) was investigated with benzyl alcohol, *iso*-propanol or *tert*-butanol. For using both benzyl alcohol and *iso*-propanol, narrow molar mass distributions ($\bar{D}$ = 1.08 and 1.07) were

obtained, whereas bimodal distributions resulted when using *tert*-butanol. The two peaks were separated by ca. a factor of two, as expected in the absence of any CTA. This suggests that tertiary alcohols should not be used in this catalysis and the bimodality may be rationalised with slower initiation rates from a tertiary alcohol compared to a secondary or primary alcohol.^[15]

Following this, mono-, bi-, tri- and hexafunctional CTAs featuring secondary alcohols were compared, namely *iso*-propanol, cyclohexanediol, cyclohexanetriol and *myo*-inositol. Well-defined polymers ($\bar{D} = 1.07$ -1.14) were obtained with all CTAs apart from *myo*-inositol. The latter features multiple hydroxyl groups in close proximity to each other and steric bulk may hamper chain-transfer.^[15]

Finally, 1,1,1-tris(hydroxymethyl)ethane featuring primary alcohols was tested and yielded a well-defined polymer ($\bar{D} = 1.11$). This is the only alcohol, which is used routinely for the synthesis of polyurethanes.^[16] In all cases, one T_g value was found, which further confirmed block miscibility.

In summary, 'switch' catalysis was successfully performed with different primary and secondary alcohols of low or medium steric bulk.

4.5. Increasing Molecular Masses

So far, polymers showing molecular masses of $10,000 \text{ g mol}^{-1}$, or less, have been synthesised. This allows for a range of oligomer applications. For example, the synthesis of polyurethanes occurs from diisocyanates and polyols, where the polyol structure determines the physical and processing properties of the resulting polyurethanes. In this case, molecular mass values for the polyol between 180 and $8,000 \text{ g mol}^{-1}$ are typically used.^[16] One other example are coating applications, where low molecular masses reduce melt viscosities and values of ca. $4,000 \text{ g mol}^{-1}$ can be used.^[17] Although both examples are of industrial relevance, higher molar masses are desirable for a variety of applications, such as thermoplastic elastomers or shape-memory materials.^[18] For this reason, three approaches to access high molar masses were investigated.

4.5.1. Increasing Monomer Loadings

By increasing the anhydride:epoxide (A:E) loading, while maintaining constant the amounts of catalyst, co-catalyst and CTA, higher molar masses should be obtained. This hypothesis was tested by gradually increasing the catalyst:monomer loading from 1:100 to 1:1000 (A:E; Figure 4. 13 and Table 4. 4). With loadings of 1:100, 1:200, 1:300 and 1:400, monomodal GPC traces were obtained, which shifted to higher molar masses. Beyond this loading, an additional, high molecular mass shoulder becomes visible until both peaks merge ($M_n=21,500 \text{ g mol}^{-1}$, $\bar{D} = 1.61$).

Surprisingly, this shoulder is higher by a factor of 2-3 from the main peak and is observed as a sharp peak ($\bar{D} < 1.10$). For all reactions at high loadings, the amount of solvent was kept constant, thereby increasing the concentration of polymer in solution, which results in higher viscosities. As a result, the polymerisation reaction should be slowed at high conversions and side-reactions might be favoured. One possible outcome could be the coupling of hydroxyl end groups *via* condensation, which may be promoted by the catalyst as an external Lewis acid and high reaction temperatures. This would result in macromolecular dimers and trimers, hence explaining the sharp peak appearance.

As an aside, one T_g value between 20 and 40°C was typically observed, indicating block miscibility over a range of molar masses.

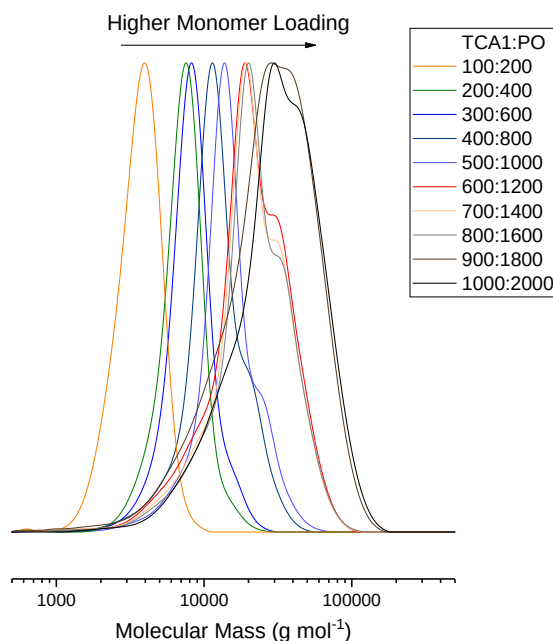


Figure 4. 13 – GPC traces of the one-pot polymerisation of TCA1/PO with various monomer loadings.

Table 4. 4 - One-pot polymerisation of TCA1/PO with various monomer loadings.^[a]

TCA1:PO	Time [d]	Conversion ^[b]		PE:PPO [wt%] ^[c]	M_n (Đ) [g mol ⁻¹] ^[d]	T_g [°C] ^[e]
		PO [%]	TCA1 [%]			
100:200	2 d	95	99	83:17	3,400 (1.12)	N. D. [#]
200:400	5 d	90	99	83:17	6,700 (1.12)	41
300:600	5 d	> 95	99	83:17	7,600 (1.13)	34
400:800	5 d	> 95	99	83:17	22,300 (1.05) 9,900 (1.11)	37, 78
500:1000	5 d	94	99	83:17	26,200 (1.05) 11,800 (1.10)	34
600:1000	10 d	> 95	99	83:17	38,500 (1.06) 13,700 (1.23)	21
700:1000	10 d	> 95	99	83:17	38,500 (1.07) 14,400 (1.21)	35
800:1000	10 d	> 95	99	83:17	38,900 (1.06) 14,600 (1.21)	24
900:1000	10 d	> 95	99	83:17	21,500 (1.61)	19
1000:2000	10 d	> 95	99	83:17	54,200 (1.09) 18,200 (1.25)	32

^[a] Conditions: [TCA1]:[PO]:[CHD]:[Cr]:[PPNCl] = X:Y:15:1:0.5 in toluene (entries 1-5: anhydride 5 M in toluene; entries 6-10 in 0.9 mL toluene) at 60 °C. ^[b] Based on ¹H NMR spectroscopy. The following chemical shifts were used: 1.04-1.00 ppm (TCA1), 3.72-3.25 ppm (PPO; the conversion was calculated based on the theoretical maximum conversion of PO). ^[c] PE content was calculated based on shifts for PE (5.85-5.55) and PPO (3.72-3.25 ppm), i.e. Integral PE/(Integral PE+Integral PPO/3). ^[d] Measured by GPC (30°C, THF) with narrow polystyrene standards. ^[e] Measured by DSC, 3rd heating cycle.

[#] Not isolated (highly soluble).

4.5.2. Decreasing Chain-Transfer Agent

In the absence of CTA, bimodal molar mass distributions are typically obtained. The two distributions are attributed to (i) chloro-initiated AB blocks (Figure 4. 14, major peak) and (ii) dihydroxyl-terminated ABA blocks, formed from bifunctional impurities (diacid or diol, Figure 4. 14, minor peak). It should be noted that this mixed chain end-group chemistry is commonly observed in ROCOP and ROP.^[19-22]

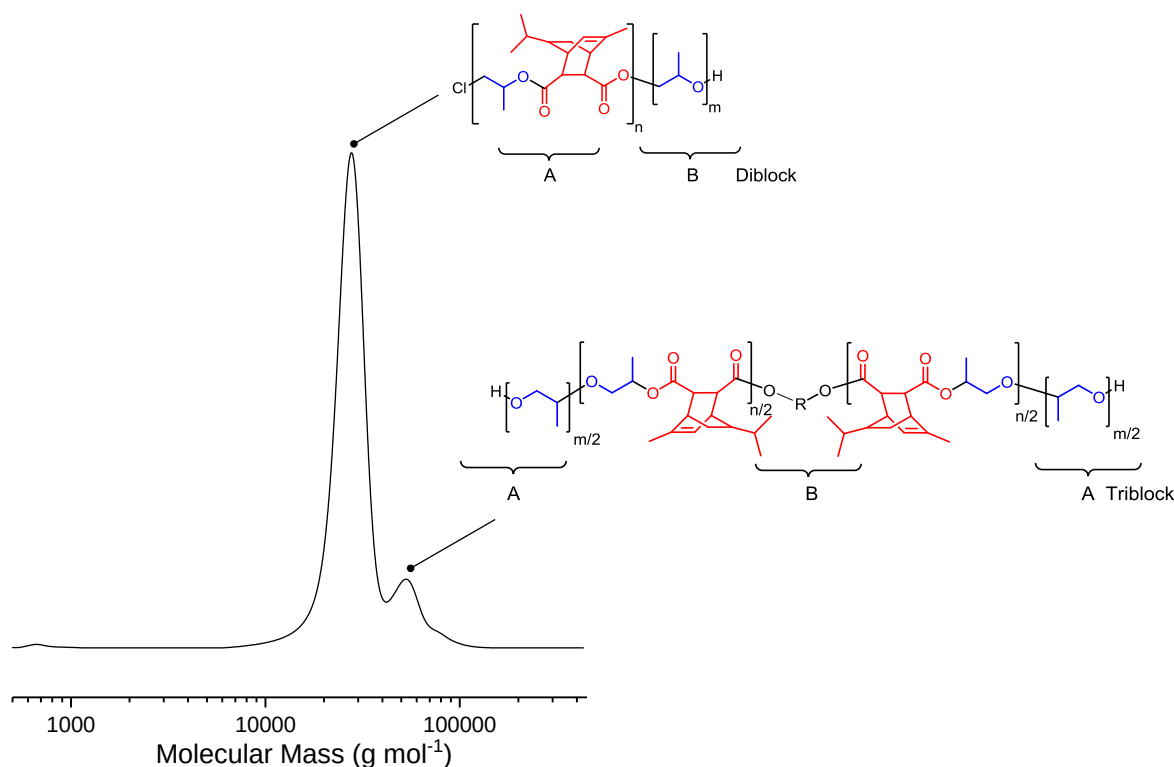


Figure 4. 14 – TCA1/PO Polymerisation in the absence of CTA.

The ABA triblock architecture is relevant for a range of potential applications. For example, the majority of thermoplastic elastomers contain this ABA triblock structure.^[23-27] Nonetheless, the use of large amounts of CTA is necessary to suppress the chloro-initiated AB diblock copolymers.

For the purpose of accessing high molar masses, the reverse was attempted, to suppress residual triblocks. It was hypothesized that lower amounts of CTA may be needed, if monofunctional CTAs are used, as only AB diblocks should be generated, which are already the major species in the absence of CTA. This was tested with different amounts of *iso*-propanol and monomodal GPC traces were obtained with six equivalents of CTA (as opposed to ten equivalents for CHD, Figure 4. 15). Although encouraging, the molar

mass was still reduced by a factor of six from 26,000 g mol⁻¹ to 5,000 g mol⁻¹, thereby yielding low molar mass material. Again, one T_g value was observed for all polymers.

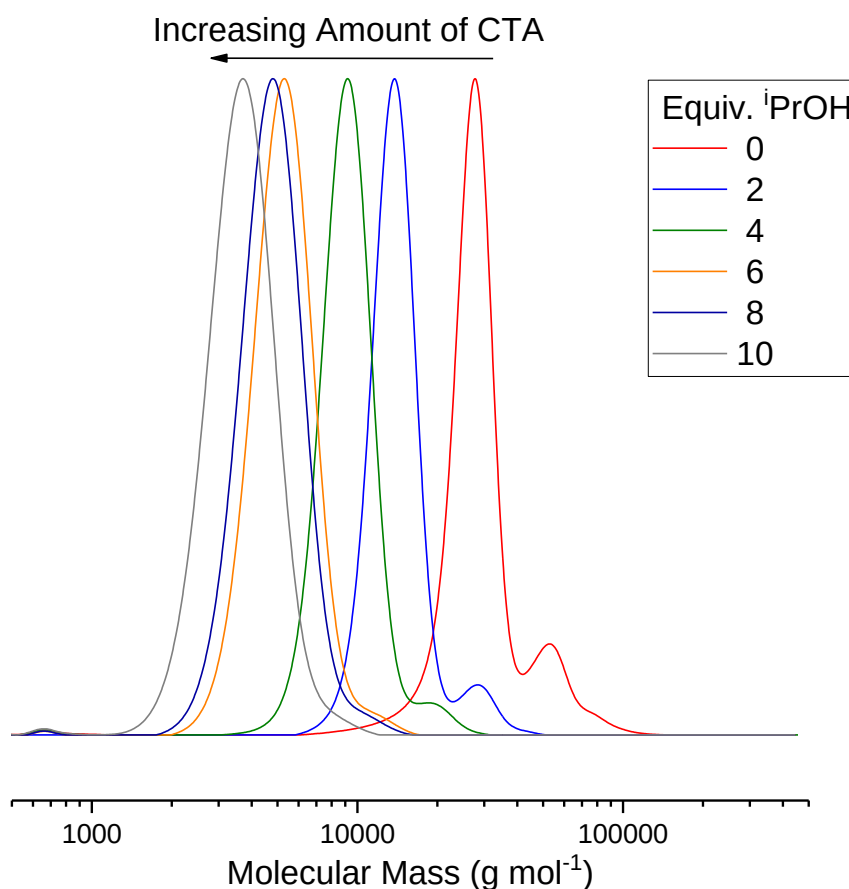


Figure 4. 15 – GPC traces for polymerisation of TCA1/PO with various amounts of *iso*-propanol.

4.5.3. Chain-Extension

Coupling of the poly(ether-*b*-ester-*b*-ether) obtained from TCA1/PO with diphenylmethane-4,4'-diisocyanate (4,4'-MDI) was investigated to chain-extend the polymer. This reaction can be considered a step-growth polymerisation, which follows a Schulz-Flory distribution. Consequently, maintaining an accurate stoichiometry between hydroxyl- and isocyanate functionalities is critical to obtain high molar masses. For this reason, the hydroxyl end groups were quantified using ³¹P{¹H} NMR spectroscopy (after the reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in the presence of bisphenol A as an internal standard). To ensure accurate integration of the two species, relaxation times were determined in a T₁-inversion recovery experiment (see appendix). Once both T₁ values were determined, integration of the two peaks revealed that the

number of hydroxyl end-groups is 9.28×10^{-3} (g equiv. / g polymer or 0.55 mmol / g polymer).

In a next step, the block copolymer was reacted with MDI (Figure 4. 16). An increase in molar mass by a factor of seven, from $3,700 \text{ g mol}^{-1}$ to $27,000 \text{ g mol}^{-1}$ was observed by GPC and the consumption of the hydroxyl-end groups was evident by ^1H NMR spectroscopy (Figure 4. 17). A slight increase in dispersity ($\bar{D} = 1.72$) was found, as expected from a step-growth polymerisation. Further purification, by filtration over silica followed by precipitation from methanol, can be used to fractionate the polymer obtain a high molar mass multiblock copolymer with a number-average molar mass of $45,600 \text{ g mol}^{-1}$ and a dispersity of 1.29. This material shows an increase in molar mass by a factor of 12, compared to the polyol precursor. This chain-extension affected the glass-transition of the materials and an increase from 27 to 65 °C was found by DSC (see appendix), which might be attributed to the increase in molar mass and/or end-group effects. As an aside, the architecture of the polymer was changed from ABA triblocks to multiblock copolymers.

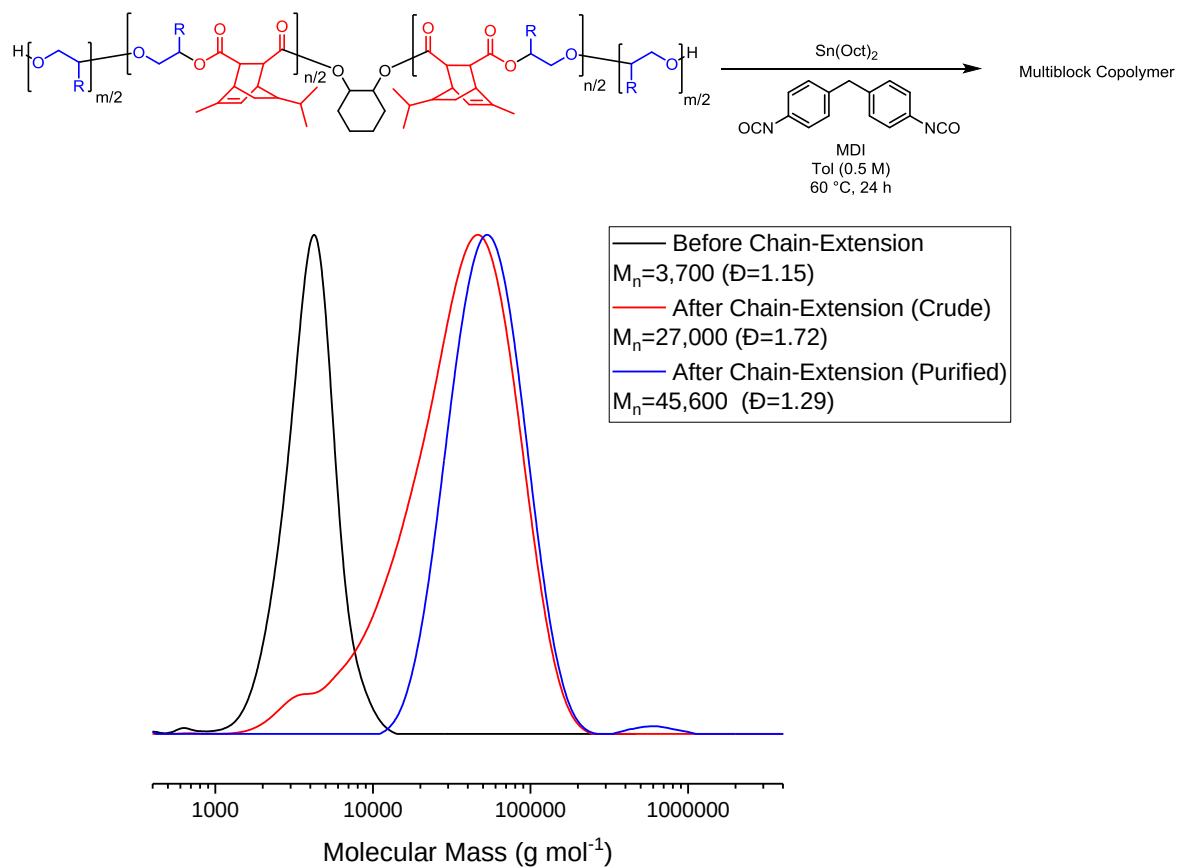


Figure 4. 16 - Chain-extension reaction of hydroxyl-terminated polymer with MDI (top). GPC traces before and after the reaction (bottom).

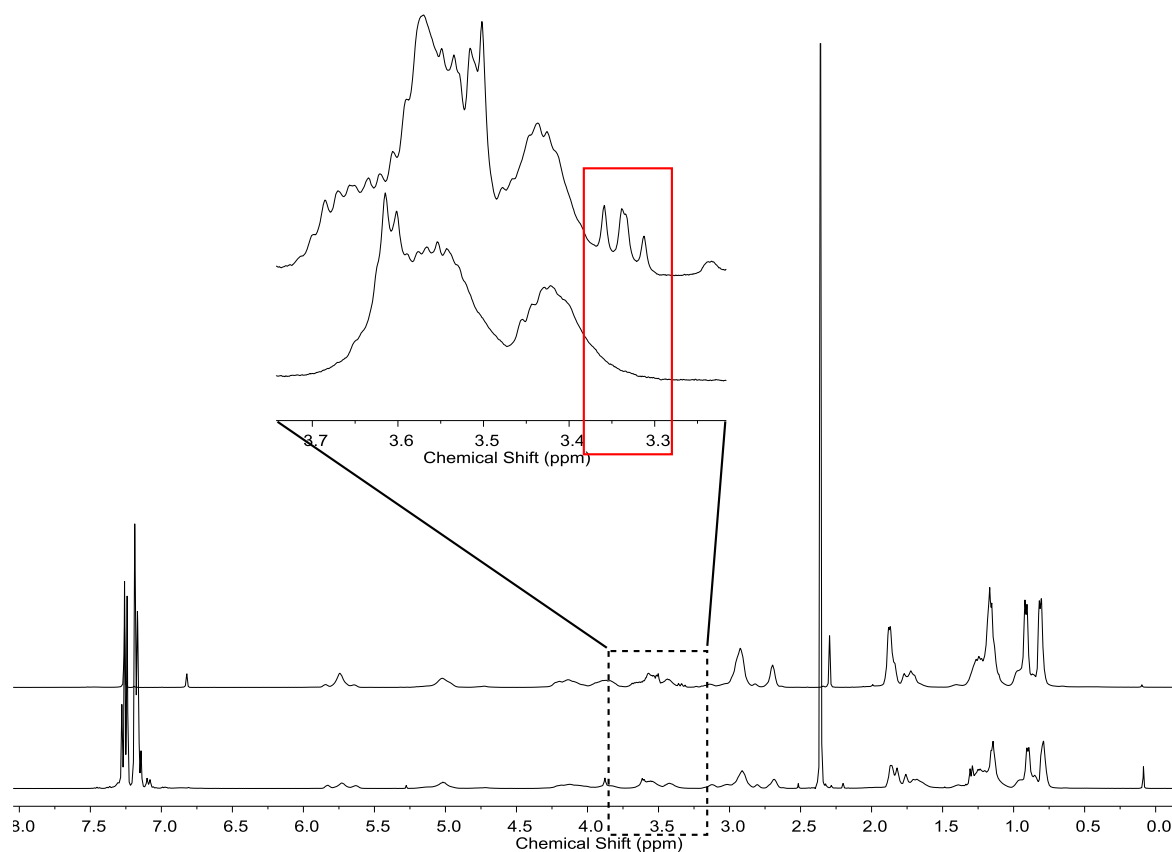
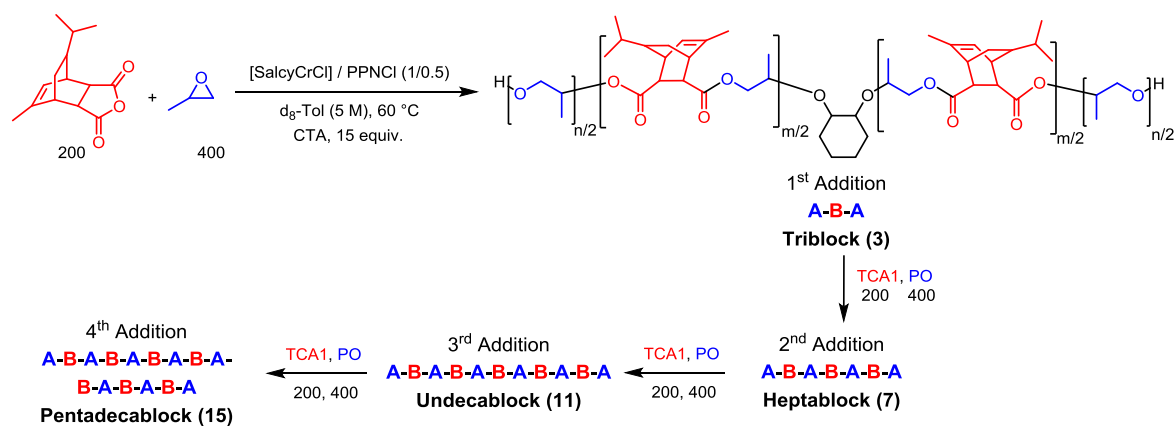


Figure 4. 17 – ^1H NMR spectra (CDCl_3 , 400 MHz) before and after chain-extension (the region of the hydroxyl end-group is enlarged).

4.6. Multiple Switching

So far, ABA triblock copolymers have been synthesised, but as an immortal polymerisation method was used, multiple monomer additions should allow access to higher block numbers. When initiating from diols (e. g. CHD), each further monomer addition yields four blocks, with one block from ROCOP and one from ROP on either side of the CTA. To test this hypothesis, the monomer mixture was added four subsequent times producing a pentadeca(15) block copolymer (Scheme 4. 3).



Scheme 4. 3 – Synthesis of multiblock copolymers.

To observe the formation of these block copolymers, the reaction mixture was analysed after each addition by ^1H NMR spectroscopy and GPC. In all cases, high conversions (>90% in PO, 99% in TCA1) were obtained and the increase in the corresponding polymer resonances (with respect to mesitylene as internal standard) were observed (Figure 4. 18, left). At the same time, an increase in molar mass was found after each step. Although monomodal molar mass distributions were maintained throughout the reaction, broadening was observed towards the end of the reaction ($M_n=17,800 \text{ g mol}^{-1}$ ($\mathcal{D}=1.38$)). This may be an effect of the long reaction times as 3-5 days were necessary to obtain high conversions after each addition and which may well result in accumulation of trace impurities. Nonetheless, this result clearly illustrates the potential of 'switch' catalysis to produce new multiblock copolymers.

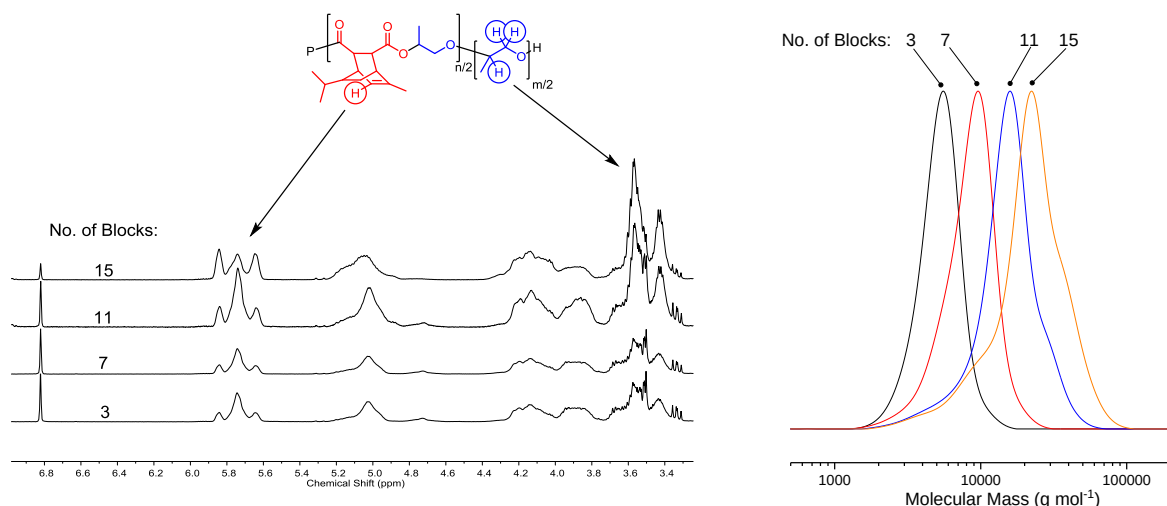


Figure 4. 18 – ^1H NMR spectra (left) and GPC traces (right) for the synthesis of multiblock copolymers after each monomer addition.

DOSY NMR spectroscopy further supported that all blocks are covalently attached to each other, as only one diffusion coefficient was observed (Figure 4.19). Thermal analysis of the multiblock copolymer, by DSC, showed one T_g value at 24°C , indicating block miscibility (see appendix). The obtained value was lower compared to the chain-extended material, which may be ascribed to lower molar masses of the multiblock material and/or end group effects.

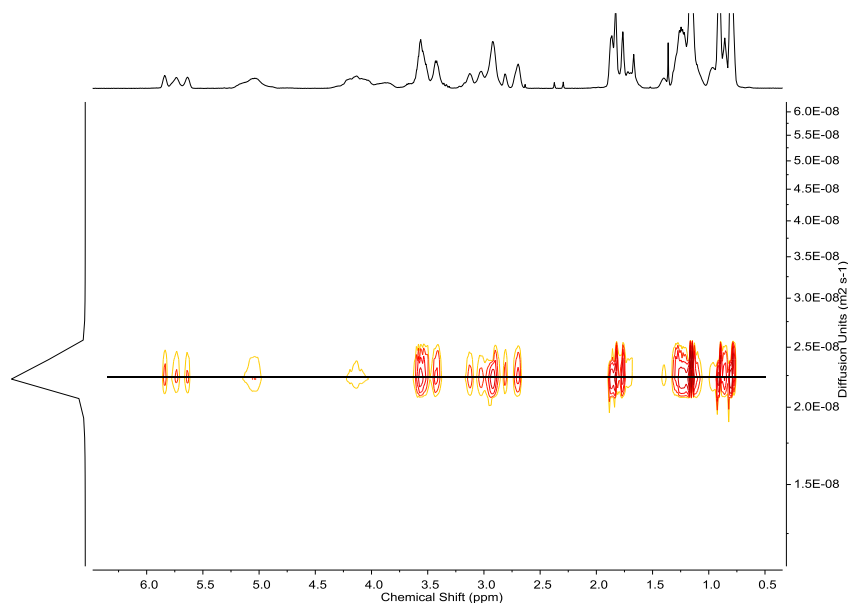


Figure 4. 19 – DOSY NMR spectrum of multiblock copolymer (Diffusion coefficient $D = 2.23 \times 10^{-8} \text{ m}^2\text{s}^{-1}$).

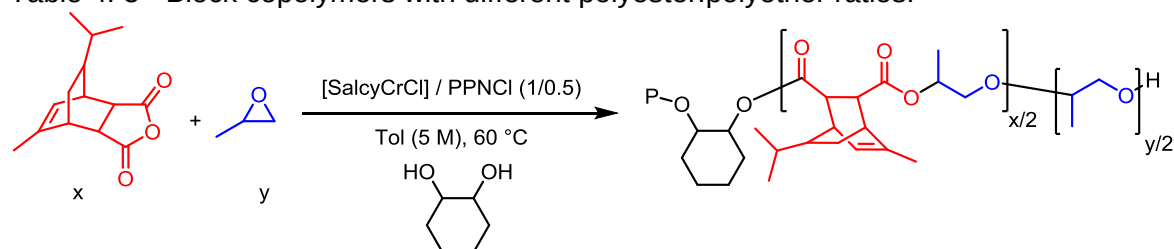
In conclusion, multiblock copolymers can be obtained from the present 'switch' catalysis with TCA1/PO by multiple monomer additions.

4.7. Copolymers with different block ratios

Although a range of block copolymers was successfully synthesised, block miscibility was usually observed. In this section, the effect of varying the relative block ratio between polyester and polyether on block miscibility was investigated.

To obtain high molar masses, the monomer loading was increased to target a theoretical weight of 20,000 g mol⁻¹ (Table 4. 5). In most cases, high conversions (> 80% PO, > 99% TCA1) and monomodal GPC traces were obtained, similar to the high loadings used previously.

Table 4. 5 - Block copolymers with different polyester:polyether ratios.^[a]



TCA1:PO [equiv.]	Time [d]	Conversion ^[b]		PE:PPO [wt%] ^[c]	M_n (Đ) [g mol ⁻¹] ^[d]	T_g [°C] ^[e]	T_g^{calc} [°C] ^[f]
		PO [%]	TCA1 [%]				
1000:950	2	99 %	> 95%	> 99	22,100 (1.09)	81	81
1020:1020	10	> 95%	99	99	40,900 (1.02) 18,300 (1.07)	73	78
820:1850	10	> 95%	99	80	22,800 (1.49)	34	36
720:2270	10	> 95%	99	70	24,100 (1.56)	-3	18
620:2680	10	> 95%	99	60	18,600 (1.56)	-1	1
510:3100	10	> 95%	99	50	17,200 (1.55)	-12	-13
410:3510	10	> 95%	99	40	15,100 (1.57)	-42	-26
310:3920 ^[g]	10	87	99	27	15,900 (1.49)	-55	-42
200:4340 ^[g]	15	85	99	16	16,100 (1.36)	-61	-53
100:4750 ^[g]	15	88	99	6	16,500 (1.31)	-66	-63
50:5120 ^[g]	15	85	99	1	20,300 (1.04) 7,200 (1.11)	-68	-67
5:5000	15	65	99	< 1	14,520 (1.03) 5,800 (1.05)	-69	-69

^[a]Molar ratio with respect to catalyst. ^[b]Based on ¹H NMR spectroscopy. The following chemical shifts were used: 1.04-1.00 ppm (TCA1), 3.72-3.25 ppm (PPO; the conversion was calculated based on the theoretical maximum conversion of PO). ^[c]Based on ¹H NMR spectroscopy of crude sample. PE content was calculated based on shifts for PE (5.85-5.55, HC=C) and PPO (3.72-3.25 ppm), i.e. Integral PE/(Integral PE+Integral PPO/3). ^[d]Measured by GPC (30°C, THF) with narrow polystyrene standards. ^[e]Measured by DSC, 3rd heating cycle. ^[f]Based on the Fox equation with $T_{g,PE}$ = 81 °C and $T_{g,PPO}$ = -68 °C.

^[g]Determined by ratio of PO:PPO (3.02-2.97 ppm, H^{PO} , vs. 3.73-3.20 ppm, $HPPO$; i.e. Integral $H^{PPO}/(H^{PPO}+H^{PO}\times 3)$).

The thermal analysis of the obtained polymers revealed one T_g value in all cases. This value could be adjusted over the range of ca. 140 °C between 73 °C and -68 °C, depending on the amount of the 'hard' PE block (Figure 4. 20, left). Moreover, the values were in agreement with the theoretical values from the Fox equation with only minor deviations (Figure 4. 20, right).

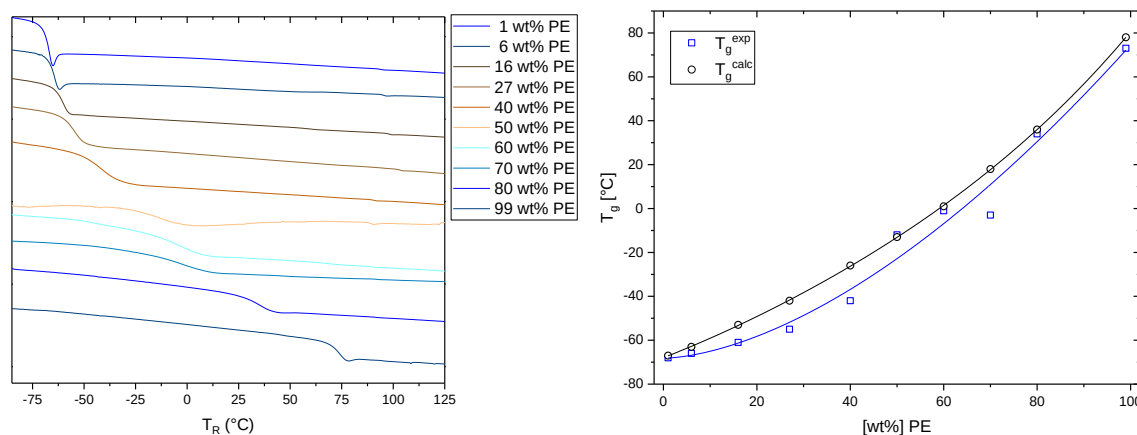


Figure 4. 20 – Thermal analysis of synthesised block copolymers. The recorded DSC thermograms are shown on the left and the obtained T_g values are compared with theoretical values (Fox equation for miscible polymers) on the right.

To summarise, a range of block compositions was obtained by changing the relative feed ratios of monomers. The polyester and the polyether blocks were miscible, as observed by DSC, over all compositions.

4.8. Expanding 'Switch' Catalysis with ϵ -Decalactone

In the last chapter, [SalcyCrCl] systems were investigated for 'switch' catalysis using CHO, anhydrides and DL. To test the effect of DL on 'switch' catalysis with PO and TCA1, the reaction of the three component mixture was monitored with ^1H NMR spectroscopy and GPC. Three different stages of the reaction were observed in the ^1H NMR spectra at different reaction times (i) TCA1/PO ROCOP, (ii) PO ROP and (iii) DL ROP (Figure 4. 21).

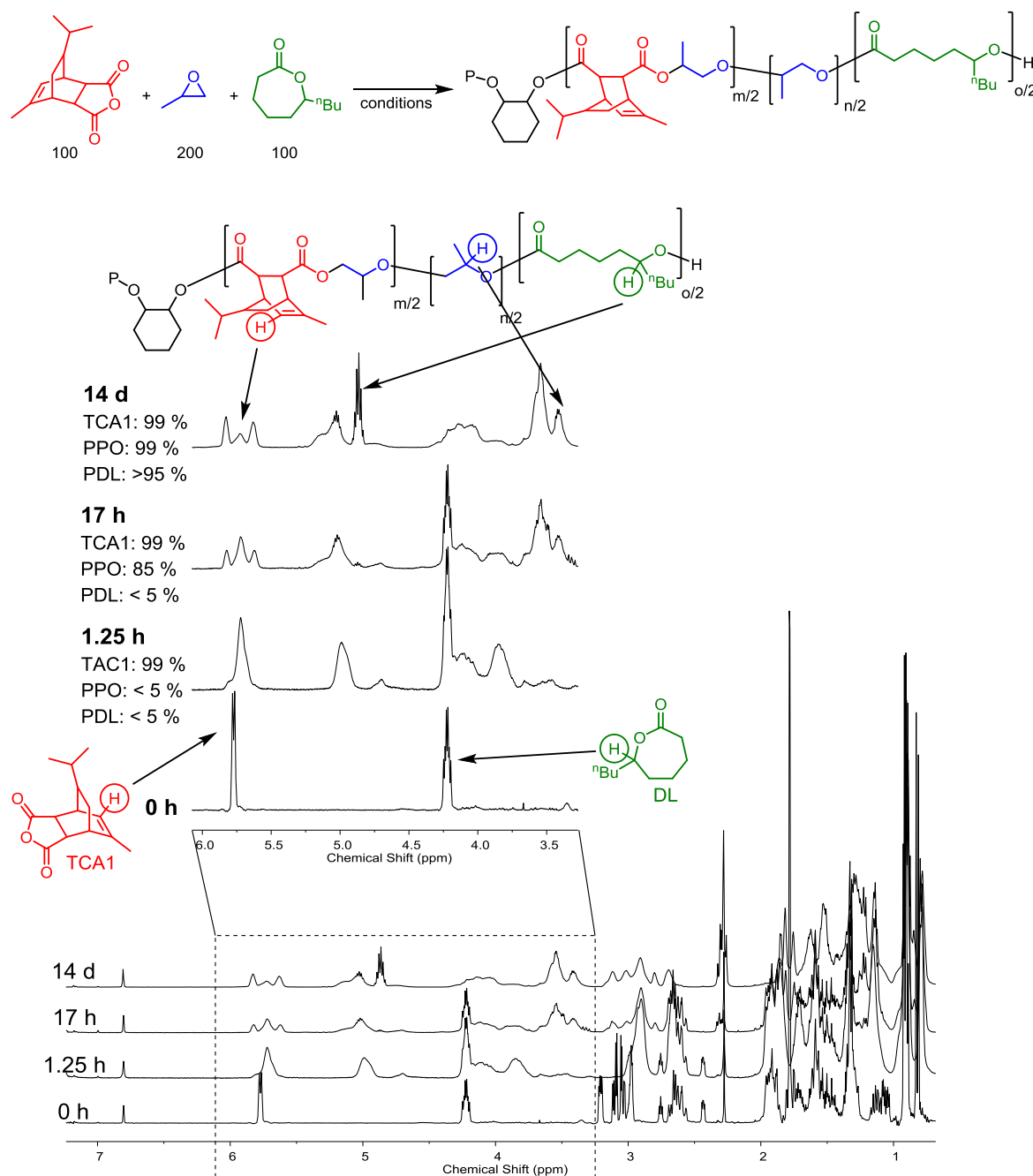


Figure 4. 21 – ^1H NMR spectra of the one-pot polymerisation of TCA1/PO/DL at different times. Reaction conditions: $[\text{Cr}]:[\text{PPNCl}]:[\text{CHD}]:[\text{TCA1}]:[\text{PO}]:[\text{DL}]=1:0.5:10:100:200:100$ in Tol (5M, 60 °C).

During the first 1.25 h, TCA1 was converted into the corresponding polyester, while no significant formation of PPO or PDL was observed. For the next 17 hours, formation of PPO occurred, similar to the previous example. In the final stage (up to 148 hours), the ROP of DL was established. Overall, all three monomers were incorporated in the expected sequence, TCA1, PO and DL.

This was further quantified in Figure 4. 22 and rate constants could be extracted for all three stages: for TCA1/PO ROCOP, $k_{obs,ROCOP} = 4.36 \text{ mol} \pm 0.04 \text{ L}^{-1} \text{ h}^{-1}$, is slightly higher than in the previous example ($k_{obs,ROCOP} = 0.78 \pm 0.02 \text{ mol L}^{-1} \text{ h}^{-1}$). This is most likely a direct consequence of the experimental setup and the quantity of aliquots removed: Whereas this reaction was performed inside the glovebox with a slightly lower number of aliquots taken, the previous reaction was transferred into the glovebox for every aliquot and a higher number of aliquots were taken. The latter inevitably results in cooling, which had a large influence on the observed rates. One further effect may be that no significant pressure is built up during the reaction as the reaction was repeatedly cooled to room temperature (PO has a boiling point of 34 °C and the reaction is performed at 60 °C), which might negatively impact the observed rates. Nonetheless, ROCOP clearly followed a zeroth order trend in anhydride. For the ROP of PO, a rate constant $k_{obs,ROP} = 0.19 \pm 0.02 \text{ h}^{-1}$ was found, which was similar to the one-pot polymerisation of TCA1/PO ($k_{obs,ROP} = 0.32 \pm 0.02 \text{ h}^{-1}$). Finally, the rate constant for the ROP of DL was determined as $k_{ROP,DL} = 0.004 \pm 0.001 \text{ h}^{-1}$.

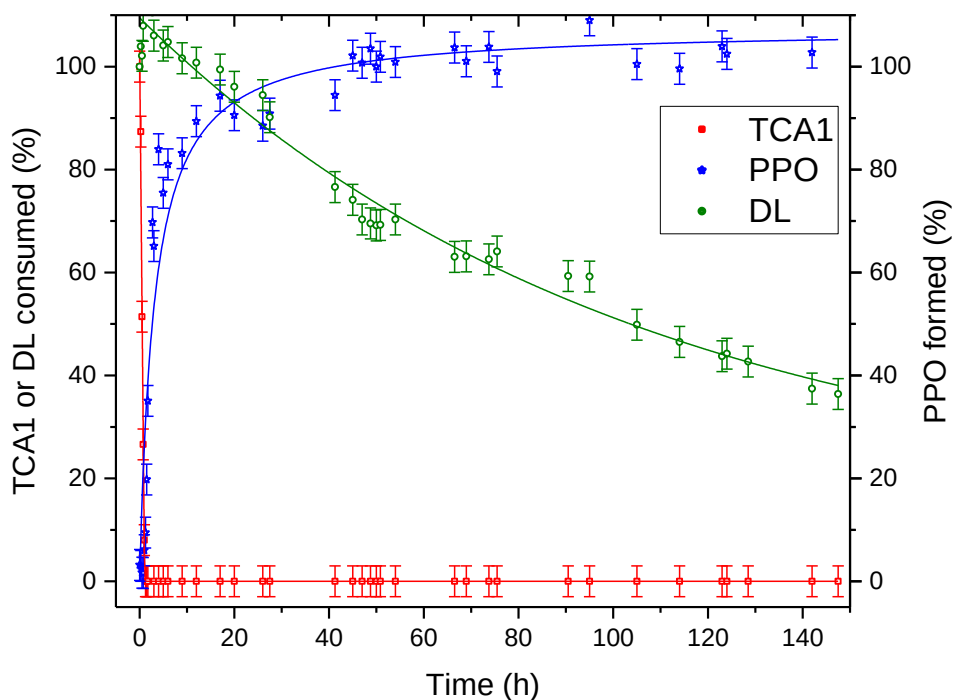


Figure 4. 22 - Conversion vs. time plot for the one-pot polymerisation of TCA1/PO/DL. Reaction conditions: [Cr]:[PPNCl]:[CHD]:[TCA1]:[PO]:[DL]=1:0.5:10:100:200:100 in Tol (5M, 60 °C).

In this example, a small tapered region between the formation of PPO and PDL was observed. Although this may not be desirable if precise blocks are targeted, it may be expected from the monomer feedstock, as two ROP mechanisms are combined. In ROP, the rate is expected to be proportional to the monomer concentration ($r_{\text{ROP}} = k_{\text{ROP}} \cdot [\text{M}]_t$). Consequently, the rate for homopolymerisation of PO should continuously decrease as the feedstock is depleted of monomer. Further, a cross-over point of equal rates between PPO and PDL formation, should be detected at $k_{\text{obs,PPO}} \times [\text{PO}]_t = k_{\text{obs,DL}} \times [\text{DL}]_0$ or at 98% consumption of PO (0.1 M). This theoretical value is in good agreement with the experimental data and at 17 hours, $94 \pm 3\%$ of PPO was formed, while $99 \pm 3\%$ of DL was unreacted (Figure 4. 23).

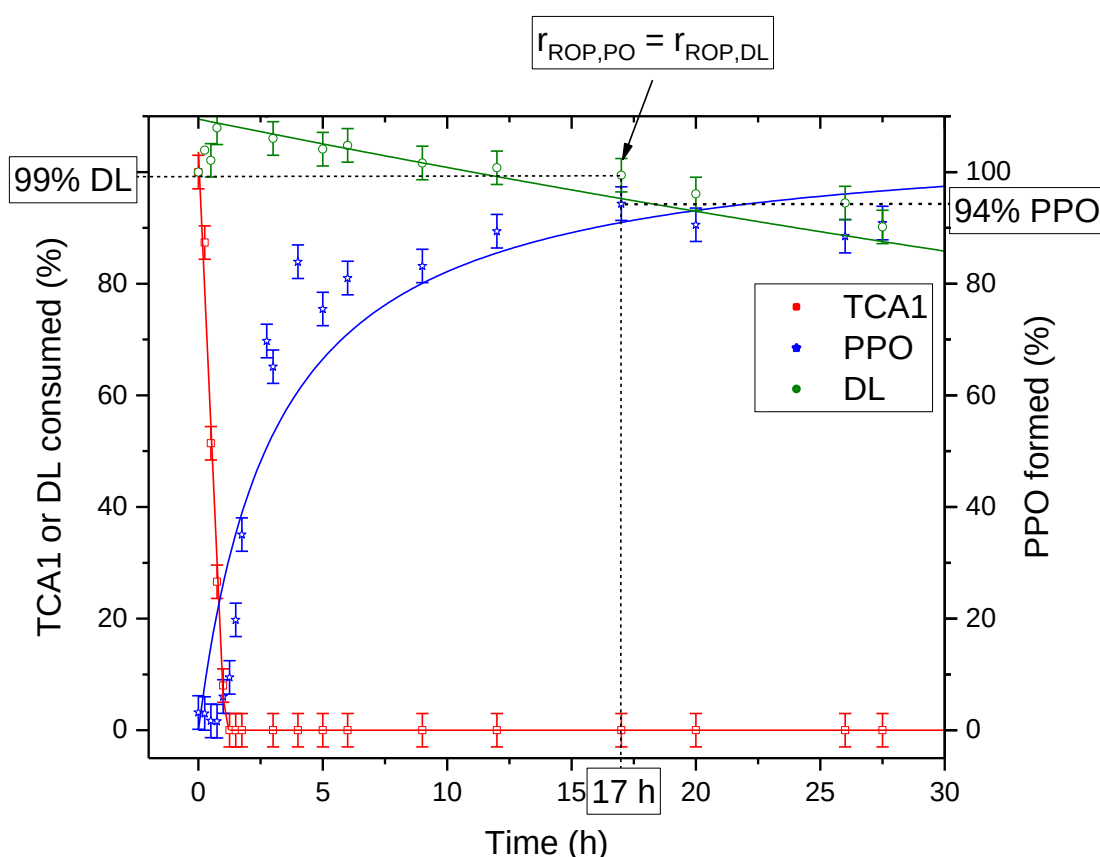


Figure 4. 23 – Extended area of conversion – time plot that shows the point at which rate of PO ROP and DL ROP are equal. Reaction conditions: $[\text{Cr}]:[\text{PPNCl}]:[\text{CHD}]:[\text{TCA1}]:[\text{PO}]:[\text{DL}]=1:0.5:10:100:200:100$ in Tol (5M, 60 °C).

Similar to before, the observed high monomer selectivity does not necessarily imply the formation of block copolymers. Thus, the reaction was further investigated by GPC, end group analysis and DOSY NMR spectroscopy to confirm block polymer formation.

Analysis by GPC showed a continuous increase in molar mass throughout the reaction, while maintaining narrow, monomodal molar mass distributions (Figure 4. 24).

Remarkably, dispersities below 1.20 were observed, even after 14 days (times necessary to complete DL ROP). At the end of the reaction, a number-average molar mass of 6,500 g mol⁻¹ was obtained.

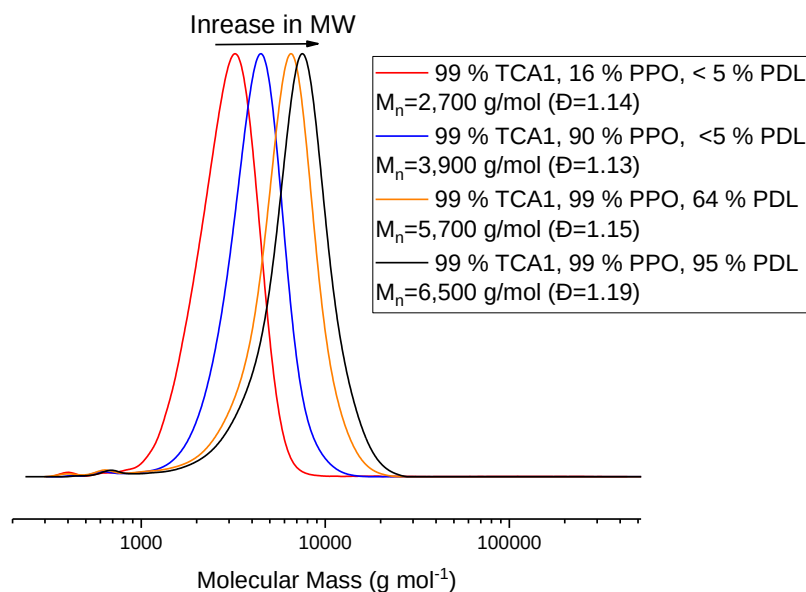


Figure 4. 24 – GPC Traces at different stages of the one-pot polymerisation of TCA1/PO/DL.

Further aliquots were taken and an exponential increase in molar mass was detected during the ROP stages, as expected from the previous kinetics (Figure 4. 25).

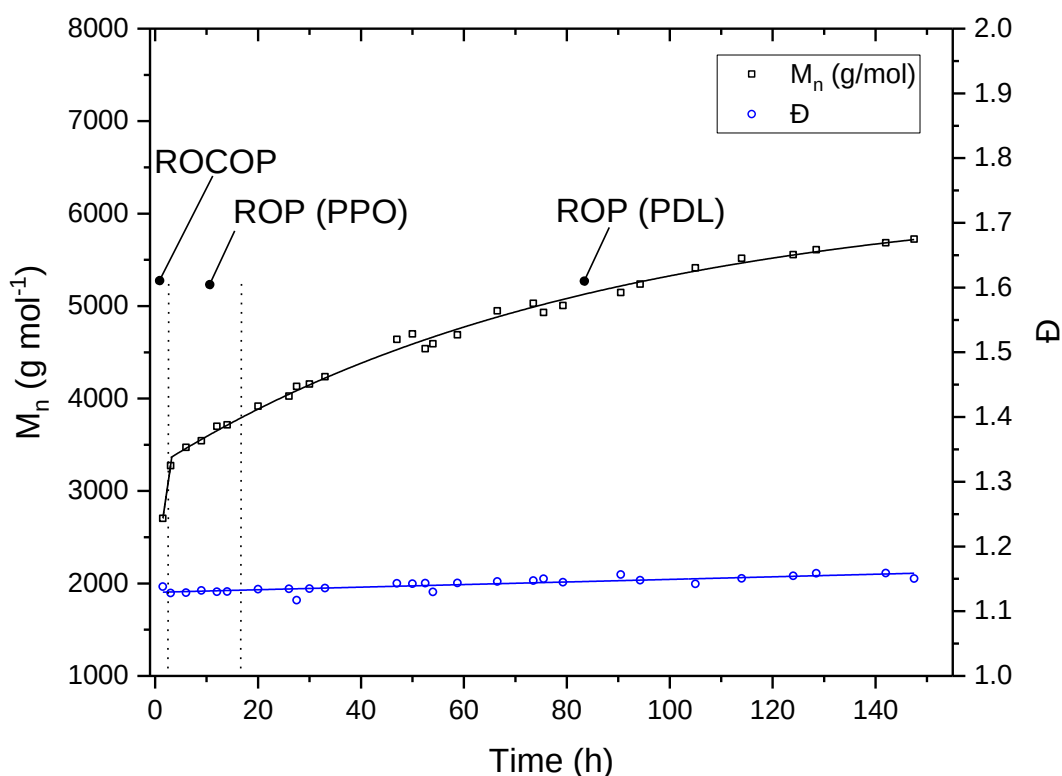


Figure 4. 25 – GPC Traces at various times of the one-pot polymerisation of TCA1/PO/DL.

Next, polymer end groups were analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, after reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (Figure 4. 26). Only one signal at 147.10 ppm was detected, which was in agreement with individually synthesised PDL and was not found for the corresponding PPO-terminated triblock copolymer (146.08 ppm).

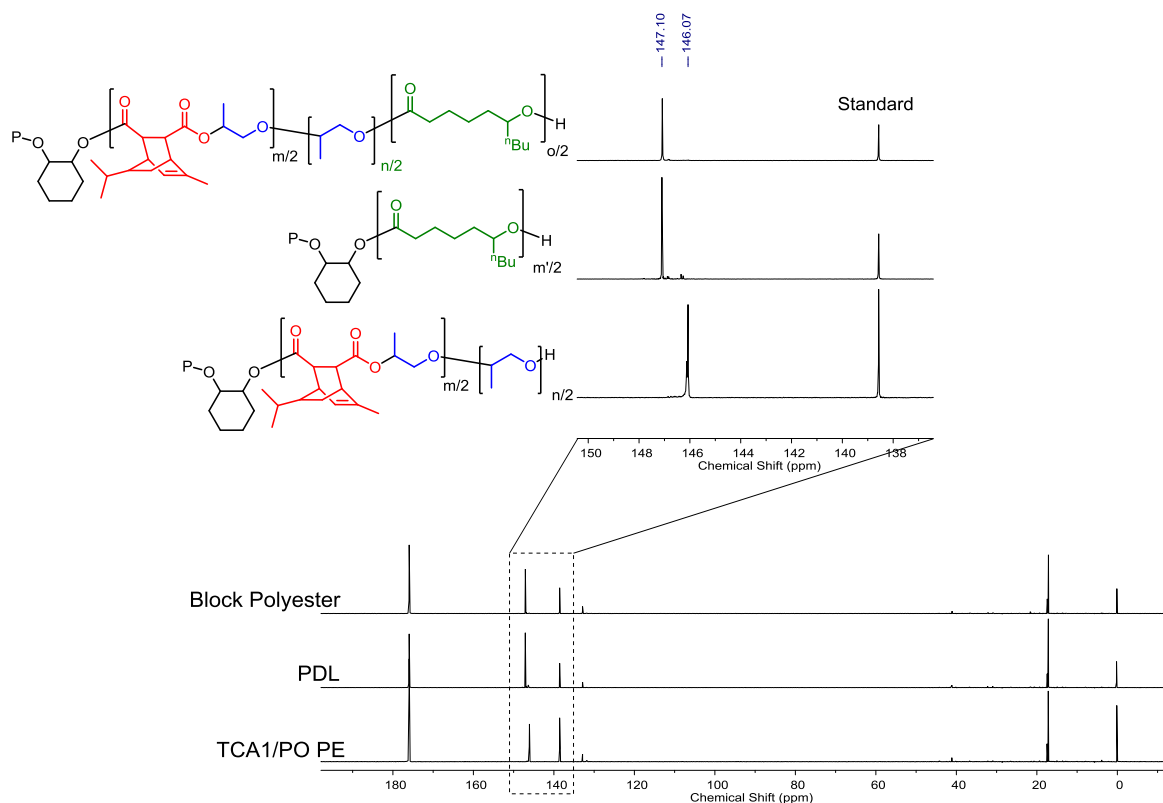


Figure 4. 26 – $^{31}\text{P}\{^1\text{H}\}$ NMR Spectrum of proposed pentablock copolymer obtained from the one-pot polymerisation of TCA1, PO and DL (A, top), PDL (B, middle) and the triblock copolymer obtained from TCA1 and PO (C, bottom) the after the reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane.

Further evidence was found by ^1H NMR spectroscopy. Although not all end-groups could be identified, due to overlapping signals, the hydroxyl end-group formed during the formation of PPO could be monitored at $\delta = 3.32$ ppm (Figure 4. 27). This resonance was absent in the starting materials or the polyester from TCA1/PO and only formed during the homopolymerisation of PPO, as expected from 'switch' catalysis with TCA1/PO (Figure 4. 16). More importantly, this end-group was consumed during the last stage of the reaction, the formation of DL, which is in agreement with the end-group essay using $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy.

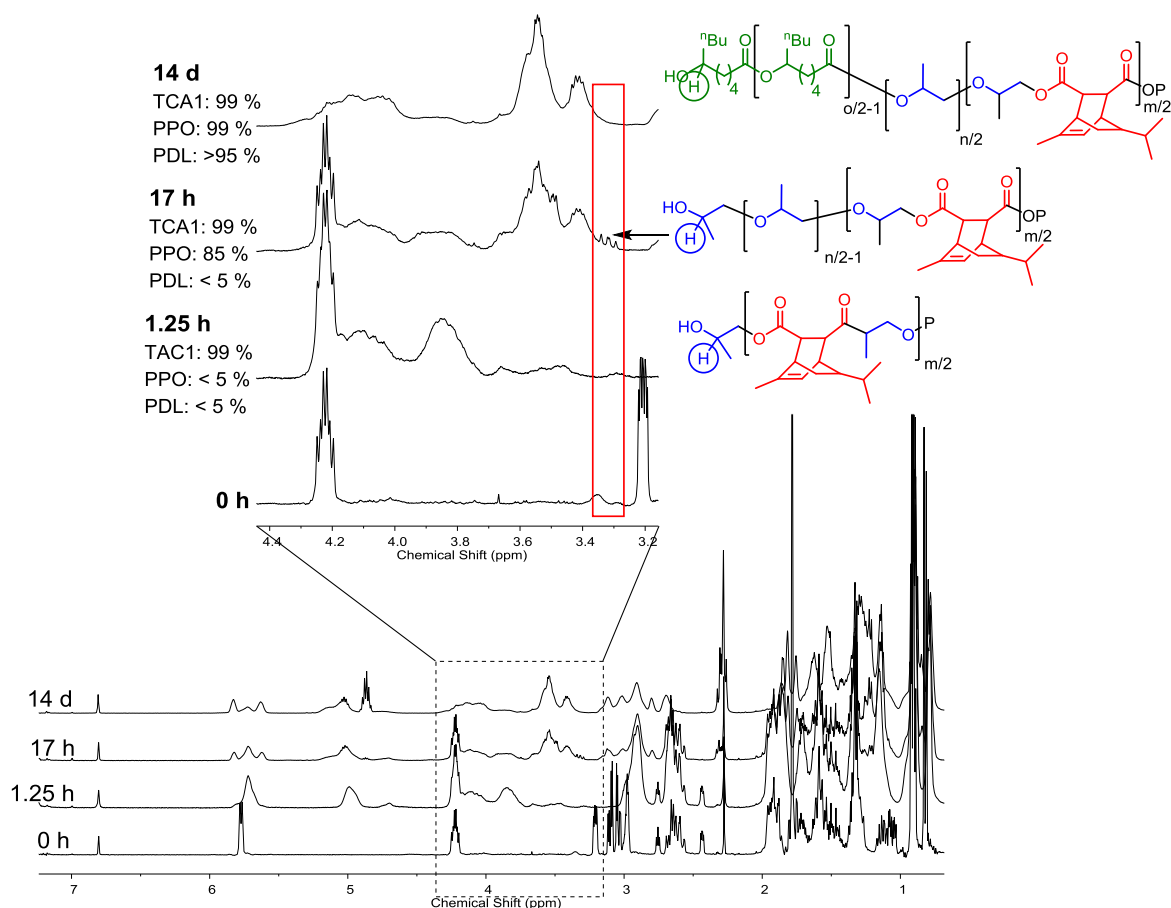


Figure 4. 27 – ^1H NMR spectra of one-pot polymerisation of TCA1/PO/DL at different times; the region relevant to hydroxyl end-groups from PPO is enlarged. Reaction conditions: $[\text{Cr}]:[\text{PPNCI}]:[\text{CHD}]:[\text{TCA1}]:[\text{PO}]:[\text{DL}]=1:0.5:10:100:200:100$ in Tol (5M, 60 °C).

The polymer was further analysed by DOSY NMR spectroscopy (Figure 4. 28). Only one diffusion coefficient was observed, suggesting that all blocks are attached to each other.

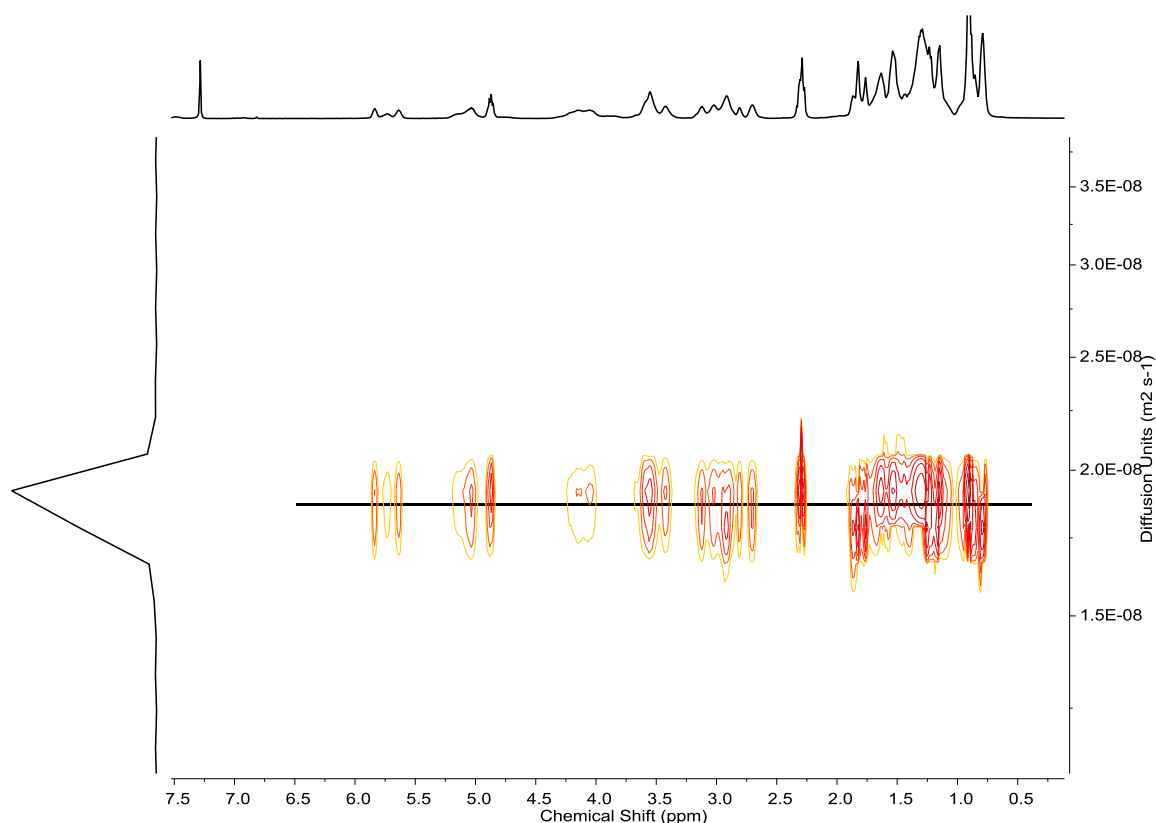
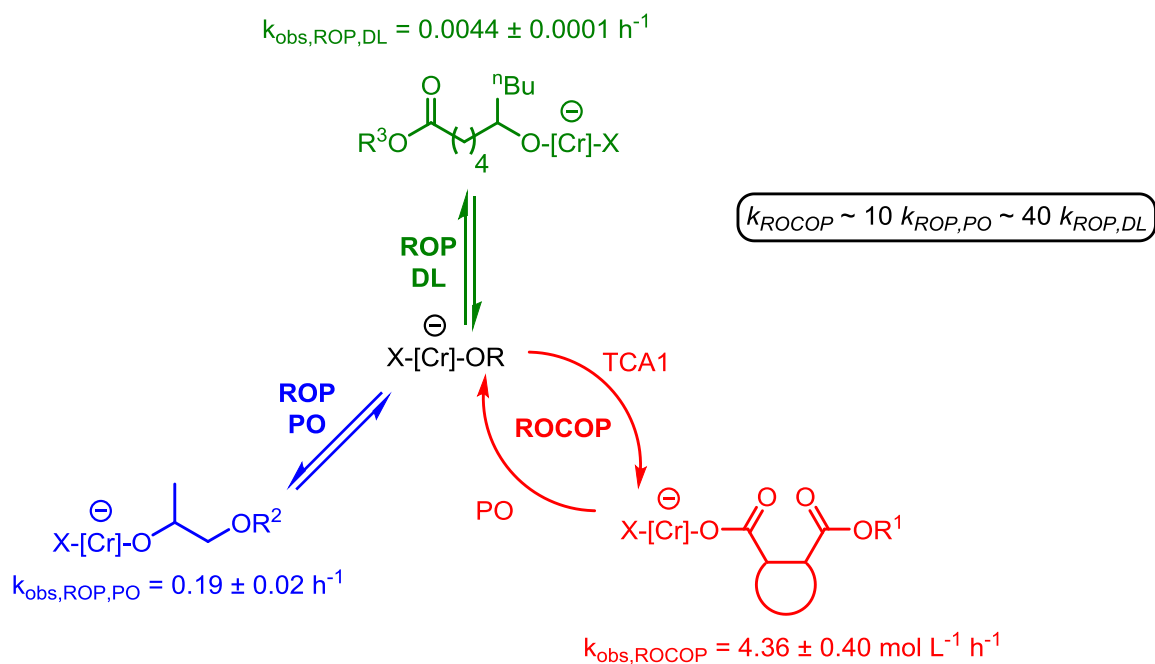


Figure 4. 28 - DOSY NMR spectrum of block copolymer obtained from TCA1, PO and DL.

All the analytical techniques strongly indicated the formation of block polymers, more precisely a pentablock copolymer. The observed order of monomer enchainment (TCA1>PO>DL) can be used to build a mechanistic hypothesis (Scheme 4. 4). The central intermediate is proposed to be a chromium alkoxide, which connects ROCOP and two ROP cycles in a similar way to catalysis in using TCA1/PO mixtures. First, the reaction proceeds through ROCOP and the resting state is likely a chromium carboxylate formed by reaction with the anhydride. The chromium alkoxide intermediate is regenerated by ring-opening of PO. Once the anhydride is fully reacted, the alkoxide continues to react with PO. Kinetic analysis revealed that the rate of the chromium carboxylate towards the ring-opening of PO is ca. 10 times faster than the reaction of the chromium alkoxide with PO. In the final step, PO is nearly fully consumed and DL ROP proceeds from a related chromium alkoxide, until the reaction is completed. Overall, the following rate coefficient order was determined: $k_{ROCOP} \sim 10 k_{ROP,PO} \sim 40 k_{ROP,DL}$. For comparison, $k_{obs,ROCOP}$ was determined by multiplying k_p with the concentration of PO.



Scheme 4.4 - Mechanistic scheme showing the key intermediates in the one-pot polymerisation of TCA1/PO/DL.

With PDL incorporated into the polymer, an additional 'soft' (low T_g) segment should result in a lower T_g value than the corresponding polymer from TCA1/PO. For the pentablock copolymer, one T_g value at -8°C was detected by DSC, which was significantly lower than the corresponding ABA triblock copolymer ($20\text{-}30^\circ\text{C}$; see appendix).

Overall, 'switch' catalysis was successfully performed with a monomer mixture comprising PO, TCA1 and DL. Thereby, three different catalytic cycles are combined and a pentablock copolymer is obtained in one step.

4.9. Post-Functionalisation Reactions

Post-functionalisation reactions are commonly used to modify polymer properties and access a wide-range of functional materials. In this chapter, one post-functionalisation has already been demonstrated: the chain-extension of hydroxyl-terminated polymers with diisocyanates. Moreover, thiol-ene reactions are used in this thesis to: (i) generate highly cross-linked polymer networks and (ii) to install side-chains in the polymer backbone. The latter was attempted with the materials obtained from 'switch' catalysis with PO.

Thiol-Ene Reactions

To illustrate that this well-established chemistry is compatible with poly(ether-*b*-ester-*b*-ether)s, the ABA triblock copolymer, based on TCA1/VPO, was reacted with *n*-butane thiol or mercaptoethanol. In both cases, the disappearance of the resonance attributed to the terminal alkene indicated high conversions to the corresponding thioether (Figure 4. 29). Moreover, analysis by GPC indicated the polymer backbone remained intact by displaying narrow, monomodal traces (Figure 4. 30).

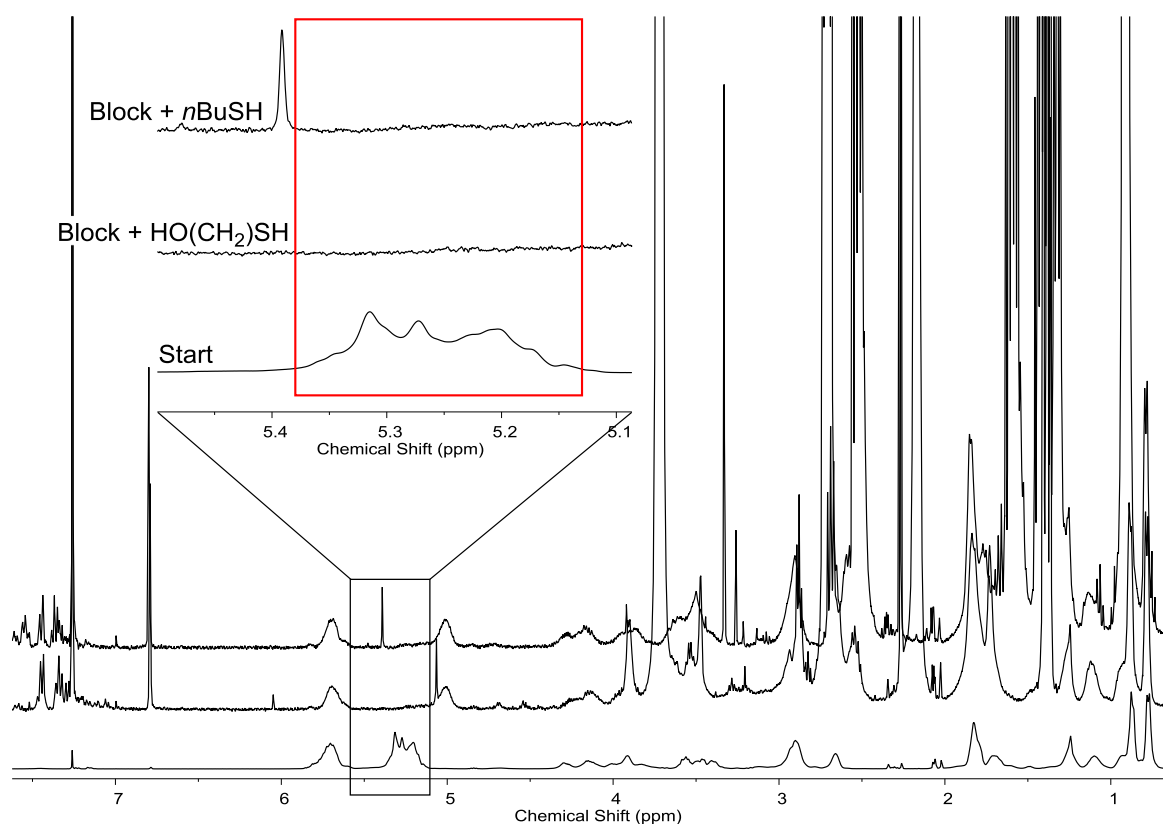


Figure 4. 29 – ^1H NMR spectra of crude reaction mixture after thiol-ene reactions.

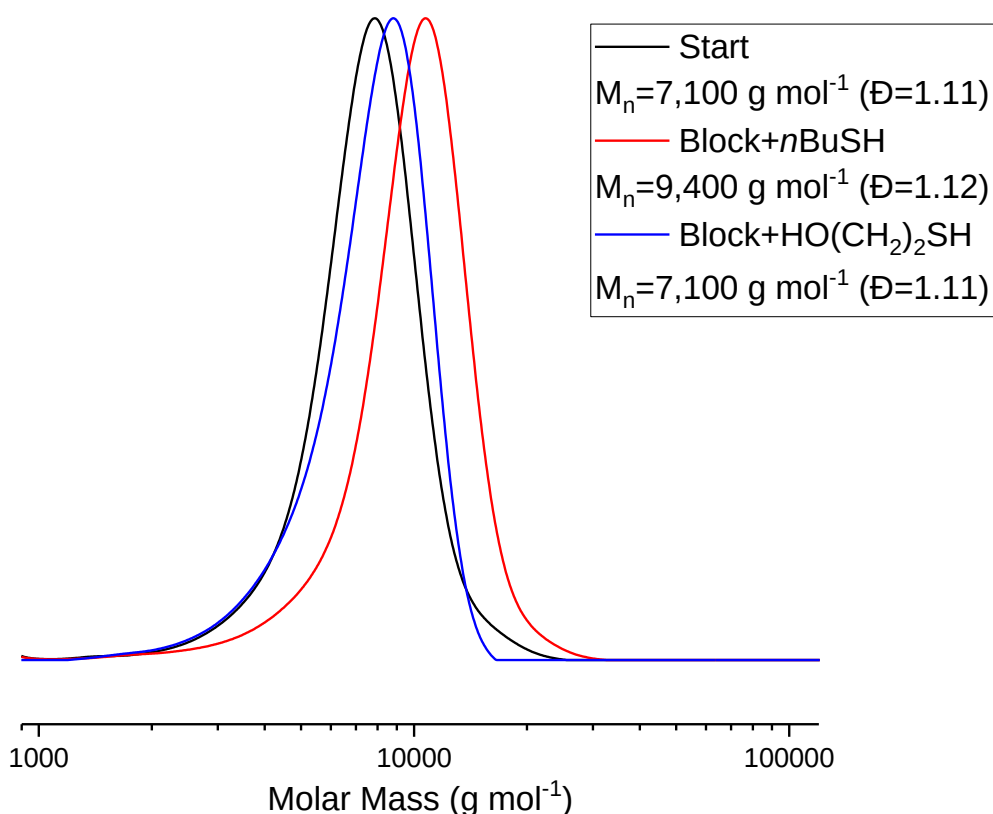


Figure 4. 30 – GPC traces before and after thiol-ene reactions.

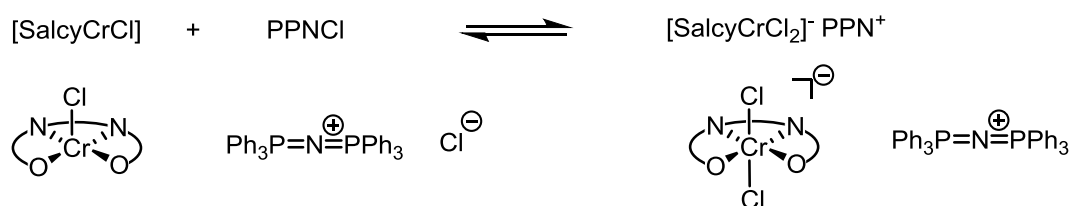
In conclusion, the obtained triblock copolymers can be used in post-functionalisation reactions to convert vinyl-functionalities in the polymer backbone into thioethers or react hydroxyl end-groups with diisocyanates (Figure 4. 16). This may provide the basis for tailored applications, as similar reactions have been used in various areas of material science.^[28-30]

4.10. Discussion

So far, 'switch' catalysis with TCA1/PO has been investigated in depth with [SalcyCrCl] / PPNCI. Several further aspects can be noted:

4.10.1. Catalyst-Co-Catalyst Equilibrium

Control reactions with only [SalcyCrCl] or PPNCI did not show the formation of poly(ester-*b*-ether)s. For this reason, the catalytically active species is proposed to be a hexacoordinate chromate species formed in an equilibrium between catalyst and co-catalyst (Scheme 4. 5).



Scheme 4. 5 – Equilibrium with [SalcyCrCl] and PPNCI.

In the presence of epoxide, the corresponding alkoxide species are formed and the equilibrium constant can be expressed as

$$K_{eq} = \frac{[RO - Cr - OR]^- [PPN]^+}{[Cr - OR] [PPN^+ RO^-]}$$

with [RO-Cr-OR][PPN]⁺ as the desired active species and [PPN⁺RO⁻] the undesired uncoordinated alkoxide, which was proposed to facilitate transesterification.

To decrease [PPN⁺RO⁻], [Cr-OR] may be increased. Consequently, the amount of the salen-chromium catalyst or PPNCI is expected to have a strong influence on dispersity. This was tested with the one-pot polymerisation of TCA1/PO/DL with various amounts of PPNCI (Table 4. 6). The expected results were detected and a significant improvement in dispersity was found with a catalyst:co-catalyst ratio of 1:0.4.

Table 4. 6 – 'Switch' catalysis with TCA1/PO/DL with different amounts of PPNCI.

Equiv. of PPNCI ^[a]	Conversion [%] ^[b]			<i>M_n</i> (Đ) [g mol ⁻¹] ^[c]
	TCA1	PO	DL	
0.2	99	99	31	4,500 (1.11)
0.4	99	99	36	5,000 (1.11)
0.6	99	99	33	5,400 (1.13)
0.8	99	99	25	5,400 (1.20)
1.0	99	99	30	5,100 (1.34)

^[a]Relative to [SalcyCrCl]. A stock solution of PPNCI (0.2 M in anhydrous MeCN) was used and the reaction time was four days in all cases. ^[b]Determined by ¹H NMR spectroscopy (TCA1: 3.23-3.17 ppm; DL: 4.26-4.19 ppm; conversion of PO was calculated from

formation of PPO: 3.71 – 3.28 ppm) after normalisation with mesitylene as internal standard; ^[c]Determined by GPC (THF, 30 °C, based on PS standards).

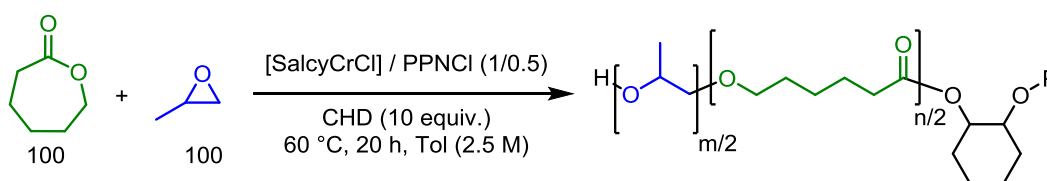
Changes in K_{eq}

By increasing the value of the equilibrium constant, the amount of $[PPN^+RO^-]$ should be reduced. This may be achieved by electronic variation of the catalyst, for example by introducing electron-withdrawing substituents (NO_2 , CN, F) in the ligand backbone, as salen-ligands are readily accessible.^[31]

4.10.2. Further Monomer Scope

Having demonstrated the successful incorporation of DL, several other lactones may be of interest for the present 'switch' catalysis.

i) ϵ -Caprolactone (CL)



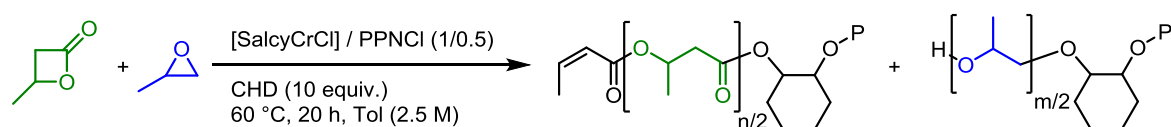
Scheme 4. 6 – One-pot polymerisation of CL/PO.

CL is a readily available, seven-membered lactone and was copolymerised with PO (Scheme 4. 6). Based on ¹H NMR spectra at various points throughout the one-pot polymerisation of CL/PO, the formation of a gradient copolymer was observed (69% PCL and 31% PPO at 20 h; see appendix for ¹H NMR spectrum). This may be explained by a larger rate constant for the ROP of CL and the point at which both ROPs are similar is achieved at lower conversion, i.e. $k_{ROP,CL} = k_{ROP,PO}$. Nonetheless, no further side-reactions were detected and narrow molar mass distributions were obtained ($M_n=5,120 \text{ g mol}^{-1}$; $\bar{D}=1.23$).

ii) β -Butyrolactone (BL)

By replacing CL with BL, the relative rates should favour the formation of block copolymers instead of gradient copolymers as a significant rate enhancement is expected for BL. As an aside, isotactic poly(hydroxyl butyrate) has been reported with chromium salphen complexes from racemic BL.^[32] Although high conversions were observed by

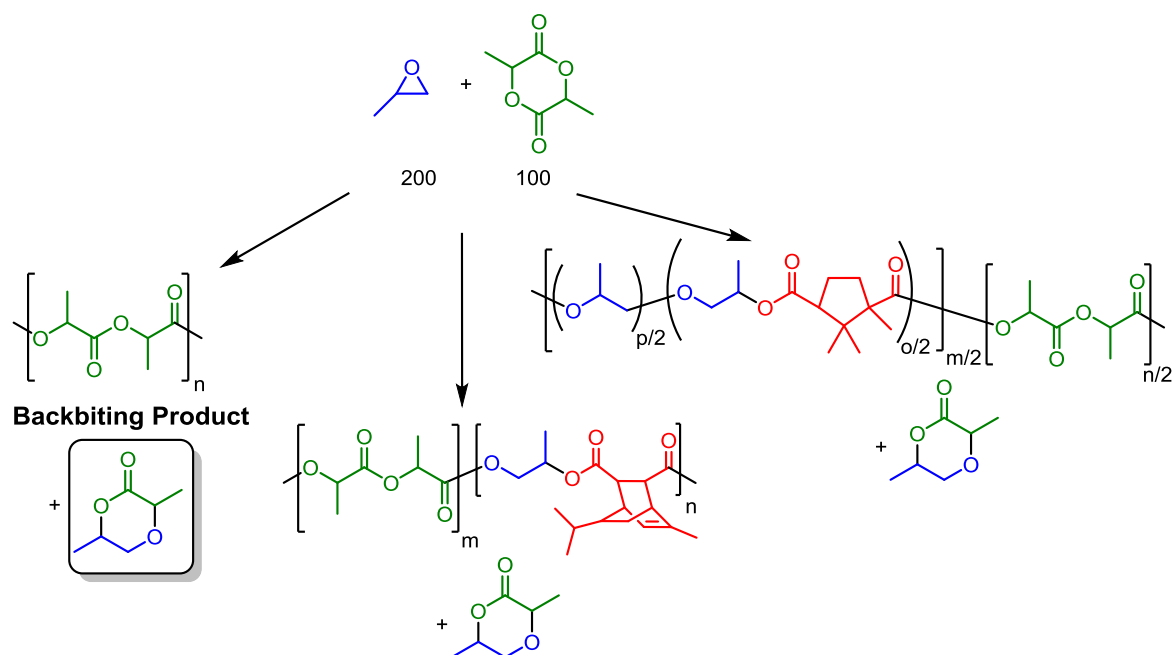
^1H NMR after 24 hours, a significant amount α,β -unsaturated end groups (crotonic esters) was detected by ^1H NMR spectroscopy (Scheme 4. 7; see appendix for spectrum). This was reported recently and strongly suggests a large portion of inactive polymer chains alongside with deactivated catalyst.^[33] For this reason, BL is not a suitable substrate in this catalysis.



Scheme 4. 7 - Copolymerisation of BL and PO with [SalcyCrCl].

iii) (Rac)-Lactide

Similar to BL, high rates were observed with lactide ($\text{TOF} > 133 \text{ h}^{-1}$), but the homopolymerisation of PO was not observed. Instead, the formation of a cyclic ester resulting from the coupling of PO and lactide was found (Scheme 4. 8, left; ^1H NMR spectrum is given in appendix). A similar back-biting reaction was reported with [TPPCrCl]/PPNCI.^[34] This suggests that PLA-*b*-PPO cannot be formed in this catalysis. However, this may be avoided by adding TCA1 to the feedstock, if the rate for the ROP of lactide is higher than the rate of ROCOP. Unfortunately, the ROCOP of TCA1/PO was performed first, followed by the ROP of lactide and the backbiting persisted (Scheme 4. 8, middle). To achieve the desired relative rates ($r_{\text{ROP,Lactide}} > r_{\text{ROCOP,Anhydride,PO}} > r_{\text{ROP,PO}}$), TCA1 was replaced with CA. The formation of PLA was indeed observed before the conversion of CA, but backbiting could not be fully suppressed (Scheme 4. 8, right)



Scheme 4.8 – 'Switch' Catalysis with PO and Lactide for [SalcyCrCl]. Reaction conditions: [SalcyCrCl]/PPNCl (1/0.5), CHD (10 equiv.), 60 °C, 20 h, Tol (2.5 M).

4.10.3. Statistical Analysis of Block Copolymers

The presented 'switch' catalysis can be classified as a chain-growth polymerisation and is thereby statistical in nature. This has a strong effect on precision-polymer synthesis since there may be a significant proportion of chains with differing structures if blocks with a small DP are synthesised. The molecular mass distribution should follow a Poisson distribution, if all blocks are of equal length, and the probability that a multiblock copolymer contains the proposed number of blocks depends upon:

$$p = (1 - e^{-\overline{DP}})^N$$

With p , the probability that all chains contain the same number of N blocks, $\overline{DP}$ as average degree of polymerisation for each block and N as the total number of blocks.^[35] This relation is illustrated in Figure 4. 31 for $\overline{DP}$ and N values ranging between 0 and 20. Herein, a pentadecablock polymer ($N = 15$) was prepared with $\overline{DP}$ of 6.6. This results in a probability of all chains containing 15 block of ~ 98%.

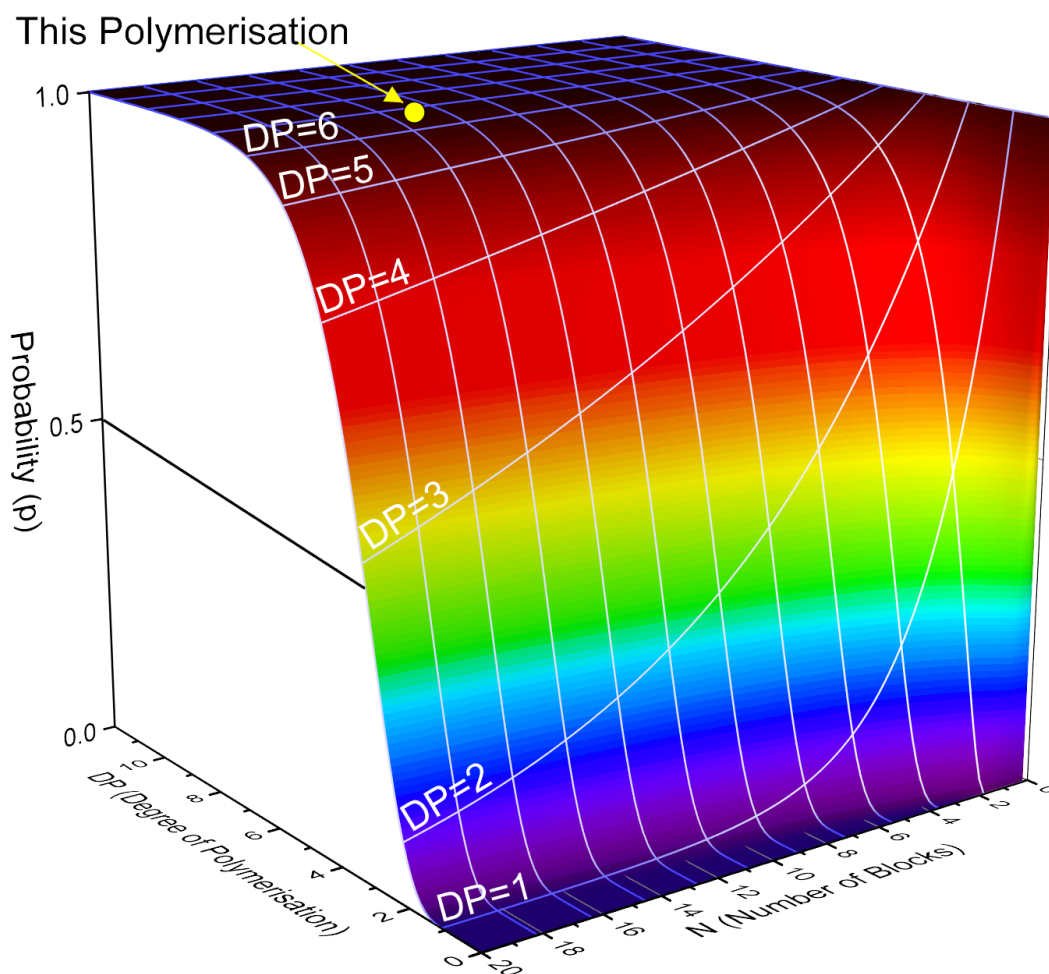


Figure 4. 31 - Probability p that all chains contain all N blocks for a given number of blocks (N) and degree of polymerisation (DP).

4.10.4. Mechanism

The chemistry of the catalytic intermediates may be further investigated. The ratio of catalyst:co-catalyst had a dramatic effect on the molar mass distribution of the polymer, which supports the relevance of the anionic, hexacoordinate chromate intermediate and suggests that ca. 50% of the chromium catalyst exist in its neutral form. Although most of this discussion has so far focussed on the chromate species and a monometallic pathway, it is also pertinent to consider a bimetallic mechanism may be possible. In detail, one chromium complex acts as a Lewis-acid for epoxide (or anhydride) activation, thereby making the monomer reactive towards nucleophilic ring-opening from the chromate species, as illustrated in Figure 4. 32. A similar bimetallic mechanism has been proposed most recently by Coates but earlier by many others to rationalise the mechanism of catalysts for PPO.^[4] Such a mechanism has also been a reoccurring theme in related catalysis with macrocyclic catalysts,^[36-37] zinc BDI catalysts^[38] and chromium and cobalt salen complexes.^[4, 10-11] Mechanistic studies would be useful to clarify the roles of the two complexes during PO-ring-opening: as shown in Figure 4. 32, metal I should be formally anionic after the ring-opening event, and the roles between metal I and II change, similar to a chain-shuttling mechanism.^[39]

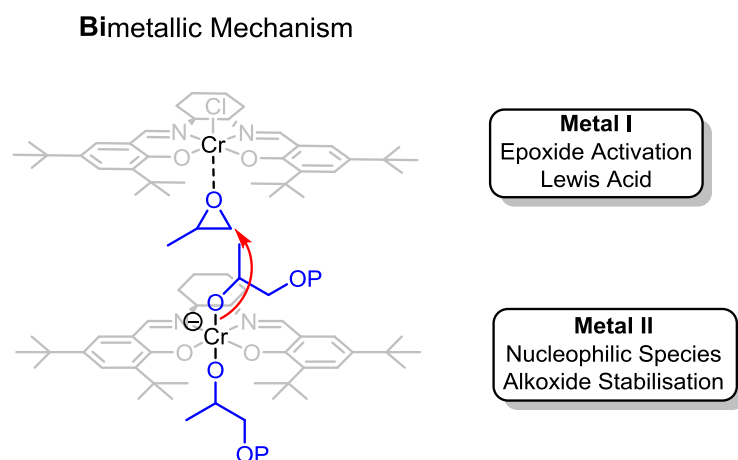


Figure 4. 32 – Bimetallic intermediate proposed during the ring-opening of PO.

More insight into the second chromate co-ligand would also help to validate the mechanism: Although two alkoxide co-ligands are shown, the active species may contain two carboxylate or one carboxylate and one alkoxide co-ligand. Further the mechanism may change and may differ between mono- and bi-metallic pathways or in the presence of anionic species from ROCOP to ROP.

To summarise, the mechanism involving metal salen complexes is not yet fully understood and a number of important questions remain unanswered.

4.11. Summary and Outlook

Block copoly(ester-*b*-ether)s have been synthesised from a mixed monomer feedstock featuring epoxides and anhydrides with a commercial chromium salen catalyst, [SalcyCrCl], in combination with PPNCI (Figure 4. 33). This catalysis enables the one-pot combination of epoxide / anhydride ROCOP and epoxide and/or lactone ROP ('switch' catalysis) and allows for the incorporation of polyether segments, compared to chapter 3. The reaction was optimised with respect to monomer scope, polymer molar masses and block structure (multiple switching). Thermal analysis of the resulting materials, by DSC, showed block miscibility over a range of block compositions. Finally, the catalysis was extended to mixtures of three monomers (PO/TCA1/DL) and post-functionalisation reactions were carried out. Overall, this is the first example of 'switch' catalysis incorporating polyether segments into a block copolymer. Future work in different areas should be considered to extend these promising results.

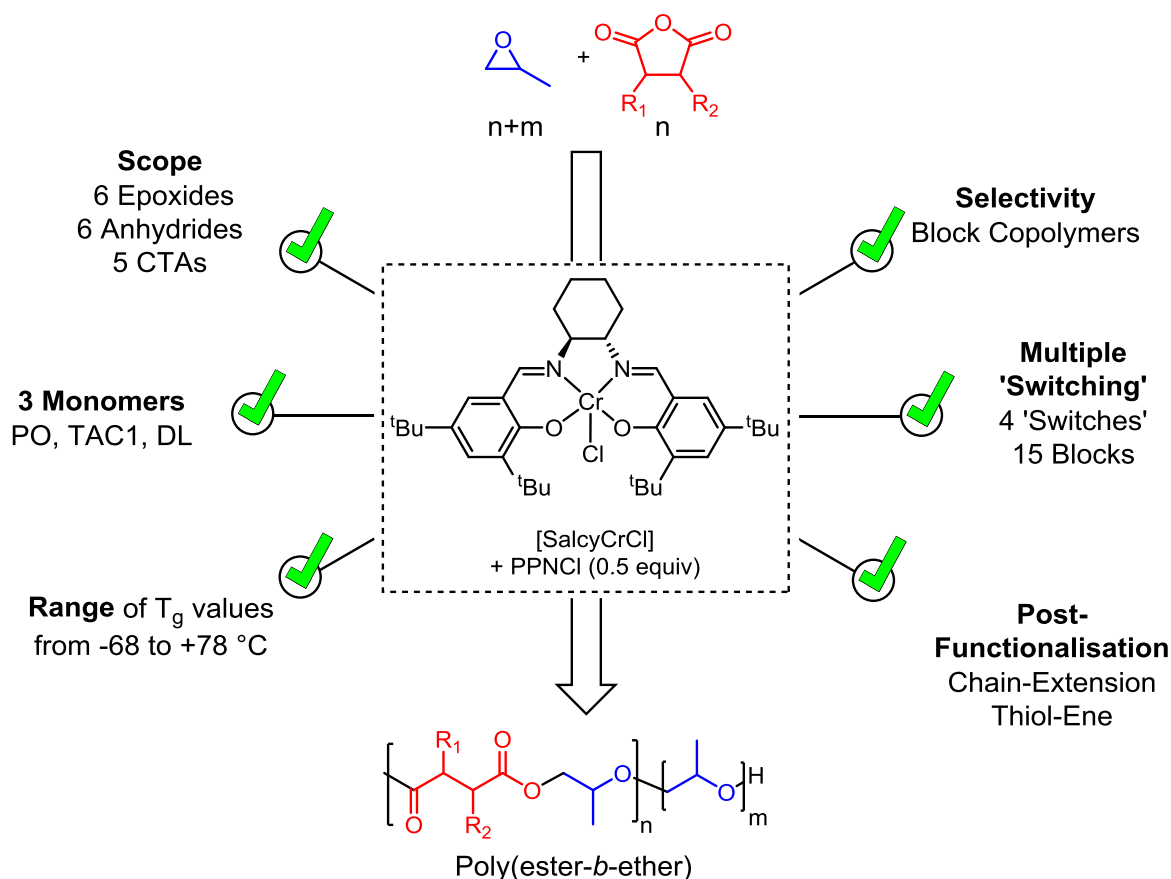


Figure 4. 33 – Key achievements in 'switch' catalysis in this chapter.

4.11.1. Catalyst Development

One major disadvantage of the catalytic system used, [SalcyCrCl]/PPNCl, is the use of chloro-initiating groups. These groups result in bimodal molar mass distributions due to initiation from chloride and from diols or dicarboxylic acids. However, monomodal molar mass distributions are necessary for the synthesis of block copolymers. One means to improve molar mass distribution could be to modify the catalytic system: recently, this has been illustrated with a non-initiating aluminium complex ([Salphen^FAl⁺OTf⁻]) and an initiating co-catalyst (PPN₂Ad). High molar masses (ca. 10,000 g mol⁻¹) and narrow molar mass distributions ($\mathcal{D} \leq 1.07$) were obtained.^[40] This alternative co-catalyst could be investigated with the corresponding chromium complexes and could make it an excellent candidate for 'switch' catalysis (Figure 4. 34).

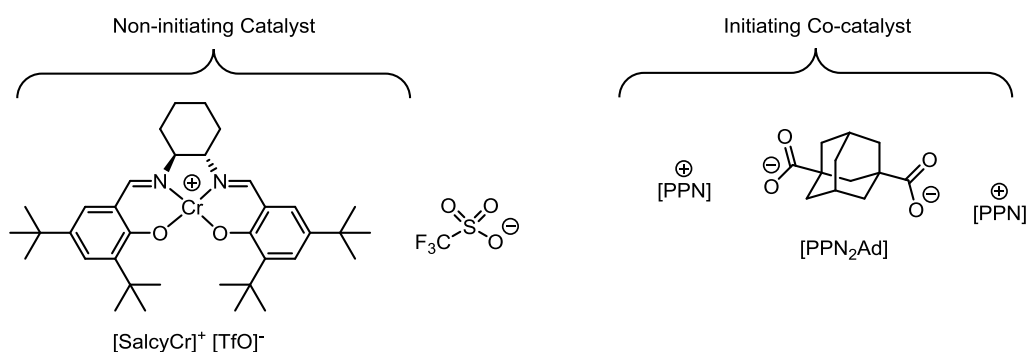


Figure 4. 34 – Proposed catalytic system for 'switch' catalysis.

Another alternative would be to electronically modify the catalyst to affect the position of the catalyst-co-catalyst equilibrium. This might allow for a wider monomer scope, particularly for anhydrides, where transesterification side-reactions were observed. For example, by changing the phenol moieties, the linker between them, or the imine-group the catalyst activity for transesterification may be modulates (Figure 4. 35).^[41-43] A combination of these changes may also enable asymmetric ROP catalysts.^[44] The formation of polyether is expected to be dependent on the metal and polyether formation is not reported using aluminium(III) catalysts.^[10, 45-49]

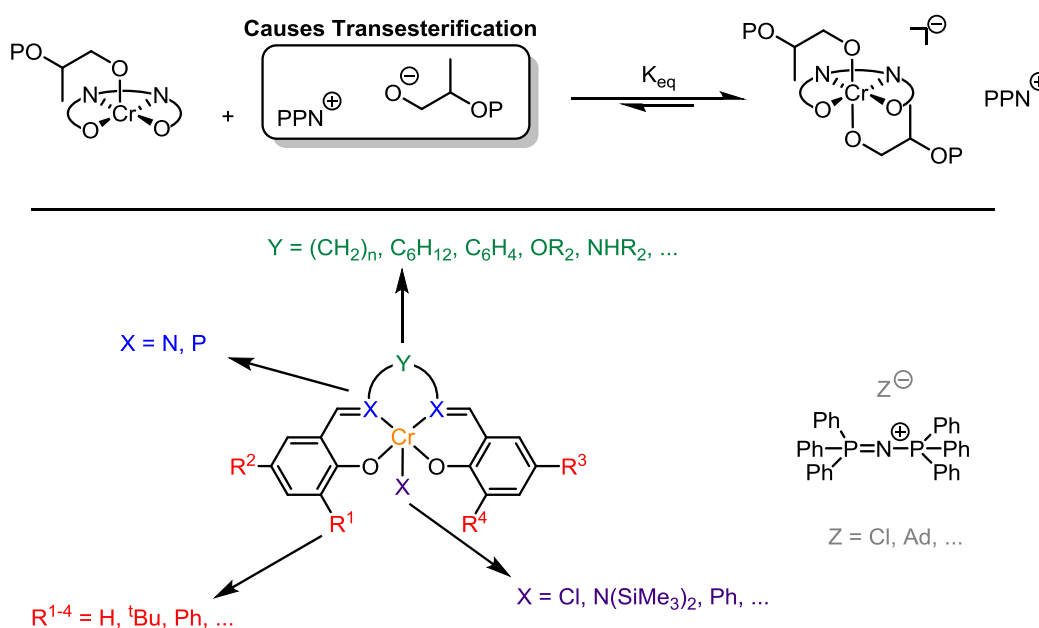


Figure 4. 35 – Catalyst-co-catalyst equilibrium (top) and possible modifications of the catalyst.

In all reactions, the addition of PPNCl, as a co-catalyst, is critical to allow for successful ‘switch’ catalysis. However, this co-catalyst introduces side-reactions and further complicates the catalytic system as multiple equilibria have to be considered.^[50] Another simplification may be achieved by tethering the co-catalyst to the ligand framework (Figure 4. 36, left).

One further disadvantage of [SalcyCrCl] catalysts is the overall slow rates, particularly for the homopolymerisation of PO. Bimetallic chromium salen catalysts could be selected for ‘switch’ catalysis, as they were successfully used for PO ROP showing turn-over frequencies of ca. 500 h⁻¹ (Figure 4. 36, right).^[4]

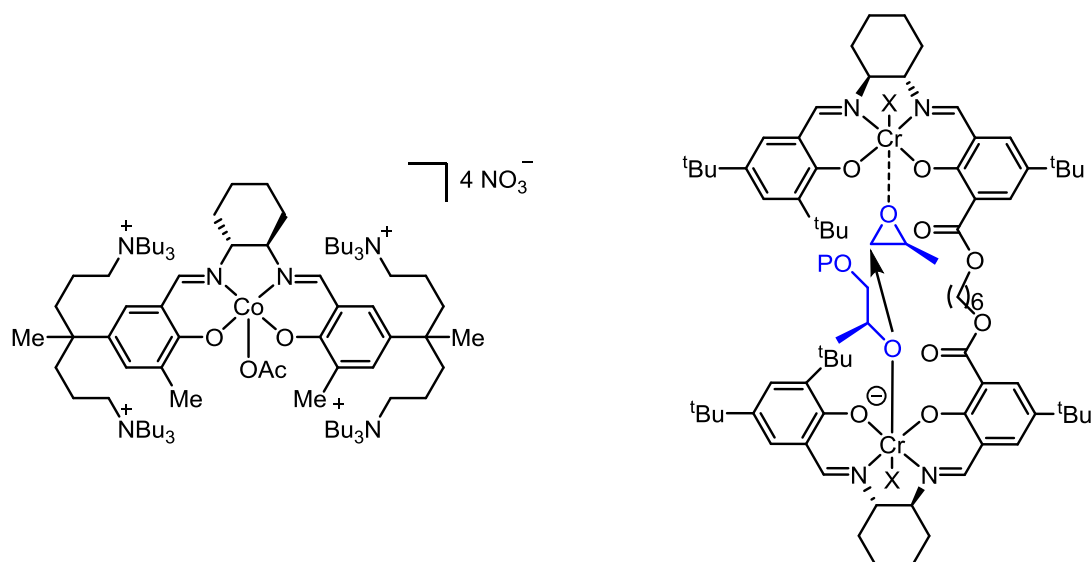
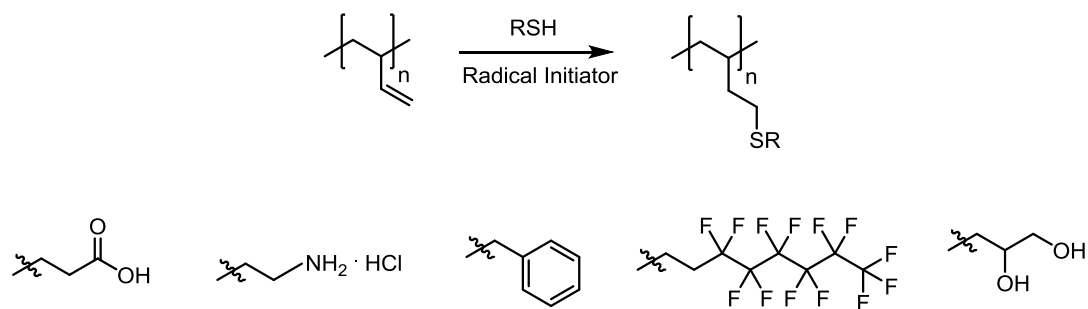


Figure 4. 36 – Alternative metal salen catalyst (left) and bimetallic chromium catalyst (right).^[4, 51]

4.11.2. Post-Functionalisation Reactions

A range of further post-functionalisation reactions should be explored using reactions such as alkene metathesis, thiol-ene reactions and copper(I)-catalyzed alkyne-azide cycloaddition (CuAAC).^[52] A range of thiol-ene reactions is shown in Scheme 4. 9, which may be used to increase χ .^[53] The reaction conditions, however, should be considered carefully to ensure that the polyester remains intact during this post-reaction.



Scheme 4. 9 – Thiol-ene reactions with poly(1,2-butadiene).^[53]

Finally, the polymers could be further functionalised through end group modification. In this catalysis, end groups can be changed easily through the choice of CTA. This has been demonstrated with propargyl alcohol as CTA followed by CuAAC to attach dyes or peptides to the polymer end groups.^[54]

4.11.3. Materials

The obtained materials may be compatible with a range of applications due to their highly tuneable glass transition temperature. Following this 'switch' approach, hydroxyl-terminated poly(ether-*b*-ester) materials with T_g values between -70 and +70 °C can be obtained. These polymers can be used for polyurethanes to access elastic foams, such as in car seats, or rigid plastics for hard surfaces.^[55]

These poly(ether-*b*-ester-*b*-ether) materials could also be useful as polymer electrolytes. In contrast to small-molecule electrolytes, polymer electrolytes can be used solvent-free, offer new designs and may be used safely with metallic lithium.^[56-60] Typically, a polyether is mixed with a lithium salt and poly(ethylene oxide) has been widely used – however, ionic conductivity is dramatically decreased below 65 °C due to crystallisation, making it difficult to use for room temperature applications.^[61] Despite several improvements to decrease crystallinity, such as adding plasticisers (fillers),^[62-63] blending with other polymers,^[64-65] or introducing comonomers,^[66-68] these performance limitations persist.^[69]

The ionic conductivity increases with temperature and at lower molar masses (reduced segmental / molecular friction). For this reason, the low molar mass polymers obtained in this catalysis could be beneficial for use as electrolytes.^[70] Moreover, the high proportion of heteroatoms, such as oxygen, combined with the low glass transition temperatures may allow high ion mobility.^[66] Interestingly, better performances were found for polyethers compared to polyesters, which was attributed to a different diffusion mechanism.^[71] Although this mechanistic change may have a negative effect on the use of copoly(ether-*b*-ester-*b*-ether)s as electrolytes, the miscible copolymers obtained here represent a new class of materials for further testing.

4.12. References

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Chapter 5

‘Switch’ Catalysis with [Salphen^FAlCl]

Block Copolyesters from commercially
relevant feedstocks

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5.1. Introduction

From a commercial perspective, an attractive feedstock for 'switch' catalysis would contain propylene oxide (PO), maleic or phthalic anhydride (PA) and (*rac*)-Lactide (LA). This is mainly due to their large-scale availability and low price. Although PO was used successfully for poly(ester-*b*-ether)s in the last chapter, 'switch' catalysis using [SalcyCrCl] has three limitations: (i) tricyclic anhydrides are necessary to avoid transesterification (block-scrambling), (ii) LA cannot be used as backbiting products are formed and (iii) the selective ROCOP cannot be performed in neat epoxide as polyether was formed.

Three different aluminium catalysts were tested but only a fluorine-substituted aluminium salphen catalyst, [Salphen^FAlCl], enabled 'switch' catalysis (Figure 5. 1). This raises fundamental questions, such as: What catalyst properties are needed for this transformation? Is [Salphen^FAlCl] only a 'match' to PO/PA/LA or can other monomer combinations be used? Can molar masses be improved above 5,000 g mol⁻¹? Are there any advantages over previously investigated 'switch' catalysts based on zinc or chromium? These questions will be investigated in detail in this chapter.

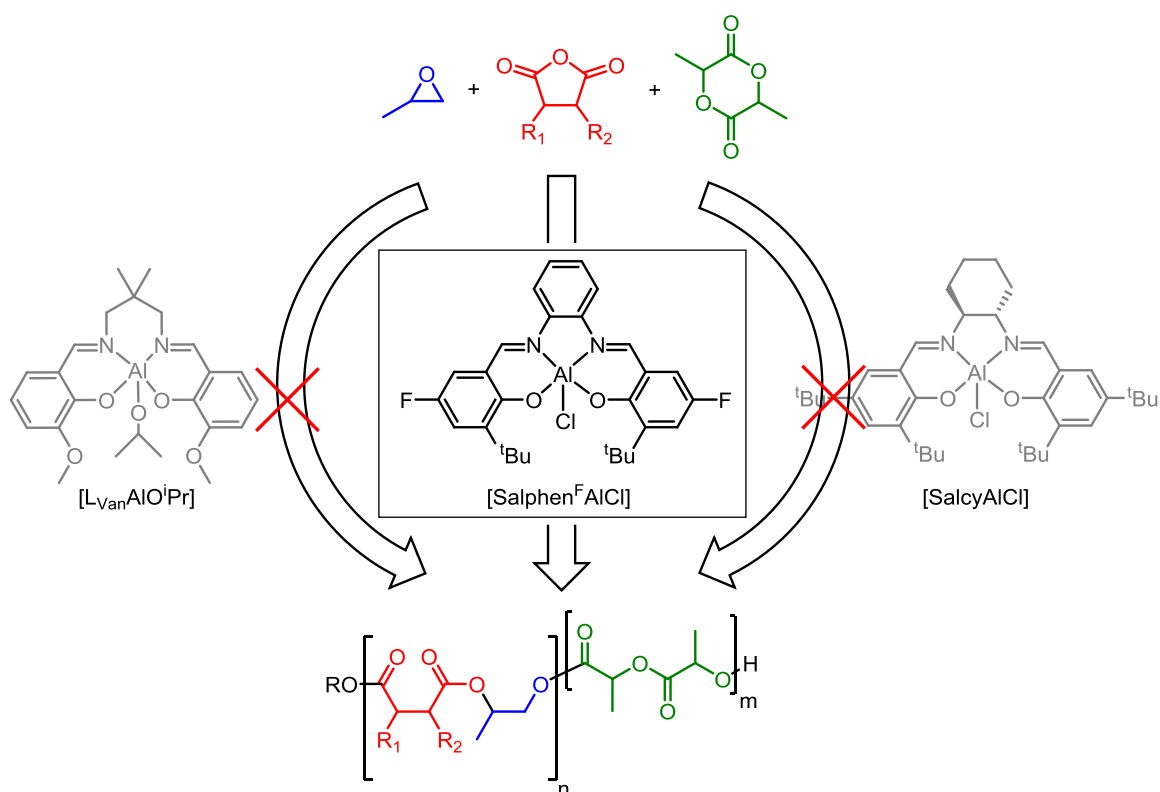


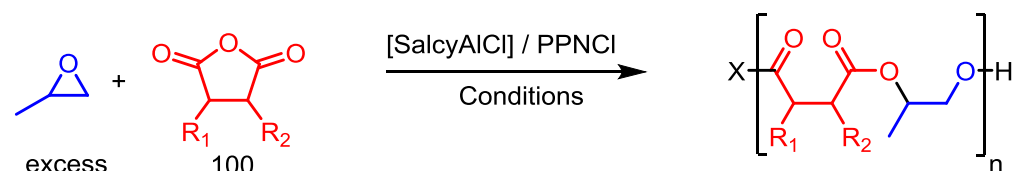
Figure 5. 1 – 'Switch' catalysis with [Salphen^FAlCl].

5.2. Catalyst Screening

5.2.1. [SalcyAlCl]

As a starting point, commercially available [SalcyAlCl] was investigated for anhydride/PO ROCOP (Table 5. 1) as aluminium complexes, compared to chromium or cobalt complexes, generally do not homopolymerise PO.^[1] The focus was on mono- and bicyclic anhydrides and succinic (SA), glutaric (GA) and phthalic anhydride (PA) were tested. High conversions and polyester vs. polyether selectivity were observed with GA and PA at room temperature; SA was unreactive even under extended reaction times (seven days). GPC analysis of the polymer formed from PO/PA showed broad molar mass distributions, which may be indicative of transesterification (see Chapters 2 and 3).

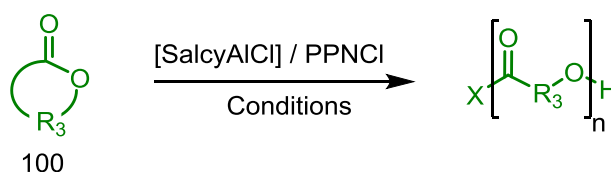
Table 5. 1 – Screening of monomers for ROCOP with [SalcyAlCl].^[a]



Anhydride	t [d]	Conversion [%] ^[b]	Selectivity [%] ^[b]	M_n (Đ) [g mol ⁻¹] ^[c]
 SA	7	< 5	N. D.	N. D.
 GA	3	99	> 95 %	N. D.
 PA	2	> 95 %	> 95 %	18,100 (1.77)

^[a] Conditions: [Catalyst]: [Co-catalyst]: [Anhydride]: [Epoxide] = 1:0.9:100:1000, room temperature. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC (THF, 30°C), based on PS standards.

Next, LA, ϵ -caprolactone (CL) and ϵ -decalactone (DL) were tested for ROP (Table 5. 2). High activity was observed with LA (TOF ~ 100 h⁻¹); CL and DL ROP were either slow (CL, TOF < 0.5 h⁻¹) or did not occur (DL). Unfortunately, the high activities for the ROP of LA were accompanied by broad GPC traces (Đ = 1.40), which again indicated transesterification.

Table 5. 2 - Screening of monomers for ROP with [SalcyAlCl].^[a]

Anhydride	t [d]	Conversion [%] ^[b]	Selectivity [%] ^[b]	M_n ($\bar{D}$) [g mol ⁻¹] ^[c]
	3	25	> 95 %	N. D.
	6	< 5	N. D.	N. D.
	1	99	> 95 %	8,700 (1.40)

^[a] Conditions: [Catalyst]:[Co-catalyst]:[Lactone]:[Epoxide] = 1:0.9:100:1000, room temperature. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC (THF, 30°C), based on PS standards.

In the one-pot polymerisation of PO/PA/CL at 60 °C, high conversions were observed, within one day. However, broad molar mass distributions ($\bar{D}$ = 1.82) were found by GPC, which was in line with transesterification or slow initiation. Similar results were obtained with LA at 60 °C (not shown). In summary, [SalcyAlCl] could not be used in 'switch' catalysis with PO, PA and lactones.

5.2.2. [L_{Van}AlOⁱPr]

A related salen aluminium catalyst featuring an *iso*-propoxide co-ligand was tested next, [L_{Van}AlOⁱPr] (Figure 5. 2). In contrast to [SalcyAlCl], which contained a chloro co-ligand, the alkoxide was expected to be a better initiating group for ROCOP and ROP, which might obviate the need for a co-catalyst and thereby reduce side-reactions.

In the absence of a co-catalyst, slow DL ROP was observed, at room temperature (TOF < 0.5 h⁻¹), and the catalyst was inactive for PA/PO ROCOP, even at elevated temperatures (60 °C). By using a catalyst-co-catalyst mixture (1:1), higher rates for ROCOP (TOF ~ 50 h⁻¹)

were observed. This catalytic system was tested for the one-pot polymerisation of PO/PA/DL next and high conversions were obtained after 24 hours (99% PA, 67% DL). Analysis of aliquots at different times of the reaction revealed that ROCOP proceeds before ROP and with high polyester vs. polyether selectivity (not shown). Further GPC analysis showed a continuous increase in molar mass throughout the reaction. Unfortunately, broad molar mass distributions were obtained, particularly during ROP (Figure 5. 2). These observations were similar to the attempted 'switch' catalysis of CHO/PA/CL with [SalcyCrCl], which suggested either transesterification or slow initiation.

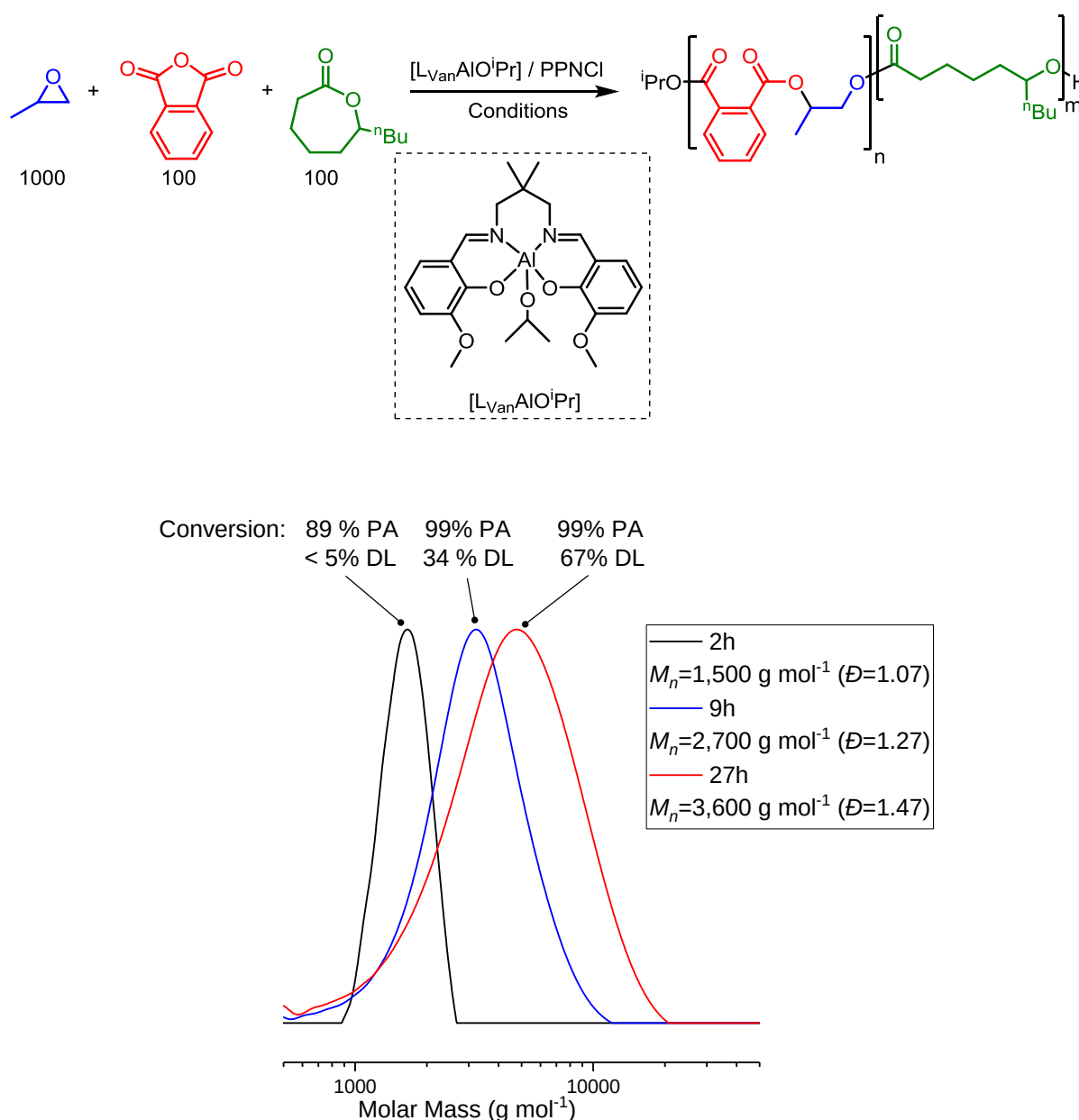


Figure 5. 2 – GPC Traces at different times of the one-pot polymerisation of PO/PA/DL with [L_{Van}AlOⁱPr]/PPNCI. Conditions: [L_{Van}AlOⁱPr]:[PPNCI]:[ⁱPrOH]:[DL]:[PO] = 1:0.9:10:100:1000, 60 °C.

Next, the amounts of PPNCl, relative to [L_{van}AlOⁱPr], were varied from 0.25 to 1.0 equivalent (Table 5. 3). In all cases, high conversions (99% PA, >95% DL) were observed after three days, accompanied by a broad dispersity (1.39<*D*<1.61). If PPNCl was replaced with DMAP, no significant improvement in dispersity was observed.

Table 5. 3 - One-pot polymerisation of PO/PA/DL with [L_{van}AlOⁱPr] and different amounts of PPNCl.^[a]

[L _{van} AlO ⁱ Pr]: [PPNCl]	Conversion [%] ^[b]		<i>M_n</i> (<i>D</i>) [g mol ⁻¹] ^[c]
	PA	DL	
1.0:0.3	99	99	3,400 (1.39)
1.0:0.5	99	99	3,400 (1.46)
1.0:0.8	99	99	3,500 (1.61)
1.0:0.9	99	99	3,500 (1.61)
1.0:1.0	99	99	3,300 (1.55)
1.0:1.0 (DMAP)	99	80	4,000 (1.27)

^[a] Conditions: [L_{van}AlOⁱPr]:PPNCl:ⁱPrOH:PA:DL 1:(0.3-1.0):10:100:100 in 1.5 mL of PO, 60 °C, 3 d; for DMAP: 30 hrs. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC (THF, 30°C), based on PS standards.

In summary, [L_{van}AlOⁱPr] could not be used for 'switch' catalysis with PO and was inactive for ROCOP in the absence of a co-catalyst. In the presence of a co-catalyst, broad mass distributions were obtained with PO/PA/DL.

5.2.3. [Salphen^FAlCl]

In 2017, a fluorine-substituted aluminium salphen catalyst ([Salphen^FAlCl]) was published, by Coates and co-workers, and an unexpected performance in ROCOP was noted: within a series of catalysts, [Salphen^FAlCl] showed only minimal transesterification and epimerization in the synthesis of polyesters.^[2] This lack of transesterification reactivity makes [Salphen^FAlCl] a promising candidate for 'switch' catalysis and this catalyst was tested with PO/PA/LA.

High rates were observed for the attempted 'switch' catalysis with full conversion of PA and LA occurring within 90 minutes. The molar mass increased throughout the reaction and more importantly, narrow monomodal molecular mass distributions were observed by GPC, even during twelve additional hours after reaction completion (Figure 5. 3). This was highly encouraging and [Salphen^FAlCl] was further investigated for 'switch' catalysis with PA/PO/LA.

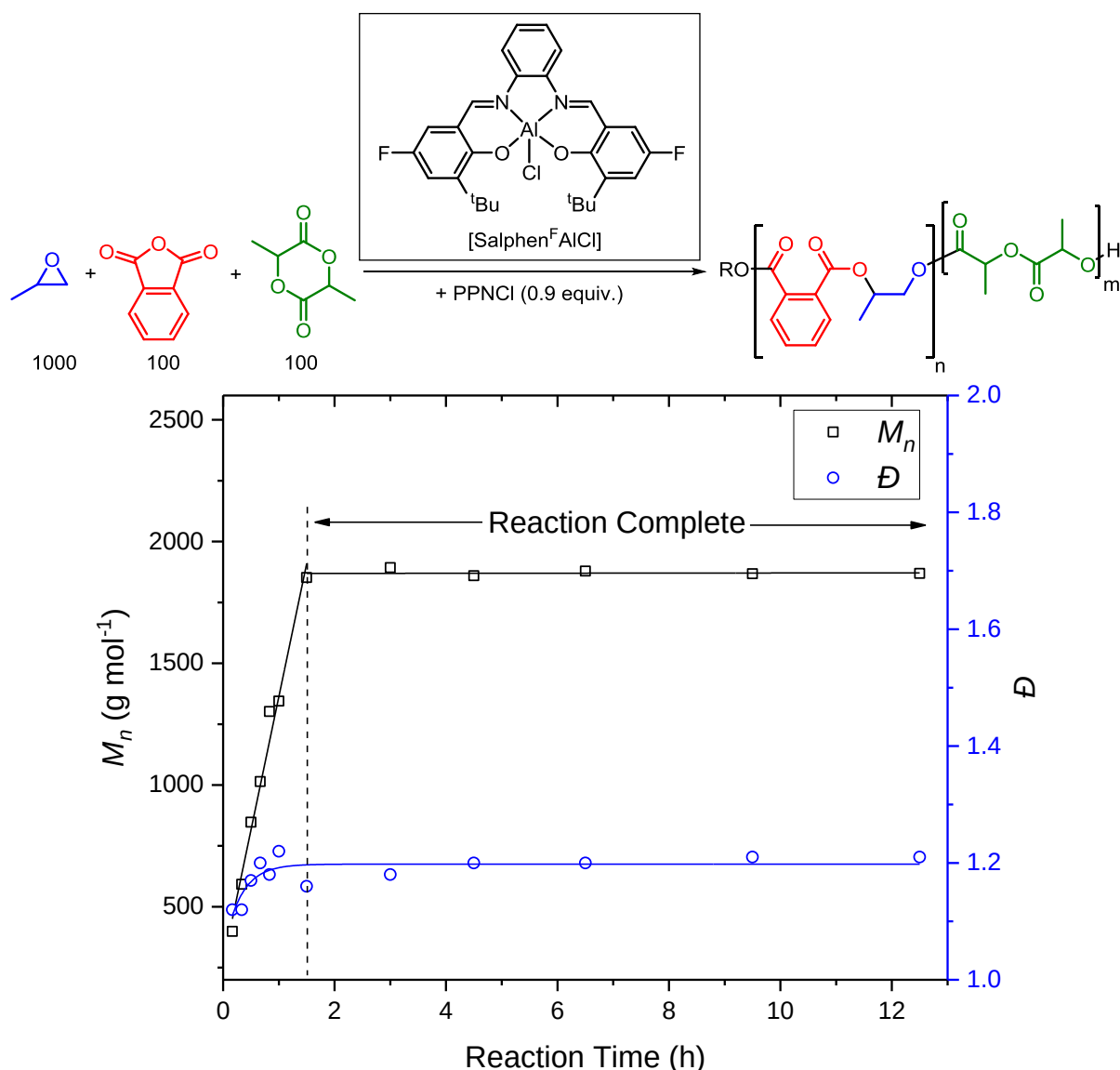


Figure 5. 3 – One-pot polymerisation of PO/PA/LA (top) and GPC analysis at different times (bottom). Conditions: [Salphen^FAlCl]:[PPNCI]:[CHD]:[PA]:[LA]:[PO] = 1:0.8:10:100:100:1000, 60°C.

Moreover, [Salphen^FAlCl] was characterised by X-ray diffraction, as its solid state structure was previously unknown (Figure 5. 4); selected bond length and angles are given in Table 5. 4. The aluminium(III) centre adopts a pseudo-octahedral geometry and is located 0.109 Å above the equatorial plane formed by the tetradenate salphen ligand and towards the chloro ligand. Al1 is coordinated by the salphen ligand in equatorial position with N1 and N2 *cis* to each other and *trans* to O1 and O2, respectively. Cl1 and a THF molecule are coordinated in axial position and all bond lengths are within the expected values of similar salen aluminium complexes (Table 5. 4). THF may be considered as a model compound for an epoxide and this structure may be considered to represent one epoxide-coordinated intermediate during ROCOP.

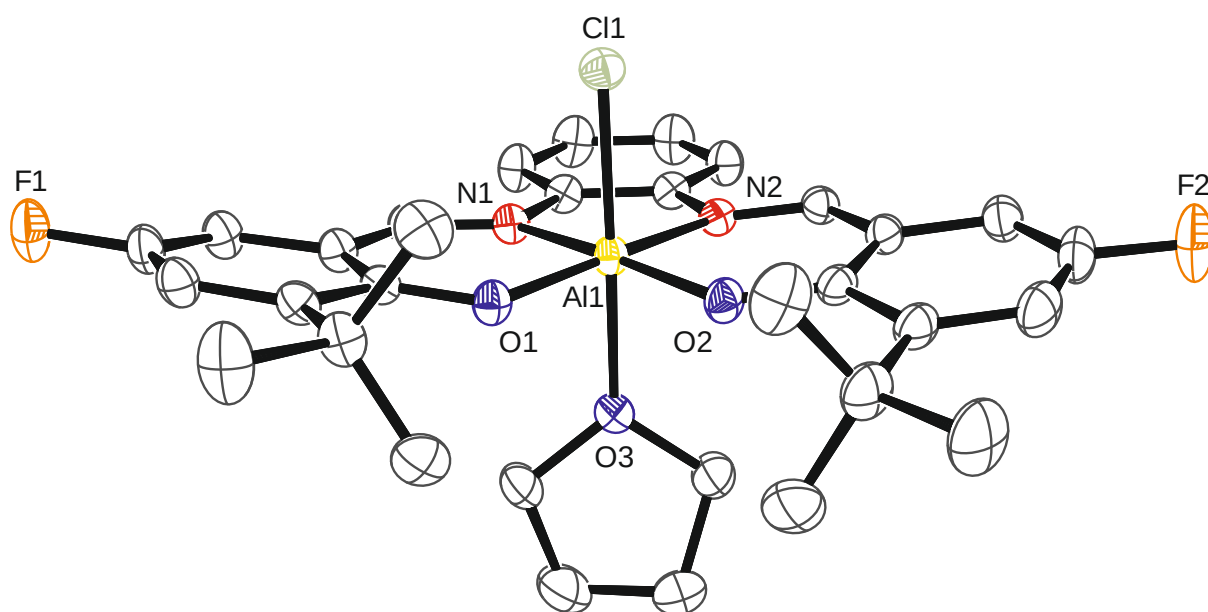


Figure 5. 4 – Solid state structure of [Salphen^FAlCl(THF)] with thermal ellipsoids at the 50% probability level; hydrogen omitted for clarity.

Table 5. 4 – Selected bond lengths and angles for [Salphen^FAlCl(THF)].

Bond	Bond length [Å]	Bond	Bond Angle [°]
Al(1)-O(1)	1.800(1)	O(1)-Al(1)-O(2)	96.19(5)
Al(1)-O(2)	1.804(1)	O(1)-Al(1)-N(1)	91.00(5)
Al(1)-N(1)	2.013(1)	O(1)-Al(1)-Cl(1)	93.88(4)
Al(1)-N(2)	1.994(1)	O(1)-Al(1)-O(3)	87.36(4)
Al(1)-O(3)	2.091(1)	N(1)-Al(1)-N(2)	80.48(5)
Al(1)-Cl(1)	2.3054(5)	O(3)-Al(1)-Cl(1)	176.22(3)

5.3. 'Switch' Catalysis of Propylene Oxide/Phthalic Anhydride/Lactide

After these encouraging results, the set guidelines for testing for 'switch' catalysis, outlined in Chapter 2, were followed.

First, the reaction was monitored by *in situ* IR and NMR spectroscopy to identify if all monomers were incorporated randomly throughout the reaction or if one (ROP) or two (ROCOP) monomers were polymerised at a time. The *in situ* IR analysis is given in Figure 5. 5 and showed that PO/PA ROCOP occurred before the polymerisation of LA. The ROP of LA was observed only once high conversions of the anhydride were achieved (> 95%), which was a key criterion for 'switch' catalysis to minimise tapered regions. In this reaction, ROCOP was slow (TOF ~ 15 h⁻¹) compared to ROP (TOF ~ 400 h⁻¹). Kinetic analysis yielded the zeroth order rate constant for ROCOP with $k_{PO-PA-ROCOP} = 8.20 \pm 0.02 \times 10^{-5} \text{ M s}^{-1}$ and the first order rate constant for ROP of $k_{LA-ROP} = 8.05 \pm 0.50 \times 10^{-3} \text{ s}^{-1}$ (see appendix). It should be noted that the rates were generally lower than in the previous screening, which was performed in a sealed vial. It is proposed that an overpressure was generated at 60 °C, which allows for reaction temperatures above the boiling point of PO (34 °C). For the *in situ* IR monitoring, the head space of the reaction is increased by a factor of ca. 10 and the built-up of pressure is less likely to occur, which may contribute to the slower rates.

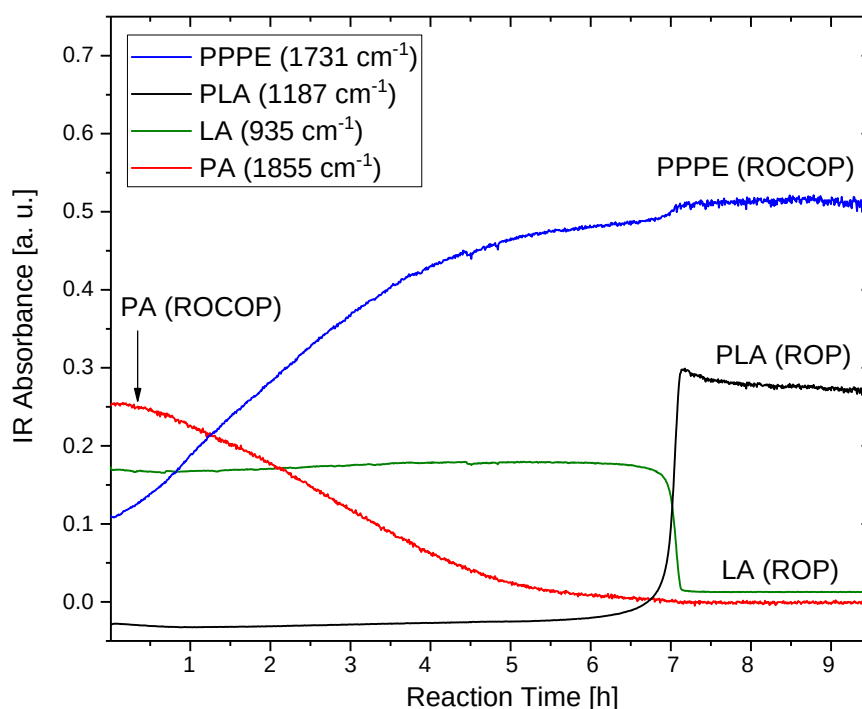


Figure 5. 5 – *In situ* monitoring of one-pot polymerisation of PO/PA/LA by IR. Conditions: [Salphen^FAlCl]:[PPNCl]:[CHD]:[PA]:[LA]:[PO] = 1:0.8:10:100:100:1000, 60°C.

Slight deviations from an idealised pseudo first order rate-law were observed at low conversions of LA. This may be a consequence of slow-initiation from the macromolecule, formed after ROCOP, similar to the chromium (chapter 3) and zinc catalysts.^[3]

The selective monomer incorporation was further confirmed by *in situ* ¹H NMR spectroscopy (Figure 5. 6). Compared to IR spectroscopy, generally lower rates were found, associated with both the dilution (the reaction was run 0.75 M in CDCl₃) and the absence of stirring (or spinning). Further differences between the techniques can be seen in the formation of a small tapered region where the consumption of LA starts at ca. 90% PA conversion (vs. >95% in IR). The rate constants could not be determined as the reactions did not clearly follow zeroth or first order rate laws. Two further observations from the monitoring by ¹H NMR spectroscopy could be noted: first, the homopolymerisation of excess PO to PPO was not observed as no resonances were found between 3.2 and 3.5 ppm. This was further confirmed by MALDI-ToF spectrometry of the polyester block obtained only from ROCOP where the only repeat unit has *m/z* = 206 in line with a perfectly alternating polyester (see appendix). Second, the stereoselective ROP of LA was not observed with ¹H NMR spectroscopy showing broad resonances at δ = 5.15 ppm.

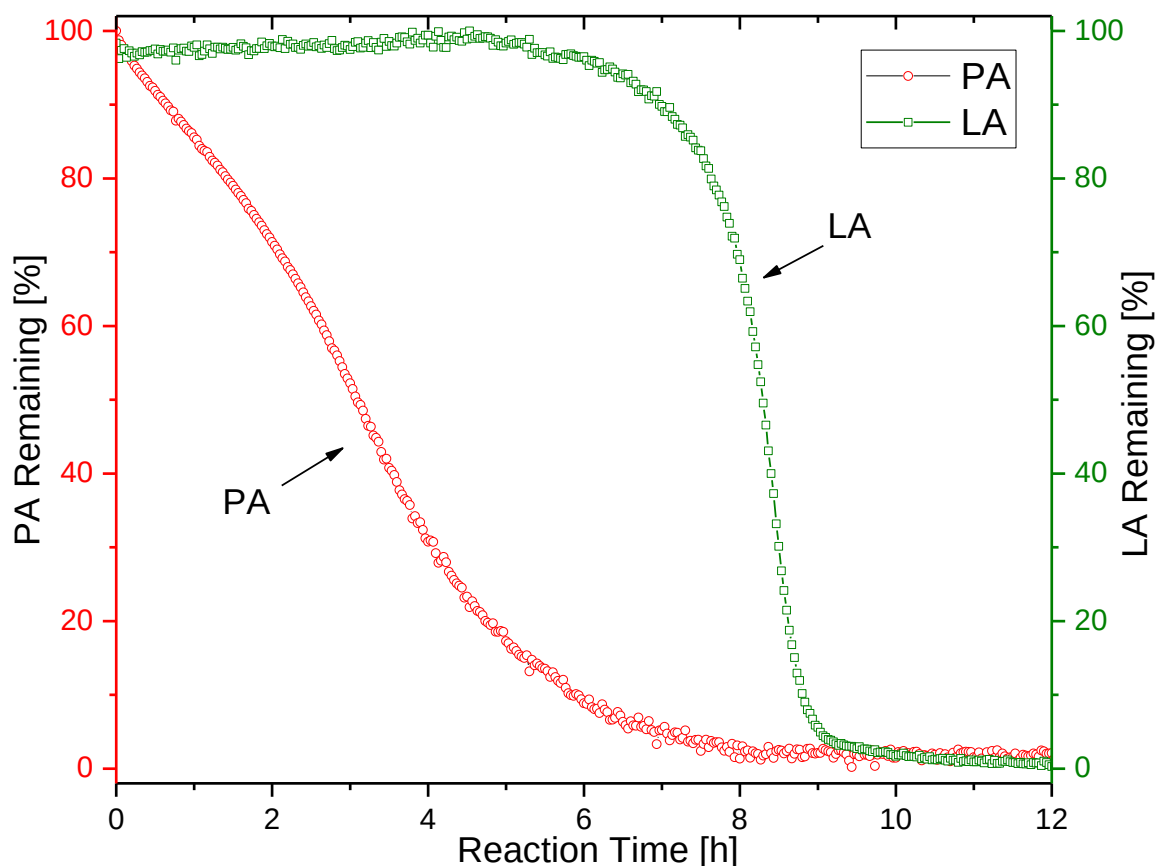


Figure 5. 6 – *In situ* IR NMR monitoring of one-pot polymerisation of PO/PA/LA. Conditions: [Salphen^FAlCl]:[PPNCl]:[CHD]:[PA]:[LA]:[PO] = 1:0.8:10:100:100:300, 60°C, 0.75 M in CDCl₃.

Next, the reaction was monitored by GPC and an increase in mass after ROCOP was observed while maintaining low dispersities (Figure 5. 7). This indicates the formation of a block copolymer, as opposed to a mixture of homopolymers, in which case the peak after ROCOP would not shift in mass and a second distribution (PLA) should be detected. The formation of a block polyester was further confirmed by comparing RI and UV traces, as only the polymer obtained from ROCOP contains a chromophore (the benzene ring in PA) and no absorption should be obtained for PLA. During 'switch' catalysis, both UV and RI traces increased continuously in mass and were identical (Figure 5. 7, bold and dashed lines).

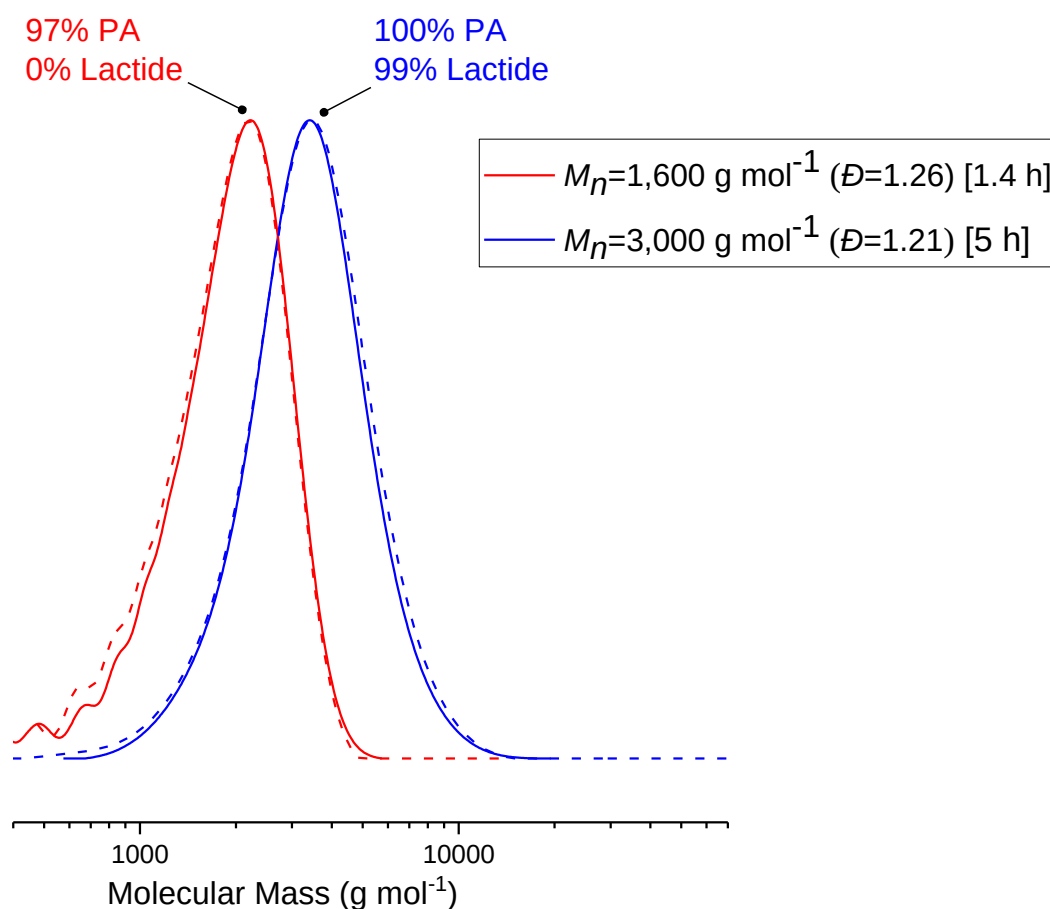


Figure 5. 7 – GPC traces of one-pot polymerisation of PO/PA/LA with [Salphen^FAlCl]/PPNCl. RI trace is given as a solid, UV trace as a dashed line. Conditions: [Salphen^FAlCl]:[PPNCl]:[CHD]:[PA]:[LA]:[PO] = 1:0.8:10:100:100:1000, 60°C.

The polymer end groups were analysed by ³¹P{¹H} NMR spectroscopy after the reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, and using bisphenol A as an internal standard (Figure 5. 8). Two different sets of signals were obtained for the homopolymers: in the case of PLA, a series of resonances at 147.2 ppm were observed with an apparent multiplet structure, which is proposed to be caused by different tetrad stereochemistry. Two well-separated signals were found for the polyester from ROCOP at 148.6 and 146.3 ppm,

which are tentatively assigned to the two different regioisomers resulting from the ring-opening of PO (Figure 5. 8, top). Consequently, the two end groups were ascribed to a primary (148.6 ppm) and a secondary alcohol (146.3 ppm); the integral ratio was 1:2 (assuming similar relaxation times). This indicates that the ring-opening of PO is predominantly sterically driven as it was preferentially ring-opened at the sterically least hindered side, yielding a secondary alkoxide. For the block copolymer, the signal at 147.2 ppm suggests a PLA end group – i. e. successful 'switch' catalysis rather than a mixture of homopolymers.

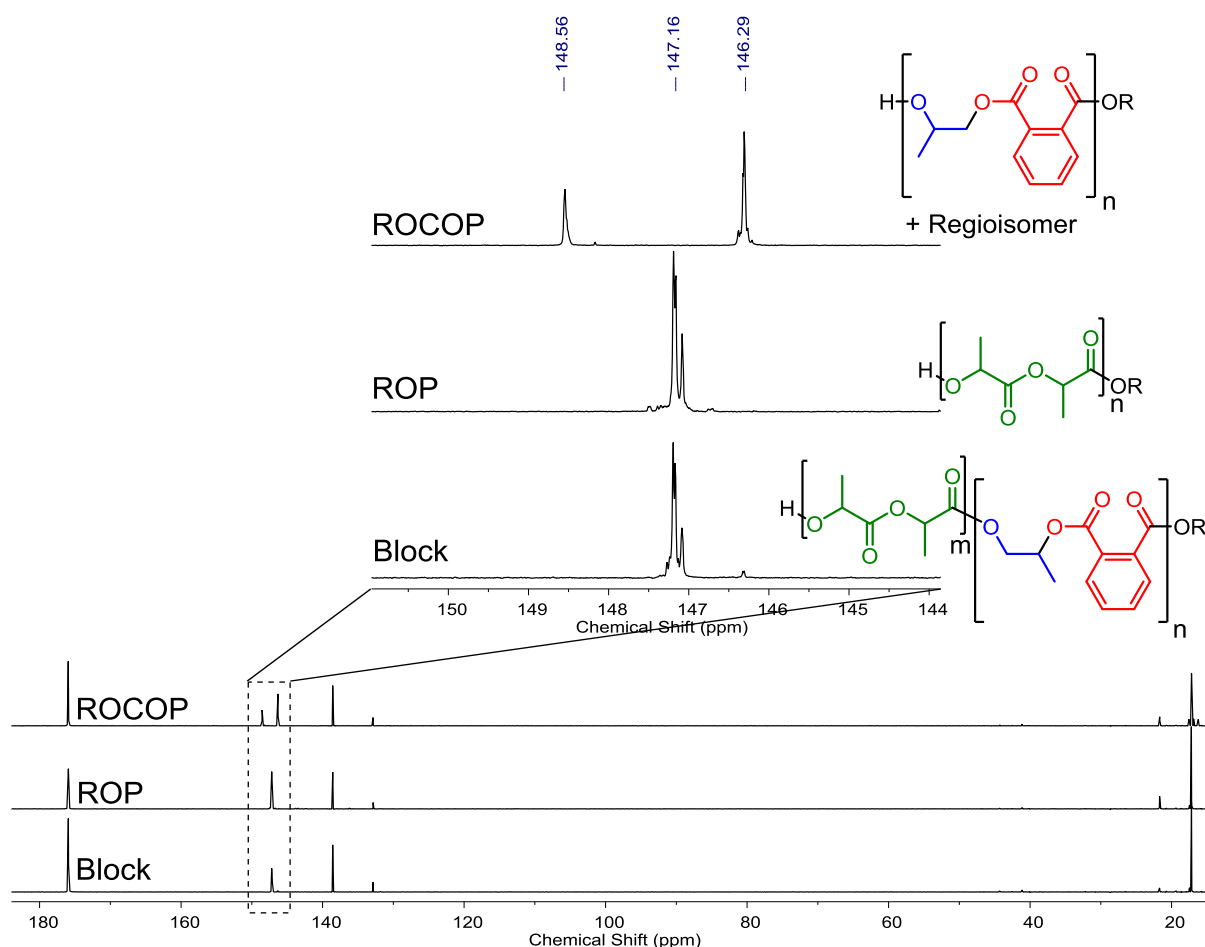


Figure 5. 8 – $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of different polyesters, after the reaction with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (bisphenol A present as internal standard).

The regioselectivity of ROCOP was also examined using $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. Linkages between primary and secondary alkoxides are observed as different 'junctions' between two epoxides and one anhydride repeat unit (Figure 5. 9). As expected from the previous end group analysis, a mixture of head-to-tail (HT), head-to-head (HH) and tail-to-tail (TT) regioisomers were found. This confirmed the low regioselectivity during ROCOP and is in agreement with a recent microstructural analysis of poly(propylene phthalate) (PPE).^[4]

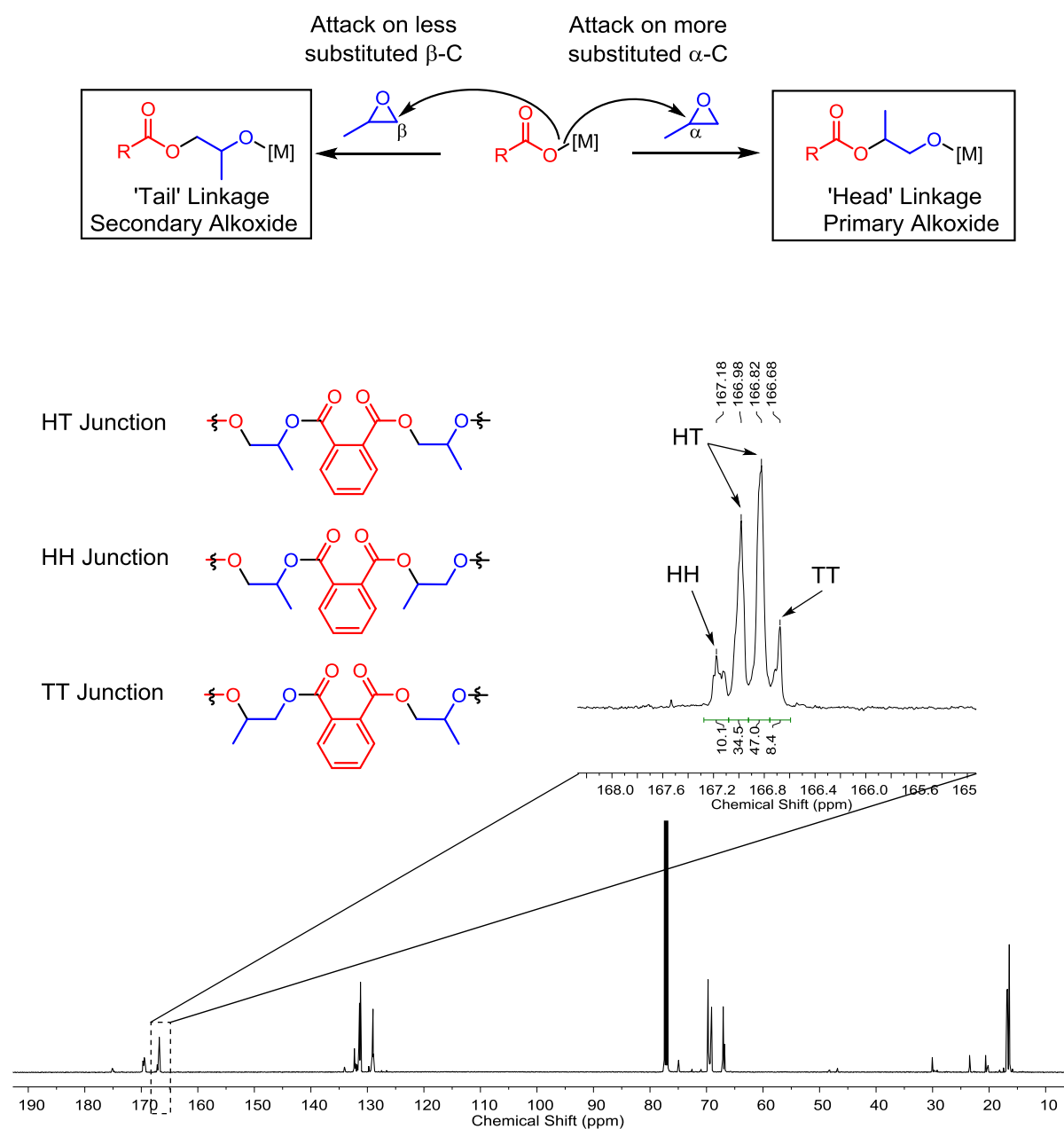


Figure 5. 9 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated block copolyester and an illustration of regioselective epoxide ring-opening.

Comparison of $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the block copolymer with the individual polyesters allowed further end group analysis in the carbonyl region: the polymer obtained from PO/PA ROCOP (PPE) showed an end group at 167.6 ppm whilst PLA showed an end group at 175.1 ppm. These different chemical shifts allow differentiation between the formation of a block copolymer vs. a mixture of homopolymers. In agreement with the previous analysis, only one end group at 175.1 ppm was detected for the block copolymer without any resonances at 167.6 ppm.

Different polymer backbone signals for the polyesters were also identified: the polymer from ROCOP showed resonances between 166.6 and 167.1 ppm, as opposed to PLA, where signals 169.1-169.8 ppm were found (Figure 5. 10). Signals at both sets of chemical shifts were found for the block copolymer but there were no further signals at intermediary chemical shifts. This observation confirms the presence of both blocks and suggests the absence of transesterification (at least within detection limits of NMR spectroscopy).

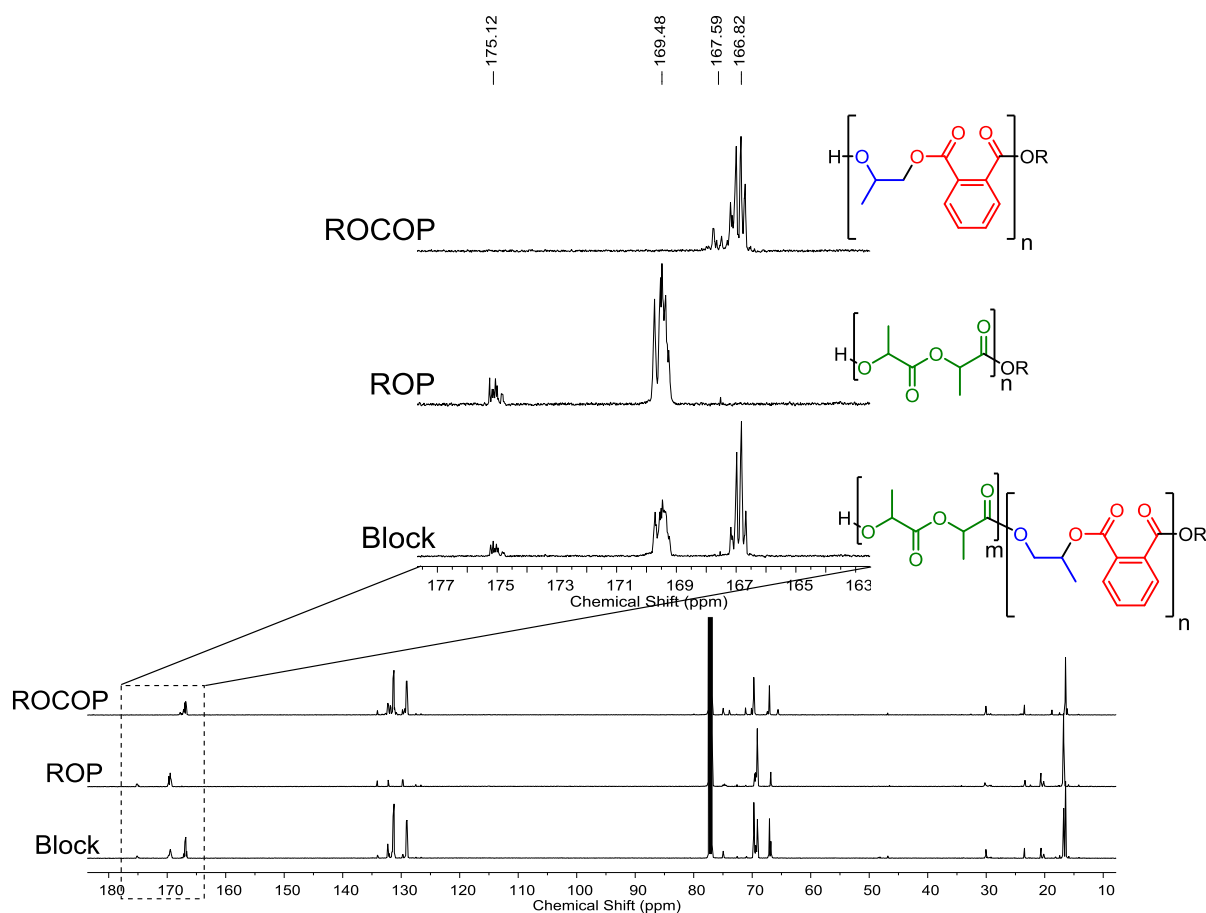


Figure 5. 10 – Comparison of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the block copolymer and the separate polymers obtained from ROP or ROCOP.

Finally, the block copolymer was analysed by DOSY NMR spectroscopy and compared to a blend of homopolymers of similar molar mass (Figure 5. 11). One diffusion coefficient was measured for the block copolymer ($D = 1.78 \times 10^{-8} \text{ m}^2\text{s}^{-1}$), whereas two diffusion coefficients were found for the blend of homopolymers ($D = 7.93 \times 10^{-6} \text{ m}^2\text{s}^{-1}$ [PLA] and $D = 7.28 \times 10^{-6} \text{ m}^2\text{s}^{-1}$ [PPE]).

In conclusion, a range of analytical tests confirmed 'switch' catalysis of PO/PA/LA using [Salphen^FAlCl], in which a triblock copolyester (PLA-*b*-PPE-*b*-PLA) was formed.

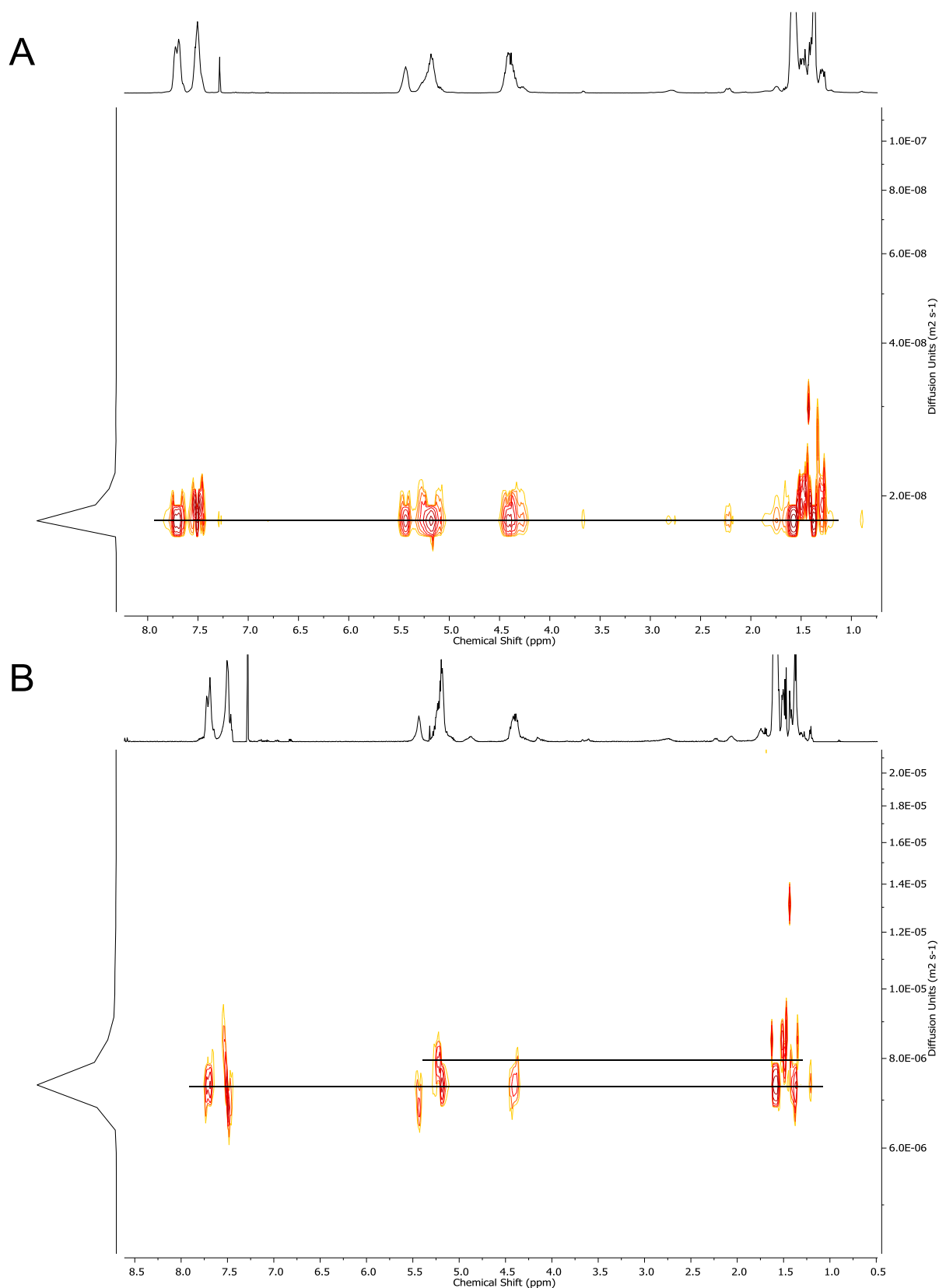
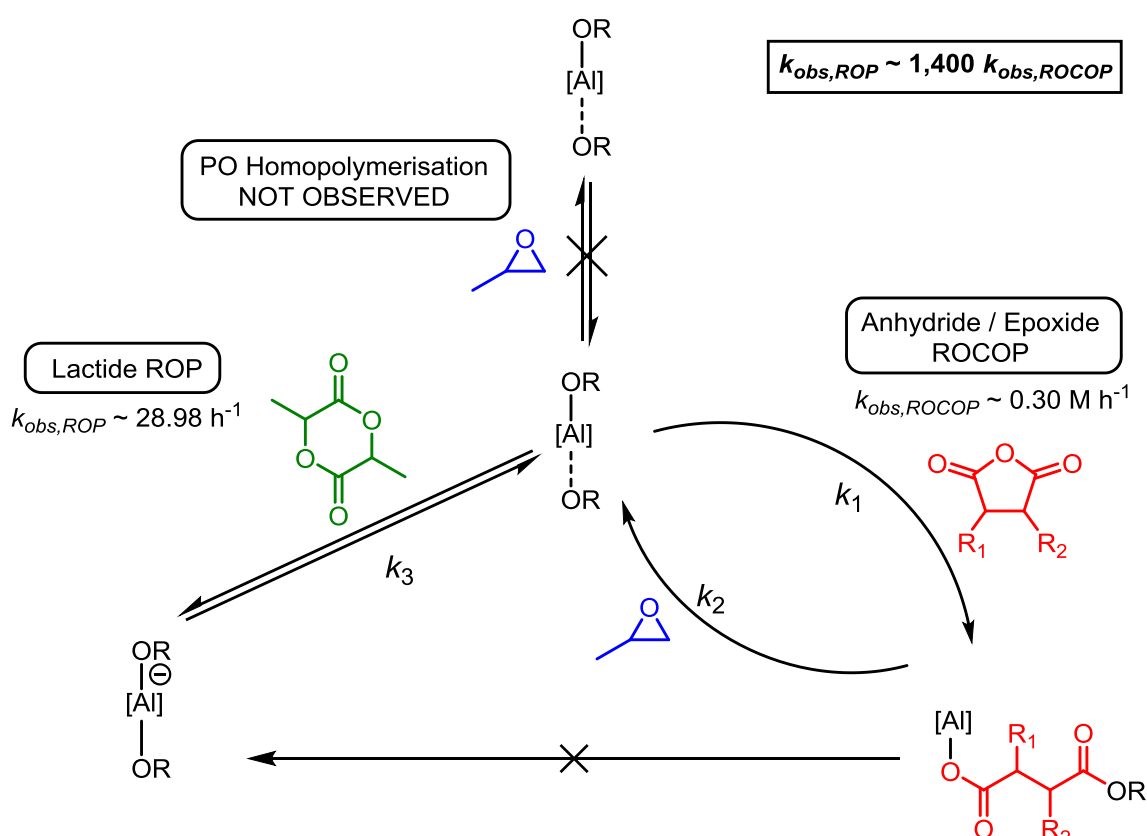


Figure 5. 11 – DOSY NMR Spectra of block copolymer (A) and blend of homopolymers (B).

5.4. Mechanistic Hypothesis

The proposed reaction mechanism involves two catalytic cycles, anhydride/epoxide ROCOP and lactide ROP (Scheme 5. 1). ROCOP is a two-step process and the anhydride is ring-opened first, which results in the formation of an aluminium carboxylate intermediate (k_1). The rate-determining step involves the reaction of the carboxylate intermediate with PO, which yields the aluminium alkoxide intermediate (k_2). Once ROCOP is complete, lactide is polymerised. The lactide ROP proceeds through a single intermediate: an aluminium alkoxide species. It is important to note that the homopolymerisation of PO was not observed.

Based on the observed rates and block selectivity, the following order is proposed for the constituent reactions: $k_1 > k_2 \gg k_3$. In other words, the fastest step in 'switch' catalysis is the ring-opening of anhydride during ROCOP, followed by the ring-opening of LA (ROP), and the ring-opening of PO is the rate-determining step.



Scheme 5. 1 – Proposed reaction mechanism for 'switch' catalysis with [Salphen^FAlCl]/PPNCl, PO/PA/LA.

Similar to [SalcyCrCl], the high selectivity for 'switch' catalysis is proposed to be caused by kinetic control and a high barrier for the reaction between the aluminium carboxylate species and the lactone (and also between the aluminium alkoxide and the epoxide). Thus, the reaction between the aluminium carboxylate intermediate is selective only for PO.

Due to its conjugated ligand, [Salphen^FAlCl] is highly coloured and this provides a visual indicator for the nature of the active species: the catalyst itself is a yellow compound with the colour being maintained in the presence of co-catalyst and during ROCOP. However, during LA ROP the colour changes to dark red. These colour changes are reversible if anhydride or lactide are re-introduced into the reaction mixture (not shown). The colour of these compounds was previously noted by Coates and co-workers and was ascribed to a neutral aluminium complex or a hexacoordinate aluminate species containing one carboxylate co-ligand (yellow) and a hexacoordinate aluminate bis-alkoxide species (red).^[5] Consequently, ROCOP is proposed to proceed through neutral or anionic species containing at least one carboxylate co-ligand, whereas bis-alkoxide intermediates are proposed for LA ROP.

It should be noted that a more detailed mechanism will require much greater insight into the precise structures of the aluminium intermediates. Such studies are recommended but were outside the scope of this thesis.

5.5. Increasing Molar Masses

So far, products with molar masses $< 5,000 \text{ g mol}^{-1}$ were obtained. It was of interest to increase molar masses and this was attempted by two approaches: (i) increasing the [monomer]:[catalyst] loading and (ii) reducing [CTA]:[catalyst] loading.

Starting from 100 equivalents of monomer with respect to the catalyst, the [monomer]:[catalyst] loading was gradually increased up to a ratio of 2000:1. In all cases, full conversions were obtained (after several days). For loadings below 1000:1, monomodal molar mass distributions were observed ($M_n = 8,500 \text{ g mol}^{-1}$; $\bar{D} = 1.13$) and at higher monomer loadings a lower mass shoulder was detected. This might be a result of the accumulation of (unidentified) monofunctional impurities at high catalyst loading and/or partial overlap between AB diblock and ABA triblock polyesters at low masses. Poor stirring at higher monomer loading might also contribute to this tailing. Nonetheless, molar masses could be significantly increased by a factor of ca. 3 by adjusting the [monomer]:[catalyst] ratio.

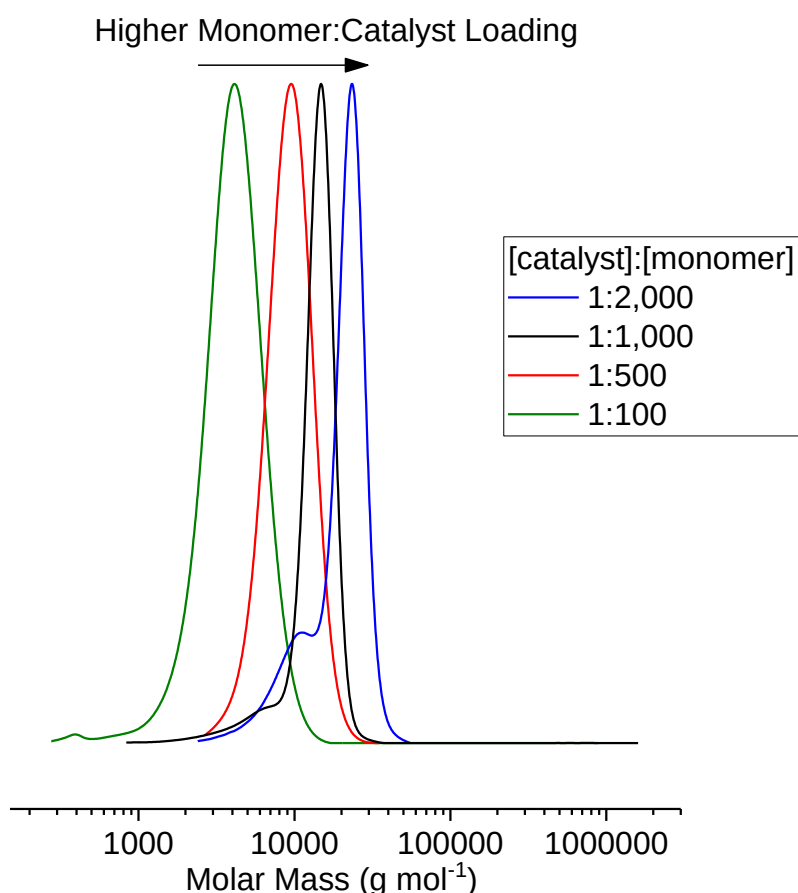


Figure 5. 12 – Effects of [monomer]:[catalyst] loading on molar mass distributions for 'switch' catalysis of PO/PA/LA with [Salphen^FAlCl].

Table 5. 5 – PO/PA/LA 'Switch' catalysis at different [monomer]: [catalyst] loadings.^[a]

[PO]:[PA]:[LA] ^[b]	Equiv. of CHD ^[b]	Conversion [%] ^[c]		M_n (Đ) [g mol ⁻¹] ^[d]
		PA	LA	
2,000:100:100	20	99	> 95	3,500 (1.28)
10,000:500:500	20	99	> 95	8,500 (1.13)
100,000:1,000:1,000	20	99	> 95	14,900 (1.10)
200,000:2,000:2,000	20	99	> 95	16,600 (1.24)

^[a] Conditions: [Salphen^FAlCl]:[PPNCl]:[CHD]:[PO]:[PA]:[LA]=1:0.8:specified equiv. in columns 1 and 2, 60 °C in neat PO. ^[b] Relative to [Salphen^FAlCl]. ^[c] Determined by ¹H NMR spectroscopy. ^[d] Determined by GPC, THF, 30 °C, using polystyrene standards.

One alternative to achieve higher masses is to lower the [CTA]:[catalyst] loading at constant monomer loading. This was optimised for a [monomer]:[catalyst] loading of 500:1 and the amount of CTA was gradually lowered from 20:1 to 10:1. With large amounts of CTA, monomodal molar mass distributions were obtained and the low-mass shoulder was only observed at loadings $\leq 12.5:1$. This is most likely due to the higher amount of AB diblock concentration caused by chloride-terminated species resulting from the reduced CTA loading.

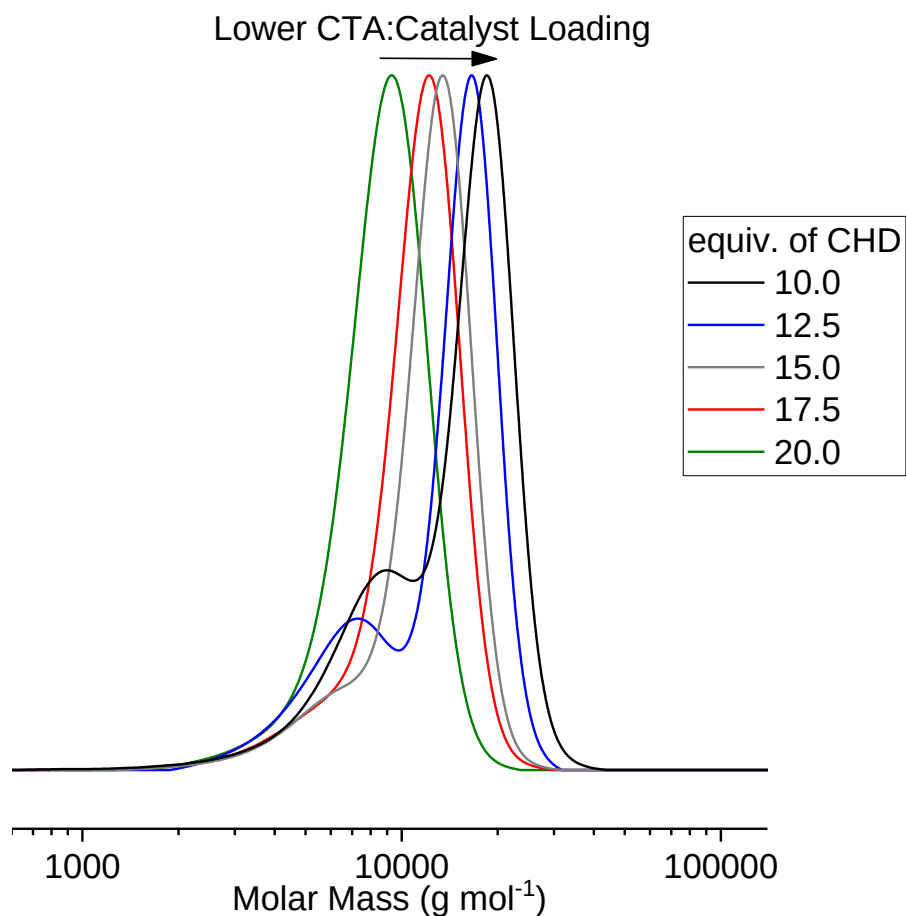


Figure 5. 13 - Effects of CTA:Catalyst loading on molar mass distribution for 'switch' catalysis of PO/PA/LA with [Salphen^FAlCl].

Table 5. 6 - PO/PA/LA 'Switch' catalysis at different [CTA]:[catalyst] loadings.^[a]

[PO]:[PA]:[LA] ^[b]	Equiv. of CHD	Conversion [%] ^[c]		<i>M_n</i> (Đ) [g mol ⁻¹] ^[d]
		PA	LA	
10,000:500:500	20.0	99	> 95	8,500 (1.13)
10,000:500:500	17.5	99	> 95	10,600 (1.15)
10,000:500:500	15.0	99	> 95	11,100 (1.17)
10,000:500:500	12.5	99	> 95	12,700 (1.26)
10,000:500:500	10.0	99	> 95	13,400 (1.23)

^[a] Conditions: [Salphen^FAlCl]:[PPNCl]:[CHD]:[PO]:[PA]:[LA]=1:0.8:specified equiv. in columns 1 and 2, 60 °C in neat PO. ^[b] Relative to [Salphen^FAlCl]. ^[c] Determined by ¹H NMR spectroscopy. ^[d] Determined by GPC, THF, 30 °C, using polystyrene standards.

In summary, molar masses above 10,000 g mol⁻¹ can be achieved by optimising [monomer]:[catalyst] and [CTA]:[catalyst] loading. However, there was a limitation to this approach and once this optimal ratio was exceeded, bimodal mass distributions were obtained. This may be the result of the accumulation of monomer impurities and/or partial overlap of AB and ABA triblock polymers at lower molar mass.

5.6. Thermal Analysis of Block Polyester from Propylene Oxide/Phthalic Anhydride/Lactide

The thermal stability of PLA-*b*-PPE-*b*-PLA with a number-average molar mass of $16,600 \text{ g mol}^{-1}$ ($\bar{D}=1.24$) was determined by TGA as $T_{d\ 5\%} = 251 \text{ }^{\circ}\text{C}$ after precipitation in methanol. The value defines the maximum temperature at which the polyester can be heated with 5% weight loss and is the upper processing limit. Further analysis, by DSC, on a polymer with $\overline{DP}=100$ and 41wt% PLA showed one T_g value at $50 \text{ }^{\circ}\text{C}$ (Figure 5. 14). This was in line with the predicated value for a miscible polymer based on the Fox equation, of $52 \text{ }^{\circ}\text{C}$. The calculated value was determined using the value for the polymers PLA, $43 \text{ }^{\circ}\text{C}$, and PPE, $60 \text{ }^{\circ}\text{C}$ (Table 5. 7). The block miscibility was further confirmed by analysis of a blend of homopolymers which also showed only a single T_g value ($46 \text{ }^{\circ}\text{C}$).

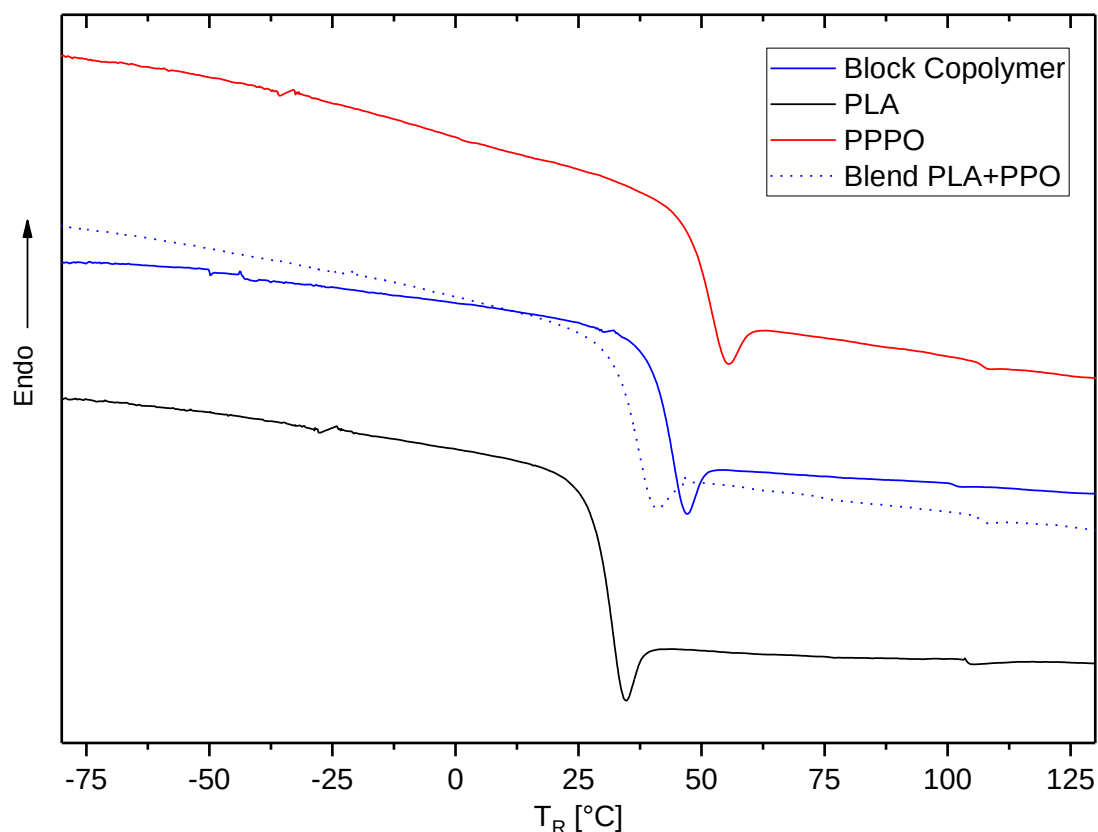


Figure 5. 14 – DSC Thermograms of PLA, PPE, PLA-*b*-PPE-*b*-PLA and 1:1 (wt%) blend of PLA and PPE.

Table 5. 7 – Polyesters used for thermal analysis.^[a]

Polymer	Conversion [%] ^[b]		M_n (Đ) [g mol ⁻¹] ^[c]	DP	T_g [°C] ^[d]
	PA	LA			
PPE	> 95	N. A.	18,000 (1.50)	100	60
PLA	N. A.	> 95	8,000 (1.70)	100	43
PLA- <i>b</i> -PPE- <i>b</i> -PLA	99	> 95	16,600 (1.24)	100, 100	50

^[a] Conditions: [Salphen^FAlCl]:[PPNCl]:[CHD]:[Monomer]=1:0.8:20:2000 in 2 mL of PO, 7 days. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, THF, 30 °C, using polystyrene standards. ^[d] Determined by DSC, 3rd heating cycle.

5.7. Substrate Scope

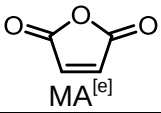
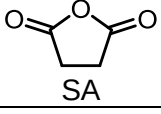
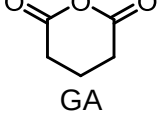
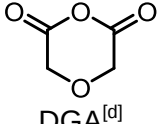
To test the versatility of this 'switch' catalysis, a range of anhydrides, epoxides and CTAs were investigated.

5.7.1. Anhydrides

Mono-, bi- and tricyclic anhydrides were tested at the limit of [monomer]:[catalyst] loading, i. e. 2,000:1, in the presence of 20 equiv. of CHD. Two five-membered anhydrides were tested, maleic anhydride (MA) and succinic anhydride (SA, Table 5. 8). For MA, monomodal mass distributions were obtained for lower [monomer]:[catalyst] loadings and if the reaction was stopped at lower conversions. For higher loadings and/or longer reaction times, partial cross-linking was observed, similar to 'switch' catalysis with [SalcyCrCl]. For SA, high conversions (>80%) and high molar masses >10,000 g mol⁻¹ were observed, alongside a bimodal mass distribution. High conversions of anhydride and lactide (99%) were found for six-membered anhydrides, glutaric anhydride (GA) and diglycolic anhydride (DGA). In both cases, low molar masses (2,000 and 6,000 g mol⁻¹) were detected. This is tentatively ascribed to competitive cyclisation reactions, caused by long reaction times necessary to complete the reaction (up to 19 days). Two T_g values were found for the polymer from PO/DGA/LA at 11 and 37 °C. The values are higher than expected for the polyester from ROCOP (-2 °C) and lower compared to atactic PLA (45-50 °C), which may be attributed to either low molar masses or partial block miscibility.^[6, 7] Interestingly, analysis by ¹H NMR spectroscopy throughout the reaction revealed the simultaneous incorporation of GA and LA (49% GA and 75% LA after seven days), which suggests the formation of random copolymers instead of block copolymers (not shown).

Table 5. 8 – PO/anhydride/LA 'switch' catalysis with different monocyclic anhydrides.



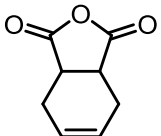
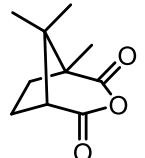
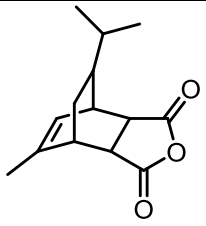
Anhydride	Reaction Time [d]	Conversion [%] ^[b]		<i>M_n</i> (<i>Đ</i>) [g mol ⁻¹] ^[c]	<i>T_g</i> [°C] ^[d]
		Anhydride	Lactide		
 MA ^[e]	1	99	22	2,200 (1.26)	N. D.
 SA	15	99	83	11,400 (1.60) 27,100 (1.25)	N. D.
 GA	19	99	99	2,100 (1.32)	N. D.
 DGA ^[d]	7	99	99	6,000 (1.46)	11 37

^[a] Conditions: [Salphen^FAlCl]:[PPNCI]:[CHD]:[PO]:[PA]:[LA]=1:0.8:20:2000:2000 in 2 mL of PO at 60 °C. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, THF, 30 °C, using polystyrene standards. ^[d] Determined by DSC (3rd heating cycle). ^[d] Conditions: [Salphen^FAlCl]:[PPNCI]:[CHD]:[PO]:[PA]:[LA]=1:0.8:10:100:100 in 1.5 mL of PO at 60 °C.

In respect to bicyclic anhydrides, tetrahydrophthalic anhydride (THPA) and camphoric anhydride (CA) were tested (Table 5. 9). In both cases, high conversions (>90%) were obtained and for CA, a low molar mass and a broad distribution was found (*M_n*=6,000 g mol⁻¹; *Đ*=1.54). Further monitoring of the reaction revealed the reverse order of reactivity: LA was consumed within three days (99% LA, 14% CA) and only during the next eleven days, CA was fully consumed. This was in agreement with previous observations with [SalcyCrCl], where CA did not follow the trends established for a range of anhydrides. Higher masses and a bimodal distribution were detected for THPA. Both materials showed two *T_g* values, at 35-37 °C and at 48 (CA) or 87 °C (THPA). Finally, TCA1 was tested as a tricyclic substrate and high conversions (99%), a high number-average molar mass (*M_n* = 14,200 g mol⁻¹) and a monomodal mass distributions with narrow dispersity (*Đ*=1.22) were obtained. Two *T_g* values were found by DSC, at 45 and 68 °C (Figure 5. 15). This was lower than expected from the polyester from TCA1/PO at 91 °C (*M_n*=17,200 g mol⁻¹, *Đ* = 1.12, >99% *cis* ester linkages) and was ascribed to low molar masses and/or a varying degree of epimerisation.^[8]

Table 5. 9 - PO/anhydride/LA 'switch' catalysis with different bi- and tricyclic anhydrides.



Anhydride	Reaction Time [d]	Conversion [%] ^[b]		M_n (Đ) [g mol ⁻¹] ^[c]	T_g [°C] ^[d]
		Anhydride	Lactide		
 THPA	5	99	92	11,000 (1.30) 4,300 (1.06)	39 85
 CA	14	99	99	6,000 (1.54)	35 48
 TCA1	7	99	99	14,200 (1.22)	45 68

^[a] Conditions: [Salphen^FAlCl]:[PPNCI]:[CHD]:[PO]:[PA]:[LA]=1:0.8:20:2000:2000 in 2 mL of PO at 60 °C. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, THF, 30 °C, using polystyrene standards. ^[d] Determined by DSC (2nd or 3rd heating cycle; see appendix).
^[d] [Salphen^FAlCl]:[PPNCI]:[CHD]:[PO]:[PA]:[LA]=1:0.8:10:100:100, 1.5 mL of PO, 60 °C.

In summary, two T_g values were observed for all materials. The first T_g value between 35 and 45 °C is ascribed to the atactic PLA block and the second to the polymer formed after ROCOP, which was dependent on the anhydride. For DGA, a 'softer' (more flexible) segment was formed (11 °C) and for CA, THPA and TCA1, a 'harder' (more rigid) block resulted in higher T_g values (48-87 °C). It should be noted that one of the transitions is typically only visible upon magnification and an example for a typical thermogram is shown in Figure 5. 15. Although more experiments are necessary to unambiguously ascribe these transitions to the different blocks, these are encouraging results as phase-separation is indicated by DSC.

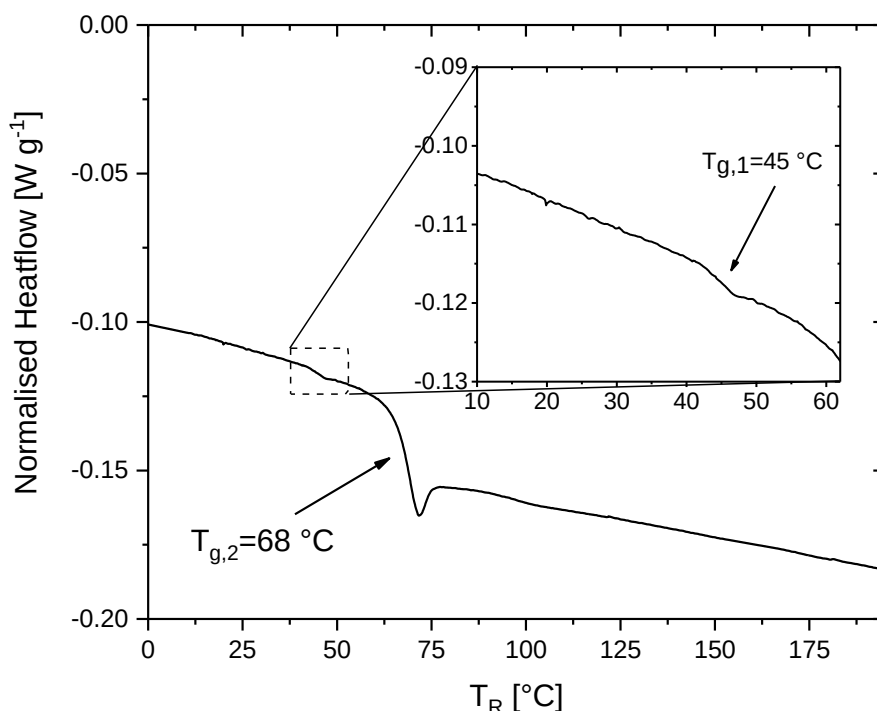
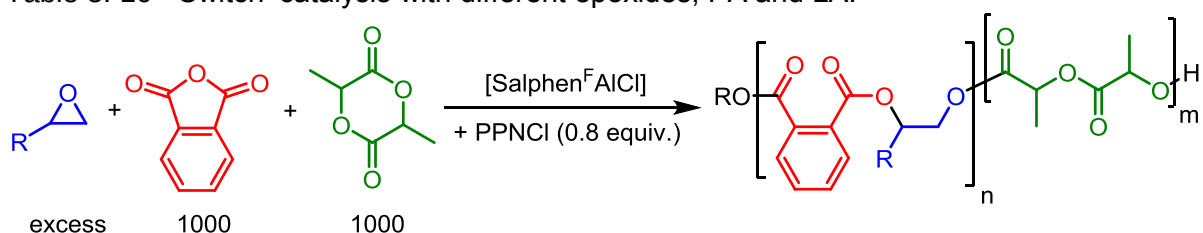


Figure 5. 15 – DSC Thermogram of polymer obtained from PO/TAC1/LA (2nd heating cycle).

5.7.2. Epoxides

Six different epoxides were tested for 'switch' catalysis with PA/LA at a [monomer]:[catalyst] loading of 1000:1 (Table 5. 10). With vinyl-propylene oxide (VPO), phenyl glycidyl ether (PGE) and 2-(2,5,8,11)-tetraoxadodecyloxirane (PEG₃-OMe-PO), high conversions of anhydride and lactide were observed (80-99%); in two cases, with *tert*-butyl glycidyl ether (BGE) and 2-ethyl hexylglycidyl ether (EHGE), no reactivity was observed. The latter might be ascribed to the high steric hindrance of the epoxide, which prevents ring-opening. For styrene oxide (SO), ROCOP was comparatively slower and LA was not consumed within 16 days. Although high molecular weights were obtained with SO, VPO and PGE, bimodal mass distributions were observed. Two explanations are possible to rationalise this observation: first, the accumulation of monofunctional trace impurities and second, a higher regioselectivity for ROCOP due to the increased steric bulk on the methine (α) group of the epoxide. This may result in a primary alkoxide as the propagating species and chain-transfer with a secondary alcohol (CHD) is slower than the propagation ($k_i/k_p < 5$). Consequently, a mixture of AB and ABA polymers is obtained. For PEG₃-OMe-PO, a surprisingly low molar mass vs. polystyrene was found ($M_n=3,200 \text{ g mol}^{-1}$; $\bar{D}=1.40$). The observed mass is likely to be inaccurate as different hydrodynamic radii are expected for partially water-soluble monomers (water-solubility is introduced through the PEG side-chain).

Thermal analysis by DSC revealed two T_g values with PGE (46 and 72 °C) and PEG₃-OMe-PO (-66 and 91°C). The polymer based on PGE follows the trend found for the variation in anhydride and the transition at 46 °C is assigned to the PLA block and the higher transition to the ROCOP polyester block. This is in contrast to PEG₃-OMe-PO, where a significantly lower value at -66 °C and higher value at 91 °C were detected. Further characterisation is necessary to fully characterise the polymeric product and rationalise the observed transitions. Nonetheless, these results demonstrate that different epoxides can be used in 'switch' catalysis.

Table 5. 10 - 'Switch' catalysis with different epoxides, PA and LA.^[a]

Anhydride	Reaction Time [d]	Conversion [%] ^[b]		M_n (Đ) [g mol ⁻¹] ^[c]	T_g [°C] ^[d]
		Anhydride	Lactide		
VPO	16	99	95	10,400 (1.20) 3,000 (1.18)	15
BGE	5	< 5	< 5	N. D.	N. D.
EHGE	5	< 5	< 5	N. D.	N. D.
SO	16	95	0	4,700 (1.05) 1,300 (1.25)	N. D.
PGE	16	99	82	22,000 (1.04) 8,400 (1.14)	46 72
PEG ₃ -OMe-PO	10	99	95	3,200 (1.40)	-66 91

^[a] Conditions: [Salphen^FAlCl]:[PPnCl]:[CHD]:[PO]:[PA]:[LA]=1:0.8:20:1000:1000 in 1.5 mL of Epoxide at 60 °C. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, THF, 30 °C, using polystyrene standards. ^[d] Determined by DSC (3rd heating cycle).

The effect of increasing the reaction temperature to 100 °C was tested with PGE due to its high boiling point (245 °C).^[9] Full conversion (99%) of PA and LA were observed after only six days, as opposed to 16 days at 60 °C, and monomodal mass distributions were obtained ($M_n=9,800 \text{ g mol}^{-1}$; $\bar{D}=1.16$). This illustrates the potential of the reaction to remain selective and produce block copolyesters even at higher reaction temperatures.

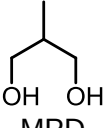
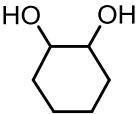
5.7.3. Chain-Transfer Agents

Different chain-transfer agents may allow access to a variety of polymer architectures. For monofunctional alcohols, AB diblock polymers are formed and for bifunctional alcohols, ABA triblock copolymers. One key criterion for the success of this approach is that the rate of chain-transfer (or initiation, k_i) should be significantly faster than the rate of chain propagation (k_p), $k_i/k_p > 5$. This was tested with two secondary and two primary alcohols for 'switch' catalysis using PO/PA/LA (Table 5. 11). In all cases, monomodal molar mass distributions were realised and for primary alcohols (benzyl alcohol and 2-methylpropane-1,3-diol), lower dispersities were obtained. The narrower dispersities might be a consequence of higher rates of initiation, differences in molar mass were unexpected and may be caused by small errors in stoichiometry on this small scale (3 – 5 μL of CTA were used).

In conclusion, different primary and secondary alcohols can be used in 'switch' catalysis but primary alcohols typically result in narrower dispersities and are therefore recommended.

Table 5. 11 – 'Switch' catalysis of PO/PA/LA with different CTAs.

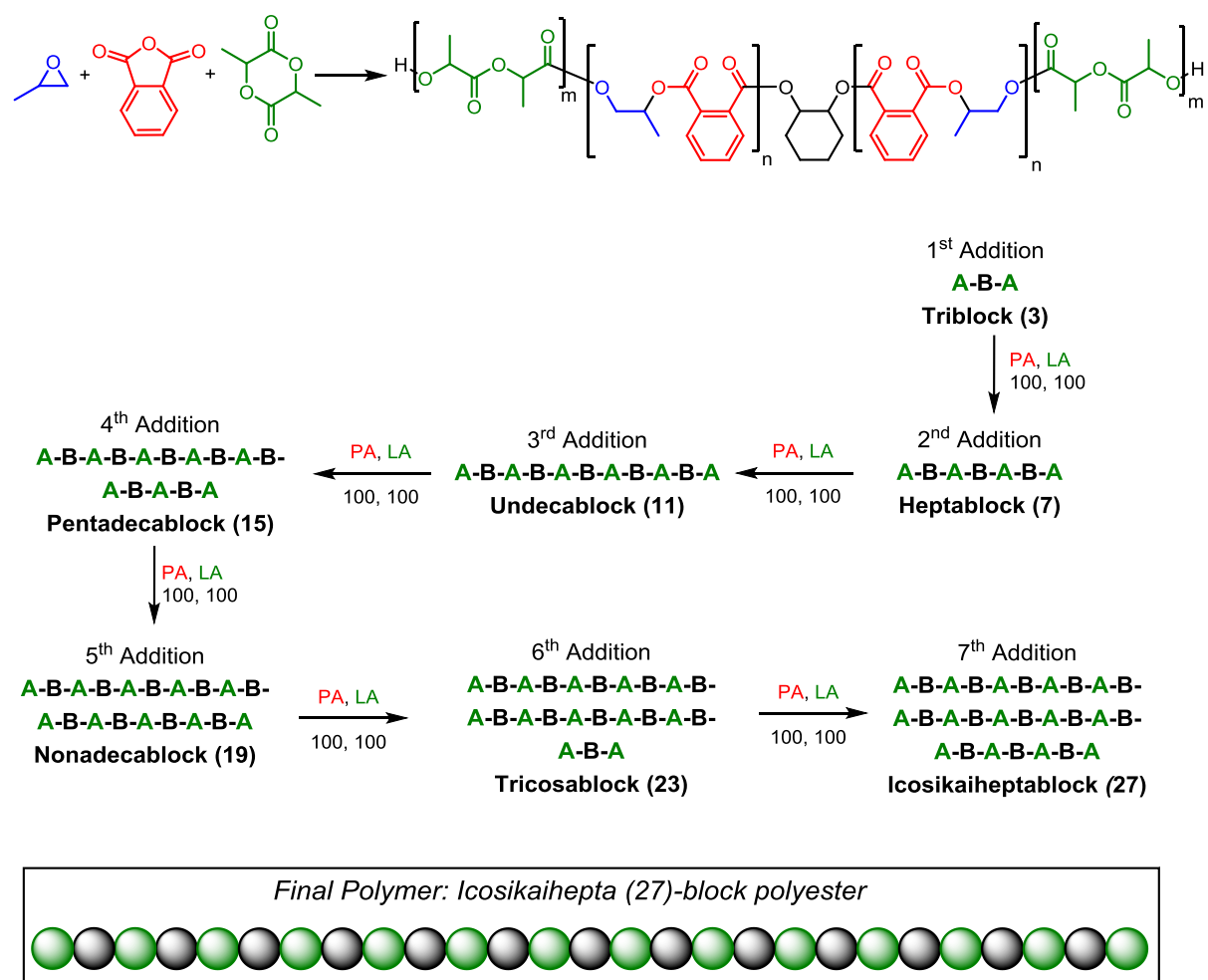
CTA	Reaction Time [d]	Conversion [%] ^[b]		$M_n (\bar{D}) [\text{g mol}^{-1}]^{[c]}$
		Anhydride	Lactide	
 BzOH	7	99	88	4,100 (1.13)
 iPrOH	7	95	93	4,400 (1.09)

 MPD	7	99	75	7,500 (1.19)
 CHD	7	99	93	8,700 (1.22)

^[a] Conditions: [Salphen^FAlCl]:[PPNCl]:[CHD]:[PO]:[PA]:[LA]:[PO]=1:0.8:20:500:500:2,000 in neat PO at 60 °C. ^[b] Determined by ¹H NMR spectroscopy. ^[c] Determined by GPC, THF, 30 °C, UV detector using polystyrene standards.

5.8. Multiple 'Switching'

In 'switch' catalysis with CHD, ABA triblock polyesters are produced from a mixture of epoxides, anhydrides and lactones. In principle, this catalysis does not have a termination step and further reactions should add more blocks to the polymer (i. e. living polymerisation). This hypothesis was tested with several additions of mixtures of PO/PA/LA; each mixture was only added once high monomer conversions were observed (99% PA, ~ 95% LA). In total, this mixture was added seven times yielding an icosikaiheptablock polyester containing 27 blocks (Scheme 5. 2). In 2016, an octablock copolyester was prepared through seven monomer additions of D- and L-LA, which is the highest number of blocks reported to date.^[10] This makes the 27 blocks prepared through this 'multi-switch' approach the leading polyester with respect to number of discrete blocks.



Scheme 5. 2 – Synthesis of multiblock copolymers via multiple monomer additions.

The intervals of the reaction were monitored by ¹H NMR spectroscopy (Figure 5. 16) and GPC (Figure 5. 17). ¹H NMR spectra clearly indicate full conversion of PA and high

conversion for LA after each step, as observed by the absence of monomer resonances ($\delta = 7.9 - 8.1$ [PA] and 5.05 ppm [LA]). At the same time, the polymer signals increased after each monomer addition, relative to mesitylene as an internal standard ($\delta = 7.3 - 7.6$ [PPE] and 5.15 ppm [PLA]). It should be noted that no polyether linkages were observed at any point during the reaction (absence of resonances between 3.4 and 3.6 ppm), suggesting a perfectly alternating polyester.

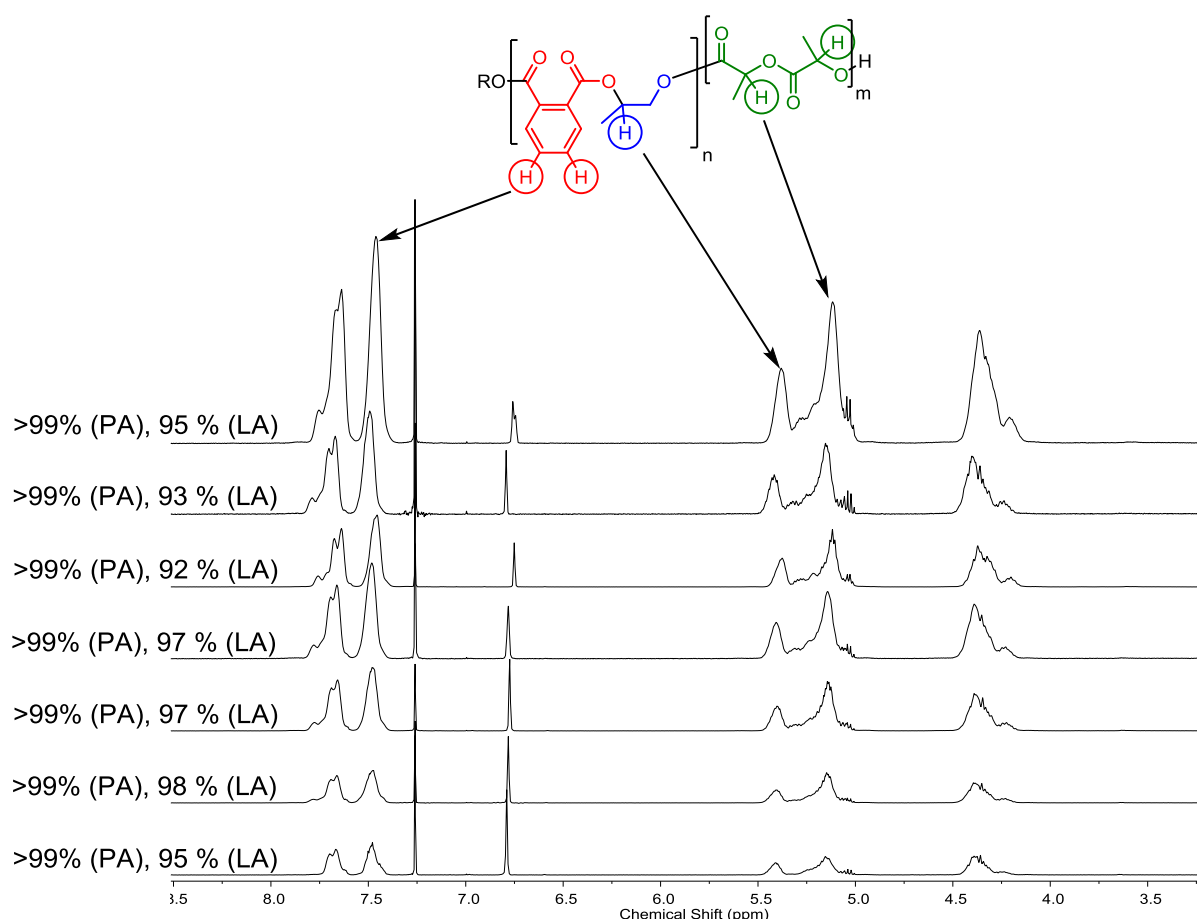


Figure 5. 16 – ^1H NMR spectra of crude reaction mixture after each monomer addition; typical reaction times: 6 hours – 2 days. Conversions are based on mesitylene (6.80 ppm) as internal standard.

Monitoring the reaction by GPC showed a continuous increase in molecular mass, after each step until a final M_n value of $23,500 \text{ g mol}^{-1}$ ($D = 1.21$). At each step, a monomodal GPC trace was observed by both RI (solid traces in Figure 5. 18) and UV detectors (dotted traces). Both traces aligned, which further confirmed the formation of a block polymer.

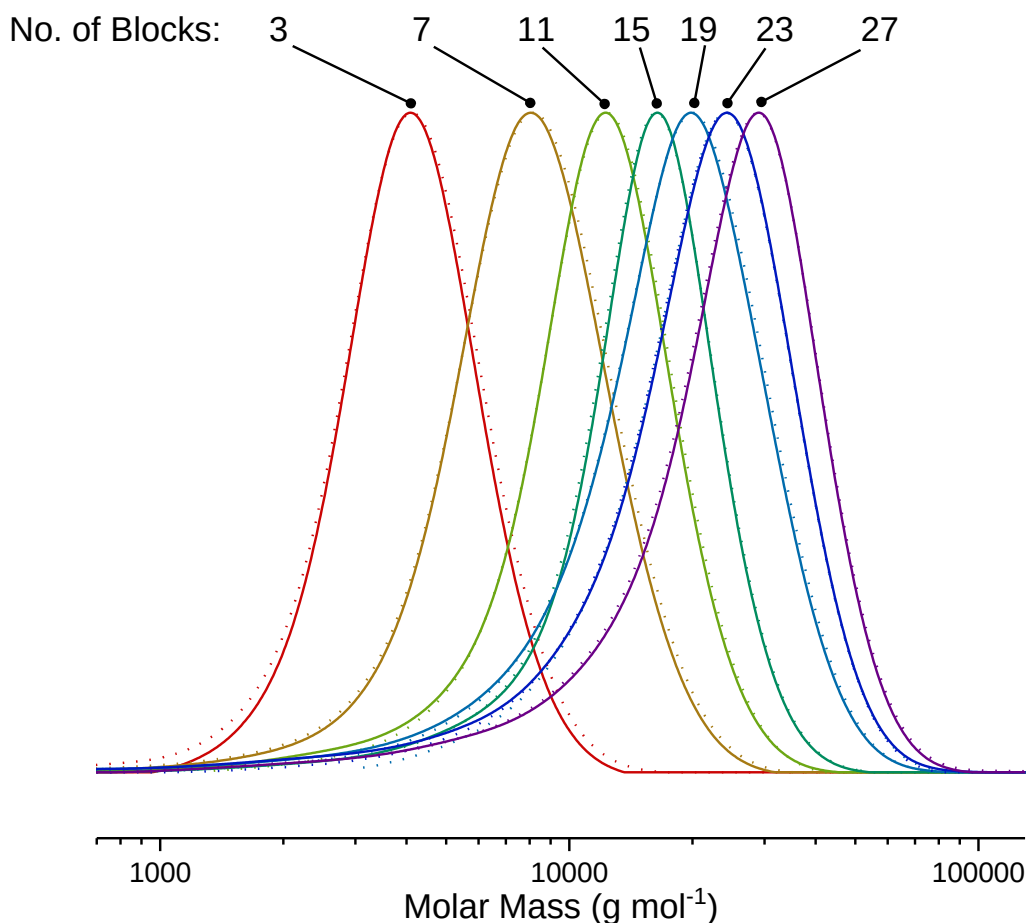


Figure 5. 17 – RI (solid) and UV (dotted) traces after each monomer addition.

Further analysis revealed a linear increase in weight after each step and the measured molar masses are similar to theoretical values (Figure 5. 18). More importantly, dispersities remained similar and narrow throughout the entire reaction ($1.18 < \bar{D} < 1.23$).

As an aside, this multiblock polymer showed one T_g value at 53 °C (Figure 5. 19). This was in agreement with the value obtained for PLA-*b*-PPE-*b*-PLA (50 °C, Figure 5. 14).

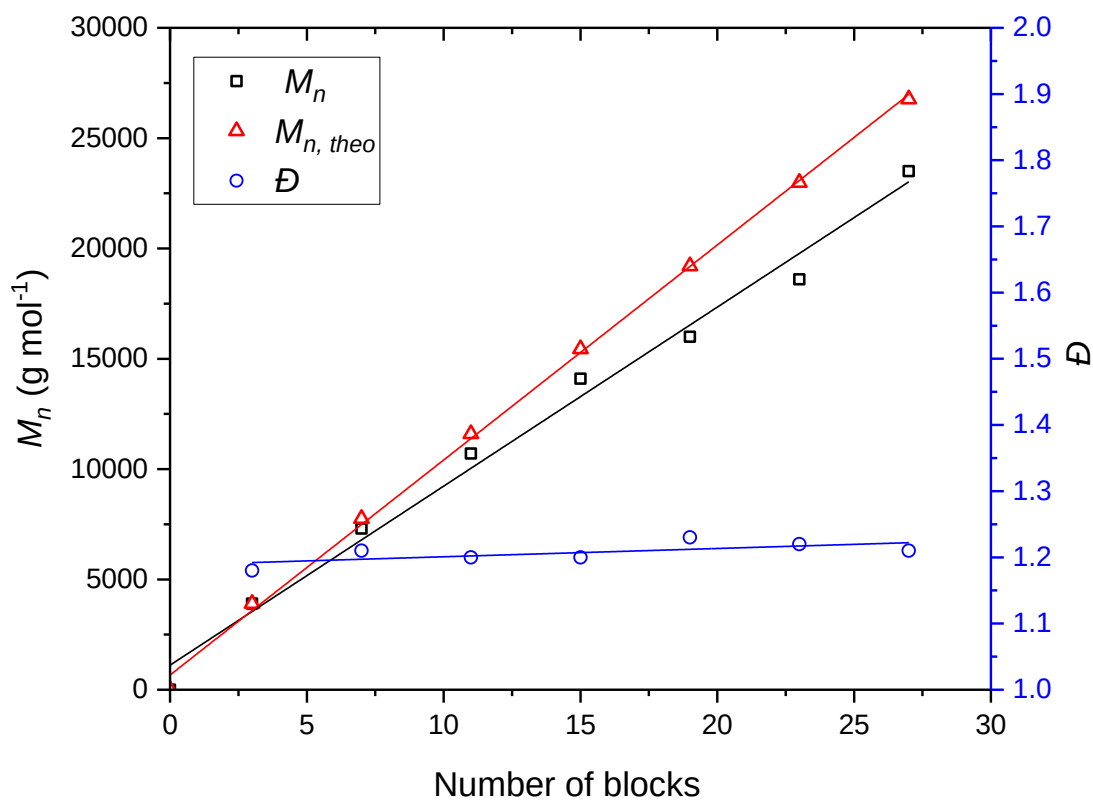


Figure 5. 18 – Evolution of M_n , $M_{n,theo}$ and $\bar{D}$ after each monomer addition.

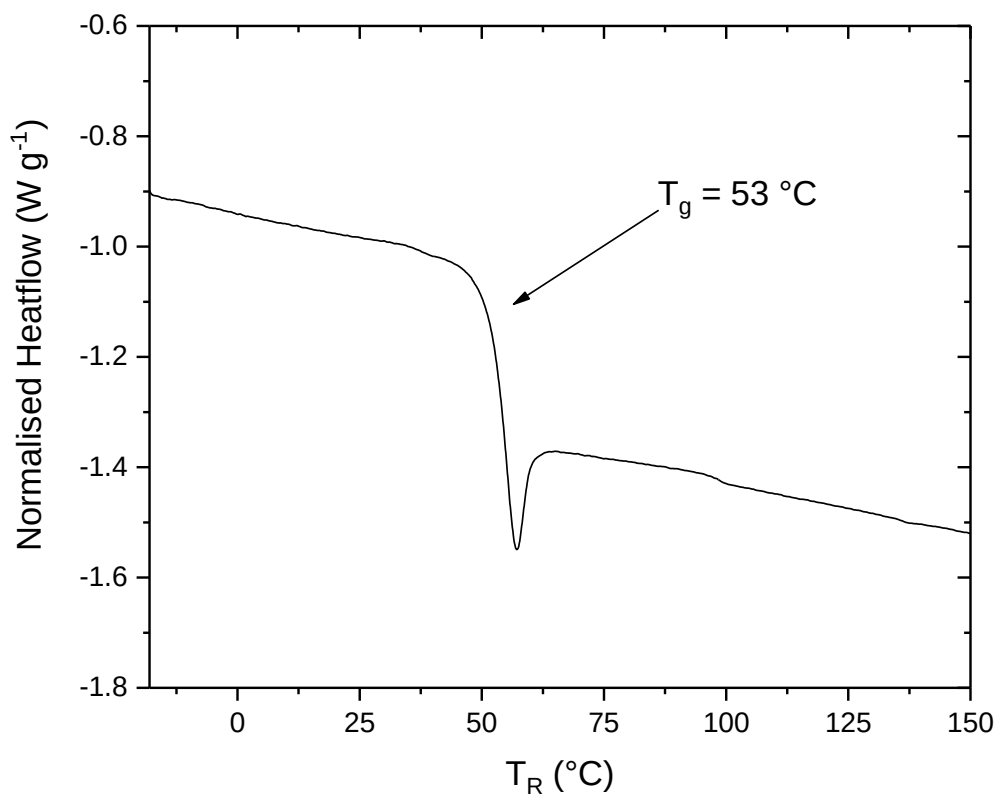
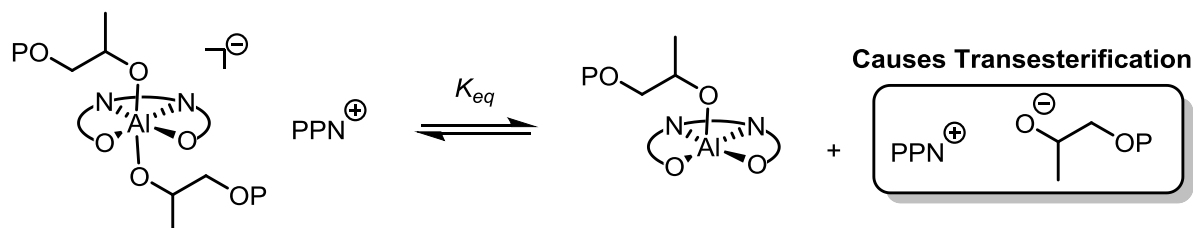


Figure 5. 19 – DSC thermogram of multiblock polymer (3rd heating cycle). The transition at ca. 95°C might be attributed to catalyst impurities (which remained after isolation from methanol).

5.9. Discussion

5.9.1. Catalyst Optimisation

The initial screening of catalysts revealed that 'switch' catalysis was only successful with [Salphen^FAlCl]; significant transesterification was observed with [SalcyAlCl] or [L_{Van}AlOⁱPr]. This transesterification is proposed to be caused by an ionic alkoxide species (stabilised by the co-catalyst), which is in equilibrium with the catalyst and co-catalyst (Scheme 5. 3).



Scheme 5. 3 – Proposed catalyst-co-catalyst equilibrium.

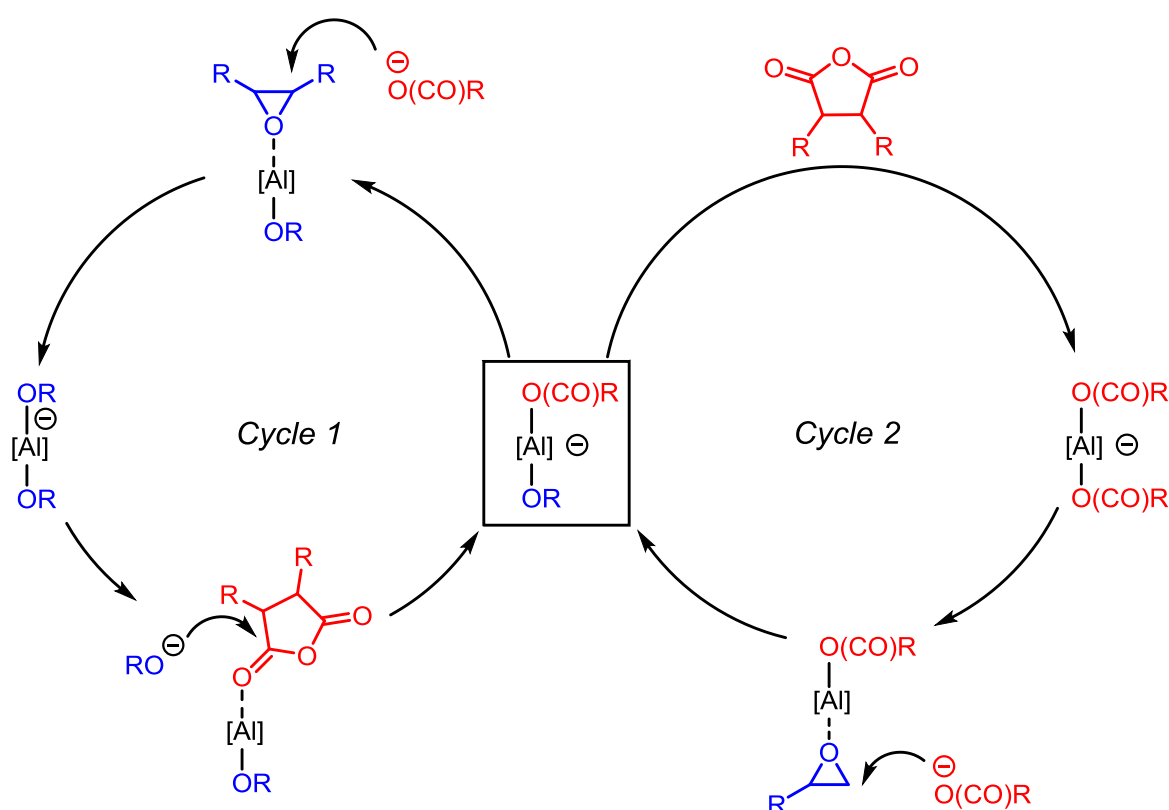
Although the use of a co-catalyst is generally undesirable, PPNCl is required to generate a catalyst active for ROCOP, a finding that holds true for all tested aluminium catalysts. It is hypothesized that the success of [Salphen^FAlCl] is connected to its electron-withdrawing fluorine substituents. As a consequence, the Lewis-acidity of the overall complex is enhanced. Thus, the above equilibrium is shifted towards the anionic aluminate species, which reduces the amount of 'free' PPN-stabilised alkoxide.

This may not be the only factor since a range of electron-withdrawing substituents were tested with related cobalt(III) complexes for ROCOP (with PO and in the presence of PPNCl) and higher rates were found for fluoro-substituted over nitro-substituted complexes, despite nitro-substituted being more electron-withdrawing.^[11] The latter substituent should favour the formation of the metalate species, increase rates and reduce side-reactions. However, these investigations were complicated by the side-reduction of cobalt(III) to cobalt(II), with the latter being inactive for ROCOP. Unfortunately, more electron-withdrawing substituents stabilise cobalt(II) which limits the range of substituents tested.

For aluminium complexes, reduction is not likely and further investigations of electron-withdrawing groups might improve understanding of this proposed catalyst-co-catalyst equilibrium.

5.9.2. Mechanism

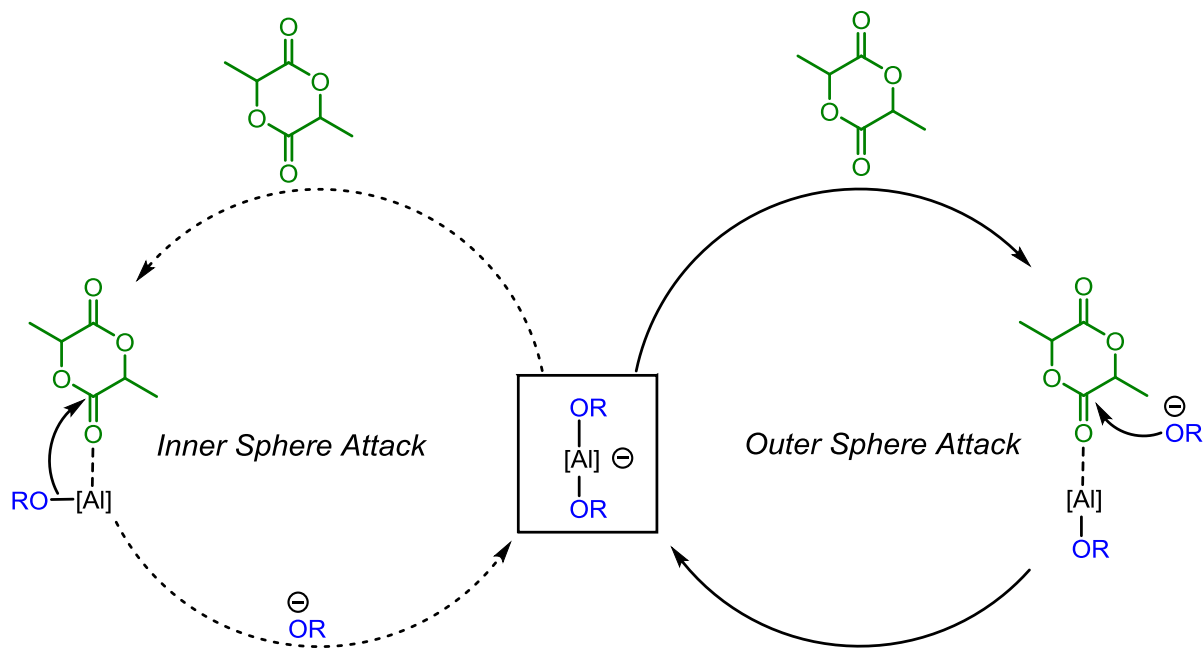
Tolman and Coates recently proposed two different mechanistic pathways for anhydride/epoxide ROCOP with [SalphenAIX] catalysts (Scheme 5. 4).^[5] Cycle 1 proceeds through a bis-alkoxide species, whereas a bis-carboxylate species is formed in cycle 2. In both pathways, the aluminium complex serves two roles: (i) epoxide and/or anhydride activation and (ii) stabilisation of the resulting ring-opened species. Interestingly, the nucleophilic species involved in ring-opening is not bound to the catalyst but an outer-sphere mechanism is proposed with the attacking species being stabilised by the co-catalyst. This emphasises the co-existence of multiple species during the catalysis and the importance of the co-catalyst.



Scheme 5. 4 – Proposed mechanism for anhydride/epoxide ROCOP.^[5]

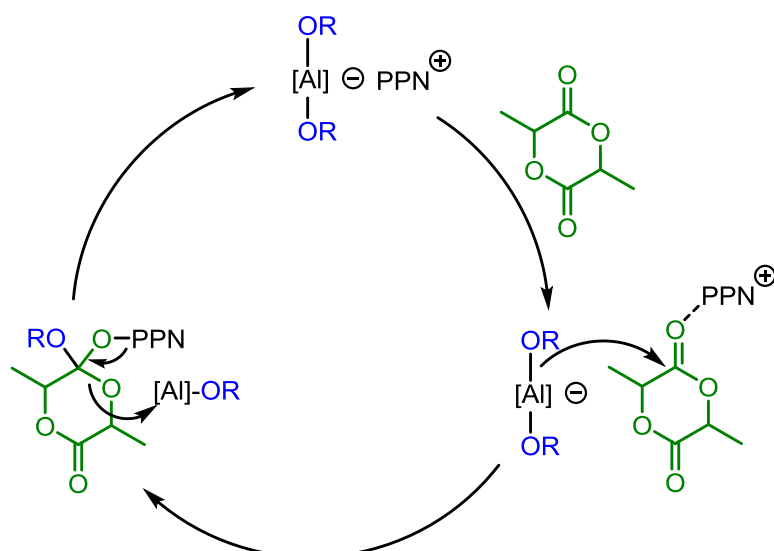
With respect to LA ROP, two mechanistic pathways are proposed (Scheme 5. 5). Starting from a bis-alkoxide intermediate, which is formed from ROCOP and indicated by the red colour, lactide is first coordinated, thereby displacing an alkoxide co-ligand. The ring-opening of lactide can now occur in two ways, either *via* an inner sphere attack, in which the alkoxide coordinated to the catalyst attacks LA (Scheme 5. 5 left), or *via* an outer sphere attack, in which the initially dissociated alkoxide attacks LA (Scheme 5. 5, right). The observed *trans*-coordination observed in the solid state of [Salphen^FAlCl] makes an inner sphere attack less

likely as spatial proximity between coordinated alkoxide and LA is not possible if the coordination geometry is maintained. Changes in the conformation of the ligand seem less likely due to its rigid aromatic backbone. Consequently, the outer sphere attack may be the preferential pathway (Scheme 5. 5, right).



Scheme 5. 5 – Proposed pathways for LA ROP.

Finally, it is worth mentioning that, in this field, mechanistic hypothesis rarely consider the catalyst/co-catalyst ion pair. For example, a possible mechanistic hypothesis for LA ROP is shown in Scheme 5. 6: Lactide is activated towards nucleophilic ring-opening by the coordination of the PPN cation. Next, one of the alkoxide co-ligands, of the aluminium complex, attacks LA and a tetrahedral intermediate is formed. The latter rearranges and the initial catalyst-co-catalyst ion pair is regenerated. It should be emphasised that is a purely theoretical consideration to illustrate the possibility for such alternative pathways.



Scheme 5. 6 – Possible pathway for LA ROP by a catalyst-co-catalyst ion pair.

5.9.3. Block Polymer Phase Separation

Block polyester phase separation may be desirable for some applications, such as thermoplastic elastomers, self-assembly and microelectronics. The propensity of phase-separation depends on a range of parameters, including the Florey-Huggins interaction parameter, χ , and the degree of polymerisation, $\overline{DP}$.^[12] Here, high M_n values $> 10,000 \text{ g mol}^{-1}$ ($\overline{DP} \sim 100$) were achieved under optimised conditions but thermal analysis indicated block miscibility. To increase χ , enantiopure L-LA was used in 'switch' catalysis, with PA and PO, to target crystalline PLLA blocks (Scheme 5. 7).

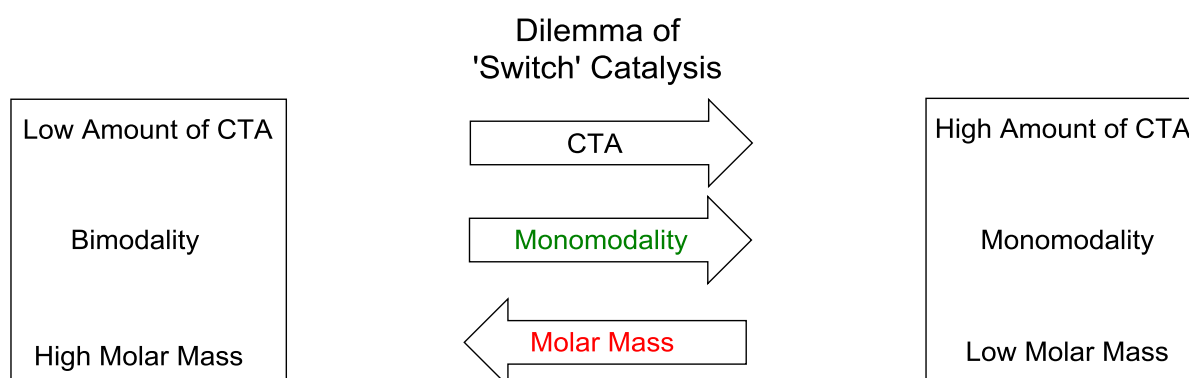


Scheme 5. 7 - 'Switch' Catalysis with PO/PA/L-LA. Conditions: neat, 60 °C, 7 days.

High conversions ($>99\%$ PA, 94% L-LA) were obtained, after seven days, and a triblock polyester with a monomodal GPC trace was obtained ($M_n = 14,900 \text{ g mol}^{-1}$, $\mathcal{D} = 1.10$). Both traces from RI and UV detector were identical. Importantly, one T_g value at $52 \text{ }^\circ\text{C}$ was obtained and no crystalline regions were detected up to $200 \text{ }^\circ\text{C}$. This was similar to a polyester from (*rac*)-LA synthesised under identical conditions ($M_n = 19,600 \text{ g mol}^{-1}$, $\mathcal{D} = 1.30$, $T_g = 51 \text{ }^\circ\text{C}$). This suggests that phase-separation cannot be induced by using LLA, despite its potential crystallinity. However, phase-separation is highly dependent on the monomer selection and was observed in other cases, for example with TCA1/PO/LA.

5.9.4. Block Polymer Molar Masses

One limitation for 'switch' catalysis with [Salphen^FAlCl] is accessing polymers with high molar masses. Although masses above 10,000 g mol⁻¹ were achieved, through careful optimisation, the requirement for excess CTA inevitably lowers molar masses. Consequently, the trade-off for these studies is to use sufficient CTA to obtain monomodal mass distributions but, at the same time, as little CTA as possible to achieve appreciable molar masses. This is the central 'dilemma' in the current 'switch' catalysis, if CTA is used, and is shown in Scheme 5. 8.



Scheme 5. 8 – The dilemma in 'switch' catalysis, if CTA is used.

This dilemma is caused by the mixture of initiating species present including chloride-groups from the catalyst and difunctional impurities, which are generated from the reaction of water with epoxides (diols) or anhydrides (dicarboxylic acids).^[13-15] Consequently, this may be improved by the choice of catalyst (and co-catalyst) and/or purity of monomers.

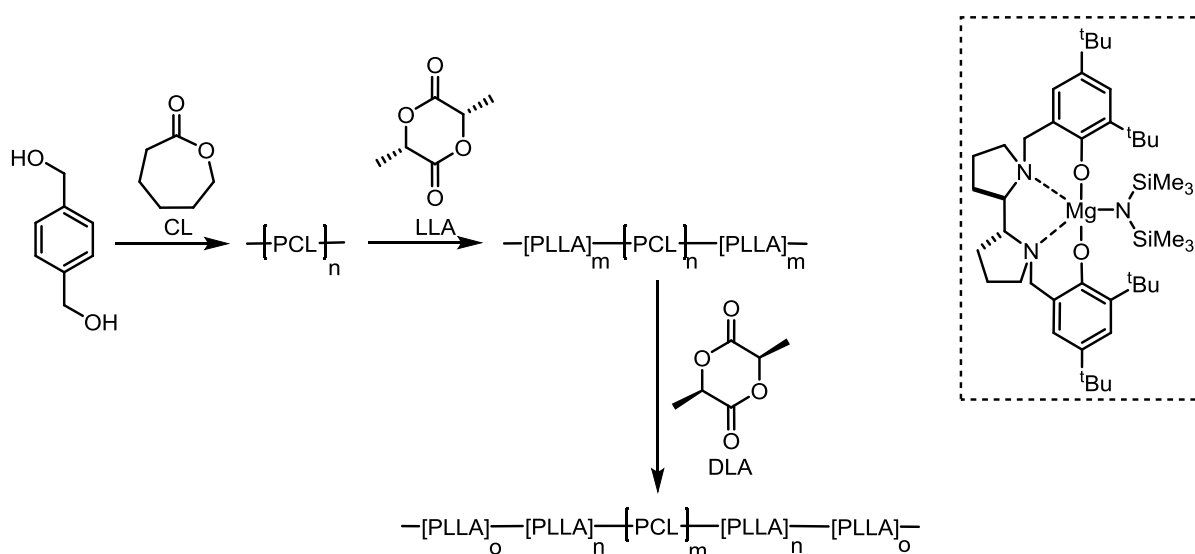
Interestingly, this challenge has mainly been discussed in ROCOP, not in ROP. Despite differences in catalysts, this might imply higher monomer purity or a more optimised purification procedure for lactones. This hypothesis was tested using a higher LA content, compared to PA, and a higher molar mass with a more narrow dispersity was detected ($M_n = 15,700$ g mol⁻¹, $\mathcal{D} = 1.06$ for [Salphen^FAlCl]:[PPNCl]:[CHD]:[PA]:[LA]=1:0.8:10:500:1000 in neat epoxide; only UV detector given). This emphasises the importance of the monomer purity and the need for standardised quantification techniques.

It should be noted that all values were given relative to polystyrene standards and have not been corrected. For this reason, the measured values may be significantly lower than the actual molar masses. For example, PLA shows a Mark Houwink correction factor of 0.58, which results in an decrease of nearly a factor of two for the corrected molar mass.^[16] However, 'such' correction factors are only applicable to homopolymers and cannot be used for block copolymers.

5.9.5. Multiblock Copolymers

The quest for very well controlled multiblock copolymers is inspired the desire to mimic biopolymers, which, from a synthetic perspective, are multiblock copolymers with base pairs or amino acids as blocks. For example, in the human genome the number of blocks reaches several billion.^[17] In that sense, the controlled synthesis of higher multiblock copolymers is a 'holy grail' for polymer synthesis.

With respect to discrete multiblock copolyesters, sequential monomer addition is most commonly used. A wide range of ABA triblock polyester have been reported and this procedure can be repeated multiple times.^[18, 19] The current state of the art is an octablock polyester based on L-LA and D-LA (2016) and heptablock polyesters with PLC and PLLA blocks (2018). Although impressive rates were obtained in these cases (TOF ~ 1,000 h⁻¹), the number of ten blocks has not been exceeded for polyesters.^[20]



Scheme 5. 9 – Multiblock polyester synthesis *via* sequential monomer addition.^[20]

Although the number of blocks is record-breaking for block copolyesters, 'switch' catalysis is a chain-growth polymerisations and inherent statistical limitations need to be considered.^[21] This has a particularly strong effect on polymerisations containing a low DP and some blocks might not incorporate monomer before 'switching' occurs, which results in an inaccurate number of blocks. Herein, a multiblock copolyester with 27 blocks ($N=27$) with an average degree of polymerisation ($\overline{DP}$) of 5 has been prepared. Following the statistical

considerations derived by Thomas and co-workers, the probability that all chains contain all N blocks is given by

$$p = (1 - e^{-\overline{DP}})^N \quad [21]$$

This relation is illustrated in Figure 5.20 and in the present example this results in a probability of 83% that all chains contain 27 blocks. It is therefore recommended to target a $\overline{DP}$ of 10 or more for the synthesis of multiblock polymers to ensure a probability of >99% that all blocks contain the proposed number of blocks.

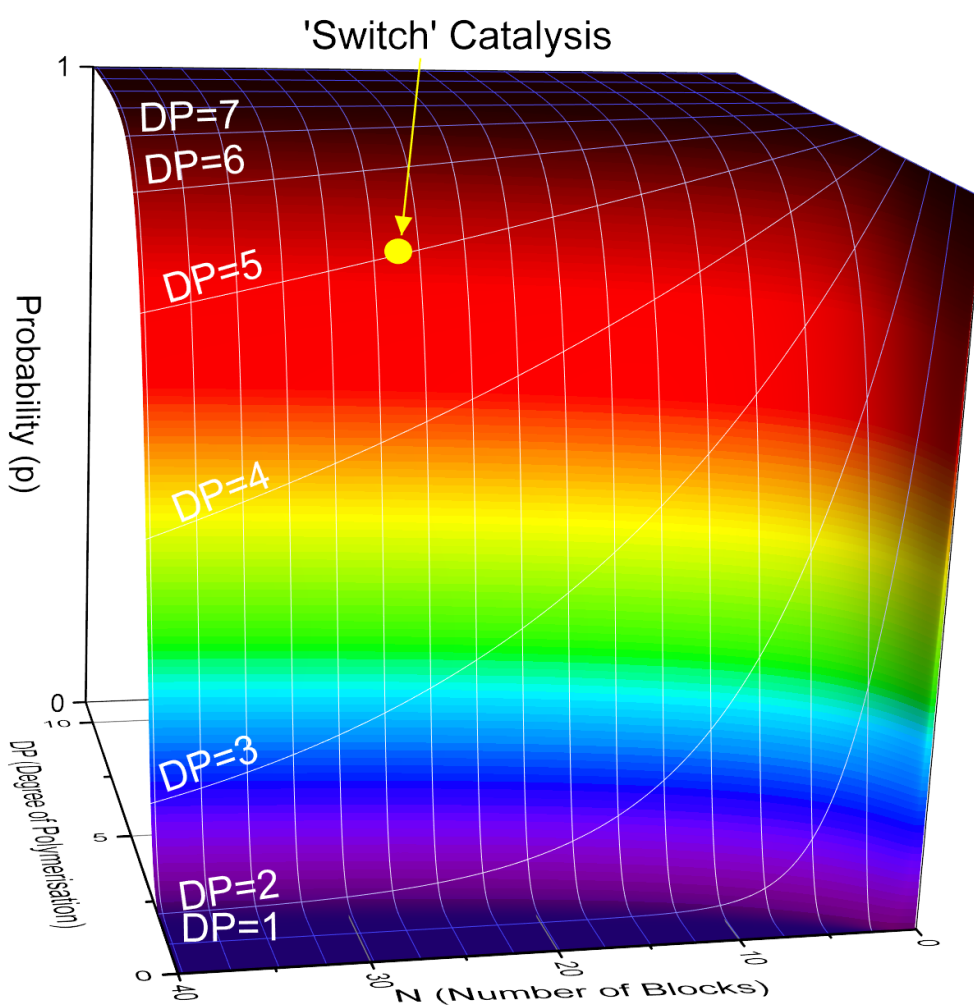


Figure 5.20 - Probability p that all chains contain all N blocks for a given number of blocks (N) and degree of polymerisation ($\overline{DP}$).^[21]

5.10. Summary and Outlook

In this chapter, 'switch' catalysis was investigated with propylene oxide, phthalic anhydride and (*rac*)-lactide. This process was previously challenging to achieve due to a range of side-reactions, including transesterification (block scrambling), polyether formation and backbiting reactions. Consequently, the choice of catalyst is important and only one out of three tested catalysts was successful. $[\text{Salphen}^{\text{F}}\text{AlCl}]$ follows the rules established recently for 'switch' catalysis and key results are summarised in Figure 5. 21. Overall, this work represents a significant development in 'switch' catalysis as: (i) all monomers are available on a large scale, (ii) it is the first example of an aluminium catalyst and (iii) an icosikaiheptablock (27) polyester was synthesised –a record-breaking multiblock copolyester.

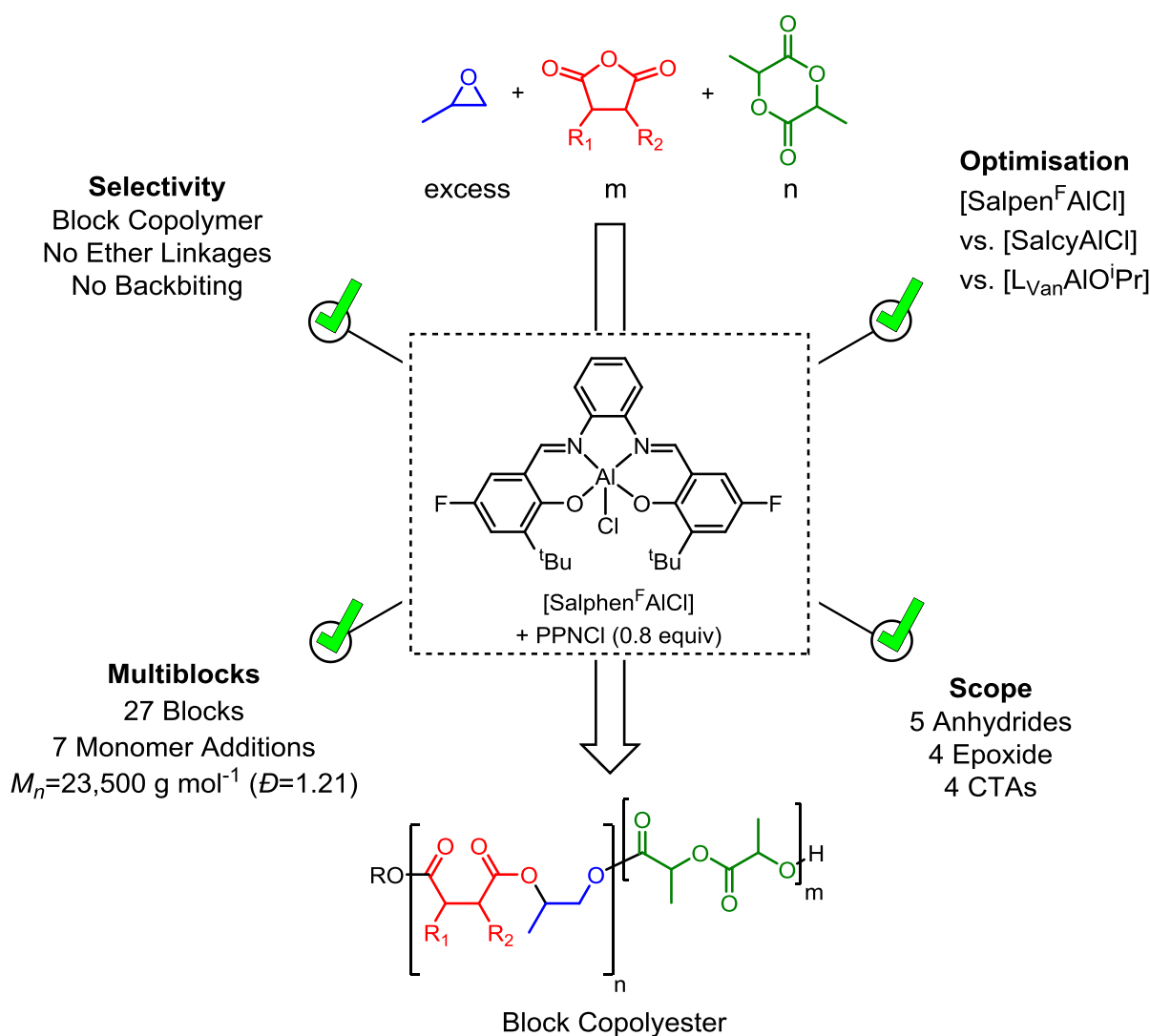
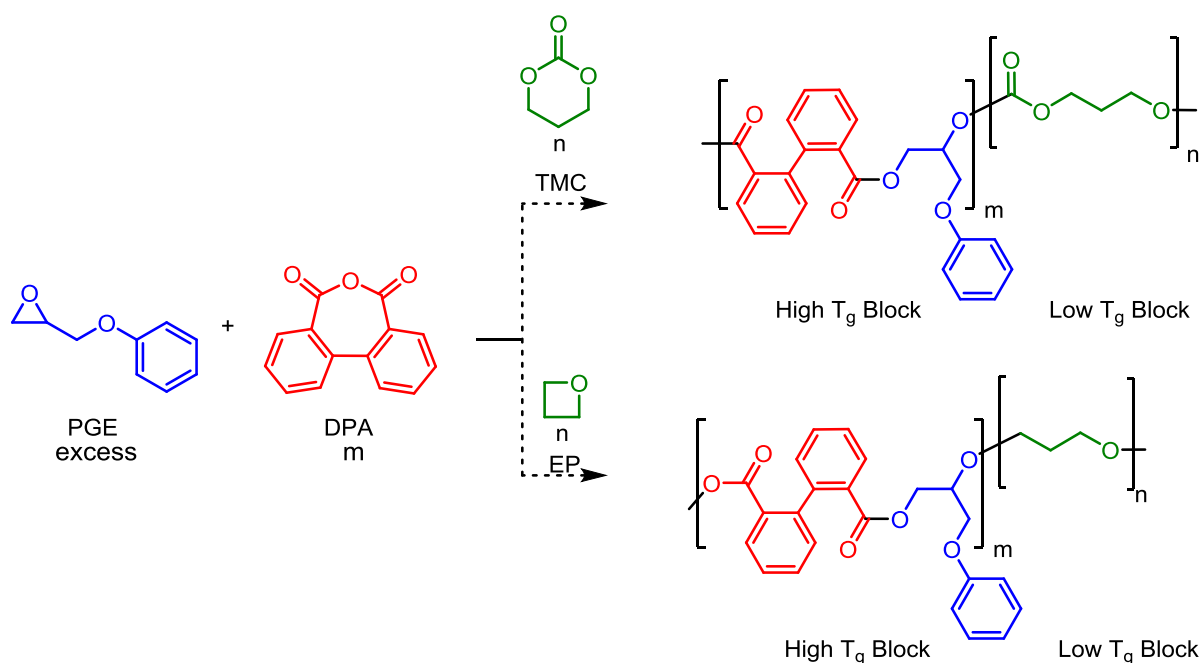


Figure 5. 21 – Key achievements in this chapter.

Although this is a promising catalyst, further work in three areas is recommended:

5.10.1. Monomers

More monomers could be used to tailor material properties. For thermoplastic elastomers, 'soft' and 'hard' blocks are combined and using [Salphen^FAlCl], the combination of diphenic anhydride (DPA) and phenyl glycidyl ether (PGE) for ROCOP and trimethylene carbonate (TMC) for ROP is proposed (Scheme 5. 10, top). The ROCOP polyester block should show a high T_g value and the ROP polycarbonate should show a value of ca. $-17\text{ }^{\circ}\text{C}$.^[22] This monomer combination would further extend the established 'switch' catalysis and allow the synthesis of poly(carbonate-*b*-ester), a class of polymers not yet investigated for metal salen catalysts. An alternative to TMC, might be the ROP of 1,3-epoxypropane (EP) to introduce polyether segments (Scheme 5. 10, bottom).



Scheme 5. 10 – 'Switch' Catalysis with PGE/DPA/TMC.

Further monomer diversity could be introduced by: (i) use of fluorinated epoxide/anhydride derivatives, (ii) protected alcohols or amine substituents, and (iii) use of hydrogen-bond acceptor with hydrogen-donor-substituted epoxides or anhydrides. The latter might allow for non-covalent and pH control of material structure.

5.10.2. Catalyst

So far, [Salphen^FAlCl] was used in combination with PPNCl and excess CTA. This results in low polymer molar masses and might be overcome by changing the initiating groups of both catalyst and co-catalyst. This principle was illustrated recently by Coates and co-workers with [Salphen^FAlOTf] and [PPN₂Ad], where only one initiating site on the co-catalyst was present (Figure 5. 22).^[23] Using this system allowed production of polymers with high molar masses up to 20,000 g mol⁻¹, $\bar{D} < 1.10$.^[23] As an aside, these reactions were performed in a mixture of acetonitrile and PO at 80 °C. Such an increase in temperature is likely to improve the observed rates for 'switch' catalysis. Finally, the catalyst might not be limited to fluorine-derivatives but other electron-withdrawing groups, such as nitro groups, are highly recommended.

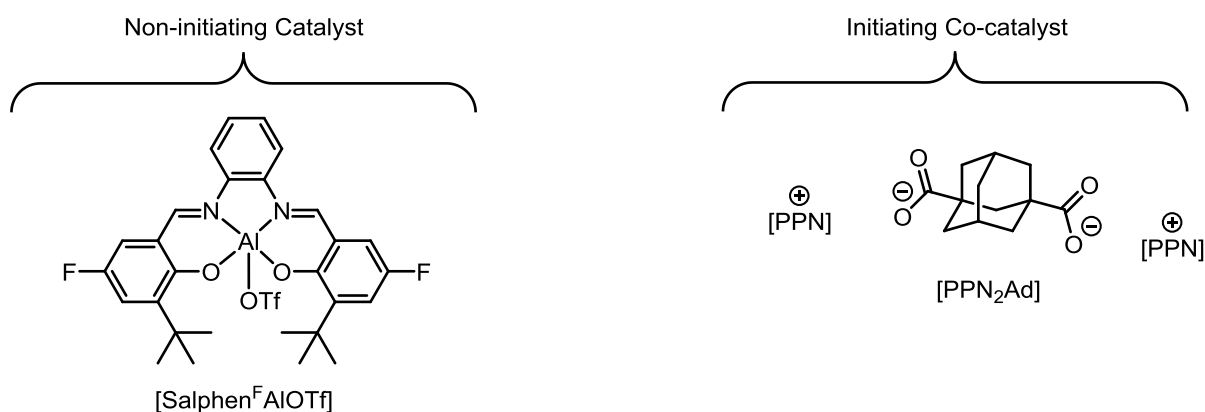


Figure 5. 22 – Structures of [Salphen^FAlOTf] and [PPN₂Ad].

5.10.3. Applications

A range of applications have already been mentioned in Chapter 3, which may apply to the block copolyesters synthesised here (coating materials, thermoplastic elastomers, plasticisers). One further application may be drug-delivery *via* polymeric micelles. Such an application may benefit from the use of isotactic PLA blocks, as a high degree of stereo-regularity improves both thermodynamic stability (critical micelle concentration (CMC)) and kinetic stability (time at which micelles remain intact below CMC).^[24, 25] As an aside, the effect of stereoregular blocks on drug loading and release behaviour was found to be dependent on the copolymer and positive effects have been found for PLA-*b*-PEG-*b*-PLA and PEG-*b*-PLA, whereas negative effects were observed for PLA-*b*-PCL.^[26-28]

5.11. References

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Chapter 6

Towards Renewable Coating Materials

A Comparison between Poly(limonene carbonate) and Poly(cyclohexadiene carbonate)

Publication: T. Stößer, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. Koning, *Polym. Chem.* **2017**, 8, 6099-6105.

6.1. Introduction

Coating materials can be found in a wide variety of everyday materials, for example floors, cars and wood surfaces, to improve resistance,^[1] increase protection^[2] and preserve structures.^[3] This high-volume market is largely based on materials prepared from fossil fuels and faces a transition towards more environmentally-friendly coating materials.^[4] The main drivers for this transition include (i) government regulations, (ii) volatile oil prices and (iii) customer demands.^[5, 6] Aliphatic polycarbonates from CO₂ and bio-based epoxides could be an attractive alternative, yet have so far been largely under-explored.

In this chapter, the overarching question to be tested is: Can (potentially) bio-based polycarbonates be used as future coating materials? In this evaluation, two polycarbonates are synthesised, cross-linked (cured) *via* thiol-ene reactions and the properties of the resulting material are evaluated. This is the first study in which coatings based on poly(limonene carbonate) (PLC) and poly(cyclohexadiene carbonate) (PCHDC), as model substrates for terminal (PLC) and internal (PCHDC) alkenes, are directly compared to each other. A selection of topics discussed in this study is outlined in Figure 6. 1.

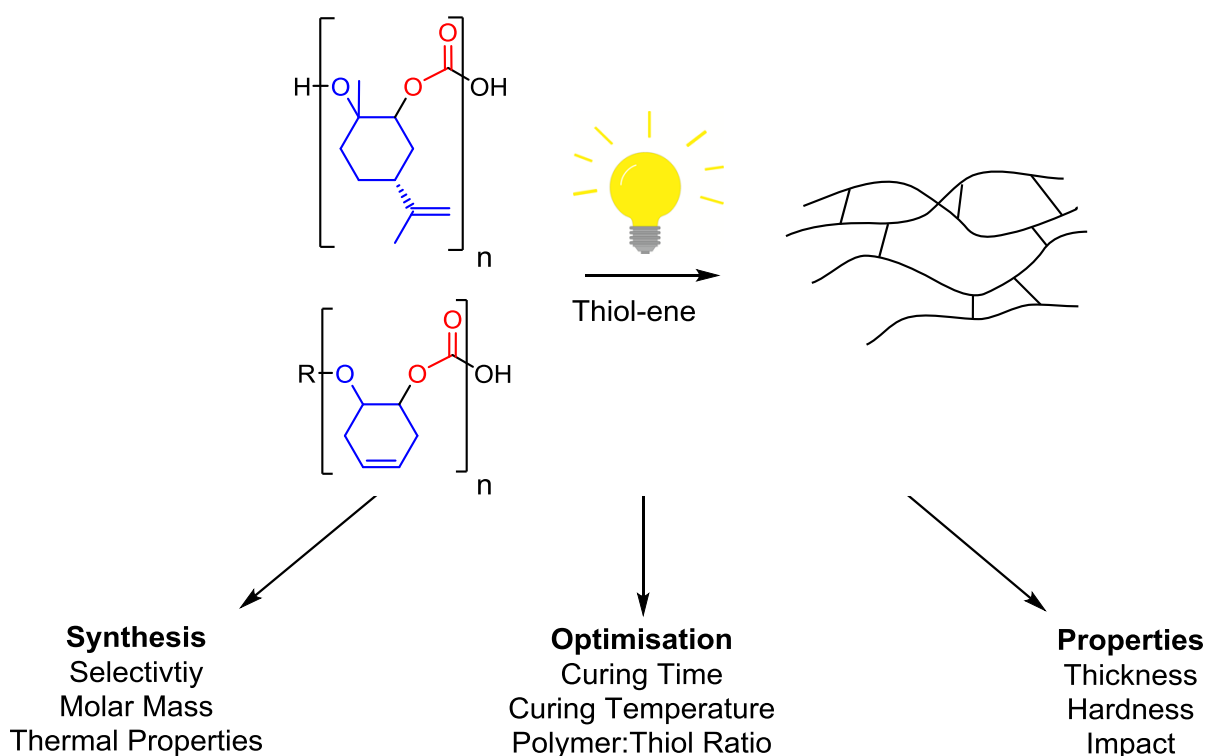
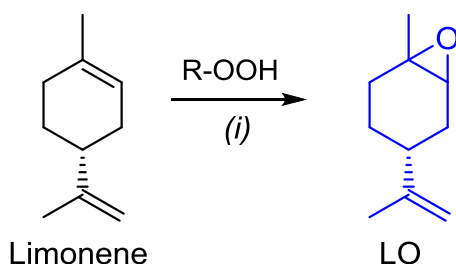


Figure 6. 1 – Key topics for the evaluation of PLC and PCHDC as coating materials covered in this chapter.

6.2 Polymer Synthesis

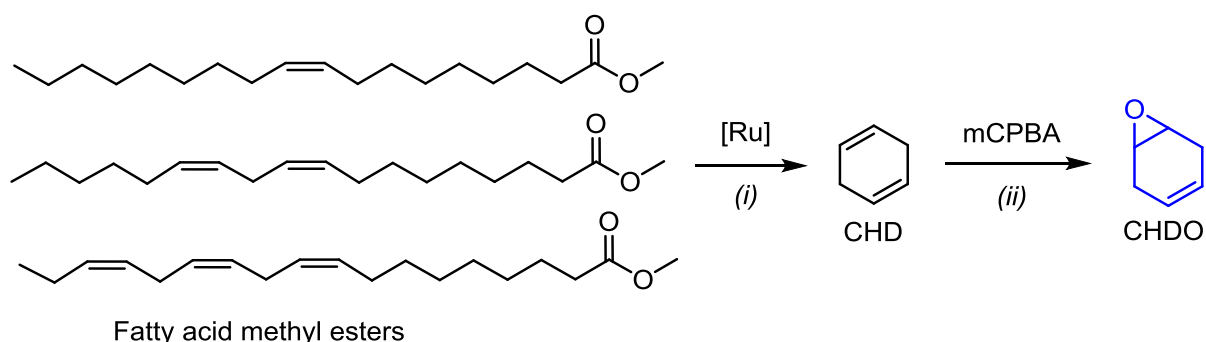
6.2.1. Synthesis of Monomers

Two polycarbonates were used in this study, PLC and PCHDC. Each polycarbonate is prepared from two monomers: an epoxide and CO₂. For PLC, the epoxide was limonene oxide (LO), which is commercially available and derived from limonene, a naturally occurring terpene found in citrus fruit peel (Scheme 6. 1).^[7-10] LO was used after drying over calcium hydride and fractional vacuum distillation (70 °C, ~ 1 mbar).



Scheme 6.1 – Synthesis of LO from limonene. Conditions: *tert*-butylhydroperoxide, Ti-MCM41, 90 °C, ethyl acetate.^[11]

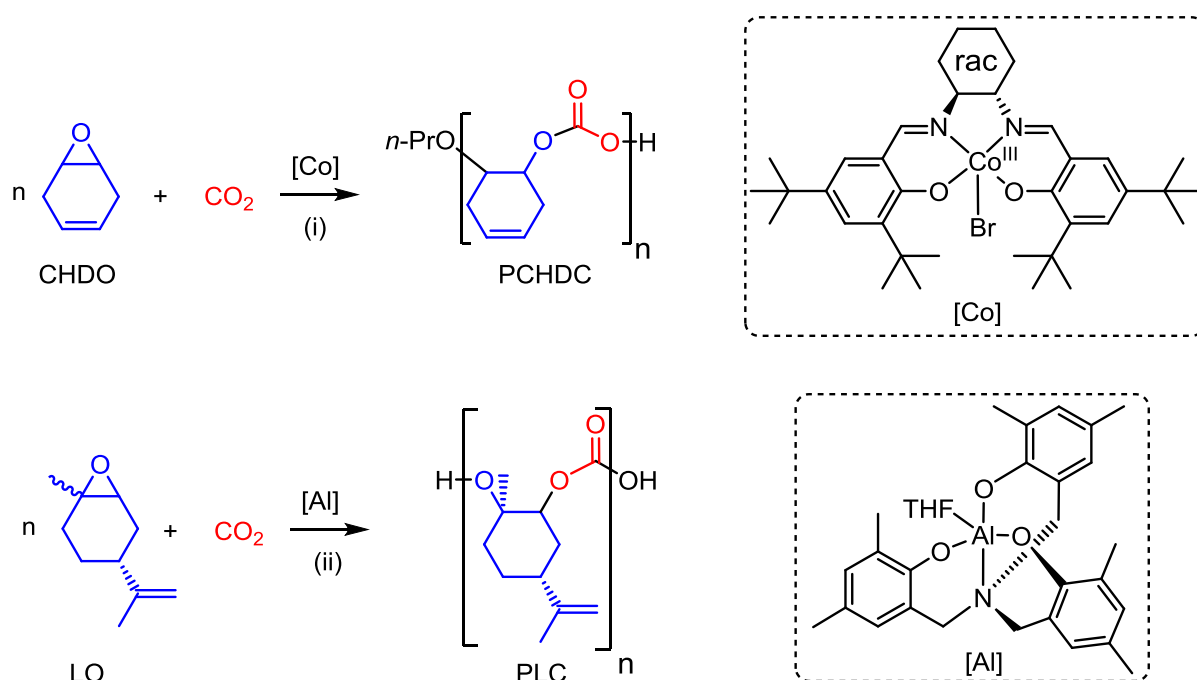
For PCHDC, the epoxide was 1,4-cyclohexadiene (CHDO) which was synthesised from 1,4-cyclohexadiene, which itself is available as a by-product in the metathesis of vegetable oil (Scheme 6. 2).^[12, 13] CHDO was synthesised by epoxidation with meta-chloroperoxybenzoic acid (mCPBA), according to literature procedures and purified by drying over calcium hydride and repeated fractional vacuum distillation (70 °C, ~ 10 mbar).^[14] The purity of CHDO was confirmed by GC-MS (see appendix).



Scheme 6.2 – Synthesis of CHD and CHDO. Conditions: (i) Metathesis catalyst (0.15 mol%), 1,4-benzoquinone (0.30 mol%), 100 °C, 10⁻² mbar, neat, 24 h;^[12] (ii) mCPBA (1.05 equiv.), NaHCO₃, DCM/H₂O (1/1), 0 °C to RT, 4 h.^[14]

6.2.2. Synthesis of Polycarbonates

CHDO was copolymerized with CO₂ in the presence of catalytic amounts (0.2 mol%) of [SalcyCoBr], PPNCI and 12 equivalents of *n*-propanol as CTA (Scheme 6. 3, top).^[14, 15] PLC was synthesised from LO and CO₂ with an aluminium trisphenolate catalyst, PPNCI (0.50 and 0.25 mol%, respectively) and water as CTA (8 equiv.; Scheme 6. 3, bottom).^[7] Low molar masses of ca. 4,000 g mol⁻¹ were targeted to reduce the melt viscosity for coating applications.^[16]



Scheme 6. 3 - Copolymerization of CHDO and CO₂. Conditions: (i) [SalcyCoBr]:[PPNCI]:[*n*-PrOH]:[CHDO] = 1:1:12:500, 20 bar, 30 °C, neat; (ii) [Al]:[PPNCI]:[H₂O]:[CHDO] = 1:0.5:8:200, 15 bar, 60 °C, neat.

For both reactions, high conversions (67-79%), high polycarbonate vs. polyether selectivity (99%) and minimal amounts of cyclic carbonate (<1%) were obtained (Table 6. 1). Molar masses, based on polystyrene standards, were lower by ca. 30% than theoretical masses and better agreement for PCHDC was achieved with a multiple-angle light-scattering (MALLS) detector. The polymerisation showed good reproducibility and comparable results were obtained in three different runs. PCHDC was purified in a three step procedure to ensure catalyst removal: (i) stirring with hexanoic acid, (ii) biphasic extraction with acetonitrile/hexane and (iii) precipitation from methanol (twice). PLC was precipitated from methanol and washed with a large excess of methanol to remove traces of catalyst. Overall yields of ca. 50% were obtained. The catalyst removal was necessary not to negatively

impact thermal and/or mechanical properties, was confirmed for both polymers by elemental analysis (not shown).

Table 6. 1 – Synthesis of PCHDC and PLC.

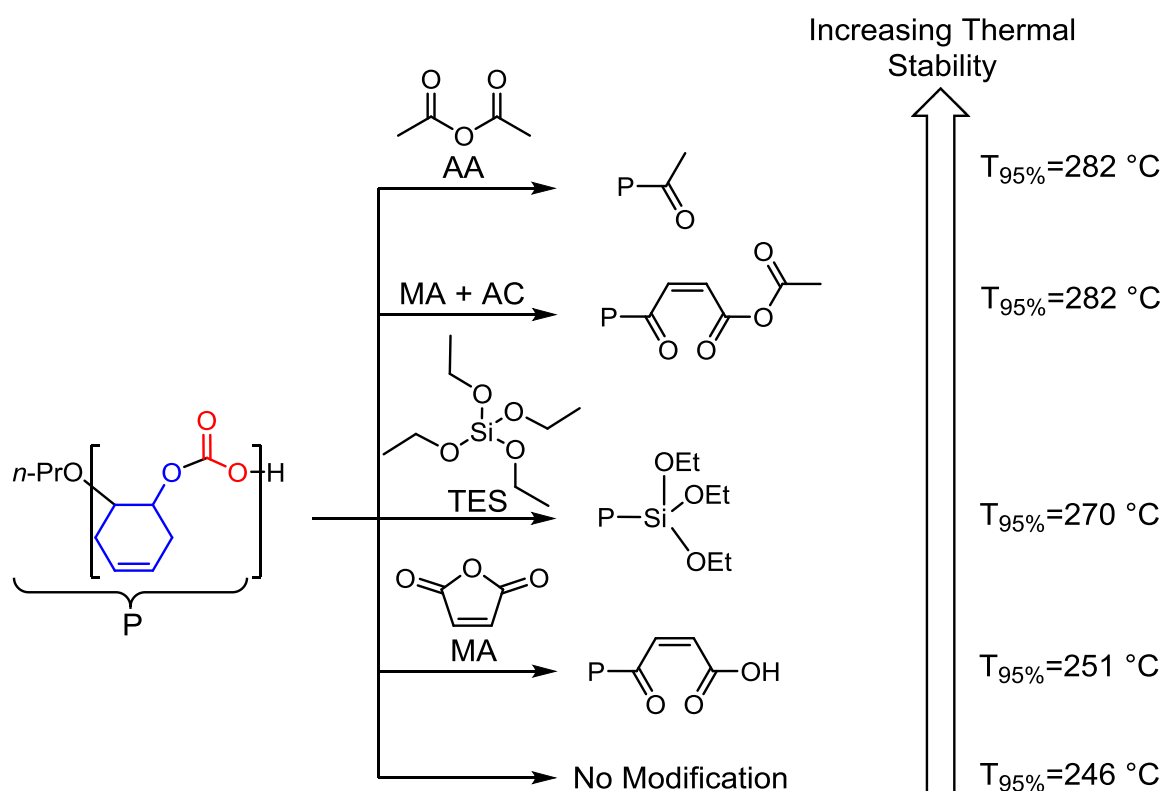
Poly- mer	T [h]	Conver- sion [%]	Selectivity [%] ^[a]		M_n^{theo} [g mol ⁻¹]	$M_n^{PS}(\bar{D})$ [g mol ⁻¹] ^[b]	$M_n^{MALLS}(\bar{D})$ [g mol ⁻¹] ^[c]	Isolated Yield [g]
			carbonate vs. ether linkage	PCHDC vs. cyclic carbonate				
PCH DC	16	79	99	99	4,660	3,340 (1.06)	4,200 (1.05)	4.8
	16	77	99	99	4,540	2,940 (1.09)	4,730 (1.13)	9.7
	20	77	99	99	4,540	2,850 (1.12)	3,770 (1.10)	4.7
PLC ^[d]	48	67	99	99	4,900	4160 (1.21)	2960 (1.18)	65.0

^[a] Selectivity determined by ¹H NMR spectroscopy based on integral ratios of polycarbonate vs. polyether (4.95 vs. 3.45 ppm) and polycarbonate vs. cyclic carbonate (4.95 vs. 3.45 ppm [PCHDC]). ^[b] Determined by SEC (THF, 30 °C) and based on polystyrene standards and given in g mol⁻¹. ^[c] Determined by SEC (THF, 30 °C) and based on multiple-angle light-scattering (MALLS) detector with a dn/dc value of 0.0851 [PCHDC] or 0.0804 mL g⁻¹ [PLC]; molar masses are given in g mol⁻¹. ^[d] Performed by C. Li at Eindhoven University (Netherlands).

As an aside, a shoulder at approximately twice the molar mass of the main peak was detected occasionally by GPC. This observation was in line with trace amounts of water which result in the hydrolysis of the epoxide and has been reported for different types of ROCOP.^[17-19]

The end groups of the polymer were further analysed by MALDI-ToF mass spectrometry. For PCHDC, only one species with a repeating unit of $m/z = 140.05$ was detected, suggesting a perfectly alternating polycarbonate, and *n*-propanol ($m/z = 60.06$) was identified as the end group. For PLC, the repeating unit ($m/z = 196.11$) was found, again indicating a perfectly alternating polycarbonate, with limonene-diol end groups. Further analysis for PCHDC by ³¹P{¹H} NMR spectroscopy, after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane, revealed only one species at 146.69 ppm, which confirmed the presence of hydroxyl-terminated chains.^[13] It should be noted that polymer end groups are not expected to have a significant influence on the reactivity of the alkene in thiol-ene reactions.

Finally, the thermal stability of PCHDC was investigated by TGA. Thermal decomposition at 5% mass loss was observed at 246 °C, which is ca. 10 °C lower than a reported higher molar mass sample ($M_n = 12,900 \text{ g mol}^{-1}$, $T_{95\%} = 255 \text{ °C}$).^[14] Increased thermal stability was observed after end group modification with maleic anhydride (MA), tetraethoxysilane (TES) and acetic anhydride (AA). In all cases, higher decomposition temperatures were observed; MA showed marginal changes of 5 °C, whereas AA showed the biggest improvement of 36 °C (Figure 6. 2). This difference may be assigned to the acid end group formed with MA, as opposed to the alkyl end group with AA. The same decomposition temperature was observed if the acid-terminated polymer was reacted with acetyl chloride (AC). This suggests that degradation predominantly occurs from the chain end and not randomly throughout the polymer backbone. Similar end group modification has recently been reported for PLC ($M_n \sim 100,000 \text{ g mol}^{-1}$) and PCHDC degrades at higher temperatures than PLC without end-capping (225 vs. 246 °C) or capped with alkyl end-capped polymers (282 vs. 241 °C).^[8]



Scheme 6. 4 – End group modification of PCHDC.

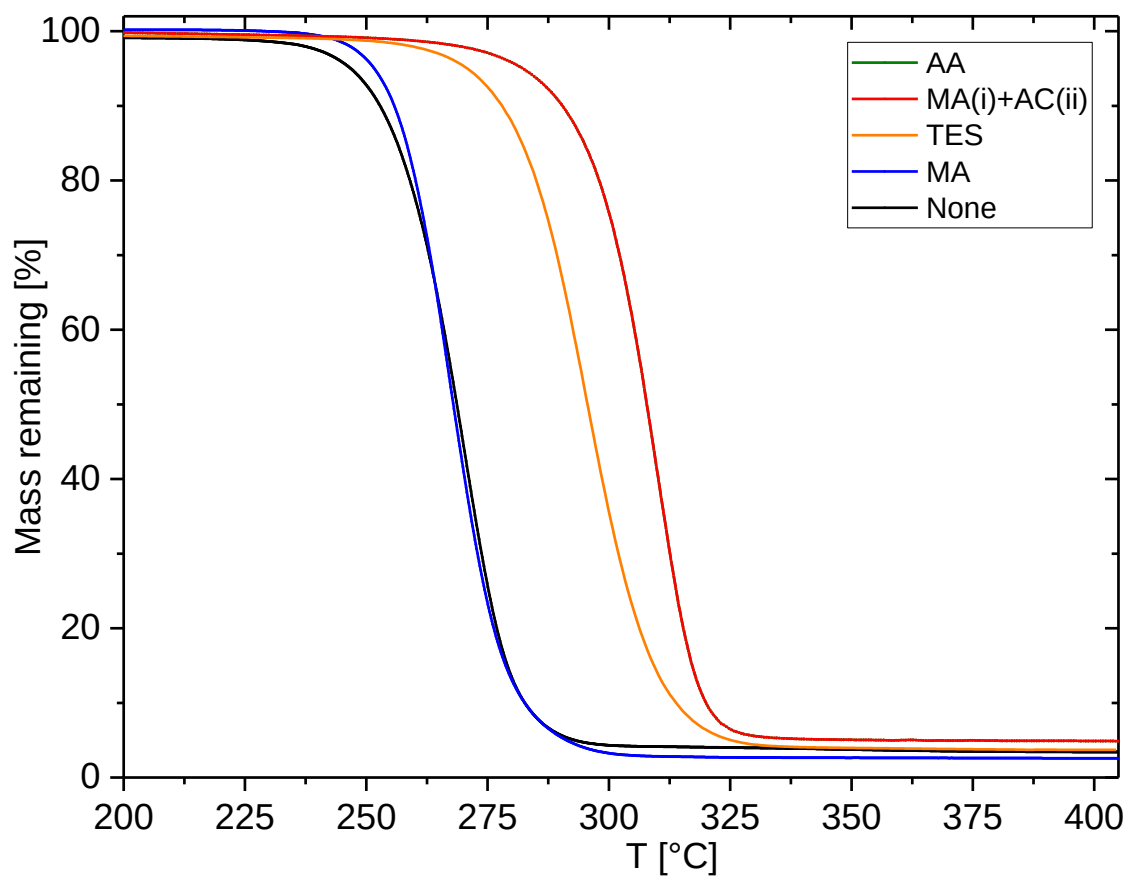
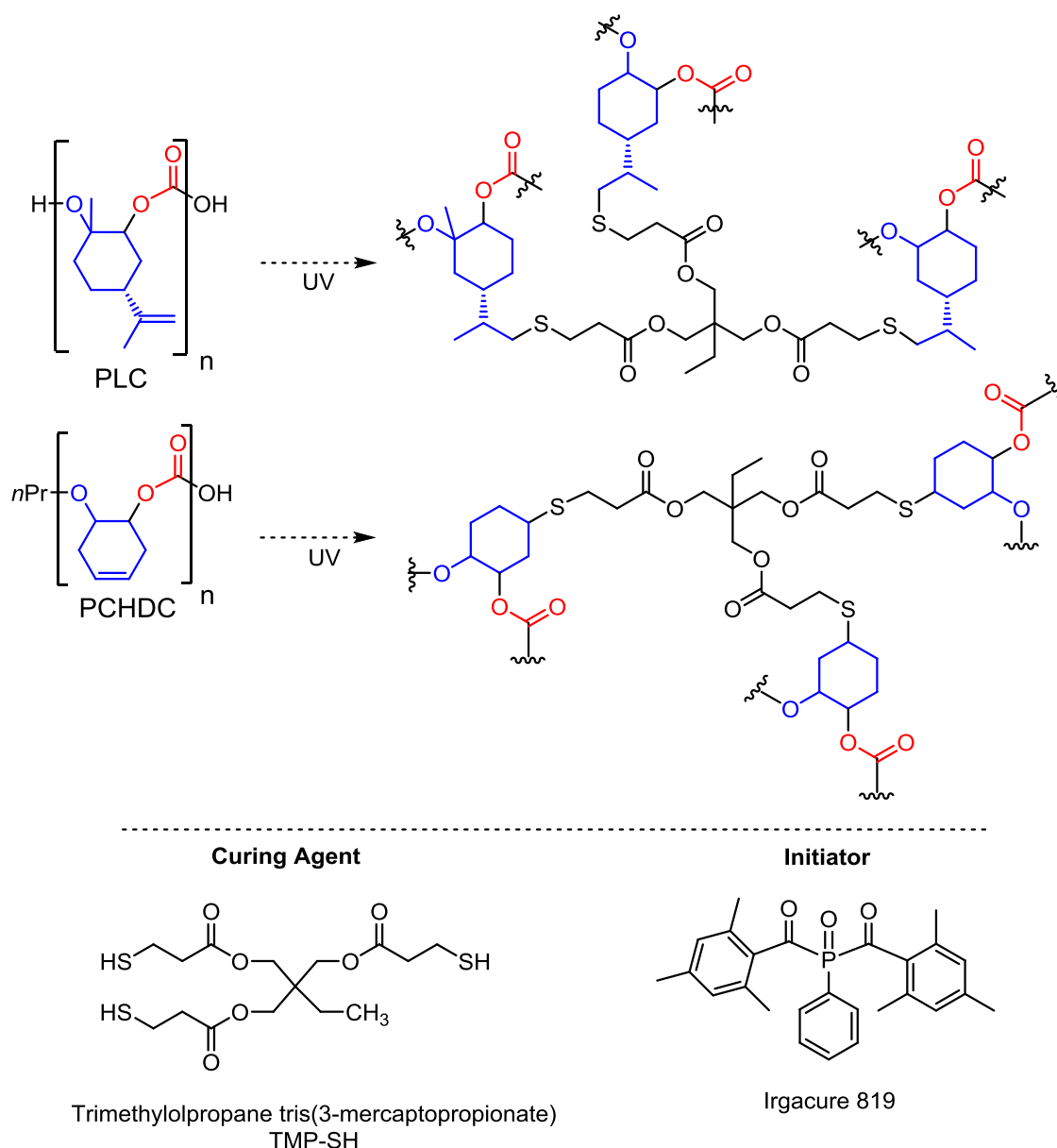


Figure 6. 2 – TGA thermograms of PCHDC and different end groups (AA and MA(i) + AC(ii) are identical).

6.3. Cross-Linking by Thiol-Ene Reactions

Both polycarbonates contain alkene functionalities, which can be further functionalised in thiol-ene reactions. The typical components in thiol-ene reactions are (i) an alkene, (ii) a thiol, (iii) a radical initiator and (iv) UV radiation.^[20-22] To achieve cross-linked materials, which is desirable for their use as coatings, a trifunctional thiol (trimethylolpropane tris(3-mercaptopropionate), TMP-SH) was used in combination with a UV-initiator (Irgacure 819).^[23, 24] Further components were PLC and PCHDC as alkenes and a conventional UV facial tanner (4x15 W). Overall, cross-linked networks shown in Scheme 6. 5 were targeted.



Scheme 6. 5 – Components and targeted cross-linked polymer networks in thiol-ene reactions.

6.3.1. Control Reactions

The curing process was monitored by Raman spectroscopy for different alkene:thiol ratios. Raman spectroscopy was the method of choice due strong resonances of thiols and the ability to examine cross-linked, insoluble materials. The successful examination of curing processes using Raman spectroscopy was used previously by Johansson and co-workers.^[9, 25-27]

Before the curing process was investigated, a range of control-reactions were conducted with curable PLC films ((C:C):(SH) = 1:1, 2 mol% Irgacure 819):

1. Stability of Curable Mixture at Daylight: Two films were casted and dried for 16 hours in the dark and in the presence of daylight. Analysis before the curing revealed minimal (5%) consumption in the dark, whereas significant (80%) conversion was found if the films were cast and dried in exclusion of daylight (see appendix). Consequently, all films were cast and dried in the dark.

2. Absorption of Operating Laser: A He-Ne laser (633nm, 8 mW) was used in the Raman spectrometer. To ensure that the laser did not degrade the initiator and thereby introduce cross-linking inside the instrument, the UV-VIS spectrum of Irgacure 819 was recorded and no absorbance was found at 633 nm (see appendix).

3. Stability with increasing Laser Power: The high intensity laser might cause local hot spots, which could degrade the polymer or further cross-link the films. This was tested by gradually increasing the laser power from 10% to 100% at constant exposure times and no changes of the PLC films were observed (see appendix).

4. Stability with increasing Laser exposure: To increase the signal-to-noise ratio, long laser exposures are typically used. So ensure that the films remain intact during longer measurements, the exposure time was gradually increased from 60 to 390 seconds per segments of 500 cm⁻¹. Again, no changes were observed (see appendix).

In summary, different control reactions confirmed that the curing process can be reliably monitored by Raman spectroscopy, if daylight is excluded.

6.3.2. Raman Spectra of Polymer/Thiol Films

As a starting point, the polymer/thiol mixture was solvent-casted on glass substrates and the films were analysed by Raman spectroscopy (Figure 6. 3). For both polycarbonates, the alkene and carbonyl functionalities were clearly visible as signals at ~ 1650 and 1750 cm^{-1} , respectively. The thiol was observed as additional resonances at 2580 cm^{-1} (S-H) and 1750 cm^{-1} ((C=O), see appendix for individual spectrum). To quantify the thiol-consumption for the optimisation studies, the mixtures without initiator were normalised to the carbonyl-signals at 1750 cm^{-1} , as an internal standard, and the integral of the thiol ($2500 - 2620\text{ cm}^{-1}$) was compared for the different measurements. The assignment of the peaks was based on closely related compounds in the literature.^[9, 25-27]

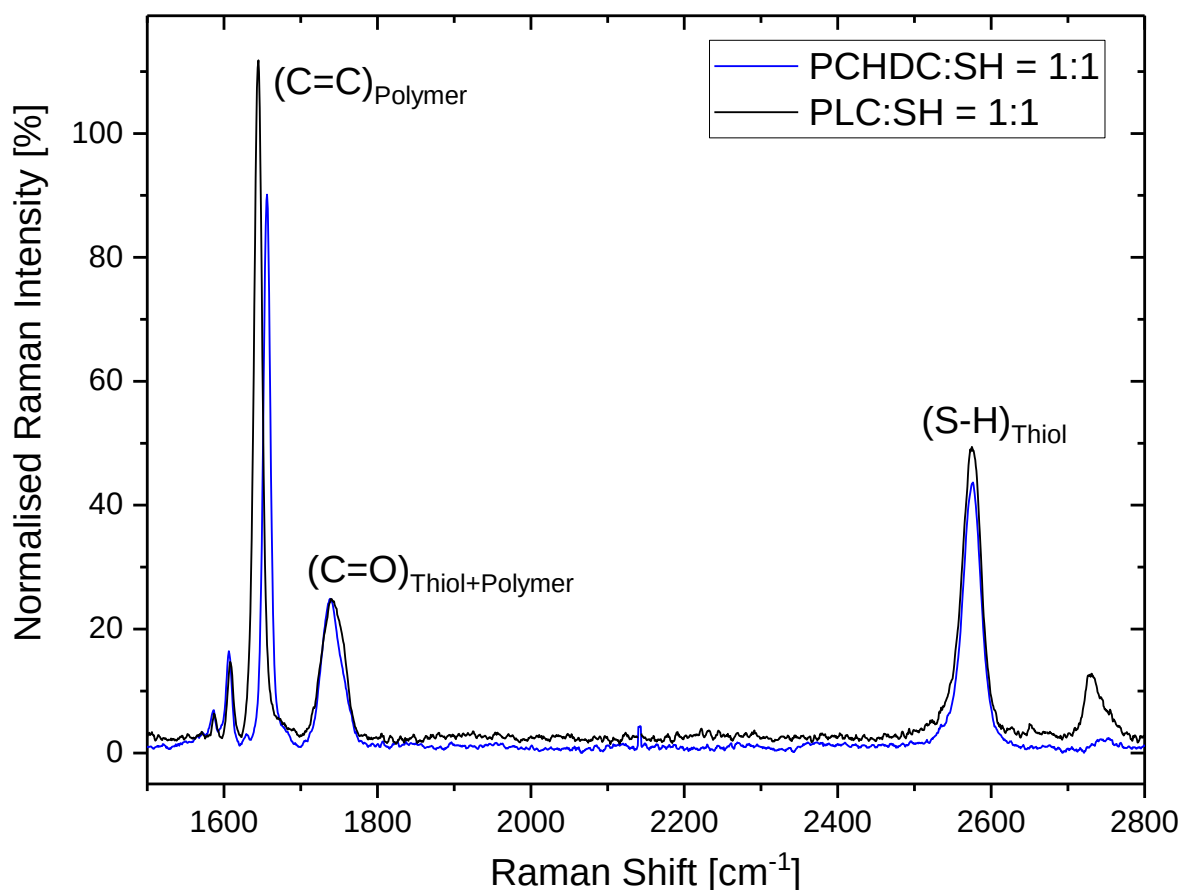


Figure 6. 3 – Normalised Raman spectra PLC or PCHDC films containing TMP-SH.

6.3.3. Optimisation of Curing Temperature

The starting points for this temperature optimisation were the T_g values of uncured films. This followed the assumption that segmental chain mobility above T_g is a key requirement for high conversions. For pure PLC, a T_g value of 92 °C was recorded, which was marginally lower than PCHDC (98 °C; Table 6. 2, entries 1 and 5). For increasing polymer:thiol ratios, the T_g values decreased stepwise from 59 °C (4:1) to 30 °C (1:1) for PLC and 54 °C (4:1) to 8 °C (1:1) for PCHDC (Table 6. 2, entries 2-4 and 6-8). In all cases, the thiol acted as a plasticiser and TMP-SH did not show a glass-transition on its own.

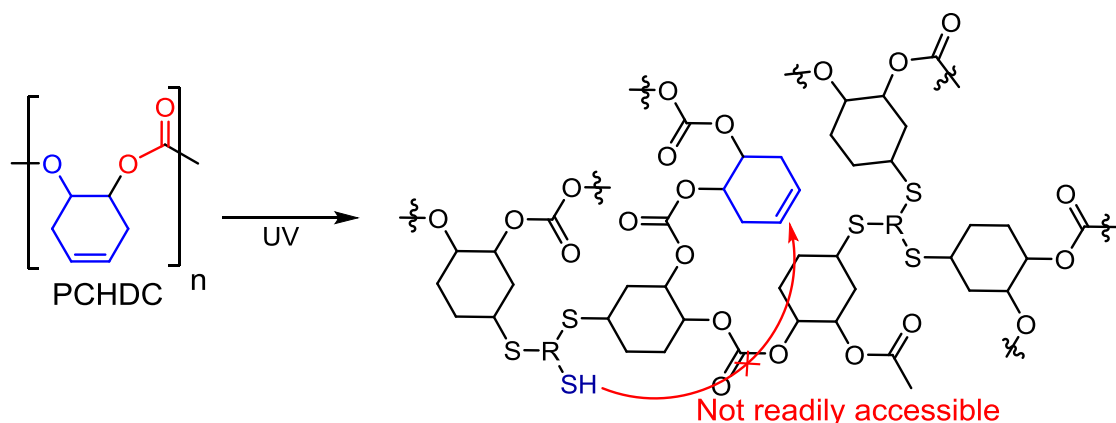
Table 6. 2 – T_g values and optimised curing temperatures for different polymer:thiol ratios.

Entry	Polymer	(C=C):(SH) ^[a]	T_g [°C] ^[b]	ΔT [°C] ^[c]
1	PLC	100% PLC	92.1	-
2	PLC	4:1	58.8	30
3	PLC	2:1	51.0	30
4	PLC	1:1	30.1	110
5	PCHDC	100% PCHDC	98.3	-
6	PCHDC	4:1	54.2	30
7	PCHDC	2:1	47.5	30
8	PCHDC	1:1	7.6	90
9	-	100% TMP-SH	-	

^[a] Molar ratio; ^[b] Determined by DSC (see appendix); ^[c] Temperature above T_g (ΔT) at which maximum conversion was determined by Raman spectroscopy (see appendix for spectra).

To test the hypothesis that curing only occurs at temperatures above T_g of the unreacted mixtures, the films were exposed to UV-radiation for 30 minutes and analysed by Raman spectroscopy. No changes were observed for the signal attributed to the thiol ($\sim 2580\text{ cm}^{-1}$), which confirmed the need for higher temperatures (see appendix). The curing temperature was now increased in 20-30 °C steps and the cured films were individually analysed by Raman spectroscopy (see appendix). These spectra were compiled in conversion vs. curing temperature diagrams and are shown Figure 6. 4. For both PCHDC and PLC, full thiol conversions were observed at temperatures of 30 °C above the T_g values of the uncured mixtures, if small amounts of thiol were used (Table 6. 2). Higher curing temperatures were necessary for equimolar alkene:thiol ratios and overall high conversions (ca. 80%) were found at 90 °C (PCHDC) and 110 °C (PLC). This was an indication of a higher degree of cross-linking compared to low alkene:thiol ratios. As the reaction proceeded and the films were increasingly cross-linked, the glass-transition temperature increased and consequently, higher curing temperatures were necessary to achieve high thiol conversions.^[28] It should be noted that the obtained conversions were all below 100%, which may be rationalised by limited mobility of the cross-linked networks beyond 80% conversion. At that point, the

unreacted functionalities are likely to be anchored within the cross-linked polymer and the reaction is proposed to be significantly hampered (Scheme 6. 6).



Scheme 6. 6 – Thiol-ene reaction at high consumption of alkene functionalities for PCHDC.

Although the reaction did not reach completion, at least two out of the three thiol functionalities were incorporated in the resin and therefore leaching of unreacted cross-linker was unlikely.

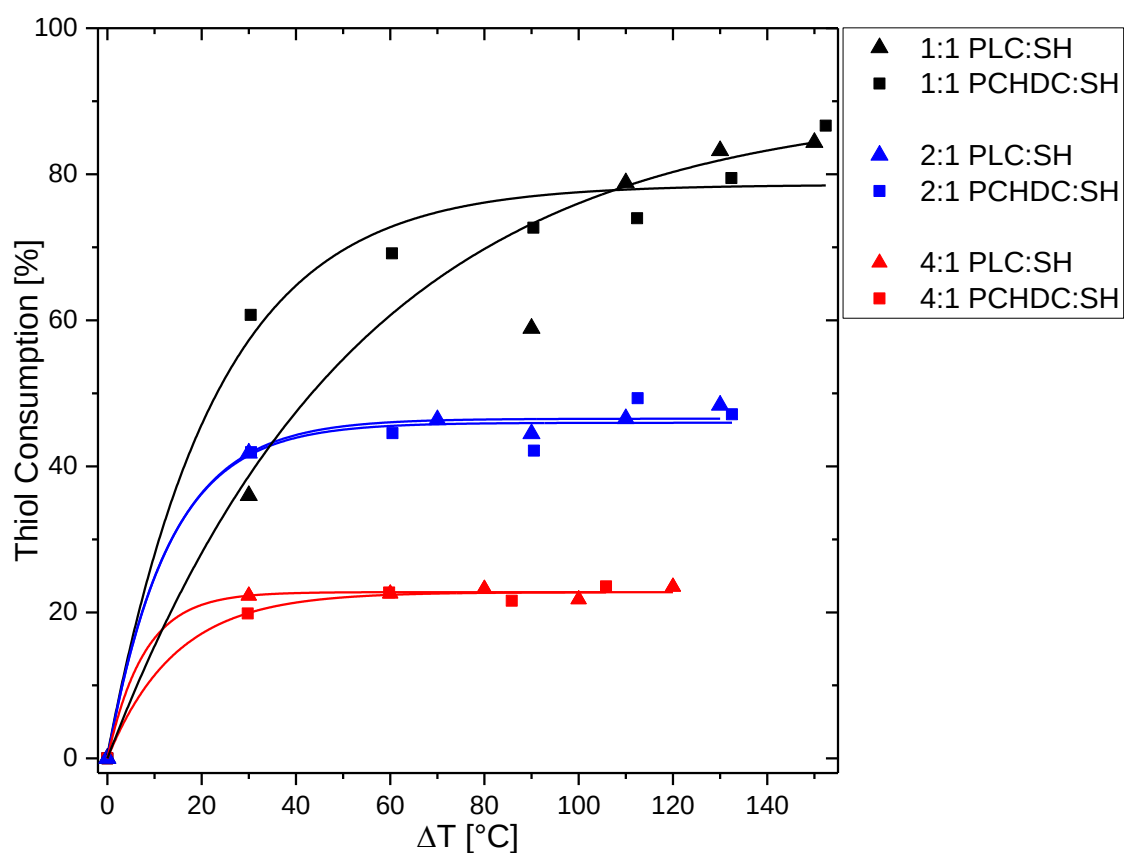


Figure 6. 4 – Thiol Consumption at various temperatures above T_g for different polymer:thiol ratios.

6.3.4. Optimisation of Curing Time

After optimal curing temperatures were found, the curing time was investigated and the solvent-cast films were cured for one to ten minutes before they were analysed by Raman spectroscopy. Selected Raman spectra were overlaid in Figure 6. 6 and with increasing curing time, the thiol-resonance gradually decreased. Based on the integral of the thiol, conversion vs. time trends could be found for different polymer:thiol ratios (Figure 6. 6). In all cases, exponential trends were observed and high conversions were detected after ten minutes; the observed values were close to the expected values from the temperature optimisation. Differences of ca. 15% were only observed for high polymer:thiol ratios, which might be attributed to the shorter reaction times (10 min vs. 30 min).

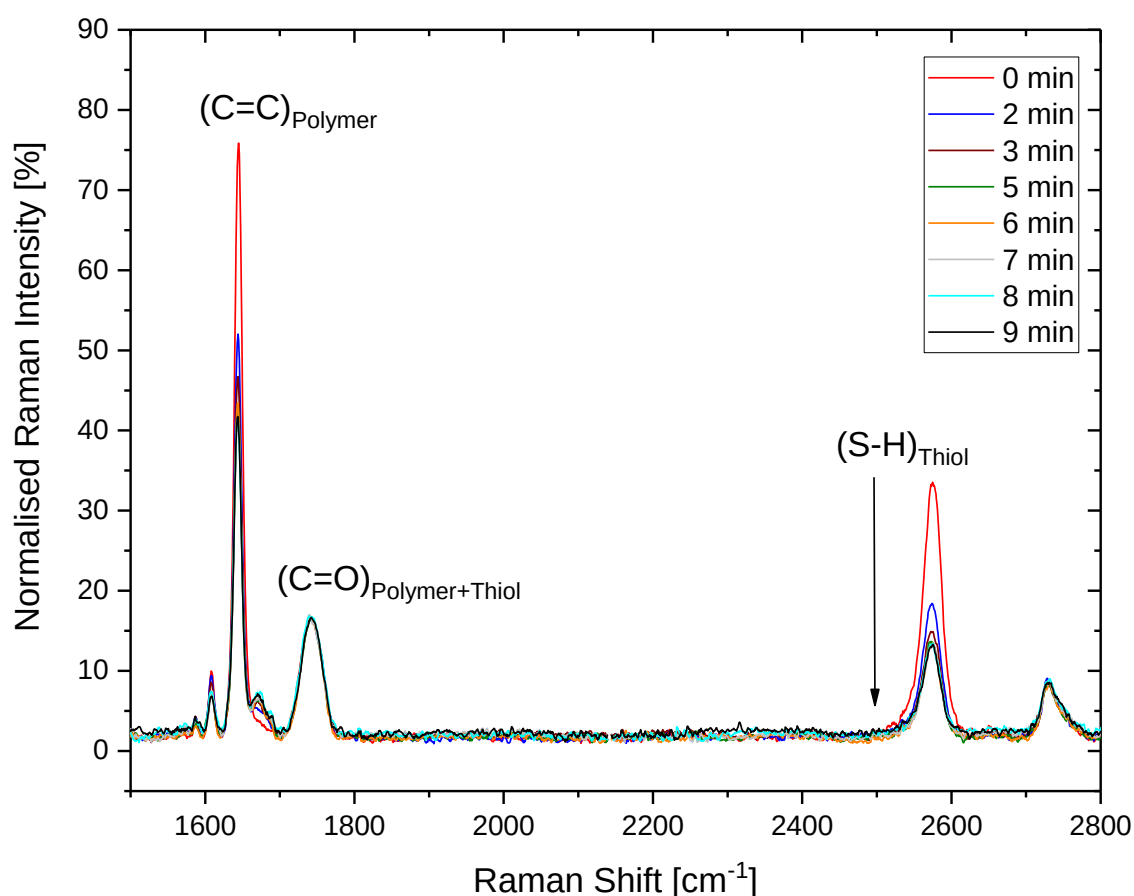


Figure 6. 5 – Normalised Raman spectra for the curing of PLC at different times (molar ratio (C=C):(SH) = 1:1, left).

Importantly, similar trends were observed for PLC and PCHDC, although PLC contained a terminal and PCHDC an internal alkene. This suggests that the nature of the alkene did not have a major influence on the thiol-ene reaction. This was an unexpected finding as reactivity differences between terminal and internal alkene were reported for reactions

conducted in solution.^[29] Consequently, this might be an effect of (i) high temperatures and (ii) casting the reaction mixture as a film. The observed rates are proposed to be diffusion-controlled.

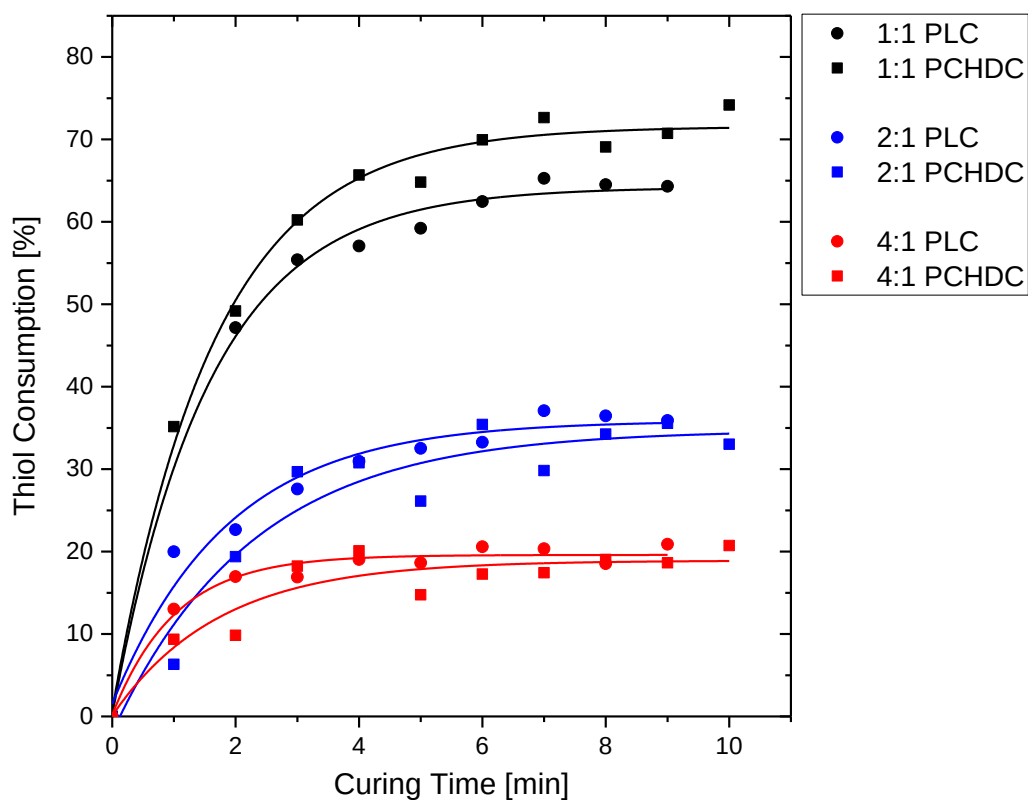


Figure 6. 6 – Thiol consumption at different curing times for PCHDC and PLC with different amounts of thiol.

6.4. Material Characterisation

For mechanical evaluation, mixtures containing polymer, curing agent and initiator were solvent-cast on aluminium plates (10 x 5 cm). These aluminium panels are commonly used in the paint industry and in a range of standardised test methods.^[30] Compared to steel, aluminium is lighter and corrosion-resistant, and therefore an attractive substrate for coating materials. Following the optimised conditions, coatings based on PCHDC and PLC for three different polymer:thiol ratios (1:1, 2:1 and 4:1) were prepared and examined by a range of techniques.

6.4.1. Appearance and Adhesion

First, the appearance of all coatings was judged. Two representative examples are shown in Figure 6. 7 and all coatings were transparent. The degree of adhesion was tested with the 'Gitterschnitt' (or crosshatch) test (ASTM D 3359), in which two perpendicular sets of six parallel cuts were applied in a distance of 1 mm with a cross-cut knife. The resulting square was then covered with an adhesive tape (adhesion strength 8 – 10 N/25 mm), which is removed after 1 second. Finally, the resulting square is rated on a scale of 0 to 5, with 5 for no detachment and 0 major detachments. All coatings had a Gitterschnitt value of 5, indicating an excellent degree of adhesion (experiment performed by C. Li, Eindhoven University, The Netherlands).



Figure 6. 7 - Photograph of coating based on PLC (left) and PCHDC (right).

6.4.2. Solvent-Resistance and Hardness

The solvent resistance was quantified by the appearance of the coating materials after 75 double-rubs with an acetone-soaked cloth ('acetone resistance'). If no changes are visible, good acetone resistance can be noted.

When small amounts of curing agent were used (polymer:thiol = 4:1), moderate acetone resistance and partial dissolution was observed as an opaque appearance of the coating (Table 6. 3, entries 3 and 6). For higher amounts of the curing agent, good acetone resistance and no optical changes after 75 acetone rubs were found (entries 1-2 and 4-5). This was in line with sufficiently cross-linked materials, as higher conversions were observed in the previous optimisation studies and better properties were expected with a higher degree of cross-linking.

The pencil hardness provides a general method to quantify scratch-resistance. In this test, calibrated pencils are used to scratch the coating material, while applying a constant pressure. Different pencils with a hardness between 8B and 8H were used and the pencil hardness was gradually increased starting from B. Once the material obtained a scratch, the coating was softer than the used pencil and the hardness value is found. For all materials, a high scratch-resistance of H-2H was measured, which clearly illustrates the benefit of cross-linking when compared the low scratch-resistance of 2B of high MW PLC ($M_n > 100,000 \text{ g mol}^{-1}$).^[8] Interestingly, higher hardness (6-8H) were found for a coating based on a mixture of polycyclohexene carbonate / poly(vinyl-cyclohexene carbonate) (Table 6. 3, entry 8). Small differences were observed between low and high polymer:thiol ratios, as expected from a higher degree of cross-linking (Table 6. 3, entries 1-3 and 4-6).

Table 6. 3 – Mechanical evaluation of coating materials.

Entry	Sample, molar ratio (C=C):(SH)	Acetone Resistance	Thickness [μm]	Pencil hardness	König hardness [s]	Impact
1	PLC, 1:1	+	40	H	109	-
2	PLC, 2:1	+	36	2H	110	-
3	PLC, 4:1	+/-	32	2H	114	-
4	PCHDC, 1:1	+	60	2H	123	-
5	PCHDC, 2:1	+	40	2H	151	-
6	PCHDC, 4:1	+/-	38	H	159	-
7	Carvone methacrylate ^{[31][a]}	+	64	2B	185	-
8	PCHC/PVCHC (50/50) ^[23]	+	9	6-8H	N. R.	+

^[a] Reported films prepared by powder coating.

The hardness was further quantified through the König test. In this method, a free-swinging pendulum rests on two metal balls, which are placed on the surface of the coating. The amplitude of the pendulum will decrease more quickly for a soft material and the oscillation will be dampened less for a hard material. In the König test, an amplitude of six degrees is set and the number of swings at which the amplitude decreased to three degrees can be measured. Generally, the measured number of swings was lower for PLC than for PCHDC (103 vs. 123 swings for polymer:thiol=1:1, Table 6. 3). This may be a result of the higher intrinsic stiffness for PCHDC, which could be a result of the absence of sterically hindered isopropenyl groups. This latter effect might increase the free volume between the polycarbonate chains for PLC, which would be in agreement with its lower T_g values. Moreover, the cross-linking agent is directly attached to the (rigid) cyclohexyl backbone of PCHDC, which is proposed to result in a stiff network. In contrast, for PLC the thiol was attached to the isopropenyl group, which might result in a more flexible cross-link. Within each polymer:thiol series, the number of swings decreased with an increasing amount of curing agent. This observation was found for both, PCHDC and PLC, and may be explained by the amount of unreacted thiol-functionalities, which might have a plasticising effect. Compared to a polymer coating prepared from carvone methacrylate, a lower number of swings was found (185 vs. 123 swings), which might be a consequence of the coating technique as solvent-free powder coating was used in the carvone experiments. Any trapped solvent should act as a plasticiser and processing by powder-coating methods is expected to result in materials with higher hardness.

6.4.3. Thickness and Impact Resistance

The thickness was measured with a coating thickness gauge. In principle, an alternating current is applied to a conducting wire, which produces an oscillating magnetic field. As the probe approaches the material, opposing currents are induced in the material. The latter is dependent on changes in the electrical conductivity, as obtained with a coating material. In all cases, coatings were solvent-cast from DCM and thicknesses between 30 and 60 μm were obtained (Table 6. 3). Typically, changes of $\pm 10 \mu\text{m}$ across the substrate were obtained. The thicknesses were reproducible if the solvent casting was automated and a constant concentration and blade speed was used (the blade is used to distribute the solution across the substrate). Generally, comparatively higher thicknesses were obtained for higher loadings of curing agent, which can be ascribed to the additional volume from larger amounts of the thiol.

The impact of the coatings ($\sim 40 \mu\text{m}$ thickness) was tested with the reverse impact test, in which a 1-kg steel ball is dropped from a height of 50 mm on the substrate (ASTM G14-04). This destructive method resulted in breaking the coating (delamination) and deformation of the substrate in all cases; an example is shown in Figure 6. 8. This might be a consequence of the thinness of the coatings, in combination with low T_g values, and thicker coatings should be beneficial to improve the impact strength.^[32] It should be noted, that related coating materials based on carvone methacrylate, lack this toughness as well. Interestingly, a coating based on PCHC/PVCHC did not lack this impact strength.^[23]



Figure 6. 8 – Picture of coating material after delamination (PLC:TMPSH = 1:1).

In summary, the polymer-based coatings can be considered as hard, but brittle materials. The most promising feature was the high scratch-resistance compared to methacrylates or uncured material.

6.4.4. Thermomechanical Properties

All cured films were further analysed by dynamic-mechanical thermal analysis (DMTA). For this purpose, free-standing films were cast in Teflon moulds and cross-linked in a second step. Raman spectroscopy indicated full thiol conversion on both sides of the films (see appendix). Based on the storage modulus vs. temperature graphs (Figure 6. 9), a glassy modulus of ca. 1 GPa was measured, which is a typical value for polymer films.^[26] This provides a measure for the stiffness of the films; PCHDC films showed higher stiffness than films based on PLC. This might be consequence of the structural differences between the two polymers, most notably the pendent isoprenyl group for PLC. Within each series, glass-transition temperatures were visible as a drop in storage modulus. These transitions were shifted to higher temperatures for larger amounts of curing agent, as expected from a higher degree of cross-linking. The rubbery plateaus, after the glass-transition, followed this trend and the highest value with 28 MPa was observed for PCHDC with equimolar amounts of thiol. These rubbery plateaus indicate cross-linked networks.

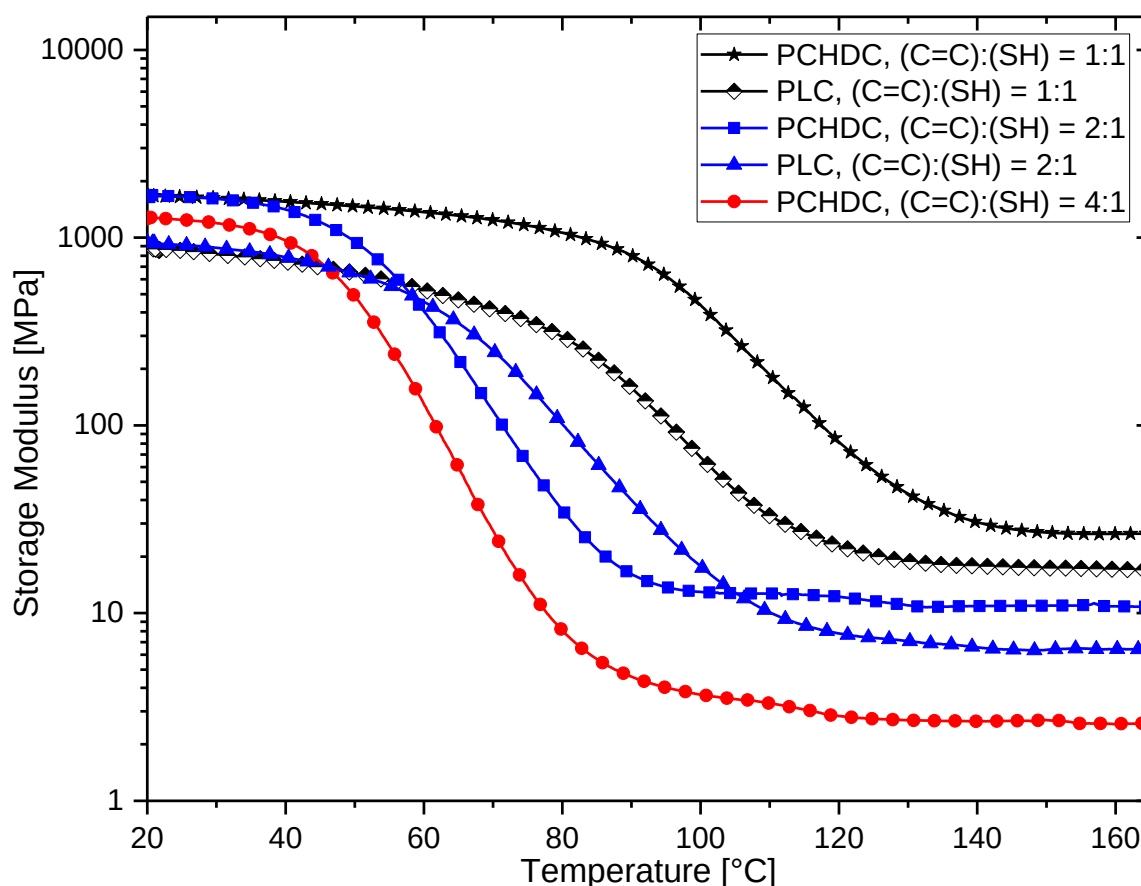


Figure 6. 9 – Storage modulus vs. temperature graph obtained from DMA (recorded by C. Li, Eindhoven University, The Netherlands). No free-standing films were obtained for PLC (C=C):(SH) = 4:1.

In the $\tan \delta$ vs. temperature curves, the glass-transition is observed as a maximum. For both series of polymers, higher T_g values were observed with larger amounts of curing agent, which indicated successful cross-linking and which was in line with earlier findings. When PLC and PCHDC were compared directly, higher T_g values were found for PCHDC for 1:1 ratios between the polymer and the thiol (113 vs. 105 °C). Surprisingly, the reverse trend was detected for polymer:thiol ratios of 2:1 (90 vs. 76 °C). Further peak analysis showed the highest full-width at half maximum for this PLC sample, suggesting a less homogeneous sample in this case, which might be the reason for the observed differences (see appendix). As an aside, the homogeneity and thickness are challenging to control as a doctor blade technique used to cast well-defined films cannot be used.

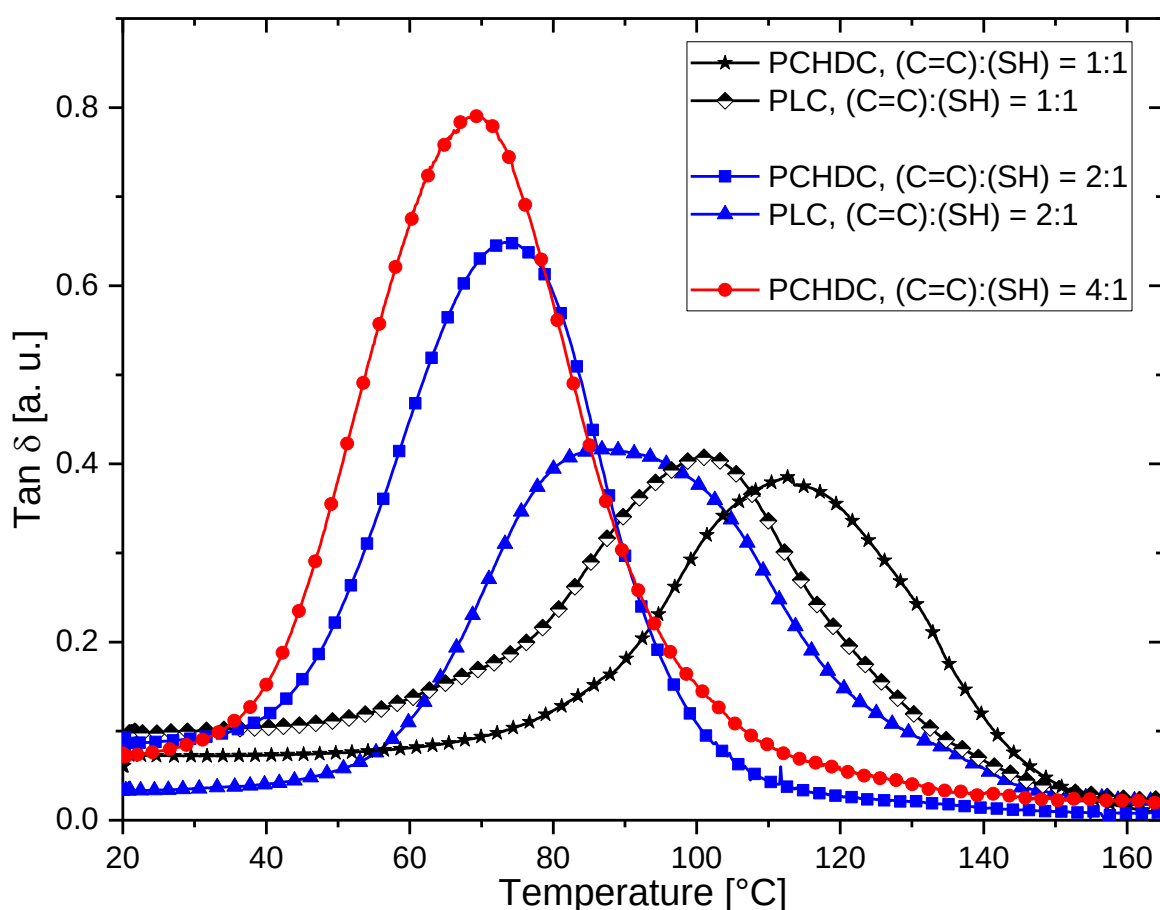


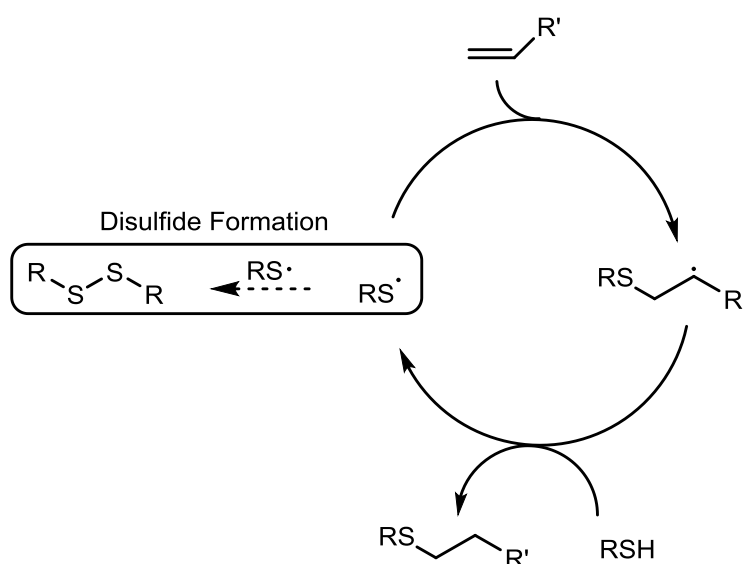
Figure 6.10 – $\tan \delta$ vs. temperature graph obtained from DMA (recorded by C. Li, Eindhoven University, The Netherlands).

In conclusion, DMTA further confirmed successful cross-linking as glass-transition temperatures increased after cross-linking. The glassy modulus was in line with typical polymer coatings and the rubbery plateau at ca. 12 MPa indicated a cross-linked network.

6.5. Discussion

6.5.1. Selectivity of Thiol-Ene Reaction

The mechanism of radical-mediated thiol-ene reactions is shown in Scheme 6. 7. Starting from a thiyl radical, which is formed from the photo-initiator and the thiol, the alkene is added in a first step, forming a carbon-centred radical. Radical chain-transfer to a second thiol results in the formation of the thiol-ene product and re-generates the initial thiyl radical.^[22] Typically, the *anti*-Markovnikov product is obtained in this formal thiol-addition across the alkene. One possible side-reaction of this process is radical recombination and the formation of disulfide linkages has been reported with polyacrylates.^[33]



Scheme 6. 7 – Mechanism for radical-mediated thiol-ene reaction and disulfide formation.^[22]

Disulfides can be detected by Raman spectroscopy between $498\text{--}511\text{ cm}^{-1}$ (ν_{S-S}) and $621\text{--}622\text{ cm}^{-1}$ ($\nu_{S,C}$).^[34, 35] For coating materials obtained from PCHDC and PLC after curing with equimolar amounts of thiol, no significant resonances were found at these shifts, which suggested the highly selective formation of the thiol-ene product (Figure 6. 11 and Figure 6. 12). This was in agreement with similar materials obtained from limonene and TMP-SH.^[36]

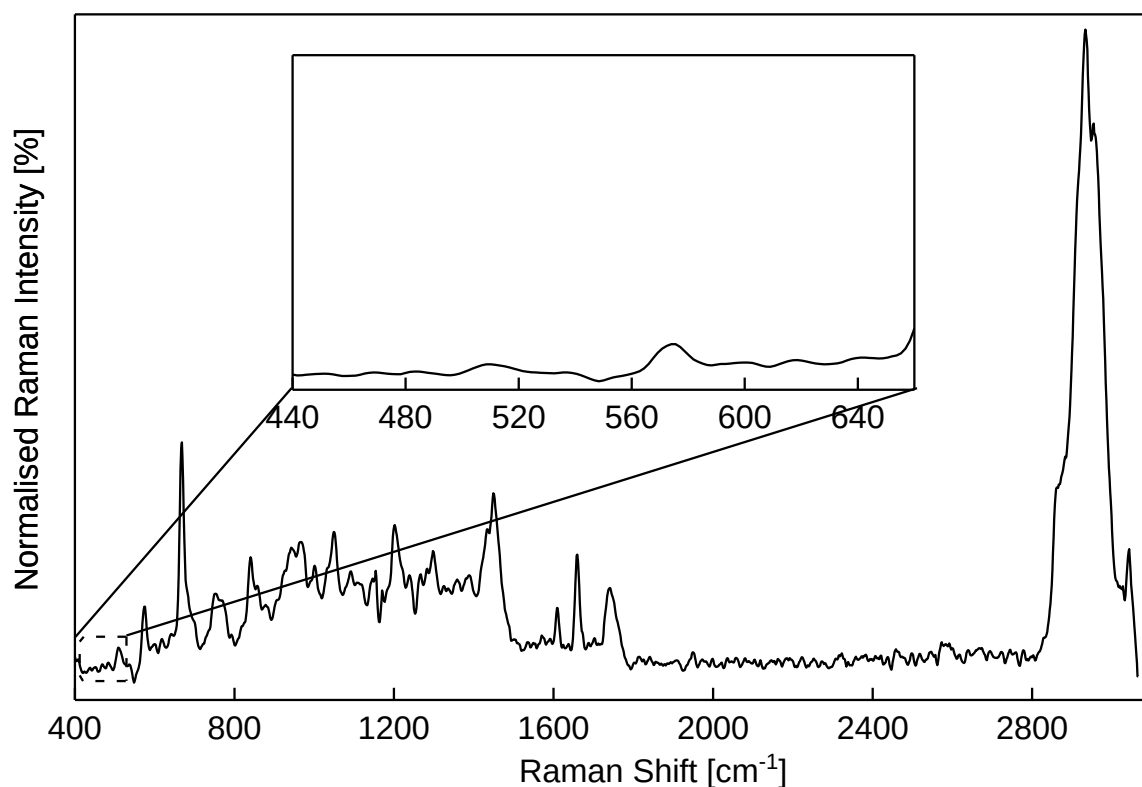


Figure 6.11 – Normalised Raman spectrum of cured PCHDC film, the relevant region for disulfide linkages is enlarged.

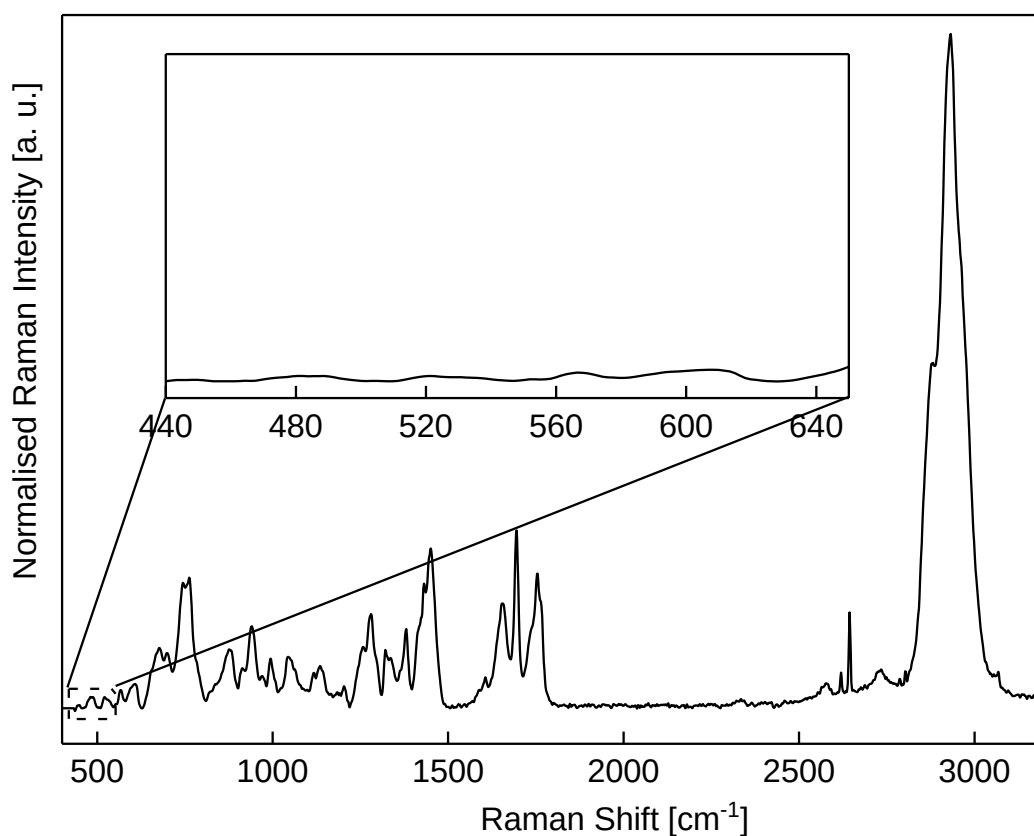
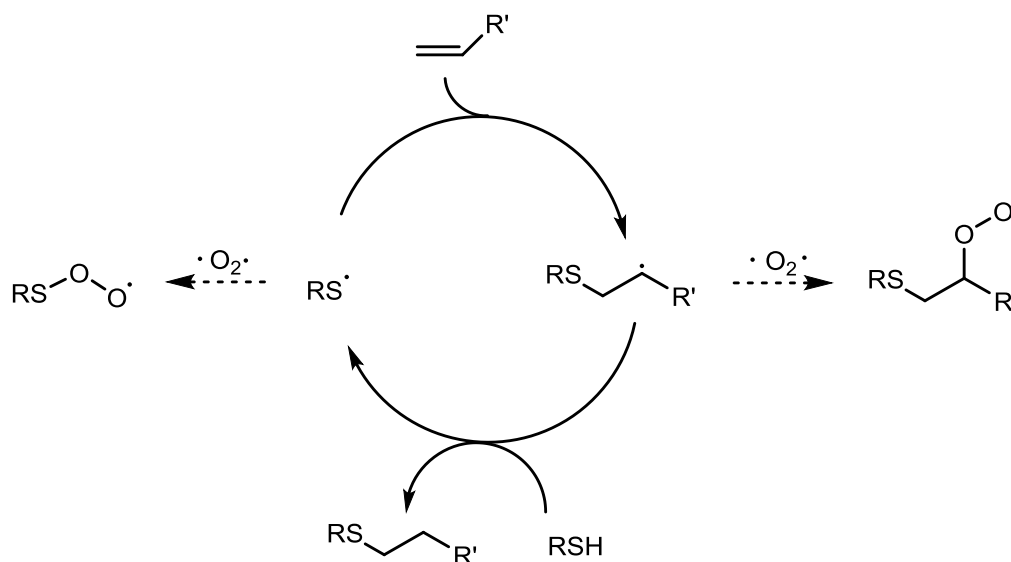


Figure 6.12 - Normalised Raman spectrum of cured PLC film, the relevant region for disulfide linkages is enlarged.

6.5.2. Effect of Oxygen

As radicals are formed during the reaction, oxygen might act as an inhibitor (Scheme 6. 8). Interestingly, thiol-ene reactions are known as air and moisture tolerant, provided the concentration of oxygen is lower than the thiol concentration.^[22] However, these reactions are commonly performed in solution and not under neat conditions as a film.



Scheme 6. 8 – Possible effects of oxygen on thiol-ene reactions.

The effect of oxygen was investigated with cured PLC films (polymer:thiol = 1:1) and the thiol-consumption was analysed by ATR-IR and Raman spectroscopy. The two complementary techniques were chosen due to their different penetration depth: whereas Raman spectroscopy allows for a depth of ca. 3 μm , ATR-IR is limited to ca. 1 μm .^[37, 38] Incomplete thiol-consumption was observed by ATR-IR, if the films were dried under air (Figure 6. 14). This is likely a result of surface inhibition by oxygen. Interestingly, high consumptions were found by Raman spectroscopy, which might be an effect of the higher penetration depth and indicated a less severe effect of oxygen-inhibition at higher sample depth. As these incomplete conversions near the surface are undesirable and plasticising effects were expected, the films were dried under nitrogen. This significantly improved the observed thiol-consumption by ATR-IR. As an aside, the thiol signals for films based on PHDC were partially overlaid by ATR-IR and were not analysed.

In conclusion, oxygen is proposed to be incorporated during the drying process under air, which inhibits thiol-ene reactions near the surface. This effect is less significant if a higher depth of the sample is analysed and can be prevented by drying under nitrogen. The latter positively affects material properties with respect to hardness and is recommended of future coating materials (see appendix).

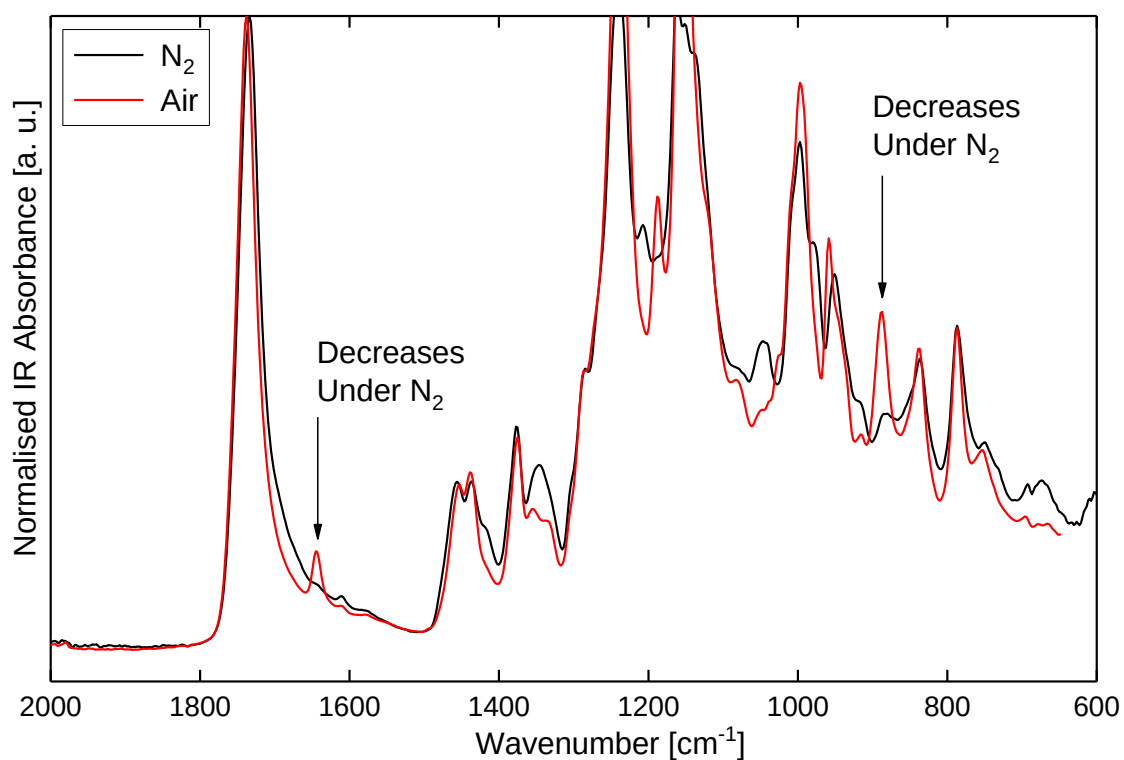


Figure 6. 13 - ATR-IR spectra of PLC films dried under nitrogen and under air; the arrows are indicative signals for C=C of the polymer (top).

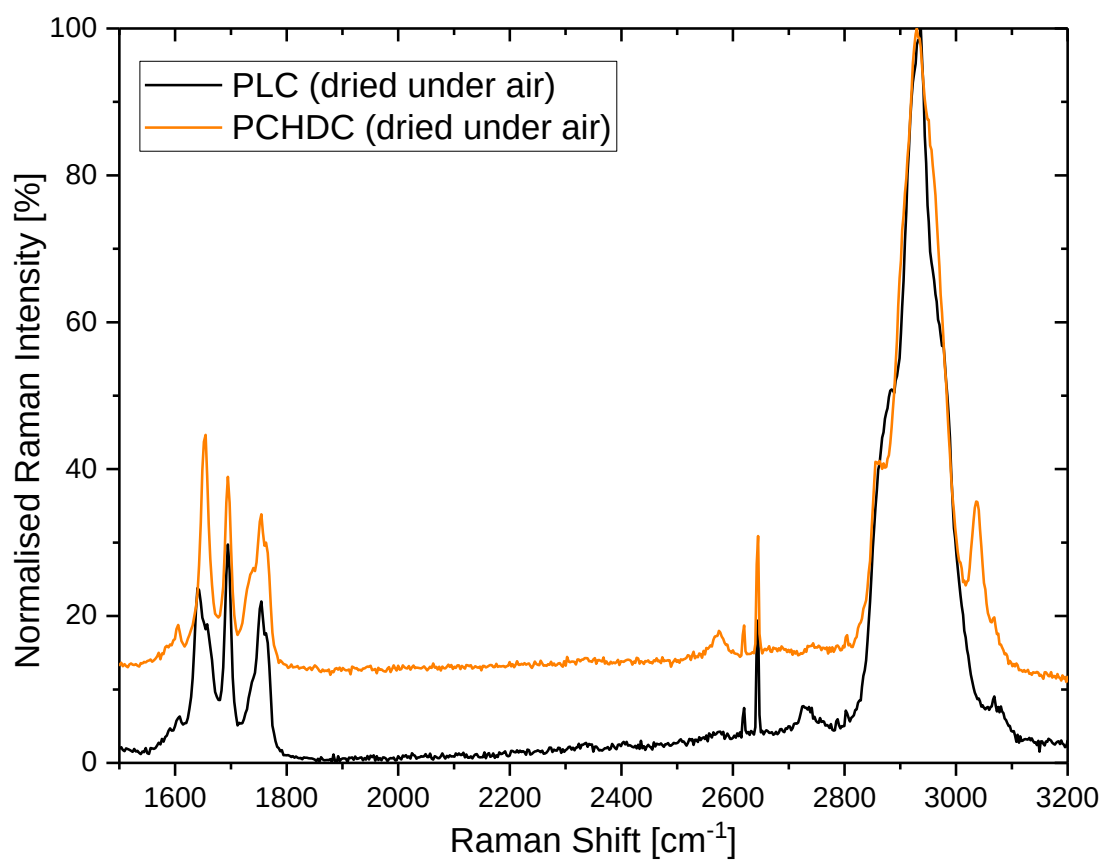


Figure 6. 14 - Raman spectra of films dried under air.

6.5.3. Choice of Initiator

A UV curing was used due to its high efficiency in thiol-ene reactions. However, this light-sensitive initiator has the practical disadvantage that significant curing was observed while the films were dried overnight after solvent-casting. To simplify the sample preparation and ensure the deliberate generation of radicals, two thermal initiators, azobisisobutyronitrile, AIBN, and dicumylperoxide, DCP, were investigated as alternatives to Irgacure 819 (Figure 6. 15).

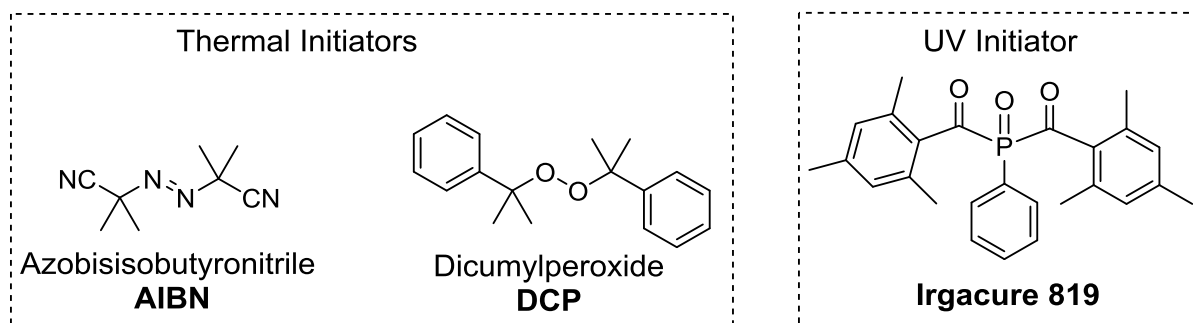


Figure 6. 15 – Structures of AIBN and DCP as thermal initiators and Irgacure 819 as UV initiator.

All initiators were tested for thiol-ene reactions with PCHDC and PLC in the presence of one equivalent of thiol. The reaction was performed at different temperatures to investigate if the choice of initiator changes the optimised conditions. For PLC, high conversions were obtained with AIBN or Irgacure 819 but DCP was less reactive at temperatures below ca. 130 °C (relative to T_g ; Figure 6. 17). Nonetheless, similar conversions, of ca. 80%, were obtained at higher temperatures and all initiators showed similar performance under these conditions. The decreased reactivity of DCP might be associated with the formation of a benzyl-type radical, which is resonance stabilised and therefore more stable compared to the phenyl-type radical generated from Irgacure 819 (Figure 6. 16).

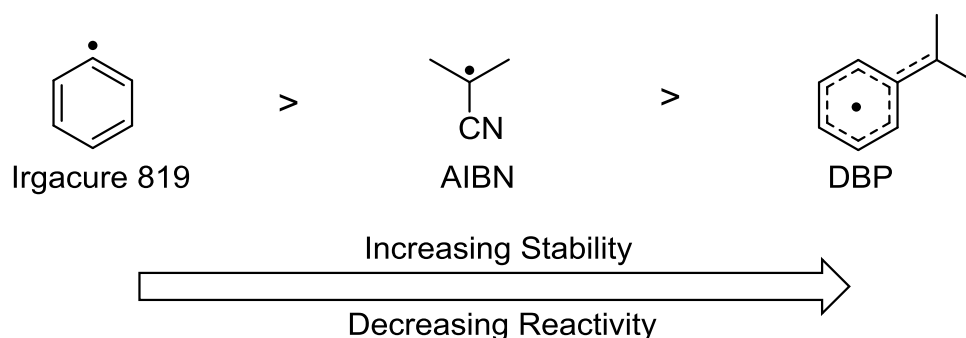


Figure 6. 16 – Proposed stability and reactivity of radicals formed from different initiators.

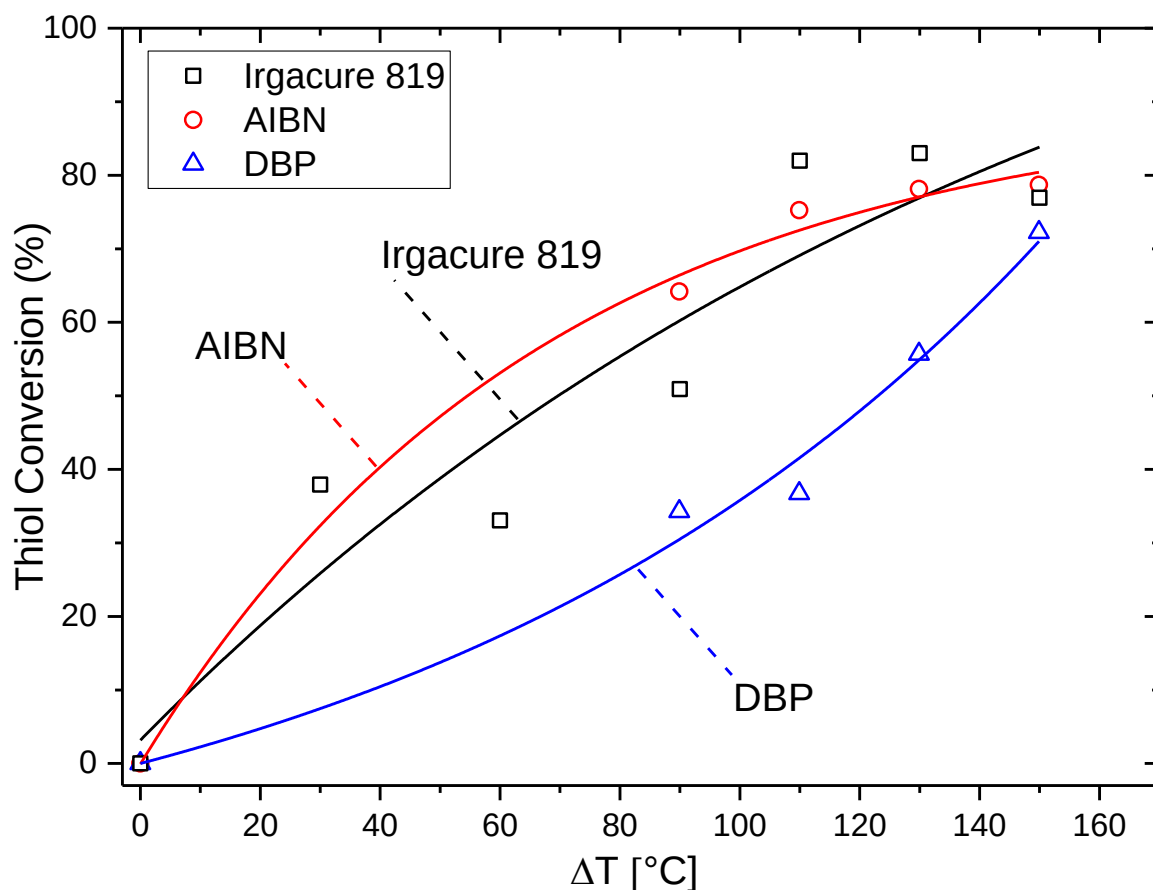
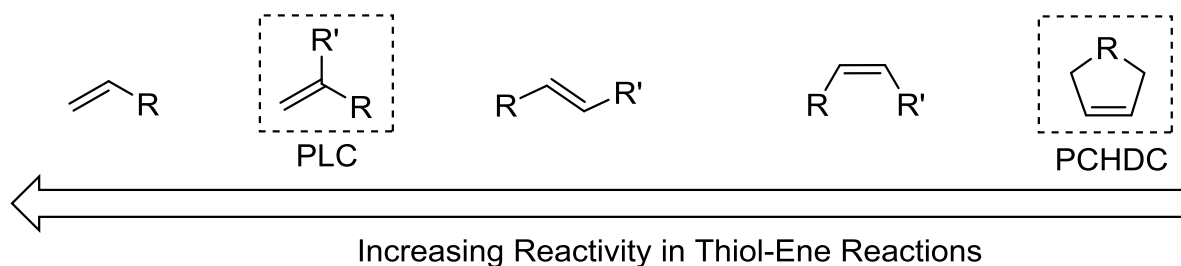


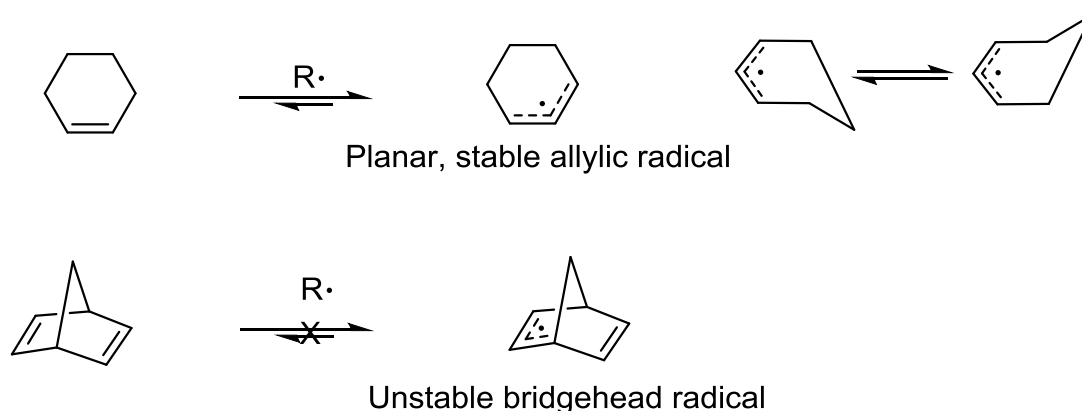
Figure 6. 17 – Thiol-ene reaction of PLC and TMP-SH with different initiators at different temperatures.

Surprisingly, significant differences between thermal and photo-initiators became evident for PCHDC and only low conversions ($\leq 20\%$) were found with thermal initiators (Figure 6. 18). This may be caused by: (i) the lower reactivity of the alkene and (ii) the reactivity of the initiating radical. In a model study by Hoyle and co-workers, the reactivity of alkenes in thiol-ene reactions was investigated and terminal alkenes, such as PLC, were found to be more reactive than internal alkenes (PCHDC). The low reactivity of cyclic alkenes, particularly cyclic *cis*-alkenes, is still not fully understood and may be attributed to a combination of ring-strain, available hydrogens for abstraction and other stereoelectronic effects.^[29]



Scheme 6. 9 – Reactivity of different alkenes in thiol-ene reactions.^[29]

The authors hypothesised that reversible hydrogen abstraction occurs as a side-reaction, which may explain the observed reactivity. In the case of cyclohexene, a planar and stable allylic radical is formed, which would make this equilibrium favourable and reduce the overall reactivity.^[39] It should be noted that a similar equilibrium is not observed for norbornene as the formation of a bridgehead radical is energetically unfavourable.^[40] For this reason, norbornene-containing polymers should be highly reactive in thiol-ene reactions, a hypothesis which was experimentally validated in for post-functionalisation reactions using PDL-*b*-PCHNBE-*b*-PDL (Chapter 3).



Scheme 6. 10 – Hydrogen abstraction from cyclohexene (top) and norbornene (bottom).

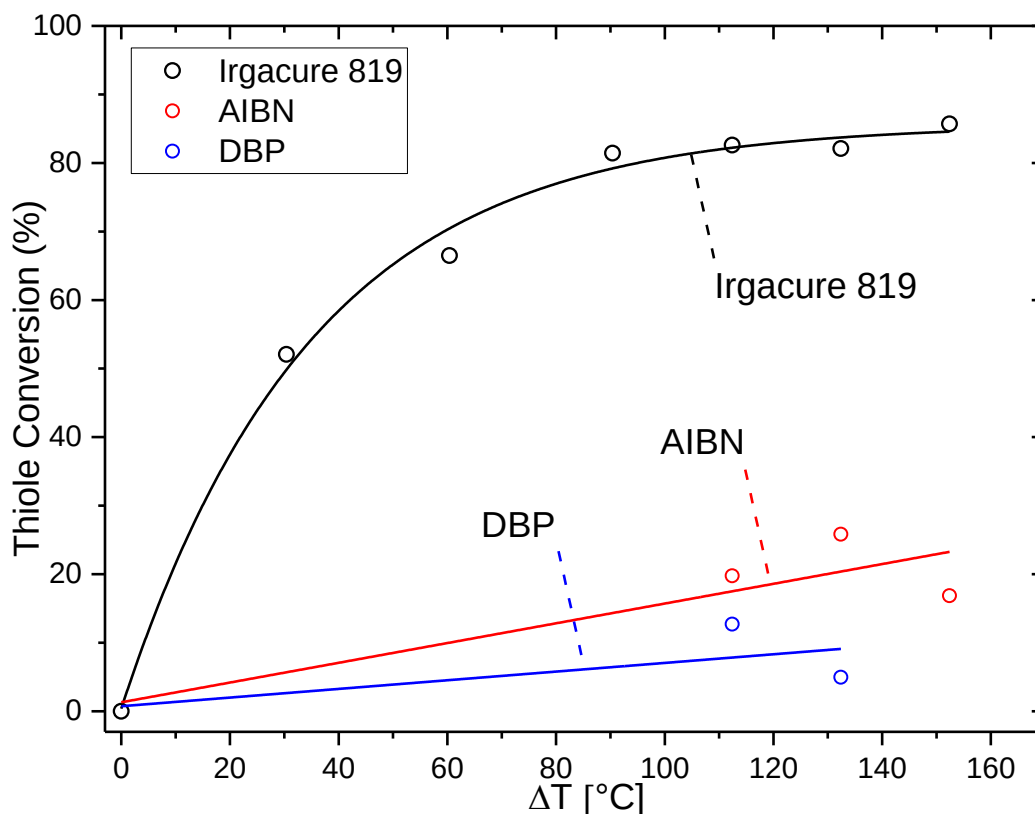


Figure 6. 18 – Thiol-ene reaction of PLC and TMP-SH with different initiators at different temperatures.

6.5.4. Comparison with Commercial Coating Materials

Direct comparisons between these materials and commercial coatings are difficult to make, mainly due to most commercial coatings being multi-component systems. The added components include pigments for colouration, binders to ensure uniformity and mixtures of solvents to control adhesion and gloss, among other additives. Moreover, coatings are tailored for a specific application and consequently suffer from individual drawbacks if they are used outside their specification. For example the structure of an anti-corrosion coating typically contains three layers (Figure 6. 19).^[41] It should be noted that each of these layers contains several chemicals.

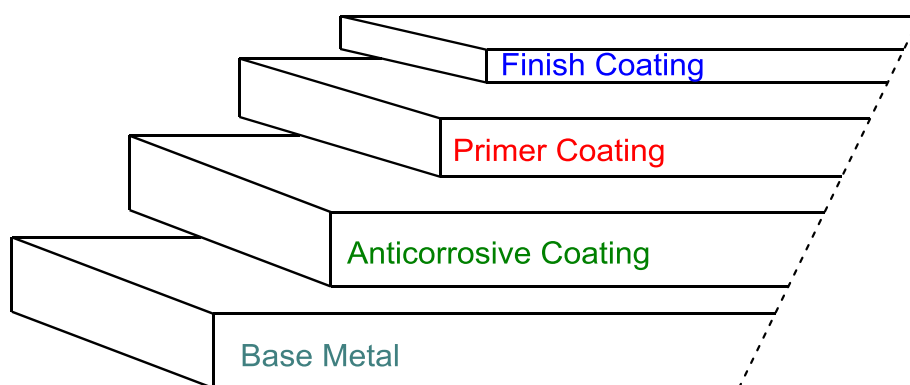


Figure 6. 19 – Example of the structure of for an anti-corrosive coating.^[41]

In contrast, here a simple two-component system was investigated. Nonetheless, the evaluation does show promising adhesion to metal (Gitterschnitt value of 5/5), good solvent resistance (no changes after 75 acetone double rubs) and hardness (2H pencil hardness, 110-160 swings for König hardness).

6.6. Summary and Outlook

Two bio-based polycarbonates, poly(limonene carbonate) and poly(cyclohexadiene carbonate), were synthesised from limonene oxide (obtainable from lemon peel) and cyclohexadiene (obtainable from vegetable oil) and CO₂.^[7, 13] The polymers were cross-linked via thiol-ene reactions with a trifunctional thiol and highly cross-linked networks were formed. The curing process was optimised by Raman spectroscopy, different polymer:thiol ratios were investigated and the material was evaluated as a future coating material. The materials showed promise as solvent and scratch-resistant coatings and further key results are summarised in Figure 6. 20.

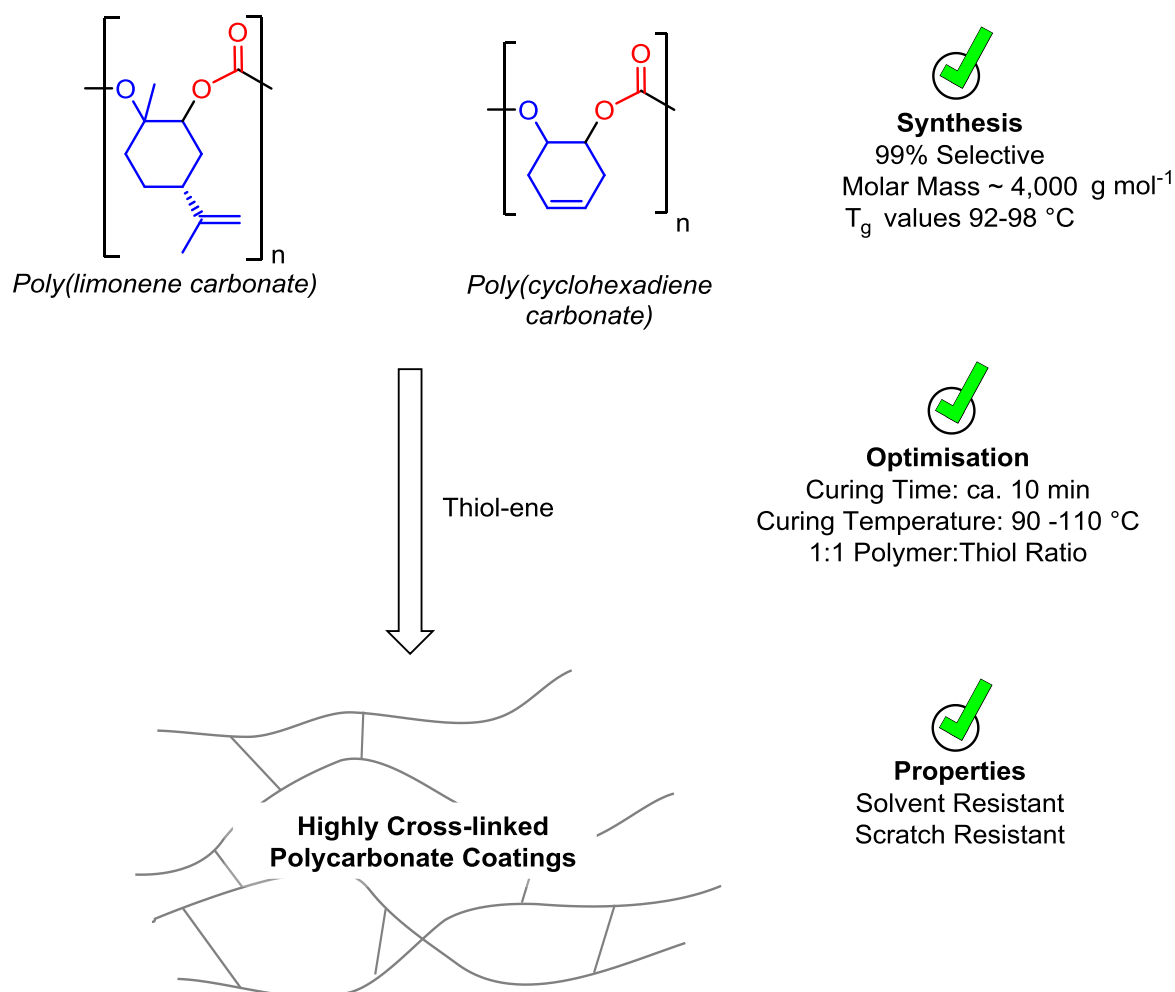


Figure 6. 20 – Key results in this chapter.

Although these are encouraging results and a first demonstration of how CO₂-based polymers could be utilised, future work in three areas should be considered.

6.6.1. Variations in Cross-Linker

A trifunctional cross-linker was used for comparability with other coatings. However, higher degrees of cross-linking may be obtained with a tetrafunctional, commercially available cross-linkers (Figure 6. 21). Other changes might address the flexibility of the cross-linker: here, an aliphatic thiol was used, which, compared to an aromatic thiol, should be more flexible. Use of more rigid cross-linkers may improve hardness or toughness of the resulting coatings.

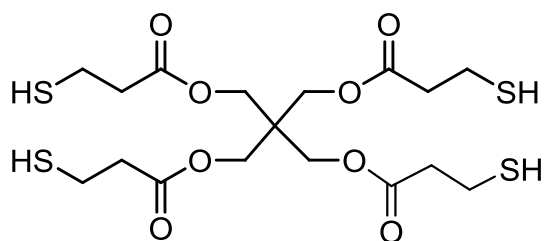


Figure 6. 21 - Pentaerythritol tetrakis(3-mercaptopropionate) as an example for a tetrafunctional, commercial curing agent.

Further changes may include the use of more sustainable solvents. So far, dichloromethane was used, which is known to be hazardous for the environment. Better solvent choices, based on environmental, health and safety (EHS) assessment and life-cycle analysis, would be methanol or ethanol.^[42]

6.6.2. Powder Coating

The selected coating technique can significantly influence the material properties of the final coating material. For protective coatings, solvent-based coatings and powder coatings are the main techniques.^[43] The first was used in this work as it is readily available, easy to use on a small scale and not associated with specialist equipment. However, improved results are generally obtained with powder coating.^[44] Powder coating is a three-step process including surface treatment (to remove dust and dirt), spraying of the powdered coating mixture and high-temperature baking as a final step (Figure 6. 22). The key difference to solvent-casting is the negative charge of the particles, which are attracted to the grounded substrate. This promotes even distribution, thickness and high adhesion.^[44, 45]

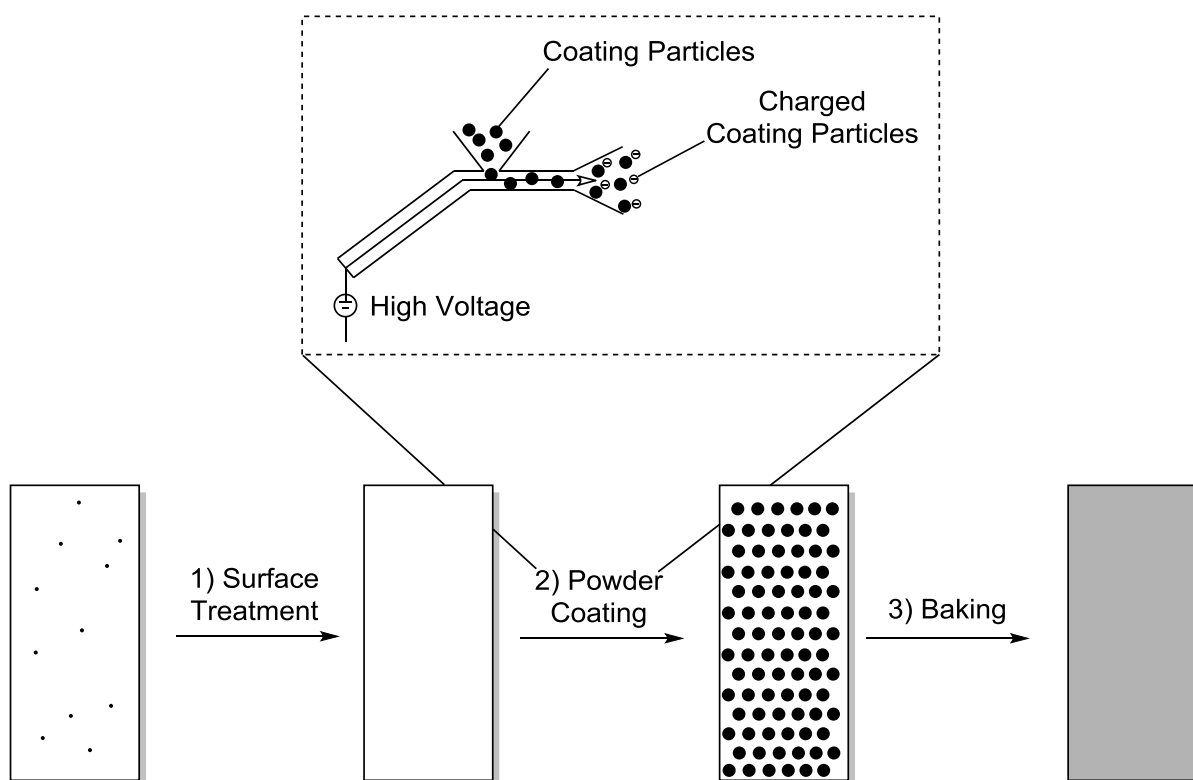


Figure 6. 22 – An illustration of powder coating.^[44]

The use of PCHDC and PLC in powder coating would allow for a better evaluation of material properties and would be a step towards further evaluation as potentially commercial coatings. Although this is an attractive technique, several additives are needed, such as flow and degassing agents as well as comparatively large amounts of polymer (ca. 30 g).^[24]

6.6.3. Additives

Finally, additives are commonly used to enhance and tailor the performance of coating materials. The use of additives would be an important step towards evaluating the full potential of these materials. Due to the range of additives available, one specific application should be targeted that benefits from the properties of the used polymers, which is a high solvent and scratch resistance. This may be useful as over varnishes to protect fridges, camera lenses and/or watches, to name only a few possible applications of these (potentially) renewable polymers.

6.7. References

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Chapter 7

New Polymerisation Catalysts
based on *ortho*-Vanillin

Preliminary Studies

7.1. Introduction

So far, two classes of ‘switch’ catalysts have been investigated, salen catalysts (chapters III-V) or dizinc catalysts (Williams and co-workers).^[1-12] A key challenge in the development of the next generation of ‘switch’ catalysts is to combine the strength of both types of catalysts, as shown in Figure 7. 1. The motivation for this chapter is to design new ‘switch’ catalysts.

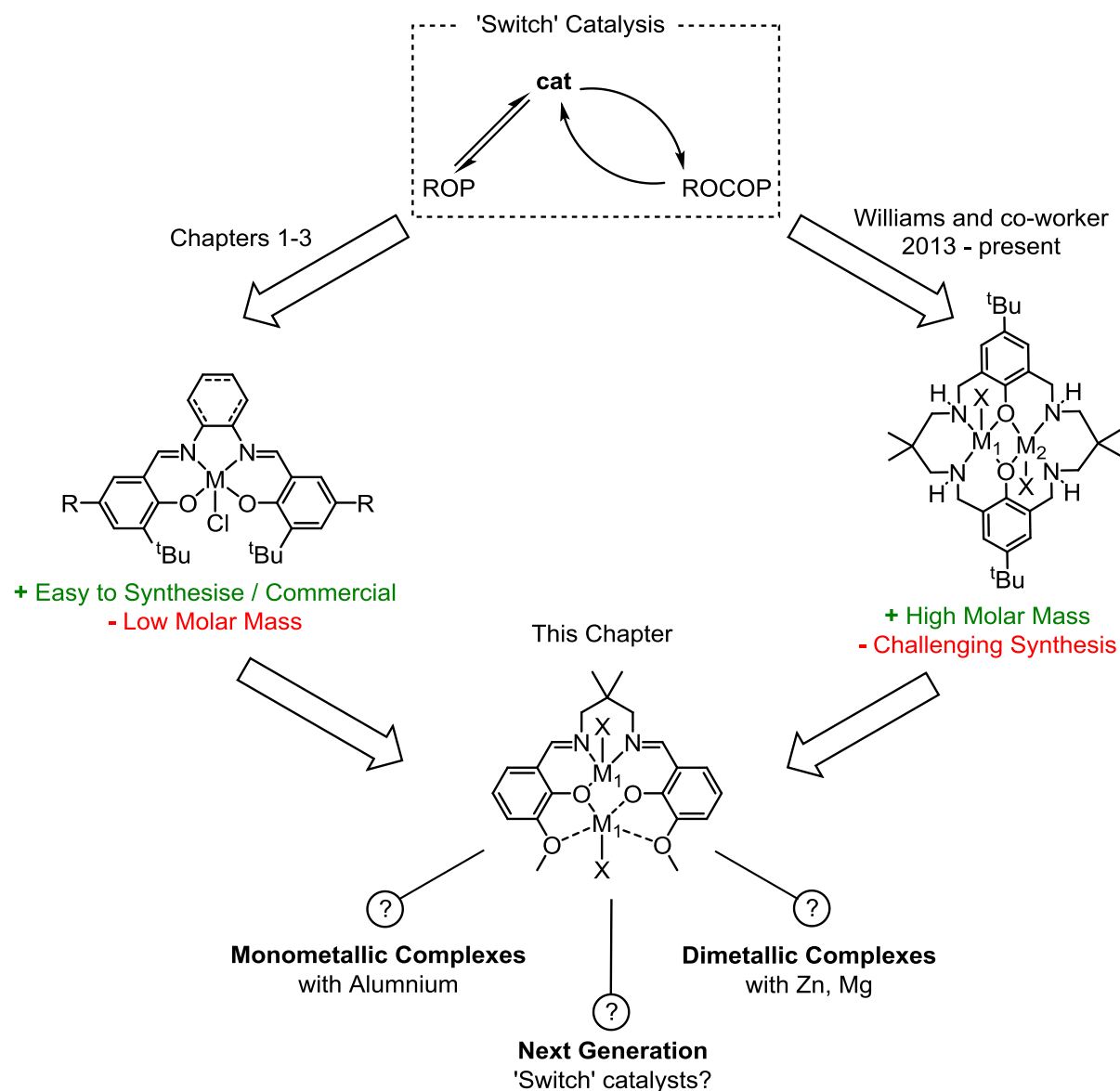
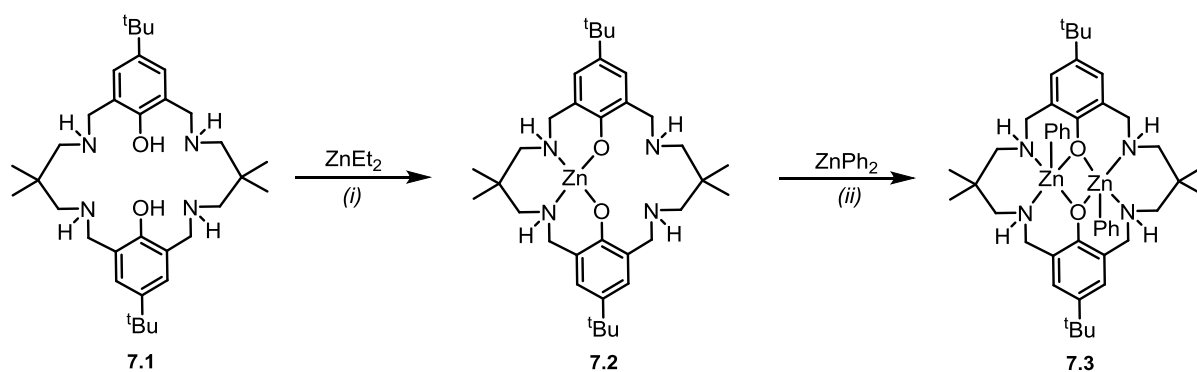


Figure 7. 1 - Development of ‘switch’ catalysis and lead questions in this chapter.

7.2. Bimetallic Zinc and Magnesium Catalysts

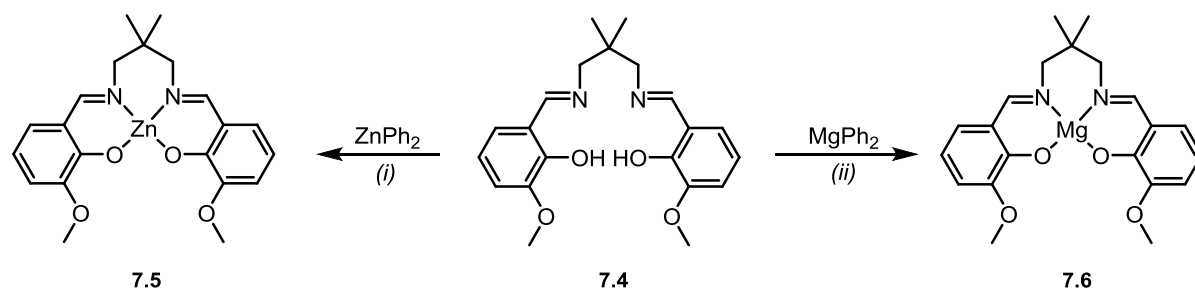
7.2.1. Mono-Zinc and Mono-Magnesium Complexes

Bimetallic complexes featuring initiating groups reactive towards alcoholysis are the synthetic target for this section. This target was inspired by: (i) high performances of dizinc catalysts for ROCOP and ROP and (ii) the ability to modify the initiating groups without the need for excessive amounts of chain-transfer agent.^[3, 13] Both of these features were recently combined in dizinc catalyst **7.3**, which was synthesised by reaction between diphenyl zinc and the protio-ligand **7.1**.^[14, 15] In a related study, the formation of mono-zinc complex **7.2** was reported by using one equivalent of diethyl zinc, and is likely an intermediate in the synthesis of **7.3**.^[15, 16]



Scheme 7. 1 – Synthesis of mono-zinc complex **7.2** and dizinc complex **7.3**. Conditions: (i) 1 equiv. ZnEt_2 , THF, -78°C , 14 h; (ii) 2 equiv. ZnPh_2 (relative to **7.1**), THF, RT, 14 h.^[15, 16]

Following the same synthetic route, the synthesis of the corresponding mono-zinc and mono-magnesium complexes, **7.5** and **7.6**, respectively, was attempted (Scheme 7. 2). Protio-ligand **7.4** was reacted with one equivalent of diphenyl zinc or diphenyl magnesium, at room temperature in THF, and full conversions were observed within minutes, as determined by ^1H NMR spectroscopy. The products were further identified by X-Ray diffraction (Figure 7. 4).



Scheme 7. 2 – Synthesis of mono-zinc complex **7.5** and mono-magnesium complex **7.6**. Conditions: (i) 1 equiv. ZnPh_2 , THF, RT, 14 h; (ii) 1 equiv. MgPh_2 , THF, RT, 14 h.

The molecular structure of **7.5** is a centrosymmetric dimer of the expected mononuclear complex (Figure 7. 2). The zinc centres were pentacoordinated by the two nitrogen atoms and two phenolic oxygen atoms of the ‘closed’ pocket of the ligand (N1, N2, O2, O3); phenolic oxygen atom O2 was shared by the neighbouring zinc centre. Each zinc centre had a τ value of 0.53 indicating a distorted trigonal bipyramidal geometry. The zinc-zinc distance of 3.1218(4) Å, which was longer than dizinc catalysts featuring a bridging acetate co-ligand based on the same ligand (~ 2.9 Å) but in line with other dinuclear catalysts (~ 3.0-3.1 Å).^[1, 17]

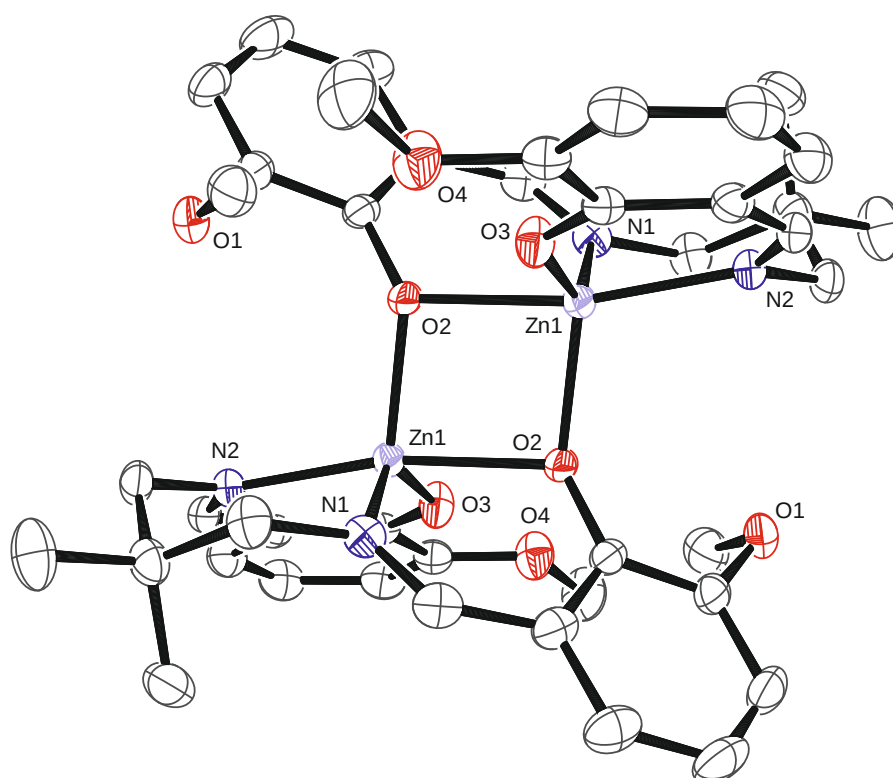


Figure 7. 2 – Molecular structure of **7.5** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 7. 1 - Selected bond lengths and angles for **7.5**.

Bond	Bond length [Å]	Bond	Bond Angle [°]
Zn1-O2	2.010(1)	N2-Zn1-O2	168.71(5)
Zn1-Zn1	3.1218(4)	O3-Zn1-N1	136.66(5)
Zn1-N1	2.098(1)	N1-Zn1-O3	136.66(5)
Zn1-N2	2.074(1)	O2-Zn1-N1	101.75(5)
Zn1-O3	1.957(1)	O2-Zn1-O3	118.25(5)

The molecular structure of **7.6** is a trimer containing three ligands and the magnesium atoms. All magnesium centres were hexacoordinated by two nitrogen and two oxygen atoms from the ‘closed’ N,N,O,O pocket of the ligand, one oxygen atom from a methoxy group and a bridging oxygen atom from a the neighbouring ligand. The magnesium-magnesium distances were 3.236(2) Å (Mg1-Mg2) and 3.225(2) Å (Mg2-Mg3), which were longer than in related dimagnesium complexes (~ 2.8 – 3.1 Å).^[18, 19] These differences may be ascribed to the steric repulsion between the three ligands in **7.6**.

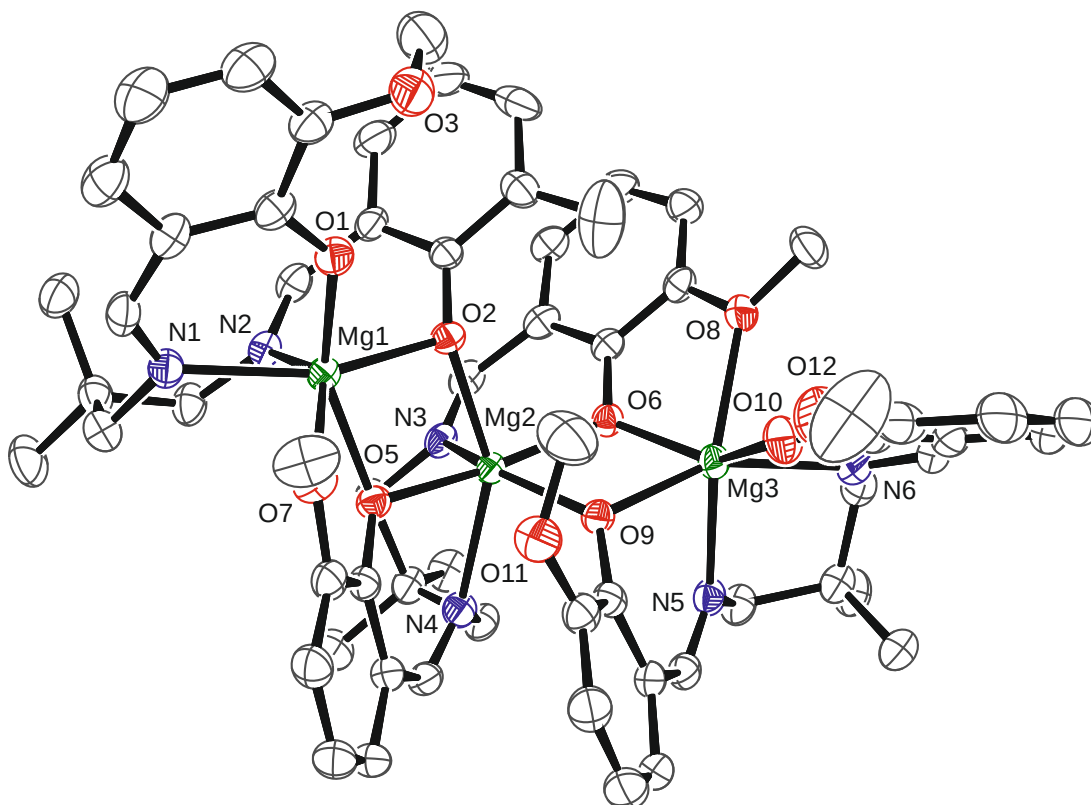


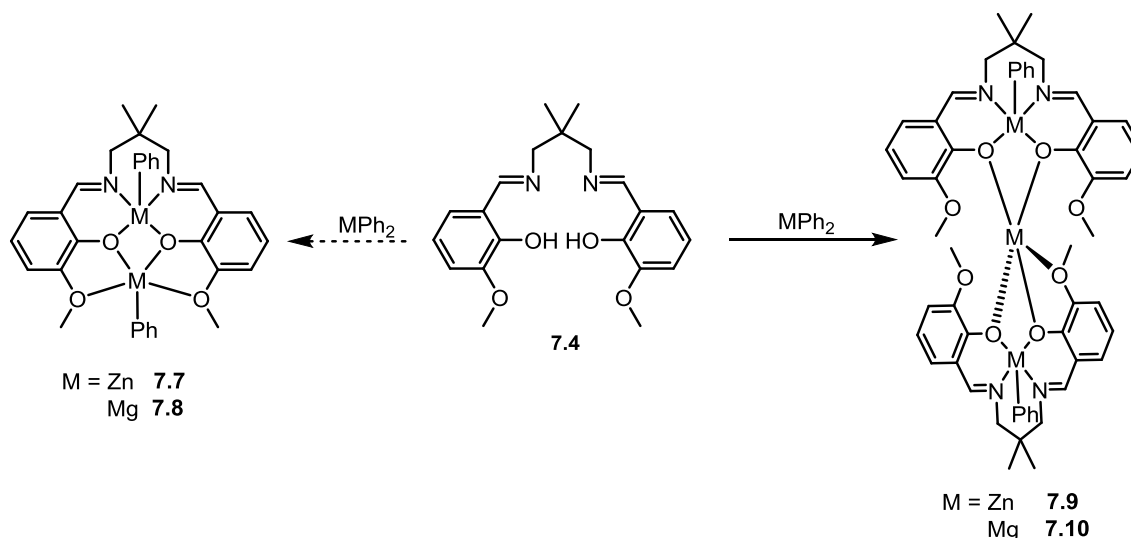
Figure 7. 3 – Molecular structure of magnesium complex **7.6** at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 7. 2 - Selected bond lengths and angles for **7.6**.

Bond	Bond length [Å]	Bond	Bond Angle [°]
Mg2-O5	2.056(3)	O2-Mg2-N4	151.4(1)
Mg2-O9	2.080(3)	O9-Mg2-N3	149.5(1)
Mg2-O6	2.073(3)	O6-Mg2-O5	170.7(1)
Mg2-O2	2.102(3)	N3-Mg2-O5	106.8(1)
Mg2-N3	2.250(3)		
Mg2-N4	2.248(3)		

7.2.2. Dimeric Zinc and Magnesium Complexes

Next, the synthesis of dizinc and dimagnesium complexes featuring phenyl co-ligands, **7.7** and **7.8**, was attempted (Scheme 7.3). Instead of the expected dimetallic species, dimerization to **7.9** and **7.10** was found by XRD.



Scheme 7.3 – Attempted synthesis of dimetallic complexes **7.7** and **7.8** and representative structure of obtained trimetallic complexes **7.9** and **7.10**. Conditions: THF, RT, 2 equiv. ZnPh_2 or MgPh_2 .

The molecular structure of **7.9** was a dimer containing two ligands, three zinc centres and two phenyl co-ligands (Figure 7.4, Table 7.3). All zinc centres were pentacoordinated; Zn1 was coordinated in the ‘closed’ pocket by two nitrogen atoms, N1 and N2, two phenolic oxygen atoms, O2 and O3 and by the carbon atom, C22, of the phenyl co-ligand. A τ value of 0.05 indicated a square pyramidal geometry. Zn2 was coordinated by four phenolic oxygen atoms, two from each ligand (O2, O3, O6, O7), and oxygen atom O5 from a methoxy substituent. A τ value of 0.15 suggested a distorted square based pyramidal geometry. The other oxygen atoms, from the methoxy substituents, were not coordinated to Zn2. Zn3 is pentacoordinated in the ‘closed’ pocket containing two phenolic oxygen atoms, O6 and O7, two nitrogen atoms, N3 and N4, and one carbon, C81, from the phenyl co-ligand. A τ value of 0.45 suggested a distorted square-pyramidal geometry. It should be noted that two structures were found in the solid state, one featuring the expected phenyl co-ligand at C81 and a second with a zinc-chloride instead of a zinc-phenyl bond (see appendix). ZnCl_2 or ZnPhCl might have been a minor impurity in ZnPh_2 .

The $\text{Zn1} \cdots \text{Zn2}$ distance is 3.2485(4) and $\text{Zn2} \cdots \text{Zn3}$ distance was 3.2593(4) Å, which was longer by ~ 0.25 Å than related biszinc complexes with the same ligand (~ 2.95 Å) and $\sim$

0.15 Å longer than dinuclear catalyst **7.3** (3.0394(4) Å).^[14] This might be a result of steric and electronic repulsion, particularly around Zn2, but is within the expected range for trizinc complexes bridged by oxygen atoms.^a

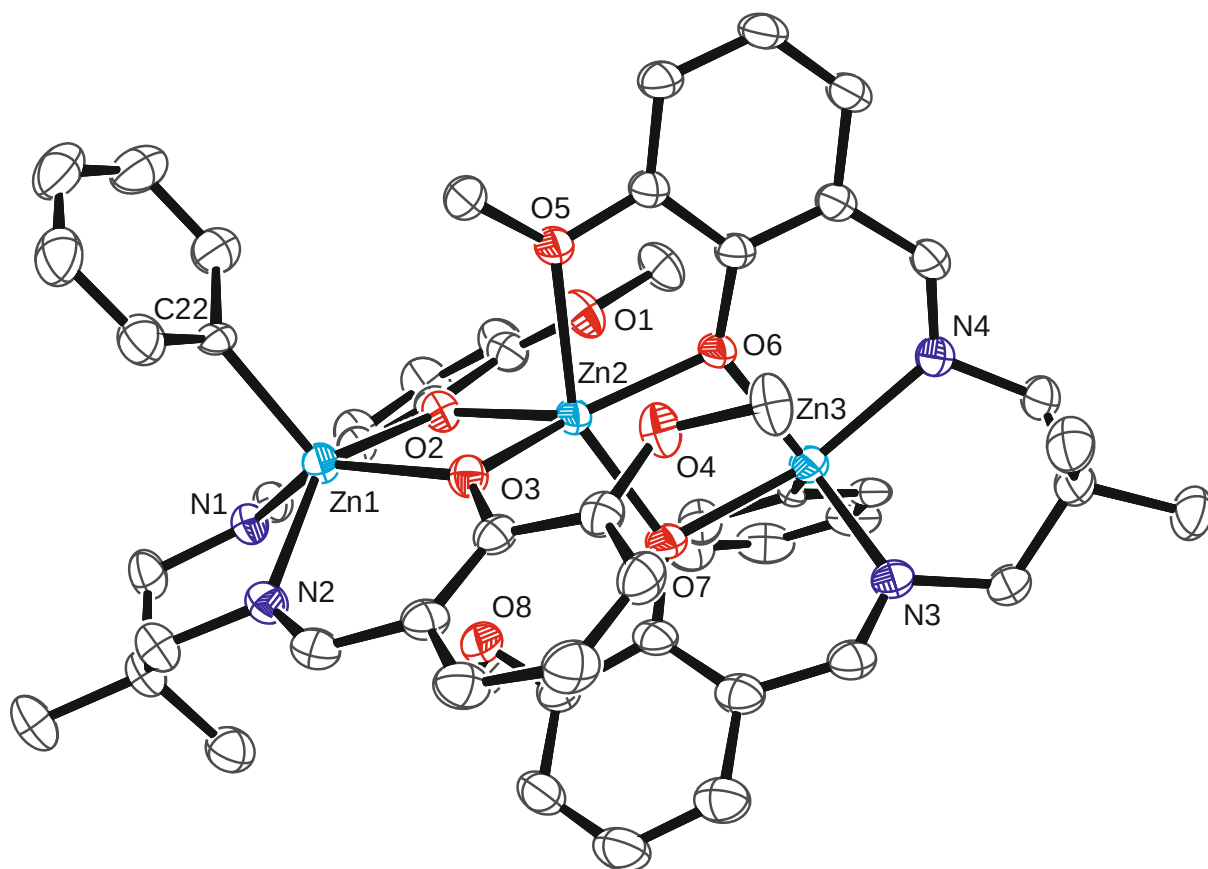


Figure 7. 4 – Molecular structure of **7.9** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

The solid-state structure of trimagnesium complex **7.10** was similar to **7.9** and contained two ligands, three magnesium centres, and two phenyl co-ligands (Figure 7. 5, Table 7. 3)). Mg2 and Mg3 were pentacoordinated in the ‘closed’ N,N,O,O-pocket of each ligand and the phenolic oxygen atoms were shared between Mg2 and Mg1 and Mg3 and Mg1. For Mg2 and Mg3, τ values of 0.42 (Mg2) and 0.01 (Mg3) were obtained indicating distorted square pyramidal geometries for both magnesium centres. Mg2 was heptacoordinated in a distorted trigonal bipyramidal geometry by four phenol oxygen atoms (O2, O3, O6, O7) and three oxygen atoms from the methoxy substituents (O1, O5, O8). The magnesium-magnesium distances were 3.1651(9) and 3.142(1) Å for Mg1···Mg2 and Mg1···Mg3, respectively, which was ~0.1 Å shorter than the mono-magnesium complex **7.6** and comparable to other dimetallic

^a Based on statistical analysis from CCDC data base from 214 structures (mean: 2.819 ± 0.126 Å; lower quantile: 2.989 Å and minimum: 2.819 Å; upper quantile: 3.161 Å and maximum: 3.418 Å). Used search fragment shown in appendix; accessed: 17/02/2018.

complexes. Similar to trizinc complex **7.9**, a second structure was found with chloro instead of phenyl co-ligands, which may indicate the contamination of the sample with trace amounts of chlorinated solvents (see appendix).

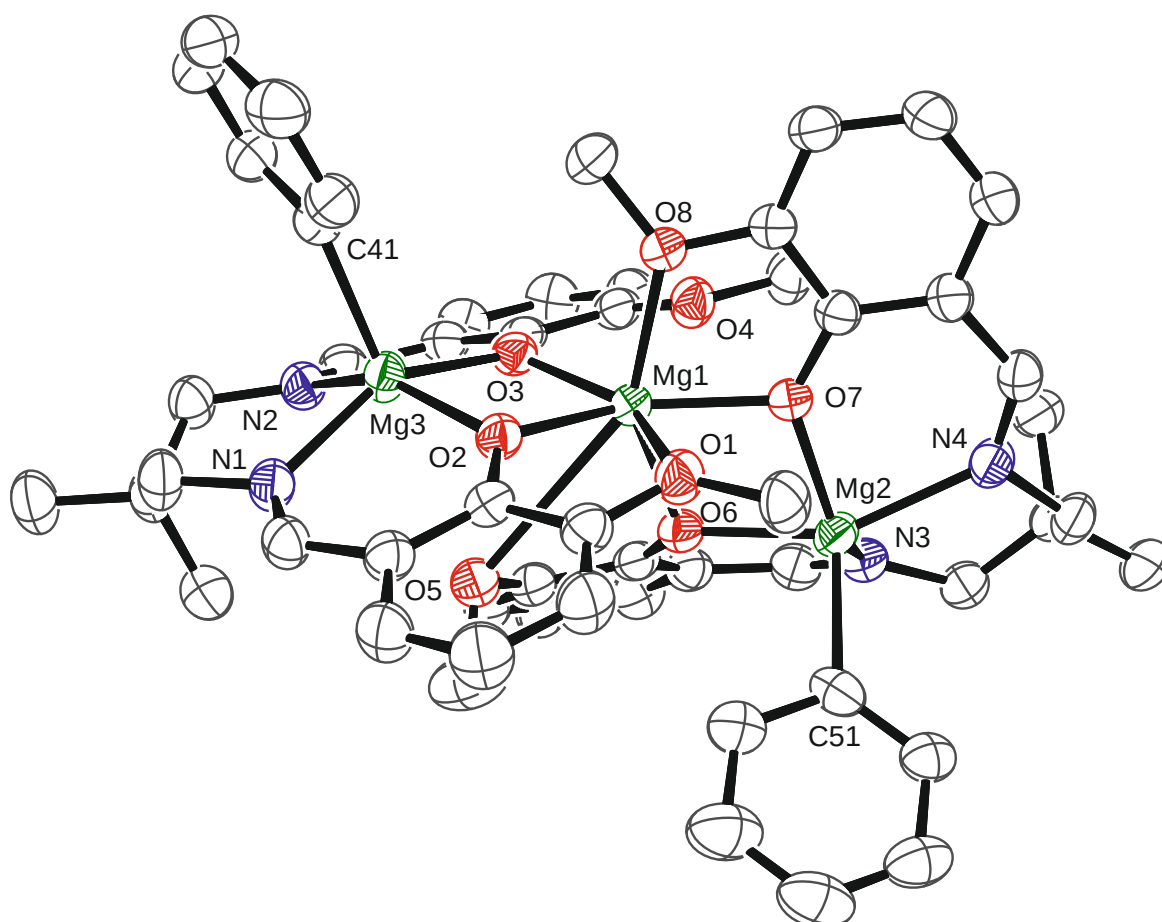


Figure 7. 5 – Molecular structure of **7.10** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

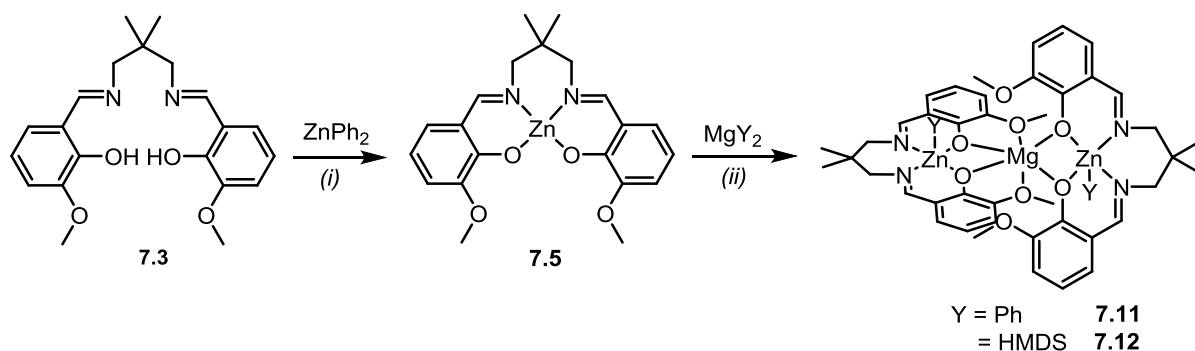
Table 7. 3 - Selected bond lengths and angles for **7.9** and **7.10**.

Complex	Bond	Bond length [Å]	Bond	Bond Angle [°]
7.9	Zn01-O2	2.167(1)	N2-Zn01-O2	142.68(6)
	Zn02-O2	2.009(1)	N1-Zn01-O3	139.88(6)
	Zn01-O3	2.101(1)	O7-Zn02-O5	150.33(6)
	Zn02-O3	2.029(1)	O3-Zn02-O6	141.39(6)
	Zn02-O6	2.016(2)	O7-Zn03-N4	149.18(7)
	Zn02-O7	2.036(1)	O6-Zn03-N3	122.06(7)
7.10	Mg1-O6	2.061(1)	N4-Mg2-O6	152.85(8)
	Mg1-O2	2.042(1)	O7-Mg2-N3	127.82(7)
	Mg1-O3	2.034(2)	O3-Mg3-N1	149.58(8)
	Mg1-O8	2.184(2)	N2-Mg3-O2	149.91(8)
	Mg1-O7	2.025(2)		

7.2.3. Heterobimetallic Complexes

So far, the targeted bimetallic complexes were not obtained and dimerization to bimetallic complexes was found instead. Although this was an undesired side-product, the structural motif might enable the synthesis of heterotrimetallic complexes of the type $M_1-M_2-M_1$. More generally, heterobimetallic complexes showed enhanced polymerisation activities for ROCOP compared to their monometallic analogues.^[3]

The synthesis of trimetallic complexes was attempted in a two-step approach in which the mono-zinc complex was formed first, in THF, and 0.5 equivalents of the magnesium reagent were added in CHCl_3 (Scheme 7. 4). The magnesium was proposed to (i) incorporate between the two ligands and (ii) provide a co-ligand for the zinc centres in the ‘closed pocket’.



Scheme 7. 4 – Synthesis of heterobimetallic complexes. Conditions: (i) ZnPh_2 (1.0 equiv.), THF, RT, 16 h, (ii) MgY_2 (0.5 equiv.), CHCl_3 , RT, 16 h.

This hypothesis was tested by reacting mono-zinc complex **7.5** with either diphenyl magnesium or magnesium bis(hexamethyldisilazide). In both cases, rather complex ^1H NMR spectra were obtained but the products were identified by XRD.

The molecular structure of **7.11** was a dimer containing two ligands, three central metals (two zinc and one magnesium atoms) and two phenyl co-ligands (Figure 7. 6). Both Zn1 and Zn2 were pentacoordinated in the ‘closed’ O,O,N,N pocket and by one carbon atom from the phenyl co-ligand. τ values of 0.06 (Zn1) and 0.44 (Zn2) suggested distorted square pyramidal coordination geometries. The distance between the metals was 3.2771(7) (Mg1...Zn2) and 3.2715(8) (Mg1...Zn1). Mg1 was heptacoordinated by four phenolic and three methoxy substituents and adopted a distorted pentagonal bipyramidal geometry.

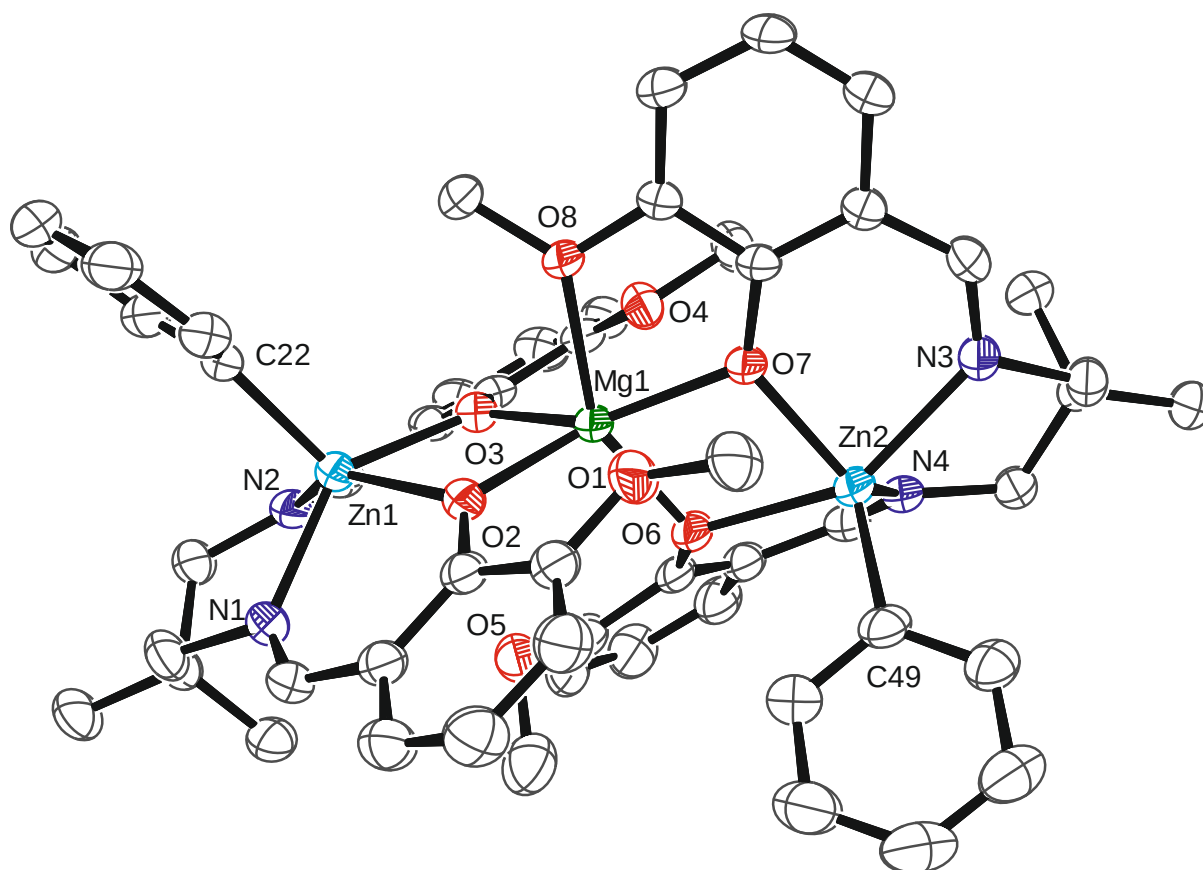


Figure 7. 6 – Molecular structure of **7.11** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

A similar structure was found for **7.12** and contained two ligands, three metal centres (Zn1, Zn2, Mg1) and two amide co-ligands (Figure 7. 7, Table 7. 4). Zn1 and Zn2 were pentacoordinated in the ‘closed’ pockets of the ligands and one nitrogen atom from the amide co-ligand. τ values of 0.40 (Zn1 and Zn2) indicated a distorted square-pyramidal coordination at the zinc centres. Mg1 was hexacoordinated by four phenolic (O2, O3, O6, O8) and two methoxy oxygen atoms (O1 and O8). The zinc-magnesium distances were 3.255(2) and 3.226(2) Å for Mg1 $\cdots$ Zn1 and Mg1 $\cdots$ Zn2, respectively, which was longer by ca. 0.1 Å than other heterobimetallic complexes, which were bridged by oxygen-donors (~ 3.1 Å).^[20, 21]

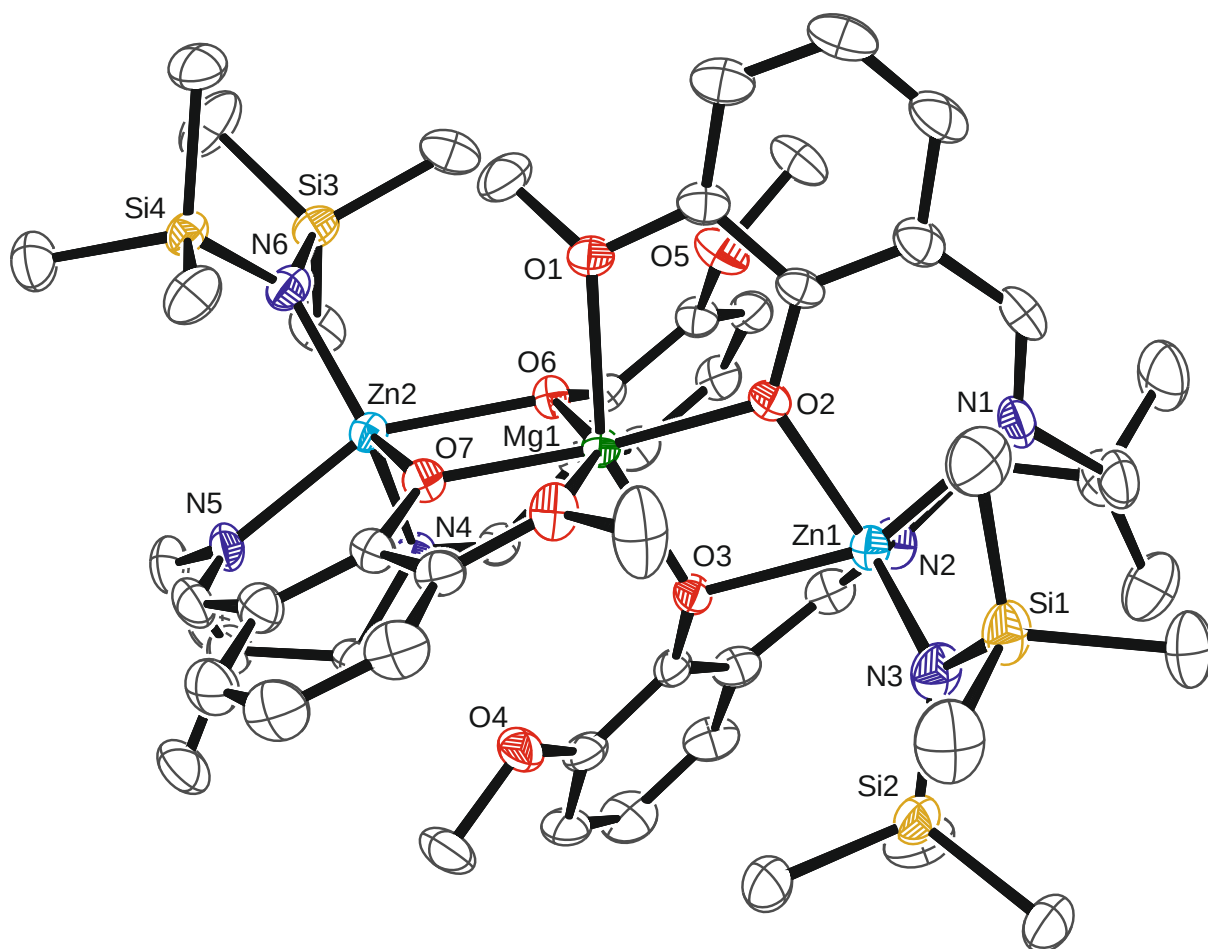


Figure 7. 7 – Molecular structure of **7.12** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

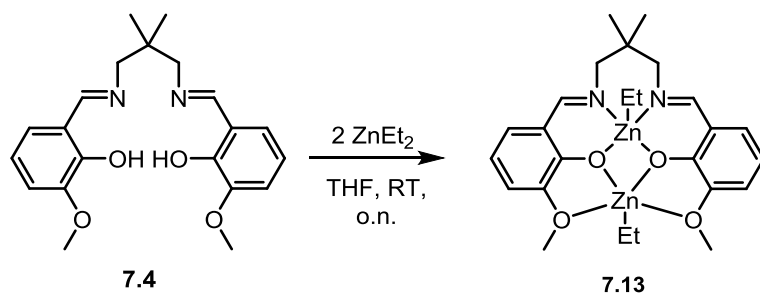
Table 7. 4 - Selected bond lengths and angles for **7.11** and **7.12**.

Complex	Bond	Bond length [Å]	Bond	Bond Angle [°]
7.11	Mg1-O1	2.685(2)	N3-Zn2-O6	148.44(6)
	Mg1-O2	2.027(2)	O7-Zn2-C49	122.31(8)
	Mg1-O3	2.037(2)	N2-Zn1-O2	142.93(6)
	Mg1-O4	2.559(2)	N1-Zn1-O3	139.33(7)
	Mg1-O6	2.022(2)		
	Mg1-O7	2.033(2)		
7.12	Mg1 O1	2.237(5)	O3-Zn1-N1	150.0(2)
	Mg1 O2	2.024(4)	N2-Zn1-N3	126.1(2)
	Mg1 O3	2.035(4)	O6-Zn2-N5	151.3(2)
	Mg1 O6	2.021(4)	N4-Zn2-N6	127.1(2)
	Mg1 O7	2.029(4)		
	Mg1 O8	2.243(5)		

7.3. Synthesis and Reactivity of Monomeric Dizinc Bis(ethyl) Complex 7.13

7.3.1. Synthesis

Although dimers were formed in the reaction of protio-ligand **7.4** with organometallic zinc or magnesium reagents, the reaction of **7.4** with two equivalents of diethyl zinc resulted in the formation of dizinc bis(ethyl) complex **7.13** (Scheme 7. 5).



Scheme 7. 5 – Synthesis of dizinc bis(ethyl) complex **7.13**.

Dizinc complex **7.13** was characterised by ^1H and ^{13}C NMR spectroscopy, elemental analysis and XRD. In the solid state, both zinc centres are pentacoordinated; Zn1 was coordinated by N1, N2, O2 and O3 in the ‘closed’ pocket and C22 from the ethyl co-ligand and showed a τ value of 0.11 consistent with a distorted square planar coordination geometry (Zn1). Phenolic oxygen atoms O1 and O3 were shared between Zn1 and Zn2, and Zn2 was further coordinated by O1 and O4 from the methoxy substituents and C24 from the ethyl co-ligand. A τ value of 0.01 indicated a square-planar geometry around Zn2. The Zn1...Zn2 distance was 3.1124(6) Å, which was slightly longer than other dizinc complexes (~ 3.0 Å) and shorter than trizinc complex **7.9** (~ 3.2 Å). The ligand is slightly bent into a ‘roof-like’ conformation and the planes formed by the benzene moieties intersected at 83.36°.

Although the complex is C_1 -symmetric in the solid state, characterisation in the solution state was consistent with C_s symmetry (chapter 9). This might indicate the presence of different conformers, which rapidly interchange on the NMR time scale.

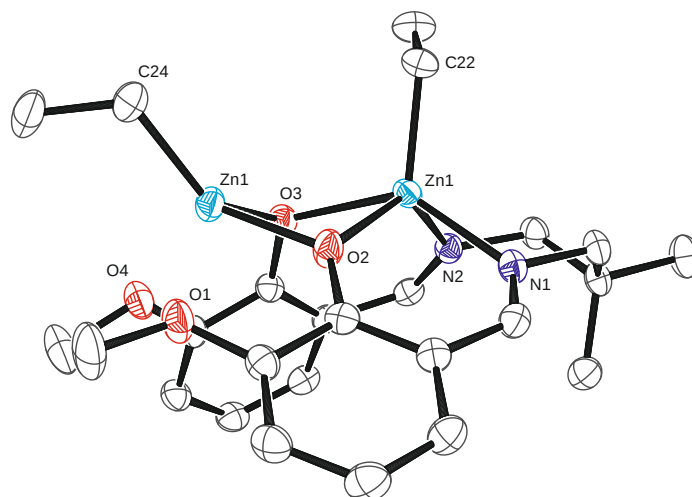


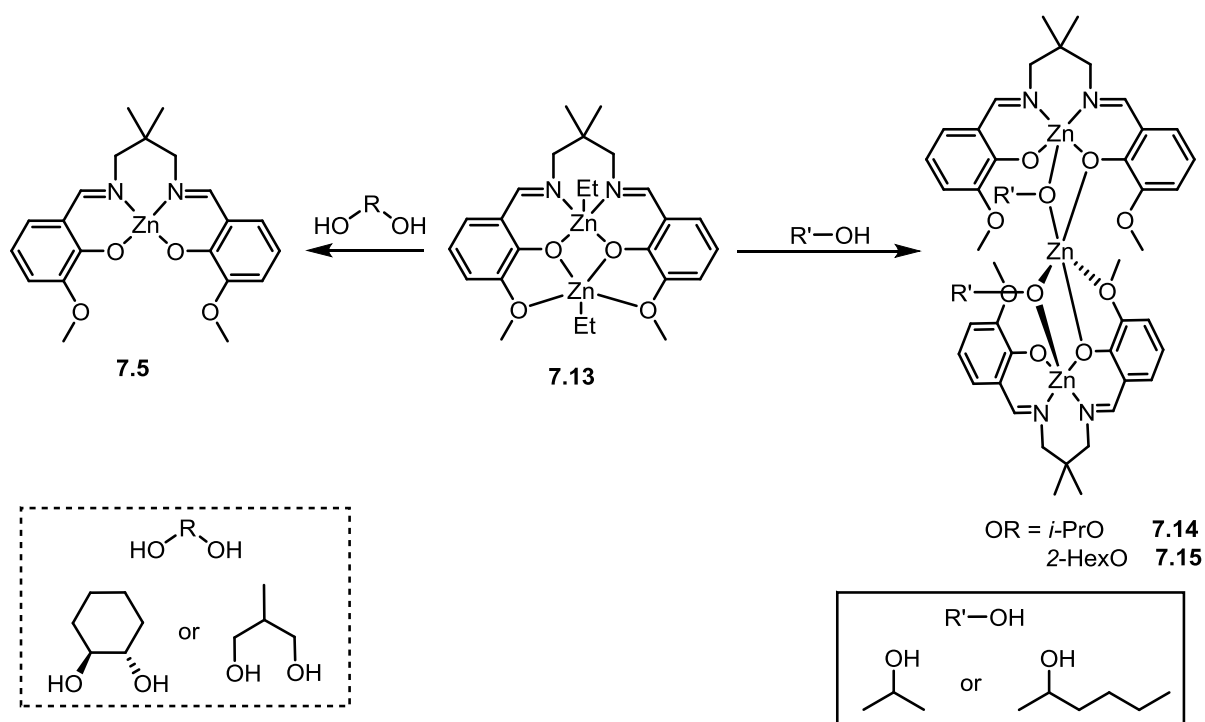
Figure 7. 8 – Molecular structure of **7.13** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 7. 5 - Selected bond lengths and angles for **7.13**.

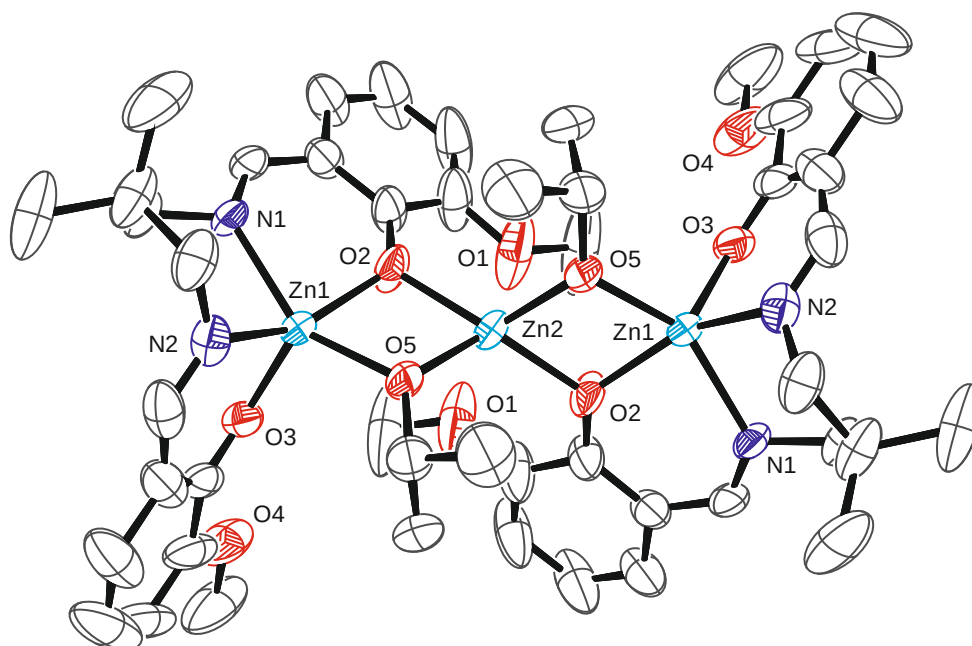
Bond	Bond length [Å]	Bond	Bond Angle [°]
Zn1-O2	2.131(2)	O2-Zn1-N2	130.38(6)
Zn1-O3	2.177(2)	N1-Zn1-O3	137.26(6)
Zn2-O1	2.494(2)	C24-Zn2-O3	130.67(8)
Zn2-O2	2.010(2)	C24-Zn2-O2	129.85(9)
Zn2-O3	2.041(2)		
Zn2-O4	2.269(2)		

7.3.2. Reaction with Alcohols

Dizinc bis(ethyl) complex **7.13** was reacted with alcohols in order to model the initiation step of any polymerisation (Scheme 7. 6). When **7.13** was reacted with *trans*-cyclohexanediol or 2-methyl-1,3-propanediol (MPD), the formation of mono-zinc complex **7.5** was observed within minutes at room temperature (Scheme 7. 6, left). This may be a consequence of the shorter distance between the oxygen atoms of 2.822(1) Å for CHD (based on XRD) and the longer distance of 3.498 Å for MPD (based on force-field geometry optimisation), compared to the Zn1...Zn2 distance of ~ 3.1 Å.^[23] Iso-propanol was tested next, as this steric limitation may not be given for a monofunctional alcohol. Interestingly, complex ¹H NMR spectra were obtained but a product was identified by XRD as a bridged dimer (Scheme 7. 6, right).

Scheme 7. 6 – Reaction of bis(ethyl) dizinc complex **7.13** with alcohols.

The molecular structure of **7.14** is a dimer containing three zinc centres and two bridging alcohol co-ligands (Figure 7. 9). Zn1 was pentacoordinated in the ‘closed’ pocket of the ligand (N1, N2, O2, O5) and O5 from one *iso*-propanol co-ligand. Phenolic oxygens O2 were shared between Zn1 and Zn2. Zn2 was hexacoordinated by O2, O1 and O5 from bridging *iso*-propanol units. The Zn1...Zn2 distance was 3.1144 Å and comparable to **7.9**.

Figure 7. 9 – Molecular structure of **7.14** with thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity.

If *iso*-propanol was replaced with sterically more hindered 2-hexanol, **7.15** was obtained. The molecular structure is similar to that of **7.14** (Figure 7. 10): the structure contains two ligands, three zinc centres and two bridging hexanol units. Zn1 is pentacoordinated in the ‘closed’ pocket (N1, N2, O2, O5) and O5 from the hexanol co-ligand; a τ value of 0.09 indicated a distorted square pyramidal geometry at Zn1. Zn2 is hexacoordinated by two phenol oxygen atoms (O2), two methoxy oxygen atoms (O1) and two oxygen atoms from the hexanol co-ligand (O5); the Zn1...Zn2 distance is 3.0987 Å, which is similar to trimetallic complexes **7.9** and **7.14**.

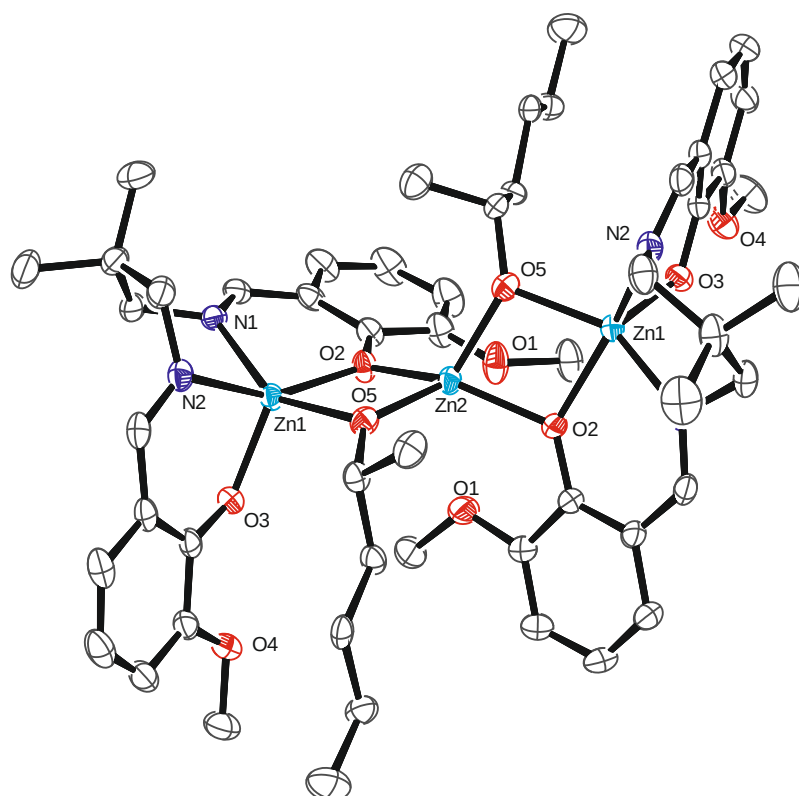


Figure 7. 10 – Molecular structure of **7.15** with thermal ellipsoids at the 25% probability level. Hydrogen atoms are omitted for clarity.

Table 7. 6 – Selected bond lengths and angles of **7.14** and **7.15**.

Complex	Bond	Bond length [Å]	Bond	Bond Angle [°]
7.14	Zn1-O2	2.064(3)	N1-Zn01-O5	147.6(1)
	Zn1-O5	1.999(2)	O2-Zn01-N2	152.1(1)
	Zn2-O1	2.539	O2-Zn01-O3	117.4(1)
	Zn2-O2	1.995	O5-Zn02-O5	113.2
	Zn2-O5	1.961	O2-Zn02-O2	145.1
7.15	Zn01 O2	2.063(1)	O5A Zn01 N1	148.5(3)
	Zn01 O5	2.03(2)	O2 Zn01 N2	153.90(8)
	Zn02 O2	1.989	O5A Zn02 O2	80.3
	Zn02 O5	1.94	O5A Zn02 O1	144.2

Next, the amount of CTA was optimised and varied between zero and ten equivalents (Figure 7. 12). Surprisingly, full monomer consumption was observed even in the absence of chain-transfer agent, although somewhat broad distributions were obtained ($M_n=56,100$ g mol⁻¹, $\bar{D}=1.43$). This might indicate the presence of alcohol as an impurity in the monomers from partial hydrolysis, which has been reported previously in ROCOP.^[24-26] A significant decrease in dispersity was found for two equivalents of CHD and masses over 20,000 g mol⁻¹ were obtained within 22 hours ($M_n=22,400$ g mol⁻¹, $\bar{D}=1.23$). Larger amounts of CTA resulted in lower molar masses, as expected, but did not affect dispersity.

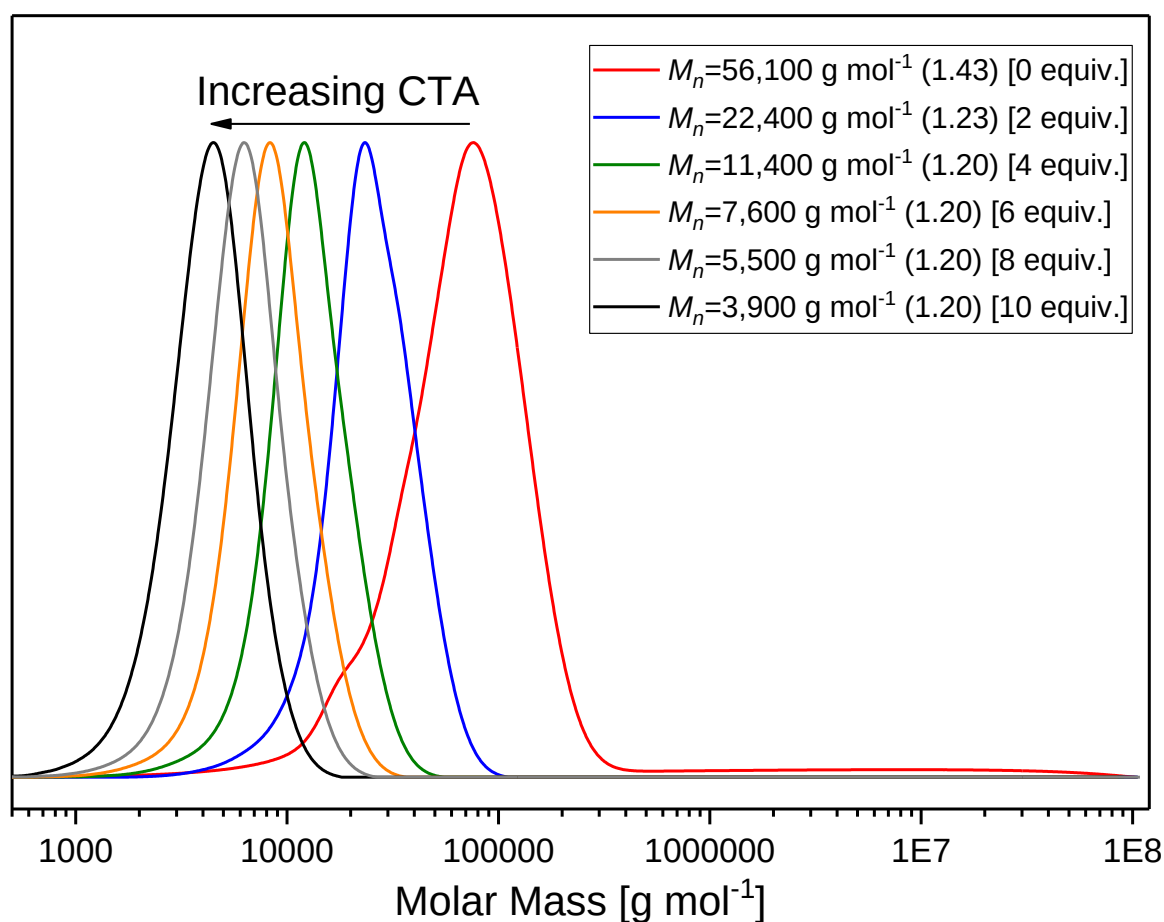


Figure 7. 12 - GPC traces for the one-pot reaction of PA, CHO, DL with different amounts of CTA (only UV detector shown). Conditions: [PA]:[CHO]:[DL]:[CHD]:[7.13]=100:200:100:(0-10):1, 100 °C.

This was an encouraging result as slightly higher molar masses were observed compared to previous ‘switch’ systems and in less than 24 hours. To gain further insight into the proposed formation of block copolymers, the reaction was monitored with addition of two equivalents of CTA (Figure 7. 13, left). Surprisingly, multiple peaks were found at short reaction times (during ROCOP), which merged over time until a monomodal GPC trace was found at full conversion ($M_n=22,400$ g mol⁻¹, $\bar{D}=1.23$). Similar findings were made with up to eight

equivalents of CTA (see appendix). Although further analysis is necessary to understand the formation of these different polymeric species, these observations may indicate: (i) the presence of different alcohols in the feedstock resulting in slow initiation (*i. e.* primary, secondary and/or tertiary) and/or (ii) the slow reaction (initiation) of zinc-ethyl bonds in **7.13** with alcohols under polymerisation conditions. A similar observation was made recently for related macrocyclic dizinc catalysts and could be overcome using zinc-amide species.^[13] The synthesis of the analogous amide complex was attempted, but a dimer was identified as the reaction product by XRD (not shown).

Nonetheless, by the addition of ten equivalents of CHD narrow, monomodal GPC traces were detected throughout the reaction by UV analysis, which continuously increased in mass as reaction proceeded (Figure 7. 13, right). This indicated the formation of block copolymers.

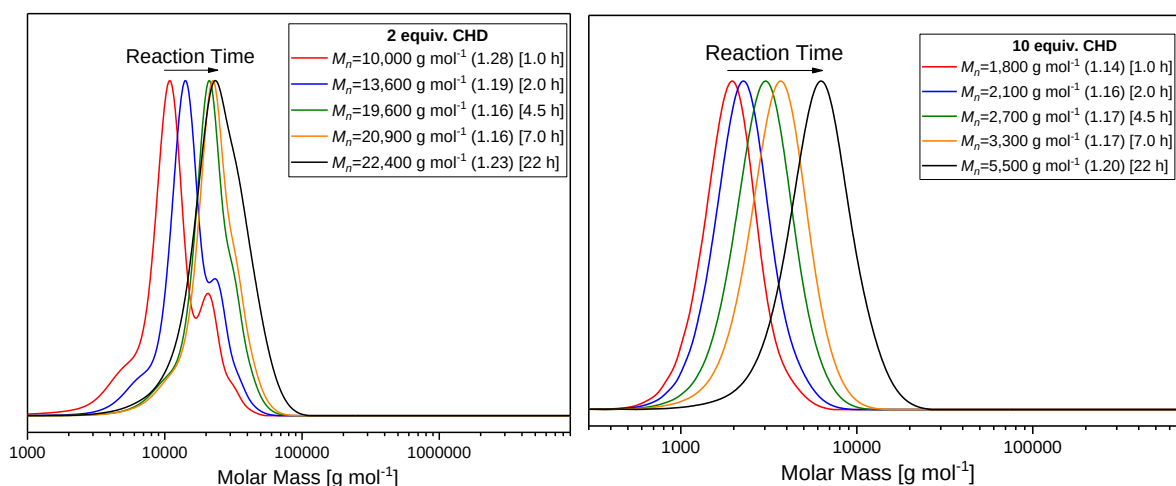


Figure 7. 13 - GPC traces at different times for the one-pot reaction of PA, CHO, DL at different times (only UV detector shown). Conditions: [PA]:[CHO]:[DL]:[CHD]:[**7.13**]=100:200:100:2-10:1, 100 °C.

The effect of CTA on the rates in ‘switch’ catalysis was further investigated by ¹H NMR spectroscopy (Figure 7. 14). PA/CHO ROCOP was fast, with TOFs $\geq 100 \text{ h}^{-1}$, and was complete within one hour (time of first aliquot), regardless of the amount of CTA. More data points were obtained for DL ROP and the rate was significantly decreased with increasing amounts of CTA, suggesting catalyst poisoning.

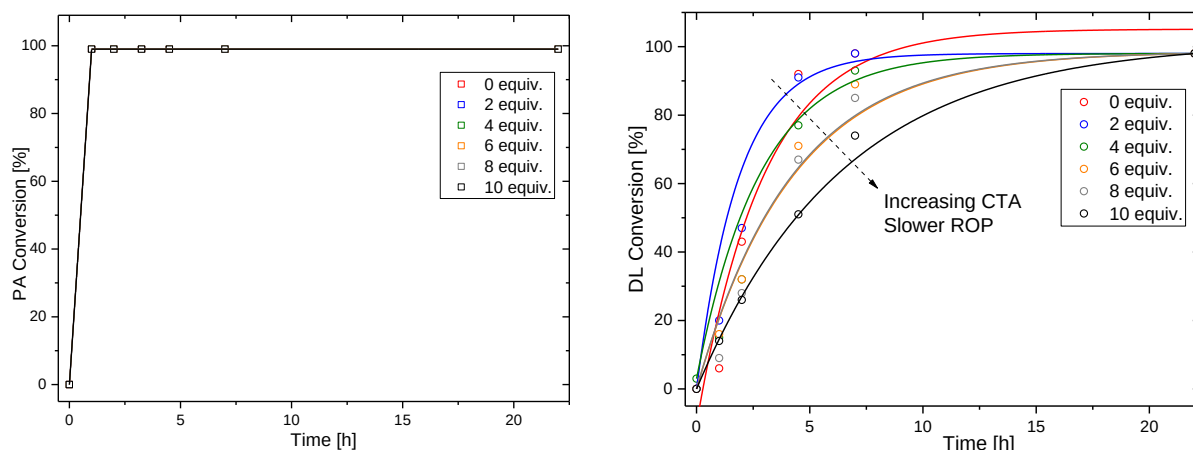


Figure 7. 14 – Conversion of PA (right; all traces are identical) and DL (left) vs. time for the one-pot polymerisation of PA, CHO, DL with different amounts of CTA. Conditions: [PA]:[CHO]:[DL]:[CHD]:[**7.13**]=100:200:100:2-10:1, 100 °C.

The observation that a less active catalyst was obtained with increasing amounts of CTA was consistent with the rapid formation of mono-zinc complex **7.5** for stoichiometric reactions with alcohol (Section 7.3.2). The decreased catalytic activity for **7.5** is expected due to (i) the absence of an initiating species and (ii) the formation of a sterically inaccessible dimer. It should be noted, however, that catalytic activity was observed even at ten equivalents of CTA, which indicates the existence of an equilibrium between mono-zinc species **7.5** and a catalytically active species. Further investigations are recommended to gain more insight into the nature of the active species and their interplay.

The sequential occurrence of ROCOP and ROP with dizinc complex **7.13** and ten equivalents of CTA, was further confirmed by *in situ* IR spectroscopy (Figure 7. 15). The observed rates were slower than observed previously by ^1H NMR spectroscopy, which might indicate: (i) the high sensitivity of **7.13** and/or (ii) slower stirring in the IR spectrometer.

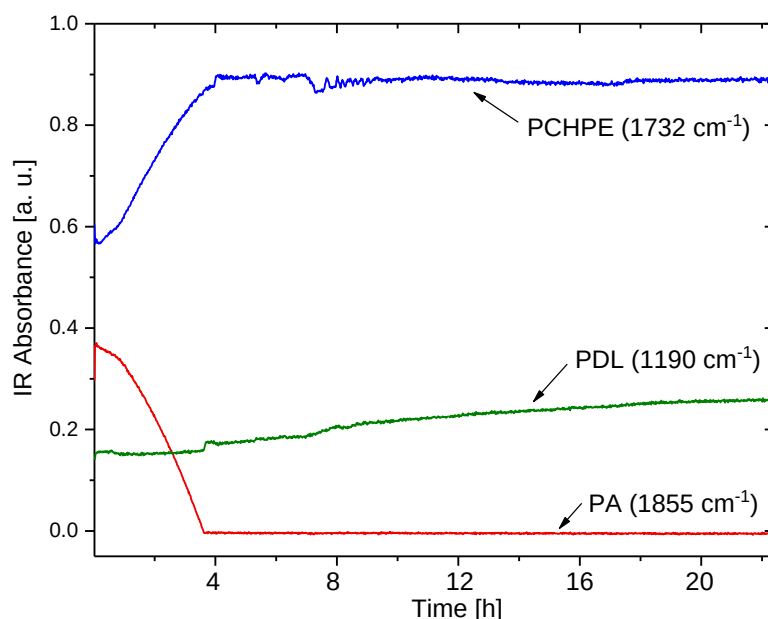


Figure 7. 15 – *In situ* IR monitoring of one-pot polymerisation of PA, CHO, DL. Conditions: [PA]:[CHO]:[DL]:[CHD]:[**7.13**]=100:200:100:10:1, 100 °C.

When dizinc complex **7.13** was used, with ten equivalents of 2-hexanol as CTA, lower rates for both ROCOP and ROP were observed by *in situ* IR spectroscopy (Figure 7. 16). As an aside, a (pseudo)-first order rate law in ROCOP was observed with CHD as CTA, but deviations were observed with 2-hexanol, which might indicate a different mechanism.

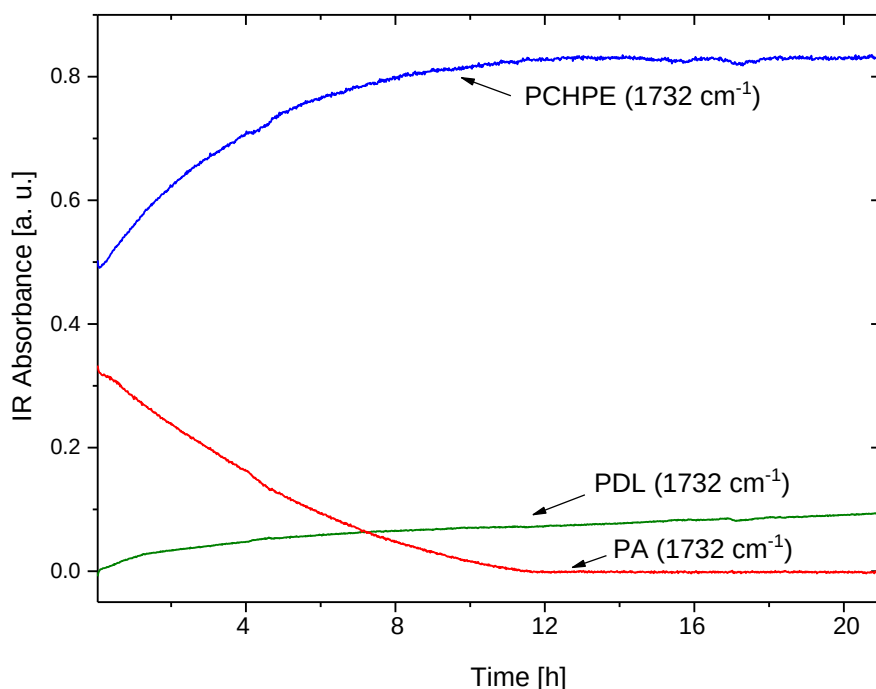


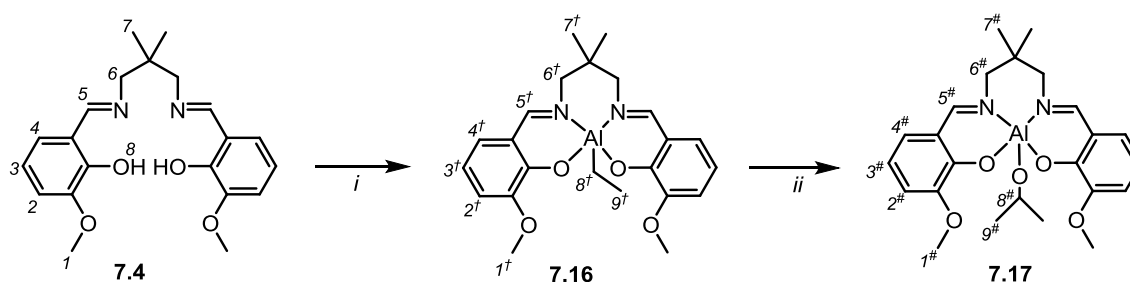
Figure 7. 16 - *In situ* IR monitoring of one-pot polymerisation of PA, CHO, DL. Conditions: [PA]:[CHO]:[DL]:[2-Hexanol]:[**7.13**]=100:110:100:10:1, Tol (5M), 100 °C.

7.4. Aluminium Catalysts

Bimetallic zinc and magnesium complexes undergo dimerization and/or catalyst deactivation. In addition to bimetallic complexes, the *ortho*-vanillin ligand can be used as a salen-derivative for the coordination to trivalent metals. In this section, various aluminium complexes were synthesized and evaluated as ‘switch’ catalysts.

7.4.1 Synthesis

Secondary alkoxides are desirable initiating groups for ‘switch’ catalysis as they model the reactivity of the propagating species for both PA/CHO ROCOP and DL ROP. For this reason, aluminium alkoxide **7.17** was synthesized by reaction of protio-ligand **7.4** with triethyl aluminium (yielding **7.16**) and the subsequent addition of an equivalent of *iso*-propanol (Scheme 7. 7).



Scheme 7. 7 – Synthesis of aluminium alkoxide complex **7.17**. Conditions: (i) triethyl aluminium (1.00 equiv.), THF, -30 °C – RT, 16 h; (ii) *iso*-propanol (1.05 equiv.), THF, RT, 16 h. Overall yields: 70-80%.

Both complexes (**7.16** and **7.17**) were analysed by ^1H and ^{13}C NMR spectroscopy (Figure 7. 17). The metalation was monitored by the consumption of the phenolic signal, at 14.14 ppm (8 in Scheme 7. 7), and significant shifts to most other signals were observed. Most significant were the changes in the imine-region, 8.32-8.06 ppm (5 and 5 † in Scheme 7. 7), 8.09 ppm (5 $^\#$). The formation of **7.16** was evident by resonances assigned to the ethyl co-ligand, at 0.01 and 0.88 ppm (5 † and 9 †). Further alcoholysis was observed as the consumption of these signals and the formation of the corresponding *iso*-propoxide species, at 4.01 and 1.00 ppm (8 $^\#$ and 9 $^\#$). The signals assigned to the methoxy substituent changed marginally by from 3.85 to 3.87 ppm (1 † and 1 $^\#$, respectively) and no other significant changes were observed. These NMR spectra suggest C_{2v} symmetry for **7.4** and C_1 -symmetry for **7.16** and **7.17**.

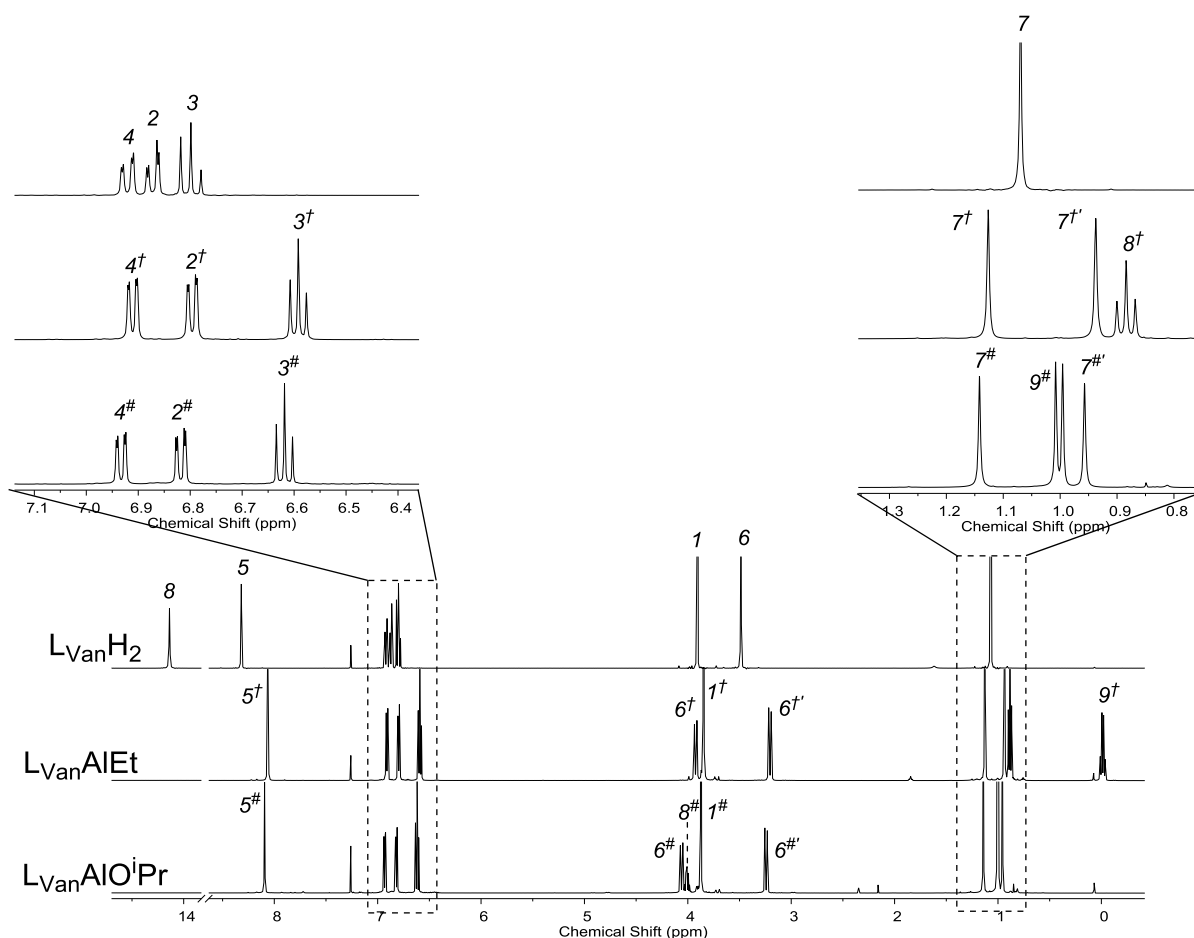


Figure 7. 17 – ^1H NMR spectra of **7.4**, **7.16** and **7.17** (CDCl_3 , 298 K, 400 MHz).

Crystals suitable for XRD were grown for **7.16** and **7.17** (Figure 7. 18 and Table 7. 7). In both complexes, the aluminium(III) centre is pentacoordinated in the ‘closed’ pocket of the ligand (O_2 , O_3 , N_1 , N_2) and adopts a distorted trigonal bipyramidal geometry ($\tau = 0.79$ (**7.16**) and 0.86 (**7.17**)). All bonds are within the expected range of $1.71\text{--}2.34$ Å for aluminium-oxygen,^b $1.92\text{--}2.15$ Å for aluminium-nitrogen^c and $1.92\text{--}2.05$ Å for aluminium-carbon bonds.^d The ligand in **7.17** is slightly less bent compared to **7.16**, as indicated by the intersection of the phenol moieties at 35° vs. 75° , which may be the result of lone-pair repulsion between the *iso*-propoxide co-ligand and the imine functionality.

^b Based on statistical analysis from CCDC data base. For $\text{Al-O}^{\text{Aromatic}}$, the following values were obtained from 42 structures: mean: 1.812 ± 0.026 Å lower quantile: 1.796 Å and minimum: 1.731 Å; upper quantile: 1.831 Å and maximum: 1.893 Å. For $\text{Al-O}^{\text{Aliphatic}}$ (10 structures): mean: 1.771 ± 0.070 Å; lower quantile: 1.735 Å and minimum: 1.716 Å; upper quantile: 1.757 Å and maximum: 1.932 Å.

^c Based on statistical analysis from CCDC data base from 122 structures: mean: 2.020 ± 0.037 Å lower quantile: 1.996 Å and minimum: 1.908 Å; upper quantile: 2.037 Å and maximum: 2.147 Å.

^d Based on statistical analysis from CCDC data base from 45 structures: mean = 1.973 ± 0.013 Å lower quantile: 1.993 Å and minimum: 1.922 Å; upper quantile: 1.980 Å and maximum: 2.047 Å.

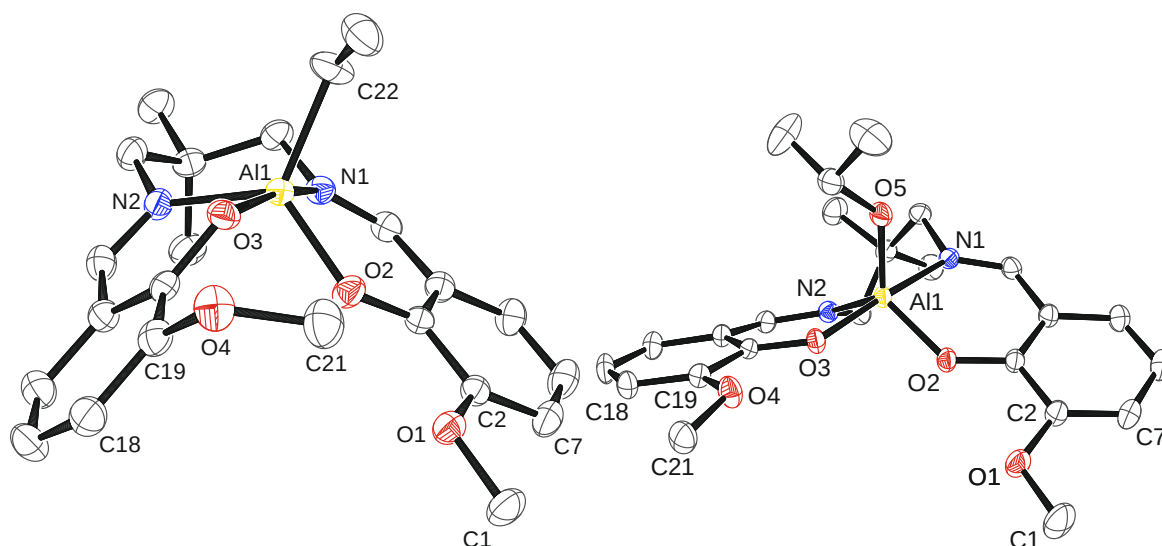
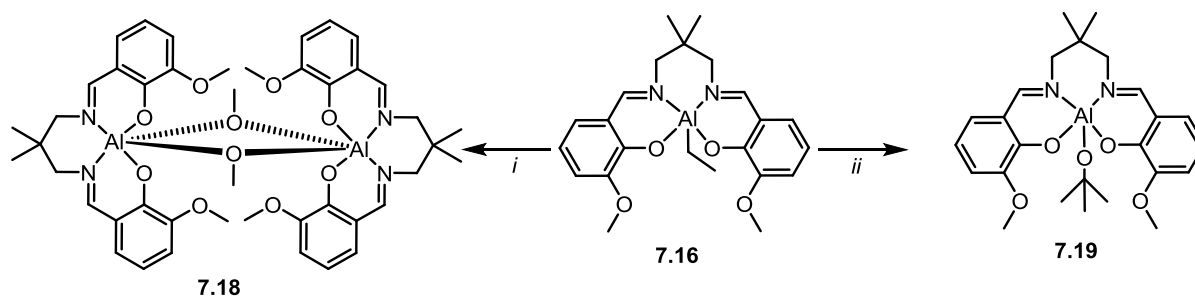


Figure 7. 18 - Molecular structure of **7.16** and **7.17** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 7. 7.

Next, aluminium ethyl complex **7.16** was reacted with methanol or *tert*-butanol to synthesize the corresponding alkoxide complexes (*Scheme 7. 8*). **7.18** and **7.19** were analysed by ^1H and ^{13}C NMR spectroscopy and XRD.



Scheme 7. 8 - Synthesis of **7.18** and **7.19**. Conditions: (i) methanol (1.05 equiv.), THF, RT, 2 h (45%), (ii) *tert*-butanol (1.05 equiv.), THF, RT, 24 h (70%).

The molecular structure of **7.18** is a dimer, bridged by two methoxy co-ligands (Figure 7. 19). Each aluminium centre is hexacoordinated, by the ‘closed’ N,N,O,O pocket of the ligand and O9 and O10, from the methoxy co-ligands, are shared between Al1 and Al2. The aluminium-aluminium distance is 2.953(1) Å, similar to other bridged aluminium salen complexes.^[27-29] This dimeric structure is in contrast to **7.19**, which exists as a monomer in the solid state. Al1 is pentacoordinated by the ligand (N1, N2, O2, O3) and the alkoxide co-ligand (O5). A τ value of 0.83 indicates a distorted trigonal bipyramidal coordination geometry and all aluminium-nitrogen or aluminium-oxygen bonds are within the expected ranges.

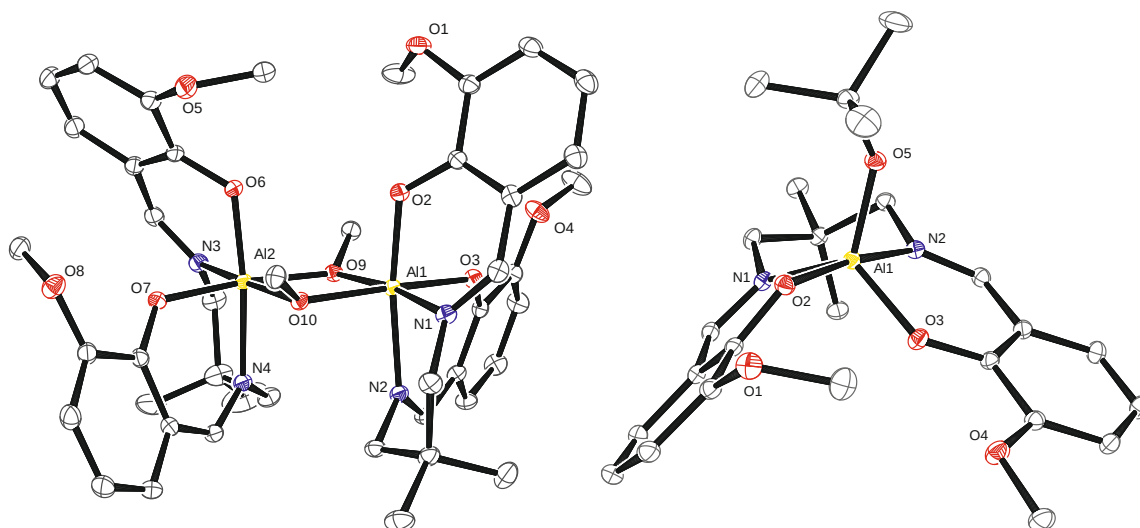
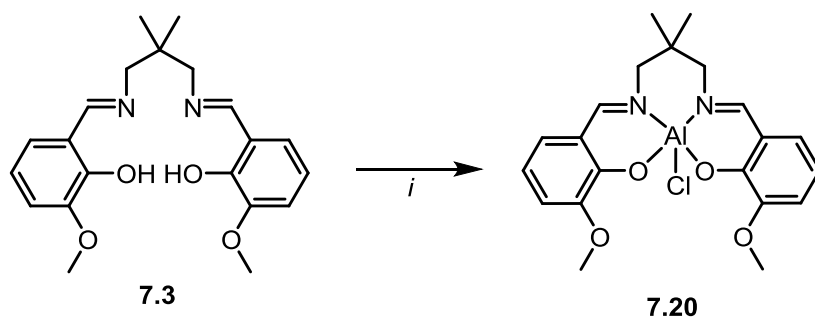


Figure 7. 19 - Molecular structures of **7.18** and **7.19** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 7. 7.

In this field of catalysis, most salen complexes are used with chloro co-ligands.^[30, 31] For comparison to these systems, the corresponding chloro complex **7.20** was synthesised by reacting a solution of **7.3**, in THF, with diethyl aluminium chloride (Scheme 7. 9).



Scheme 7. 9 – Synthesis of **7.20**. Conditions: AlEt_2Cl (1.05 equiv.), THF, RT, 2 h (75%).

The solid-state structure of **7.20** contains the expected monomeric aluminium chloro complex and a coordinated pyridine molecule (crystals grown from pyridine; Figure 7. 20). Al1 is hexacoordinated by the ‘closed’ pocket of the ligand (N1, N2, O2, O3) in equatorial and Cl1 and N3 (from pyridine) in axial position. All bond lengths are within the expected range and the *trans* coordination of pyridine to the chloro co-ligand may be relevant to the coordination geometry during epoxide binding under polymerisation conditions.

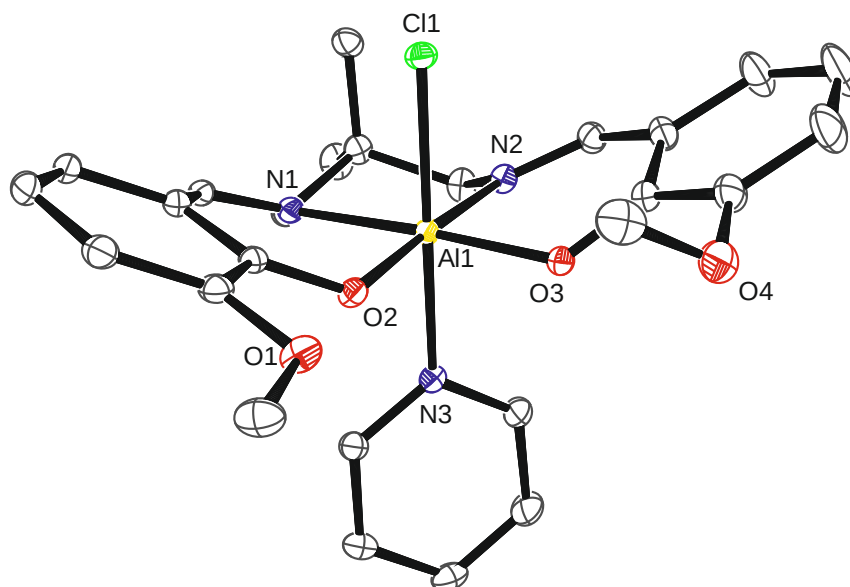


Figure 7. 20 – Molecular structure of **7.20** with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Table 7. 7.

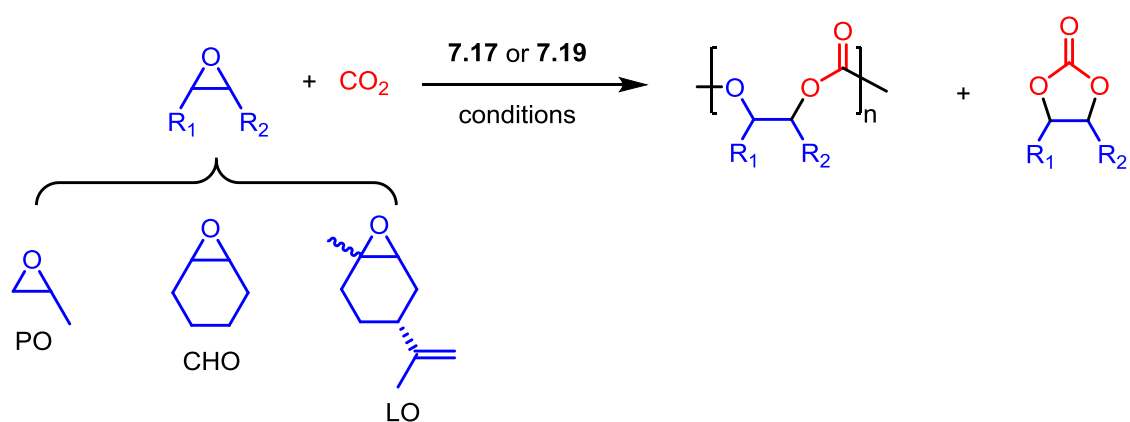
Table 7. 7 - Selected bond lengths and angles for **7.16-7.20**.

Complex	Bond	Bond length [Å]	Bond	Bond Angle [°]
7.16	Al1-C22	1.983(3)	O3-Al1-N1	167.8(1)
	Al1-O2	1.801(2)	N2-Al1-C22	119.9(1)
	Al1-N1	2.083(2)	O2-Al1-C22	120.5(1)
7.17	Al01-O5	1.741(1)	N1-Al01-O3	173.16(6)
	Al01-O2	1.791(1)	N2-Al01-O5	118.20(6)
	Al01-N1	2.043(1)	O5-Al01-O2	121.36(6)
7.18	Al1-O3	1.859(2)	N2-Al1-O2	170.4(1)
	Al1-N1	2.065(3)	Al1-O9-Al2	102.4(1)
	Al1-O10	1.888(2)	O10-Al1-O9	77.85(9)
7.19	Al1-O2	1.824(1)	O2-Al1-N2	171.22(5)
	Al1-N1	2.010(1)	O3-Al1-O5	120.58(5)
	Al1-O5	1.740(1)	O3-Al1-N1	121.21(5)
7.20	Al1-N3	2.085(1)	N3-Al1-Cl1	178.76(5)
	Al1-Cl1	2.3166(5)	N1-Al1-N2	90.18(6)
	Al1-N1	2.026(1)	O3-Al1-N2	88.11(6)

7.4.2. Activity for Epoxide / Carbon Dioxide ROCOP

Next, the aluminium complexes were tested for epoxide/ CO_2 ROCOP (Table 7. 8). Three epoxides were investigated: propylene oxide (PO), cyclohexene oxide (CHO) and limonene oxide (LO, 60:40 *cis:trans*-mixture). In all cases, no reaction was observed if aluminium alkoxides **7.19** and **7.17** were used without PPNCl or DMAP as a co-catalyst. The coupling of PO or CHO and CO_2 was observed with *iso*-propoxide **7.17** and PPNCl, however, cyclic carbonate was obtained as the main product, under various conditions.

Table 7. 8 – Epoxide/ CO_2 copolymerisation with **7.17** or **7.19**.



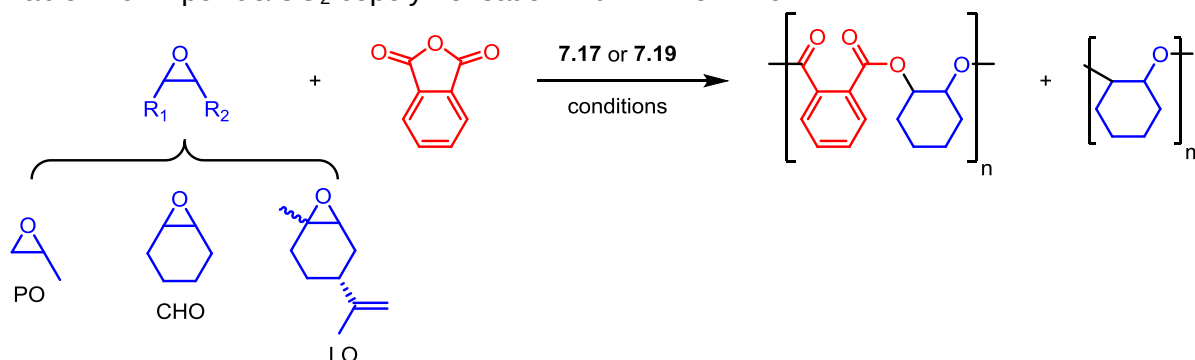
Cat. / Co-Cat. ^[a]	Epoxide	Conditions				Conversion [%] ^[b]	Selectivity [%] ^[b]
		c [mol l ⁻¹]	T [°C]	t [d]	bar		
7.17	LO	Neat	100	2	40	< 5	N. D.
	LO	Neat	120	3	40	< 5	N. D.
7.17 + PPNCl	LO	Neat	120	2	40	< 5	N. D.
7.17 + DMAP	LO	Neat	120	2	40	< 5	N. D.
7.19	LO	5	100	2	40	< 5	N. D.
7.17 + PPNCl	CHO	Neat	80	1	40	69	7 ^[c]
7.17 + PPNCl	PO	Neat	40	48	40	> 95	< 5
	PO	Neat	40	48	40	96	< 5
	PO	Neat	60	48	20	89	< 5
	PO	Neat	RT	72	40	97	< 5
7.17 + DMAP	PO	Neat	60	72	40	> 95	< 5

^[a] 1/1 ratio unless specified. ^[b] Determined by ^1H NMR spectroscopy. ^[c] The following products were obtained: PCHC (7%), *cis*-CHC (87%), *trans*-CHC (6%)

7.4.3. Activity for Epoxide / Anhydride ROCOP

For epoxide/anhydride ROCOP, all three epoxides (LO, CHO and PO) were tested with PA. In the case of anhydrides, low polyether vs. polyester selectivity was found for *tert*-butoxide complex **7.19**, if run neat and without co-catalyst. For LO/PA, high selectivity and the preferential enchainment of *cis*-LO was observed in the presence of PPNCI. Similar results were found with CHO and polyether was the main product, if the reactions were run in neat epoxide. With PO, no reaction was detected by ^1H NMR spectroscopy with the *tert*-butoxide derivative **7.19**, which might indicate the initiation is hindered from a tertiary alkoxide (a full list of reactions is given in the appendix). High selectivity was observed for *iso*-propoxide derivative **7.17**; however, accompanied by broad dispersities, which may indicate transesterification as a side-reaction (not shown).

Table 7. 9 - Epoxide/ CO_2 copolymerisation with **7.17** or **7.19**.



Cat. / Co-Cat. ^[a]	Epoxide	Conditions			Conversion [%] ^[b,c]	Selectivity [%] ^[b]
		c [mol l ⁻¹]	T [°C]	t [d]		
7.19	LO	Neat	100	1	> 95	20
7.17 + PPNCI ^[d]	Cis-LO	5	100	1	> 95	> 95
	Trans-LO	5	100	1	> 95	> 95
	LO	5	100	1	> 95	> 95
	CHO	Neat	100	1	> 95	< 5
7.19 + PPNCI	CHO	Neat	100	1	> 95	> 95
7.19	PO	Neat	60	1	< 5	N. D
7.17 + DMAP	PO	Neat	60	1	> 95	> 95

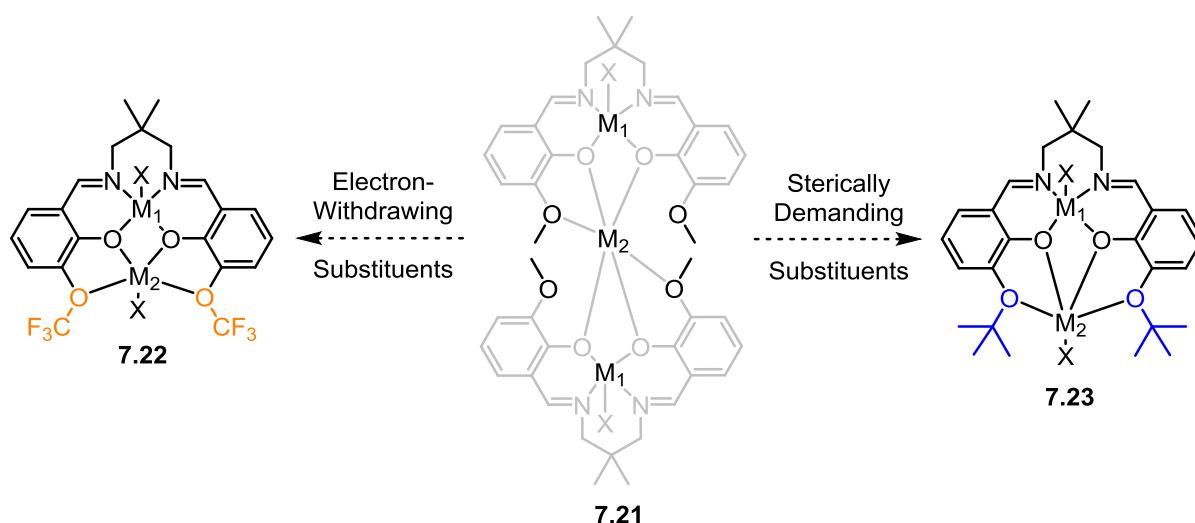
^[a] 1/1 ratio unless specified. ^[b] Determined by ^1H NMR spectroscopy. ^[c] Relative to anhydride. ^[d] Loading: cat:anhydride:PO=1:100:200. List of experiments given in appendix. ^[d] [*cis*-LO]:[PA]:[**7.15**]=110:100:1; $M_n=8,300 \text{ g mol}^{-1}$ ($\bar{D}=1.26$)

Finally, the catalyst was tested for lactone ROP and high activities were found for CL at room temperature (TOF > 1,000 h⁻¹) and DL at room temperature (TOF ~ 10 h⁻¹).

7.5. Discussion

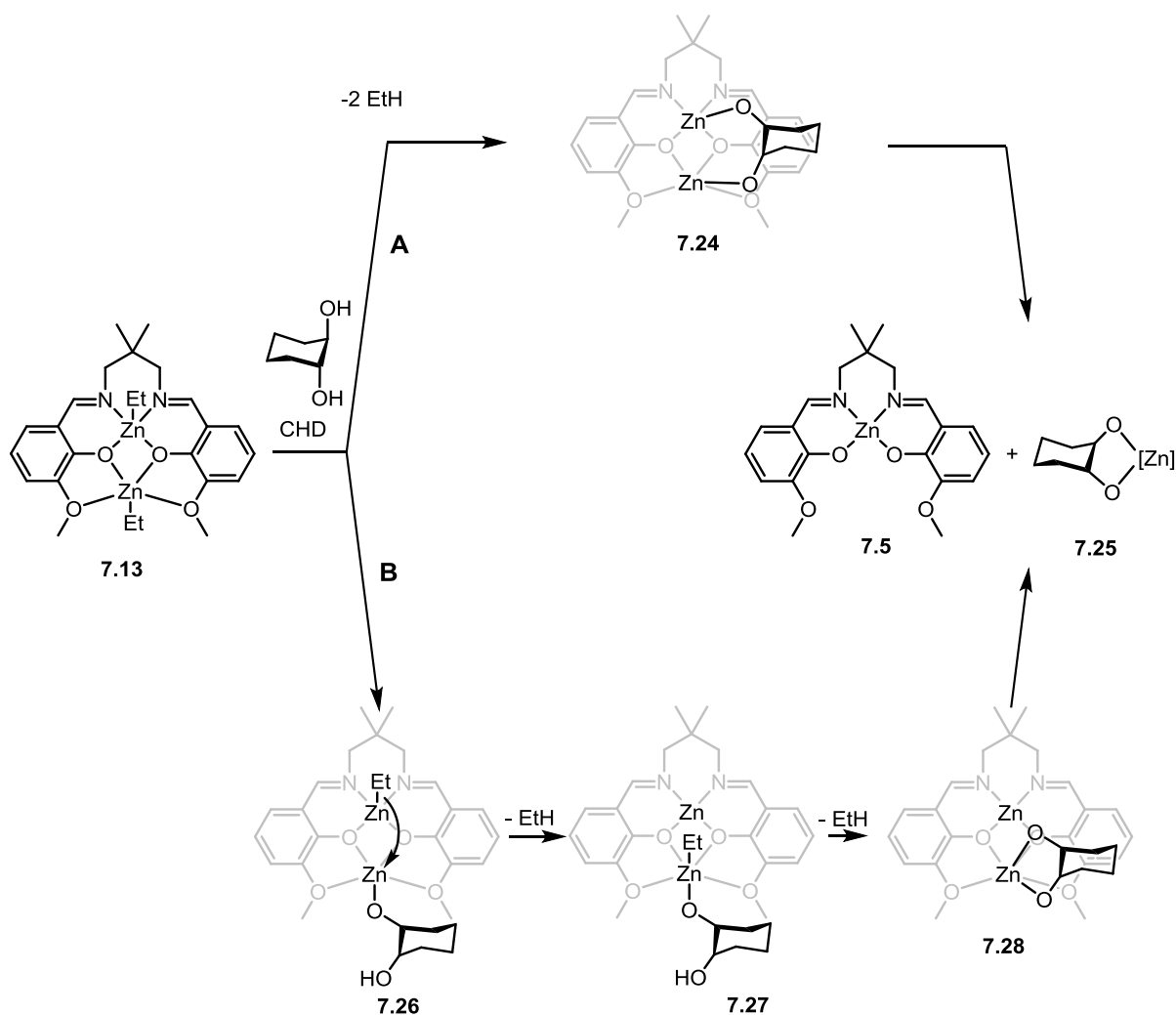
7.5.1. Zinc and Magnesium Complexes

Dimerization was frequently observed in the attempted synthesis of dizinc and dimagnesium complexes and bis(ethyl) dizinc complex **7.13** was the only example of a monomeric complex. This propensity to dimerize may be a result of the methoxy substituents, which act as donors to bridge between the two ligands. To reduce dimerization, the introduction of sterically more hindered substituents (O^iPr , O^iBu) or electron-withdrawing groups of the methoxy substituents (i. e. OCF_3) is proposed.



Scheme 7. 10 – Proposed changes in the ligand scaffold and their effect on dimerization.

Dizinc complex **7.13** yielded mono-zinc complex **7.5** upon reaction with CHD (Scheme 7. 6). Two mechanistic pathways are proposed to rationalise the finding (Scheme 7. 11): (A) concerted reaction of CHD with both zinc-ethyl bonds in one step to form **7.24**, which rearranges to mono-zinc complex **7.5** and bisalkoxide **7.25** or (B) the stepwise reaction of CHD with **7.13**. The latter possibility includes the transient formation of a mixed zinc-ethyl zinc-alkoxide species, **7.26**, which rearranges the zinc-ethyl in the ‘closed’ pocket to the zinc centre in the ‘open’ pocket and yields **7.27**. The reaction of the remaining alcohol group with the ethyl co-ligand then results in the formation of **7.28**, which features a zinc centre without any co-ligand in the ‘closed’ pocket and a second zinc centre with two alkoxide co-ligands in the ‘open’ pocket. Finally, liberation of the zinc centre in the ‘open’ pocket forms mono-zinc complex **7.5** and bisalkoxide **7.25**. This last rearrangement is shared by both mechanistic pathways and should be entropically favoured, which makes the formation of **7.5** and **7.25** under polymerisation conditions (100°C) likely.

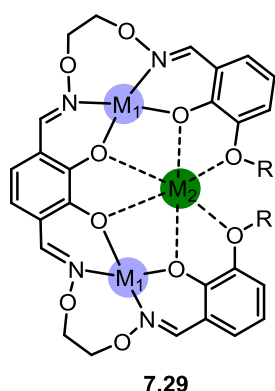
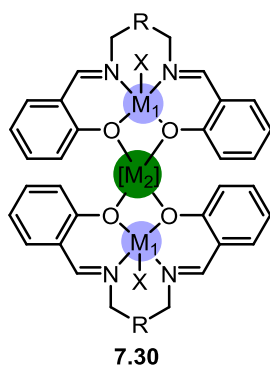
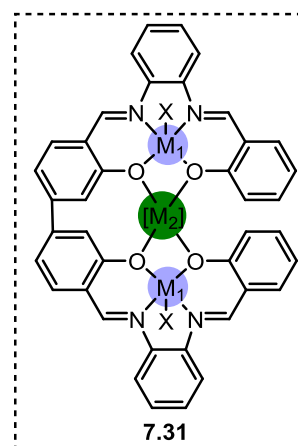


Scheme 7. 11 – Proposed pathways A and B for the formation of **7.5** from **7.13** and CHD.

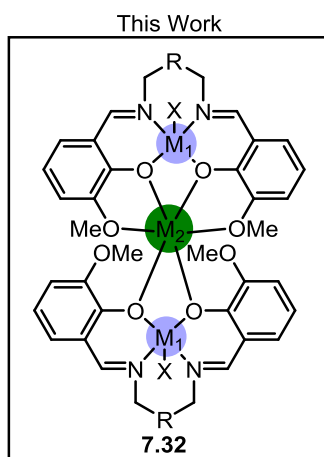
Although the nature of the catalytically active species from **7.13** and CHD is still unknown, a bimetallic mechanism may be considered in which **7.5** acts as a Lewis acid to activate the monomer towards nucleophilic attack from bisalkoxide (or biscarboxylate) species **7.25**. Such a hypothesis would be in line with related bimetallic zinc catalysts, in which one zinc centre activates the epoxide and the second zinc centre delivers the nucleophile. It is therefore recommended that this notion is further tested in the future.

Finally, heterobimetallic complexes **7.12** and **7.13** could be highly attractive polymerisation catalysts as they (i) feature different metals in close proximity to each other and (ii) contain a co-ligand reactive towards alcoholysis (Ph or HMDS). As an aside, only three examples of this structural motif ($\text{Zn1} \cdots \text{O} \cdots \text{Mg1} \cdots \text{O} \cdots \text{Zn2}$) are currently known in the solid state, two of which are cubane-like structures obtained from controlled alcoholysis of mixtures of dimethyl zinc and dimethyl magnesium (not shown).^[20] A literature review of heterobimetallic trinuclear complexes shows that only few examples have been crystallographically characterised

(Figure 7. 21). In detail, **7.29** was used for cation recognition and the templated synthesis of macrocycles.^[32, 33] However, in these complexes M_1 and M_2 are coordinatively saturated without co-ligands, which limits their use for polymerisations. Trimetallic complexes of type **7.30**, which are based on salen ligands, have been used for aromatic halogenations ($M_1=M_2=Cu(II)$) and oxidation reactions ($M_1=Ni(II)$, $M_2=Mn(II)$).^[34, 35] These complexes can be tethered and **7.31** has been recently used for the formation of cyclic carbonates with $M_1=Zn$, $M_2=Zn/Mg$, $X=I$, OAc (complexes containing OAc co-ligands were slightly less active).^[36]



Crystallographically
Characterised for
 $M_1=Zn$, $X=I$, $M_2=Mg$



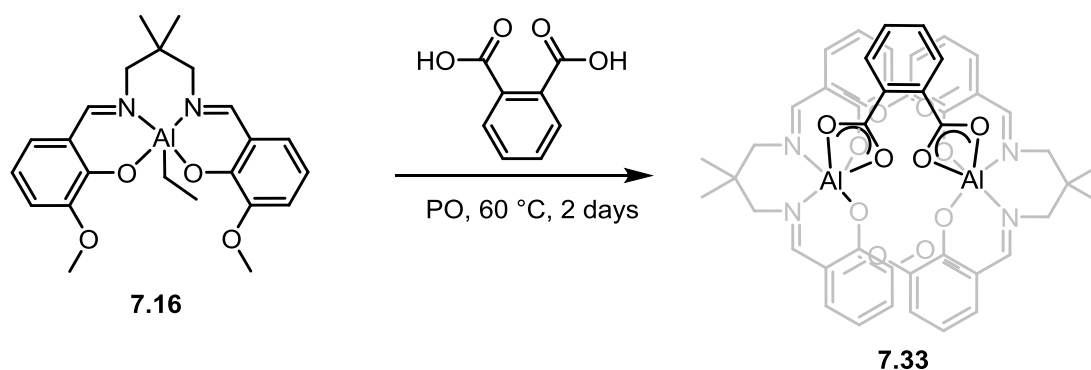
Crystallographically
Characterised for
 $M_1=Zn$, $X=Ph$ or $HDMS$, $M_2=Mg$

Figure 7. 21 – Selected trinuclear catalysts.

7.5.2. Aluminium Complexes

The aluminium complexes were generally more active ROP catalysts than commercially available [SalcyAlCl] (TOF $\sim 200 \text{ h}^{-1}$ vs. 0.1 h^{-1}) and activities for ROCOP were comparable (not shown). This increased activity may be a direct consequence of the electron-donating effect of the methoxy substituents and the flexible dimethyl propane diimine backbone.

So far, only alkoxides were tested as initiating groups, however, in epoxide/anhydride ROCOP, alkoxide and carboxylate intermediates are formed. For this reason, aluminium carboxylates should be viable initiating species. These complexes could be prepared by reacting **7.16** with the corresponding carboxylic acid and may be more stable than the corresponding alkoxides. If ABA triblocks are targeted, which may be useful for a range of applications, a difunctional initiating group should be chosen, such as 1,2-diphthalic acid. This complex was synthesised and characterised by XRD (Figure 7. 22).



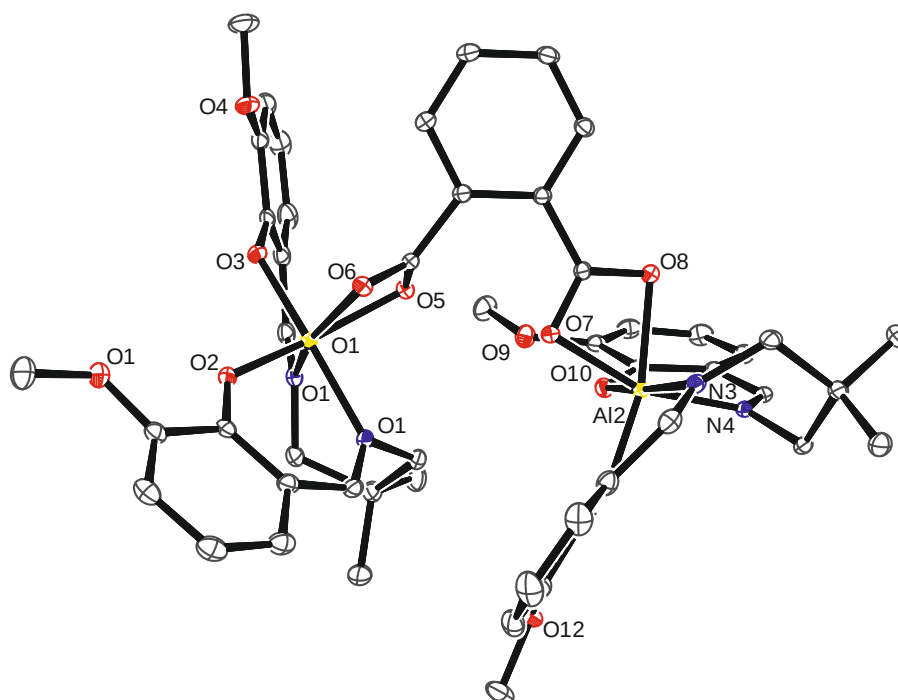
Scheme 7. 12 – Synthesis of **7.33**.

As expected, the two aluminium centres are bridged by the phthalic acid. Al1 and Al2 are hexacoordinated by the ‘closed’ N,N,O,O pocket of the ligand and each aluminium centre is coordinated by one carboxylate functionality of phthalic acid (η -2 coordination). The Al1...Al2 distance is 5.8591(6) Å, similar to other bridged dialuminium complexes^e; all bond lengths were within the expected ranges.

^e Based on statistical analysis from CCDC data base from 723 structures (mean: 4.537 ± 0.027 Å; lower quantile: 3.396 Å and minimum: 2.612 Å and; upper quantile: 5.315 Å and maximum: 8.287 Å). Used search fragment: Al-O-X(Any)-O-Al; accessed: 17/02/2018.

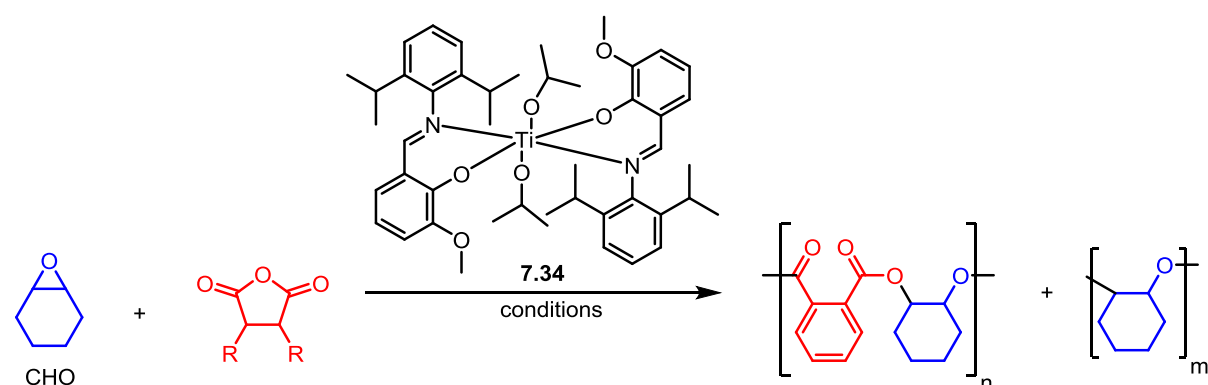
Table 7. 10 – Selected bond lengths and angles for **7.33**.

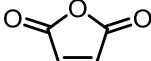
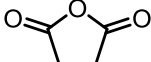
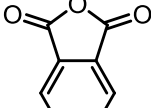
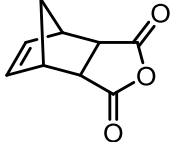
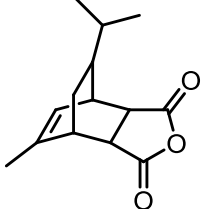
Bond	Bond length [Å]	Bond	Bond Angle [°]
Al1-O5	1.976(1)	N2-Al1-O3	175.04(5)
Al1-O6	2.023(1)	O5-Al1-O6	65.78(4)
Al2-O8	2.029(1)	O10-Al2-N4	173.33(5)
Al2-O7	1.9631(9)	O7-Al2-O8	65.86(4)

Figure 7. 22 – Molecular structure of **7.33** at the 50% probability level. Hydrogen atoms are omitted for clarity.

7.5.3. Titanium Complexes

Titanium complexes, such as **7.34**, were investigated in a separate study for lactone ROP and ethylene polymerisation and showed promising activities.^[37] These catalysts are readily available, highly crystalline and contain alkoxide initiating groups. **7.34** was tested for CHO/anhydride ROCOP (Table 7. 11). Unfortunately, only low polyester vs. polyether selectivity was obtained with mono- and bicyclic anhydrides and no activity was observed with tricyclic anhydrides. Nonetheless, the imine functionality is tuned easily and a library of ligand scaffolds is readily available (not shown).

Table 7. 11 Testing of **7.34** for ROCOP.^[a]

Anhydride	Conditions		Conversion [%] ^[b]		Selectivity [%] ^[b]
	T [°C]	t [h]	Anhydride	CHO	
 MA ^[c]	60	20	28	90	15
	80	28	43	> 95	25
	100	16	> 95	> 95	25
 SA ^[d]	60	20	< 5	< 5	N. D.
	80	28	57	93	63
	100	16	< 5	75	70
 PA ^[e]	60	20	< 5	< 5	< 5
	80	28	39	57	34
	100	16	54	100	29
 NBA ^[f]	60	20	< 5	< 5	N. D
	80	28	< 5	< 5	N. D
 TCA1 ^[g]	60	20	< 5	< 5	N. D
	80	28	< 5	< 5	N. D

^[a] Conditions: [CHO]:[Anhydride]:[**7.34**] = 120:100:1, Tol(5 M). ^[b] Determined by ¹H NMR spectroscopy. ^[c] The following chemical shifts were used: 7.02 (MA) vs. 6.1-6.5 ppm (Polyester) and 3.13 (CHO) vs. [3.1-3.6/2 ppm (polyether) + 6.1-6.5/2 (polyester)]; selectivity was determined for polyester vs. polyether signal. ^[d] 2.98 (SA) vs. 2.60 (polyester); selectivity: 2.60 ppm /2 (polyester) vs. 3.1-3.6 (polyether). ^[e] 7.80-8.00 (PA) vs 7.50-7.30 (polyester); selectivity: 7.30 (polyester) vs. 3.1-3.6 (polyether). ^[f] 6.32 ppm (NBA). ^[g] 5.78 ppm (TCA1).

7.6. Summary and Outlook

The properties of a good ‘switch’ catalyst are proposed to be: (i) high rates for ROCOP and ROP, (ii) minimal side-reactions, such as transesterification and (iii) initiating group reactive towards alcoholysis. In this chapter, new ‘switch’ catalysts, based on ligand **7.3**, were investigated and key results of this catalyst development are summarised in Figure 7. 23. In brief, four conclusions can be made: First, reaction of **7.3** with diphenyl zinc (or diphenyl magnesium) results in dimers. This structural motif can be exploited for the synthesis of dimeric, heterobimetallic complexes. Second, reaction of **7.3** with diethyl zinc yielded a monomeric dizinc ethyl complex which was a promising ‘switch’ catalyst. Third, reaction of this dizinc catalyst with monofunctional alcohols resulted in dimers which showed only low activities in polymerisations and finally, monomeric aluminium complexes were efficient ‘switch’ catalysts in the presence of a co-catalyst.

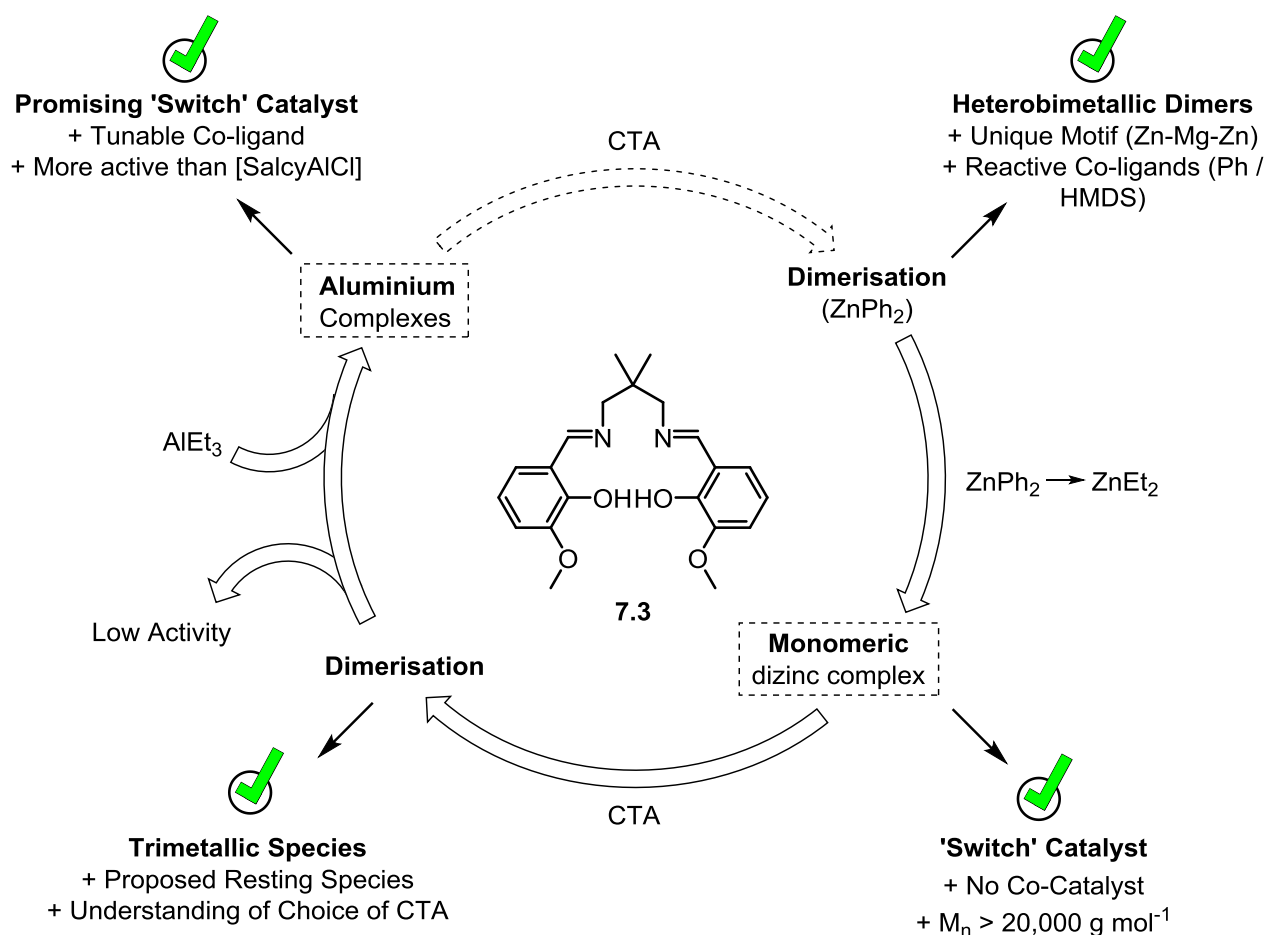
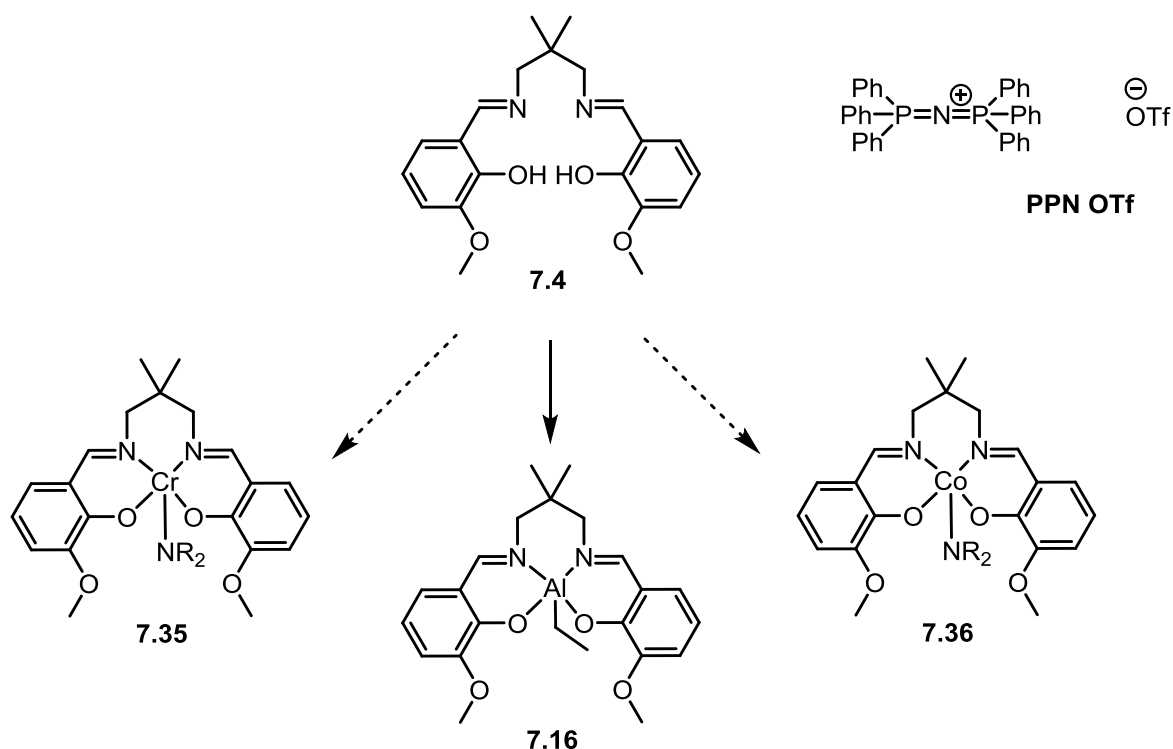


Figure 7. 23 – Catalyst developments in this chapter.

7.6.1. Chromium and Cobalt Analogues

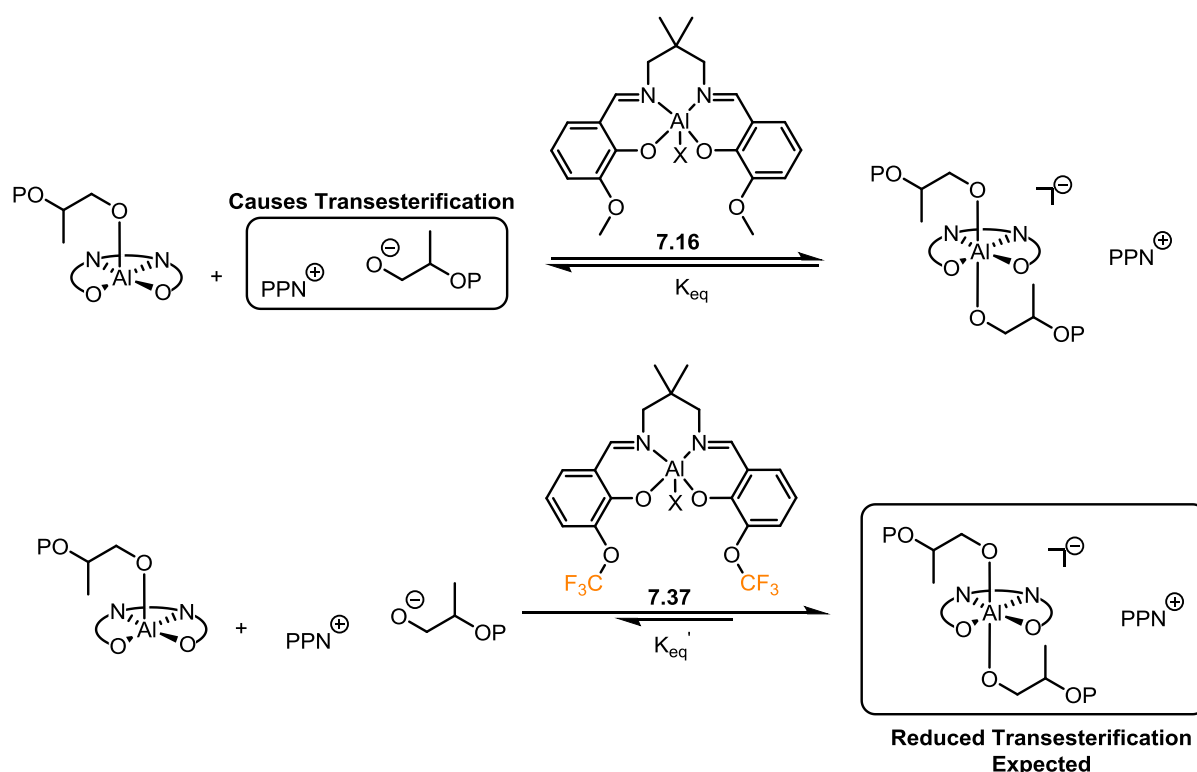
In this first investigation of aluminium catalyst **7.16**, increased activities for ROCOP and ROP compared to [SalcyAlCl] were found. Two modifications are proposed, first, the use of these complexes with co-catalyst [PPNOTf] is proposed to reduce the amount of initiating species. [PPNOTf] is readily available from [PPNCl] and [NaOTf] via salt metathesis.^[38] It also would be worth investigating similar catalysts based on chromium(III) and cobalt(III) as large activity / selectivity differences between the three metals were found for related porphyrin catalysts.^[39-41] Ideally, this investigation should be focussed on co-ligands reactive towards alcoholysis, such as amides (**7.21** and **7.22**)



Scheme 7. 13 - Proposed chromium and cobalt complexes based on **7.4**.

7.6.2. Aluminium Trifluoro-Methoxy Derivatives

Transesterification was suspected for anhydride / PO ROCOP (based on high dispersities ($\bar{D} \geq 1.30$)). This is a known challenge and so far, only one catalyst, [Salphen^FAlCl] (chapter 5), is reported to overcome this limitation.^[42] It is proposed that an equilibrium between catalyst and co-catalyst exists and the presence of a PPN-stabilised alkoxide introduces transesterification.^[42] The position of this equilibrium seems to be affected by introducing more electron-withdrawing salen ligand substituents, such as fluorine. A future target for these catalysts may be to replace the methoxy-substituent with trifluoromethoxy groups. Other electron-withdrawing groups may also be targeted but are either not commercially available or involve challenging (not impossible).



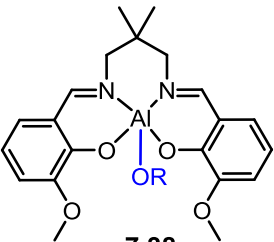
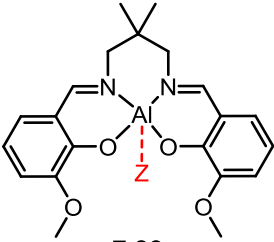
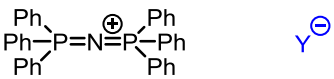
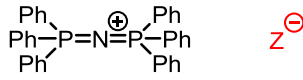
Scheme 7. 14 - Proposed catalyst co-catalyst equilibria for methoxy-derivative **7.16** and trifluoro-derivative **7.37**.

7.6.3. Catalyst Co-Catalyst Relation

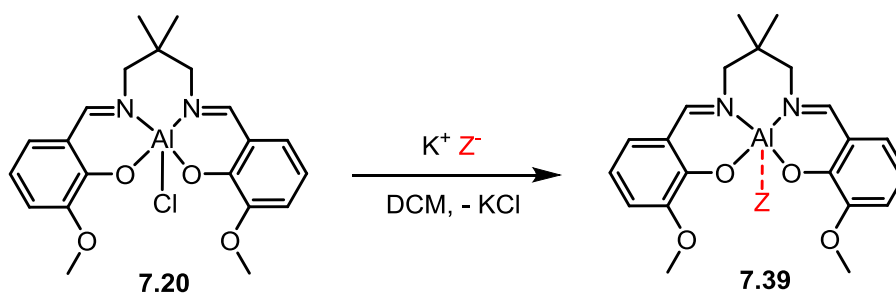
The aluminium catalysts are only active and selective when a co-catalyst is used. This is a similar scenario to catalysts described in chapters III-V. As these *ortho*-vanillin aluminium complexes are (i) readily available, (ii) mostly crystalline and (iii) allow the straight-forward analysis by ^1H NMR spectroscopy, this catalyst co-catalyst interplay could be further investigated. Most importantly, these studies would not only apply to catalysts based on *ortho*-vanillin but may be applicable for the whole ‘salen’ family.

To achieve high molar masses, the number of initiating species needs to be minimized. Recently, Coates and co-workers used a non-initiating aluminium catalyst with a tosylate (OTs) co-ligand, and a sterically hindered PPN-carboxylate to achieve significantly higher masses.^[38] Testing of the combinations shown in Table 7. 12 is proposed to shine light on the nature of the catalyst / co-catalyst equilibrium.

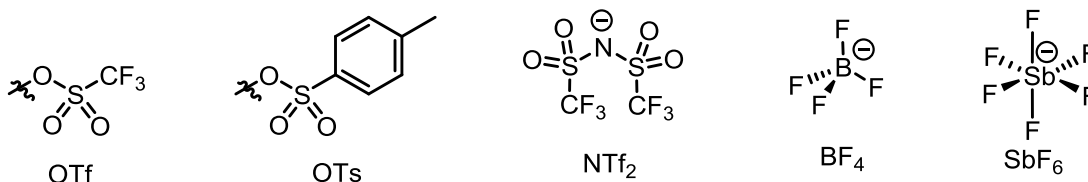
Table 7. 12 – Proposed catalyst co-catalyst study.

	 7.38 Initiating Catalyst	 7.39 Non-Initiating Catalyst
 7.40 Initiating Co-Catalyst	<p>+ Active</p> <p>- Large Amounts of CTA (Chapters 3-5)</p>	<p>?</p> <p>Expected (Ref. 19):</p> <p>+ Active</p> <p>+ Low Amounts of CTA</p>
 7.41 Non-Initiating Catalyst	<p>?</p> <p>Assumed:</p> <p>+ Active</p> <p>+ Low Amounts of CTA</p>	<p>?</p> <p>Assumed:</p> <p>- Inactive</p>

The selection of species **7.38-7.41** is proposed to affect polymer properties and/or activity. It is hypothesized to be particularly important for copolymerisations using PO, where transesterification is a major challenge. For this reason, a primary alkoxide is proposed for **7.38** to ensure fast initiation. A dimer was obtained when methanol was used and, therefore, sterically more hindered primary alkoxides are recommended to prevent dimerization, such as benzyl alcohol or *iso*-butanol. For **7.39**, weakly-coordinating anions are recommended, such as triflate, tosylate, NTf and others (Scheme 7. 15).

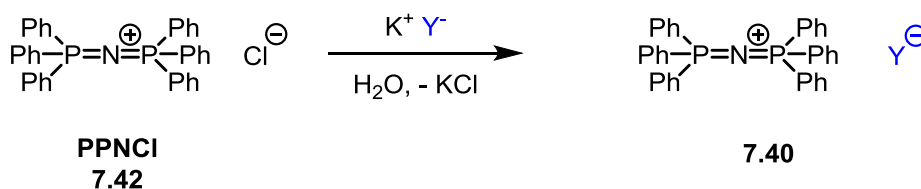


Z = Weakly Coordinating Anion

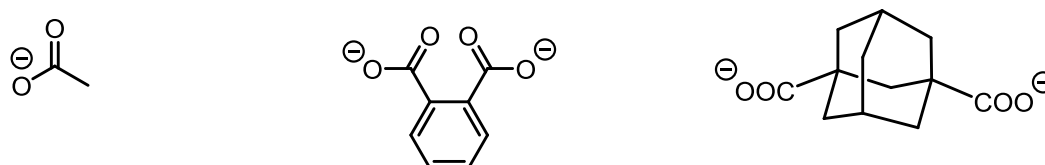


Scheme 7. 15 – Proposed complexes for **7.39** (ionic character of Al---Z bound expected to increase from left to right).

With respect to non-initiating PPN compounds, similar weakly coordinating anions as for **7.39** are suggested for **7.41**. The initiating counterparts are proposed to be carboxylates with different steric bulk, which are available through salt metathesis from PPNCl (Scheme 7. 16).



Y = Carboxylate



Scheme 7. 16 – Proposed synthesis of **7.40**. Steric bulk is expected to increase from left to right.

7.5. References

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Chapter 8

Summary and Outlook

8.1 Summary

The main topic of this thesis is the one-pot combination of ring-opening copolymerisation (ROCOP) and ring-opening polymerisation (ROP) to access oxygenated block copolymers ('switch' catalysis). So far, this approach was limited to dizinc catalysts and three main advances are presented here (Figure 8. 1). First, [SalcyCrCl] was used as the first commercially available chromium catalyst for the synthesis of block copolyesters based on cyclohexene oxide (CHO)/anhydrides/ ϵ -decalactone (DL). Second, [SalcyCrCl] could be used with propylene oxide (PO), a monomer unknown in 'switch' catalysis, and poly(ester-*b*-ether)s could be accessed as a new class of materials. The third advance was the synthesis of block copolyesters from mixtures of PO/anhydrides/(*rac*)-Lactide with [Salphen^FAlCl]. This is a unique feedstock as each monomer is available on a (potentially) industrially relevant scale. In separate studies, two polycarbonates, poly (limonene carbonate) and poly(cyclohexadiene carbonate), were tested as future coating materials and new catalysts for 'switch' catalysis were developed based on *ortho*-vanillin.

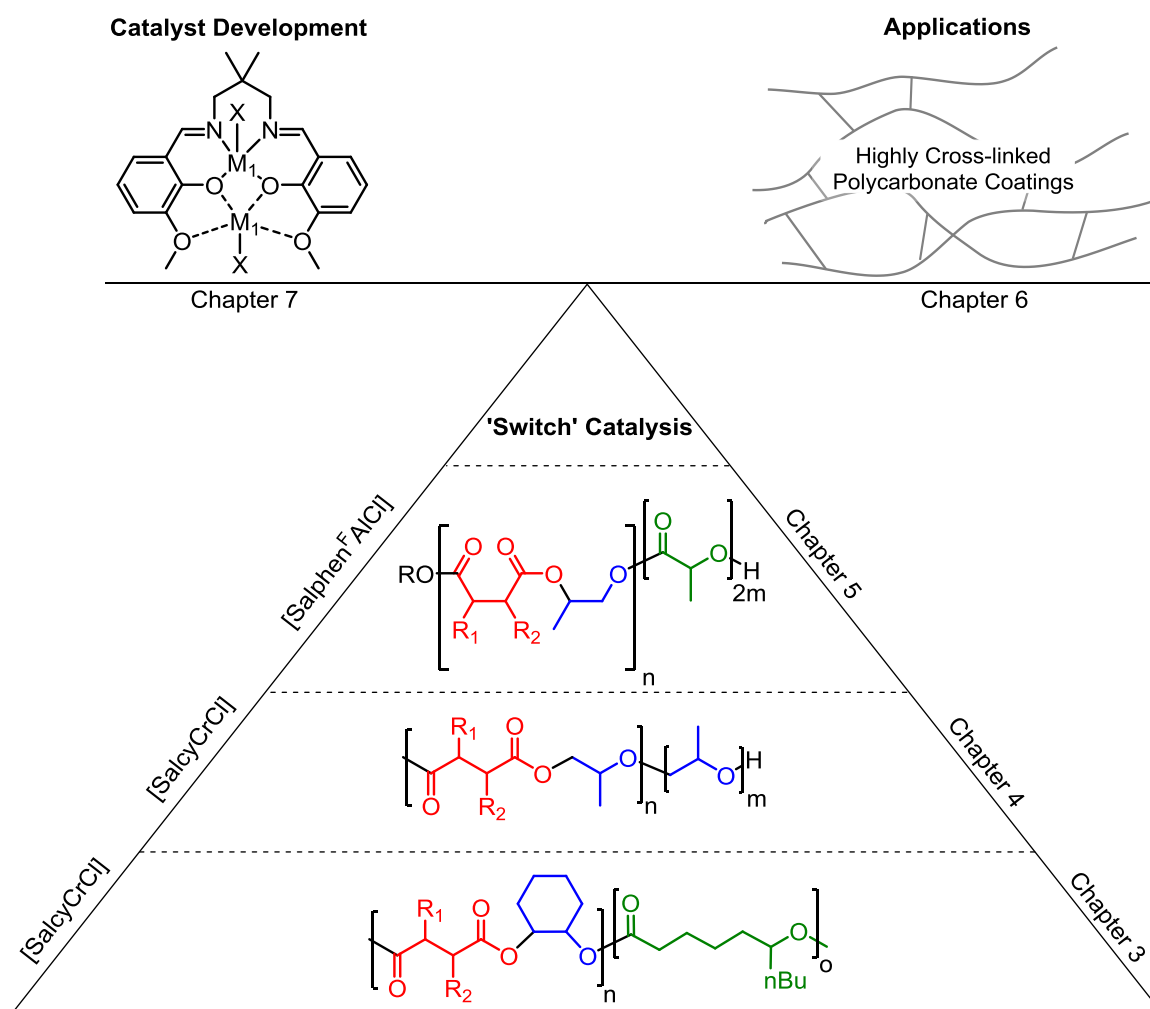


Figure 8. 1 – Thesis summary.

8.2 Outlook

8.2.1 Future 'Switch' Catalysts

Sophistication and Simplification

A wide range of catalysts has been reported for lactone ROP and epoxide/anhydride ROCOP.^[1-12] For 'switch' catalysis, two directions may be possible, first, expanding into more sophisticated materials by coupling stereoselective ROP with stereoselective ROCOP and second, further simplifying the system to allow its wide-spread and potential industrial use (Figure 8. 2). The first option may be achieved through metal complexes reported for *iso*-selective lactide ROP, or other cyclic esters, and the second alternative could focus on metal salts, such as aluminium trifluoromethanesulfonate, or metal alkyls, such as diethyl zinc (with or without further additives).^[13-21]

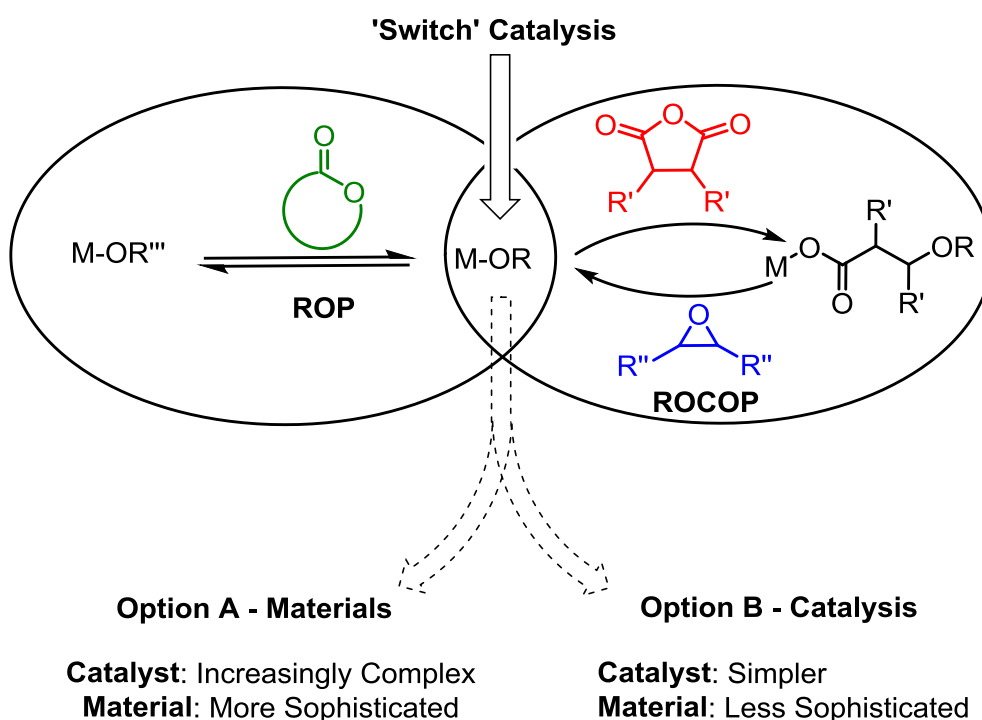


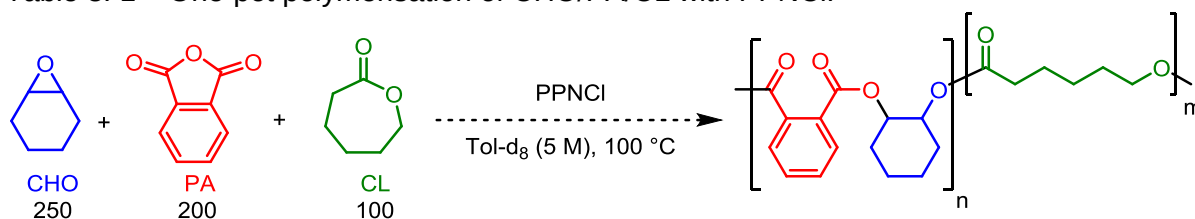
Figure 8. 2 – Two possible future directions in 'switch' catalysis.

Each option has individual advantages/disadvantages and ideally, both options are combined. For increasingly complex catalysts, challenging multi-step synthesis is involved but the resulting materials may be attractive as they currently are under-explored and difficult to synthesise by other means. For option B, the challenge of using 'simple' catalysts is the reduced control of the polymerisation, particularly with respect to polyester vs. polyether selectivity and/or transesterification. Ideally, such catalysts (or initiators) would be commercially available on a large scale and only require minimal synthesis, if any.

PPNCl as ‘Switch’ Catalyst

PPNCl, which was used as a co-catalyst in most parts of this work, has been reported for CHO/anhydride ROCOP and similar phosphanes or ammonium salts are known ROP catalysts.^[22-24] For this reason, PPNCl was tested for ‘switch’ catalysis with CHO/PO/CL (Table 8. 1). With various amounts of CHD, high conversions of all reactants can be achieved after several days, which is typically accompanied by broad dispersities. The latter indicates transesterification at high CL conversions. Unfortunately, PPNCl is not an active catalyst for DL ROP, even in the presence of triethyl borane as an external Lewis acid (not shown).^[25] For this reason, PPNCl is not recommended for ‘switch’ catalysts for this particular feedstock. Nonetheless, this preliminary testing illustrates the potential of an organocatalyst to be considered as a future ‘switch’ catalyst.

Table 8. 1 – One-pot polymerisation of CHO/PA/CL with PPNCl.^[a]



CHD [equiv.] ^[b]	Conversion [%] ^[c]		Selectivity [%] ^[c]	M_n (Đ) [g mol ⁻¹] ^[d]
	PA	CL		
0	> 95	28	> 95	20,950 (1.04) 7,560 (1.21)
5	> 95	68	> 95	10,600 (1.23) 2,700 (1.13)
10	> 95	17	> 95	4,540 (1.28)
15	> 95	88	> 95	6,970 (1.50)
20	> 95	95	> 95	7,680 (1.91)

^[a]Conditions: 100°C , toluene (5 M), 3 days. ^[b]Relative to [PPNCl]. ^[c]Determined by ^1H NMR spectroscopy. ^[d]Determined by GPC (RI detector, 30°C , relative to PS standards).

Phosphazenes as ‘Switch’ Catalysts

Phosphazenes are strong, weakly nucleophilic Brønsted bases, which contain at least one phosphorus(V) atom bound to one imine and three (peralkylated) amine functionalities (triaminoimino phosphoranes). The general structure of a phosphazene base is shown in Figure 8. 3 and these compounds can be categorised according to the number of P=N functionalities, which can vary between one and seven ($\text{P}_1\text{-P}_7$; Schwesinger and co-workers).^[26-28]

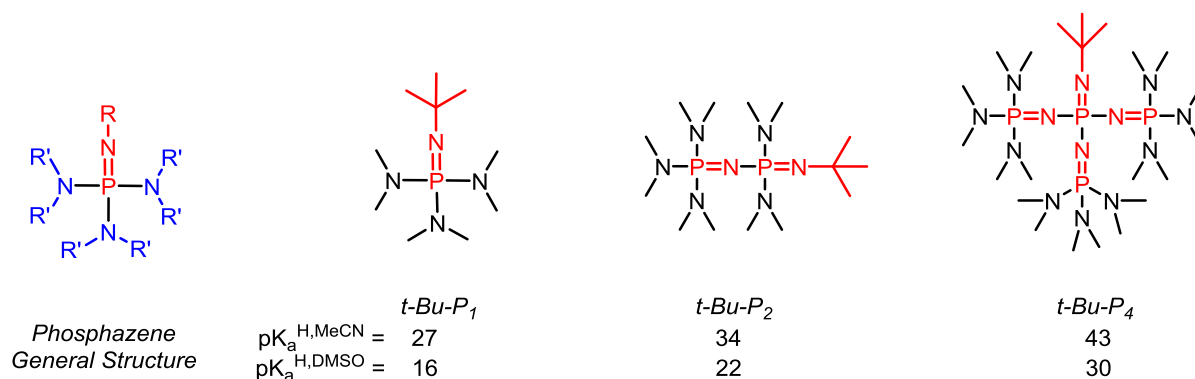
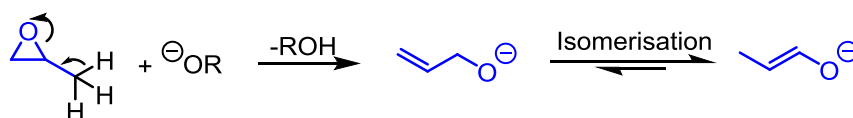


Figure 8. 3 – General structure of phosphazene base, commercial derivatives and their pK_a^{H} values.^[29]

Phosphazenes have been reported for ROP of several monomers and epoxides, cyclic esters, cyclosiloxanes are briefly discussed here:^[29-32] with respect to epoxides, a library of polyethers has been published with $t\text{-Bu-P}_4$ including polymers based on ethylene oxide, allyl glycidyl ether and styrene oxide. In most cases, immortal ROP was observed with a linear increase in mass with conversion and low dispersities ($\bar{D} < 1.2$).^[11] Interestingly, propylene oxide was the most challenging monomer due the formation of an allyl alkoxide (Scheme 8. 1).^[33]



Scheme 8. 1 – Formation of allyl alkoxide in the polymerisation of PO.^[33]

Regarding cyclic esters, three observations can be noted: (i) most catalysts (initiators) are active for ROP, (ii) TOFs are generally low, apart from lactide ROP, and (iii) transesterification occurs at high conversions.^[34-38] Nonetheless, low dispersities ($\bar{D} < 1.2$) were found if polymerisations are stopped at conversions of 80% or below and better control is typically obtained with less basic catalysts/initiators ($t\text{-Bu-P}_1 < t\text{-Bu-P}_2 < t\text{-Bu-P}_4$). In all cases, an ‘alcohol-activated’ mechanism is proposed and alkoxides or alcohols are key intermediates in ROP (Scheme 8. 2, left). Interestingly, this is not the case for β -lactone ROP, which proceeds through carboxylates and high conversions were reported ($M_n = 21,000 - 450,000 \text{ g mol}^{-1}$; $\bar{D} = 1.1-1.5$).^[39] The ROP of cyclosiloxanes has been investigated with $t\text{-Bu-P}_4$ and poly(methyl(phenyl)siloxane) with masses of ca. $250,000 \text{ g mol}^{-1}$ and moderate

dispersities ($\mathcal{D} = 1.5$) being reported; lower masses and dispersities were obtained for poly(dimethylsiloxane) with *t*-Bu- P_1 ($M_n \sim 3,000 \text{ g mol}^{-1}$, $\mathcal{D} = 1.23$).^[40-43]

Recently (2017), phosphazenes were used for epoxide/anhydride ROCOP with *t*-Bu- P_1 and dispersities as low as 1.05 and molar masses up to $100,000 \text{ g mol}^{-1}$ reported.^[22, 25, 44-46] A key requirement for successful ROCOP was the adjustment of the pK_a (pK_a^H) values to ensure deprotonation of the carboxylic acid formed after anhydride ring-opening and protonation of the alkoxide formed after epoxide ring-opening (Scheme 8. 2, right). Thus, the pK_a^H value for the phosphazene base should be > 11 (pK_a of benzoic acid), < 28 (methanol) and < 30 (*tert*-butyl acetate; Figure 8. 4).^[47-49]

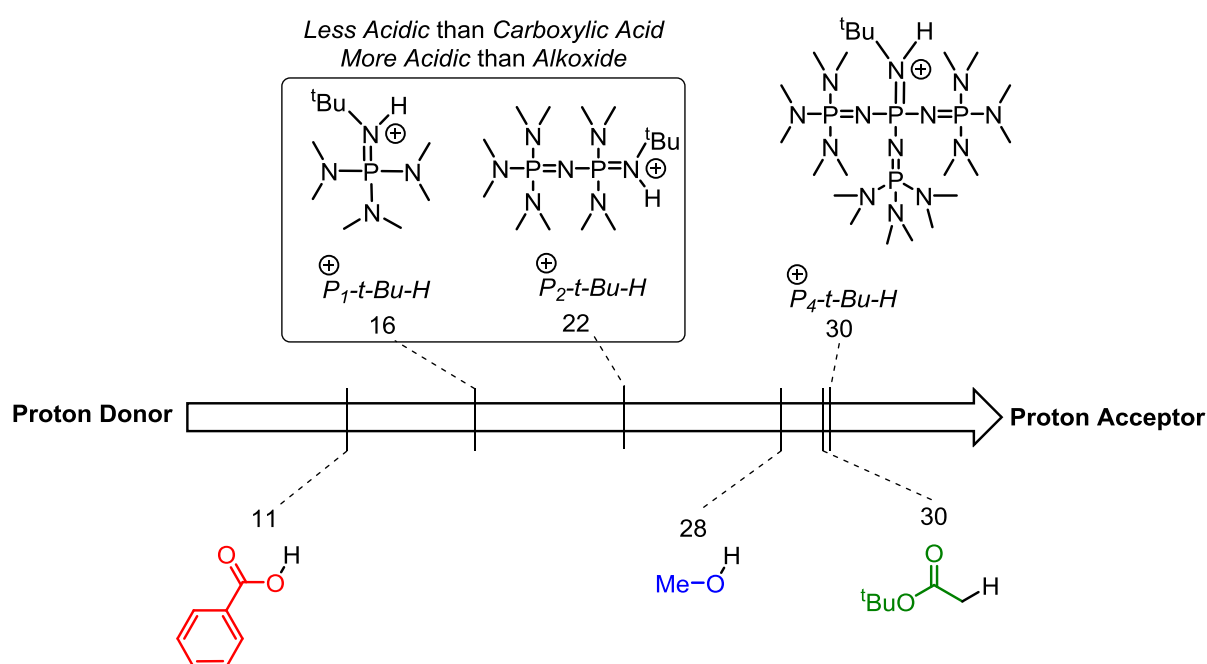
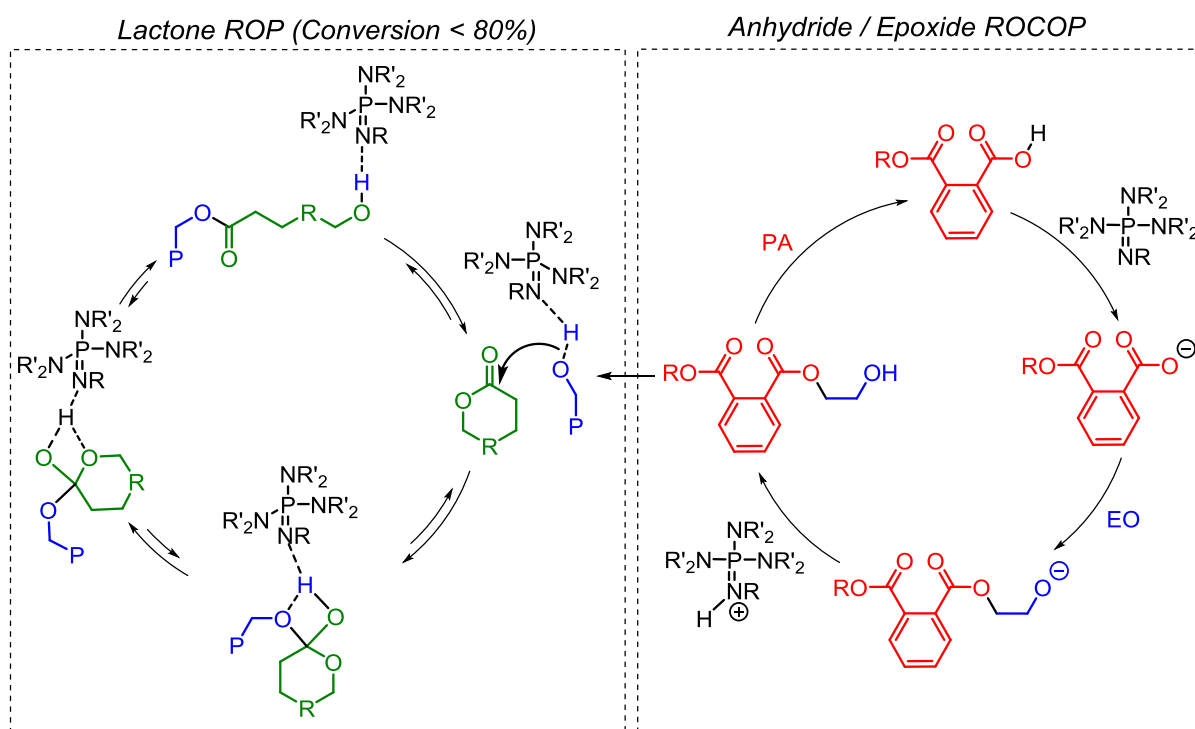


Figure 8. 4 – Acid dissociation constants for different species in DMSO.^[47-49]

Based on the successful use of phosphazenes for ROP and ROCOP, two different ‘switches’ are proposed: First, the coupling of anhydride/epoxide ROCOP with lactone ROP is suggested as a starting point due to its similarity with ‘switch’ catalysis investigated in this thesis (Scheme 8. 2). It is assumed that ROCOP proceeds first and is followed by lactone ROP. It should be noted that both steps are expected to be slow ($\text{TOF} \sim 1 \text{ h}^{-1}$) but may be accelerated upon heating. It is further recommended to quench the lactone ROP before full conversion is reached to maintain relatively narrow dispersities. As an aside, lactide may be significantly faster but is likely to proceed before ROCOP and transesterification may occur

at high conversions of lactide and during ROCOP. One promising substrate variation may be β -lactones, which did not seem to suffer from transesterification reactions.



Scheme 8. 2 – Proposed ‘switch’ catalysis with anhydride/epoxide ROCOP and lactone ROP.

Second, ‘switch’ catalysis between cyclosiloxane ROP and anhydride/epoxide ROCOP is proposed. This may allow the synthesis of *hard-soft-hard* poly(siloxane-*b*-ester)s if bifunctional CTAs are used. These materials would feature the common triblock architecture of thermoplastic elastomers. Although the mechanism for ROP is still unknown, it is hypothesised to proceed through alkoxides or alcohols, which is the basis for the coupling with ROCOP.

In summary, phosphazenes are attractive ‘switch’ catalysts as these are (i) commercial catalysts, (ii) well-controlled ROCOP and ROP has been reported if the reagents and catalysts are chosen well, (iii) new classes of silicone-containing polymers may be possible and (iv) organocatalytic ‘switch’ catalysis is currently unknown.

8.2.2 The Benefit of Bimodal Molar Mass Distributions

For the synthesis of block copolymers, monomodal molar mass distributions were of high importance and the catalysis was optimised to achieve this goal. This procedure was based on the assumption that the shape and dispersity of the GPC trace allows evaluation of the polymeric species in solution. One example are bimodal distributions, which were assigned to a low-mass, monofunctional (AB) species and a high-mass, bifunctional (ABA) species (see chapter 3 for details). Although this interpretation is valuable for block copolymers, bimodality is not *per se* a disadvantage for the resulting material properties. In fact, the synthesis of polyethylene with bimodal molar mass distribution was described as a 'breakthrough'.^[50] A typical structure-property-process relation is shown in Figure 8.5 and the low molar mass chains allow for good processability due to its low viscosity and the high molar mass chains are beneficial for properties (strength) by acting as a cross-linker.^[51, 52]

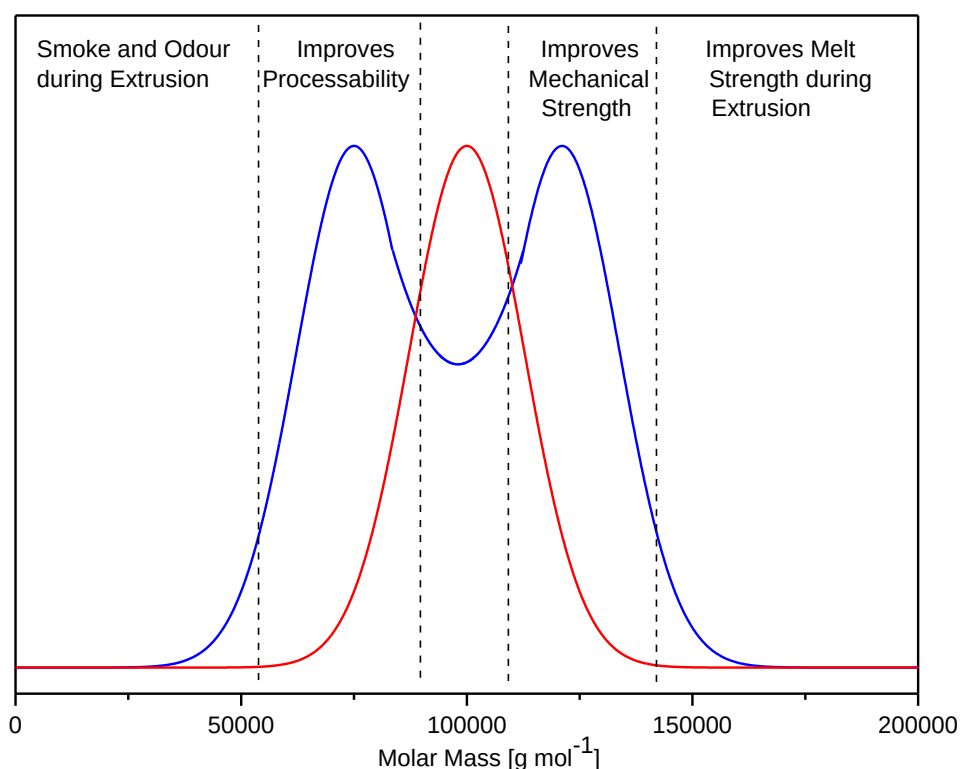


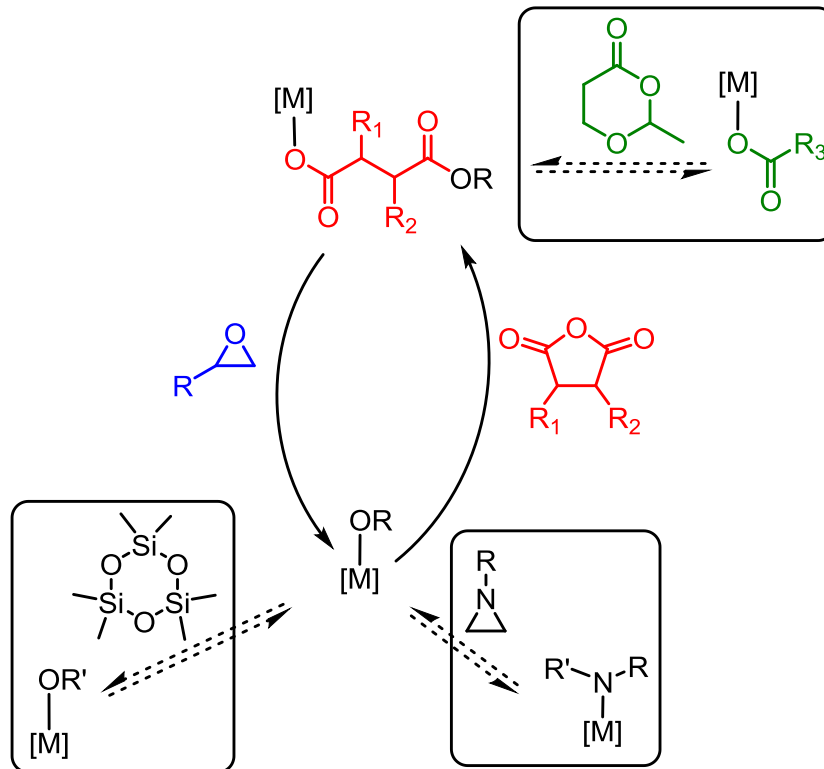
Figure 8.5 – Comparison of mono- and bimodal GPC traces and properties of different molar mass fractions (idealised curves plotted, descriptions can be found in the appendix).^[50]

It should be emphasised that polyolefins and polyesters are slightly different materials and monomodal molar mass distributions are essential for the formation of block copolymers. Nonetheless, interesting material properties may be obtained with polymers that feature mixtures of species.

8.2.3 Future Monomers

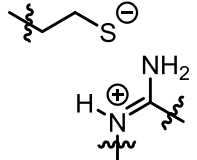
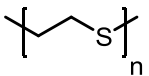
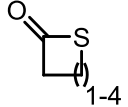
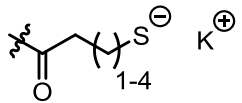
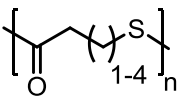
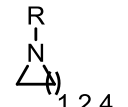
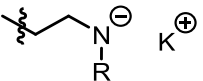
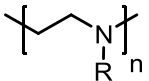
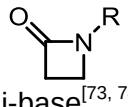
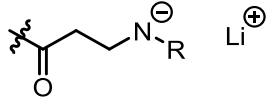
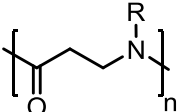
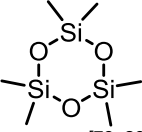
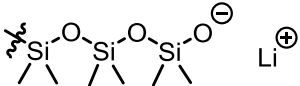
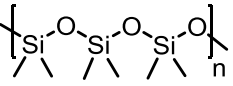
The investigated monomers in this thesis cover epoxides, anhydrides and lactones. Suggestions for further monomers include cyclic carbonates or fluorine-containing epoxides to access a wide range of T_g values ($-47 < T_g < 150$; $105 < T_m < 175$ (if observed)).^[53-55]

An alternative would be the incorporation of other types of polymerisations in ‘switch’ catalysis. The first recommendation would be ROP that proceeds through a metal carboxylate, such as the ROP of esteracetal shown in Scheme 8. 3 (top).^[56] Further choices may include anionic polymerisations and a selection is given in Table 8. 2. The most promising ROP would proceed through an alkoxide species to maintain a ‘shared’ intermediate in ‘switch’ catalysis, which would apply to siloxanes (Scheme 8. 3, left). This would be of particular relevance for ‘ultrahigh χ block copolymers’, which phase-separate at molar masses as low as $3,000 \text{ g mol}^{-1}$ for poly(3-hydroxystyrene-*b*-dimethylsiloxane).^[57] Interestingly, this polymerisation is dominated by lithium alkyls as initiators and metal catalysts commonly used for ROCOP have not yet been tested for this polymerisation.^[58-60] One further alternative would be to couple ROCOP with the ROP of aziridines, which can be achieved with potassium alkoxides as initiators (Scheme 8. 3, right).^[61, 62]



Scheme 8. 3 – Possible extensions of ‘switch’ catalysis.

Table 8. 2 – Selection of different ROPs which follow an anionic mechanism.^[63]

Functional Group Ref	Structure Catalyst	Nature of Propagating species	Polymer	Properties	Comment
Thioether ¹ [64, 65]	 DBU			High-refractive index materials ^[66]	Oxidation possible ^[67]
Thiolactone [68]	 K-base ^[61, 62] Li-base ^[61, 62] DBU ^[68]			Improved thermal properties compared to polyesters ^[68]	Regioselectivity: Acyl substitution energetically favoured over S _N 2. ^[68]
Amine [69]	 K-base ^[69] Organocat. ^[70]			Used in genetics (gene delivery) ^[71]	R = sulphonamides as activating group (alcohol/water-tolerant) ^[72]
Lactam [73, 74]	 Li-base ^[73, 74]			Biomedical applications (similar to proteins). ^[75-78]	Acyl PG typically used. ^[73, 74]
Siloxane [79]	 Li-base ^[79, 80]			Low T _g polymers ^[80]	Modified easily with vinyl-derivative in hydrosilylation ^[80]

¹ Radical polymerisation (via thiol-ene reaction) possible.

8.3. Future Challenges

8.3.1. Monomer Purity

High monomer purity is crucial to achieve high molar masses and well-defined block copolymers. Most common impurities are formed by hydrolysis of epoxides and anhydrides, i.e. diols and dicarboxylic acids, which act as chain-transfer agents and thereby lower molar masses.

A range of purification procedures for two commonly used monomers, PO and PA, is shown in Table 8. 3. Besides the purification procedure, varying degrees of purity between batches of crude monomers are likely and up to ten different compounds were identified in crude LO by GC, including unreacted limonene, mono- and bifunctional alcohols from hydrolysis and rearrangement as well as limonene dioxide.^[81]

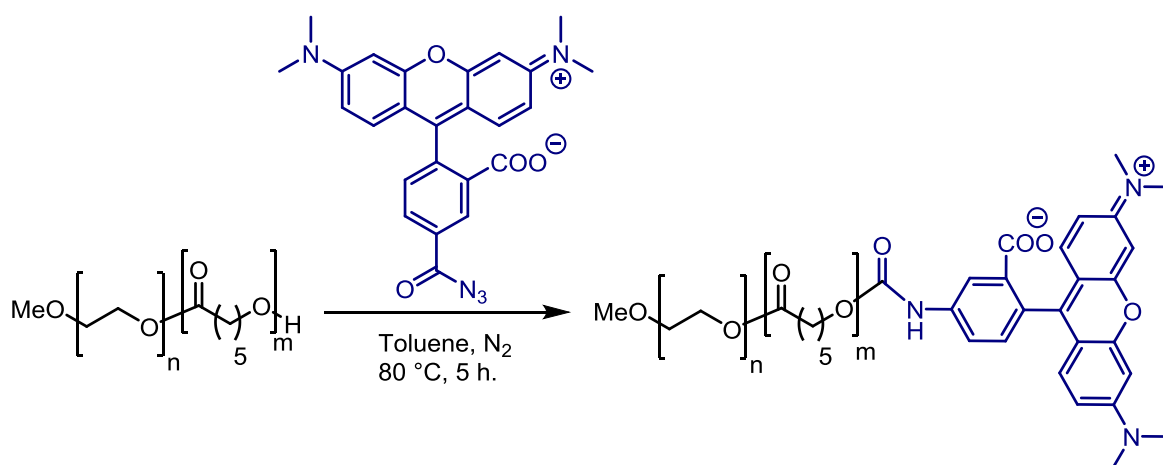
Table 8. 3 – Purification procedures for PO and PA.

Monomer	Purification	Reference
PO	Stirred over calcium hydride, fractional vacuum distillation	[25]
	Cryo-condensation (vacuum transfer)	[82]
	Cryo-condensation after drying over sodium hydride	[83]
	Cryo-condensation after reacting with <i>n</i> -butyllithium	[84]
PA	Dissolved in benzene, recrystallised from chloroform, sublimation	[85]
	Sublimation, recrystallisation from acetic anhydride	[84]
	Recrystallisation from benzene	[86]

The accurate quantification of these impurities is a key challenge, particularly at high [monomer]:[catalyst] loadings. Importantly, the impurity should be quantified relative to the catalyst, not the monomer. For example, to achieve PDL with a molar mass of 100,000 g mol⁻¹, a catalyst loading of ca. 600:1 is necessary. Consequently, ca. 1.5‰ of an impurity would be equal to a 1.5:1 mixture of the impurity and the catalyst. If a polymer purity of 99% is targeted, the detection limit should not exceed 10 ppm - under anhydrous conditions.

One promising technique would involve fluorescence spectroscopy due to its high sensitivity and excellent S/N ratio.^[87] With alcohols or diacids as the assumed impurities, a direct coupling with isocyanates is available, which has been demonstrated with polyesters.^[88, 89] In this reaction, a commercial acyl azide can be used, which rearranges to the corresponding isocyanate *in situ* (Curtius rearrangement) and reacts with the alcohol end groups (Scheme 8. 4). This end-capping had no effects on the self-assembly behaviour of the block

copolymer and could be used to monitor cell uptake. Typically, concentrations of 1 μM or less were analysed.^[88, 89]



Scheme 8. 4 – End-capping of poly(ethylene glycol-*b*-caprolactone) with tetramethyl rhodamine.^[88, 89]

8.3.2. Polymer Analysis

The range of characterisation techniques outlined in chapter 2 offers several indicators for block copolymers. Nonetheless, block copolymers are challenging to analyse with respect to end-groups, formation of cyclic species and/or contamination of homopolymers. For this reason, two further characterisation techniques are suggested, (i) multidimensional mass spectrometry and (ii) 2D GPC analysis. The coupling of different MS techniques has recently been demonstrated with poly(propylene fumarate) with MALDI/ESI or tandem fragmentation.^[90] This allows for separation of different polymeric species based on their drift time and gradual fragmentation of individual species, which may be applied to block copolymers. One alternative is the two-dimensional GPC in which the second dimension may be liquid chromatography (LC), which has been established for the analysis of peptides.^[91]

8.3.3. Polydispersity

The use of polydispersity as a measure of the ‘spread’ of molar mass distributions is well established in polymer science. The introduction of $\bar{D}$ (equ.1) has a historic background as different techniques were developed to measure either the number-average molar mass (M_n ; osmometry, cryoscopy, ebullioscopy (boiling point elevation)) or the weight-average molar

mass (M_w , light scattering, ultracentrifugation); $\mathcal{D}$ enabled the comparison between these values.^[92-95]

$$\mathcal{D} = \frac{M_w}{M_n} \quad (1)$$

Apart from this common definition, $\mathcal{D}$ is a function of the relative standard deviation (σ/μ) with μ as the number-average molar mass (equ. 2).^[93]

$$\mathcal{D} = 1 + \frac{\sigma^2}{\mu^2} \quad (2)$$

Thus, $\mathcal{D}$ is a relative quantity and high molar mass polymers have a larger standard deviation than a low mass polymer with identical $\mathcal{D}$: Polymer 1 with $M_{n,1} = 5,000 \text{ g mol}^{-1}$ and $\mathcal{D} = 1.2$ has an absolute standard distribution of $2,230 \text{ g mol}^{-1}$ and polymer 2 with $M_{n,2} = 100,000 \text{ g mol}^{-1}$ and $\mathcal{D} = 1.2$ has a standard deviation of $44,700 \text{ g mol}^{-1}$ – in each case, this corresponds to a relative standard deviation of 44.7%. Importantly, dispersity and relative standard deviation do not have a linear correlation (Figure 8. 6) and the standard deviation is doubled between $\mathcal{D}=1.20$ and $\mathcal{D}=1.80$, which may be counter-intuitive. For this reason, the relative standard deviation may be added to illustrate the breadth of molar mass distributions. Nonetheless, dispersity is a well-established concept that allows a first comparison between polymers and to evaluate the success of a polymerisation.

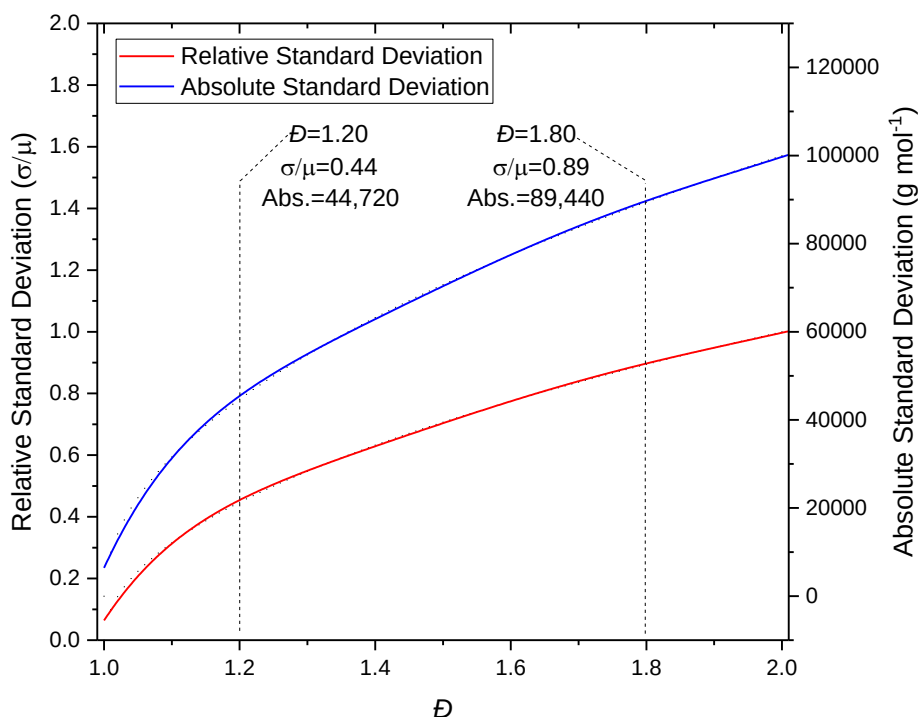


Figure 8. 6 – Relative and absolute standard deviation for a polymer with $M_n=100,000 \text{ g mol}^{-1}$ and various dispersities. Plotting functions are given in the appendix.^[93]

8.4. Closing Remarks

The majority of today's block copolymers are based on hydrocarbons and, although truly transforming and life-changing applications have been developed, their degradability is a major societal challenge.^[96] In this context, oxygenated polymers are commonly considered more sustainable alternatives and particularly oxygenated block copolymers may offer unique features.^[97, 98] One example are negative χ -values which allow attraction between chemically different polymers and can for example be used for PLA toughening;^[99] key in adjusting the χ parameter for oxygenated block copolymers is the carbon-oxygen ratio.^[100] Understanding the complicated thermodynamics of these oxygenated polymers will undoubtedly go hand in hand with the development of future materials. Easy access to a variety of these polymers will therefore be essential. This is the strength of 'switch' catalysis as an enabler of oxygenated block copolymers with different monomers (carbon-oxygen ratios), architectures (AB, ABA, multiblock) and weights (2,000 – 20,000 g mol⁻¹).

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Chapter 9

Experimental Procedures and Characterisation Data

9.1. Materials

Unless specified, all chemicals were purchased from commercial suppliers (Sigma Aldrich, Fischer, VWR, Alfa Aesar, Acros Organics, Strem Chemicals [metal catalysts and metal-organic precursors], Fluorochem). Anhydrous solvents were obtained from a SPS-800 system by M Braun, degassed by bubbling with nitrogen for one hour or three freeze-pump-thaw cycles and stored over activated molecular sieves. Deuterated solvents (>98%, Sigma Aldrich or Cambridge Isotope Laboratories) and mesitylene (98%, Aldrich) were stirred over calcium hydride for at least 24 hours, transferred under high vacuum, degassed with three freeze-pump-thaw cycles and stored inside the glovebox over activated molecular sieves. Research grade carbon dioxide (BOC, 99.99%) was dried by passing through two MicroTorr purifier columns (flow rate < 0.5 standard litre per minute). Methylene diphenyl diisocyanate was sublimed under high vacuum and stored inside the glovebox at – 30 °C.

Monomer Synthesis

Cyclohexadiene oxide (CHDO)^[1] and TCA1^[2] were synthesised according to literature procedures.

Ligand / Catalyst / Co-Catalyst Synthesis

[SalcyCoBr]^[3-5], [Salphen^FAlCl]^[6] and ligand **7.4**^[7] were prepared according to literature procedures. Bis(triphenylphosphoranylidene)ammonium chloride (PPNCl, 97%, Aldrich) was recrystallised from anhydrous acetonitrile / diethyl ether, dried at 40 °C overnight and stored in a nitrogen-filled glovebox.

Purification of Anhydrides

Phthalic anhydride (99%, Aldrich) was purified by stirring in dry benzene overnight, filtering off insoluble impurities, evaporation of the remaining solution and recrystallisation in hot (anhydrous) chloroform. Sublimation under high vacuum (10⁻² mbar, 80 °C) yielded phthalic anhydride, which was stored in a nitrogen-filled glovebox. TCA1 was recrystallised from acetone and sublimed under high vacuum before use. All other anhydrides were sublimed under high vacuum at least once and stored inside the glovebox.

Purification of Epoxides

(±)-Propylene oxide (PO, 99%, Sigma Aldrich) was purified by fractional distillation after drying over calcium hydride overnight. Cyclohexene oxide (CHO, 98%, Sigma Aldrich) was reacted with sodium hydride and methyl iodide and then purified by fractional vacuum distillation.^[8] 1,4-Cyclohexadiene oxide (CHDO) was dried overnight over calcium hydride, distilled under reduced pressure multiple times (3-5 times; ~10 mbar, ~70 °C), stored under nitrogen and used within one week.

Purification of Lactones

(Rac)-Lactide (LA, 99%, Sigma Aldrich) was recrystallised from anhydrous toluene and sublimed under high vacuum three times. The obtained solid was stored in the glovebox at -30 °C. ϵ -Decalactone (99%, DL, Sigma Aldrich) was dried over calcium hydride and purified by fractional vacuum distillation.

Purification of Chain-Transfer Agents and Thiols

Trans-1,2-cyclohexanediol (CHD, 98%, Aldrich) was recrystallised from anhydrous ethyl acetate, dried at 40 °C under high vacuum overnight and stored inside the glovebox. All thiols were dried over calcium hydride, distilled under nitrogen and stored in the glovebox.

9.2. Characterisation Techniques

Attenuated Total Reflection - Infrared Spectroscopy (ATR-IR)

IR spectra were recorded on a Perkin Elmer Spectrum 100 (FT-IR) with an AT-IR crystal or a Varian FT-IR 3100 spectrophotometer (Golden Gate). All the IR measurements were performed in the reflection mode at a resolution of 4 cm⁻¹.

For *in situ* monitoring by ATR-IR, a Mettler-Toledo ReactIR 4000 spectrometer with a MCT detector and a silver halide DiComp probe was used. The reported plots were obtained after one or two point baseline corrections and the monitored bands were selected from the overlap of individual IR spectra of monomer and polymers (see appendix).

Thermo-Gravimetric Analysis (TGA)

TGA was performed on a Netzsch 'Jupiter' simultaneous DSC/TGA. Ca. 10 mg were placed inside an aluminium heating pan and the sample was linearly heated at a rate of 20 °C min⁻¹ under a flow of nitrogen of 60 mL min⁻¹.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was performed on a Q800 DMTA (TA instruments) equipped with a film fixture for tensile testing. Film tension DMTA measurements were performed on rectangular dry film samples between 20 and 180 °C, with a heating rate of 3 °C min⁻¹. The tests were performed in the controlled strain mode with a frequency of 1 Hz, an oscillating amplitude of 0.12 μ m, and a force track of 125%. The spectra were recorded by C. Li (Eindhoven University, The Netherlands).

Differential Scanning Calometry (DSC)

DSC thermograms were recorded on a DSC4000 (Perkin Elmer) or a Mettler Toledo DSC 3 Star calorimeter under nitrogen at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. First, the sample was kept at $25\text{ }^{\circ}\text{C}$ for 1 minute, then heated to $160\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$, kept for 1 minute and cooled down to $-90\text{ }^{\circ}\text{C}$ and kept for 1 minute. This heating / cooling cycle was then repeated three times and the data from the second or third heating cycle is reported. The flow rate of nitrogen was kept at 80 mL min^{-1} throughout the measurement.

Elemental Analysis (EA)

EA was measured at London Metropolitan University (by Mr. Stephen Boyer) using a Carlo Erba Flash 2000 Elemental Analyser.

Matrix-Assisted Laser Desorption/Ionization – Time of Flight Mass Spectrometry (MALDI-ToF)

Mass spectrometry was performed on a MALDI micro MX micromass instrument with dithranol as matrix (10 mg mL^{-1}), potassium trifluoroacetate (10 mg mL^{-1}) or sodium trifluoroacetic acid (10 mg mL^{-1}) as additive, and THF as solvent. The polymer (ca. 10 mg mL^{-1}), the matrix and the additive were mixed in a ratio of 1/4/1 (v/v) and ca. $5\text{ }\mu\text{L}$ were spotted on the MALDI plate three times.

NMR Spectroscopy

^1H -NMR and $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra were measured on a Bruker Avance III HD nanobay NMR equipped with a 9.4T magnet (^1H 400.2 MHz, ^{13}C 100.6 MHz), a Bruker Avance NMR equipped with a 11.75T magnet and a ^{13}C detect cryoprobe (^1H 500.3MHz, ^{13}C 125.8MHz) or a Bruker AV 400 (^1H 400 MHz, ^{13}C 100 MHz) instrument. All spectra were recorded in CDCl_3 , pyridine- d_5 or THF- d_8 .^[9]

Size Exclusion Chromatography (SEC)

Molar masses were determined by SEC on an Agilent PL GPC-50 instrument, with HPLC grade THF (flow rate: 1.0 mL min^{-1}) after calibration with near monodisperse polystyrene standards. Samples were dissolved in THF (ca. 10 mg mL^{-1}) and filtered through a $2\text{ }\mu\text{m}$ filter before injection. Characterisation by SEC-MALLS was performed on a Shimadzu LC-20AD, with two mixed bed PSS SDV linear S columns (flow rate 1.0 mL min^{-1}). Dn/dc values were determined with an external RID detector (Knauer) with three different concentrations of the polymer of interest. Typically, the logarithmic molar mass (x-axis) was plotted against the normalised mass fraction of the molar mass, $w(\log M)$, although the y-axis was omitted for clarity.

X-Ray Diffraction

Crystal structures were recorded and solved by Dr. C. B. Durr. The crystal sample was isolated in a nitrogen-filled glovebox, covered in oil and mounted on MiTeGen MicroMounts before being cooled to 150 K (Oxford Cryosystems). Diffraction data was collected on an Oxford Diffraction Supernova diffractometer with Cu K $_{\alpha}$ ($\lambda = 1.5417 \text{ \AA}$) radiation, processed in CrysAlisPro and solved by SHELXT (Full-matrix least-squares refinements based on F2 were performed in SHELXL-1413 as part of the WinGX package).^[10]

Raman Spectroscopy

Raman spectra were recorded on a LabRAM Infinity N $^{\circ}$ 3/81F spectrometer from Horiba Jobin Yvon Ltd. using a He-Ne Laser (633 nm, 8 mW) with a pinhole of 200 μm and a magnification of 50x (Olympus LMPlanFI 50x/ $_{0.50}$). Acquisition times varied between 180 and 300 seconds and the number of scans was set to 1 or 2 (depending on the quality of the spectra). Accumulated spectra were smoothed by adjacent averaging (5 points) and peaks caused by residual radiation were removed before processing ('cosmic peaks'). To determine the conversion, the signal between 2520 and 2620 cm^{-1} was integrated and compared after normalisation of the carbonyl peak at 1750 cm^{-1} . To take the (C=C):(SH) ratio into account, the obtained ratios were multiplied by the theoretical conversion (i. e. the ratios yield values between 1 and 0; the multiplication with the theoretical conversions (25, 50, 100 for 4:1, 2:1, 1:1, respectively) transforms the numbers into meaningful percentages). For all the films, freshly made polymers and new reagents were used; significant background fluorescence was recorded for samples that were casted ca. 6 months after the preparation of the polymers (including samples that were recorded before the curing). However, no changes were detected by ^1H NMR, which suggests the stability of the materials. This effect was not further investigated and may be attributed to microstructural changes during the long-term drying process.

Raman spectra shown in Figs. 6.11 – 6.14 were recorded on a Jobin Yvon (Horiba) spectrometer using a He-Ne laser at a wavelength of 632 nm, which was controlled by a motorised stage. Confocal Raman microscopy depth profiling was performed in air, thus the focus was slightly shifted due to refraction of the transparent polymer films. 100 $\times$ magnification objectives (Olympus) with a 400- μm pinhole were used and a laser step increment of 3 μm was set for CRM depth profiling. Small differences in the spectra were detected depending on the spectrometer.

9.3. Experimental Procedures

Synthesis of Oxygenated Block Polymers

Inside a nitrogen-filled glovebox, the catalyst, co-catalyst, chain-transfer agent, monomers, internal standard (mesitylene) and solvent were added to a flame-dried vial equipped with a magnetic stir bar (rare-earth stir bars recommended) and sealed tightly with melamine-cap containing a Teflon inlay. The vial was further sealed with electrical isolation tape (poly(vinyl chloride)) and a rubber band around the area where the lid ends to ensure tightness over a longer period of time. The polymerisations were monitored by regular aliquoting inside the glovebox (ca. 0.1 mL removed) and analysis by ^1H NMR and GPC; a systematic error of $\pm 3\%$ was estimated based on differences in signal processing and weighing. Once the targeted conversions were observed, more monomer was added or the reaction was quenched. To quench the reaction, the vial was exposed to air and evaporated to dryness under high vacuum. The remaining solid was then dissolved in a small amount of DCM and isolated by precipitation from hexane, pentane or methanol. Typical amounts include: [SalcyCrCl] (1 equiv., 4.4 mg, 7.0 μmol), PPNCI (1 equiv., 20 μL of a stock solution of 50 mg PPNCI in 250 μL dry acetonitrile [equivalent to 4.0 mg, 7.0 μmol]), CHD (10 equiv., 8.0 mg, 70 μmol), anhydride (200 equiv., 1.39 mmol), CHO (250 equiv., 180 μL , 1.74 mmol), DL (200 equiv., 240 μL , 1.39 mmol) and toluene- d_8 (550 μL to obtain a 2.5 M solution in anhydride). All reactions were analysed by ^1H NMR spectroscopy and GPC.

End Group Assay with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane^[11]

The procedure was previously reported by Spyros and co-workers.^[11] First, a stock solution was prepared from bisphenol A (400 mg), $[\text{Cr}(\text{acac})_3]$ (5.5 mg) and pyridine (10 mL) and stored over molecular sieves. The polymer was dissolved in CDCl_3 (100 mg mL^{-1}) and 40 μL of this stock solution were added before the phosphorus agent (30 μL) was added. The mixture was allowed to react for at least 30 minutes and then analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy after calibration against the internal standard (bisphenol A, 138.57 ppm).

Thiol-Ene Reactions

Inside the glovebox, the block polymer (i. e. 100 mg, $M_n=4,000$ g mol^{-1} ($\bar{D}=1.28$), $\text{mol}\%(\text{PCHNBE})\text{:mol}\%(\text{PDL})=1.00\text{:}1.02$ [$\text{wt}\%(\text{PCHNBE})\text{:wt}\%(\text{PDL}) = 58\text{:}42$], 1.00 equiv.), 2-2-dimethoxyphenylacetophenone (10.0 mg, 0.10 equiv.) and butanethiol (30 μL , 0.27 mmol, 10 equiv.) or mercaptoethanol (30 μL , 0.43 mmol, 15 equiv.) were dissolved in CDCl_3 (0.5 mL) and transferred to a vial. The vial was sealed with a cap and irradiated at room temperature with a UV lamp (Philips Facial Tanner HB172, 4x15 W) at a distance of ca. 10 cm for 2 hours.

Chain-Extension with Methylene Diphenyl Diisocyanate

Inside the glovebox, methylene diphenyl diisocyanate (MDI, 72 mg, 0.288 mmol, 1.10 equiv. with respect to [OH]), the block copolymer (1.0 g, $M_n=4,000$ g mol⁻¹ ($\bar{D}=1.28$), $M_{n,theo}=8,420$ g mol⁻¹, mol%(PCHNBE):mol%(PDL)=1.00:1.02 [wt% (PCHNBE):wt% (PDL) = 58:42], 1.00 equiv.) and tin(II) 2-ethylhexanoate (0.1 mL of a stock solution with the concentration 10 mg mL⁻¹) were added to a 25 mL Schlenk flask, dissolved in ca. 5.0 mL of toluene and heated at 60 °C for 1.5 – 12 hours. The polymer was isolated by precipitation from methanol. In some cases, the quantity of hydroxyl end groups was not calculated but determined by ³¹P{¹H} NMR spectroscopy after the end group assay described above.

Polyester Degradation with Lithium Aluminium Hydride

The procedure reported by Coates and co-workers was followed.^[12] Typical amounts were: lithium aluminium hydride (0.50 g, 13.17 mmol), polyester (0.32 g) or the anhydride (0.16 g, 0.97 mmol).

Transesterification with DBU

The polyester (30 mg), DBU (1.0 mg) and toluene-d₈ (0.5 mL) were added to a J Young's NMR tube in the glovebox and left to react under polymerisation conditions (100 °C, 3 days). The ¹³C{¹H} NMR spectra of the original polymer and the polymer exposed to DBU were compared.^[13]

Epoxide/CO₂ Copolymerisations

The polymerisation reactor (20 or 100 mL high pressure vessel manufactured by Parr Instruments) was dried at 140 °C overnight, cooled under high vacuum and flushed for ca. 2 minutes with a stream of CO₂. A mixture of monomer (6 mL), catalyst, co-catalyst and chain-transfer agent (if used) were then injected into the vessel under a stream of CO₂. Alternatively, the reactor was loaded and sealed inside the glovebox. The vessel was then pressurised with carbon dioxide (5-40 bar) and stirred at ca. 1,000 rpm for the specified time. After depressurising, the crude mixture was analysed by NMR spectroscopy and SEC. The polymers were isolated by dissolving in DCM and precipitation from methanol. For PCHDC, a different purification procedure was followed: the crude polymer was dissolved in DCM, hexanoic acid (1 mL) was added, and the solution was stirred for 2 hours at room temperature. After evaporation, the obtained solid was dissolved in acetonitrile and extracted with *n*-hexane. The solution was then evaporated to dryness, dissolved in DCM, and precipitated in methanol (two times) and the pure polymer was obtained after drying under high vacuum at 40 °C.

ATR-IR Monitoring

The general polymerisation procedure was followed with the following differences: First, a three neck flask suitable for the instrument was used (glassware was dried at 140 °C overnight and cooled under high vacuum) and high amounts were used, i.e. PO (2.5 mL, 1000 equiv., 3.6 mmol), PA (780 mg, 100 equiv., 357 µmol), LA (950mg, 100 equiv., 357 µmol), CHD (41.5 mg, 10 equiv., 357 µmol), [Salphen^FAlCl] (16.6 mg, 1 equiv., 35.7 µmol) and PPNCI (16.4 mg, 0.8 equiv., 28.6 µmol).

Monitoring by ¹H NMR Spectroscopy

PO (78 µL, 150 equiv., 370 µmol), PA (55 mg, 50 equiv., 370 µmol), LA (54 mg, 50 equiv., 74 µmol), CHD (9 mg, 10 equiv., 74 µmol), [Salphen^FAlCl] (3.5 mg, 1.0 equiv., 7.4 µmol), PPNCI (3 mg, 0.8 equiv., 5.9 µmol) and mesitylene (10 µL, 10 equiv., 74 µmol) were added to a Young's Tap NMR tube with 0.5 mL of CDCl₃ inside the glovebox, sealed, and added to a 500 MHz NMR instrument preheated to 60 °C. Every 120 seconds, a ¹H NMR spectrum was recorded (number of scans=8; number of dummy scans=0). In total, 435 NMR spectra were collected, which were processed in Mestrenova (automatic baseline correction and phasing) after normalising against mesitylene.

Synthesis of Multiblock Polyesters

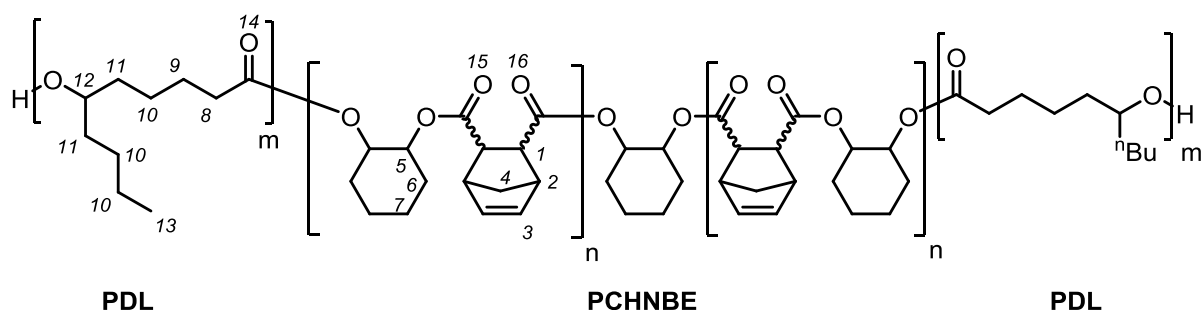
The general procedure outlined above was followed after mesitylene (10 equiv.) was added to the reaction mixture. After each monomer addition, the reaction was left to react at the specified temperature for at least 20 hour before aliquots were taken inside the glovebox and conversions were analysed by ¹H NMR spectroscopy and GPC. It should be noted that the solution became highly viscous, particularly at higher block numbers, and additional epoxide or solvent (1 mL) was added and the reaction transferred to a larger vial, if necessary. The final polymer was purified as described above.

Sample Preparation of Coating Materials (Small Scale)

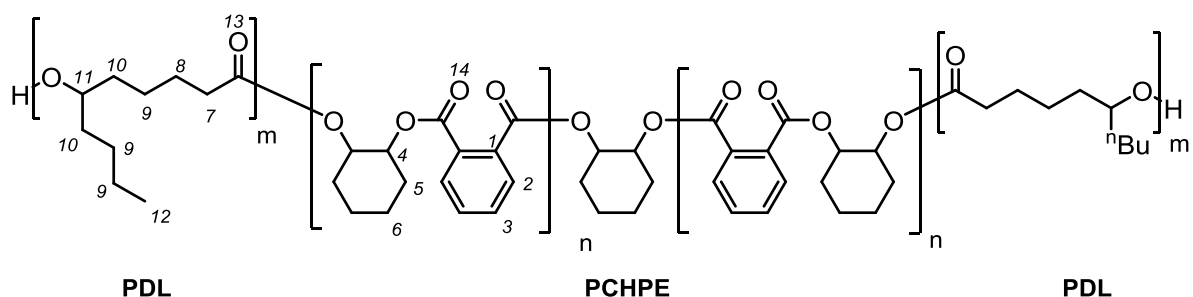
The polymers (40 mg for poly(cyclohexadiene carbonate) (PCHDC) and 67 mg for poly(limonene carbonate) (PLC)) were dissolved in DCM (80 µL) and the curing agent trimethylolpropane tris(3-mercaptopropionate) (for molar ratios (C=C):(SH) = 1:1, 2:1 and 4:1 63, 32 and 16 µL of a stock solution of 121 mg in 0.2 mL), and the initiator Irgacure 819 (24 µL from a stock solution of 10 mg per 0.1 mL) were added. This solution (10 µL) was applied to a glass slide and left to dry overnight, in a well-ventilated fume hood. The obtained films were positioned in a drying tube, which was placed in a heated oil bath (silicon oil), and irradiated for a defined amount of time with a UV lamp (Philips Facial Tanner HB172, 4x15 W) in a distance of ca. 10 cm. All work was done under exclusion of light, mainly by protecting the samples in boxes covered with aluminium foil.

Sample Preparation of Coating Materials for Mechanical Testing

Polymer (1.0 g of PCHDC or 1.4 g of PLC), curing agent (955 mg, 478 and 239 mg for 1:1, 2:1 and 4:1, respectively) and initiator (Irgacure 819, 60 mg) were dissolved in chloroform (2 mL). The solution was then applied on an aluminium plate (10 cm x 5 cm) with a doctor blade set to 250 μm , in a room designed for work with UV-sensitive compounds. The plate was dried in a fume hood overnight, placed on a heating plate, under nitrogen atmosphere, and irradiated for 30 minutes with a UV lamp at a distance of ca. 10 cm. Free-standing films for DMTA were cast in a Teflon mold.

9.4. Characterisation Data for selected Polymers

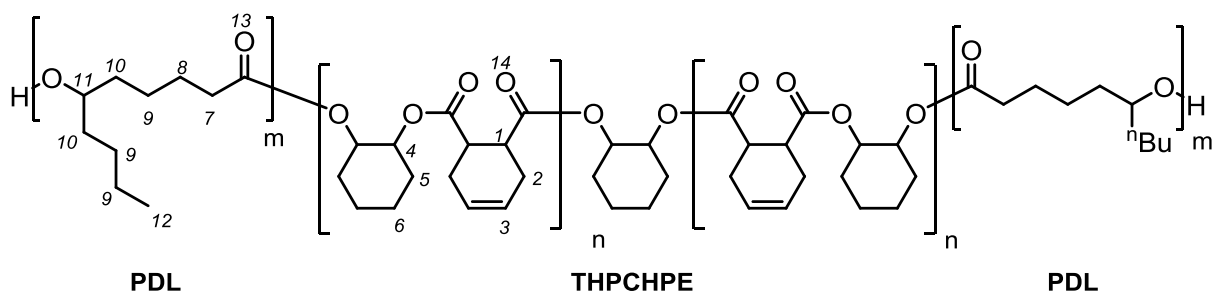
^1H NMR (500 MHz, CDCl_3) δ = 6.36-6.03 (m, 1.00 H, H^3), 4.84-4.71 (m, 1.35 H, $\text{H}^{5,12}$), 3.58 (m, 0.12 H, $\text{H}^{12\text{-Endgrp}}$), 3.37-3.11 (m, 1.80 H, $\text{H}^{1,2}$), 2.25 (m, 0.79 H, H^8), 1.98 (m, 1.09 H, H^6), 1.70 – 1.56 (m, 2.01 H, $\text{H}^{7,9}$), 1.55 – 1.45 (m, 1.54 H, H^{11}), 1.46 – 1.38 (m, 1.01 H, $\text{H}^{4,11\text{-Endgrp}}$), 1.38 - 1.15 (m, 4.44 H, $\text{H}^{4',6',7',10}$), 0.87 (m, 1.22 H, H^{13}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 173.6-171.2 ($\text{C}^{14,15,16}$), 137.7-133.5 (C^3), 73.98 (C^5), 73.8-72.6 (m, C^{11}), 71.76 (s, $\text{C}^{12\text{-Endgrp}}$), 48.6-48.0 (C^4), 47.0-45.6 ($\text{C}^{8/1\text{Junction},1,2}$), 37.3-37.2 ($\text{C}^{11\text{-Endgrp}}$), 34.7-34.4 (C^8), 33.9-33.8 (C^{11}), 30.02 (C^6), 27.9-27.6 (C^{10}), 25.3-23.4 ($\text{C}^{7,9}$), 22.8-22.6 (C^{10}), 14.21 (C^{13}) ppm.



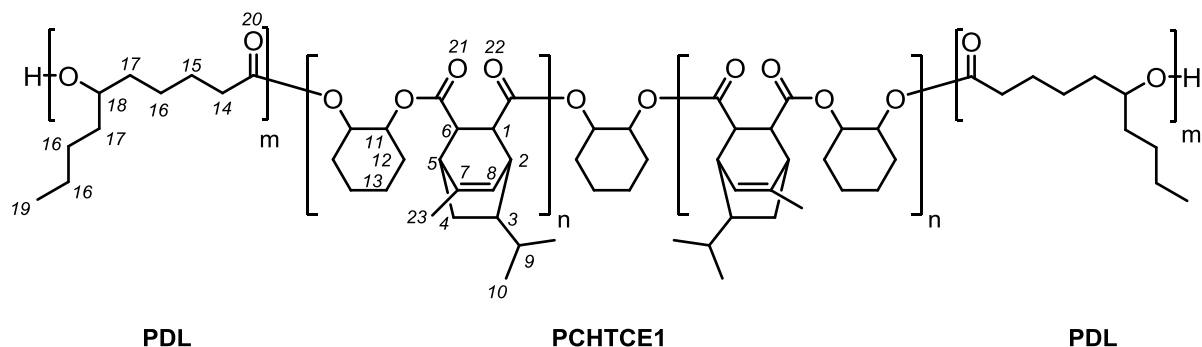
^1H NMR (500 MHz, CDCl_3) δ = 7.59-7.40 (m, 1.00 H, $\text{H}^{2,3}$), 5.14 (m, 0.44 H, H^4), 4.85 (m, 0.24 H, H^{11}), 3.58 (m, 0.04H, $\text{H}^{11\text{-Endgroup}}$), 2.27 (m, 0.92 H, $\text{H}^{7,5}$), 1.76-1.63 (m, 0.52 H, $\text{H}^{6,8}$),

1.51-1.28 (m, 1.94 H, $H^{5,10,6,9}$), 0.88 (m, 0.67 H, H^{12}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ = 173.51-172.98 (C^{13}), 166.68 (C^{14}), 132.04 (C^1), 131.07 (C^2), 128.79 (C^3), 74.77-73.89 ($C^{4,4-Junction*}$), 73.32 (C^{11}), 71.65 ($C^{11-Endgrp*}$), 37.23-37.07 ($C^{10-Endgrp}$), 34.50 (C^7), 33.81-33.74 (C^{10}), 29.91($C^{5,9-Endgrp}$), 27.86-27.46 (C^9), 25.01 (C^8), 23.41 (C^6), 22.76-22.58 (C^9), 14.10-14.02 (C^{12}) ppm.

* Cannot be distinguished from hydroxyl-terminated PCHPE-chains (in which case $C^{4-Junction}$ would be $C^{4-Esterlinkage}$ and $C^{11-Endgrp}$ would be $C^{4-Hydroxyl}$).

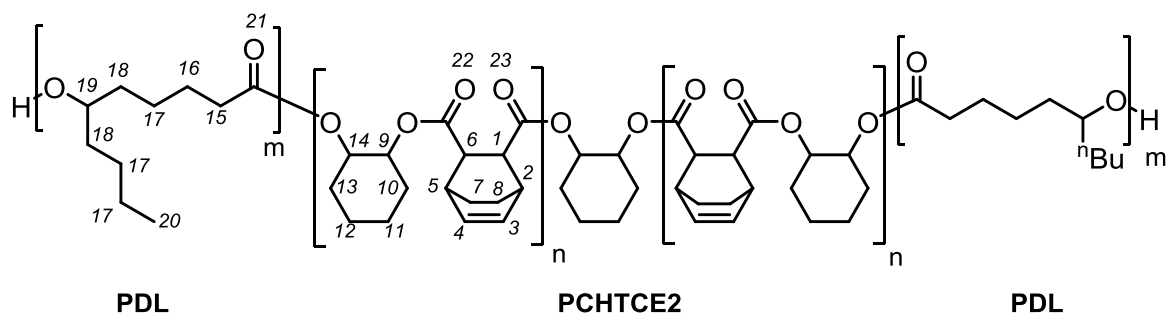


^1H NMR (500 MHz, $CDCl_3$) δ = 5.61 (m, 1.00 H, H^3), 4.86-4.79 (m, 1.32 H, $H^{1,11}$), 3.58 (m, 0.13 H, $H^{11-Endgrp}$), 2.97-2.79 (m, 1.03 H, $H^{1,1-Junction}$), 2.46 (m, 0.84 H, H^2), 2.26 (m, 1.59 H, $H^{2,7}$), 1.98 (m, 1.31 H, $H^{2-Junction,5}$), 1.68 (m, 2.16 H, H^6), 1.52 (m, 1.43 H, $H^{8,10}$), 1.32 (m, 4.41 H, $H^{10-Endgrp,5,9}$), 0.87 (m, 1.10H, H^{12}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ = 173.63-173.44 (C^{13}), 172.55 (C^{14}), 125.26 (C^3), 74.00 (C^{11}), 73.27 (C^4), 71.77 ($C^{11-Endgrp}$), 41.03 ($C^{1-Junction}$), 39.80 (C^1), 37.35 (C^{10}), 37.19 (C^7), 34.62-33.93 (C^8), 29.90 (C^5), 27.98-27.58 ($C^{9,2-Junction}$), 25.85-25.13 (C^8), 23.33 (C^6), 22.70 (C^9), 14.14 (C^{12}) ppm.

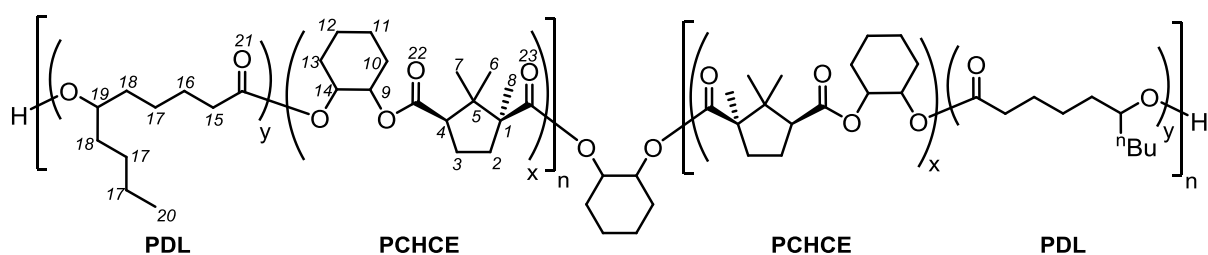


^1H NMR (500 MHz, $CDCl_3$) δ = 5.80-5.57 (m, 1.00 H, H^8), 4.84-4.65 (m, 2.87 H, $H^{1,6,18}$), 3.58 (m, 0.16 H, $H^{18-Endgrp}$), 2.97-2.66 (m, 3.86 H, $H^{2,5,1,6}$), 2.26 (m, 1.92 H, H^{14}), 2.08-1.83 (m, 3.09 H, H^{12}), 1.83-1.70 (m, 2.14 H, $H^{9,23}$), 1.70-1.56 (m, 3.84 H, $H^{4,15}$), 1.56-1.45 (m, 3.84 H, $H^{17,3}$), 1.44-1.16 (m, 10.63 H, $H^{12,13,16}$), 1.16-1.00 (m, 1.15 H, H^9), 0.89-0.80 (m, 6.37 H,

$H^{10,19}$, 0.80-0.66 (m, 2.99 H, $H^{10'}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ = 173.51-171.68 ($C^{20,21,22}$), 124.32-121.11 (C^8), 73.88 ($C^{11,18}$), 71.64 ($C^{18-Endgrp}$), 48.96-44.53 ($C^{2,5,1,6}$), 38.88-31.69 ($C^{2,5,1,6}$), 37.23 (C^{16}), 34.50 (C^{14}), 33.81 (C^{17}), 33.20-32.12 (C^9), 31.69-32.12 ($C^{2,5,1,6}$), 29.80 (C^{12}), 27.85 (C^{17}), 27.46 (C^{13}), 25.25-25.01 ($C^{15,16}$), 22.76 ($C^{17,Endgrp}$), 22.58 ($C^{4,16}$), 21.17 ($C^{10,23}$), 20.21 ($C^{10',23}$), 14.01 (C^{19}) ppm.

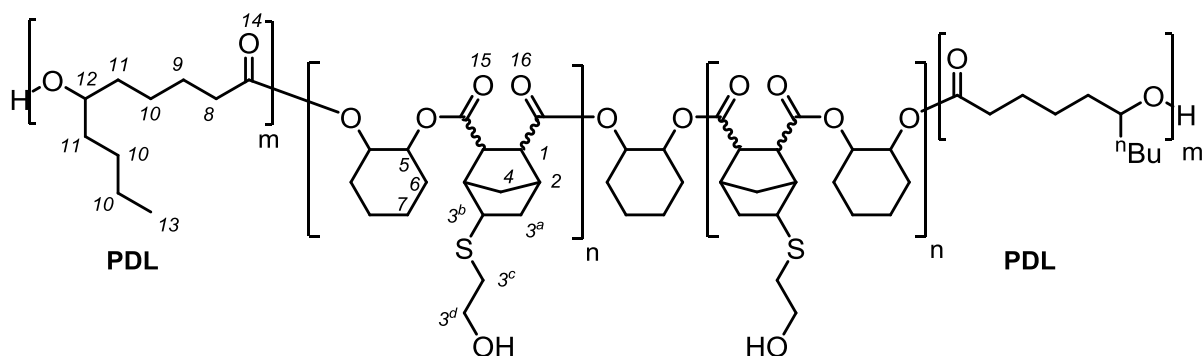


^1H NMR (500 MHz, $CDCl_3$) δ = 6.32-6.13 (m, 1.00 H, $H^{3,4}$), 4.84-4.68 (m, 1.35 H, $H^{9,14,19}$), 3.58 (m, 0.09 H, $H^{19-Endgroup}$), 2.93-2.85 (m, 1.89 H, $H^{2,5}$), 2.26 (m, 0.77 H, H^{15}), 1.97 (m, 1.05 H, $H^{10,13}$), 1.64 (m, 2.24 H, $H^{15,11,12}$), 1.50 (m, 2.04 H, H^{18}), 1.28 (m, 5.27 H, $H^{7,8,10',13,16,17}$), 1.10 (m, 0.24 H, $H^{17-Endgroup}$), 0.87 (m, 1.15 H, H^{20}) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ = 173.63-171.92 ($C^{21,22,23}$), 74.01 (C^{19}), 73.01 ($C^{4,9}$), 71.75 ($C^{19-Endgroup}$), 47.96-45.42 ($C^{2,5}$), 37.34 ($C^{7,8,10,13,16,17}$), 34.70 (C^{15}), 34.61 (C^{18}), 33.93-22.88 ($C^{7,8,10,13,16,17}$), 22.69 ($C^{17-Endgroup}$), 14.13 (C^{20}) ppm.

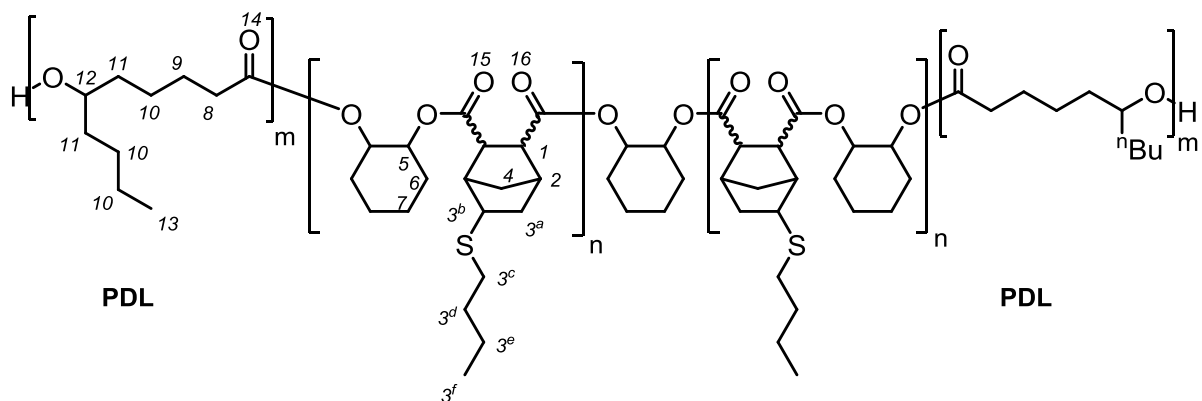


^1H NMR (500 MHz, $CDCl_3$) δ = 4.83 (m, 1.00 H, $H^{9,14,19}$), 3.56 (m, 0.05 H, $H^{19-Endgroup}$), 2.69 (m, 0.34 H, H^4), 2.50 (m, 0.34 H, H^2), 2.25 (m, 0.64 H, H^{15}), 2.10 (m, 0.37 H, H^3), 1.99 (m, 0.74 H, $H^{10,13}$), 1.79-1.73 (m, 0.29 H, $H^{3'}$), 1.68 (m, 0.97 H, H^{16}), 1.62-1.55 (m, 0.65 H, H^{16}), 1.50 (m, 1.20 H, H^{18}), 1.46-1.33 (m, 2.24 H, $H^{2',10',13',11,12}$), 1.26 (m, 1.54 H, H^{17}), 1.19-1.13 (m, 2.18 H, $H^{6,7,8}$), 0.86 (m, 0.97 H, H^{20}), 0.74 (m, 1.04 H, $H^{6,7,8}$) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ = 175.12 ($C^{22,23}$), 174.92 ($C^{22,23}$), 173.85 (C^{21}), 173.65 (C^{21}), 173.53 ($C^{22,23}$), 173.10 ($C^{22,23}$), 74.21 ($C^{9,14,19}$), 71.95 ($C^{19-Endgroup}$), 56.64-56.32 (C^5), 53.48-53.15 (C^4), 46.85

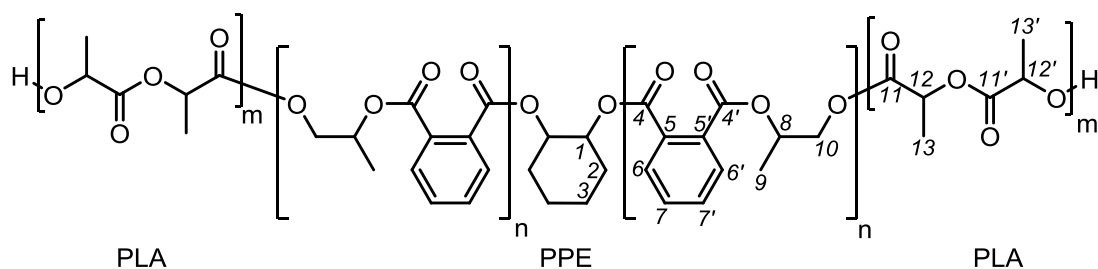
(C¹), 37.57-37.40 (C^{2,10,13}), 34.93-34.84 (C²⁰), 34.15-34.08 (C¹⁸), 32.82 (C²), 30.28 (C^{10,13}), 27.80 (C¹⁷), 25.60-22.70 (C^{3,6,7,8,16,18}), 25.27 (C^{16,17}), 22.92 (C^{11,12}), 21.91 (C^{6,7,8}), 21.43 (C^{6,7,8}), 14.36 (C²⁰) ppm.



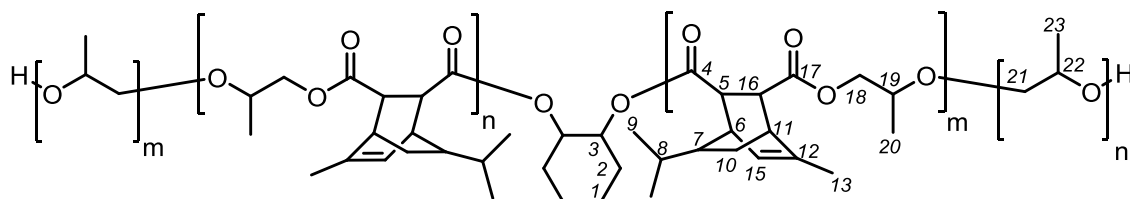
¹H NMR (400 MHz, CDCl₃) δ = 5.00-4.53 (m, 1.00 H, H^{5,12}), 3.93-3.62 (m, 0.84 H, H^{3d}), 3.62-3.48 (m, 0.15 H, H^{12-Endgrp}), 3.47-3.02 (m, 0.61 H, H^{1,2}), 2.97-2.34 (m, 2.47 H, H^{3a,b,c,b-OH}), 2.34 – 2.13 (m, 0.61 H, H⁸), 2.12-1.84 (m, 1.03 H, H⁶), 1.84-1.55 (m, 1.98 H, H^{7,9}), 1.55-1.44 (m, 1.14 H, H¹¹), 1.44-0.96 (m, 4.30 H, H^{4,4',6',7',10,11-Endgrp}), 0.93-0.73 (m, 0.90 H, H¹³) ppm.



¹H NMR (400 MHz, CDCl₃) δ = 4.92-4.47 (m, 1.00 H, H^{5,12}), 3.60-3.31 (m, 0.20 H, H^{12-Endgrp}), 3.30-2.77 (m, 0.71 H, H^{1,2}), 2.76-2.29 (m, 2.04 H, H^{3a,b,c}), 2.31 – 2.10 (m, 0.45 H, H⁸), 2.10-1.81 (m, 0.98 H, H⁶), 1.82-1.41 (m, 3.49 H, H^{3d,e,7,9,11}), 1.41-0.96 (m, 4.48 H, H^{3f,4,4',6',7',10,11-Endgrp}), 0.94-0.70 (m, 1.73 H, H^{3f,13}) ppm.



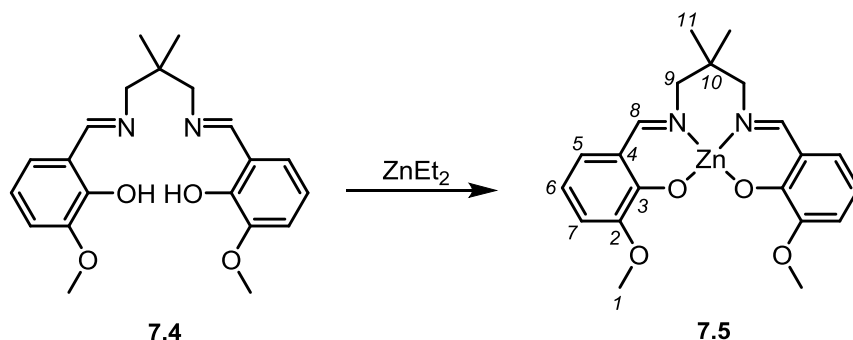
^1H NMR (500 MHz, CDCl_3) δ = 7.67 (m, 2.00 H, $\text{H}^{6/6'}$), 7.59 – 7.38 (m, 2.11 H, $\text{H}^{7/7'}$), 5.42 (m, 0.83 H, H^8), 5.31 – 4.99 (m, 2.03 H, $\text{H}^{1+12/12'-\text{Junction}/12-\text{Endgrp}}$), 4.49 – 4.18 (m, 2.21 H, $\text{H}^{10,10-\text{Junction}}$), 2.96 – 2.61 (m, 0.20 H, $\text{H}^{12-\text{Endgrp}-\text{OH}}$), 2.28 – 2.14 (m, 0.18 H, $\text{H}^{2/2'}$), 1.90 – 1.67 (m, 0.33 H, $\text{H}^{3/3'}$), 1.66 – 1.45 (m, 6.02 H, $\text{H}^{13/13'+13/13'-\text{Endgrp}}$), 1.44 – 1.10 (m, 3.24 H, $\text{H}^{9,13-\text{Junction}}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 175.13 ($\text{C}^{11-\text{Endgrp}}$), 169.51 ($\text{C}^{11/11'}$), 166.82 ($\text{C}^{4/4'}$), 132.34 ($\text{C}^{5/5'}$), 131.22 ($\text{C}^{6/6'}$), 129.01 ($\text{C}^{7/7'}$), 74.95 (C^1), 69.72 (C^{10}), 69.11 ($\text{C}^{13/13'}$), 67.05 (C^8), 30.06 (C^2), 23.46 (C^3), 20.62 ($\text{C}^{13-\text{Endgrp}}$), 16.86 ($\text{C}^{12/12'}$), 16.43 (C^9) ppm.



^1H NMR (400 MHz, CDCl_3) δ = 5.81-5.61 (m, 1.00 H, H^{15}), 5.21-4.84 (m, 0.94 H, $\text{H}^{19/19-\text{Jct}}$), 4.77-4.58 (m, 0.08 H, H^3), 4.31-3.71 (m, 2.09 H, $\text{H}^{18,18',23-\text{Endgrp}}$), 3.67-3.27 (m, 2.23 H, $\text{H}^{21,22,21-\text{Endgrp}}$), 3.18-2.76 (m, 3.25 H, $\text{H}^{5,11,16}$), 2.72-2.55 (m, 0.90 H, H^6), 2.08-1.77 (m, 2.96 H, $\text{H}^{1/2/13}$), 1.76-1.53 (m, 1.66 H, $\text{H}^{7,8}$), 1.41-1.00 (m, 6.93 H, $\text{H}^{1/2/10,20,23,20-\text{Jction}}$), 0.97-0.59 (m, 7.35 H, $\text{H}^{9/1/2}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 174.30 – 171.75 ($\text{C}^{4/17}$), 141.54 (C^{12}), 124.36 ($\text{C}^{15/15-\text{Junction}}$), 123.19 – 121.33 (C^{15}), 76.01 – 75.13 (C^{22}), 74.80 ($\text{C}^{22/21-\text{Junction}}$), 74.53 ($\text{C}^{22/21-\text{Endgrp}}$), 74.33 – 72.76 (C^{21}), 69.26 – 67.94 (C^{19}), 66.04-65.67 (C^{18}), 48.72-44.50 ($\text{C}^{5,11,16}$), 41.13 ($\text{C}^{20-\text{Junction}}$), 38.72 ($\text{C}^{5/6/11/16/7}$), 37.06 – 35.62 ($\text{C}^{5/11/16/7}$), 33.33 ($\text{C}^{6/11/15/16}$), 32.03 (C^{10}), 21.26 ($\text{C}^{13/9/20}$), 20.93 ($\text{C}^{13/7/8}$), 20.83 – 20.19 ($\text{C}^{13/7/8}$), 18.54–17.13 ($\text{C}^{23/20/9}$) ppm.

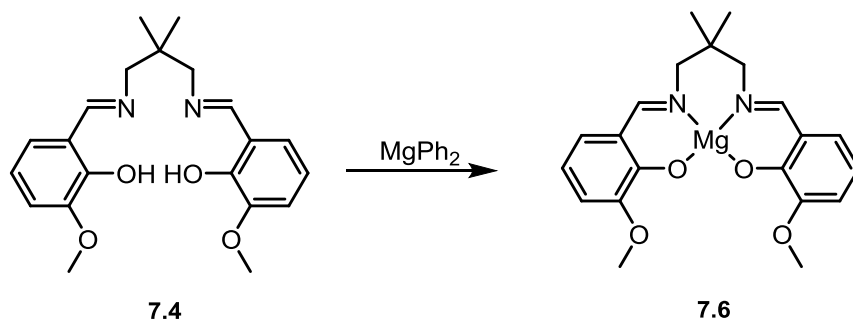
9.4. Synthesis and Characterisation Data for Complexes

Synthesis of Mono-zinc Complex 7.5

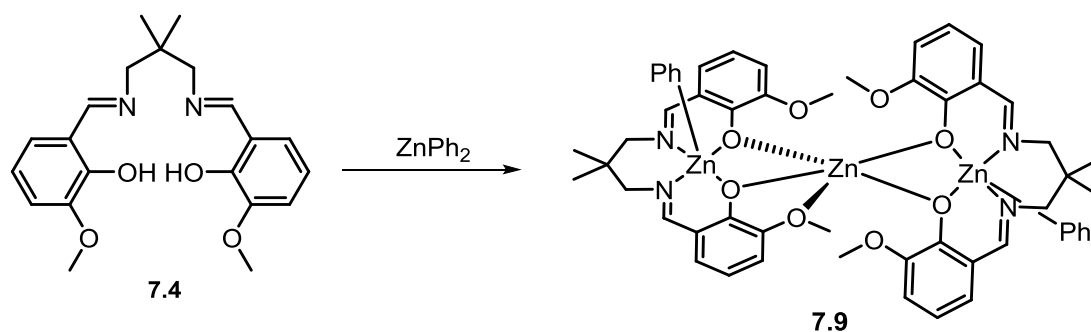


At -30 °C, diethyl zinc (167 mg, 1.35 mmol, 1.00 equiv.) was added to a solution of **7.4** (500 mg, 1.35 mmol, 1.00 equiv.) in THF (5 mL) and stirred for two hours. The suspension was centrifuged, washed with THF twice and dried under vacuum. Yield: 440 mg (75%, 1.01 mmol). ^1H NMR (400 MHz, CDCl_3) δ = 7.85 (s, 1H, H^8), 6.80 (dd, J = 7.7, 1.7 Hz, 1H, H^7), 6.66 (dd, J = 7.9, 1.7 Hz, 1H, H^5), 6.45 (t, J = 7.7 Hz, 1H, H^6), 3.74 (s, 3H, H^1), 3.49 (bs, 2H, H^9), 0.87 (s, 3H, H^{11}) ppm.^[14]

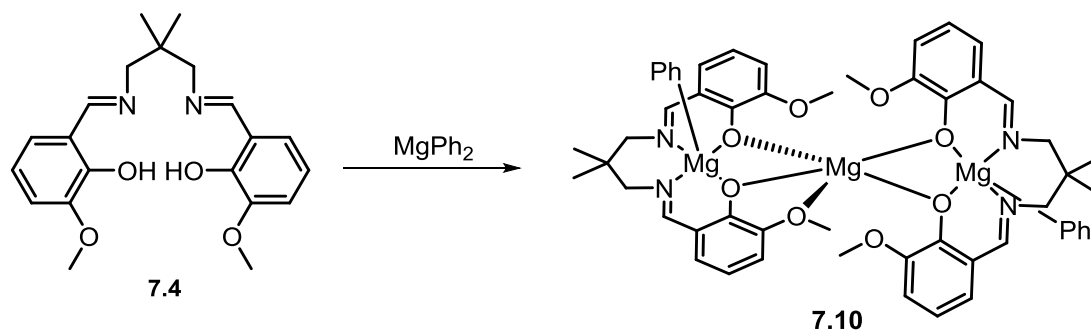
Synthesis of Mono-magnesium Complex 7.6



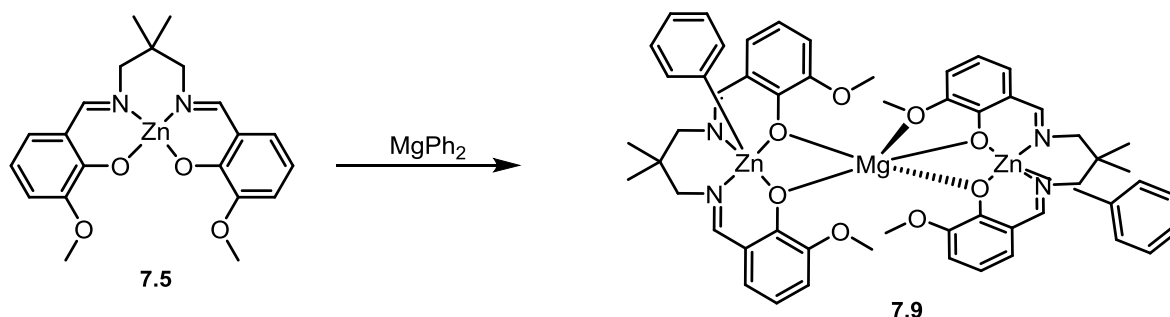
Diphenyl magnesium (7 mg, 40 μmol , 1.00 equiv.) was added to a solution of **7.4** (15 mg, 40 μmol , 1.00 equiv.) in CDCl_3 (0.5 mL). Single crystals were obtained by vapour diffusion with pentane.^[14]

Synthesis of Trizinc (bisphenyl) Complex 7.9

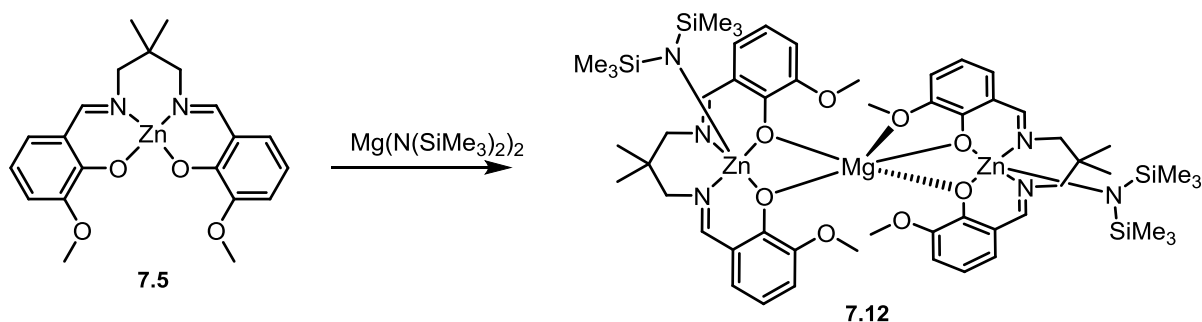
In an NMR tube, **7.4** (15 mg, 40 μmol , 1.00 equiv.) was dissolved in THF- d_8 (0.5 mL) and mesitylene (2 μL , 13 μmol , 0.33 equiv.) was added as an internal standard. Diphenyl zinc (18 mg, 81 μmol , 2.00 equiv.) was added and the reaction mixture was analysed after 15 minutes, 1 hour and 2 hours by ^1H NMR spectroscopy (see appendix). Single crystals were obtained from vapour diffusion with pentane.

Synthesis of Trimagnesium (bisphenyl) Complex 7.10

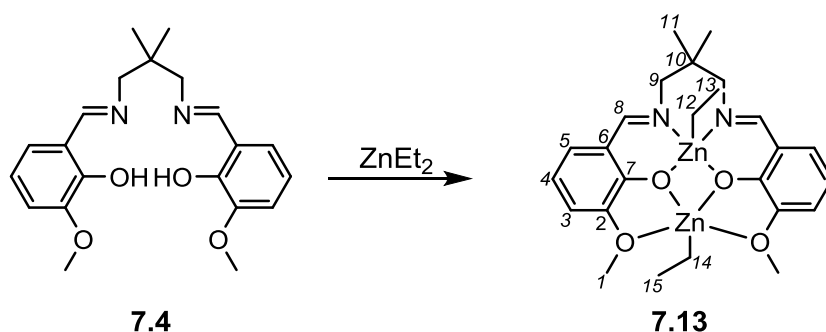
In an NMR tube, **7.4** (15 mg, 40 μmol , 1.00 equiv.) was dissolved in THF- d_8 (0.5 mL) and mesitylene (2 μL , 13 μmol , 0.33 equiv.) was added as an internal standard. Diphenyl magnesium (15 mg, 81 μmol , 2.00 equiv.) was added and the reaction mixture was analysed after 15 minutes, 1 hour and 2 hours (see appendix). Over time, a solid precipitated which was washed twice with THF and dried. Single crystals were obtained from vapour diffusion of the solid in CDCl_3 with pentane.

Synthesis of Heterotrimetallic (diphenyl) Complex 7.11

In an NMR tube, diphenylmagnesium (4 mg, 20 μmol , 1.00 equiv.) was added to a solution of **7.5** in THF-d_8 (0.5 mL) and reacted for ca. 20 hours. Single crystals were obtained by vapour diffusion with pentane. ^1H NMR (400 MHz, THF-d_8) δ = 8.34 (d, J = 1.8 Hz, 1H, $\text{H}^{8/22}$), 7.37 (s, 1H, $\text{H}^{\text{HC=N}}$), 7.28 – 7.21 (m, 2H, H^{Aryl}), 6.97 (dd, J = 8.0, 1.7 Hz, 1H, H^{Aryl}), 6.85 – 6.72 (m, 5H, H^{Aryl}), 6.62 – 6.51 (m, 2H, H^{Aryl}), 6.40 (dd, J = 7.9, 1.7 Hz, 1H, H^{Aryl}), 6.32 (t, J = 7.8 Hz, 1H, H^{Aryl}), 4.08 (d, J = 11.7 Hz, 1H, H^{NCH_2}), 3.79 (s, 1H), 3.41 (d, J = 12.9 Hz, 1H, H^{NCH_2}), 3.38 (s, 3H, $\text{H}^{1/16}$), 3.18 (d, J = 11.8 Hz, 1H, H^{NCH_2}), 2.90 (s, 3H, H^{OMe}), 2.73 (d, J = 12.8 Hz, 1H, H^{NCH_2}), 1.00 (s, 3H, H^{CH_3}), 0.88 (s, 3H, H^{CH_3}) ppm.

Synthesis of Heterotrimetallic (bis(hexamethyldisilazide)) Complex 7.12

In an NMR tube, magnesium bis(hexamethyldisilazide) (4 mg, 12 μmol , 1 equiv.) was added to a solution of **7.5** (10 mg, 24 μmol , 2 equiv.) in CDCl_3 (0.5 mL) and reacted for ca. 20 hours. The resulting NMR spectrum is shown in the appendix; single crystals were obtained by vapour diffusion with pentane.

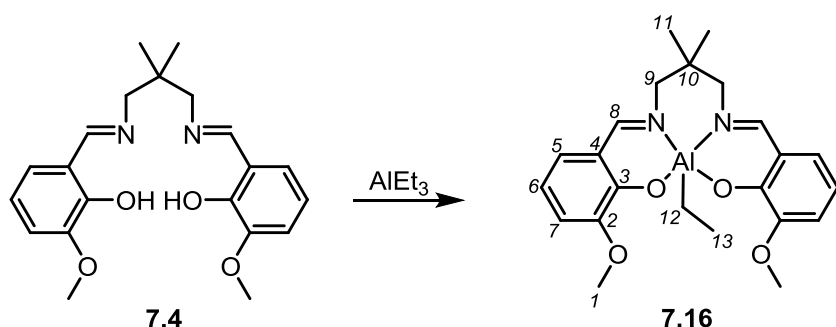
Synthesis of Dizinc (bisethyl) Complex 7.13

Diethylzinc (1.34 g, 10.80 mmol, 2.00 equiv.) was added dropwise to a cooled solution (-30 °C) of **7.4** (2.00 g, 5.40 mmol, 1.00 equiv.) in THF (30 mL). After ca. 2 hours, the yellow solution was concentrated and purified by crystallisation (vapour diffusion of THF solution with pentane). Overall yield: 1.80 g (3.24 mmol, 60%). ^1H NMR (500 MHz, THF- d_8) δ = 7.98 (s, 2H, H⁸), 6.83 (dd, J = 7.8, 1.6 Hz, 2H, H⁵), 6.72 (dd, J = 8.0, 1.6 Hz, 2H, H³), 6.40 (t, J = 7.8 Hz, 2H, H⁴), 4.22 (d, J = 11.3 Hz, 2H, H⁹), 3.93 (s, 6H, H¹), 3.12 (d, J = 11.3 Hz, 2H, H⁹), 1.28 (t, J = 8.2 Hz, 3H, H^{13/15}), 1.20 (t, J = 8.1 Hz, 3H, H^{13/15}), 1.08 (s, 3H, H¹¹), 0.67 (s, 3H, H¹¹), 0.42 (q, J = 8.1 Hz, 2H, H^{13/15}), 0.06 (d, J = 8.1 Hz, 2H, H^{13/15}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, THF- d_8) δ = 168.00 (C⁸), 158.00 (C⁷), 150.43 (C²), 127.50 (C⁵), 120.10 (C⁶), 113.86 (C⁴), 113.38 (C²), 75.24 (C⁹), 56.38 (C¹), 37.37 (C¹⁰), 27.47 (C¹¹), 21.94 (C¹¹), 14.35 (C^{13/15}), 13.31 (C^{13/15}), -0.96 (C^{14/12}), -1.61 (C^{14/12}) ppm. EA: Found (calcd. for C₂₅H₃₄N₂O₄Zn₂): C, 53.75 (53.88); H, 6.01 (6.15); N 4.93 (5.03)%.

Synthesis of trizinc (bisalkoxide) complexes 7.14 and 7.15

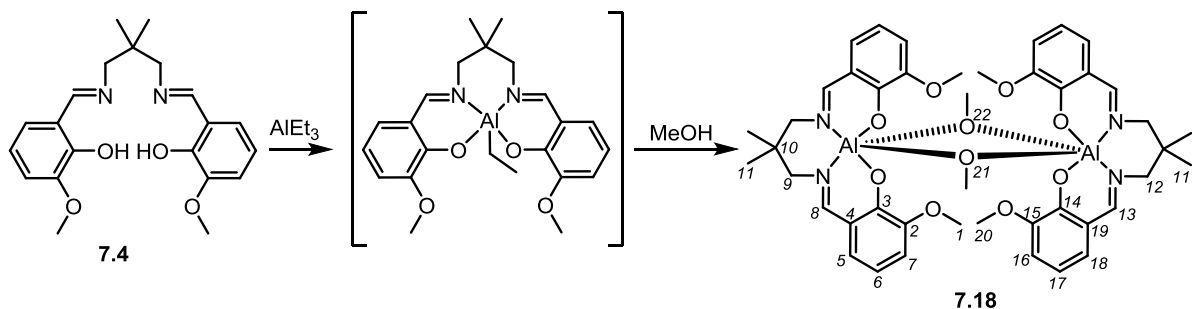
In an NMR tube, 20 mg of **7.13** (35.9 μmol , 1.00 equiv.) was dissolved in 0.5 mL of dry CDCl₃ and 2.00 equiv. of the corresponding alcohol was added. Crystals suitable for XRD were obtained by vapour diffusion with pentane.

Synthesis of Aluminium Ethyl Complex 7.16



Triethyl aluminium (154 mg, 1.35 mmol, 1.00 equiv.) was added dropwise to a solution of **7.4** (500 mg, 1.35 mmol, 1.00 equiv.) in THF (10 mL), which was cooled to $-30\text{ }^{\circ}\text{C}$. After stirring for two hours at room temperature, the solvent was removed and the solid was washed three times with pentane. Single crystals were obtained from vapour diffusion with acetonitrile / pentane. Yield: 400 mg (0.945 mmol, 70%). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ = 8.06 (s, 2H, H^8), 6.91 (dd, J = 7.7, 1.7 Hz, 2H, H^7), 6.80 (dd, J = 7.9, 1.6 Hz, 1H, H^5), 6.60 (t, J = 7.8 Hz, 2H, H^6), 3.93 (d, J = 12.0 Hz, 2H, H^9), 3.85 (s, 6H, H^1), 3.21 (d, J = 12.1 Hz, 2H, H^9), 1.13 (s, 3H, H^{11}), 0.94 (s, 3H, H^{11}), 0.88 (t, J = 8.0 Hz, 3H, H^{13}), -0.01 (q, J = 8.0 Hz, 2H, H^{12}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 169.08 (C^8), 157.77 (C^3), 151.91 (C^2), 124.93 (C^5), 119.13 (C^7), 117.99 (C^4), 115.65 (C^6), 71.06 (C^9), 56.98 (C^1), 36.22 (C^{10}), 26.04 (C^{11}), 23.29 (C^{13}), 10.10 (C^{12}) ppm.

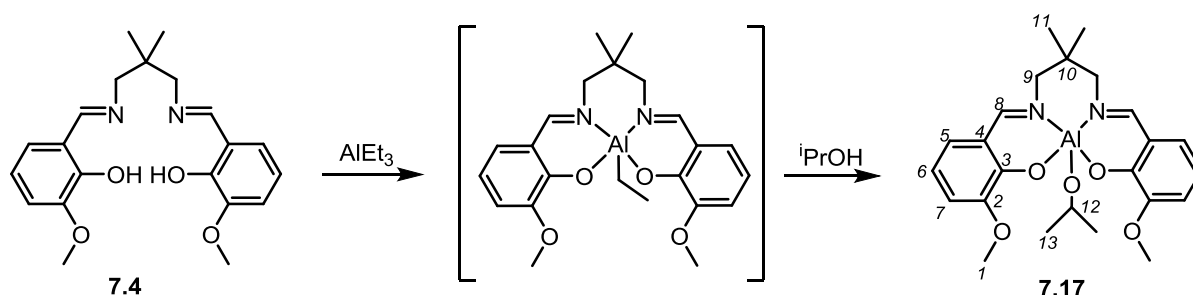
Synthesis of Dialuminium (bismethoxy) Complex 7.18



Ligand **7.4** (2.0 g, 5.40 mmol, 1.00 equiv.) was dissolved in THF (10 mL) and cooled to $-30\text{ }^{\circ}\text{C}$ in the freezer of the glovebox. Triethyl aluminium (617 mg, 5.40 mmol, 1.00 equiv.) were added then dropwise and the resulting solution stirred for 2 hours at room temperature before methanol (220 μL , 5.67 mmol, 1.05 equiv.) was added. Ca. 10 mL of THF were added to this suspension and the precipitate was filtered off after stirring at room temperature for 48 hours. Finally, the solid was washed with pentane three times and dried. Crystals suitable for XRD were obtained by vapour diffusion from CHCl_3 / pentane. Overall

yield: 0.86 g (37%, 2.02 mmol). ^1H NMR (500 MHz, CDCl_3) δ = 7.99 (s, 1H, H^8), 7.87 (s, 1H, H^{13}), 6.95 (s, 1H, H^7), 6.85 (m, 3H, $\text{H}^{5,17,19}$), 6.50 (m, 2H, $\text{H}^{6,18}$), 4.22 (d, J = 10.0 Hz, 1H, H^{12}), 3.91 (s, 1H, H^1), 3.71 (d, J = 12.8 Hz, 1H, H^9), 3.38 (s, 1H, H^{20}), 3.14 (s, 1H, $\text{H}^{21/22}$), 3.00 (d, J = 12.5 Hz, 1H, H^9), 2.71 (d, J = 10.0 Hz, 1H, H^{12}), 0.91 (s, 1H, H^{11}), 0.71 (s, 1H, H^{11}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 169.01 (C^8), 166.38 (C^{13}), 161.01 (C^3), 160.00 (C^{15}), 152.37 (C^2), 151.74 (C^{16}), 126.28 (C^5), 124.79 (C^{19}), 121.11 (C^{14}), 120.89 (C^{17}), 120.86 (C^4), 120.16 (C^7), 114.51 (C^6), 113.76 (C^{18}), 73.90 (C^9), 71.70 (C^{12}), 58.72 (C^1), 57.86 (C^{20}), 51.05 (C^{21}), 36.86 (C^{10}), 26.49 (C^{11}), 22.74 (C^{11}) ppm. EA^i : Found (calcd. for $\text{C}_{22}\text{H}_{27}\text{AlN}_2\text{O}_5$): C, 61.75 (61.96); H, 6.47 (6.38); N, 6.40 (6.57)%.

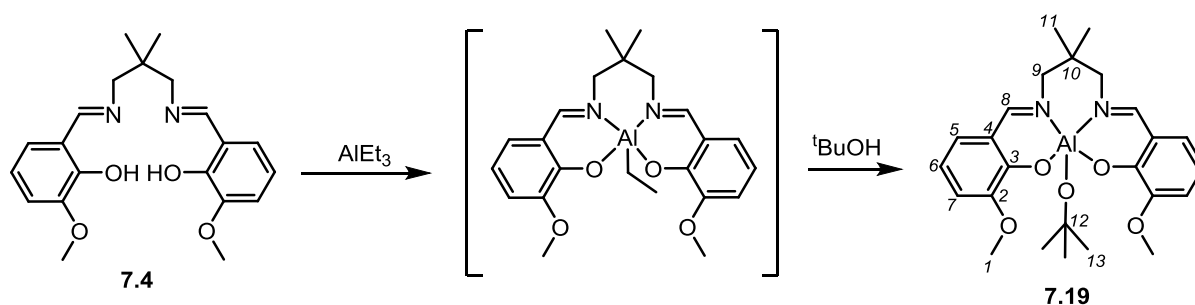
Synthesis of Aluminium Isopropoxide Complex 7.17



Ligand **7.4** (555 mg, 1.50 mmol, 1.00 equiv.) was dissolved in THF (5 mL) and the resulting solution cooled to $-30\text{ }^\circ\text{C}$. Triethyl aluminium (184 mg, 1.50 mmol, 1.00 equiv.) was added dropwise and the solution stirred for two hours before *iso*-propanol (116 μL , 1.50 mmol, 1.00 equiv.) was added. After stirring at room temperature overnight, the precipitate was filtered off, washed with pentane and dried *in vacuo*. Crystals suitable for XRD were obtained by vapour diffusion from CDCl_3 / pentane. Overall yield: 477 mg (1.05 mmol, 70%). ^1H NMR (500 MHz, CDCl_3) δ = 8.09 (s, 2H, H^8), 6.93 (dd, J = 7.7, 1.6 Hz, 2H, H^7), 6.82 (dd, J = 7.9, 1.6 Hz, 2H, H^5), 6.62 (t, J = 7.8 Hz, 2H, H^6), 4.06 (d, J = 12.1 Hz, 2H, H^9), 4.00 (s, J = 6.1 Hz, 1H, H^{12}), 3.87 (s, 6H, H^1), 3.24 (d, J = 12.1 Hz, 2H, H^9), 1.14 (s, 3H, H^{11}), 1.00 (d, J = 6.1 Hz, 6H, H^{13}), 0.96 (s, 3H, H^{11}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3) δ = 169.58 (C^8), 157.60 (C^3), 151.64 (C^2), 124.82 (C^5), 118.92 (C^7), 117.83 (C^4), 115.75 (C^6), 70.26 (C^9), 63.02 (C^{12}), 56.83 (C^1), 35.89 (C^{10}), 27.61 (C^{13}), 25.83 (C^{11}), 24.44 (C^{11}) ppm. EA : Found (calcd. for $\text{C}_{24}\text{H}_{31}\text{AlN}_2\text{O}_5$): C, 63.29 (63.42); H, 6.77 (6.88); N 6.24 (6.16)%.

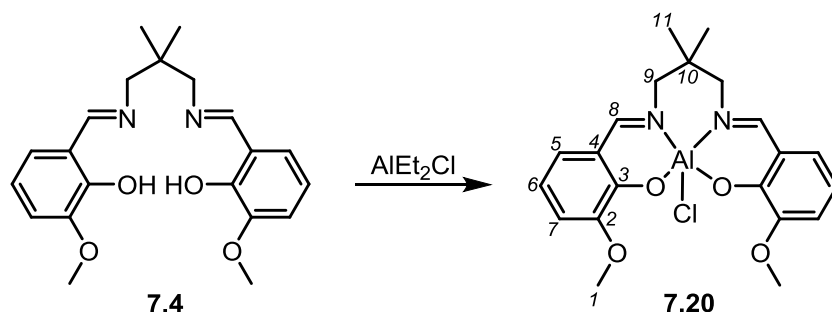
ⁱ Recorded by W. Diment.

Synthesis of Aluminium *tert*-Butoxide Complex 7.19



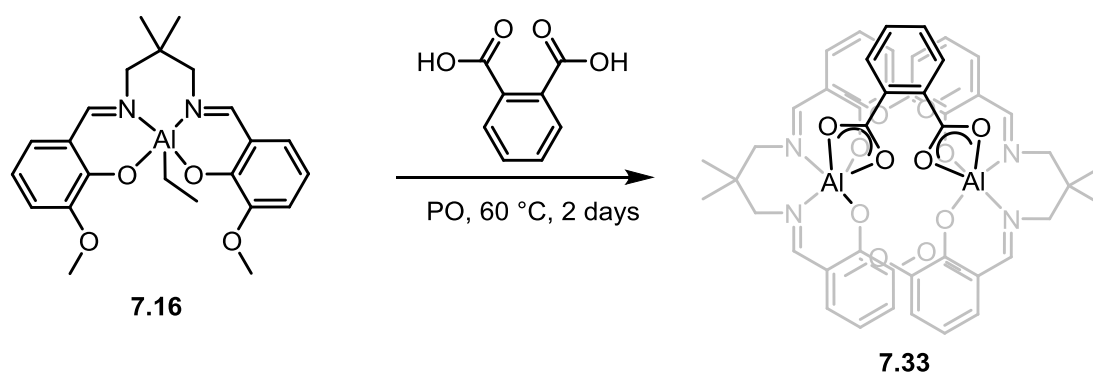
Ligand **7.4** (2.00 g, 5.40 mmol, 1.00 equiv.) was dissolved in THF (20 mL) and cooled to $-30\text{ }^{\circ}\text{C}$. Triethyl aluminium (663 mg, 5.40 mmol, 1.00 equiv.) was added dropwise and after 1 hour, *tert*-butanol (0.44 g, 5.90 mmol, 1.1 equiv.) was added. The precipitate formed after ca. 24 hours and was filtered off, washed with pentane and dried under vacuum. Yield: 1.66 g (3.54 mmol, 66%). ^1H NMR (400 MHz, CDCl_3) δ = 8.04 (s, 2H, H^8), 6.96 (dd, J = 7.8, 1.7 Hz, 2H, H^7), 6.83 (dd, J = 7.8, 1.7 Hz, 2H, H^5), 6.60 (t, J = 7.8 Hz, 2H, H^6), 4.26 (d, J = 11.9 Hz, 2H, H^9), 3.94 (s, 6H, H^1), 3.18 (d, J = 11.9 Hz, 2H H^9), 1.15 (s, 12H, H^{11+13}), 0.93 (s, 3H, H^{11}) ppm.

Synthesis of Aluminium Chloro Complex 7.20



Diethylaluminium chloride (171 mg, 1.42 mmol, 1.05 equiv.) was added dropwise to a solution of **7.4** (500 mg, 1.35 mmol, 1.00 equiv.) in THF (10 mL), which was cooled to $-30\text{ }^{\circ}\text{C}$. After stirring the resulting suspension for two hours at room temperature, the solvent was removed and the solid was washed three times with pentane. Single crystals were obtained from vapour diffusion with pyridine / pentane. Yield: 435 mg (1.01 mmol, 75%). ^1H NMR (500 MHz, pyridine- d_5) δ = 8.30 (s, 2H, H^8), 7.00 (m, 4H, H^{7+5}), 6.59 (t, J = 7.8 Hz, 2H, H^6), 5.29 – 3.94 (bs, 1H, H^9), 3.78 (s, 6H, H^1), 3.60 – 2.50 (bs, 1H, H^9), 0.83 (bs, 6H, H^{11}) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, pyridine- d_5) δ = 169.71 (C^8), 159.86 (C^3), 152.73 (C^2), 126.40 (C^5), 122.10 (C^7), 119.36 (C^4), 115.47 (C^6), 72.29 (C^9), 57.61 (C^1), 37.31 (C^{10}), 24.93 (C^{11}) ppm.

Synthesis of Bisaluminium (Dicarboxylate) Complex **7.33**



In an NMR tube, aluminium ethyl complex **7.16** (35 mg, 82.4 μmol , 1.00 equiv.) was dissolved in propylene oxide (0.5 mL) and phthalic acid (14 mg, 82.4 μmol , 1.00 equiv.) was added. The resulting mixture was heated at 90 °C overnight and single crystals were obtained upon cooling.

9.5. References

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Applications, Synthesis and Catalyst Design for Oxygenated Polymers

APPENDIX

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Figure S 3. 54	COSY NMR spectrum of polymer based on TCA2, CHO, DL.
Figure S 3. 55	HSQC NMR spectrum of polymer based on TCA2, CHO, DL.
Figure S 3. 56	¹³ C{ ¹ H} NMR spectrum of polymer based on TCA2, CHO, DL. Traces of PPNCI were observed at 129.8, 132.2 and 134.1 ppm.
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Figure S 3. 58	Conversion of TCA2 and DL and formation of polyester 5s time. Data was obtained after normalization with mesitylene as internal standard.
Figure S 3. 59	<i>In situ</i> monitoring of IR band of TCA2 at 1850 cm ⁻¹ .
Figure S 3. 60	GPC chromatograms at different conversions.
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Figure S 3. 62	MALDI of polymer based on TCA2/CHO/DL (after 1 h, 94% TCA2 and 1% DL conversion). Five species were detected: circle: m/z = [116.08 (cyclohexandiol) + (276.14 x n) (PCHTCE2) + 38.96 (K ⁺)] (n = 3 ~ 17); square: m/z = [34.97 (Cl.) + 98.07 (CHO) + 1.01 (H.) + (276.14 x n) (PCHTCE2) + 38.96 (K ⁺)] (n = 3 ~ 13); triangle: m/z = [18.01 (H ₂ O) + (276.14 x n) (PCHTCE2) + 38.96 (K ⁺)] (n = 3 ~ 7); diamond: m/z = [98.07 (CHO) + (276.14 x n) (PCHTCE2) + 38.96 (K ⁺)] (n = 3 ~ 7); star: m/z = [116.08 (cyclohexandiol) + (214.08 x n) (PCHTCE2) + (170.13 x m) (PDL) + 38.96 (K ⁺)] (n = 4 ~ 12).
Figure S 3. 63	¹ H NMR spectrum of polymer based on CA/CHO/DL.
Figure S 3. 64	COSY NMR spectrum for polymer based on CA/CHO/DL.
Figure S 3. 65	HSQC NMR spectrum for polymer based on CA/CHO/DL.
Figure S 3. 66	¹³ C{ ¹ H} NMR spectrum based on CA/CHO/DL. Traces of PPNCl were observed at 129.8, 132.2 and 134.1 ppm.
Figure S 3. 67	¹ H NMR spectra for the polymerization of CA, CHO and DL.
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Figure S 3. 69	GPC chromatograms at different conversions for the polymerization of CA/CHO/DL.
Figure S 3. 70	¹ H NMR spectra of crude (bottom) and isolated (top) polymer based on CA/CHO/DL.
Figure S 3. 71	MALDI of one-pot polymerization of CA/CHO/DL (after 19 h, 67% CA and 14% DL conversion). The series shows four species: star and triangle: m/z = [116.08 (cyclohexandiol) + (280.17 x n) (PCHCE) + (170.13 x m) (PDL) + 38.96 (K ⁺)] (n = 3 ~ 16 and m = 1 for star and n = 2 ~ 11 and m = 2 for triangle); circle: m/z = [116.08 + (cyclohexandiol) + (280.17 x n) (PCHCE) + 38.96 (K ⁺)] (n = 4 ~ 16); square: m/z = [34.97 (Cl.) + 98.07 (CHO) + 1.01 (H.) + (280.17 x n) (PCHCE) + 38.96 (K ⁺)] (n = 4 ~ 5).
Figure S 3. 72	³¹ P{ ¹ H} NMR after end-group assay with different polymers.
Figure S 3. 73	¹ H NMR spectrum of isolated polyester after post-functionalization with mercapto ethanol.
Figure S 3. 74	¹ H NMR spectrum of isolated polyester after post-functionalization with butane thiol.
Figure S 3. 75	GPC Trace obtained from one pot polymerisation of CHO, PA, LA and CO ₂ .
Figure S 3. 76	DSC Thermogram of polymer obtained from one pot polymerisation of CHO, PA, LA and CO ₂ .
Figure S 3. 77	DOSY NMR of polymer obtained from one pot polymerisation of CHO, PA, LA and CO ₂ .
Figure S 3. 78	³¹ P{ ¹ H} NMR spectrum of polymer obtained from one pot polymerisation of CHO, PA, LA and CO ₂ after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane (only region relevant to alcohols shown).
Table S 3. 1	Optimisation of CTA for ROP, ROCOP and Switch catalysis. ^[a]
Table S 3. 2	Integrals based on ¹ H NMR spectra (after normalization with mesitylene) and calculated conversions. Signals were based on the following shifts: 4.45 (NBA), 4.45-4.92 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. An error of ± 3% was applied to all plots; the conversion of CHO at the end of the reaction was determined as 74 % (data not shown).
Table S 3. 3	Block polyesters with variable compositions and properties.
Table S 3. 4	Integrals based on ¹ H NMR spectra (after normalization with mesitylene as

	internal standard) and calculated conversions. Signals were based on the following shifts: Signals were based on the following shifts: 7.87-8.08 (PA), 4.78 – 5.30 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 76 % (data not shown).
Table S 3. 5	Integrals based on ^1H NMR spectra (after normalization with mesitylene) and calculated conversions. Signals were based on the following shifts: 6.60 (THPA), 4.67-4.95 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 79 % (data not shown).
Table S 3. 6	Integrals based on ^1H NMR spectra (after normalization with mesitylene) and calculated conversions. Signals were based on the following shifts: 3.21 (TCA1), 4.45-4.92 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 77 % (data not shown).
Table S 3. 7	Integrals based on ^1H NMR spectra (after normalization with mesitylene as internal standard, Figure) and calculated conversions used for Fig. S 68. Signals were based on the following shifts: 6.80 (TCA2), 4.22 (DL), 4.95 – 4.45 (polyester) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 67 % (data not shown).
Table S 3. 8	Integrals based on ^1H NMR spectra (after normalization with mesitylene as internal standard) and calculated conversions. Signals were based on the following shifts: 1.00 (CA), 3.13 (CHO), 4.22 (DL), 4.74 – 5.00 (polyester) ppm. The conversion of CHO at the end of the reaction was determined as 80 % (data not shown).
Table S 3. 9	$^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of different polymers after end-group assay.

Chapter 4

Figure S 4. 1	^1H NMR spectra at different times of the one-pot polymerization of TCA1/PO. The arrows indicate the signals used for the conversion vs. time plots.
Figure S 4. 2	Consumption of TCA1 in one-pot reaction of TCA1/PO. Conversion vs. time data was based on integrals from ^1H NMR spectroscopy after normalizing against mesitylene as an internal standard. The following errors were applied: y-axis ± 0.15 M and x-axis ± 0.08 h.
Figure S 4. 3	Concentration of PO vs. time data was based on integrals of PPO from ^1H NMR spectroscopy after normalizing against mesitylene as an internal standard. The following errors were applied: y-axis ± 3 % and x-axis ± 0.08 h.
Figure S 4. 4	GPC traces during the one-pot polymerization of TCA1/PO.
Figure S 4. 5	MALDI Spectrum of crude sample of one-pot polymerization of TCA1/PO after 2h (25% polyesterformation, < 5% polyether formation, $M_n=1,790$ g mol $^{-1}$ ($\bar{D}=1.13$). The peaks correspond to a perfectly alternating polyester ($n \cdot 292.167$ with $n=2-11$) + CHD (116.08) + K^+ (38.96). A second distribution with a repeating unit of $m/z=74.00$ was assigned to polysiloxane, a common trace impurity in high-resolution mass spectrometry (not shown). ^[4, 5]
Figure S 4. 6	T_1 -Inversion recovery experiment for peaks at 138 and 146 ppm in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. T_1 values were determined as 2.992 s and 2.415 s after exponential fitting ($I_t=I_0+P\cdot\exp(-t/T_1)$) for 138 and 144 ppm, respectively.
Figure S 4. 7	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of block copolymer with $D_1 = 5 \cdot 2.992$ s (as determined above; 128 scans). Based on this integration, 27.3 μmol [OH] /

	50.0 mg [Polymer] are present (calculated from standard, the integral 1.00 corresponds to 40 μ L of a stock solution of 40 mg / mL (1.6 mg), which, in turn is equivalent to 14.0 μ mol of [OH]).
Figure S 4. 8	^1H NMR Spectrum of block copolymer.
Figure S 4. 9	H, H COSY NMR Spectrum of block copolymer.
Figure S 4. 10	$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of polymer obtained from TCA1/PO.
Figure S 4. 11	$\text{Ln}([\text{Cr}^{\text{Carboxylate}}]_t/[\text{Cr}^{\text{Carboxylate}}]_0)$ vs. time plot to determine the rate constant. Data based on IR data.
Figure S 4. 12	$\text{Ln}([\text{Cr}]_t/[\text{Cr}]_0)$ vs. time plot to determine the rate constant. Data based on IR data.
Figure S 4. 13	DSC Thermograms of polymers before and after chain-extension.
Figure S 4. 14	Monomodal (top) and bimodal (bottom) GPC traces of substrates shown Table 4.1 after six days.
Figure S 4. 15	DSC Thermograms for substrates shown in Table 4.1.
Figure S 4. 16	DSC Thermograms for polymer based on <i>tert</i> -butyl glycidyl ether / TCA1.
Figure S 4. 17	DSC Thermogram for polymer based on glycidyl hexadecyl ether / TCA1.
Figure S 4. 18	DSC Thermogram for polymer based on 2-ethylhexyl glycidyl ether / TCA1.
Figure S 4. 19	GPC traces of one-pot reactions of different epoxides with TCA1.
Figure S 4. 20	GPC Traces of polyethers (blue), polyesters (red) and polyester- <i>b</i> -polyethers (black) with different PO derivatives.
Figure S 4. 21	GPC Traces of the one-pot polymerization of different anhydrides with PO.
Figure S 4. 22	TCA1/PO 'Switch' catalysis with different monomer:catalyst loadings.
Figure S 4. 23	DSC Thermograms of polymers based on different TCA1/PO ratios.
Figure S 4. 24	DSC Thermogram of polymer obtained from TCA1:PO = 400:800.
Figure S 4. 25	DSC Thermograms for polymer obtained from TCA1/PO with different amounts of <i>iso</i> -propanol. The transitions at high temperatures were assigned to catalyst residues (see below).
Figure S 4. 26	GPC Traces of PPO samples in the presence of TCA1 (5 equiv., black) and the absence of TCA1 (blue).
Figure S 4. 27	DSC Thermograms of PPO samples (with 5 equiv. of TCA1 [black] and in the absence of TCA1 [blue]).
Figure S 4. 28	DSC Thermogram PPNCI.
Figure S 4. 29	DSC Thermogram [SalcyCrCl].
Figure S 4. 30	GPC traces of TCA1/PO 'Switch' catalysis with selected alcohols.
Figure S 4. 31	DSC thermograms of TCA1/PO 'Switch' catalysis with selected alcohols.
Figure S 4. 32	GPC traces of TCA1/PO 'Switch' catalysis with selected alcohols.
Figure S 4. 33	DSC thermograms of TCA1/PO 'Switch' catalysis with selected alcohols. The full range is shown on top and the enlarged region (80 – 120 $^{\circ}\text{C}$) is shown on the bottom.
Figure S 4. 34	GPC traces for Polymers with different monomer loadings.
Figure S 4. 35	DSC Thermogram of multiblock copolymer based on TCA1/PO. The second <i>transition</i> is ascribed to catalyst residues.
Figure S 4. 36	GPC traces of polymers based on TCA1/PO with different block ratios.
Figure S 4. 37	DSC Thermogram of polymer obtained from PO/TCA1/DL. The transition at ca. 90 $^{\circ}\text{C}$ is ascribed to catalyst residues.
Figure S 4. 38	^1H NMR Spectrum for polymer obtained from PO/TCA1/DL.
Figure S 4. 39	$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum for polymer obtained from PO/TCA1/DL.
Figure S 4. 40	^1H NMR Spectrum for polymer obtained from PO/CA.
Figure S 4. 41	$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum for polymer obtained from PO/CA.
Figure S 4. 42	^1H NMR Spectrum for polymer obtained from PO/CA.
Figure S 4. 43	$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum for polymer obtained from PO/CA.
Figure S 4. 44	^1H NMR Spectrum for polymer obtained from 2-EHGE/TCA1.
Figure S 4. 45	$^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum for polymer obtained from 2-EHGE/TCA1.

Figure S 4. 46	¹ H NMR Spectrum for polymer obtained from VPO /TCA1.
Figure S 4. 47	¹³ C{ ¹ H} NMR Spectrum for polymer obtained from VPO/TCA1.
Figure S 4. 48	¹ H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA and PO. Conditions: [CL]:[PO]:[CHD]:[SalcyCrCl]:[PPNCl] = 200:200:10:1:0.5, Tol (2.5 M), 60 °C, 20 h.
Figure S 4. 49	¹ H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA and PO. Conditions: [LA]:[PO]:[CHD]:[SalcyCrCl]:[PPNCl] = 200:200:10:1:0.5, Tol (2.5 M), 60 °C, 20 h. Assignments of the backbiting product are given below.
Figure S 4. 50	¹ H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA, TCA1 and PO. Conditions: [LA]:[TCA1]:[PO]:[CHD]:[SalcyCrCl]:[PPNCl] = 100:100:200:10:1:0.5, Tol (2.5 M), 60 °C, 20 h.[6]
Figure S 4. 51	¹ H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA, CA and PO. Conditions: [LA]:[CA]:[PO]:[CHD]:[SalcyCrCl]:[PPNCl] = 100:100:200:10:1:0.5, Tol (2.5 M), 60 °C, 14 h.
Figure S 4. 52	¹ H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of BL and PO. Conditions: [BL]:[PO]:[CHD]:[SalcyCrCl]:[PPNCl] = 100:200:10:1:0.5, Tol (2.5 M), 60 °C, 24 h.[6]
Table S 4. 1	Integrals based on ¹ H NMR spectroscopy used for conversion vs. time plots
Table S 4. 2	<i>M_n</i> (g mol ⁻¹) and <i>Đ</i> values of GPC traces during the one-pot polymerization of TCA1/PO.
Table S 4. 3	One Pot Polymerisation of TAC1 with Different PO-Derivatives with Higher Monomer Loading.
Table S 4. 4	Synthesis of Homo- and Block copolymers with different Epoxides.
Table S 4. 5	Anhydride Scope and used ¹ H NMR Shifts.
Table S 4. 6	Polymerisation of TCA1/PO with different monomer loadings and 10 equiv. of CHD.
Table S 4. 7	One-pot polymerization of TCA1/PO with various amounts of <i>iso</i> -propanol as CTA.
Table S 4. 8	Polymerisation of TCA1/PO with different alcohols (15 equiv.)

Chapter 5

Figure S 5. 1	Kinetic analysis of <i>in situ</i> IR plot (conditions are given in experimental section).
Figure S 5. 2	MALDI Spectrum of PPE.
Figure S 5. 3	MALDI Spectra of PLA.
Figure S 5. 4	¹ H NMR spectrum of isolated polyester; the region relevant to the formation of polyether between 3.0 and 4.0 ppm is enlarged (polyether should be observed as broad resonances in this area).
Figure S 5. 5	¹ H NMR spectrum of the one-pot polymerisation of TCA1/PO/LA
Figure S 5. 6	GPC trace of polymer obtained from TCA1/PO/LA.
Figure S 5. 7	IR spectra of monomers and polymers.
Figure S 5. 8	Extended region of IR spectra for PA and PPE.
Figure S 5. 9	Extended region of IR spectra for LA and PLA.
Figure S 5. 10	¹ H NMR spectrum of isolated polymer.
Figure S 5. 11	¹³ C{ ¹ H} NMR spectrum of isolated polymer.
Figure S 5. 12	¹ H, ¹ H TOCSY NMR spectrum (only region relevant to junction unit shown).
Figure S 5. 13	¹ H, ¹ H TOCSY NMR spectrum (only region relevant to junction unit shown).

Figure S 5. 14	^1H , ^1H COSY NMR Spectrum of PLA- <i>b</i> -PPE- <i>b</i> -PLA.
Figure S 5. 15	DSC Thermogram of Polyester based on PO/CA/LA.
Figure S 5. 16	DSC Thermogram of Polyester based on PO/CA/LA.
Figure S 5. 17	DSC Thermogram of Polyester based on PO/CA/LA.
Table S 5. 1	Fitting parameters based on Figure S 5. 1.

Chapter 6

Figure S 6. 1	GC-MS Spectrum of CHDO.
Figure S 6. 2	^1H NMR (400 MHz, CDCl_3) of PCHDC.
Figure S 6. 3	^1H NMR of crude PCHDC (400 MHz, CDCl_3). The signals at 5.94, 4.97, and 3.25 ppm are characteristic of the cyclic carbonate, PCHDC and CHDO, respectively. No signal was found at 3.45 ppm (polyether signal).
Figure S 6. 4	(PS)-SEC traces of PCHDC. A: monomodal traces (run 1 and run 2 refer to independently synthesised samples); B: bimodal traces. Fit function for peak 1: $f(x) = -0.03838 + (139830/(1106\sqrt{(\pi/2)}))\exp(-2((x-2740)/1106)^2)$; peak 2: $f(x) = -0.03838 + (56666/(1981\sqrt{(\pi/2)}))\exp(-2((x-5265)/1981)^2)$. M_n if both peaks were not considered separately: 2850 g mol ⁻¹ (1.12). For SEC-MALLS, dn/dc was determined to be 0.0851 mL g ⁻¹ (not shown). Reported molar masses are relative to polystyrene.
Figure S 6. 5	MALDI-ToF spectrum of poly(cyclohexadiene carbonate). The series shows $m/z = [60.06 \text{ (propanol)} + (140.05 \text{ n}) \text{ (PCHDC)} + 38.96 \text{ (K}^+)]$ ($n = 17 \sim 33$). Y-Axis: Intensity (a. u.), x-axis: m/z .
Figure S 6. 6	$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (400 MHz, CDCl_3) of PCHDC after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane (bisphenol A used as an internal standard). The peaks at 175.9, 146.7, 138.6, 132.9 ppm correspond to the phosphorus agent, the OH end-group (after the reaction), bisphenol A and the hydrolysed phosphorus agent, respectively.
Figure S 6. 7	(PS)-SEC trace of PLC. For SEC-MALLS, dn/dc was determined to be 0.0804 mL/g (not shown).
Figure S 6. 8	MALDI-ToF spectrum of poly(limonene carbonate). The series shows $m/z = [18.01 \text{ (water)} + \text{limonene oxide (152.12)} + (196.11 \times n) \text{ (PLC)} + 38.96 \text{ (K}^+)]$ ($n = 4 \sim 15$).
Figure S 6. 9	DSC thermograms of (A) PCHDC and (B) PLC. All DSC thermograms, the heat flow (W g ⁻¹ , y-axis) is displayed versus the temperature (°C, x-axis). Heating rate: 10 °C min ⁻¹ .
Figure S 6. 10	DSC thermograms of uncured (C=C):(SH) = 1:1 films for PCHDC (A) and (B) PLC. Heating rate: 10 °C min ⁻¹ .
Figure S 6. 11	DSC thermograms of uncured (C=C):(SH) = 2:1 films for PCHDC (A) and (B) PLC. Heating rate: 10 °C min ⁻¹ .
Figure S 6. 12	DSC thermograms of uncured (C=C):(SH) = 4:1 films for PCHDC (A) and (B) PLC films. Heating rate: 10 °C min ⁻¹ .
Figure S 6. 13	Raman Spectrum of TMP-SH.
Figure S 6. 14	UV-6S spectrum of Irgacure 819.
Figure S 6. 15	Raman spectra of PLC film after casting and curing in the presence of daylight and the exclusion of daylight ((C:C):(SH) = 1:1, 2 mol% Irgacure 819).
Figure S 6. 16	Raman spectra of PLC film at different laser power ((C:C):(SH) = 1:1, 2 mol% Irgacure 819).
Figure S 6. 17	Raman spectra of PLC film with different laser exposure times ((C:C):(SH) = 1:1, 2 mol% Irgacure 819).
Figure S 6. 18	Individual Raman spectra for the curing of PCHDC:TMPSH = 1:1 at

	different temperatures.
Figure S 6. 19	Individual Raman spectra for the curing of PCHDC:TMP SH = 4:1 at different temperatures.
Figure S 6. 20	Individual Raman spectra for the curing of PCHDC:TMP SH = 4:1 at different temperatures.
Figure S 6. 21	Individual Raman spectra for the curing of PLC:TMP SH = 1:1 at different temperatures.
Figure S 6. 22	Individual Raman spectra for the curing of PLC:TMP SH = 2:1 at different temperatures.
Figure S 6. 23	Individual Raman spectra for the curing of PLC:TMP SH = 4:1 at different temperatures.
Figure S 6. 24	Individual Raman spectra for the curing of PCHDC:TMP SH = 4:1 at different times.
Figure S 6. 25	Individual Raman spectra for the curing of PCHDC:TMP SH = 2:1 at different times.
Figure S 6. 26	Individual Raman spectra for the curing of PCHDC:TMP SH = 4:1 at different times.
Figure S 6. 27	Individual Raman spectra for the curing of PLC:TMP SH = 1:1 at different times.
Figure S 6. 28	Individual Raman spectra for the curing of PLC:TMP SH = 2:1 at different times.
Figure S 6. 29	Individual Raman spectra for the curing of PLC:TMP SH = 4:1 at different times.
Figure S 6. 30	Fitting for $\tan \delta$ vs. temperature graphs used to determine FWHM values.
Figure S 6. 31	ATR-IR spectra of top and bottom of films dried under nitrogen.
Table S 6. 1	Data for Fitting with Gauss Model
Table S 6. 2	Material properties for samples dried under nitrogen and air (data collected in collaboration with C. Li, Eindhoven University, The Netherlands).
Table S 6. 3	Determination of Crosslink-Density.

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Figure S 7. 1	^1H NMR spectrum of 7.4 in CDCl_3 .
Figure S 7. 2	^1H NMR spectrum of 7.5 in CDCl_3 .
Figure S 7. 3	^1H NMR spectrum of 7.6 (crude mixture).
Figure S 7. 4	^1H NMR spectra of crude mixture containing 7.9 in THF-d_8 .
Figure S 7. 5	^1H NMR spectrum of isolated 7.10 in CDCl_3 .
Figure S 7. 6	^1H NMR spectra of crude mixture containing 7.10 in THF-d_8 .
Figure S 7. 7	^1H NMR spectrum of 7.9 in THF-d_8 .
Figure S 7. 8	^1H NMR spectrum of 7.9 in CDCl_3 .
Figure S 7. 9	^1H NMR spectrum of 7.13 in THF-d_8 .
Figure S 7. 10	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7.13 in THF-d_8 .
Figure S 7. 11	^1H NMR spectrum of 7.16 in CDCl_3 .
Figure S 7. 12	^1H NMR spectrum of 7.16 in CDCl_3 .
Figure S 7. 13	^1H NMR spectrum of 7.18 in CDCl_3 .
Figure S 7. 14	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7.18 in CDCl_3 .
Figure S 7. 15	^1H NMR spectrum of 7.17 in CDCl_3 .
Figure S 7. 16	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7.17 in CDCl_3 .
Figure S 7. 17	^1H NMR spectrum of 7.19 in CDCl_3 .
Figure S 7. 18	^1H NMR spectrum of 7.20 in pyridine- d_5 .
Figure S 7. 19	$^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 7.20 in pyridine- d_5 .

Figure S 7. 20	Molecular structure of 7.10 with chloro co-ligands with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.
Figure S 7. 21	Molecular structure of 7.11 with chloro co-ligands with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.
Figure S 7. 22	Anhydride / epoxide ROCOP with 7.19 .
Figure S 7. 23	Optimisation of conditions for CHO/PA ROCOP with 7.19 .
Table S 7. 1	ROP with 7.19 .

Chapter 8

Table S 8. 1	Functions used for Figure 8.5 (part 1/2).
Table S 8. 2	Functions used for Figure 8.5 (part 2/2).
Table S 8. 3	Functions used for Figure 8.6.

¹H NMR Spectra of Selected Monomers

Epoxides

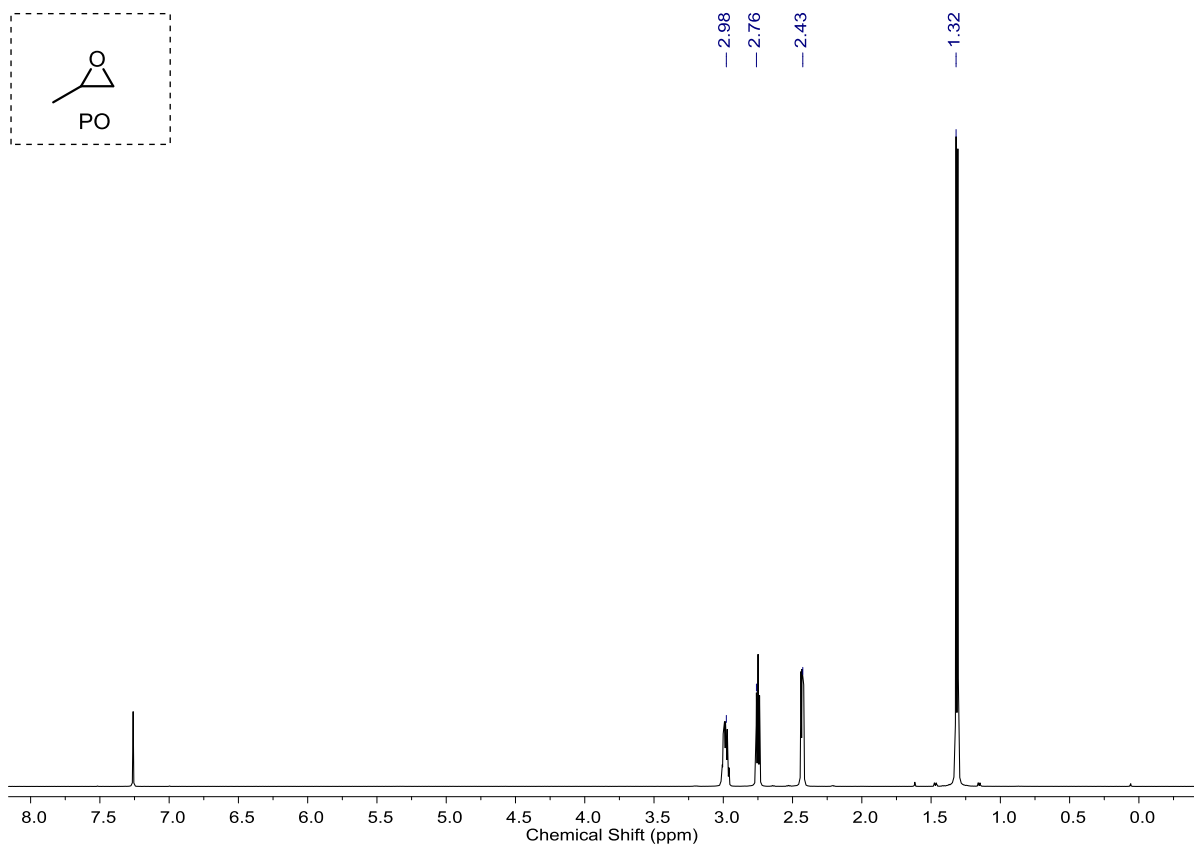


Figure S 1. 1 – ¹H NMR Spectrum of PO (400 MHz).

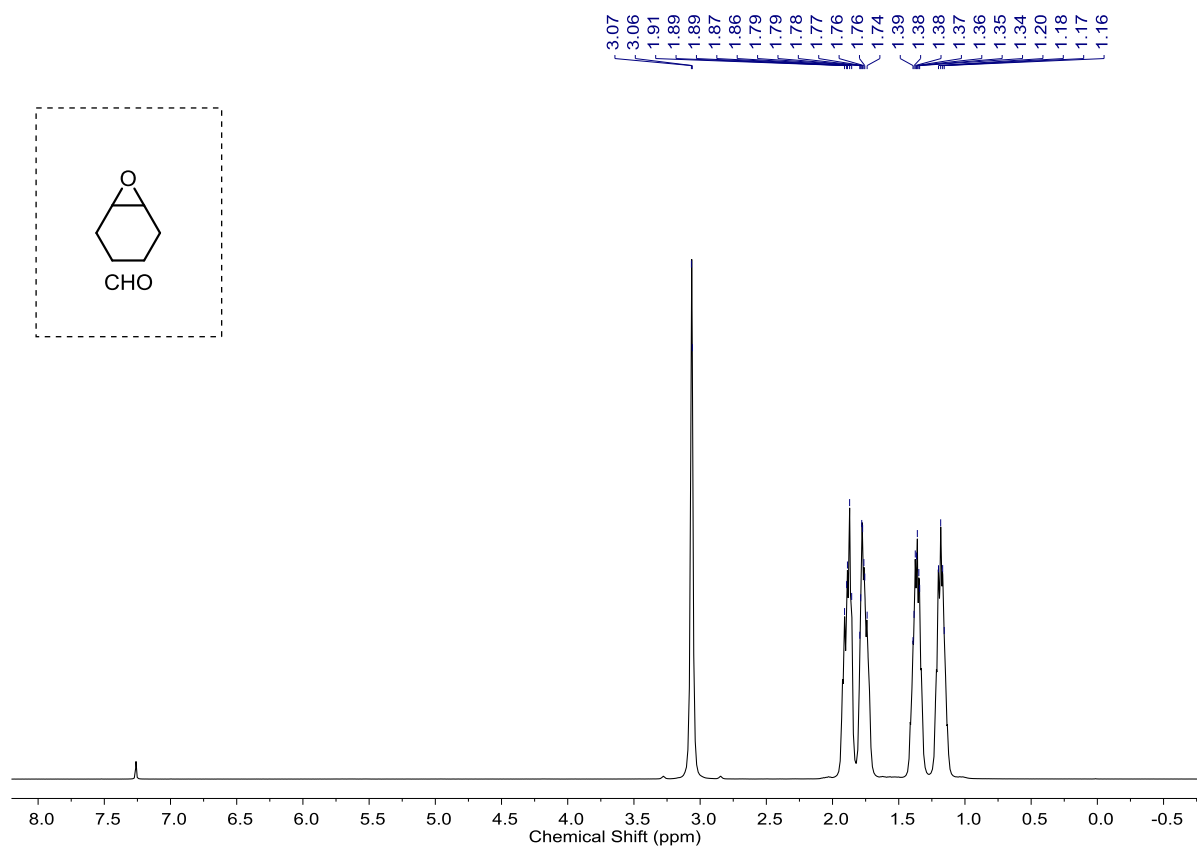


Figure S 1. 2 – ¹H NMR Spectrum of CHO (400 MHz).

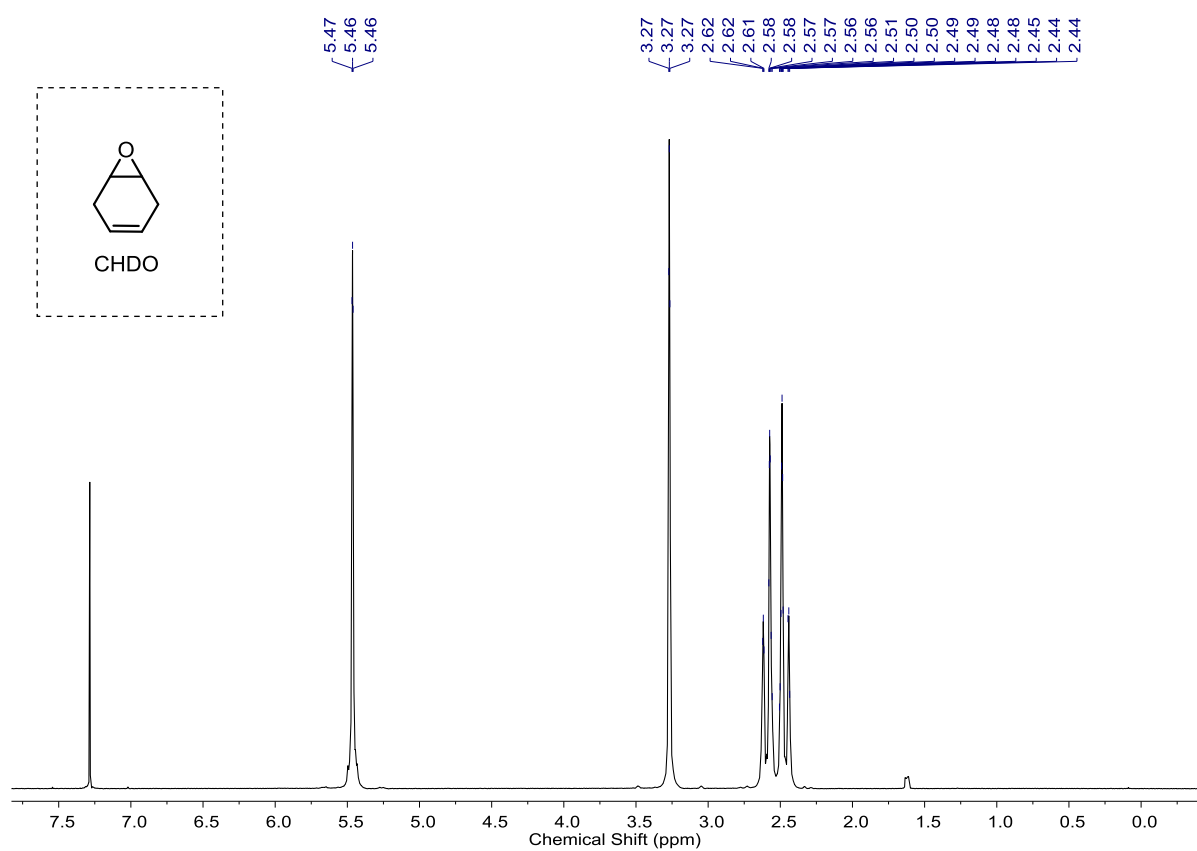


Figure S 1. 3 – ¹H NMR Spectrum of CHDO (400 MHz).

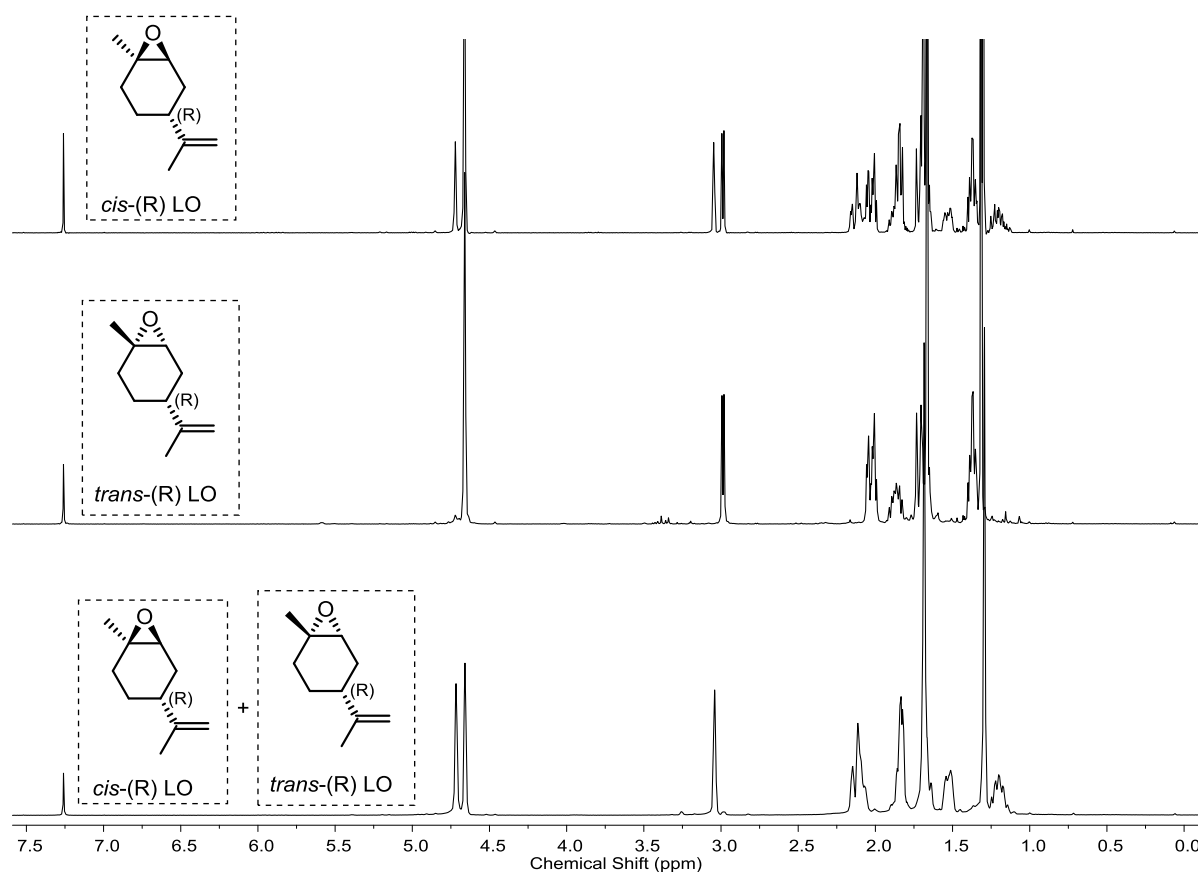


Figure S 1. 4 – ¹H NMR Spectrum of *cis* and *trans* LO (400 MHz).

Anhydrides

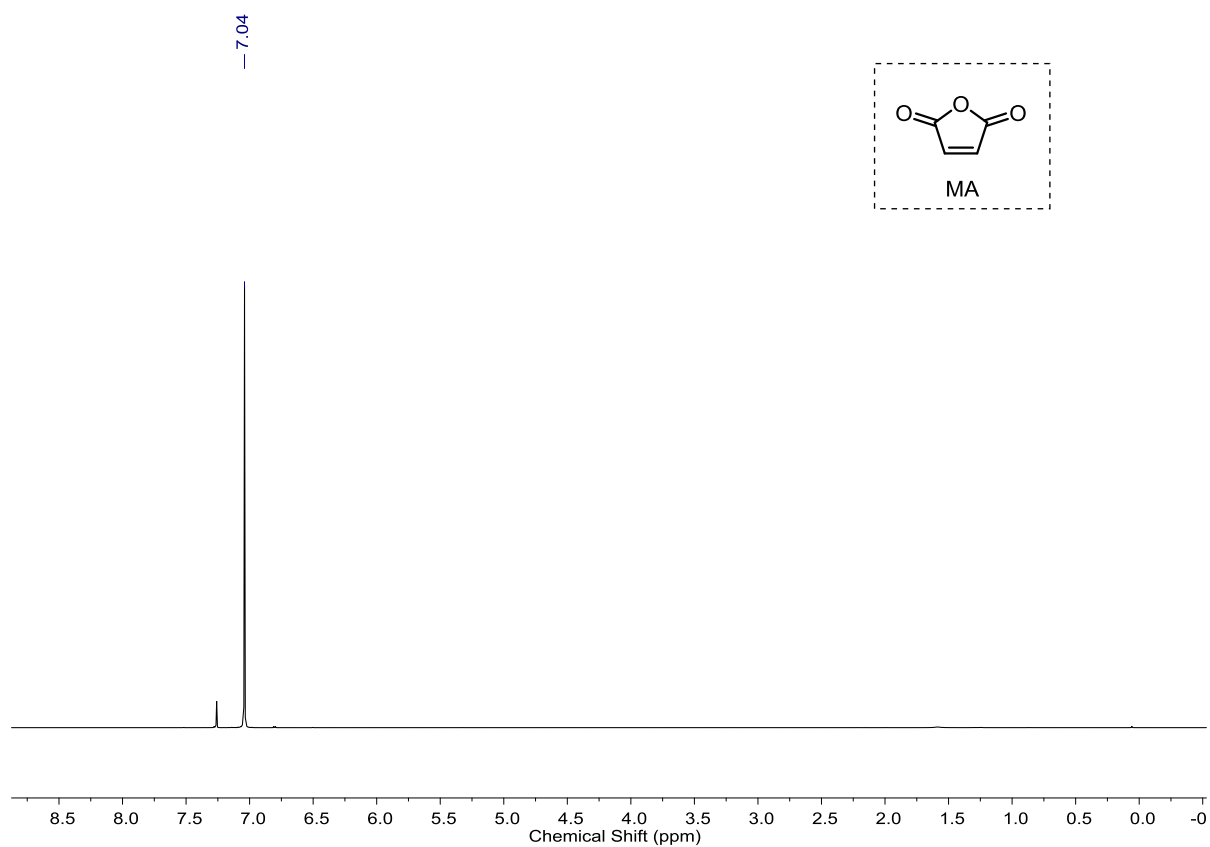


Figure S 1. 5 – ¹H NMR Spectrum of MA (400 MHz).

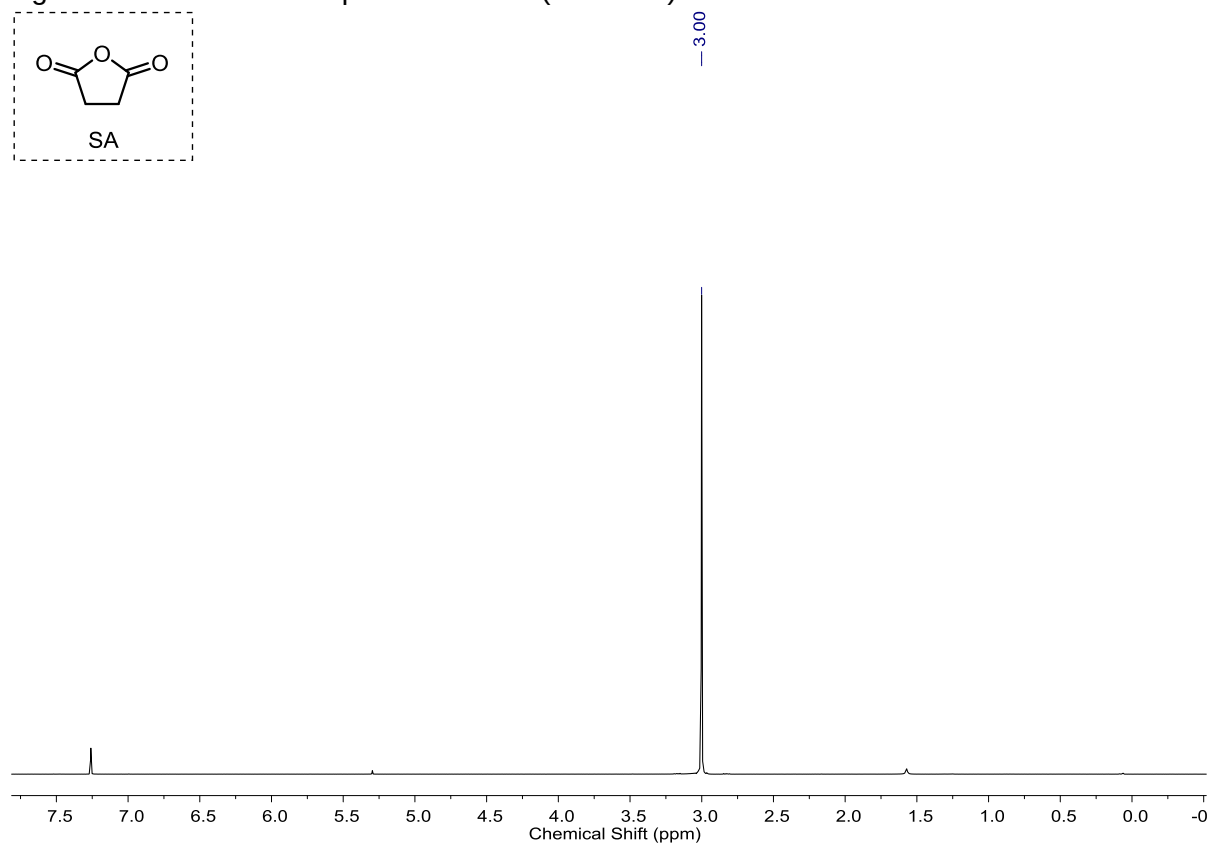


Figure S 1. 6 – ¹H NMR Spectrum of SA (400 MHz).

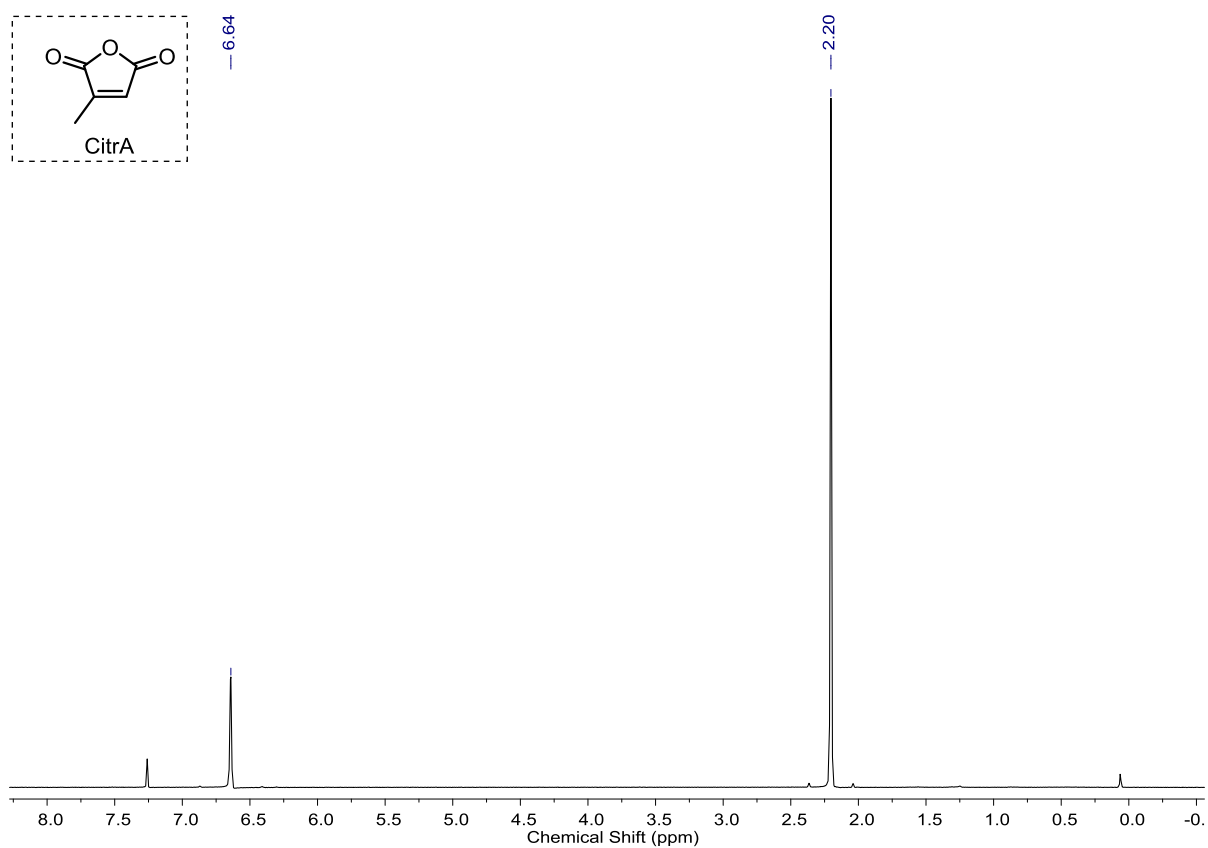


Figure S 1. 7 – ¹H NMR Spectrum of CitrA (400 MHz).

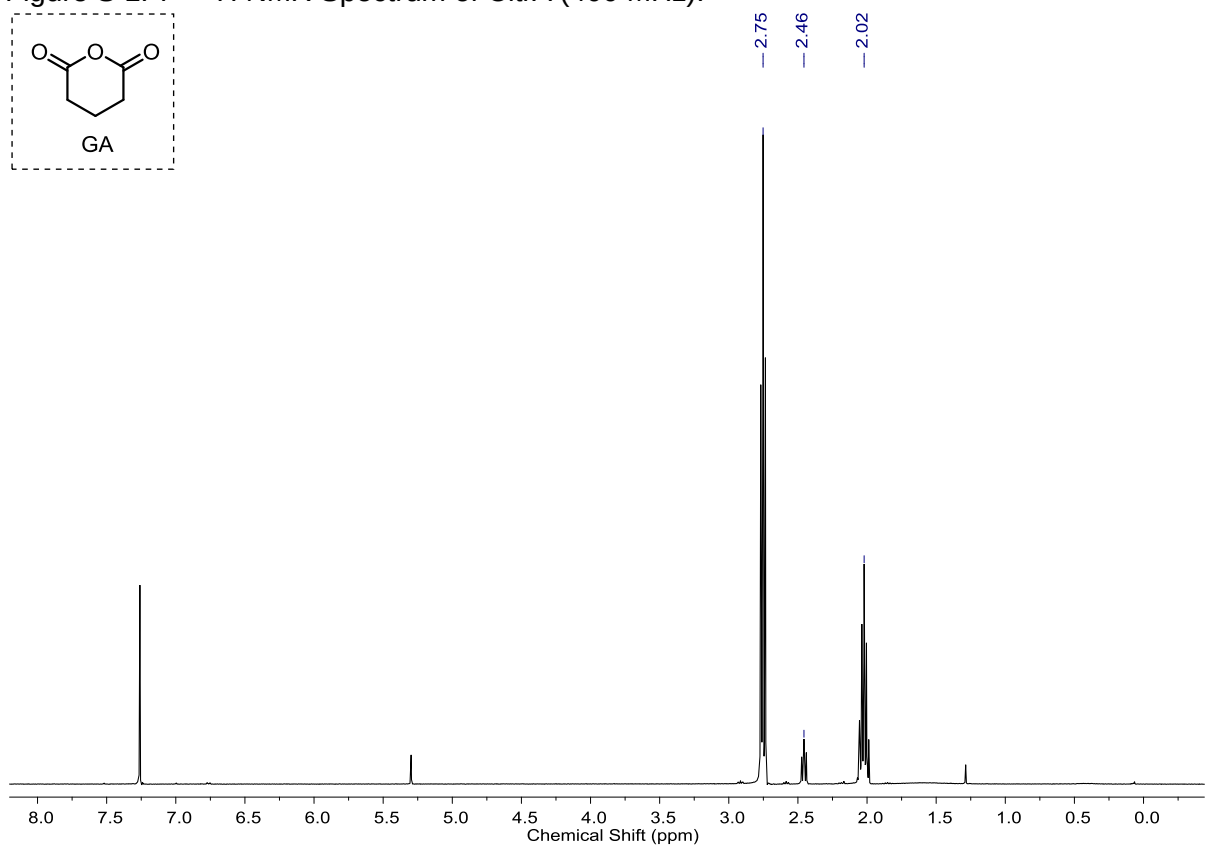


Figure S 1. 8 – ¹H NMR Spectrum of GA (400 MHz).

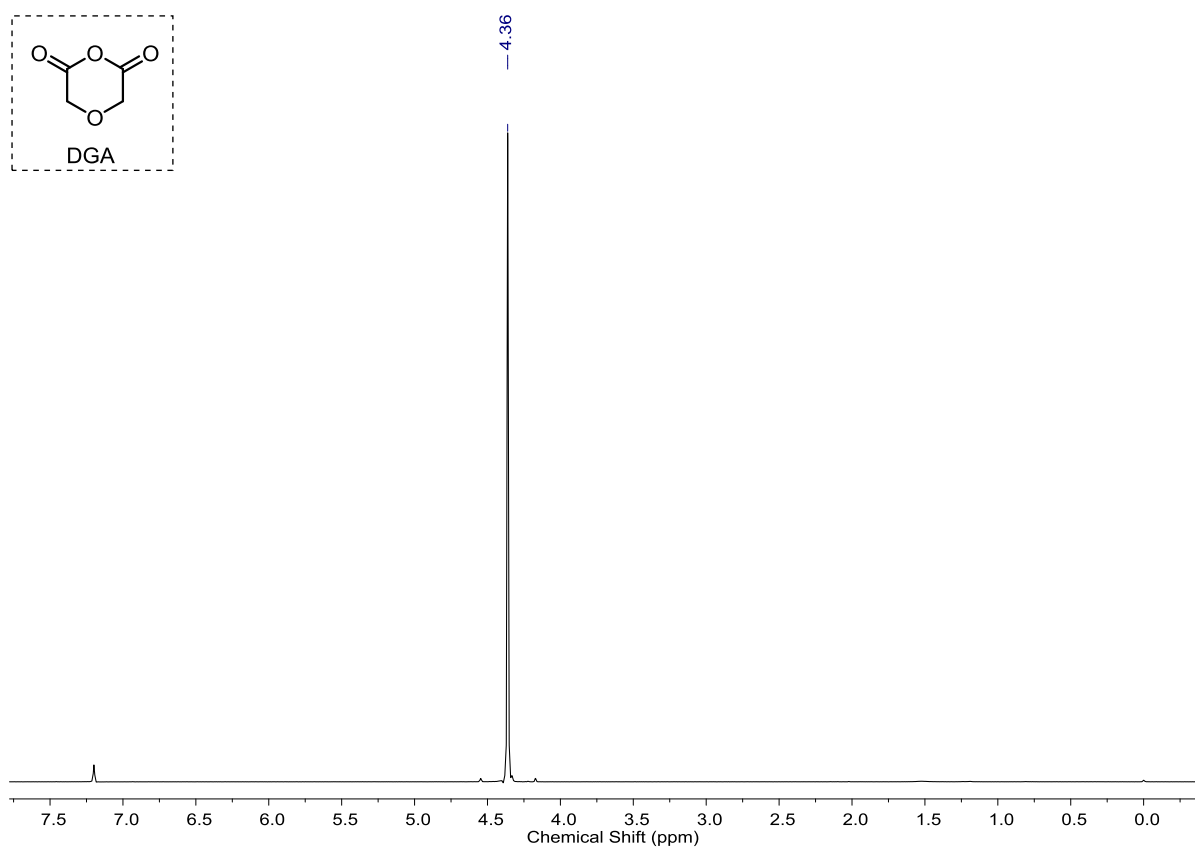


Figure S 1. 9 – ¹H NMR Spectrum of DGA (400 MHz).

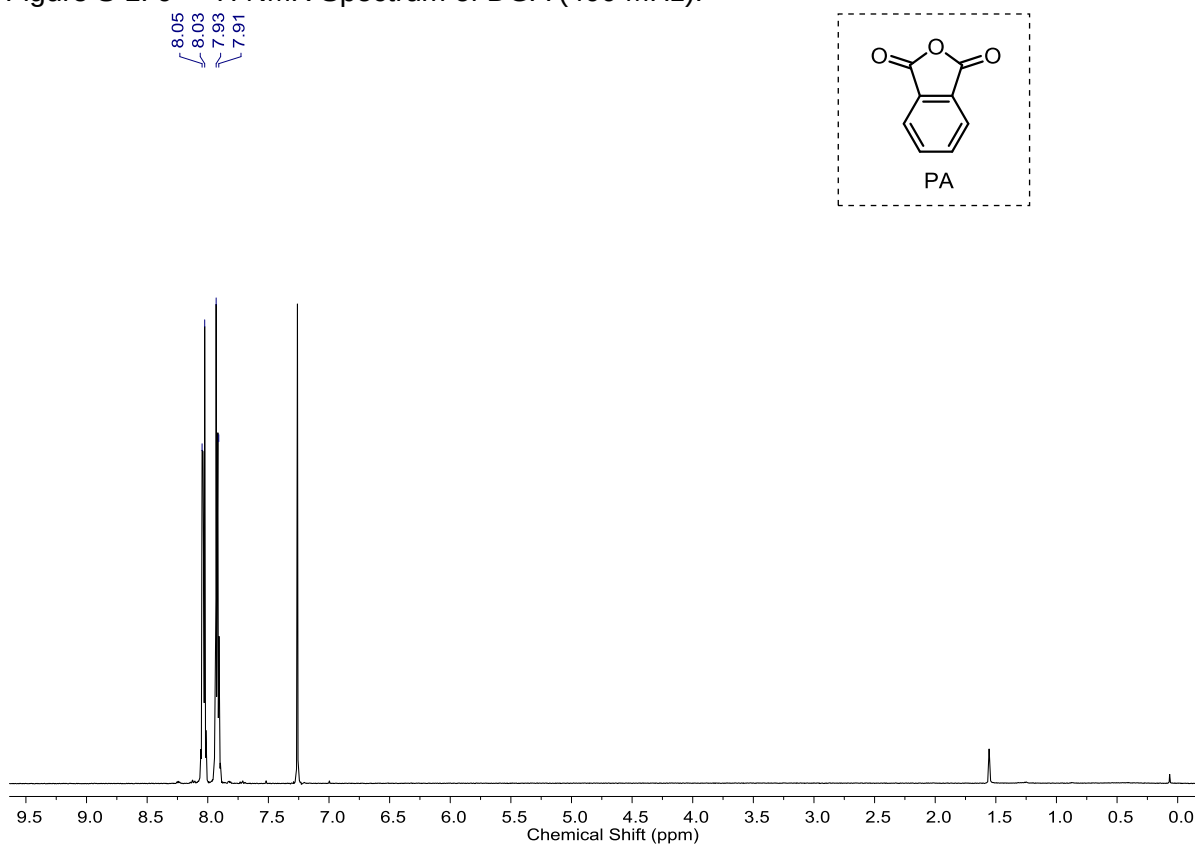


Figure S 1. 10 – ¹H NMR Spectrum of PA (400 MHz).

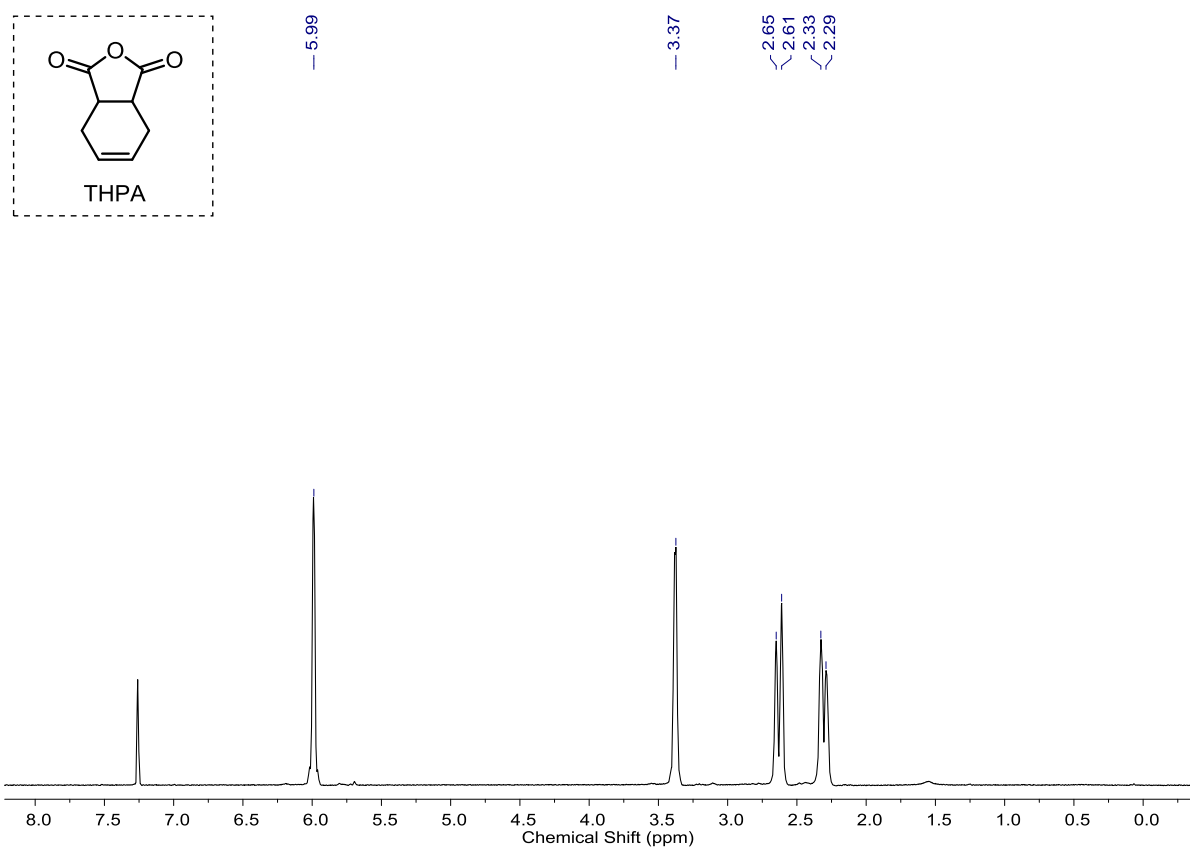


Figure S 1. 11 - ¹H NMR Spectrum of THPA (400 MHz).

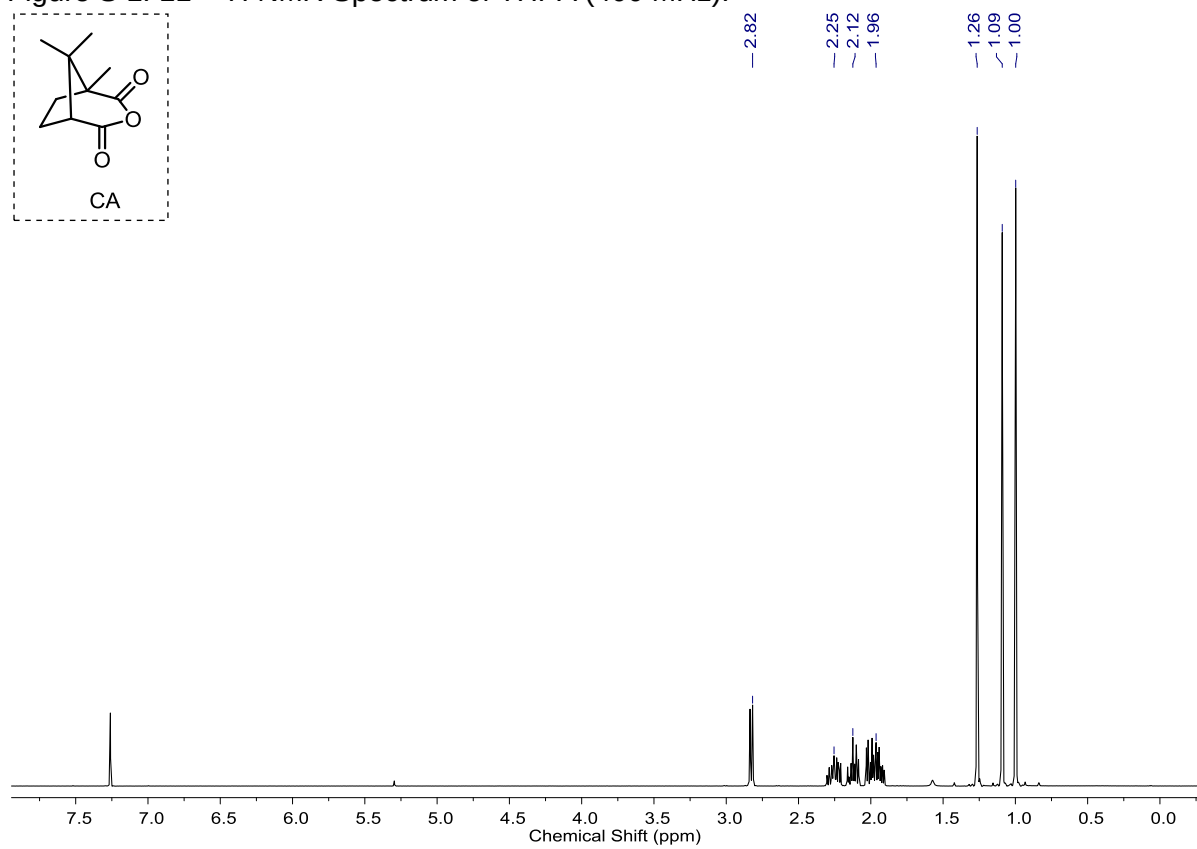


Figure S 1. 12 - ¹H NMR Spectrum of CA (400 MHz).

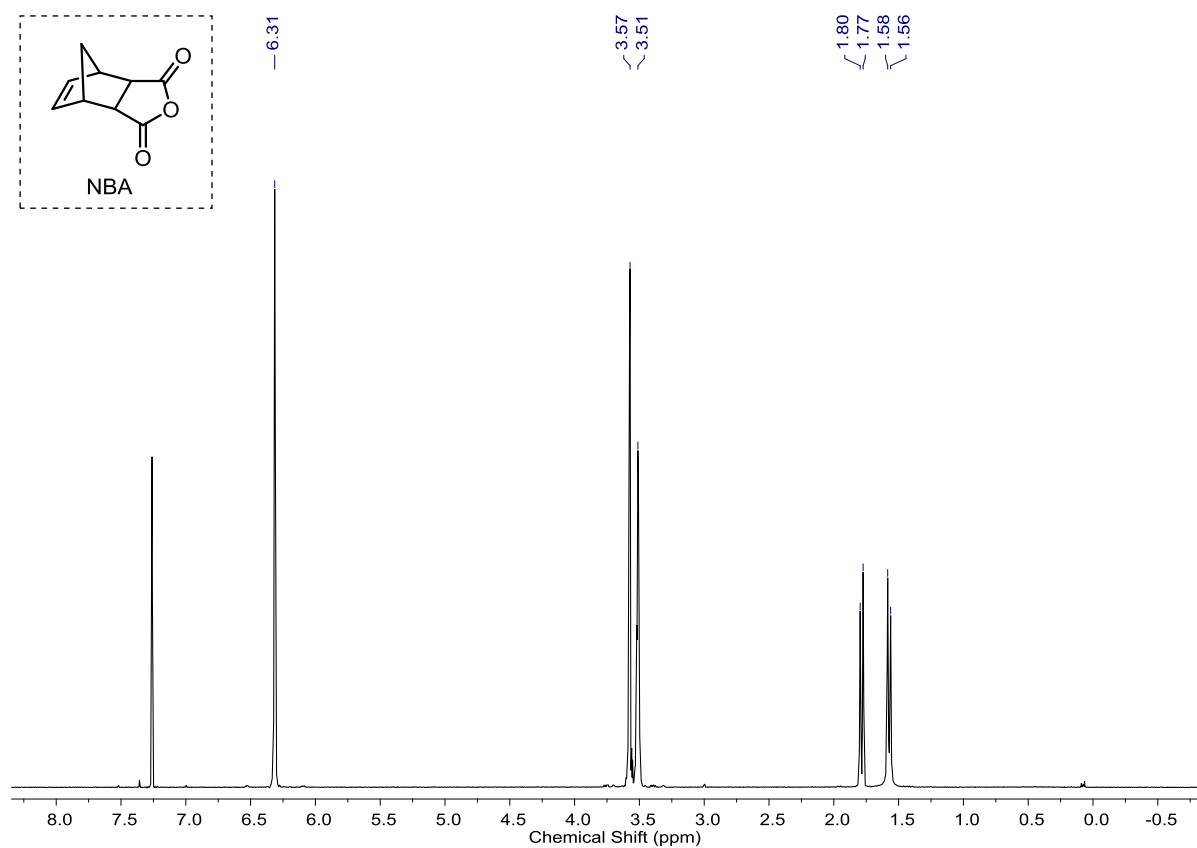


Figure S 1. 13 – ¹H NMR Spectrum of NBA (400 MHz).

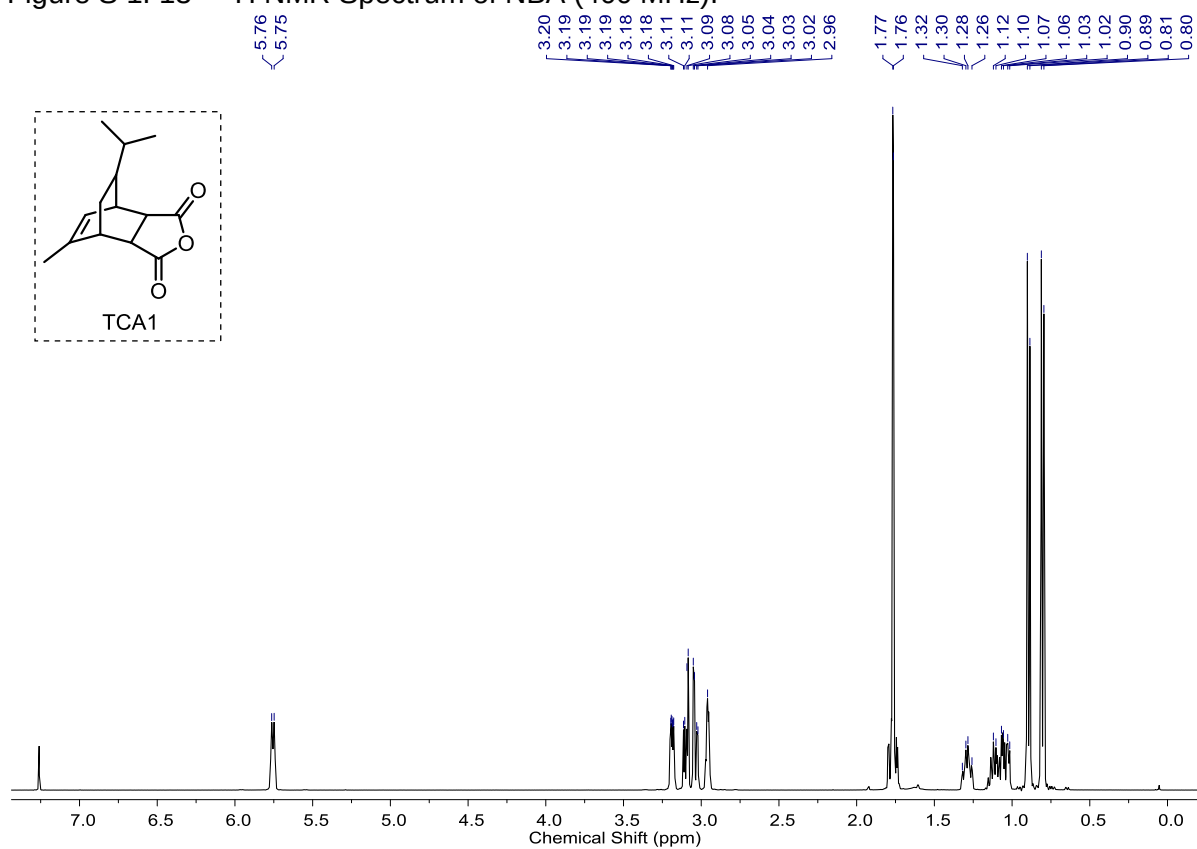


Figure S 1. 14 – ¹H NMR Spectrum of TCA1 (400 MHz).

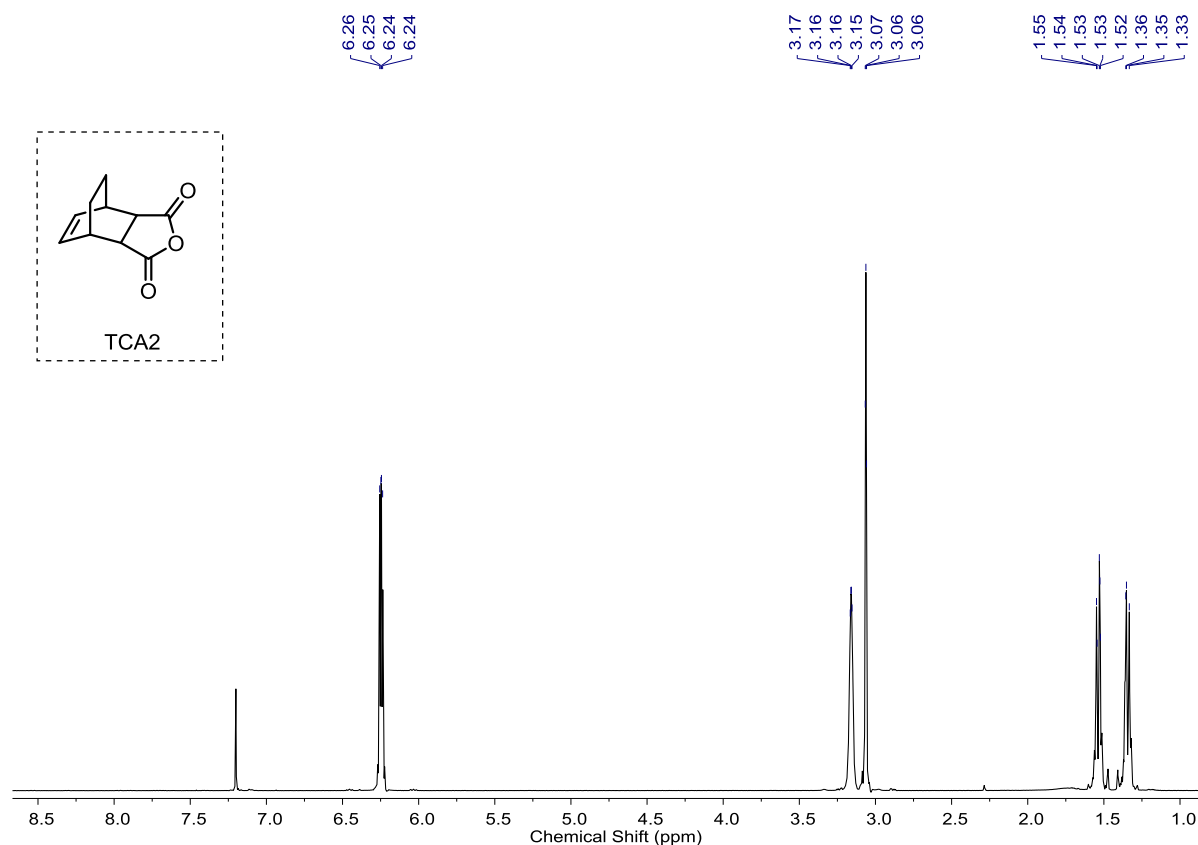


Figure S 1. 15 – ¹H NMR Spectrum of TCA2 (400 MHz).

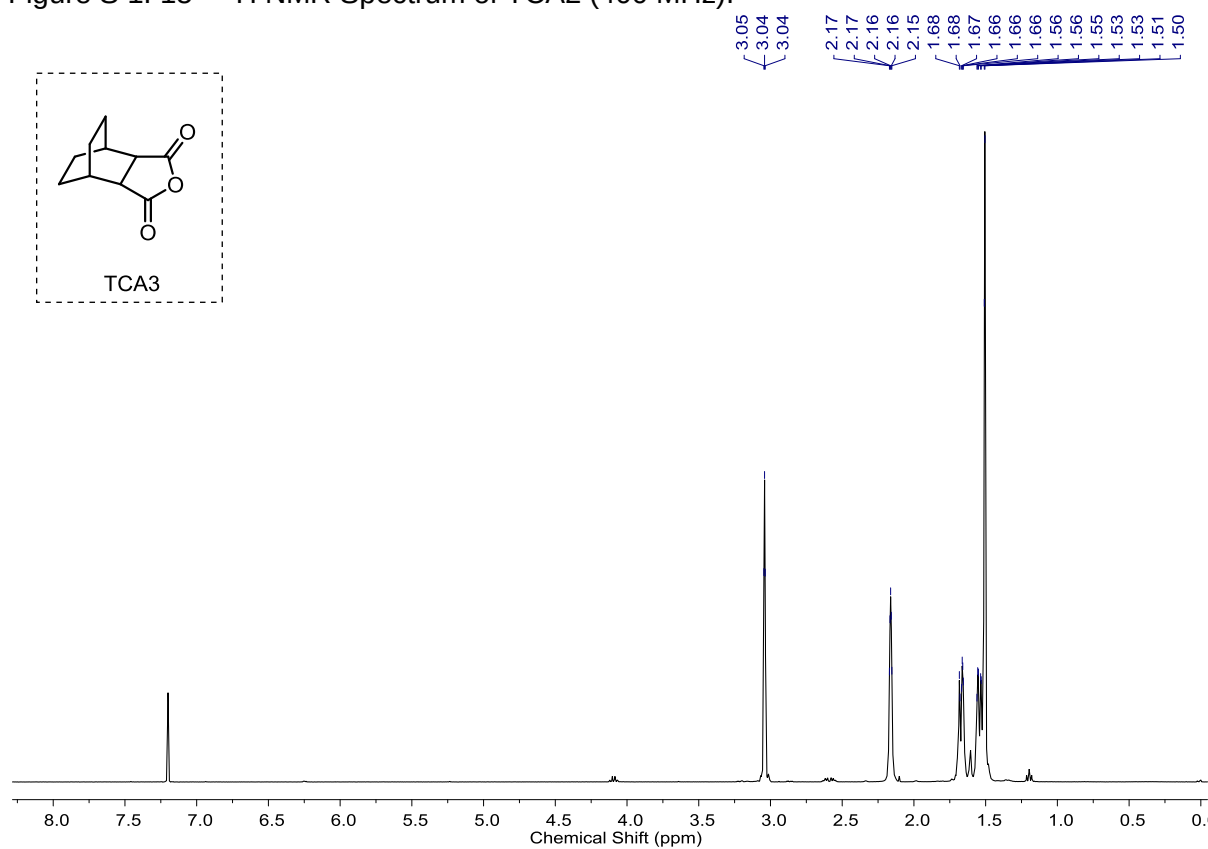


Figure S 1. 16 – ¹H NMR Spectrum of TCA3 (400 MHz).

Lactones

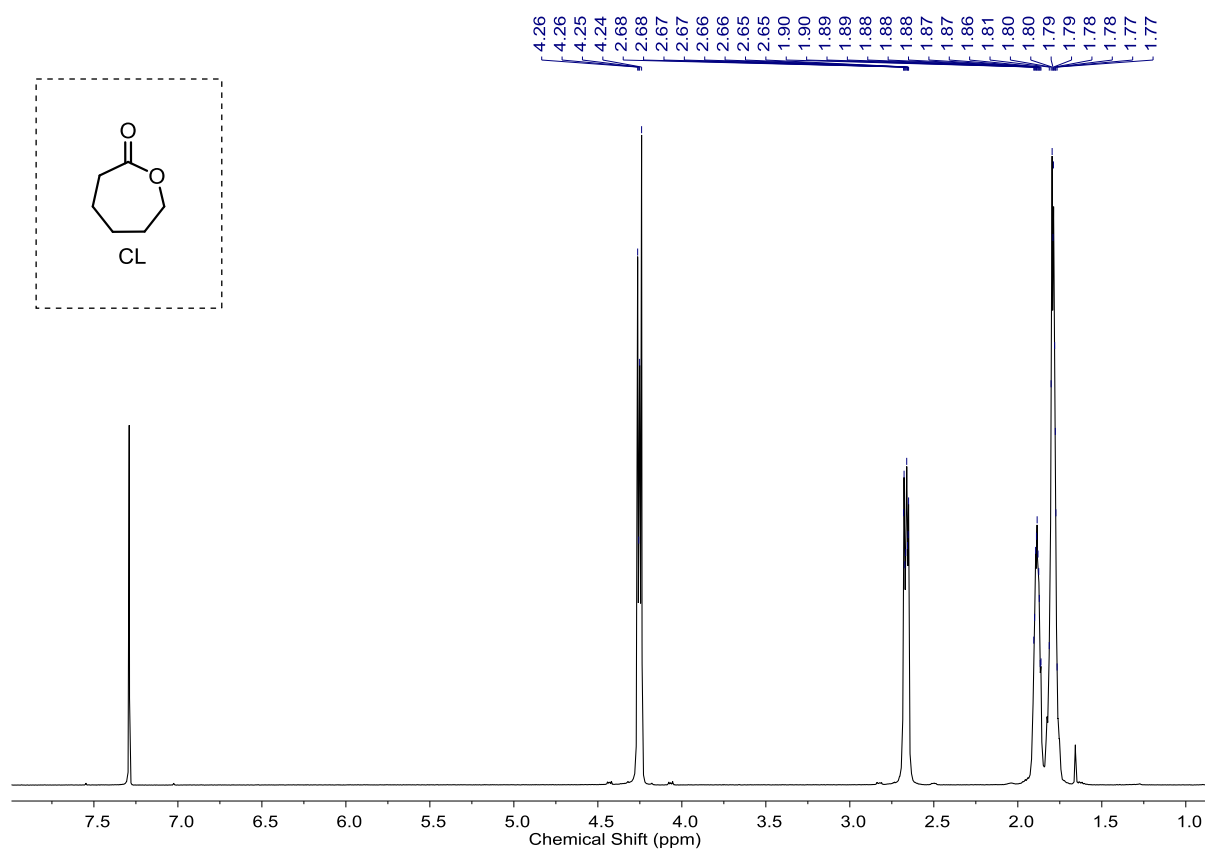


Figure S 1. 17 – ¹H NMR Spectrum of CL (400 MHz).

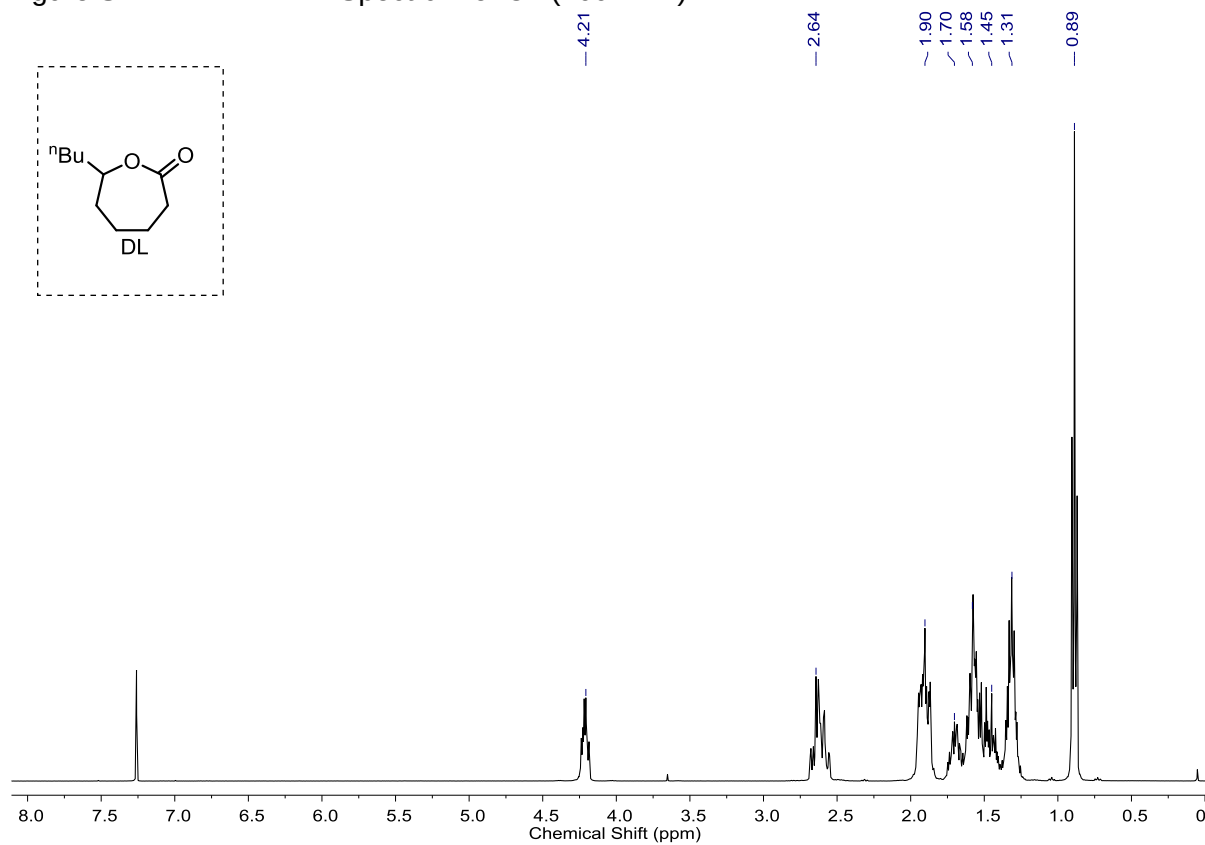


Figure S 1. 18 – ¹H NMR Spectrum of DL (400 MHz).

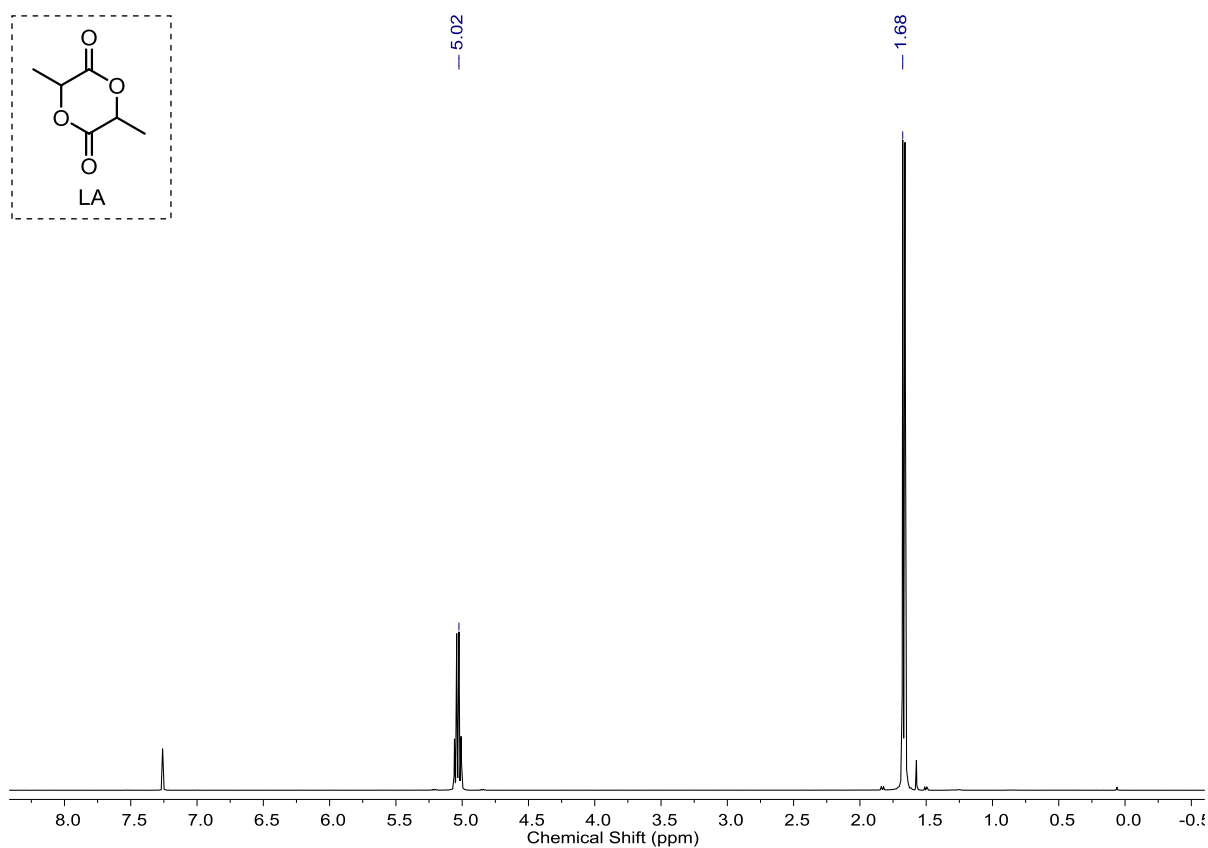


Figure S 1. 19 – ¹H NMR Spectrum of LA (400 MHz).

Poly(cyclohexene oxide)

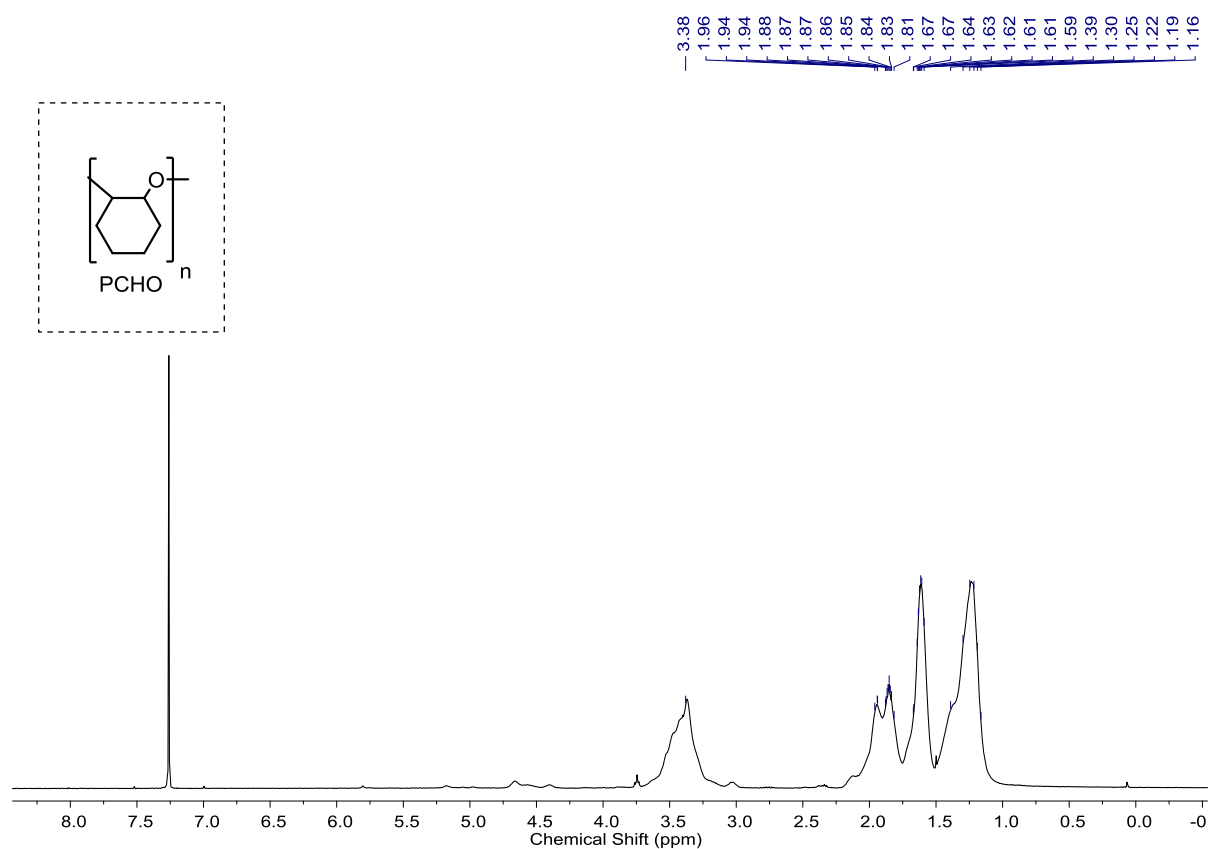


Figure S 1. 20 – ¹H NMR Spectrum of PCHO (400 MHz).

Chapter 1 – Introduction. ‘Switch’ Catalysis and Post-Functionalisation Modification

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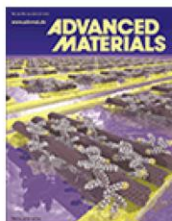


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	Monomer 1 (50-100)	$y = b$	b = offset	b = 0
	Monomer 2 (0-54)	$y = b$	b = offset	b = 100
	Monomer 2 (55-100)	$y = y_0 + Ae^{R_0 x}$	A = start value r_0 = rate y_0 = offset	x substituted with (x-55) A = 100 r_0 = -0.15 y_0 = 0

Chapter 3 - 'Switch' Catalysis with [SalcyCrCl]. Part I - Cyclohexene oxide

Based on: T. Stößer and C. K. Williams, *Angew. Chem. Int. Ed.*, **2018**, 57, 6337-6341.

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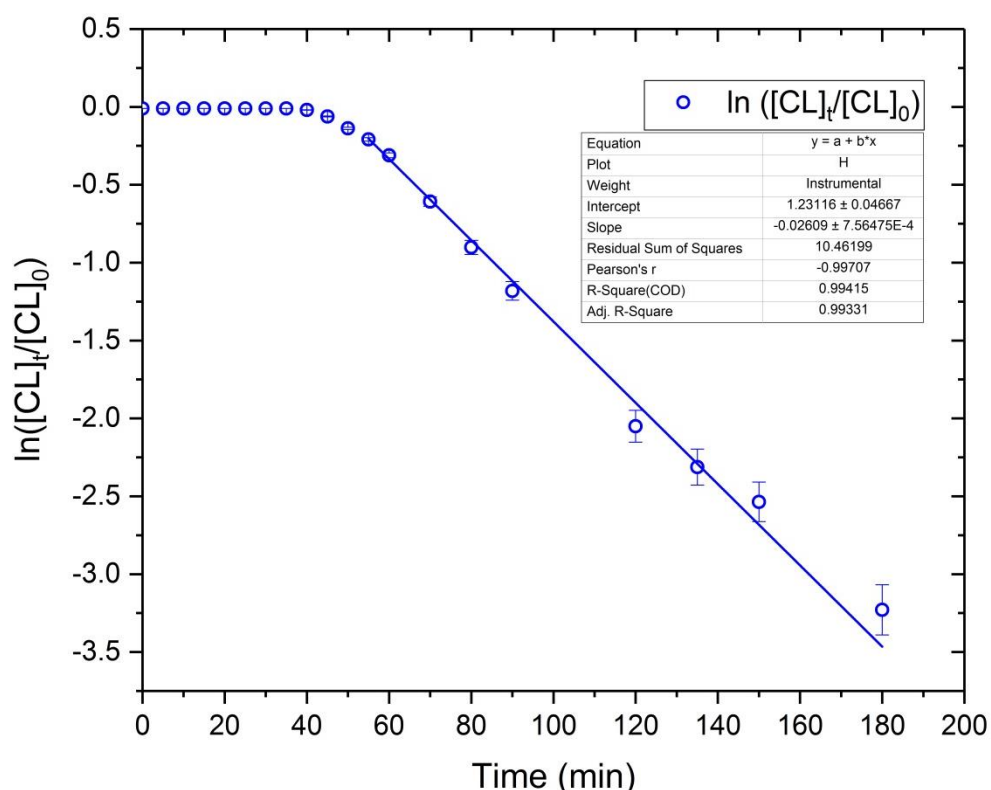


Figure S 3. 2 - $\ln([CL]_t/[CL]_0)$ vs. time plot to determine the rate constant for the polymerisation of CL in the one-pot polymerisation of PA/CHO/CL. Data based on ^1H NMR.

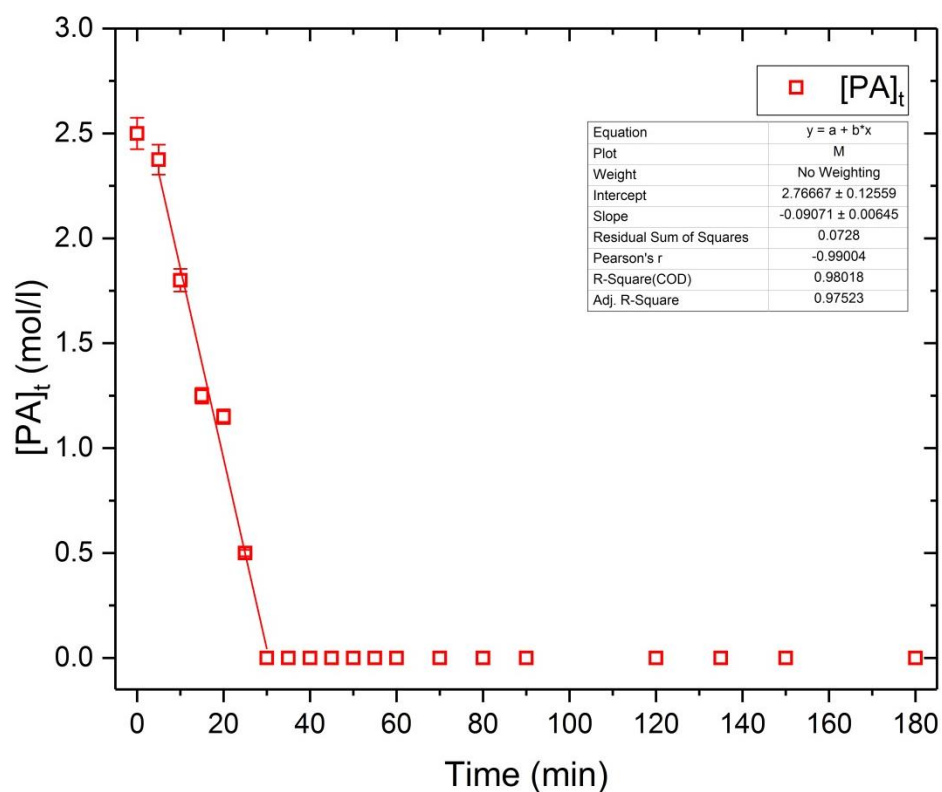


Figure S 3. 3 – $[PA]_t$ vs. time plot to determine the rate constant for the ring-opening copolymerisation of PA/CHO in the one-pot polymerisation of PA/CHO/CL. Data based on ^1H NMR.

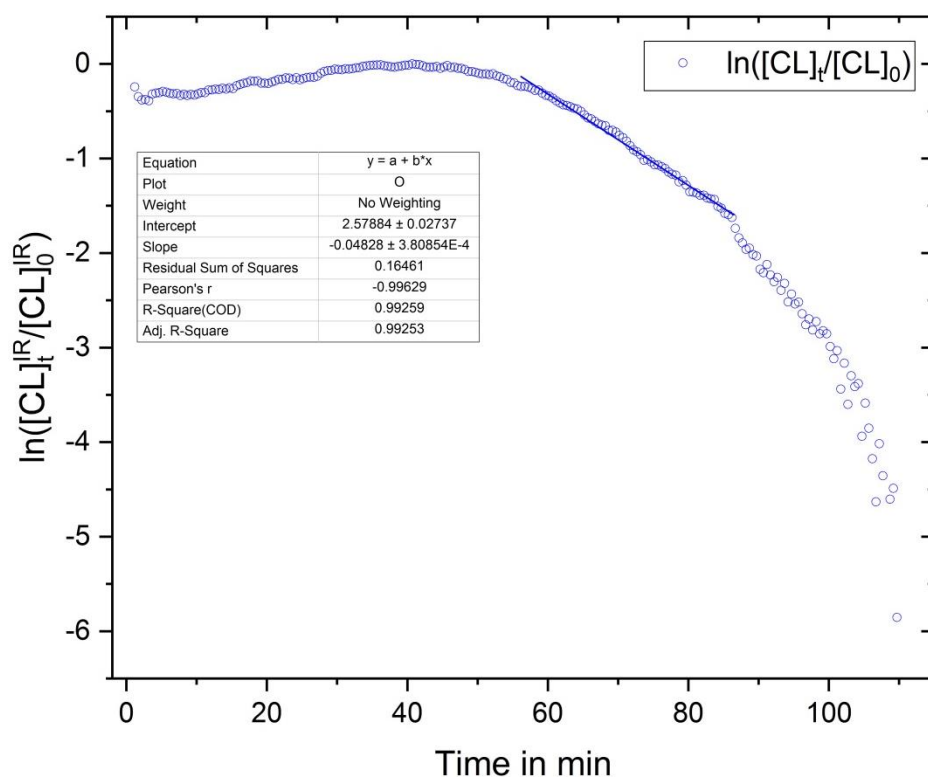


Figure S 3. 4 - $\ln([CL]_t/[CL]_0)$ vs. time plot to determine the rate constant for the polymerisation of CL in the one-pot polymerisation of PA/CHO/CL. Data based on *in situ* IR.

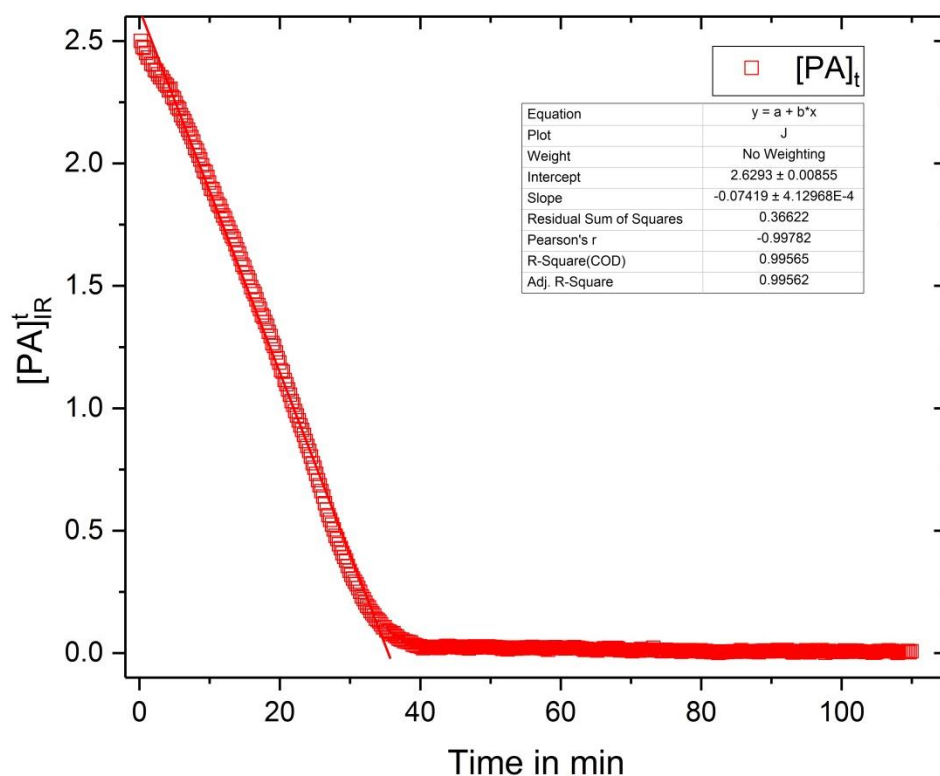


Figure S 3. 5 - $[PA]_t$ vs. time plot to determine the rate constant for the ring-opening copolymerisation of PA/CHO in the one-pot polymerisation of PA/CHO/CL. Data based on *in situ* IR.

Optimization of ROCOP and ROP

Table S 3. 1 - Optimisation of CTA for ROP, ROCOP and Switch catalysis.^[a]

Polymer	Eq of CHD	Conversion (%) ^[b]	M_n (Đ) ^[c]	$M_{n,theo}$ ^[d]
PDL	0	94	37,600 (1.02) 13,500 (1.21)	34,100
PDL	5	99	9,300 (1.07) 3,860 (1.07)	6,800
PDL	10	99	3,520 (1.15)	3,520
PDL	15	99	2,620 (1.14)	2,390
PDL	20	99	2,160 (1.15)	1,820
PCHNBE ^[e]	0	99	15,900 (1.11) 6,310 (1.07)	52,500
PCHNBE	5	99	8,200 (1.04) 3,410 (1.06)	10,500
PCHNBE	10	99	6,860 (1.05) 2,270 (1.18)	5,300
PCHNBE	15	99	1,640 (1.17)	3,610
PCHNBE	20	99	1,590 (1.21)	2,740
PDL- <i>b</i> -PCHNBE- <i>b</i> -PDL ^[f]	0	99 / 5	3,220 (1.48)	36,700
PDL- <i>b</i> -PCHNBE- <i>b</i> -PDL	5	99 / 97	8,740 (1.11) 3,270 (1.12)	16,800
PDL- <i>b</i> -PCHNBE- <i>b</i> -PDL	10	99 / 94	4,430 (1.20)	8,560
PDL- <i>b</i> -PCHNBE- <i>b</i> -PDL	15	99 / 95	3,140 (1.18)	5,770

PDL- <i>b</i> -PCHNBE- <i>b</i> -PDL	20	99 / 96	2,990 (1.18)	4,370
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^[a] Reaction conditions: DL:CHO:[SalcyCrCl]:PPNCl=200:50:1:1, Tol (2.5 M), 100°C, 3d. For PCHNBE, 250 equiv. of CHO were added. ^[b] Determined by ¹H NMR spectroscopy from the normalised integrals for DL and NBA. ^[c] Determined by GPC, calibrated using PS standards, in THF and at 30 °C. It should be noted that these are uncorrected values. ^[d] Calculated based on weight of monomers (170.25 for DL, 262.31 for NBA + CHO) and CHD end group (116.15). Example: $n(\text{CHD}) + (200 \cdot \text{conversion} \cdot \text{Monomer}) / (\text{CTA})$. ^[e] 6d. ^[f] 10d. The table is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

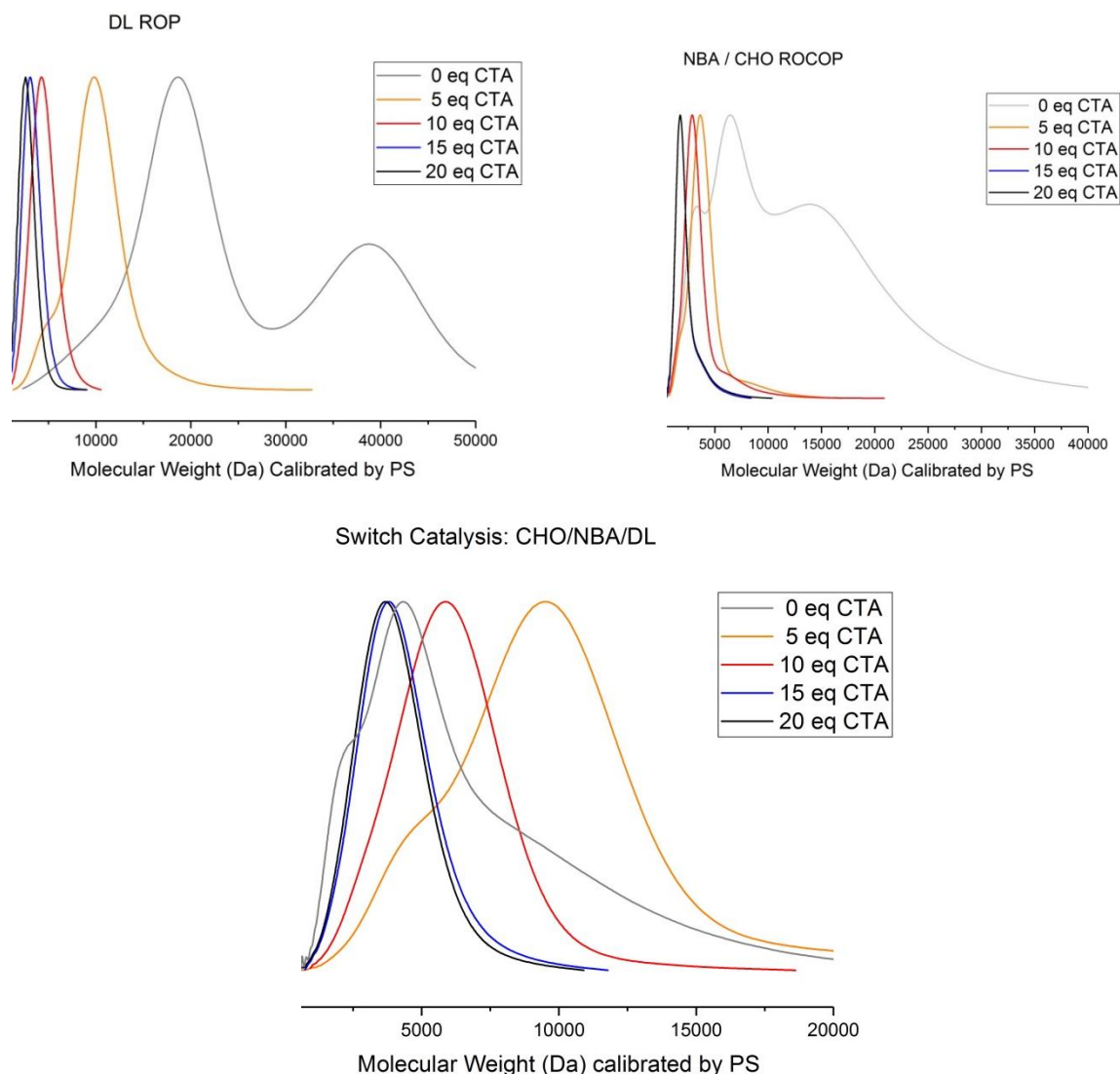


Figure S 3. 6 – GPC traces for ROP of DL (top, left), ROCOP of NBA and CHO (top, right) and the polymerization of DL/NBA/CHO, using [SalcyCrCl] with various amounts of *trans*-1,2-cyclohexanediol (CHD) as CTA. Conversions, M_n and $\bar{M}_w$ values are given in Table S1. It should be noted that bimodal molecular weight distributions were obtained in the absence of CTA – this can be ascribed to monofunctional, chloro-initiated chains (first distribution) and dihydroxyl-terminated chains caused by residual amounts of water and / or bifunctional impurities in the monomers (i. e. residual amounts of diols for epoxides or dicarboxylic acids for anhydrides; second distribution). This has been described for zinc and magnesium catalysts (see also Figure S3).^[1, 2] The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

MALDI Analysis at 40% NBA conversion (ca. 1 % DL conversion)

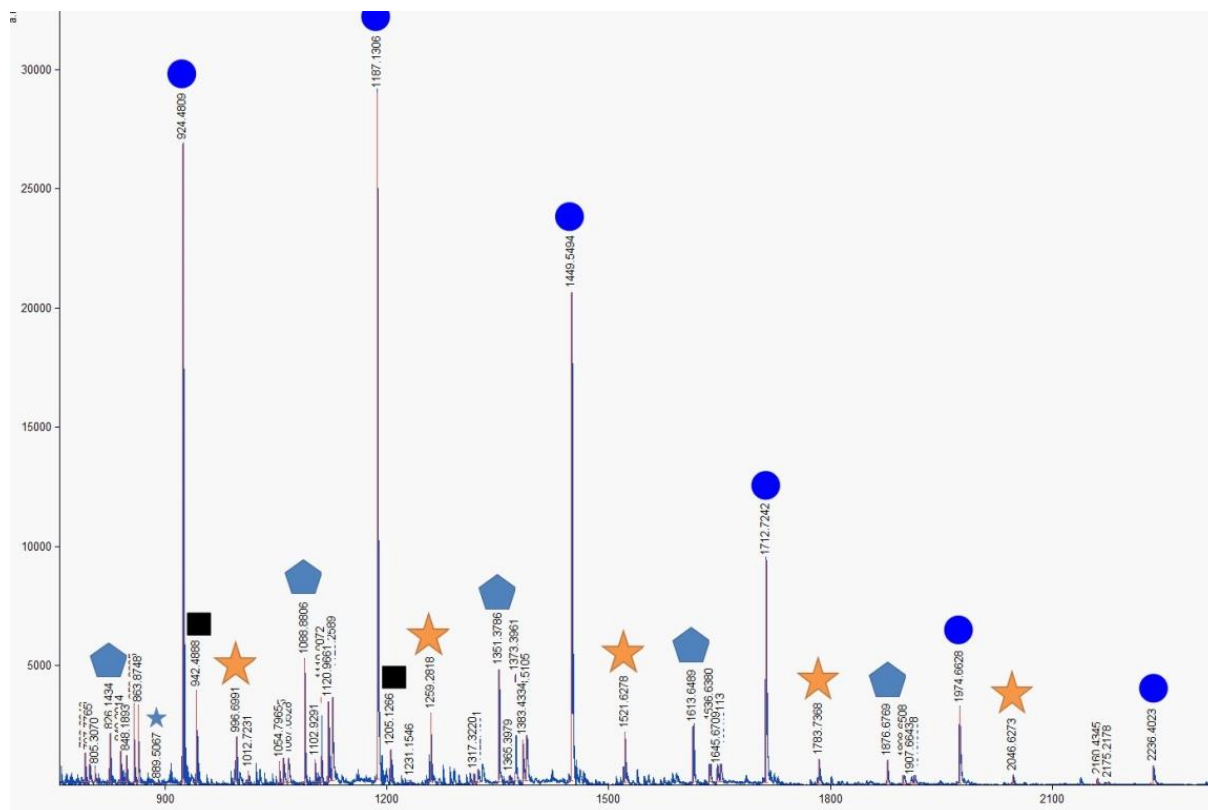


Figure S 3. 7 – MALDI of crude sample of NBA/CHO/DL ‘Switch’ catalysis. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

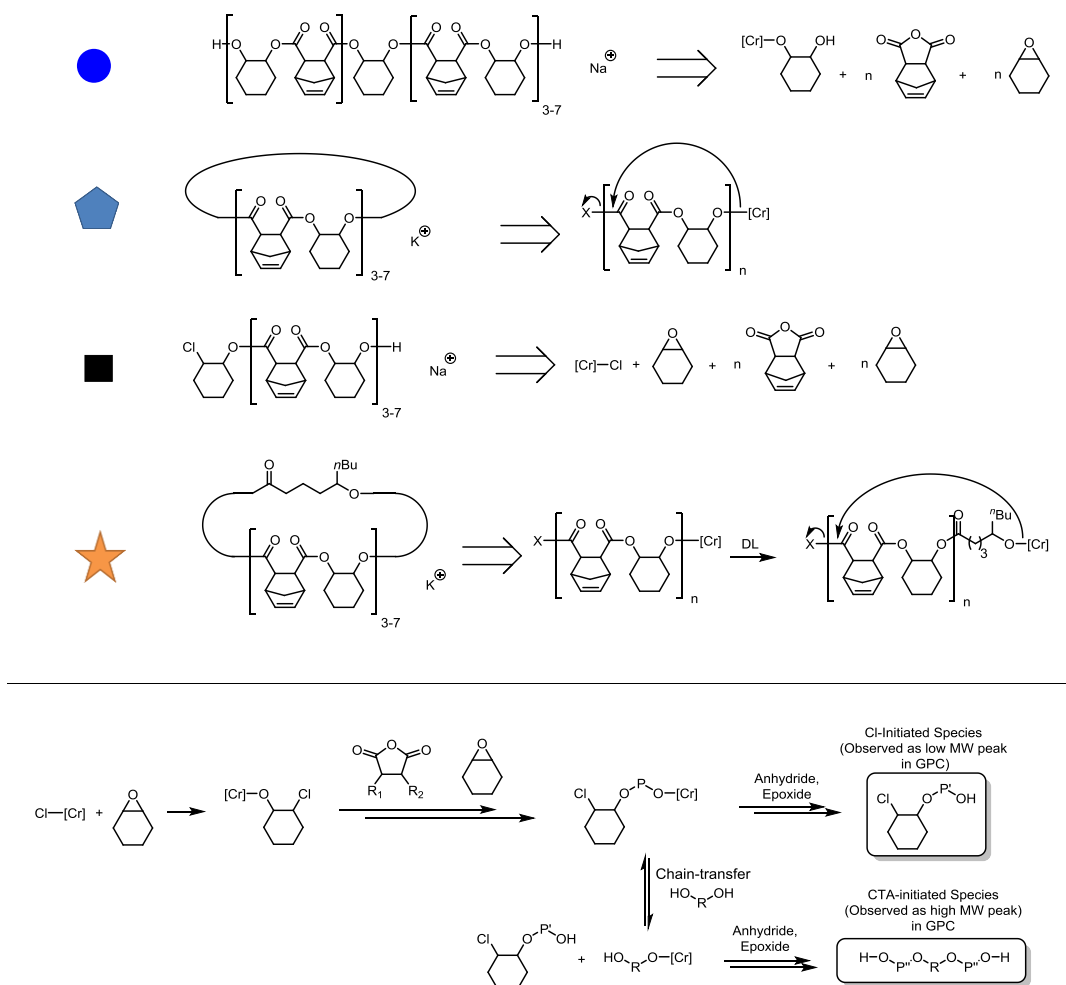


Figure S 3. 8 – Typical region of the MALDI-ToF spectrum with assignment of species present and possible rationale for their formation (top). A detailed explanation for the formation of chloro- and dihydroxyl-terminated chains in the presence of (trace)-amounts of bifunctional impurities is provided (bottom); the co-catalyst was not taken into account.^[1, 2] The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

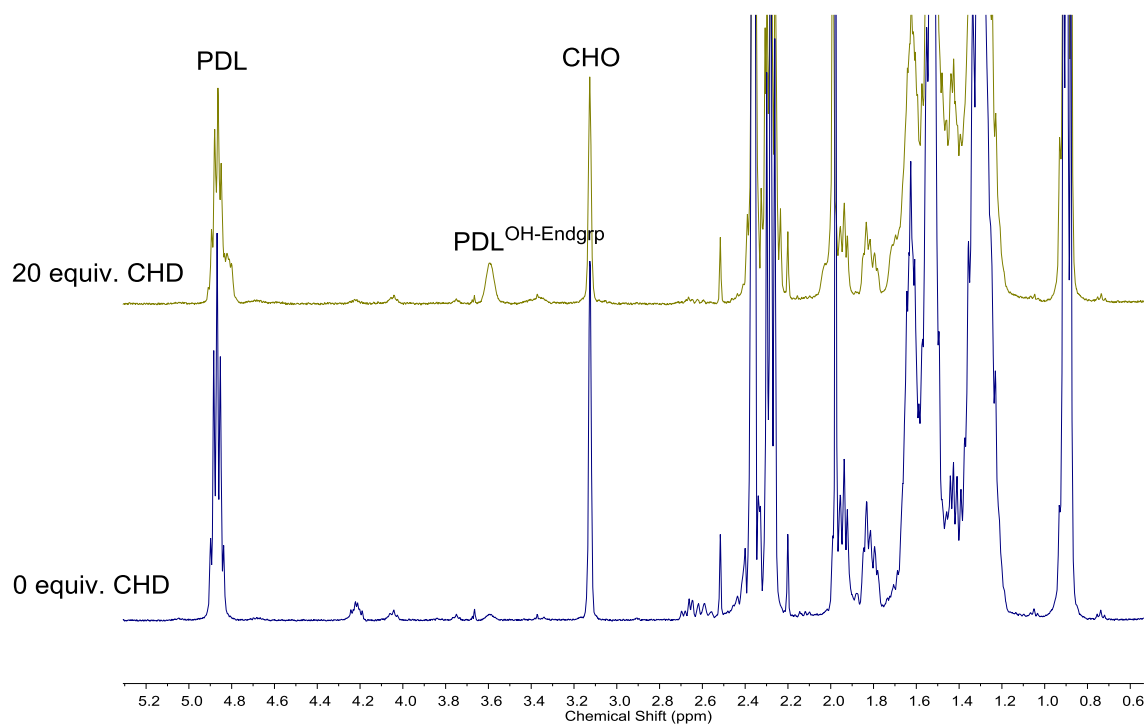


Figure S 3. 9 - Representative ^1H NMR spectra of crude samples for the homopolymerisation of DL with 20 and 0 equivalents of CHD. The absence of poly(cyclohexene oxide) at 3.4 – 3.6 ppm should be noted. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

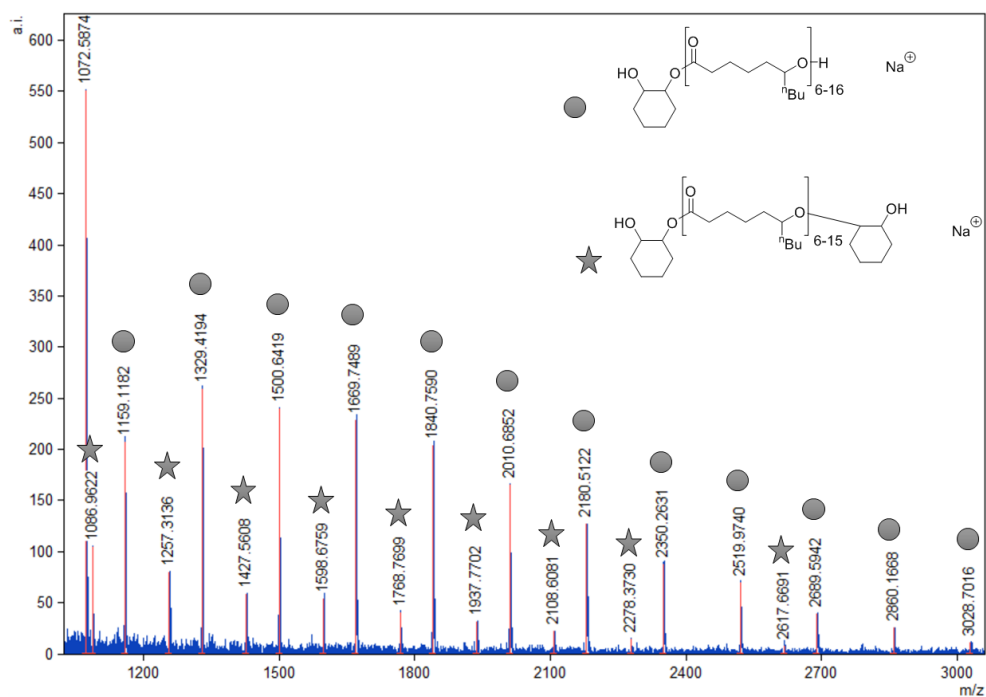


Figure S 3. 10 - Representative MALDI spectrum for a crude sample of PDL (20 equiv. of CHD). No polyether linkages were detected. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Monitoring of Polymerization of NBA/CHO/DL

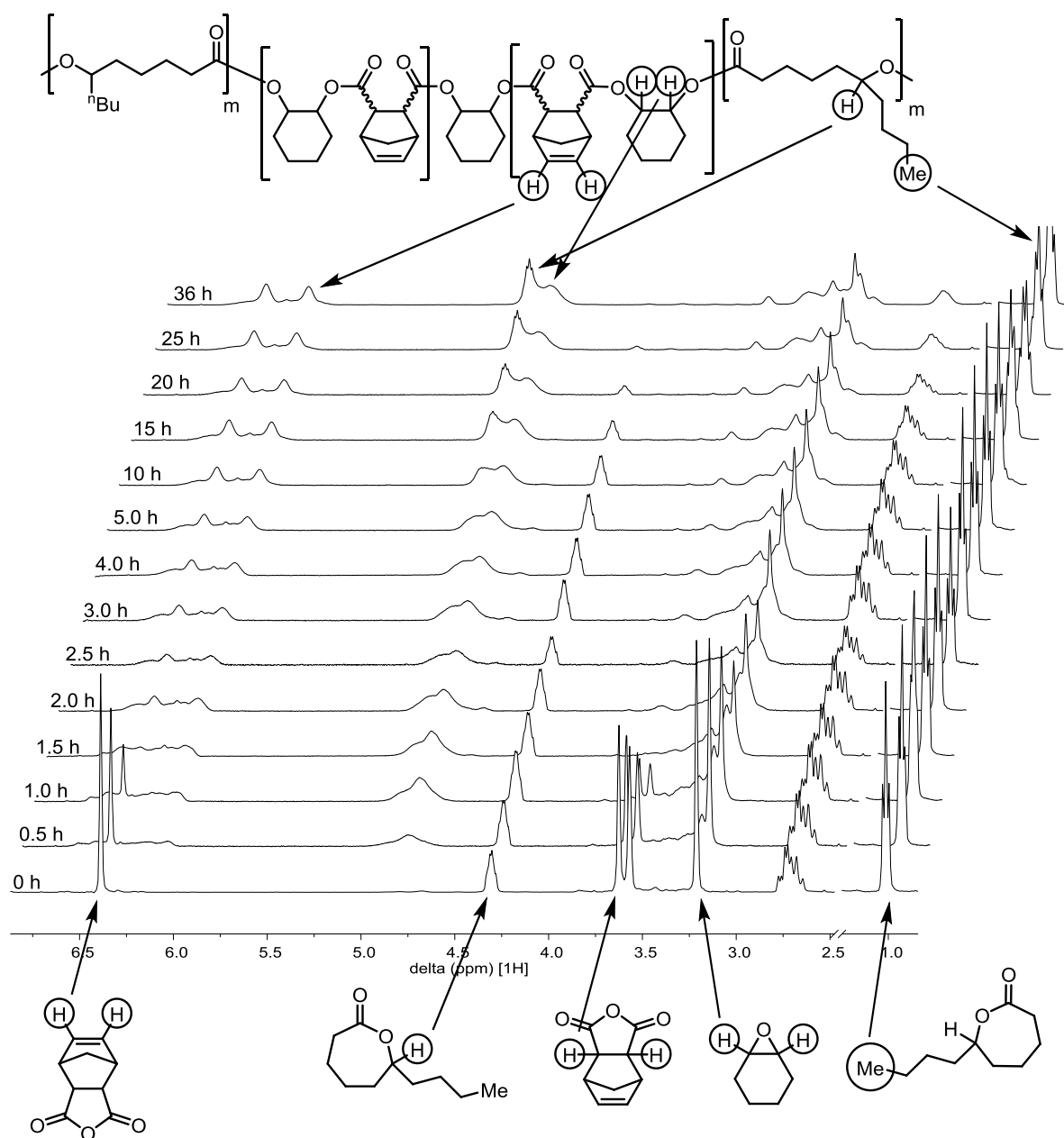


Figure S 3. 11– ^1H NMR spectra for polymerization using NBA/CHO/DL. Polymerization conditions: [SalcyCrCl]:PPNCl:CHD:NBA:CHO:DL = 1:1:10:100:125:100, Tol- d_8 (2.5 M), 100 $^\circ\text{C}$. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 2- Integrals based on ^1H NMR spectra (after normalization with mesitylene) and calculated conversions. Signals were based on the following shifts: 4.45 (NBA), 4.45-4.92 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. An error of $\pm 3\%$ was applied to all plots; the conversion of CHO at the end of the reaction was determined as 74 % (data not shown). The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Time (h)	NBA (Integral)	NBA (%)	DL (Integral)	DL (%)	Polyester (Integral)	Polyester (%)
0	531	100	143	97.9	0	0
0.5	320	60.2	146	100	124	26.4
1	121	22.7	140	95.8	215	45.9
1.5	0	0	142	97.2	275	58.7
2	0	0	137	93.7	281	60.0
2.5	0	0	140	95.8	287	61.3
3	0	0	134	91.7	272	58.1
4	0	0	129	88.2	281	60.0
5	0	0	127	86.8	280	59.8
10	0	0	102	69.6	305	65.1
15	0	0	65	44.1	350	74.7
20	0	0	32	21.3	340	72.6
25	0	0	11	6.8	393	83.9
36	0	0	1	0	468	100

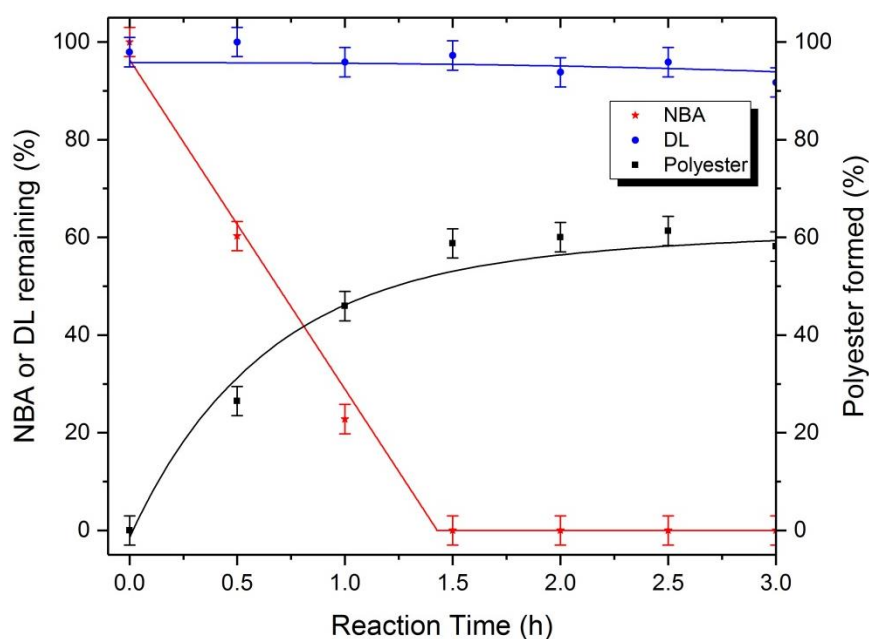


Figure S 3. 12 – Plot showing conversion of NBA and DL over the first 3 hours of the reaction. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

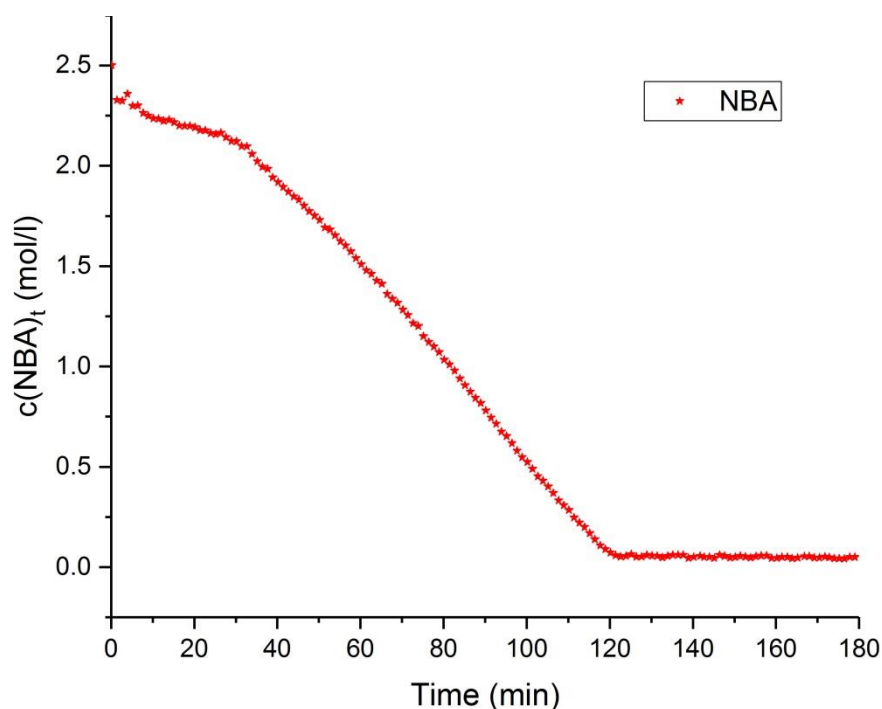


Figure S 3. 13 - *In situ* monitoring of IR band of NBA at 1850 cm^{-1} . The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Isolation of PDL-*b*-PCHNBE-*b*-PDL

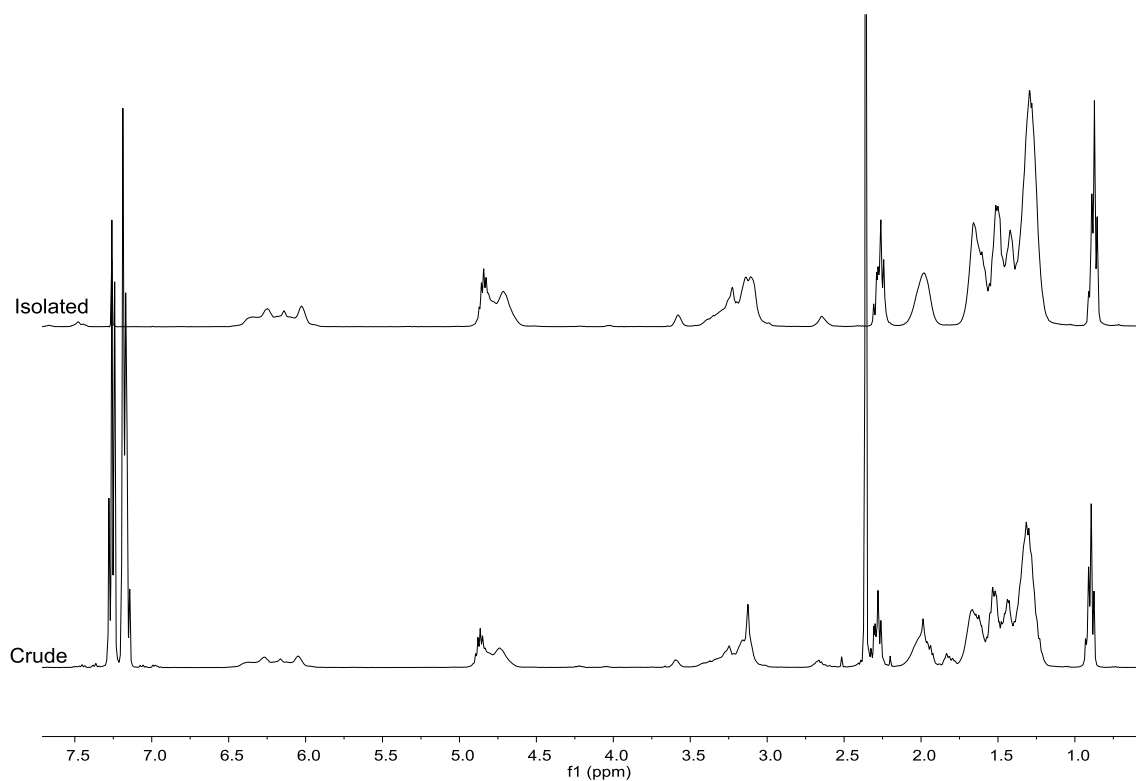


Figure S 3. 14- ^1H NMR spectra of crude (bottom) and isolated (top) polymer based on NBA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

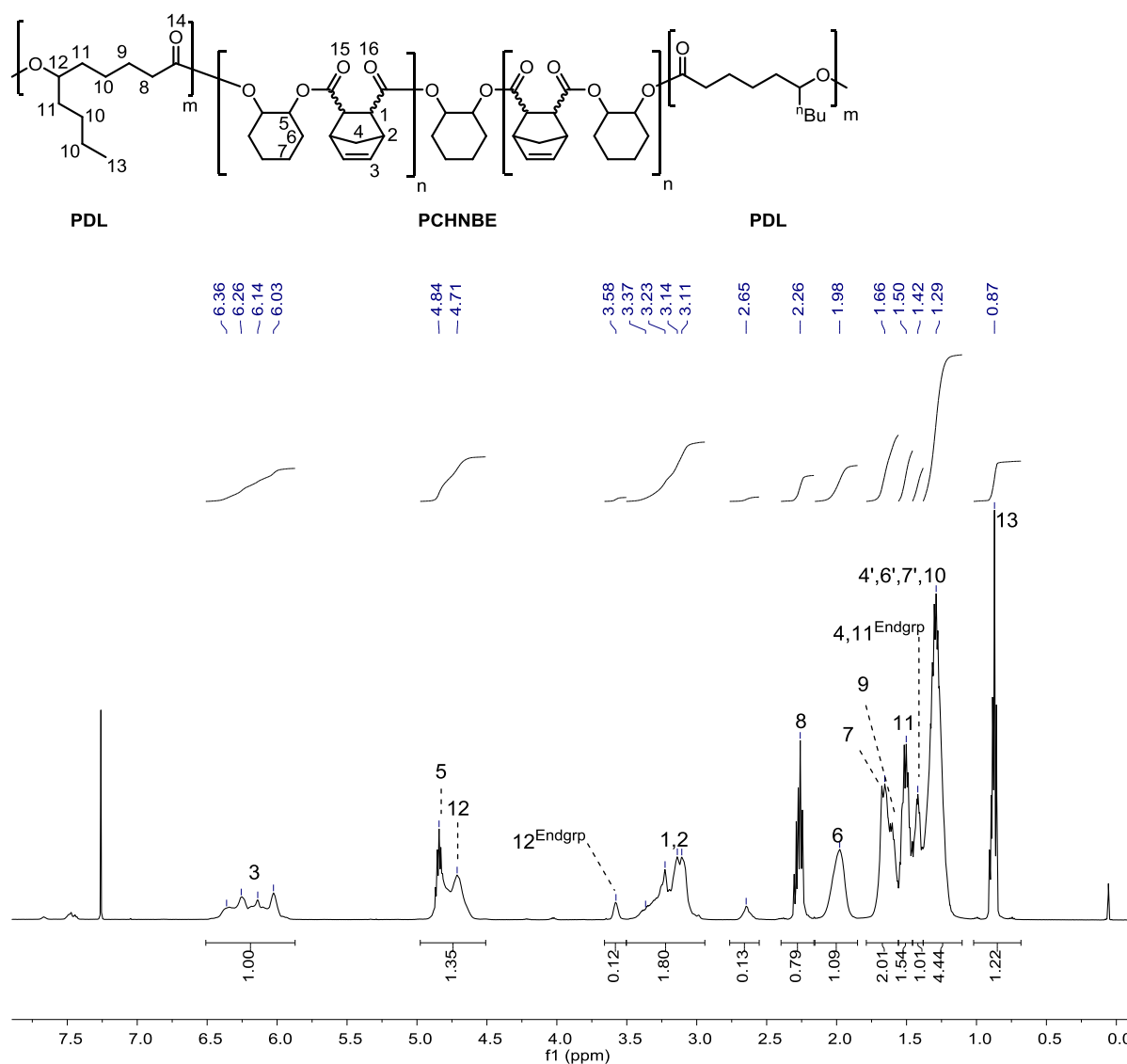


Figure S 3. 15 – ^1H NMR spectra of isolated polymer based on NBA/CHO/DL. Traces of PPNCl are observed at 7.5 ppm. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

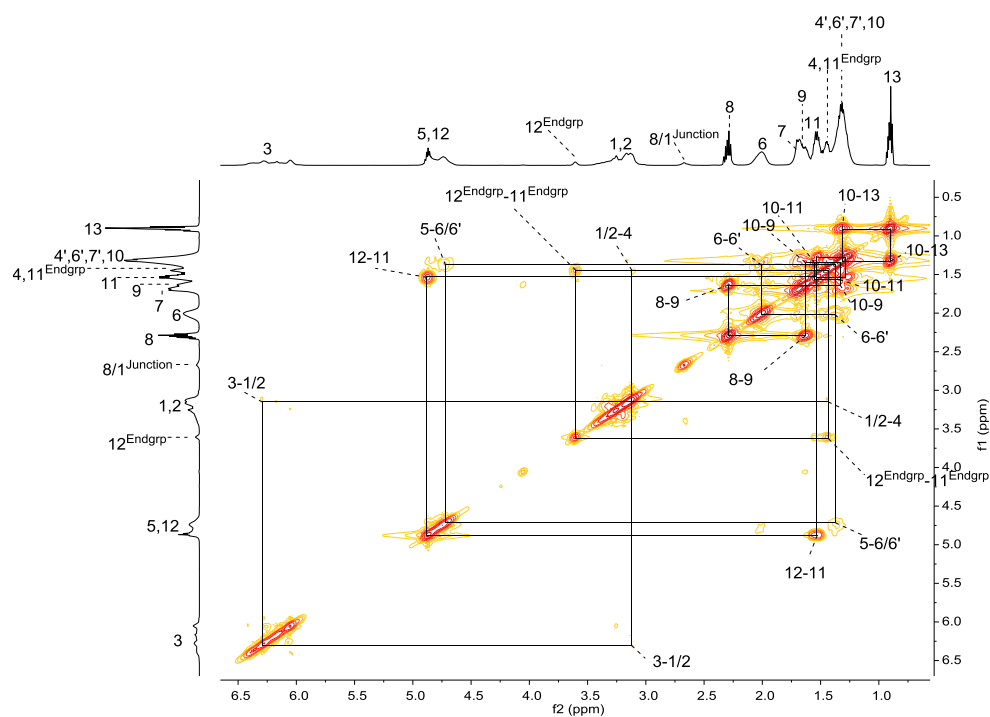


Figure S 3. 16 - COSY NMR spectrum of isolated polymer based on NBA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

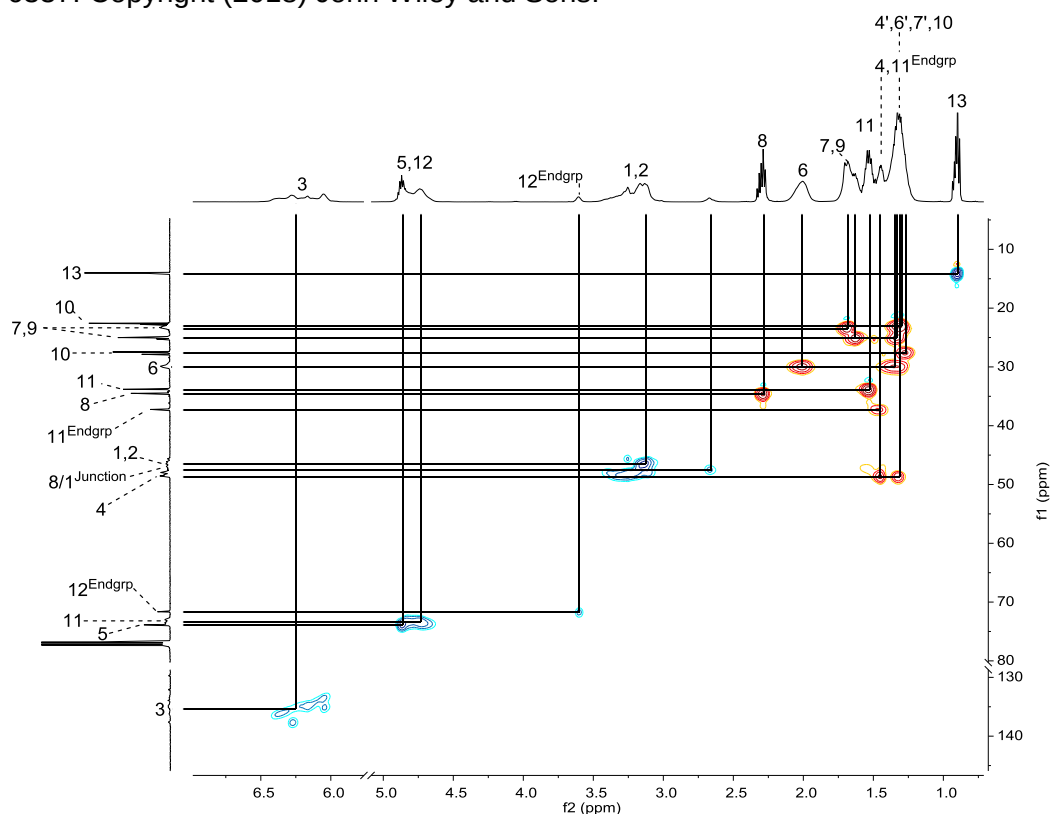


Figure S 3. 17 - HSQC NMR spectrum of isolated polymer based on NBA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

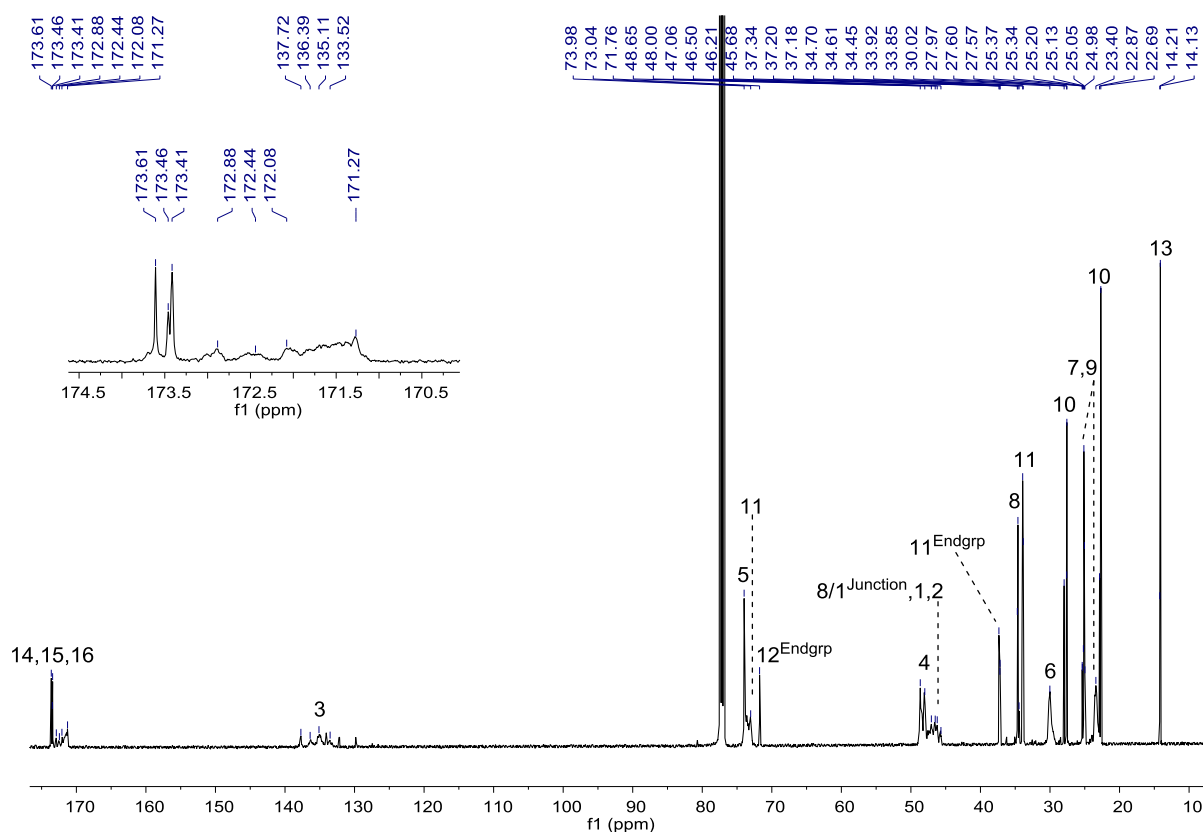
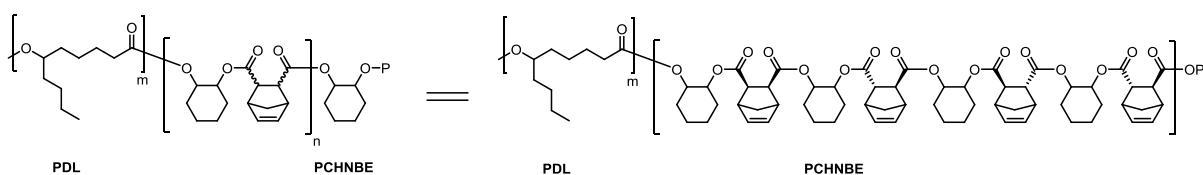


Figure S 3. 18 - $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated polymer based on NBA/CHO/DL. Traces of PPNCI are observed at 129.8, 132.2 and 134.1 ppm. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

It is proposed that the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum was complicated by the a mixture of cis and trans-ester linkages (66:34; likely to be distributed randomly throughout the polymer backbone), as illustrated below (reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.):



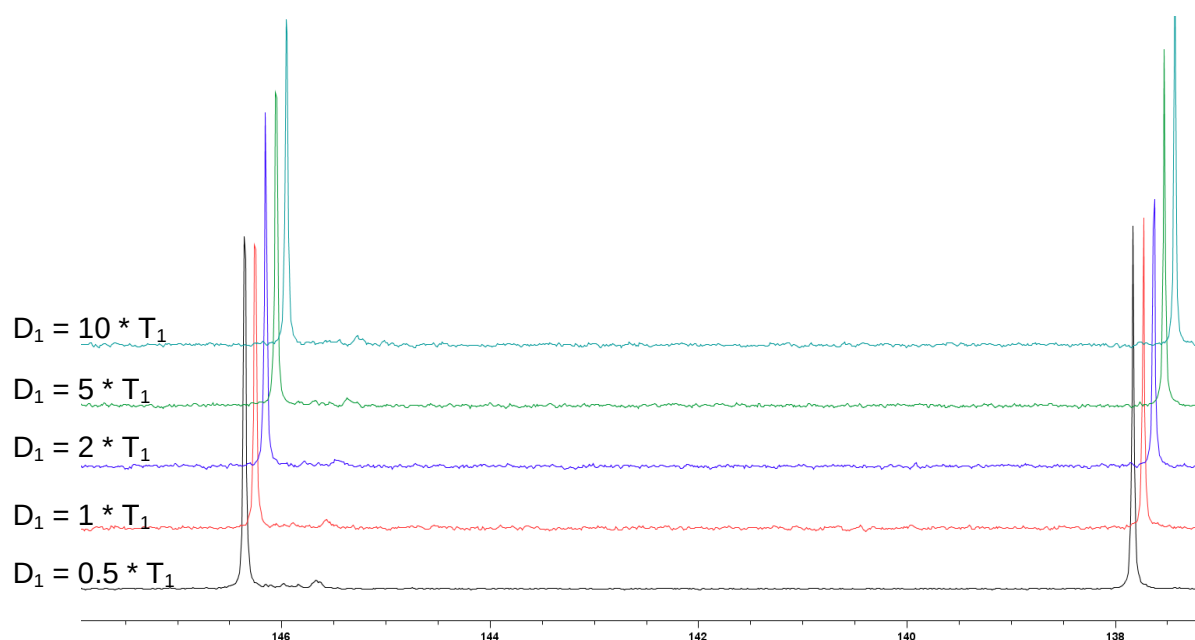


Figure S 3. 19 - ^{13}P $\{^1\text{H}\}$ NMR spectra after reacting (PDL-*b*-PCHNBE-*b*-PDL) with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane at various recycle delays (D_1) to account for the different relaxation times (T_1). The presence of only one peak at 147.2 ppm should be noted at all relaxation times (indicating PDL endgroups and the absence of PCHNBE endgroups).

Thermal Analysis of polyesters with different PCHNBE:PDL block ratios

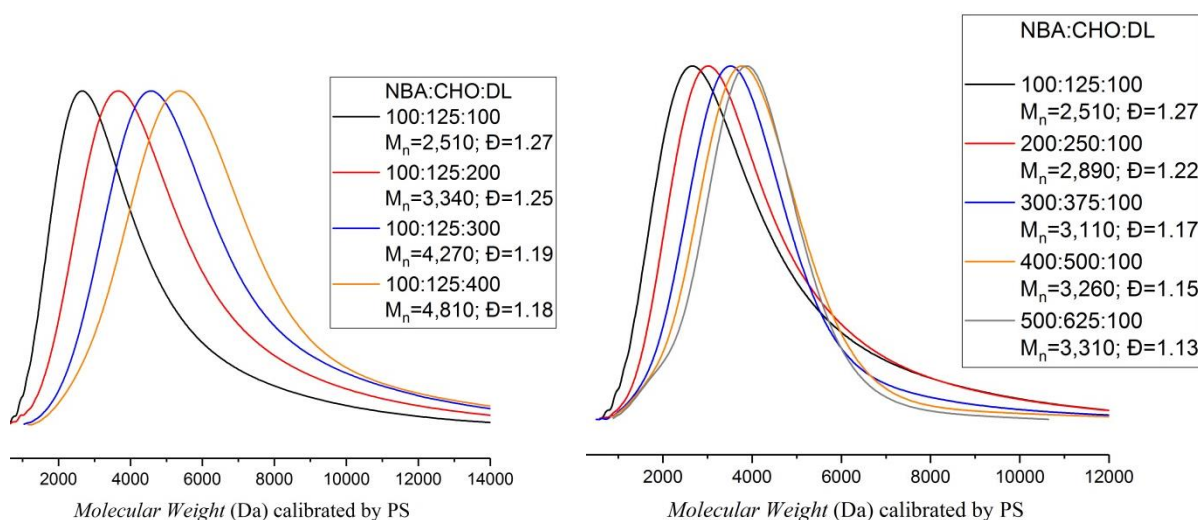


Figure S 3. 20 - GPC chromatograms for block polyesters based on NBA, CHO, DL for different block ratios. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 3 - Block polyesters with variable compositions and properties. The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

NBA:CHO:DL ^[a]	PCHNBE:PDL ^[b]	wt% PCHNBE: wt% PDL ^[c]	M_n (Đ) ^[c]	T _g (°C) ^[d]	T _{g,calc} (°C) ^[e]
100:125:400	1:4	27:73	4,810 (1.18)	-30	-28
100:125:300	1:3	34:66	4,270 (1.19)	-21	-21
100:125:200	1:2	44:56	3,340 (1.25)	-4	-10
100:125:100	1:1	61:39	2,510 (1.27)	26	13
200:250:100	2:1	76:24	2,890 (1.22)	57	36
300:375:100	3:1	82:18	3,110 (1.17)	71	46
400:500:100 ^[f]	5:1	89:11	3,260 (1.15)	84	60
500:625:100 ^[g]	16:1	96:4	3,310 (1.13)	111	73

^[a] Molar ratio of starting materials; generally both processes proceed to >95% monomer conversion (Fig. S22). ^[b] Molar ratio of the polyester blocks based on conversion of starting materials (Fig. S22). ^[c] Weight fractions of polyester blocks; calculated from molar ratios. ^[c] Determined by GPC, THF, 30 °C, using polystyrene standards to calibrate the instrument (Fig. S21). ^[d] Determined by DSC measurements from -90 – 160 °C at 10°C/min and taken from the third heating cycle (Figs. S23). ^[e] Based on Fox Equation with T_g(PCHNBE)=82°C and T_g(PDL)=-54°C. ^[f] ~ 80% DL conversion. ^[g] ~ 30% DL conversion.

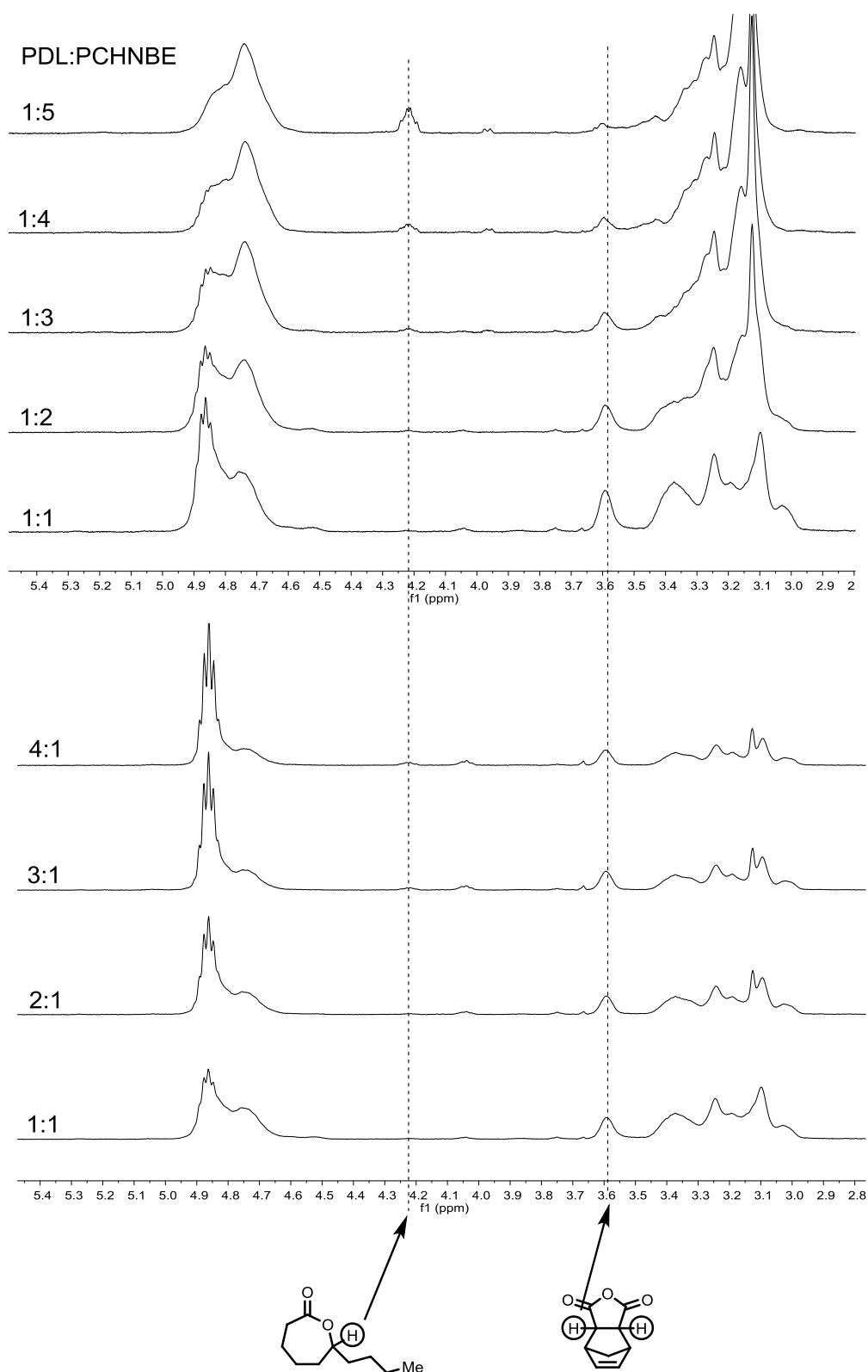


Figure S 3. 21– ^1H NMR spectra of crude block copolymers based on different NBA:CHO:DL ratios. It should be noted that conversions of 99% were obtained in all cases apart from PDL:PCHNBE = 1:5 or 1:4 (DL conversions were 80% and 30%, respectively). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

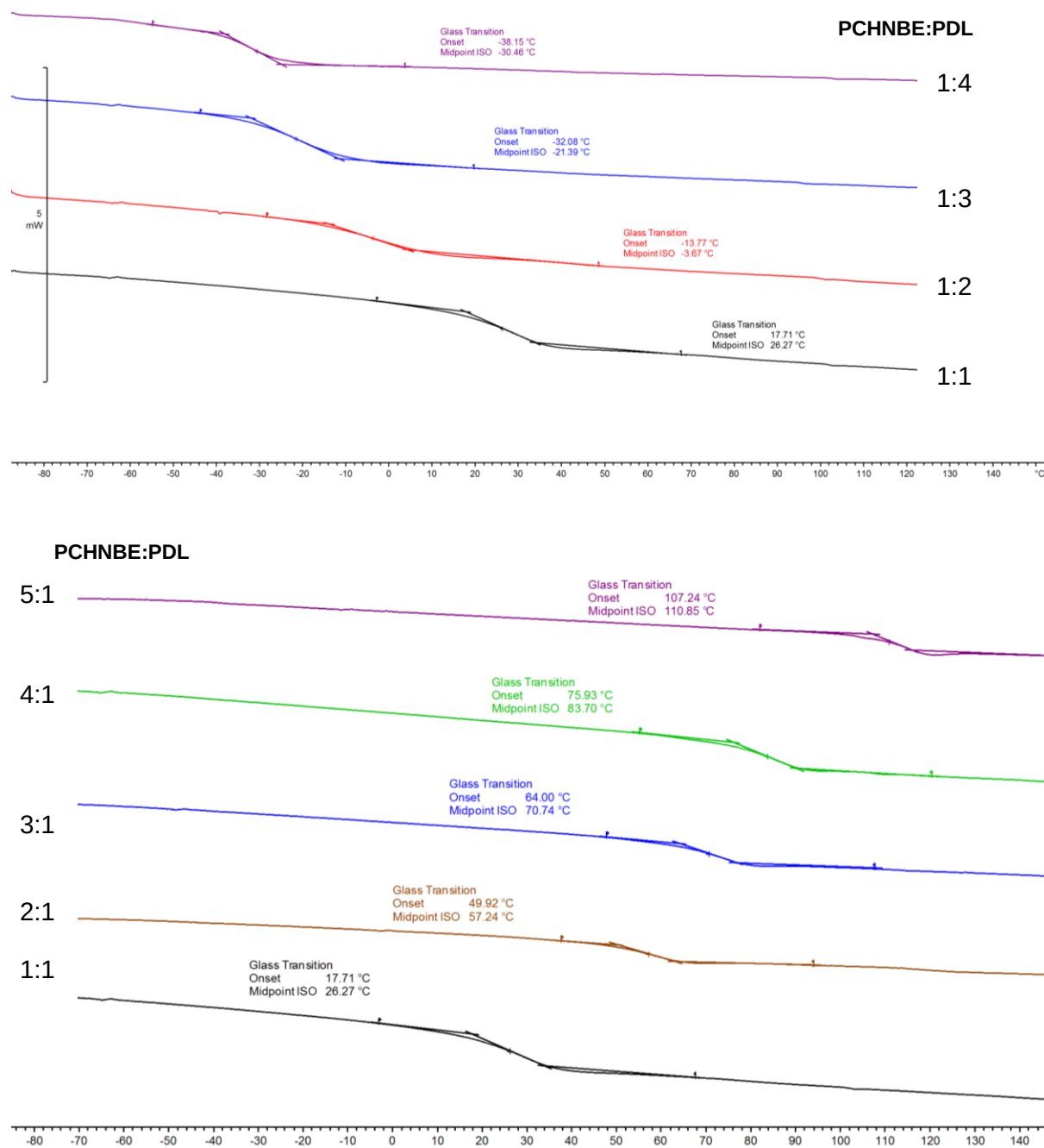


Figure S 3. 22 - DSC thermograms for block polyester based on NBA/CHO/DL at different compositions. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

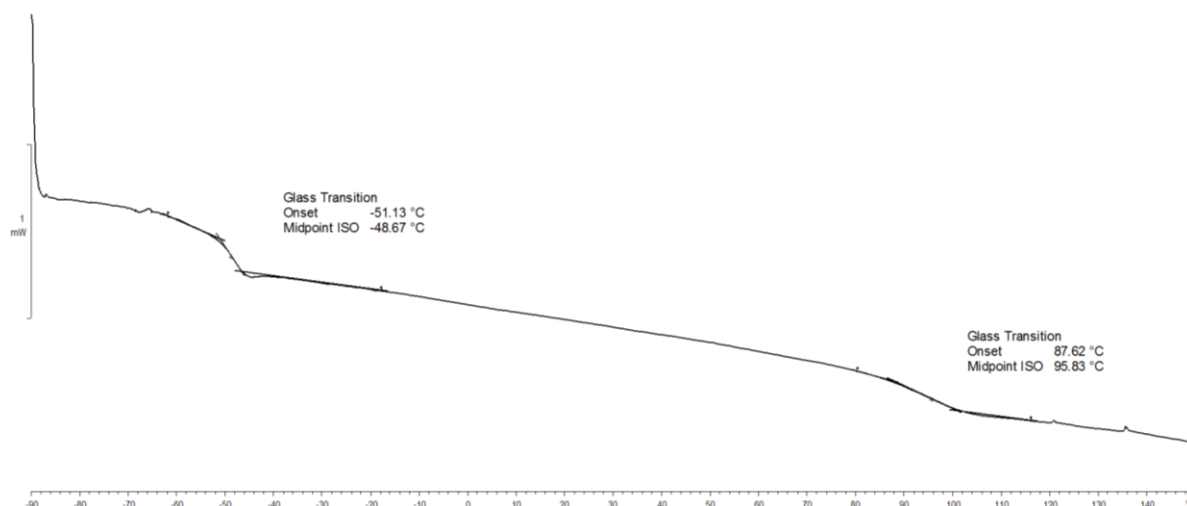


Figure S 3. 23 - DSC thermograms for mixture of homopolymers (molecular weight for PDL: $M_n=4,880$ g/mol ($\bar{D}=1.12$); for PCHNBE: $M_n=5,330$ g/mol ($\bar{D}=1.35$)). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Characterisation data for Polymer based on PA/CHO/DL

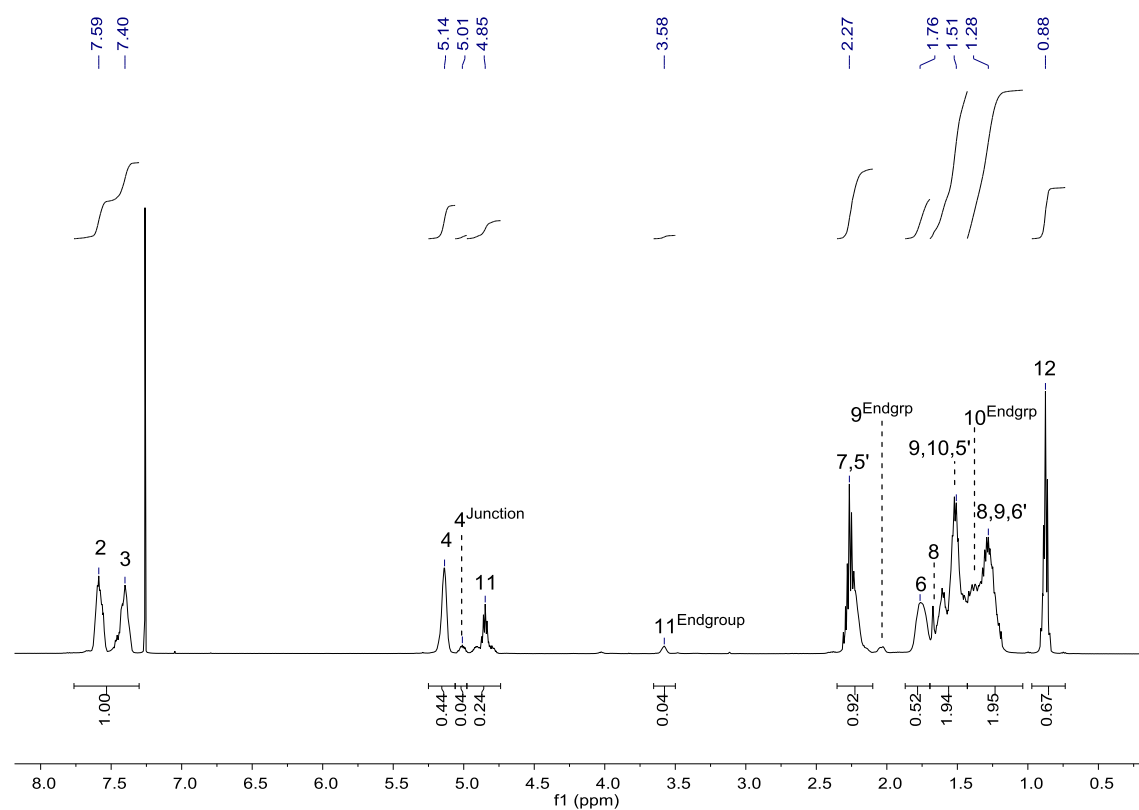


Figure S 3. 24 – ^1H NMR spectrum of polymer based on PA, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

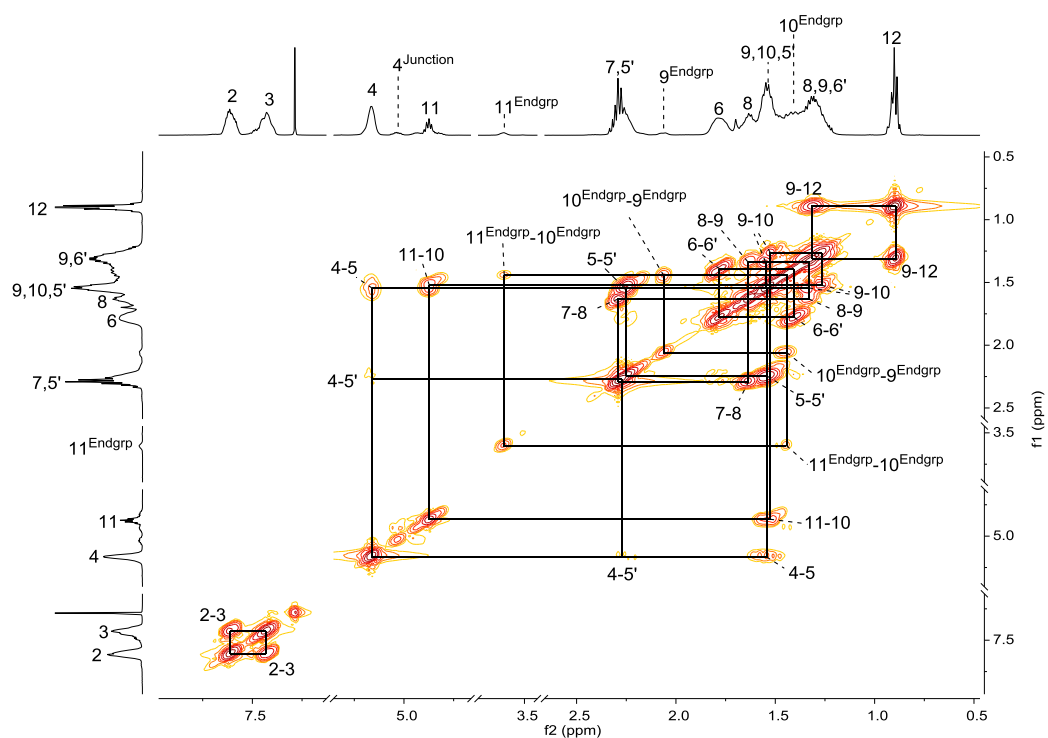


Figure S 3. 25 - COSY NMR spectrum of polymer based on PA, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

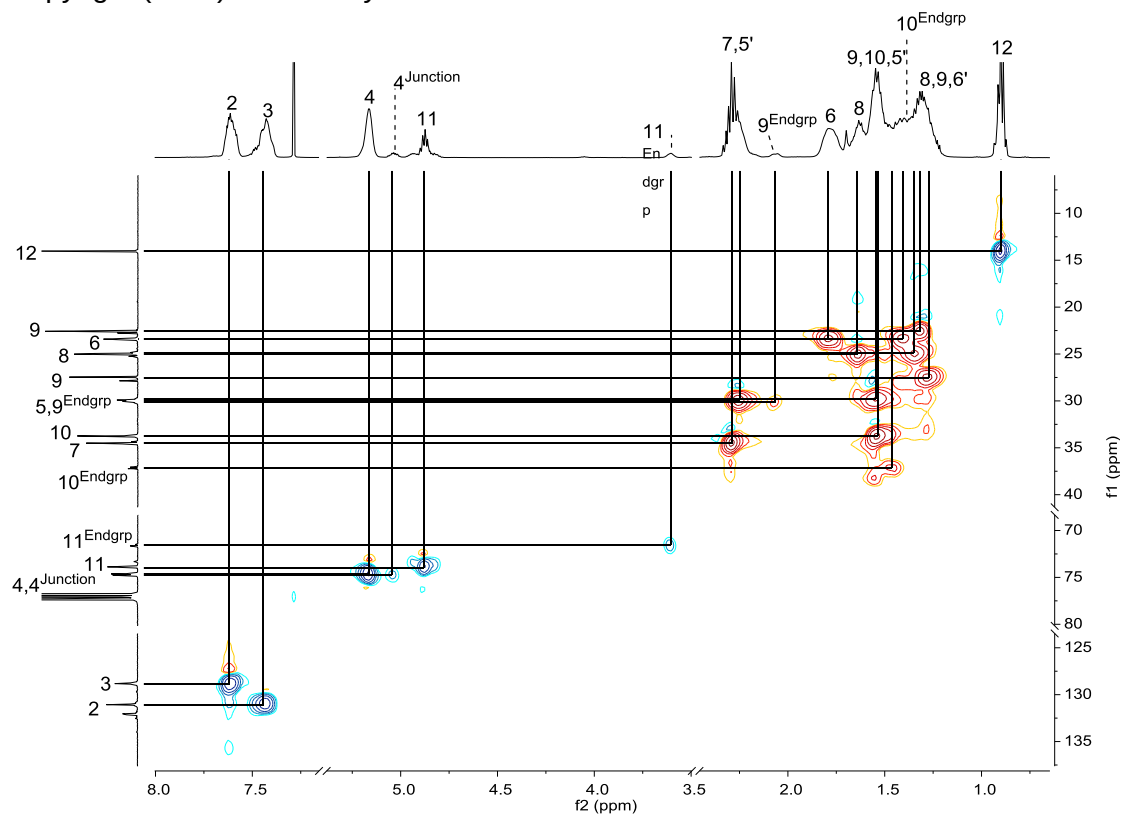


Figure S 3. 26 - HSQC NMR spectrum of polymer based on PA, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

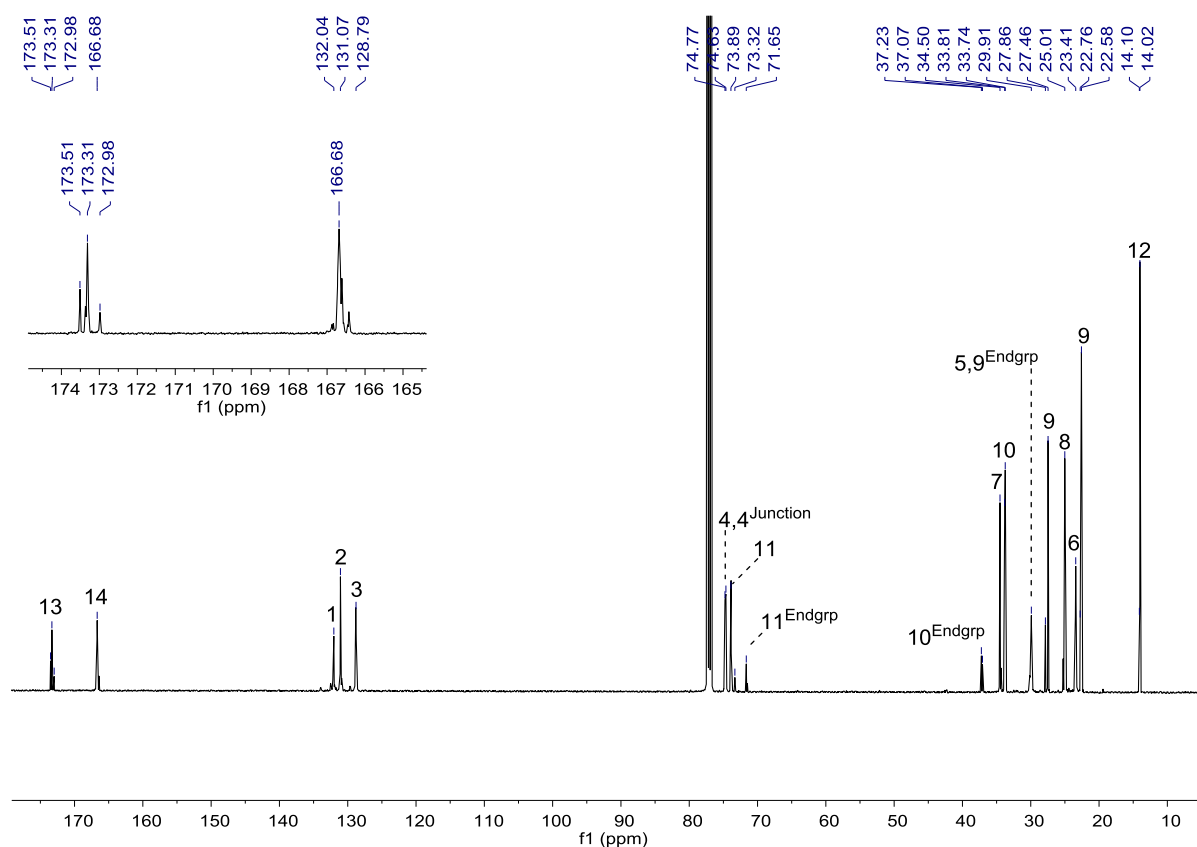


Figure S 3. 27 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polymer based on PA, CHO, DL. Traces of PPNCl were observed at 129.8, 132.2 and 134.1 ppm. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

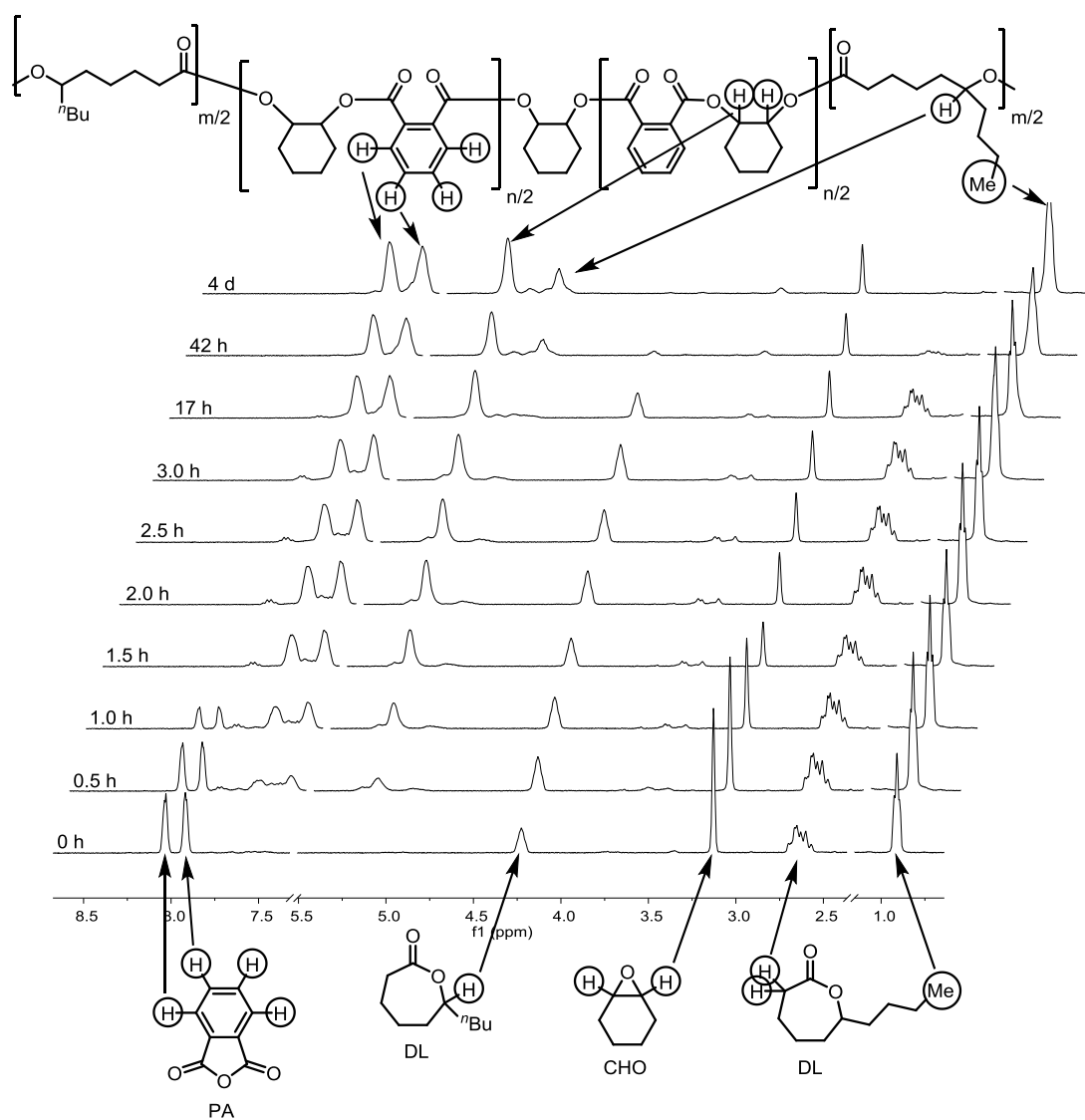


Figure S 3. 28 - ^1H NMR spectra of polymerization of PA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

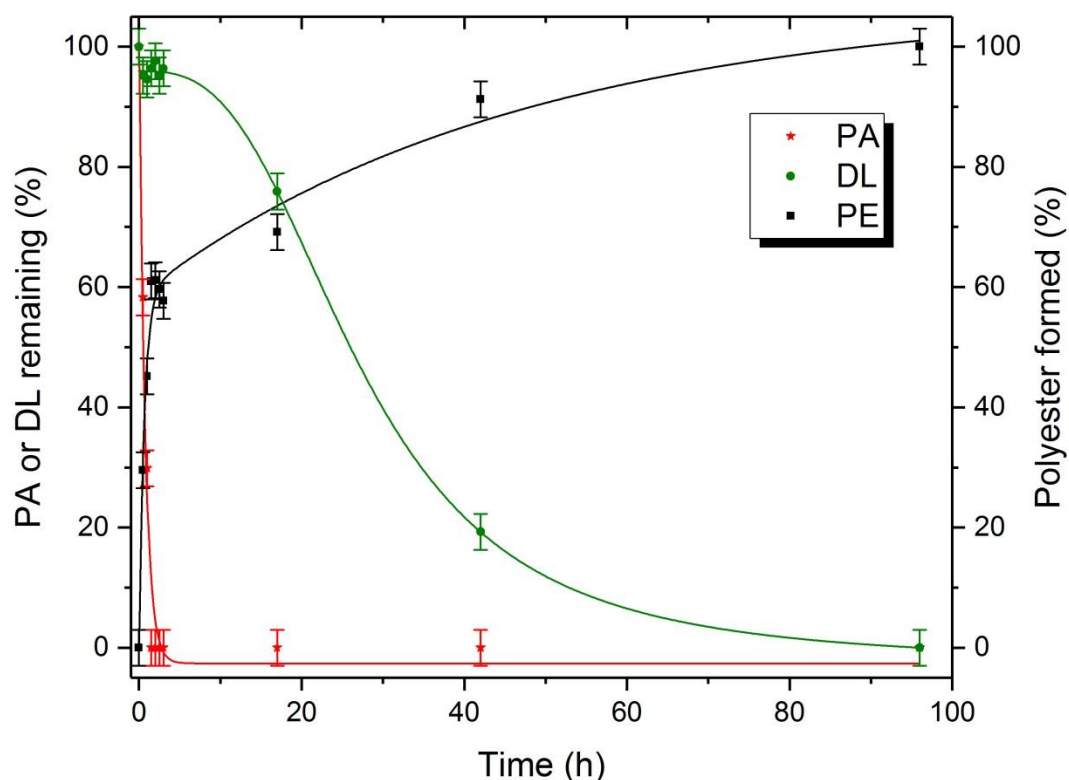


Figure S 3. 29 - Conversion of PA and DL and formation of polyester. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 4 - Integrals based on ^1H NMR spectra (after normalization with mesitylene as internal standard) and calculated conversions. Signals were based on the following shifts: Signals were based on the following shifts: 7.87-8.08 (PA), 4.78 – 5.30 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 76 % (data not shown). The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Time (h)	Integral PA	PA (%)	Integral DL	DL (%)	Integral Polyester	Polyester (%)
0	499	100	166	100	0	0
0.5	291	58.3	158	95.1	155	29.5
1	149	29.8	157	94.5	237	45.1
1.5	0	0	160	96.3	320	60.9
2	0	0	162	97.5	321	61.1
2.5	0	0	158	95.1	317	59.6
3	0	0	160	96.3	312	57.7
17	0	0	126	75.9	342	69.1
42	0	0	32	19.2	400	91.2
96	0	0	0	0	423	100

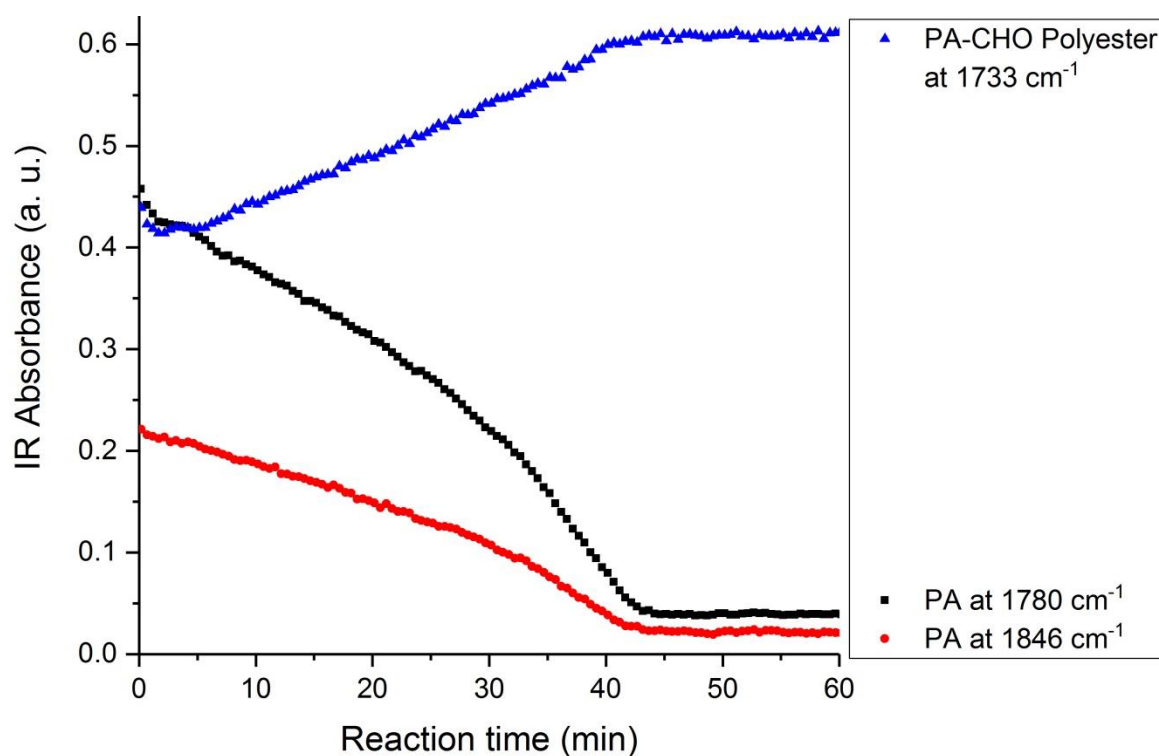


Figure S 3. 30 - *In situ* monitoring of one-pot polymerization of PA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

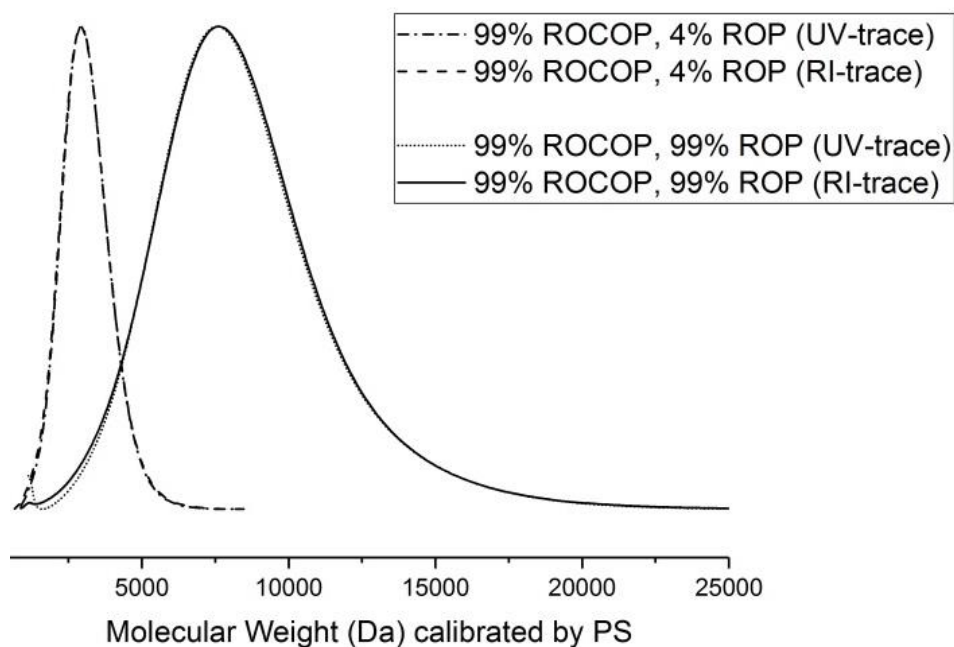


Figure S 3. 31 – Comparison of GPC chromatograms after ROCOP (left peaks) and at the end of the reaction (right peaks); UV traces are shown in dots and RI traces as bold (or dashed) lines. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

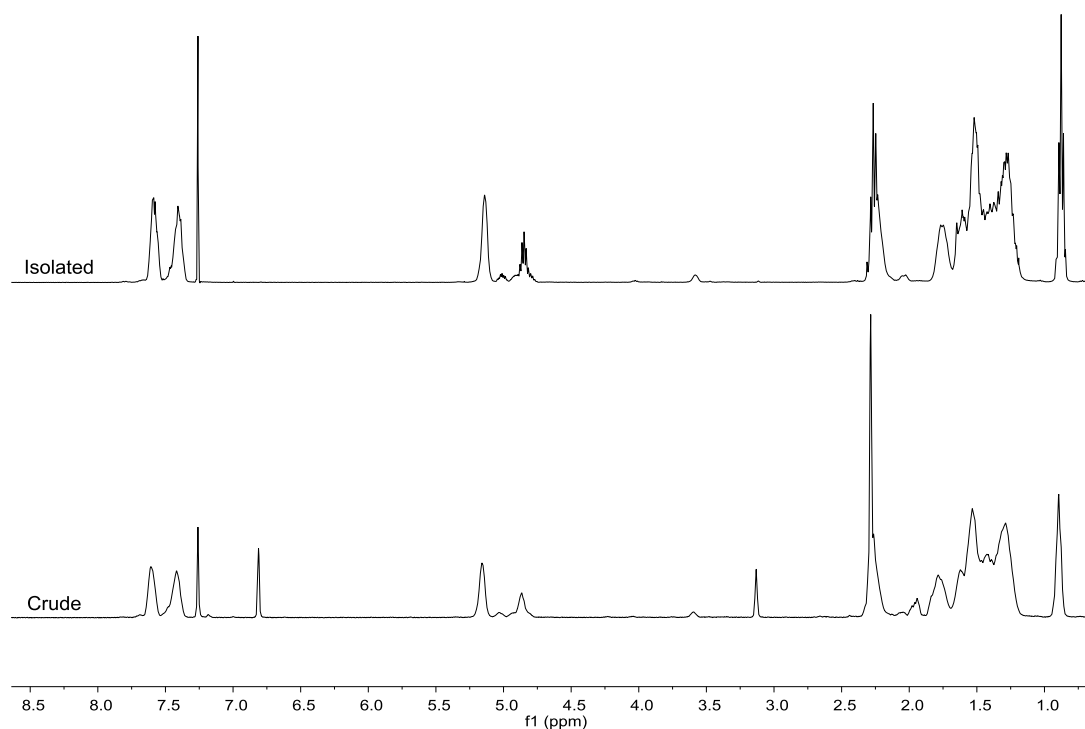


Figure S 3. 32 – ^1H NMR spectra of crude (bottom) and isolated (top) polymer based on PA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

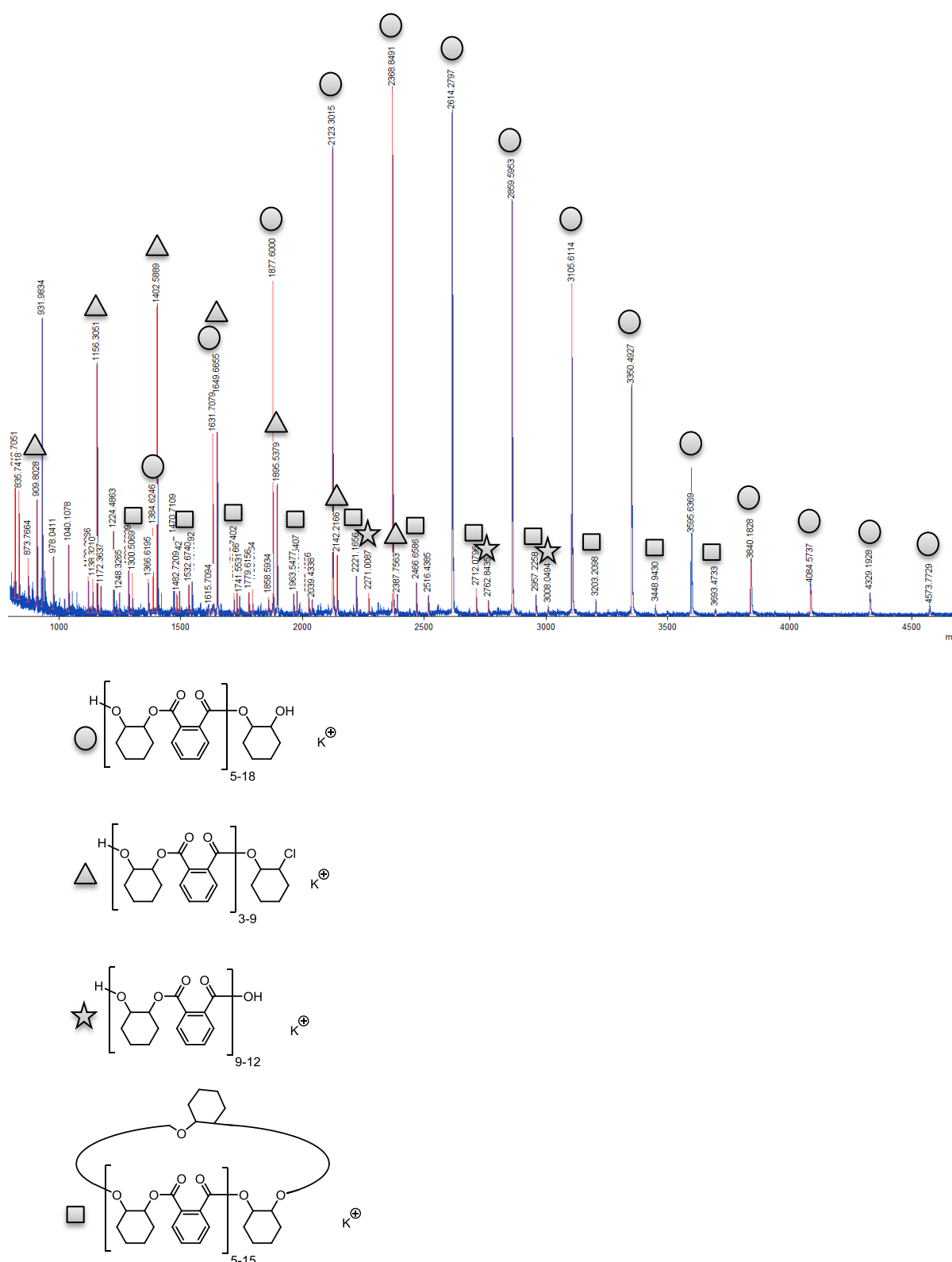


Figure S 3. 33 – MALDI of polymerization of PA/CHO/DL (after 1.5 h, 99% PA and 4% DL conversion). Four species were detected: circle: $m/z = [116.08 (\text{cyclohexandiol}) + (246.09 \times n) (\text{PCHPE}) + 38.96 (\text{K}^+)]$ ($n = 5 \sim 18$); triangle: $m/z = [34.97 (\text{Cl}^-) + 98.07 (\text{CHO}) + 1.01 (\text{H}^-) + (246.09 \times n) (\text{PCHPE}) + 38.96 (\text{K}^+)]$ ($n = 3 \sim 9$); star: $m/z = [18.01 (\text{H}_2\text{O}) + (246.09 \times n) (\text{PCHPE}) + 38.96 (\text{K}^+)]$ ($n = 9 \sim 12$); square: $m/z = [98.07 (\text{CHO}) + (246.09 \times n) (\text{PCHPE}) + 38.96 (\text{K}^+)]$ ($n = 5 \sim 15$). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Characterisation data for Polymer based on THPA/CHO/DL

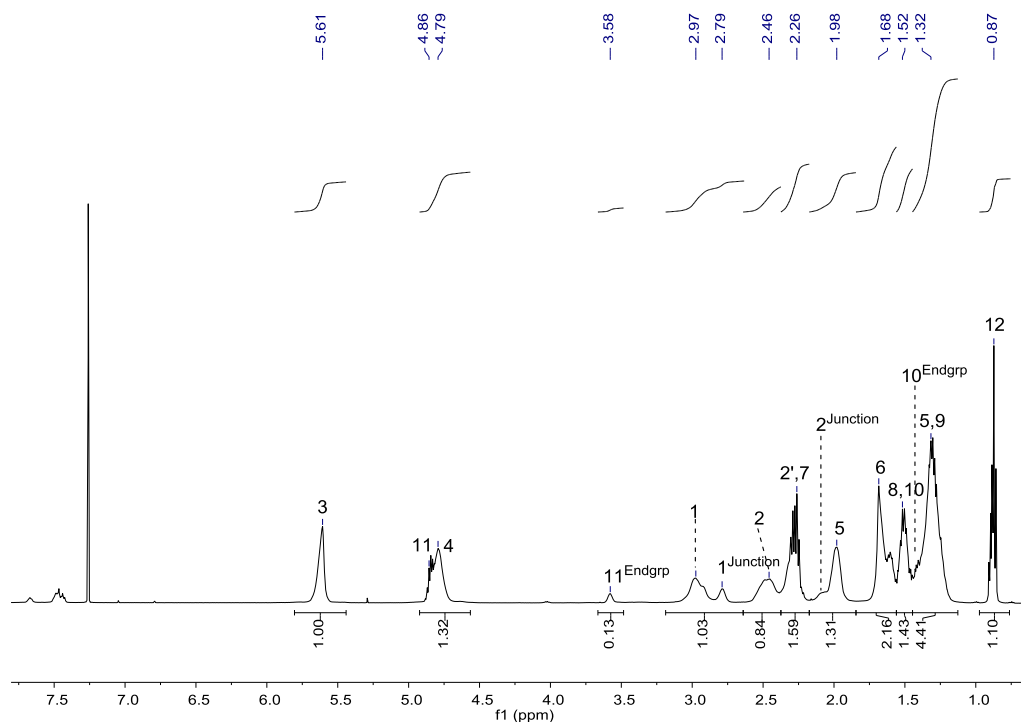


Figure S 3. 34- ^1H NMR spectrum of polymer based on THPA, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

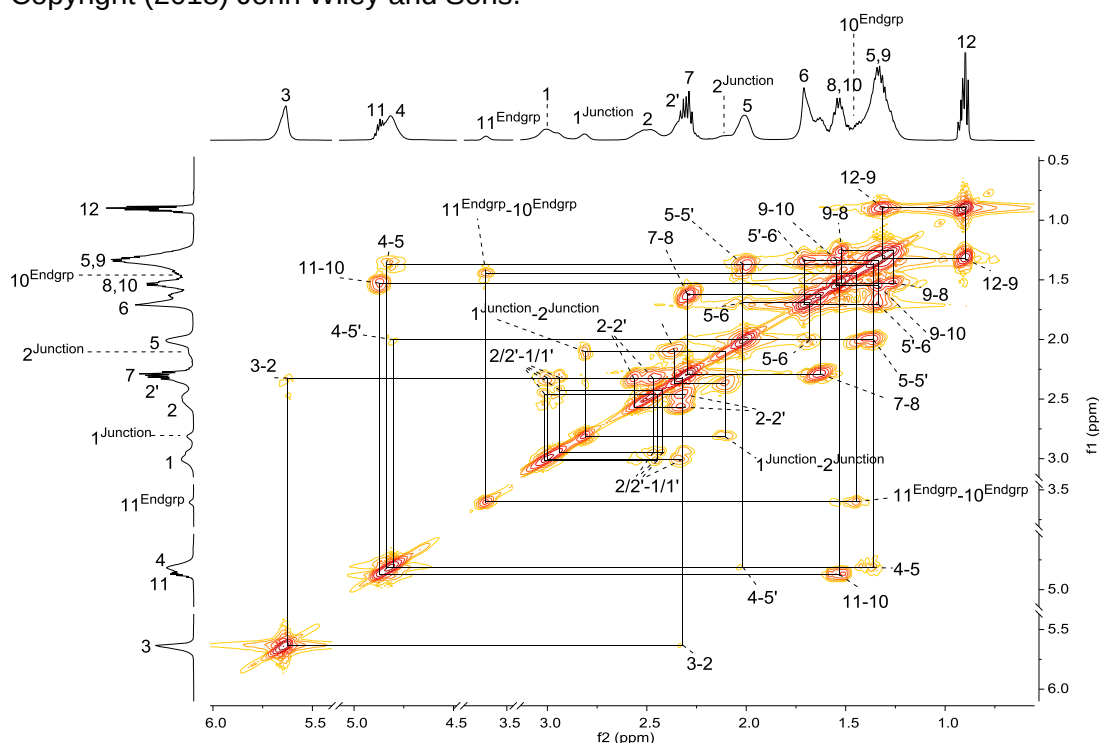


Figure S 3. 35 - COSY NMR spectrum of polymer based on THPA, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

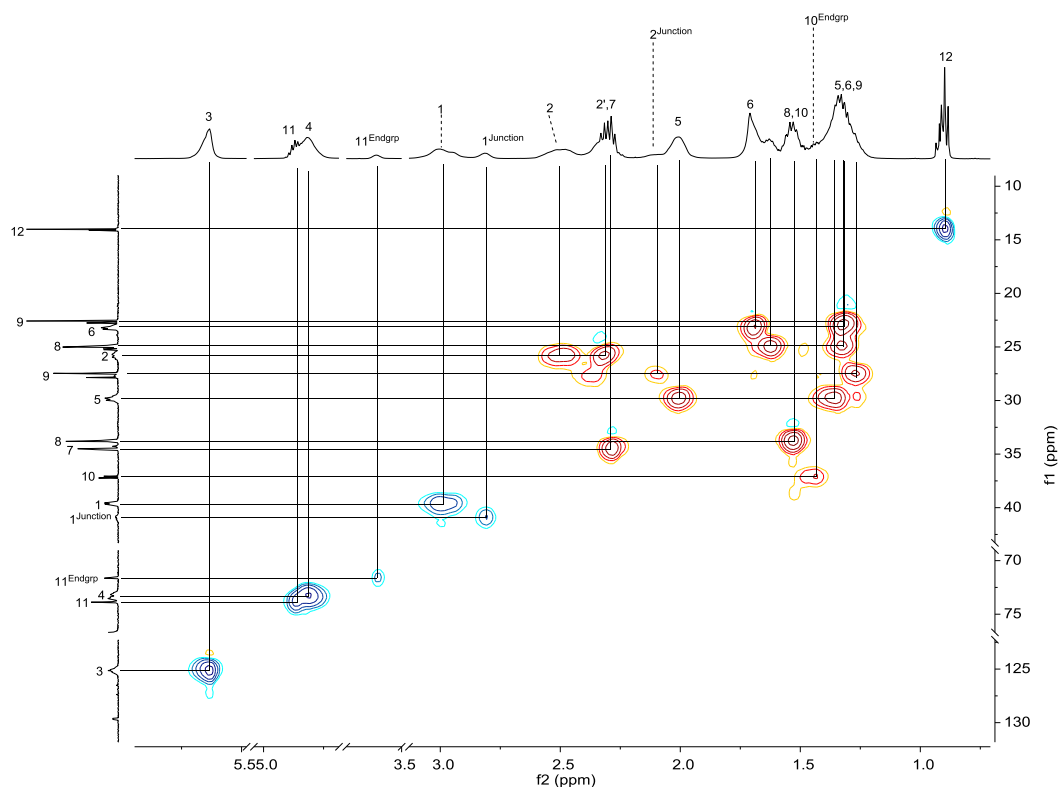


Figure S 3. 36 - ^1H , ^{13}C -HSQC of polymer based on TPHA, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

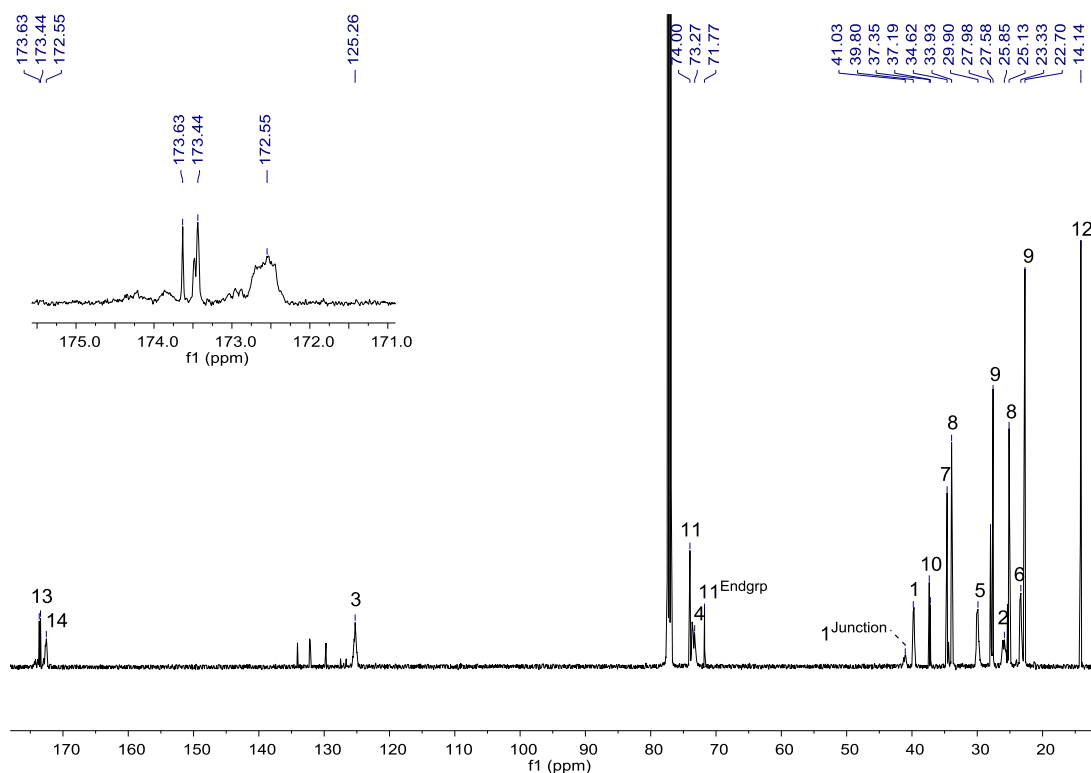


Figure S 3. 37 - $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polymer based on TPHA, CHO, DL. Traces of PPNCI were observed at 129.8, 132.2 and 134.1 ppm. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

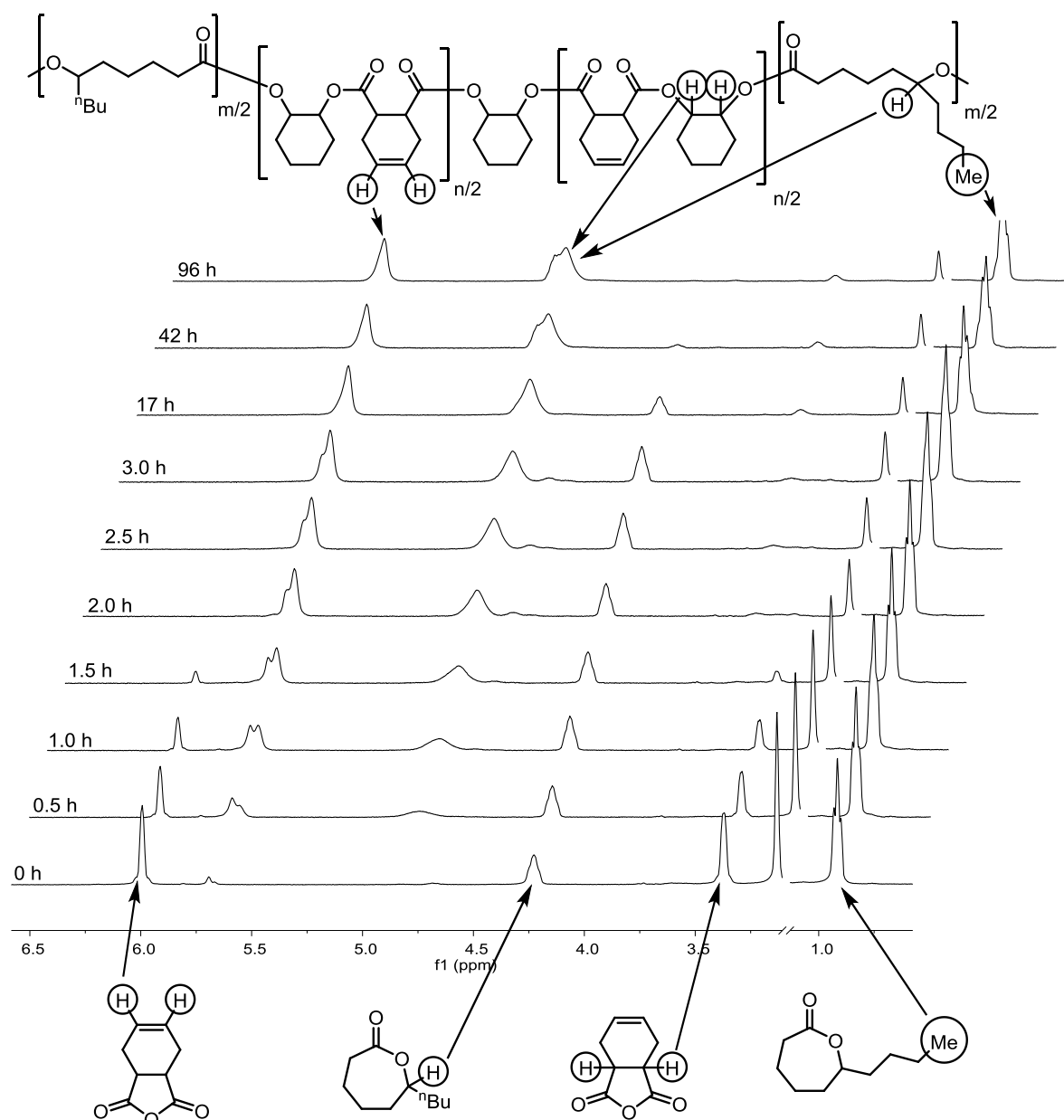


Figure S 3. 38 - ^1H NMR spectra of polymerization of THPA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

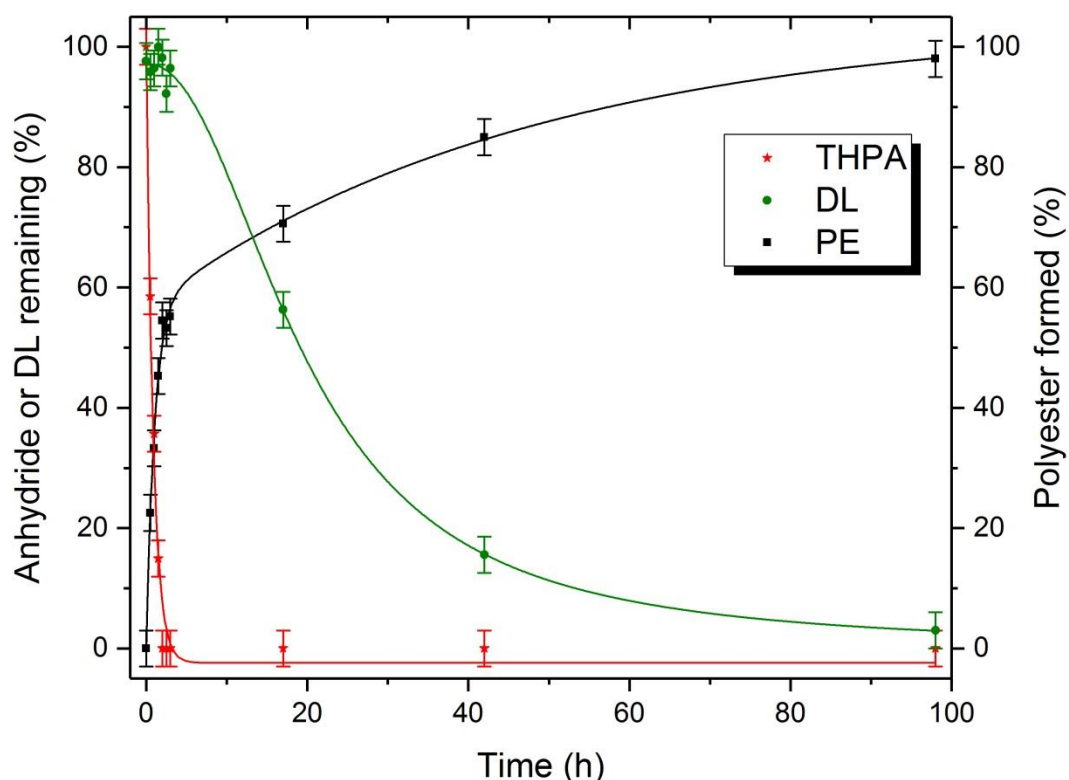


Figure S 3. 39 - Conversion of THPA and DL and formation of polyester. Data is given below. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 5 - Integrals based on ^1H NMR spectra (after normalization with mesitylene) and calculated conversions. Signals were based on the following shifts: 6.60 (THPA), 4.67-4.95 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 79 % (data not shown). The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Time (h)	Integral THPA	THPA (%)	Integral DL	DL (%)	Integral Polyester	Polyester (%)
0	241	100	163	97.6	0	0
0.5	141	58.5	160	95.8	105	22.5
1	86	35.6	161	96.4	155	33.2
1.5	36	14.9	167	100	211	45.2
2	0	0	164	98.2	254	54.5
2.5	0	0	154	92.2	248	53.2
3	0	0	161	96.4	257	55.1
17	0	0	94	56.2	329	70.6
42	0	0	26	15.5	396	84.9
96	0	0	6	3	420	98

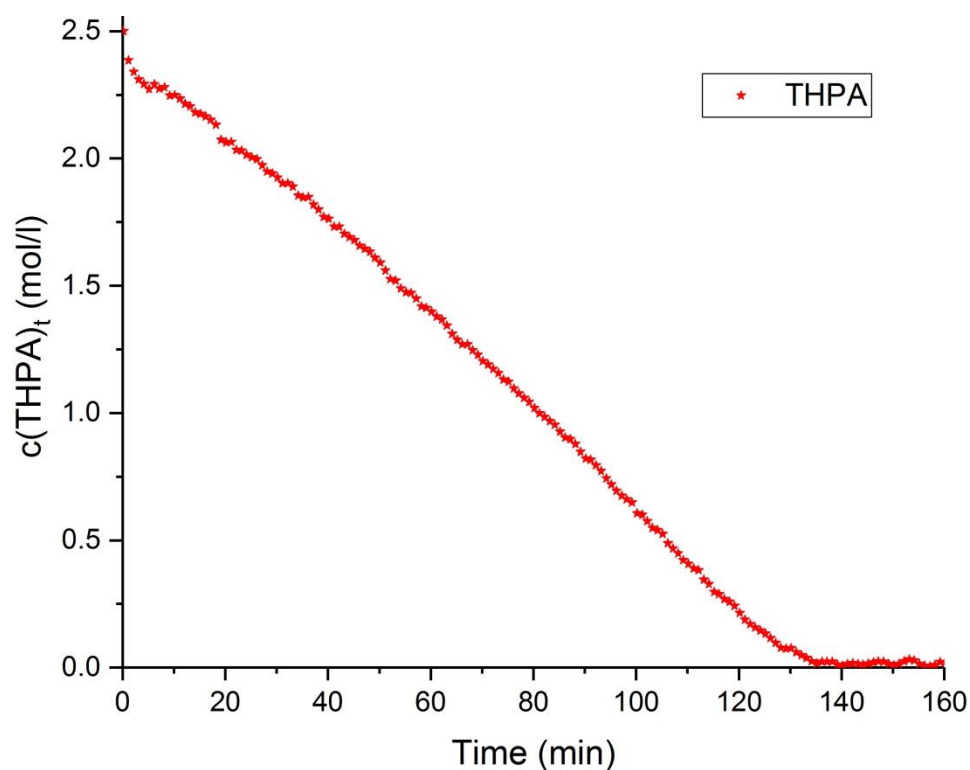


Figure S 3. 40 - *In situ* monitoring of IR band of THPA at 1850 cm^{-1} . The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

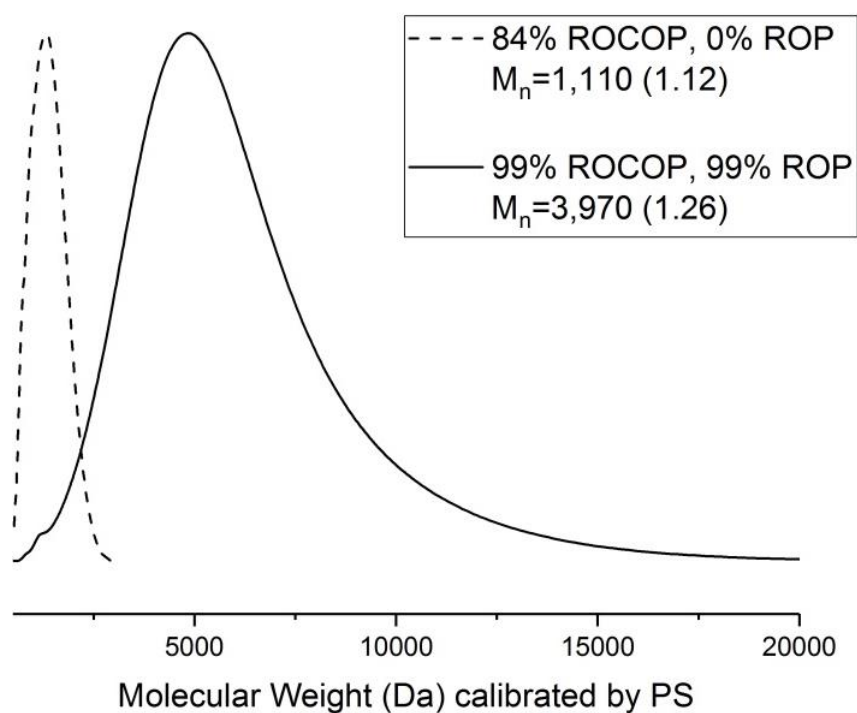
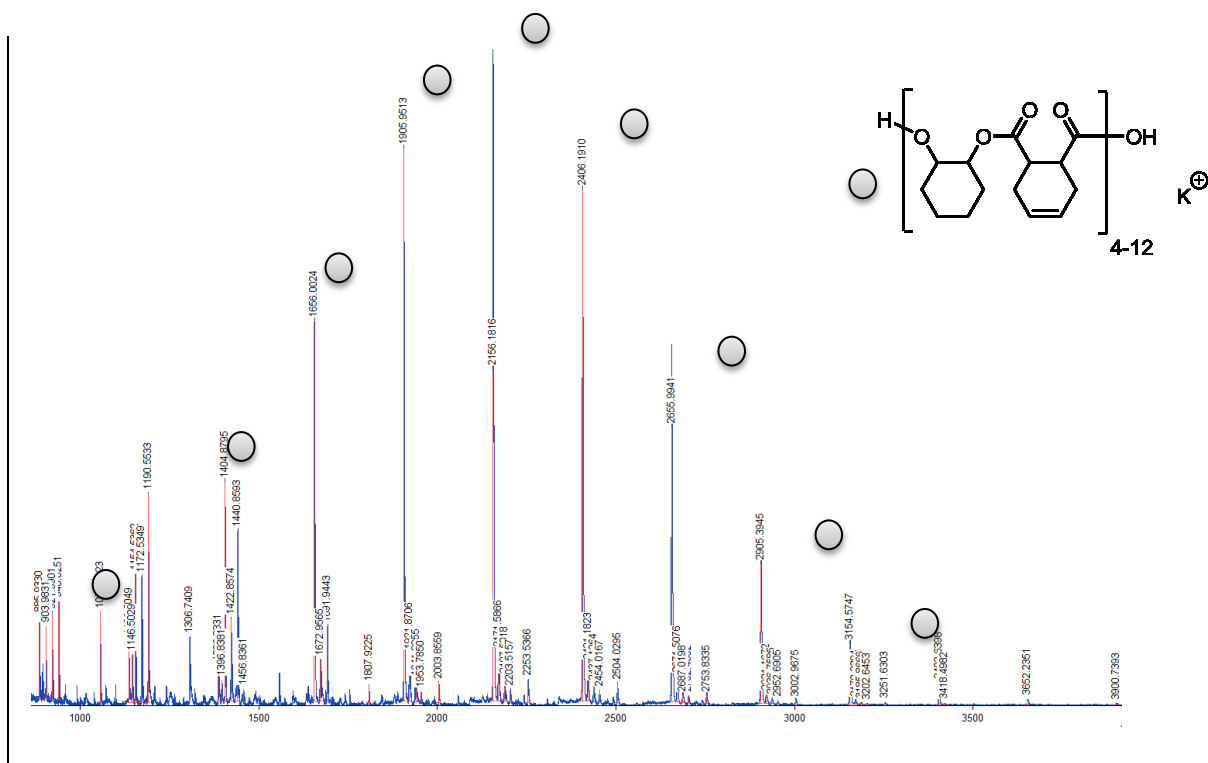


Figure S 3. 41 –GPC chromatograms at 84% conversion of ROCOP and at the end of the reaction. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.



Characterisation data for Polymer based on TCA1/CHO/DL

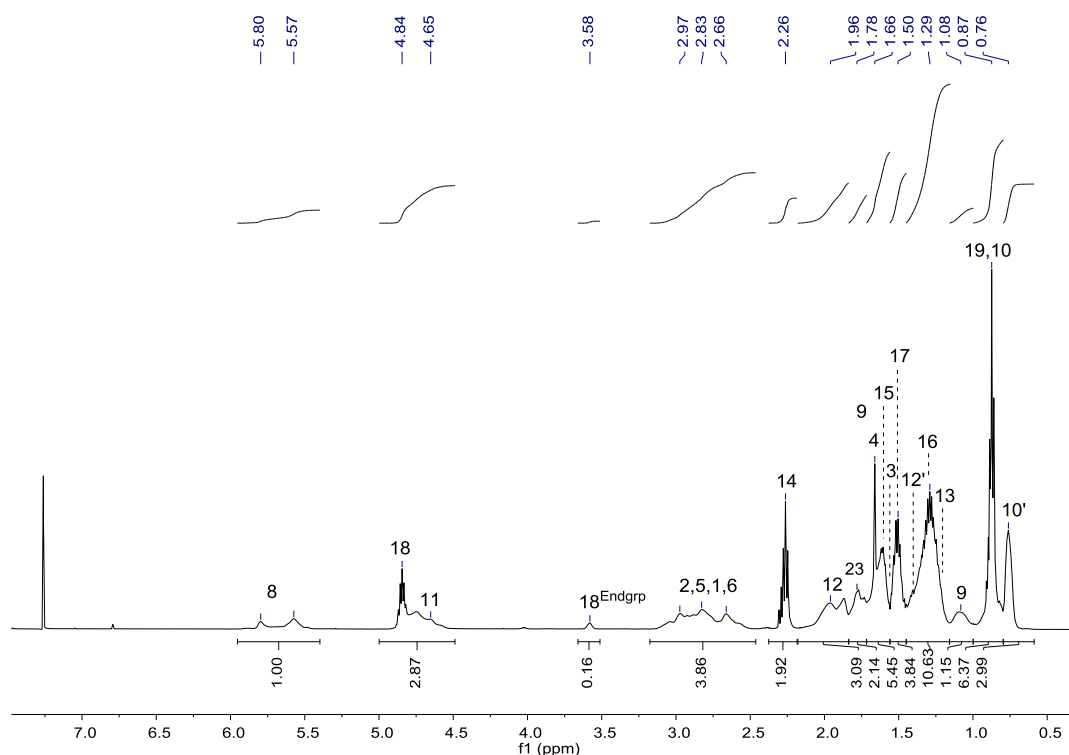


Figure S 3. 44 - ^1H NMR spectrum of polymer based on TCA1, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

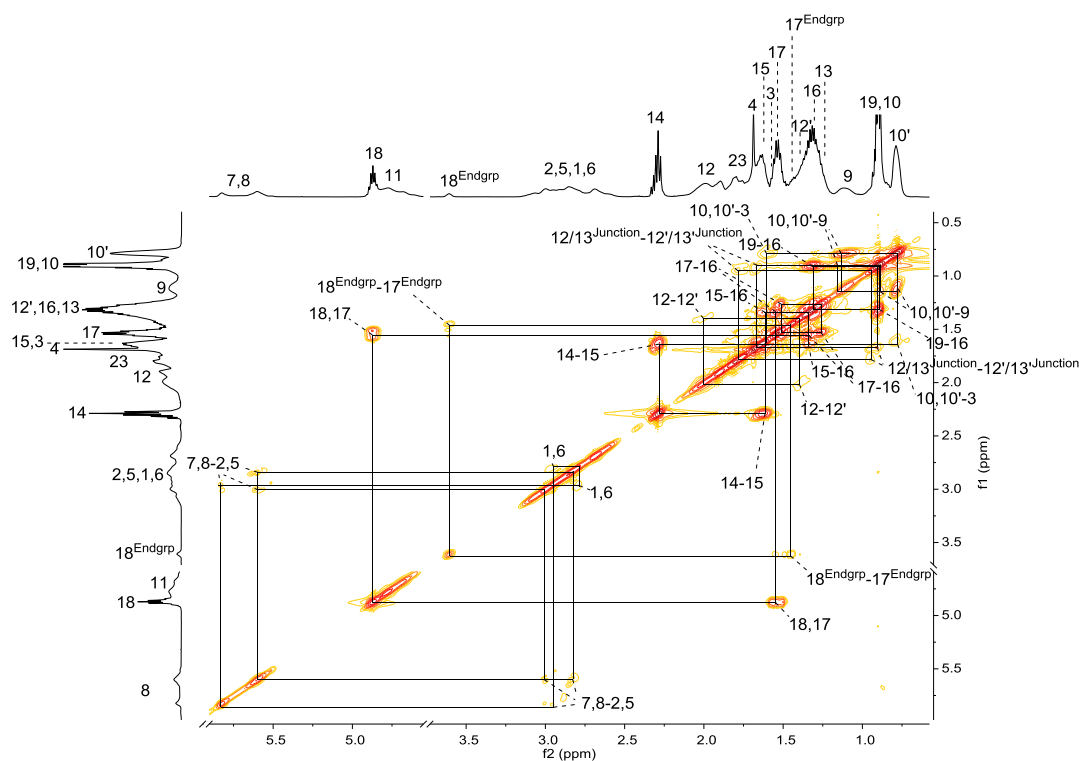


Figure S 3. 45 - COSY NMR spectrum of polymer based on TCA1, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

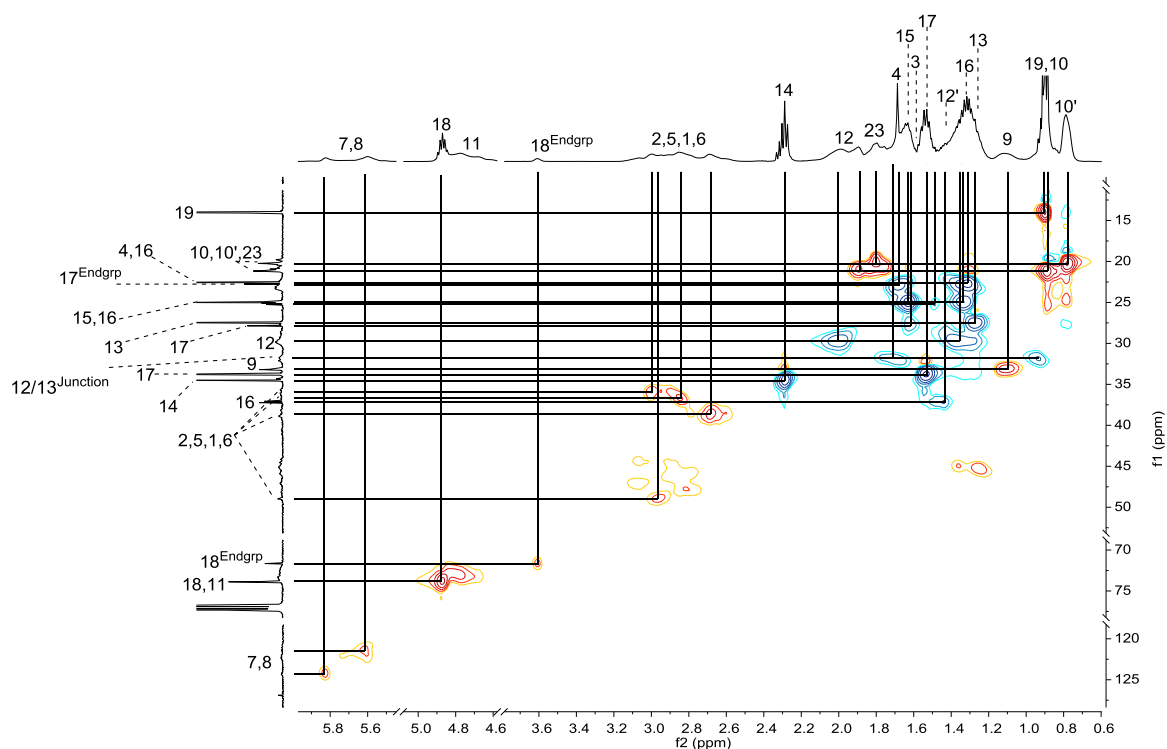


Figure S 3. 46 - HSQC NMR spectrum of polymer based on TCA1, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

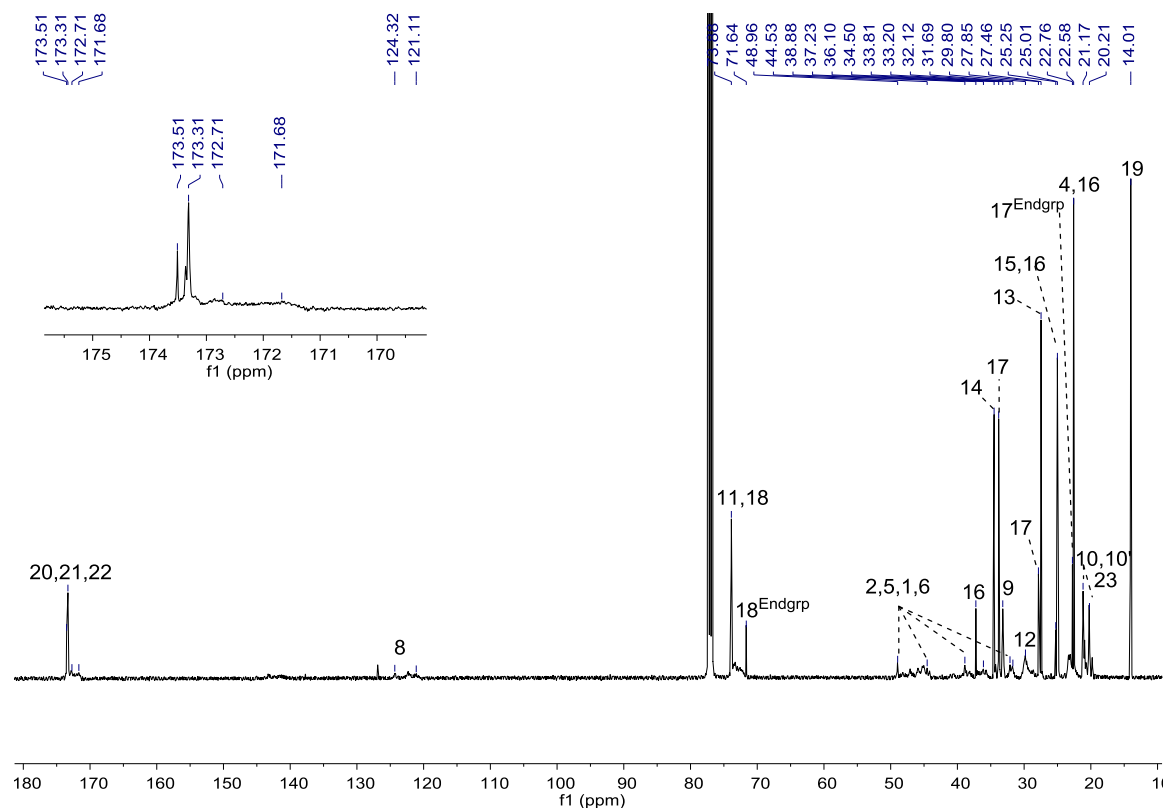


Figure S 3. 47 - $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polymer based on TCA1, CHO, DL. Traces of PPNCl were observed at 129.8, 132.2 and 134.1 ppm. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

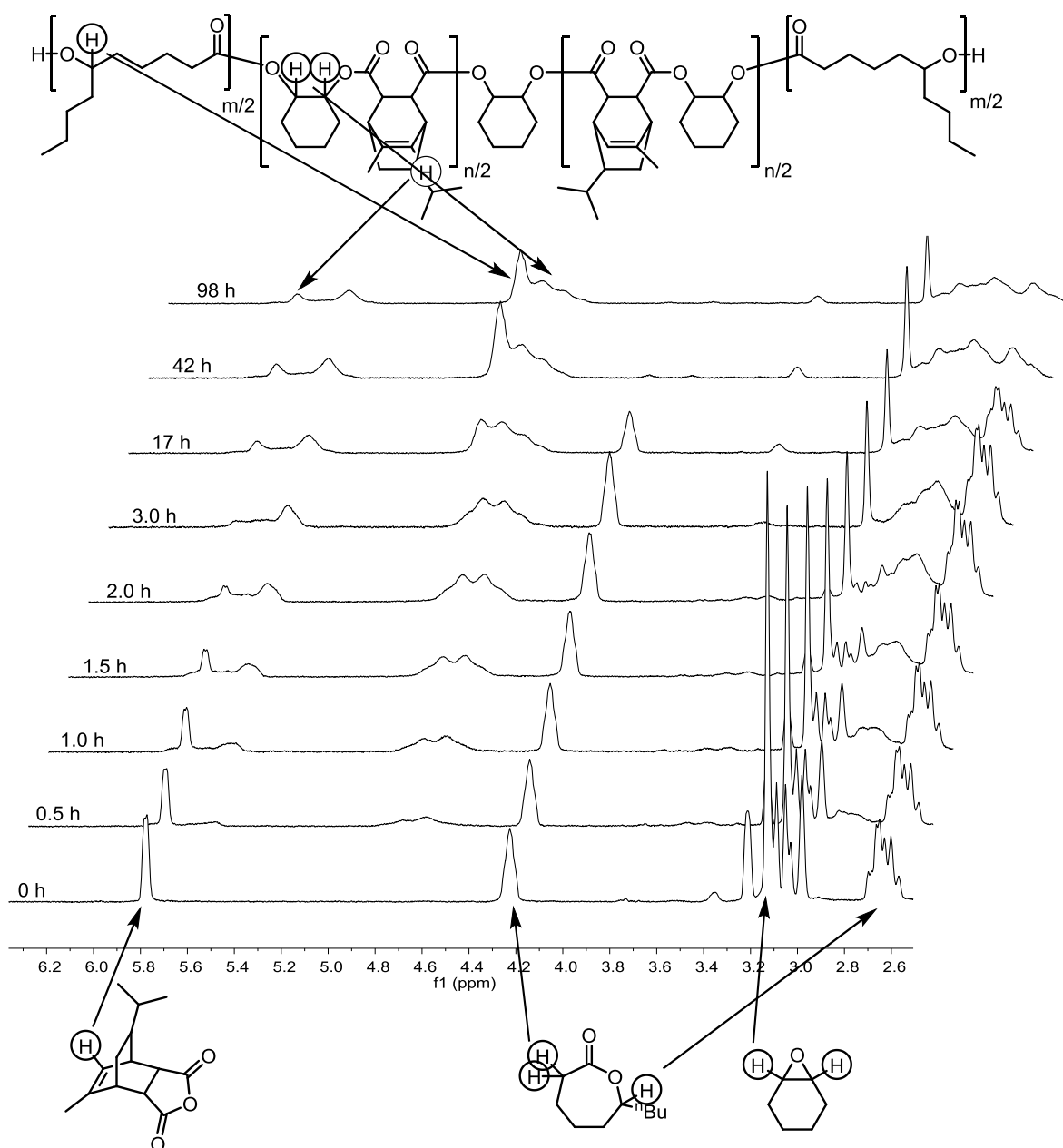


Figure S 3. 48 - ^1H NMR spectra of one-pot polymerization of TCA1/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

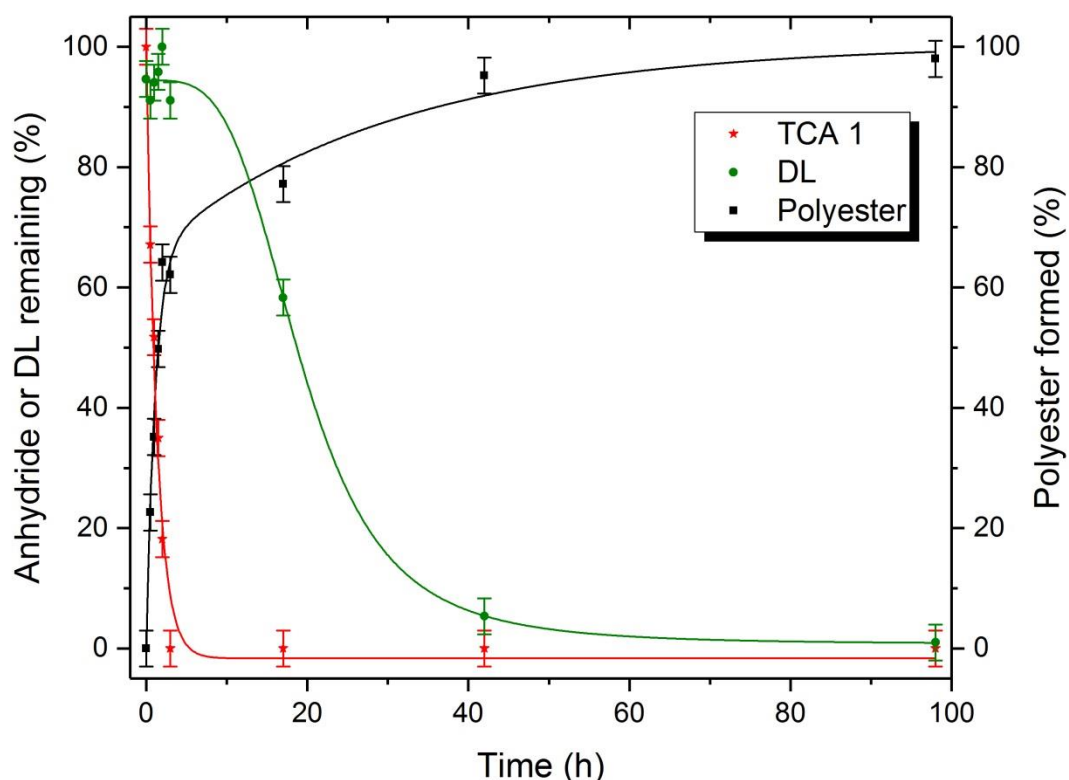


Figure S 3. 49 - Conversion of TCA1 and DL and formation of polyester Data was obtained after normalization with mesitylene as internal standard. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 6 - Integrals based on ^1H NMR spectra (after normalization with mesitylene) and calculated conversions. Signals were based on the following shifts: 3.21 (TCA1), 4.45-4.92 (Polyester), 4.23 (DL) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 77 % (data not shown). The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Time (h)	Integral TCA1	TCA1 (%)	Integral DL	DL (%)	Integral Polyester	Polyester (%)
0	143	100	159	94.6	0	0
0.5	96	67.1	153	91.0	99	22.6
1	74	51.7	158	94.0	154	35.1
1.5	50	34.9	161	95.8	218	49.7
2	26	18.1	168	100	281	64.1
3	0	0	153	91.0	272	62.1
17	0	0	98	58.3	338	77.1
42	0	0	9	5.3	417	95.2
96	0	0	2	1	430	98.0

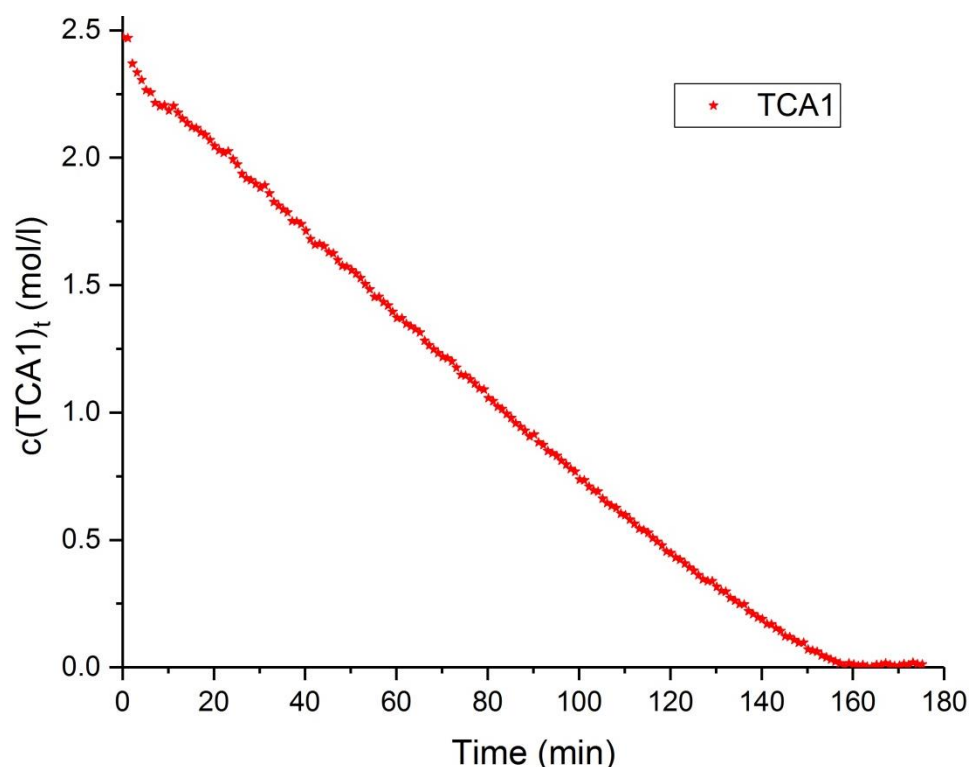


Figure S 3. 50 - *In situ* monitoring of IR band of TCA1 at 1850 cm^{-1} . The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

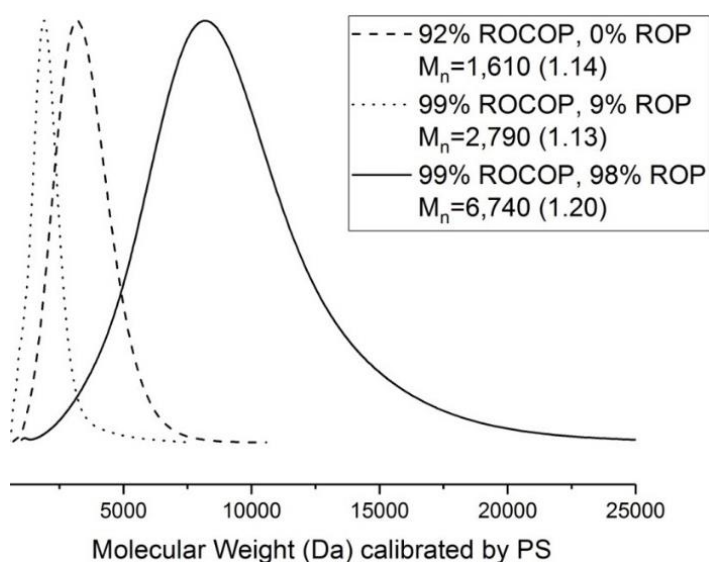


Figure S 3. 51 –GPC chromatogram at different conversions for TCA1/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

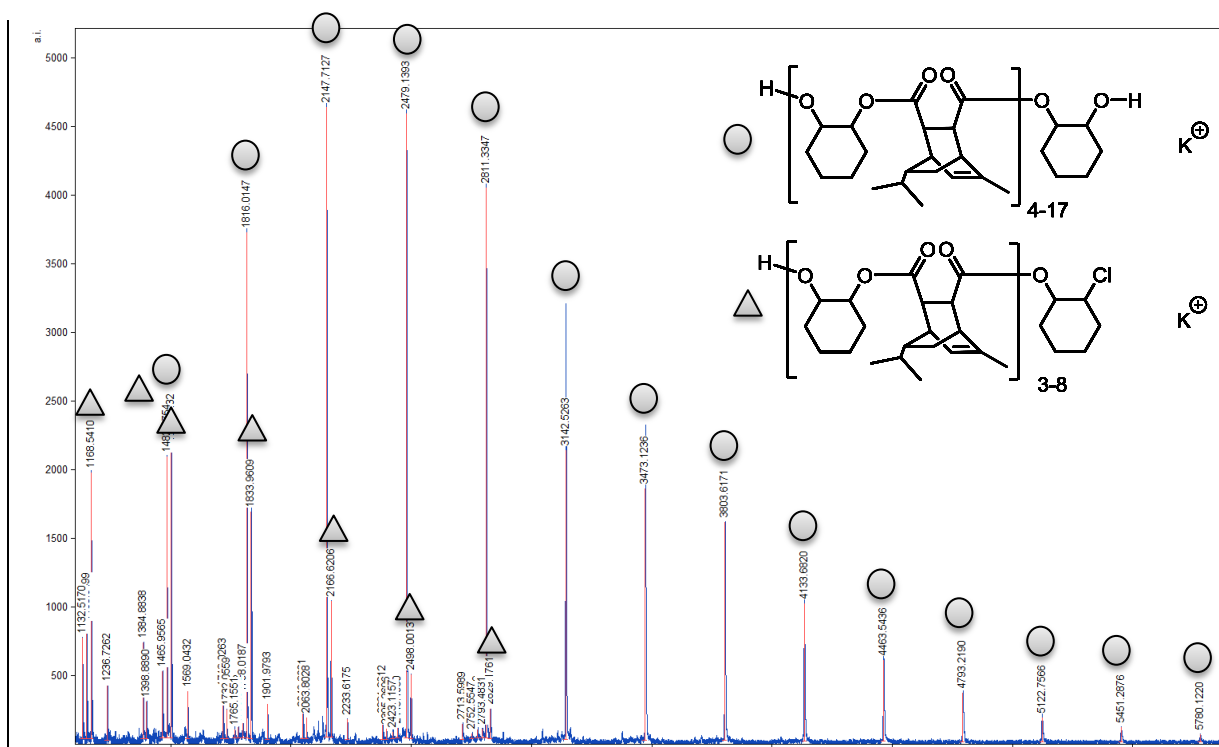


Figure S 3. 52 – MALDI of one-pot polymerization of TCA1/CHO/DL (after 2 h, 82% TCA1 and 0% DL conversion). Two species were detected: circle: $m/z = [116.08 \text{ (cyclohexandiol)} + (332.2 \times n) \text{ (PCHTCE1)} + 38.96 \text{ (K}^+)]$ ($n = 5 \sim 18$); triangle: $m/z = [34.97 \text{ (Cl)} + 98.07 \text{ (CHO)} + 1.01 \text{ (H)} + (332.2 \times n) \text{ (PCHTCE1)} + 38.96 \text{ (K}^+)]$ ($n = 3 \sim 8$). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

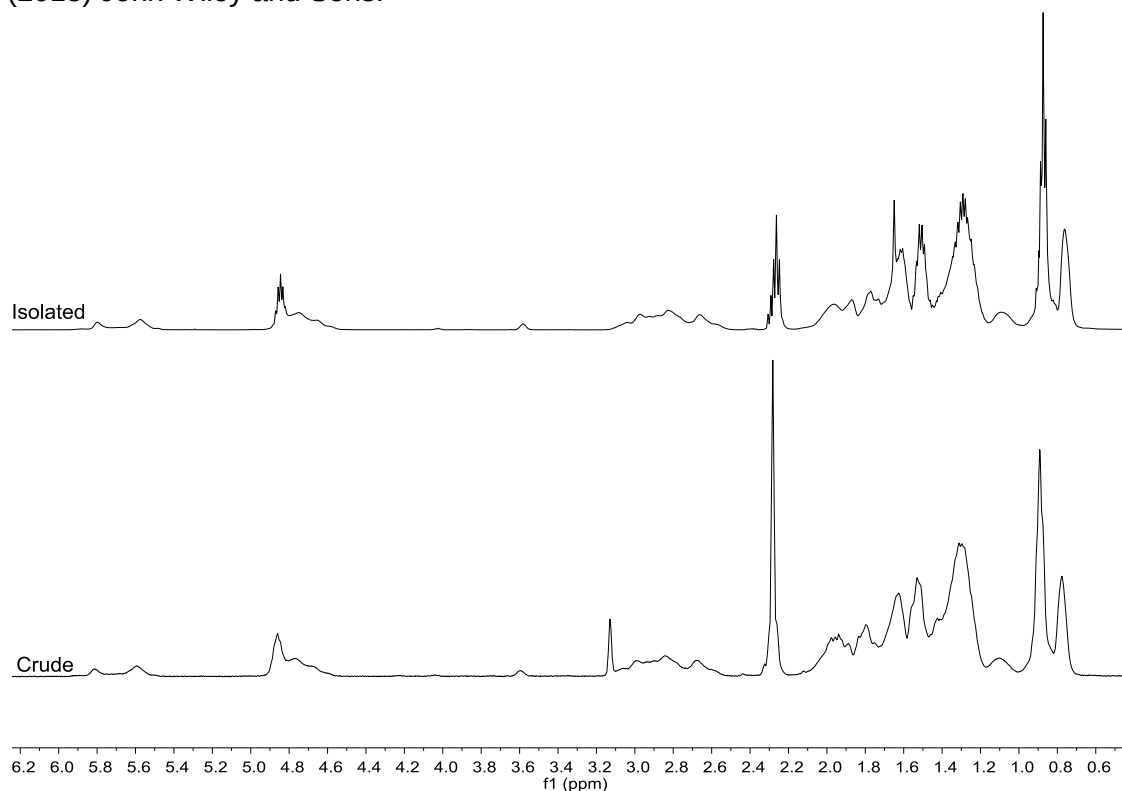


Figure S 3. 53 – ^1H NMR spectra of crude (bottom) and isolated (top) polymer based on TCA1/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Characterisation data for Polymer based on TCA2/CHO/DL

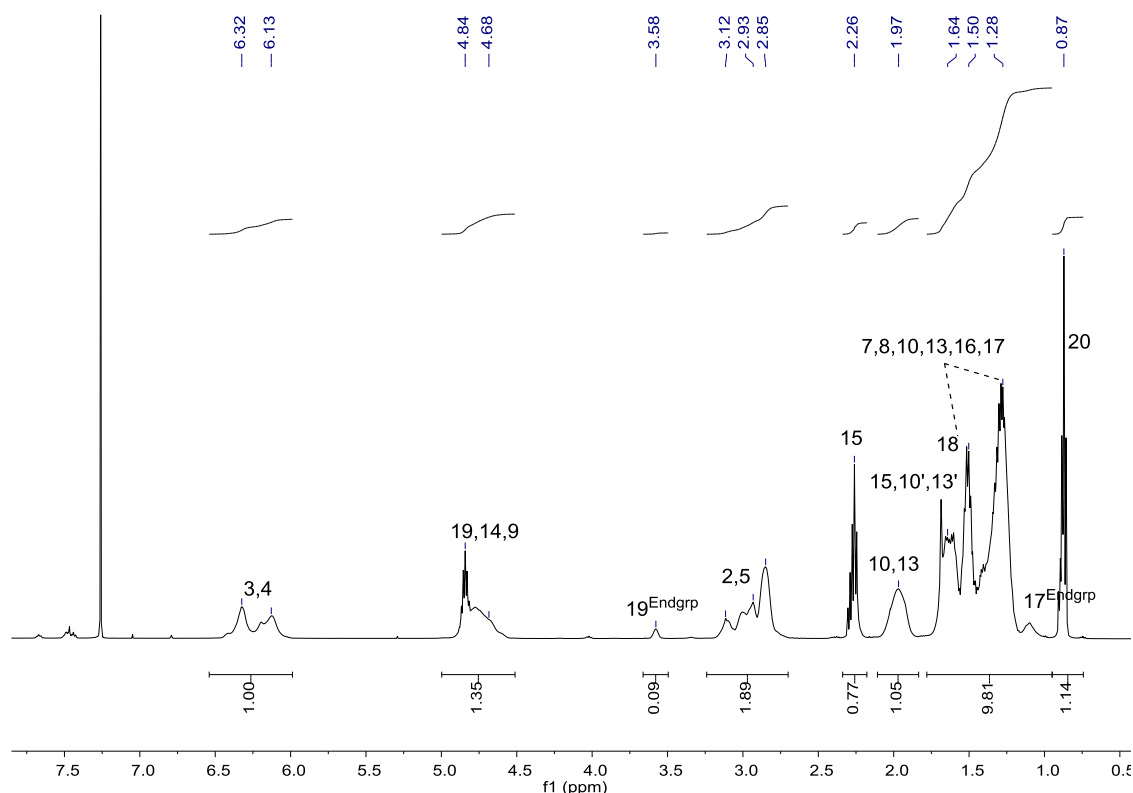


Figure S 3. 54 – ^1H NMR spectrum of polymer based on TCA2, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

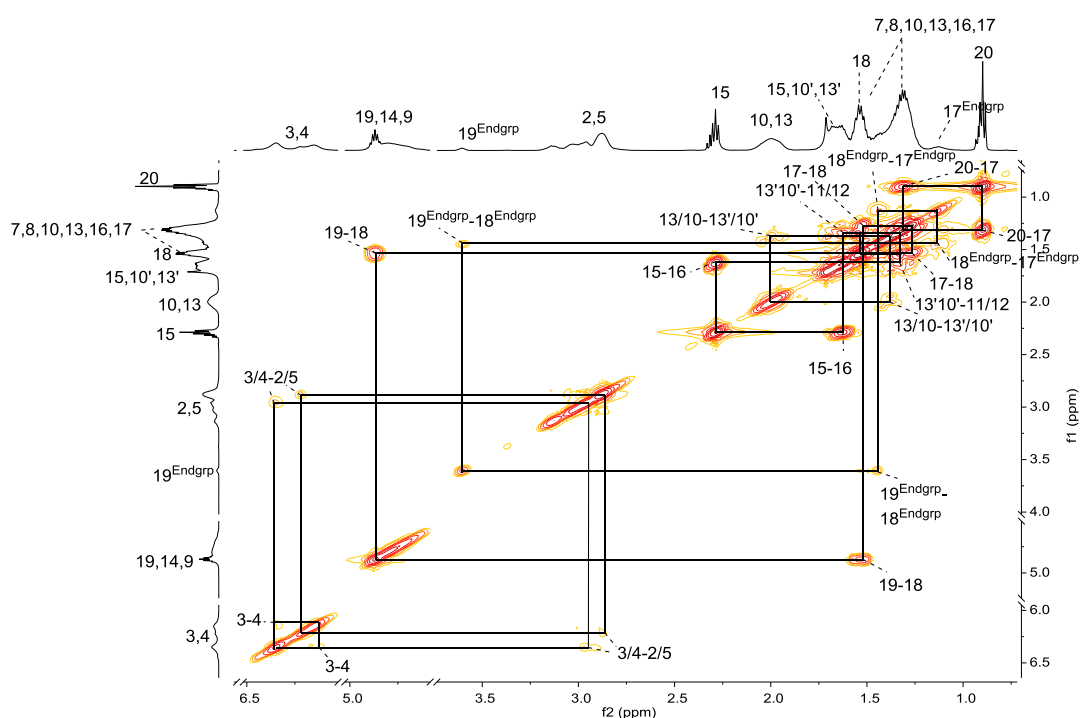


Figure S 3. 55 - COSY NMR spectrum of polymer based on TCA2, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

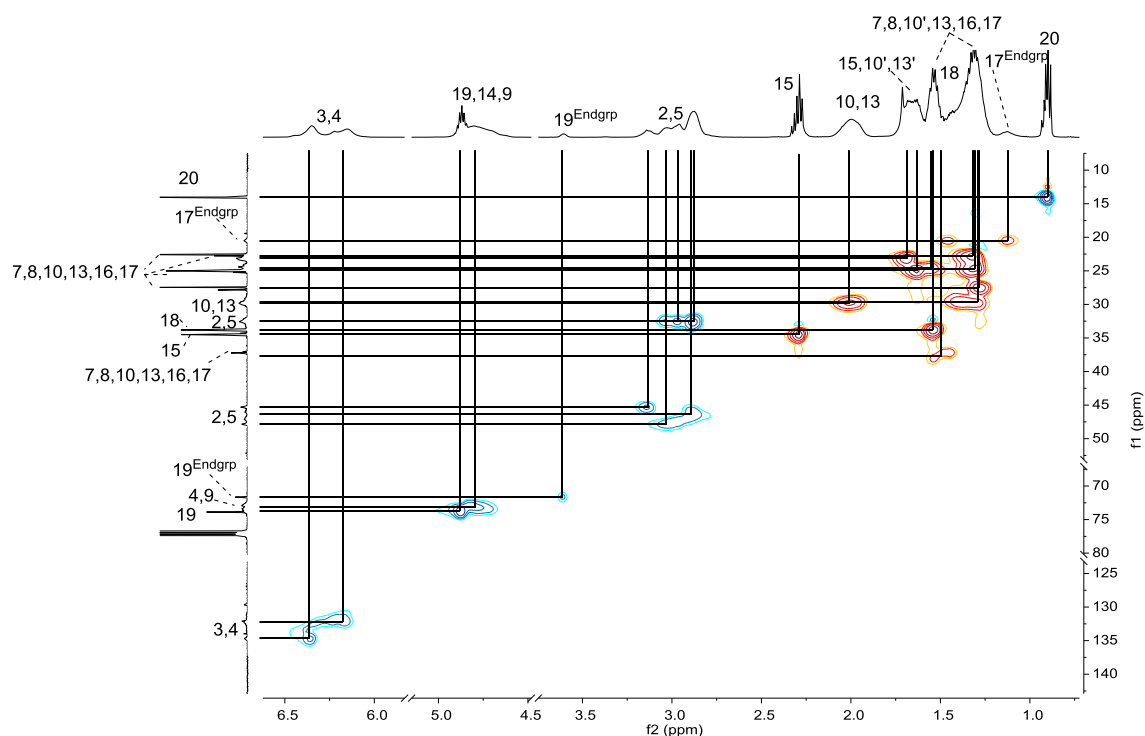


Figure S 3. 56 - HSQC NMR spectrum of polymer based on TCA2, CHO, DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

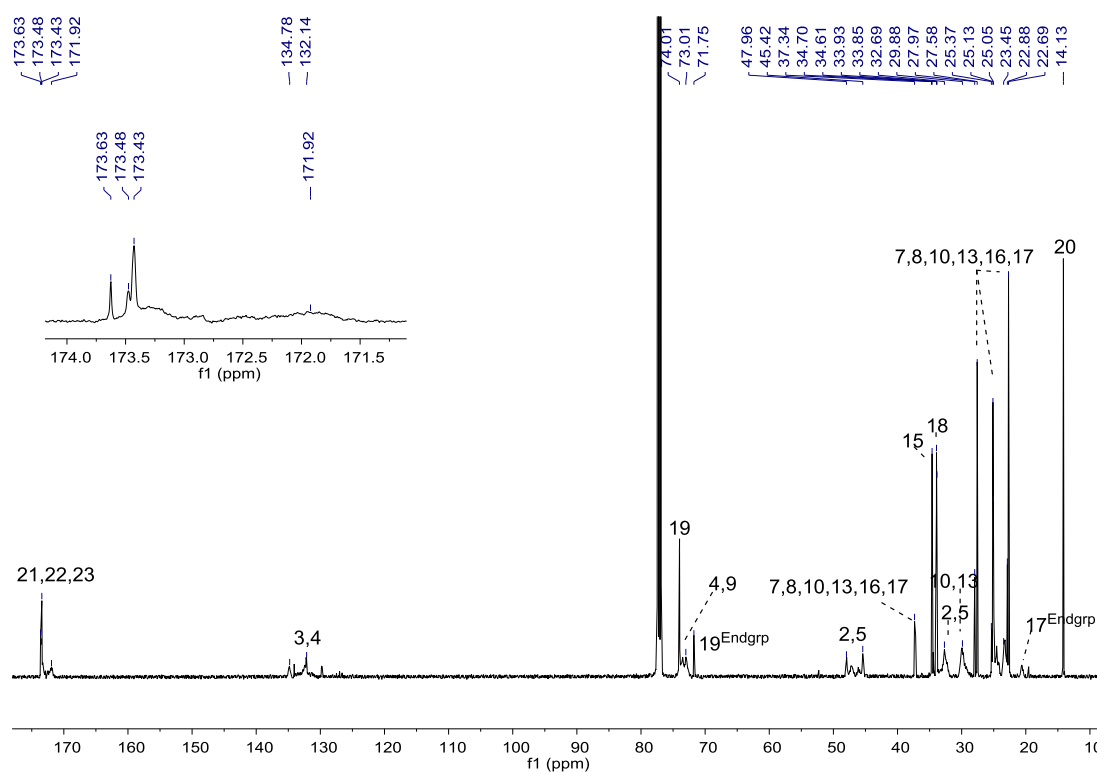


Figure S 3. 57 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of polymer based on TCA2, CHO, DL. Traces of PPNCI were observed at 129.8, 132.2 and 134.1 ppm. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

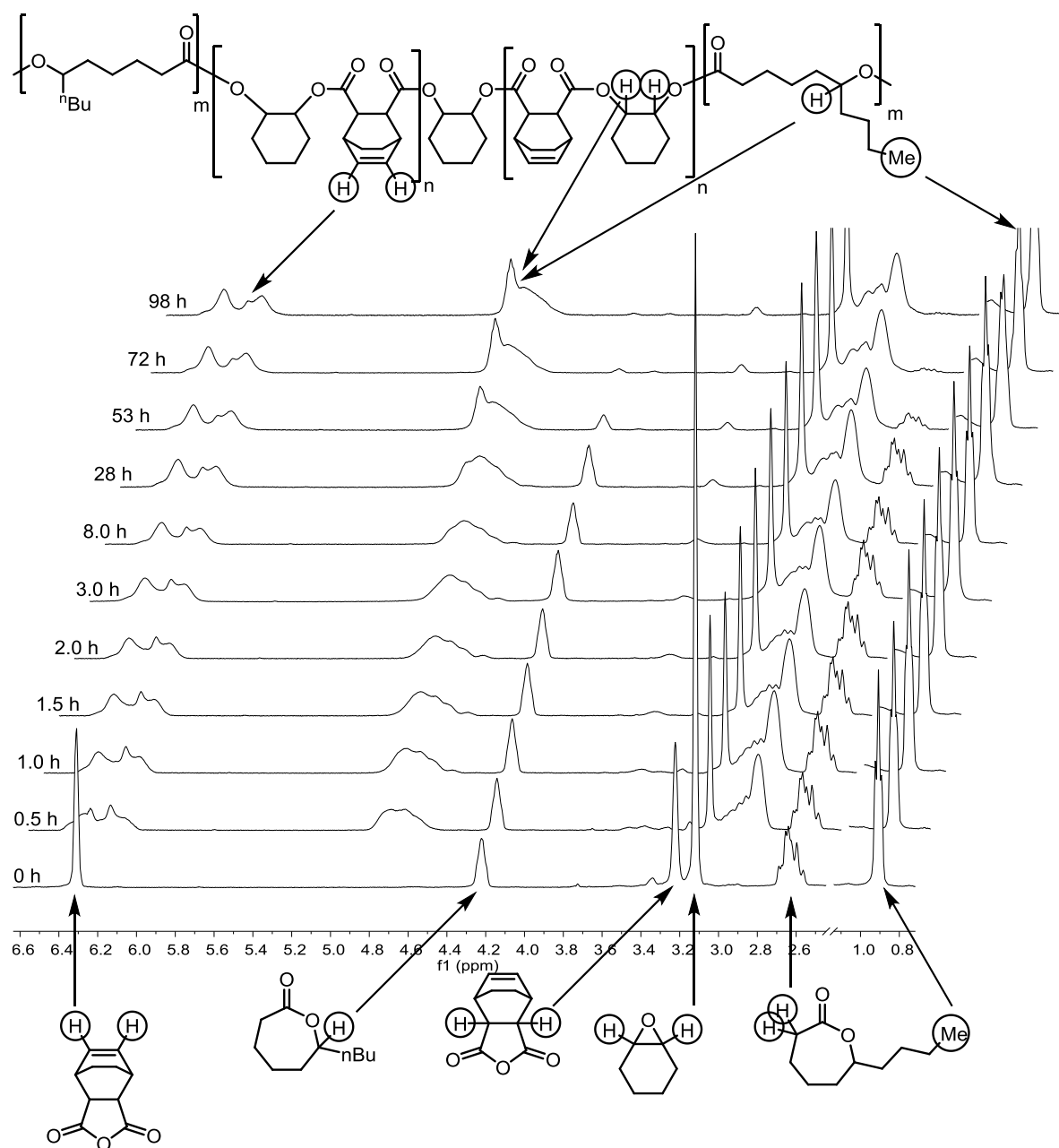


Figure S 3. 58 - ^1H NMR spectra of the polymerization of TCA2/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

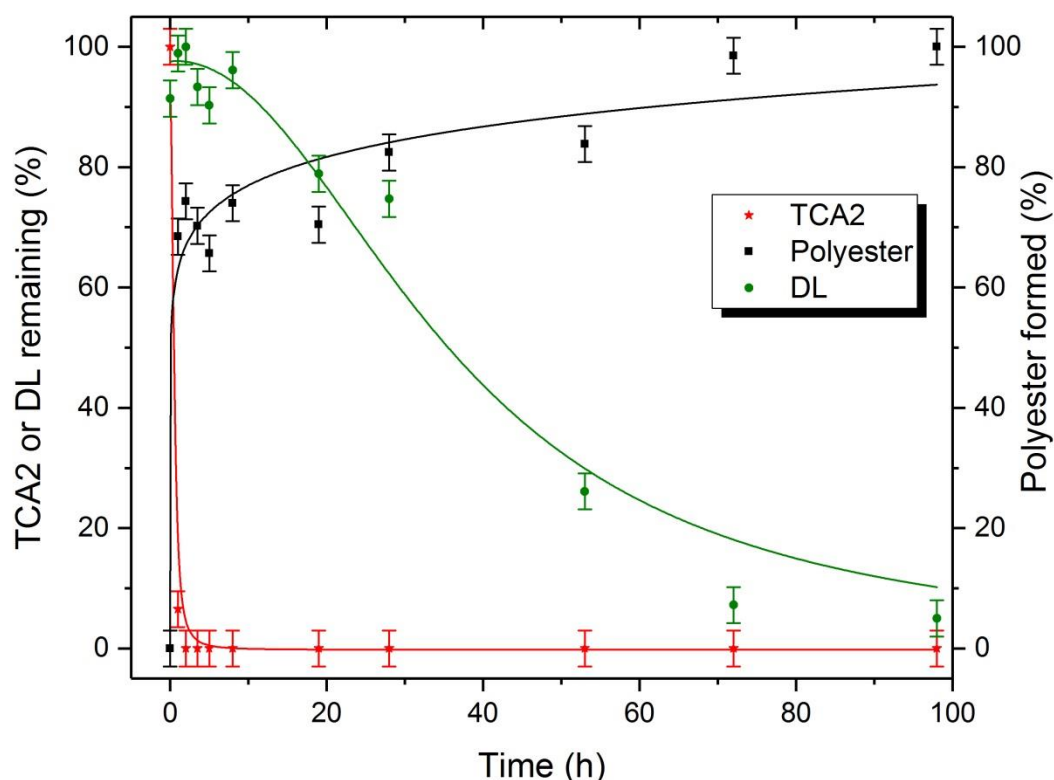


Figure S 3. 59 - Conversion of TCA2 and DL and formation of polyester 5s time. Data was obtained after normalization with mesitylene as internal standard. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 7 - Integrals based on ^1H NMR spectra (after normalization with mesitylene as internal standard, Figure) and calculated conversions used for Fig. S 68. Signals were based on the following shifts: 6.80 (TCA2), 4.22 (DL), 4.95 – 4.45 (polyester) and 3.10 (CHO) ppm. The conversion of CHO at the end of the reaction was determined as 67 % (data not shown). The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Time (h)	Integral TCA2	TCA2 (%)	Integral DL	DL (%)	Integral Polyester	Polyester (%)
0	628	100	329	91.3	0	0
1	41	6.5	356	98.8	690	68.4
2	0	0	360	100	749	74.3
3.5	0	0	336	93.3	708	70.2
5	0	0	325	90.2	662	65.6
8	0	0	346	96.1	746	74.0
19	0	0	284	78.8	710	70.4
28	0	0	269	74.7	831	82.4
53	0	0	94	26.1	845	83.8
72	0	0	26	7.2	993	98.5
98	0	0	18	5	1008	100

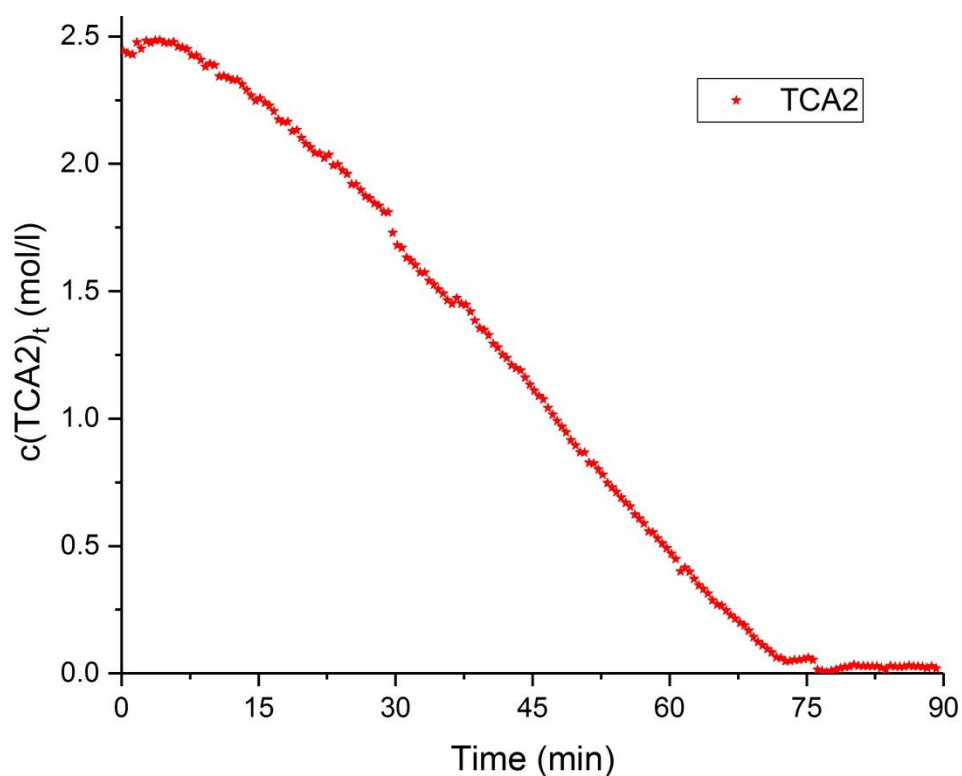


Figure S 3. 60 - *In situ* monitoring of IR band of TCA2 at 1850 cm^{-1} . The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

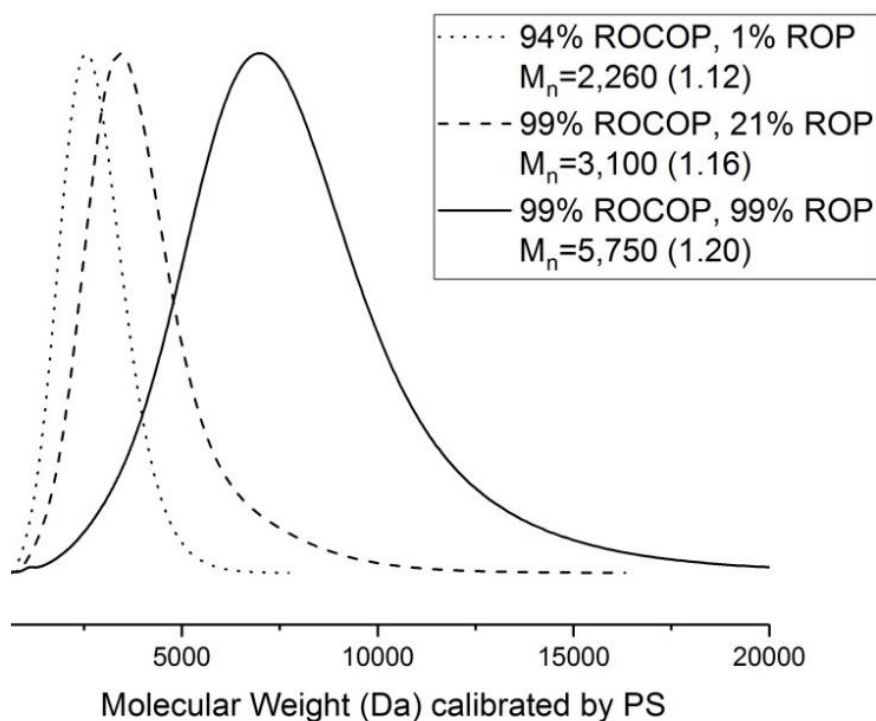


Figure S 3. 61 - GPC chromatograms at different conversions. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

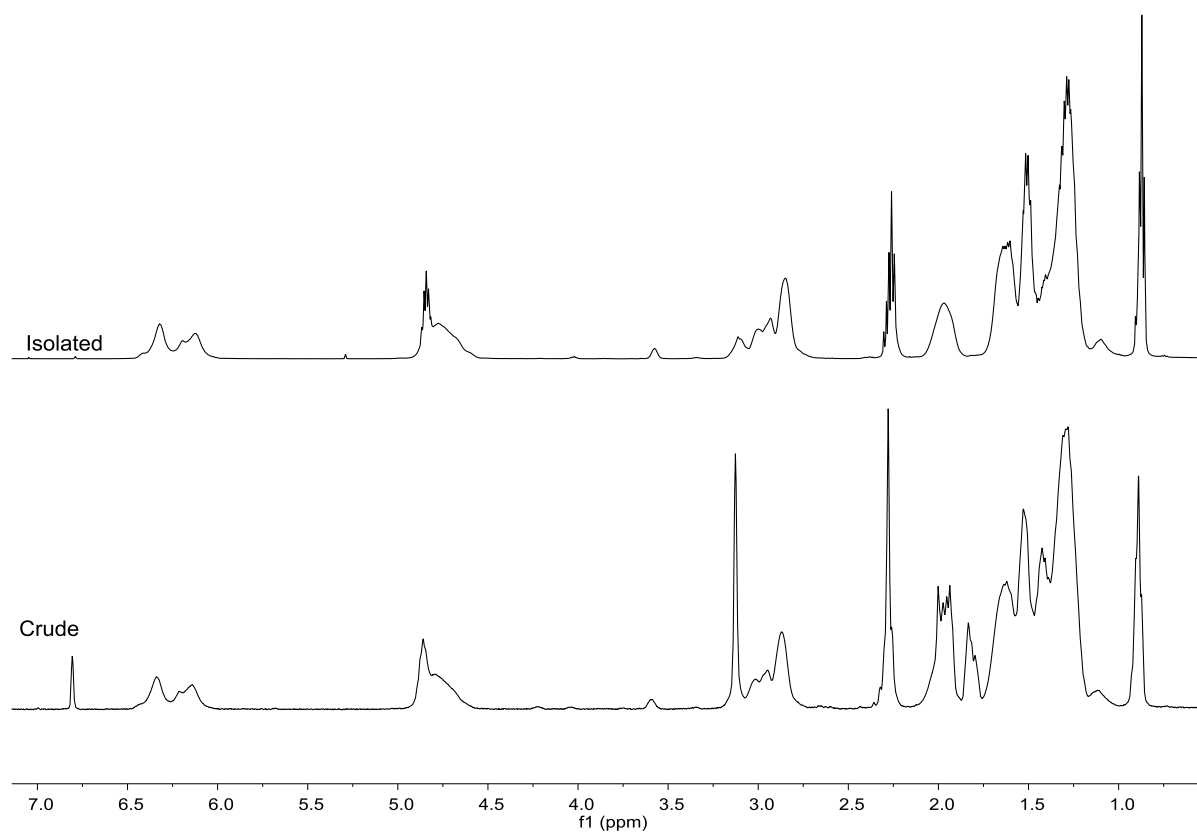


Figure S 3. 62 – ^1H NMR spectra of crude (bottom) and isolated (top) polymer based on TCA2/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

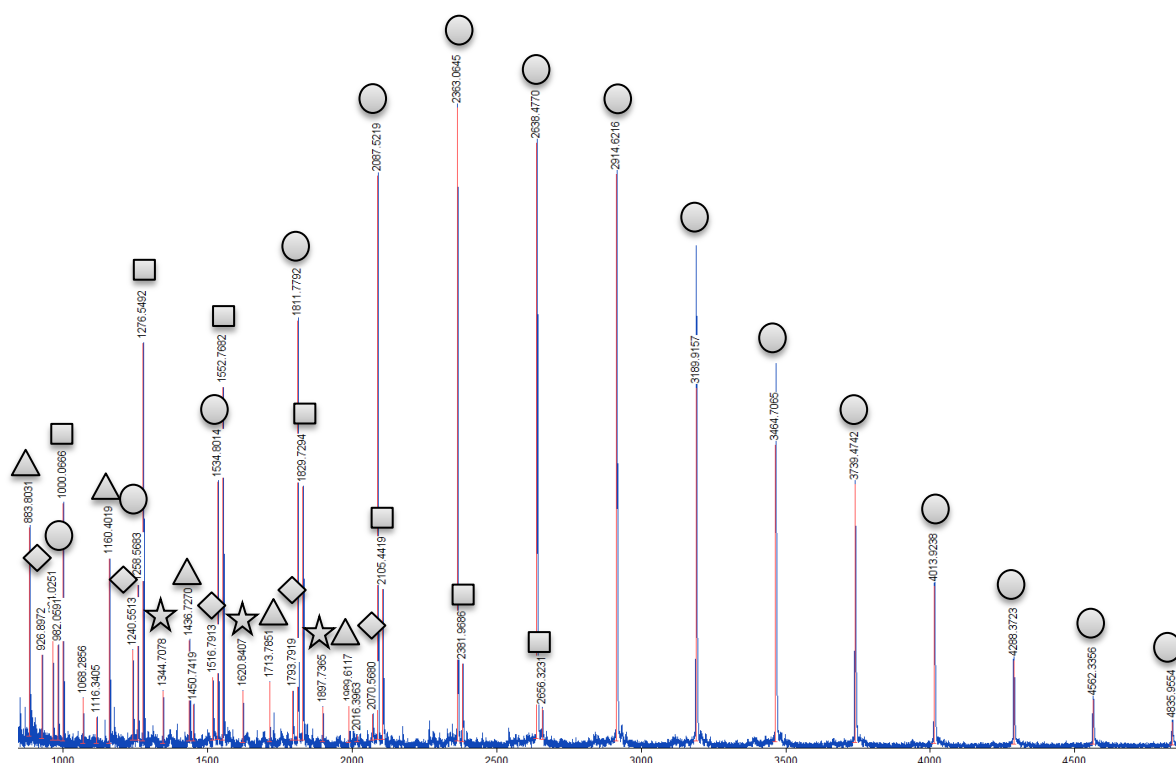
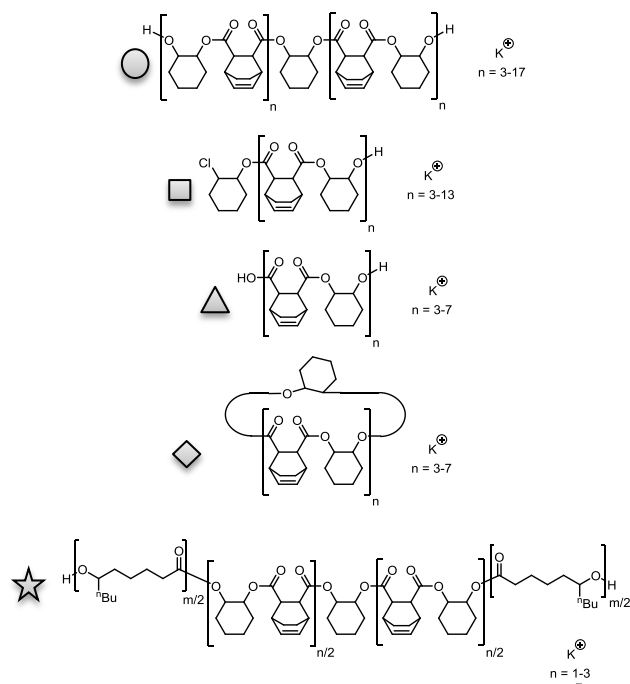


Figure S 3. 63 – MALDI of polymer based on TCA2/CHO/DL (after 1 h, 94% TCA2 and 1% DL conversion). Five species were detected: circle: $m/z = [116.08 \text{ (cyclohexandiol)} + (276.14 \times n) \text{ (PCHTCE2)} + 38.96 \text{ (K}^+)]$ ($n = 3 \sim 17$); square: $m/z = [34.97 \text{ (Cl)} + 98.07 \text{ (CHO)} + 1.01 \text{ (H)} + (276.14 \times n) \text{ (PCHTCE2)} + 38.96 \text{ (K}^+)]$ ($n = 3 \sim 13$); triangle: $m/z = [18.01 \text{ (H}_2\text{O)} + (276.14 \times n) \text{ (PCHTCE2)} + 38.96 \text{ (K}^+)]$ ($n = 3 \sim 7$); diamond: $m/z = [98.07 \text{ (CHO)} + (276.14 \times n) \text{ (PCHTCE2)} + 38.96 \text{ (K}^+)]$ ($n = 3 \sim 7$); star: $m/z = [116.08 \text{ (cyclohexandiol)} + (214.08 \times n) \text{ (PCHTCE2)} + (170.13 \times m) \text{ (PDL)} + 38.96 \text{ (K}^+)]$ ($n = 4 \sim 12$). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Characterisation data for Polymer based on CA/CHO/DL

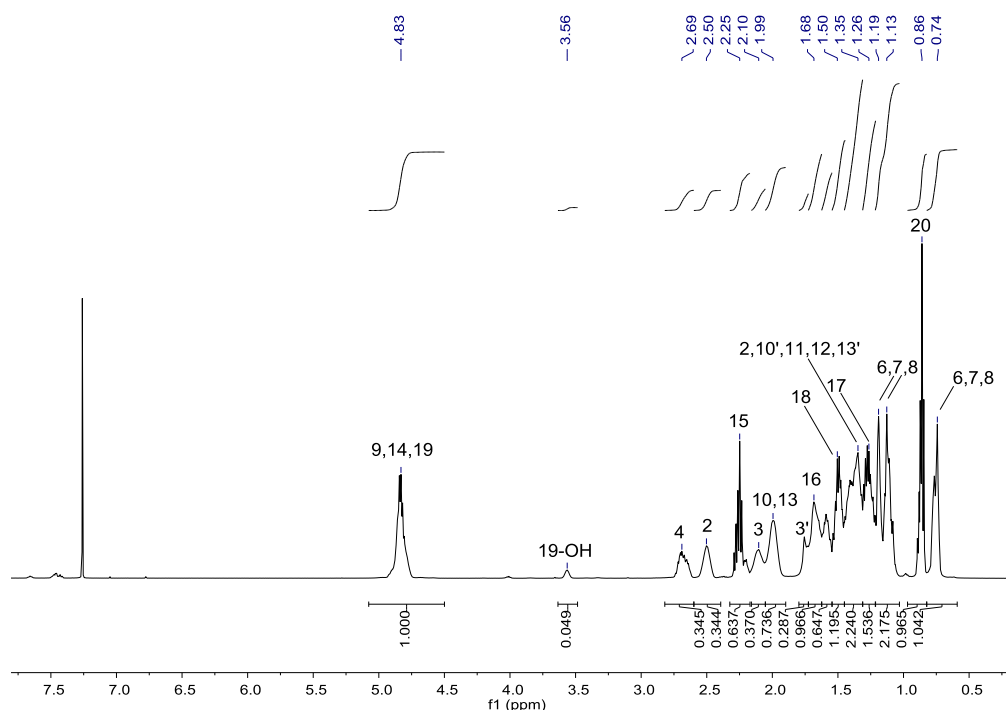


Figure S 3. 64 ^1H NMR spectrum of polymer based on CA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

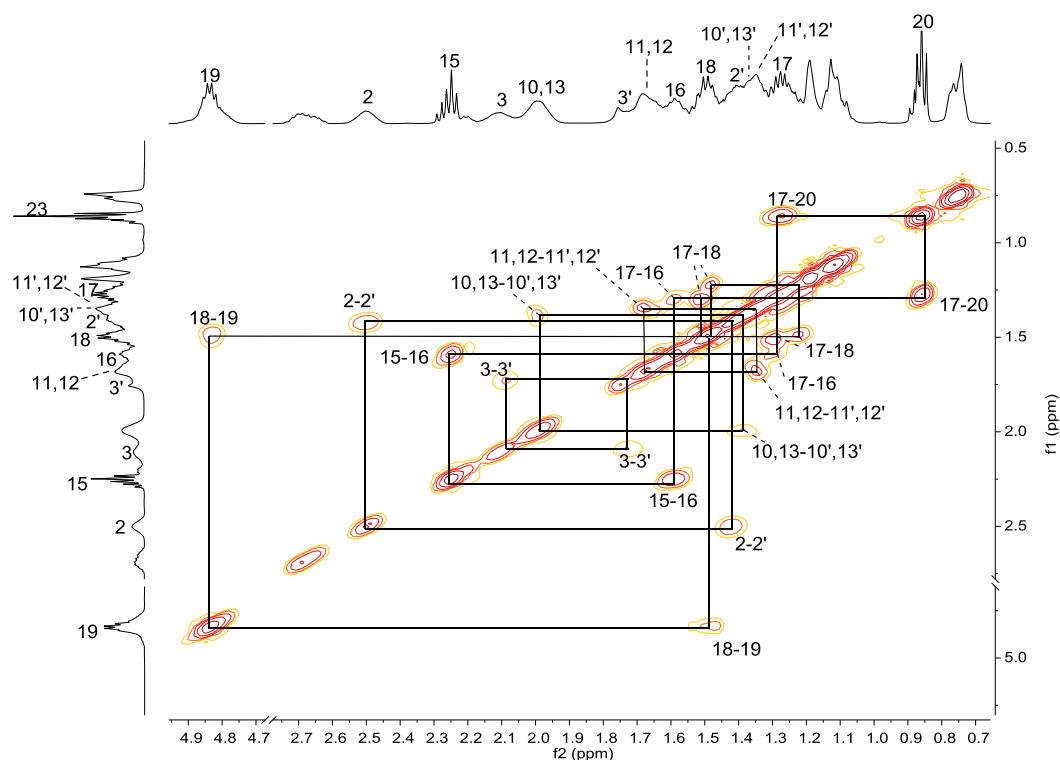


Figure S 3. 65 - COSY NMR spectrum for polymer based on CA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

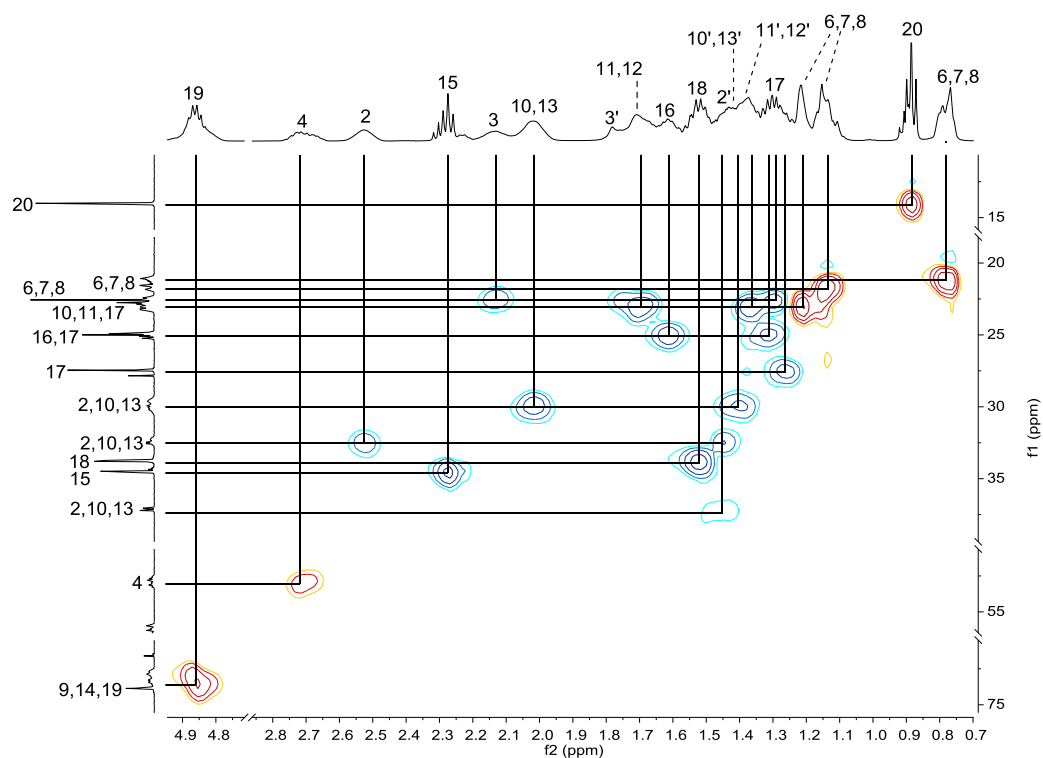


Figure S 3. 66 - HSQC NMR spectrum for polymer based on CA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

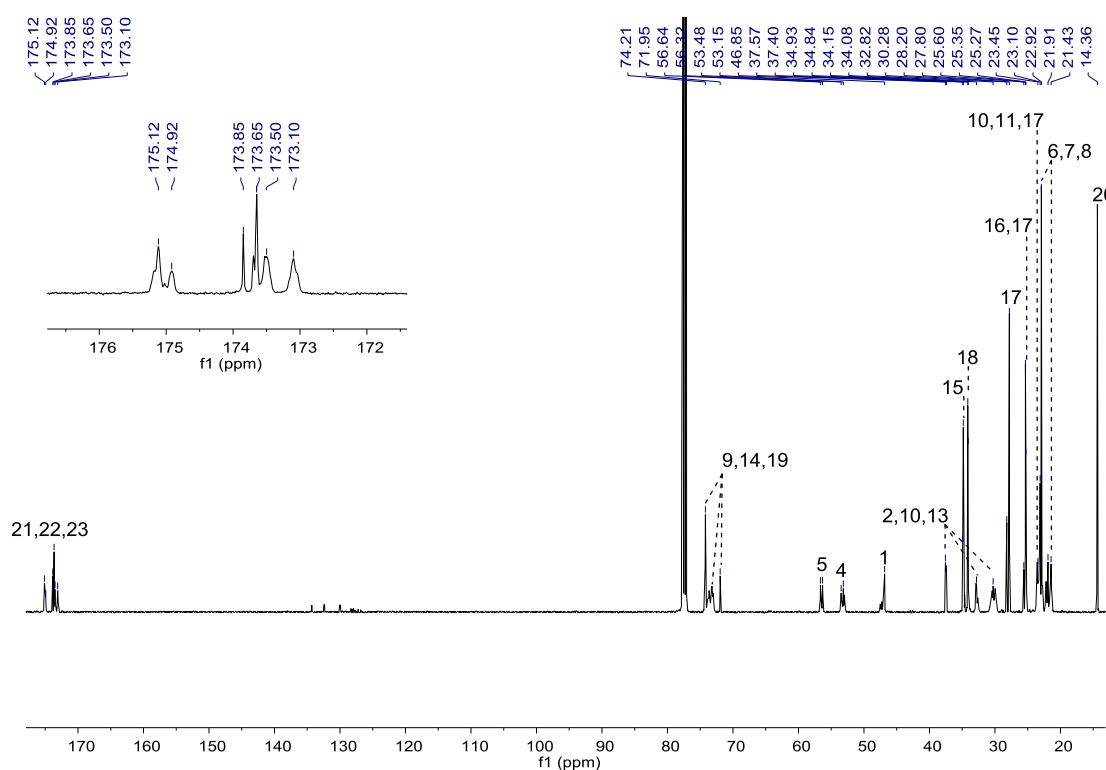


Figure S 3. 67 - $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum based on CA/CHO/DL. Traces of PPNCI were observed at 129.8, 132.2 and 134.1 ppm. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

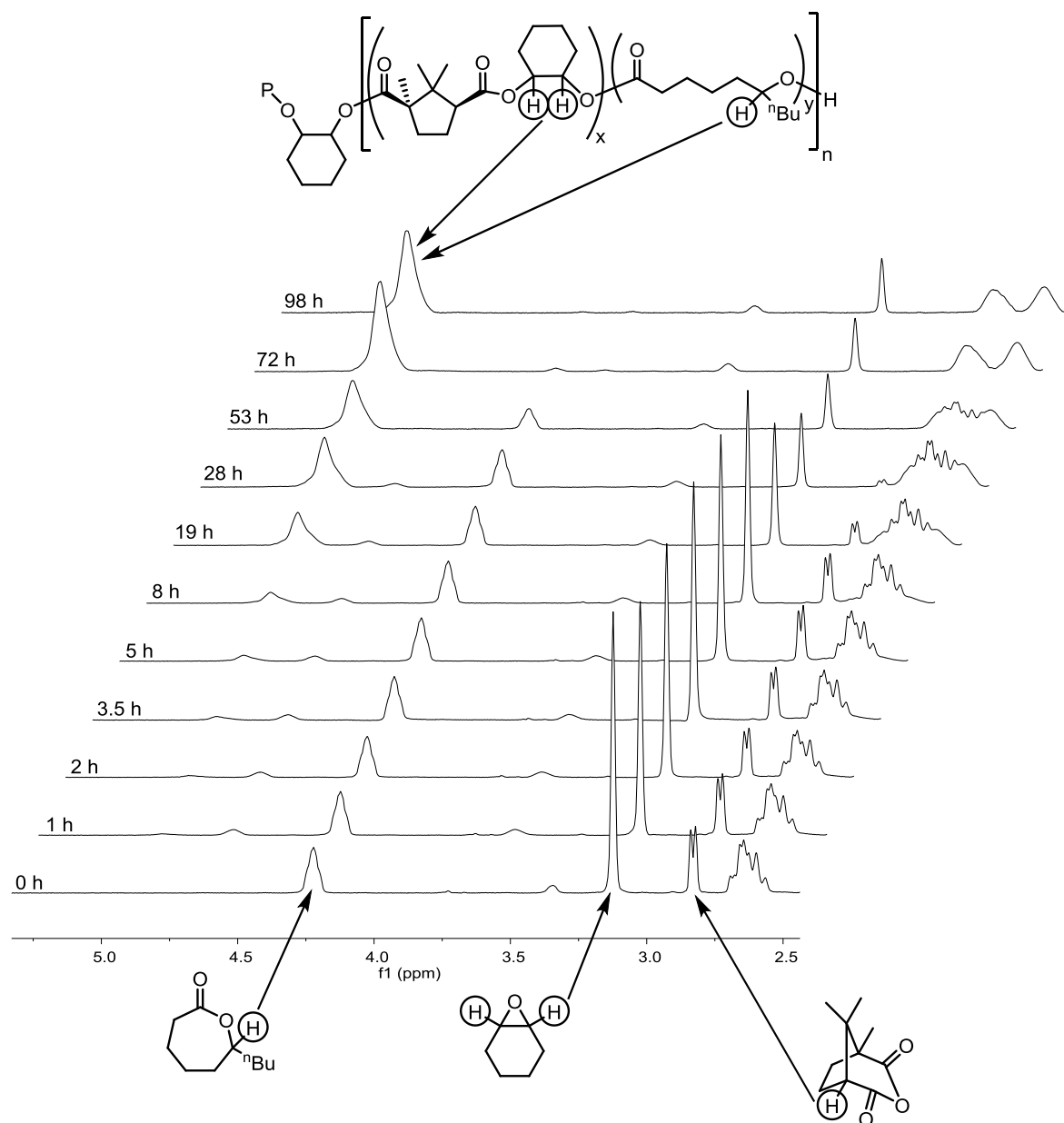


Figure S 3. 68 – ^1H NMR spectra for the polymerization of CA, CHO and DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

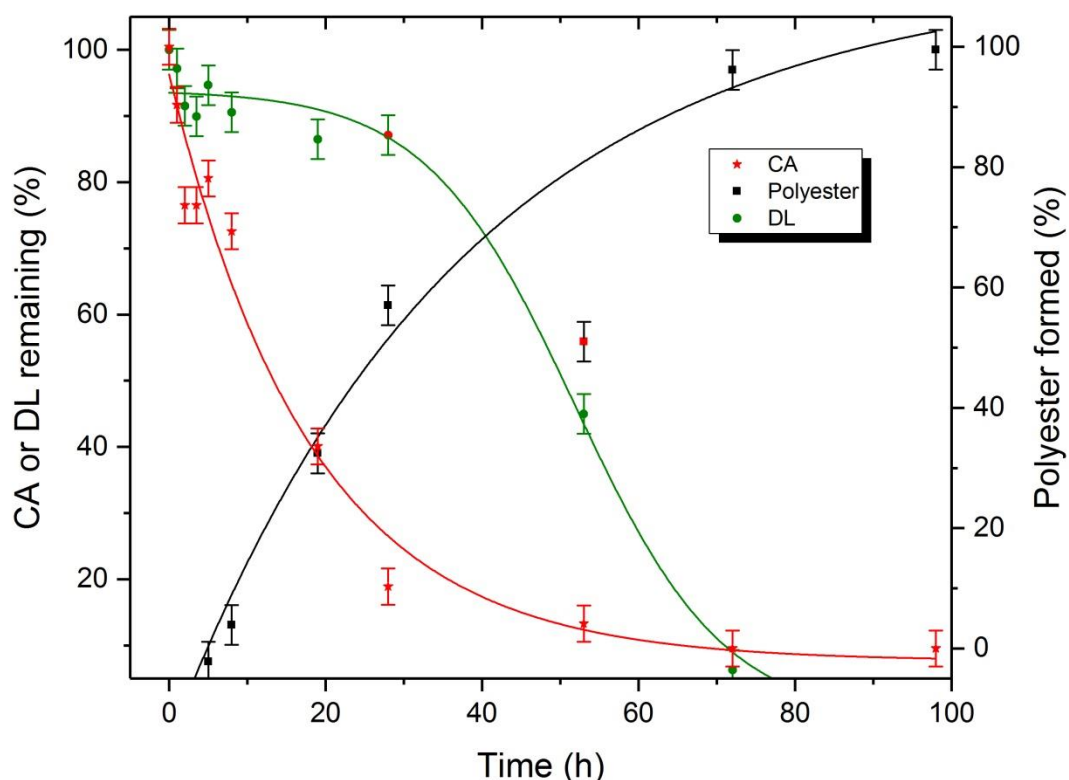


Figure S 3. 69 - Conversion of CA, CHO and DL and formation of polyester. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 8 - Integrals based on ^1H NMR spectra (after normalization with mesitylene as internal standard) and calculated conversions. Signals were based on the following shifts: 1.00 (CA), 3.13 (CHO), 4.22 (DL), 4.74 – 5.00 (polyester) ppm. The conversion of CHO at the end of the reaction was determined as 80 % (data not shown). The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Time (h)	Integral CA	CA (%)	Integral DL	DL (%)	Integral Polyester	Polyester (%)
0	923	100	318	100	0	0
1	834	90.3	309	97.1	13	1.4
2	680	73.6	291	91.5	16	1.7
3.5	680	73.6	286	89.9	24	2.5
5	721	78.1	301	94.6	70	7.5
8.5	640	69.3	288	90.5	121	13.0
19	310	33.5	275	86.4	361	39.0
28	95	10.2	277	87.1	568	61.41
53	38	4.1	143	44.9	517	55.8
72	0	0	20	6.2	897	96.9
95	0	0	4	1.2	925	100

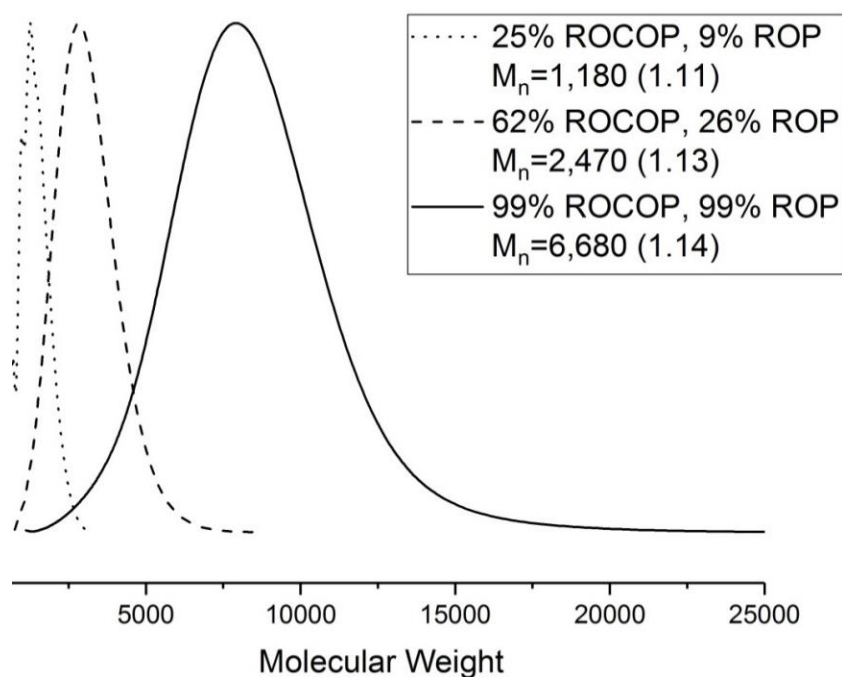


Figure S 3. 70 - GPC chromatograms at different conversions for the polymerization of CA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

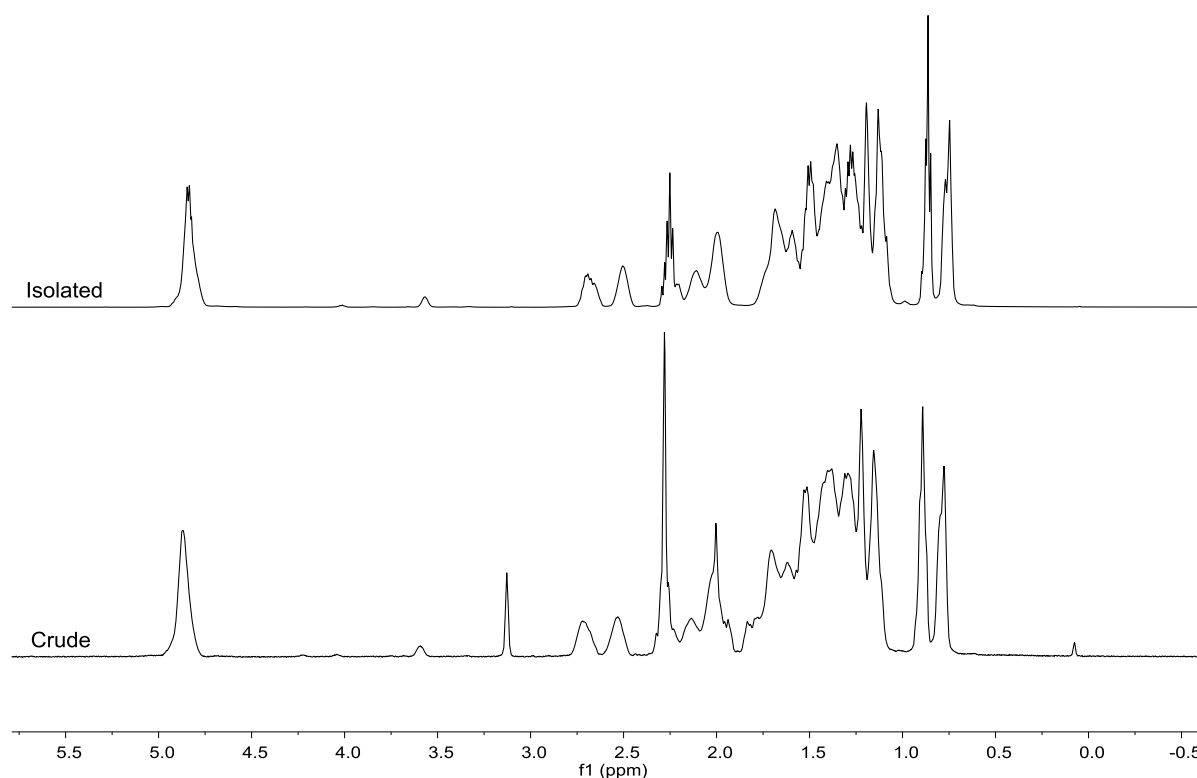


Figure S 3. 71 - ^1H NMR spectra of crude (bottom) and isolated (top) polymer based on CA/CHO/DL. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

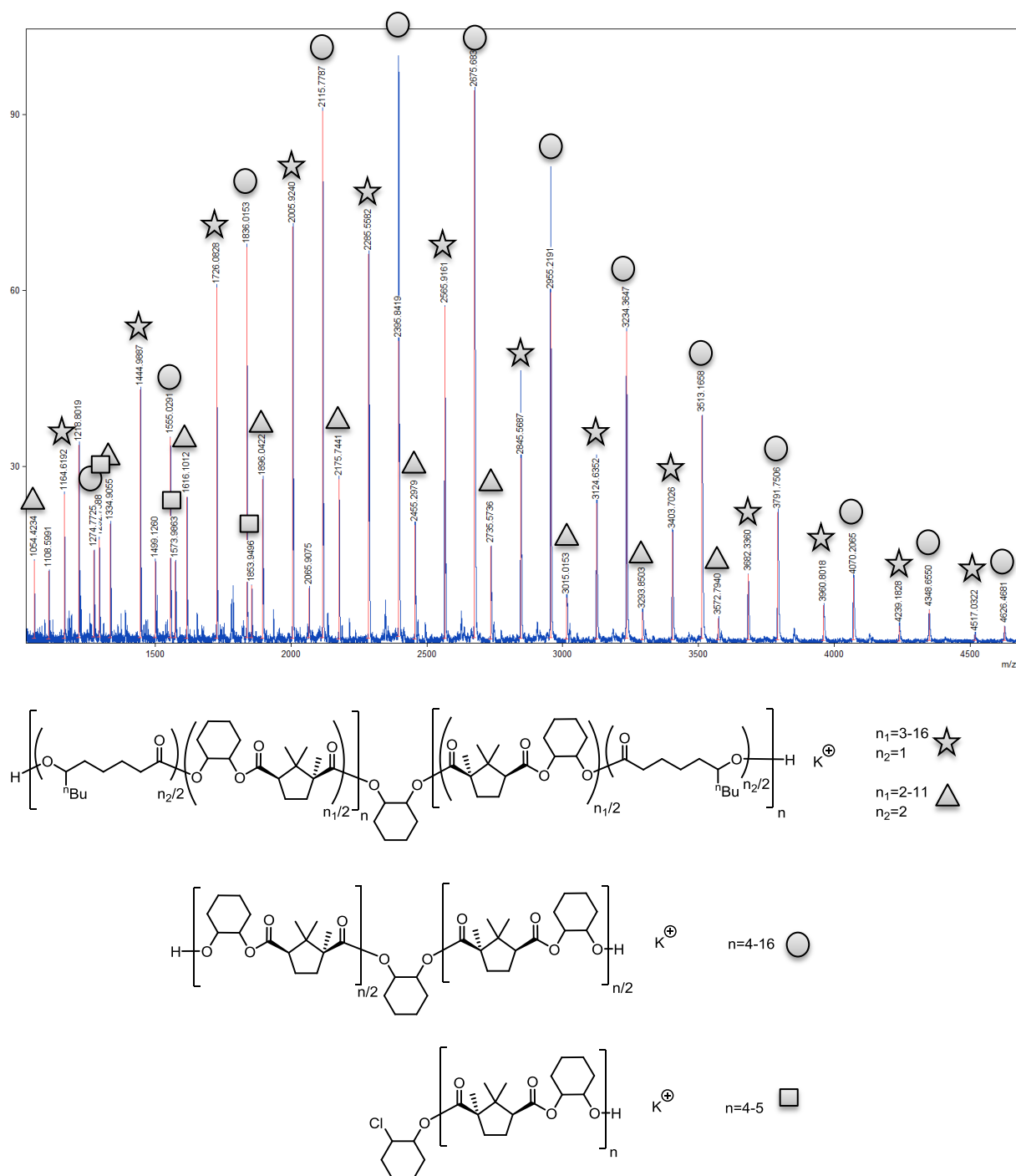


Figure S 3. 72 – MALDI of one-pot polymerization of CA/CHO/DL (after 19 h, 67% CA and 14% DL conversion). The series shows four species: star and triangle: $m/z = [116.08 \text{ (cyclohexandiol)} + (280.17 \times n) \text{ (PCHCE)} + (170.13 \times m) \text{ (PDL)} + 38.96 \text{ (K}^+)]$ ($n = 3 \sim 16$ and $m = 1$ for star and $n = 2 \sim 11$ and $m = 2$ for triangle); circle: $m/z = [116.08 + \text{(cyclohexandiol)} + (280.17 \times n) \text{ (PCHCE)} + 38.96 \text{ (K}^+)]$ ($n = 4 \sim 16$); square: $m/z = [34.97 \text{ (Cl)} + 98.07 \text{ (CHO)} + 1.01 \text{ (H)} + (280.17 \times n) \text{ (PCHCE)} + 38.96 \text{ (K}^+)]$ ($n = 4 \sim 5$). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

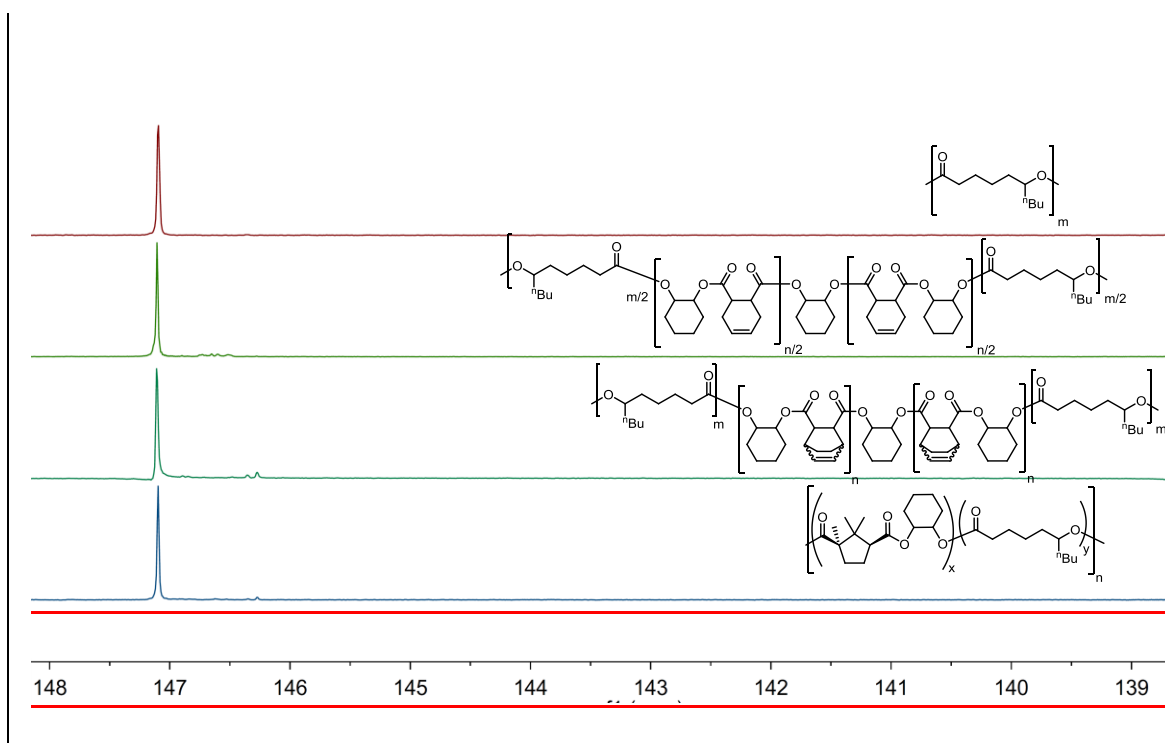
End-group analysis with $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy

Figure S 3. 73 – $^{31}\text{P}\{^1\text{H}\}$ NMR after end-group assay with different polymers. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Table S 3. 9 – $^{31}\text{P}\{^1\text{H}\}$ NMR chemical shift of different polymers after end-group assay. The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Anhydride in Backbone	$^{31}\text{P}\{^1\text{H}\}$ Shift (ppm)	Integral-ratio PDL:ROCOP
THPA	146.6	86:14
TCA2	146.2, 146.3	92:8
CA	146.3	98:2

Characterisation data for Polymer obtained after thiol-ene reaction with mercaptoethanol

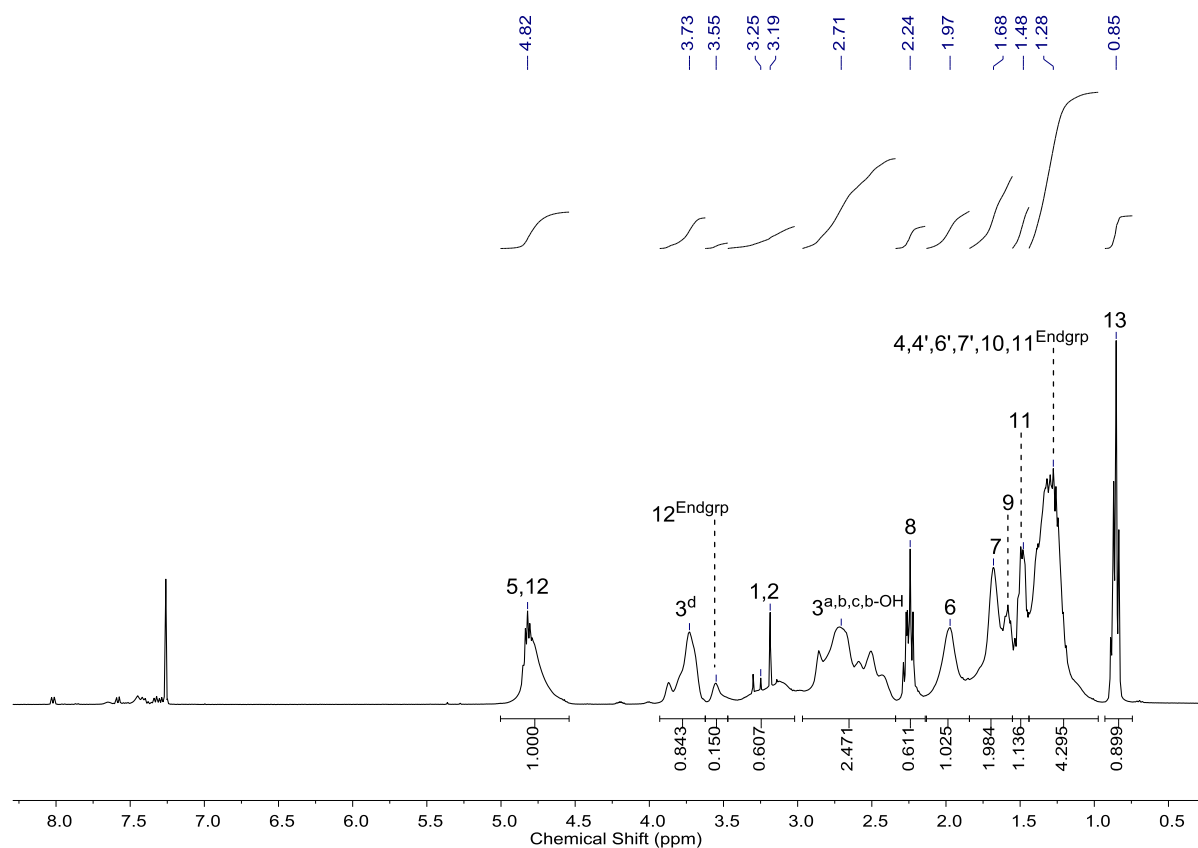


Figure S 3. 74 – ^1H NMR spectrum of isolated polyester after post-functionalization with mercapto ethanol. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

Characterisation data for Polymer obtained after thiol-ene reaction with butane thiol

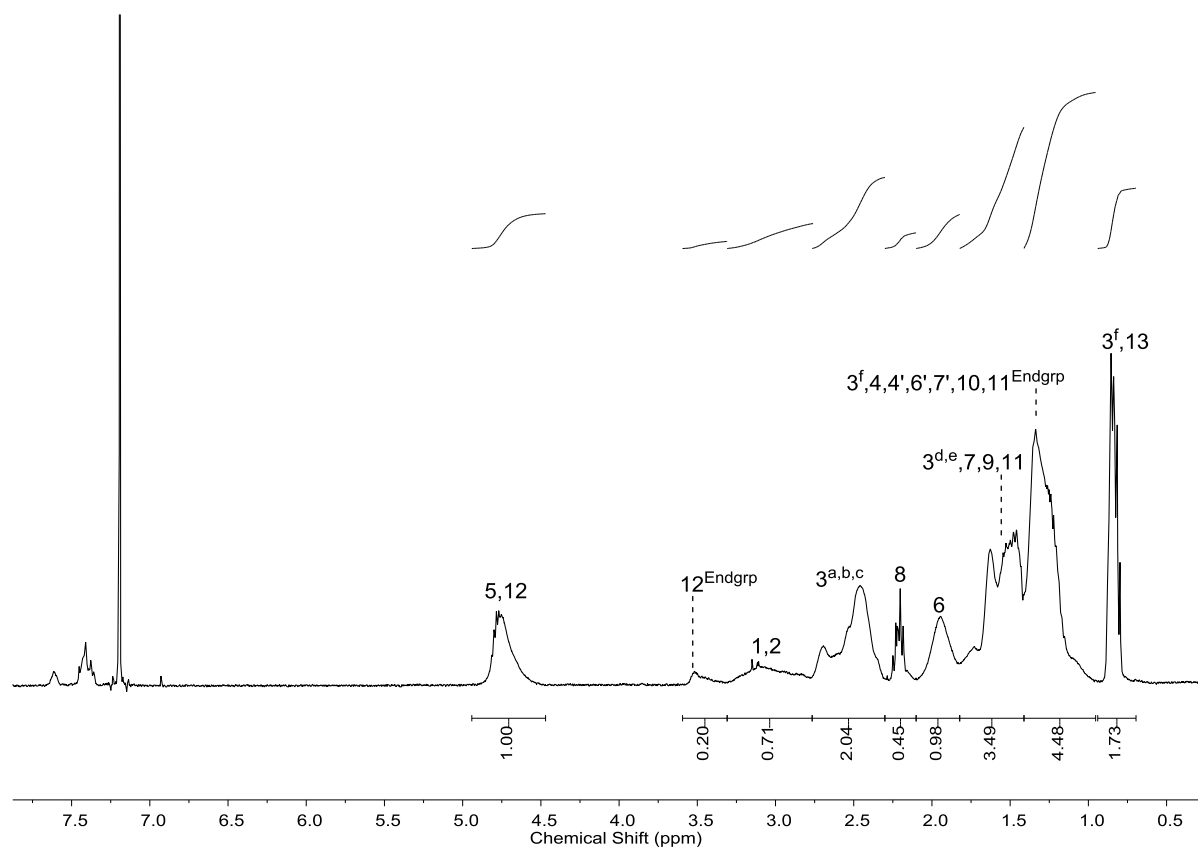


Figure S 3. 75 – ^1H NMR spectrum of isolated polyester after post-functionalization with butanthiol. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, 57, 6337. Copyright (2018) John Wiley and Sons.

One-Pot Polymerisation of CHO, PA, LA, CO₂

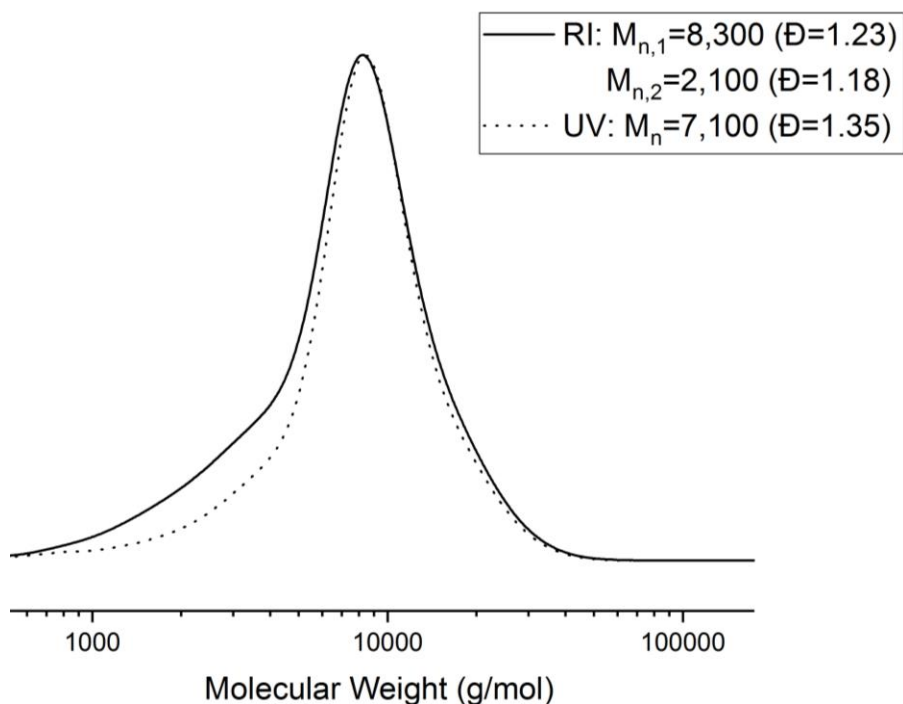


Figure S 3. 76 – GPC Trace obtained from one pot polymerisation of CHO, PA, LA and CO₂.

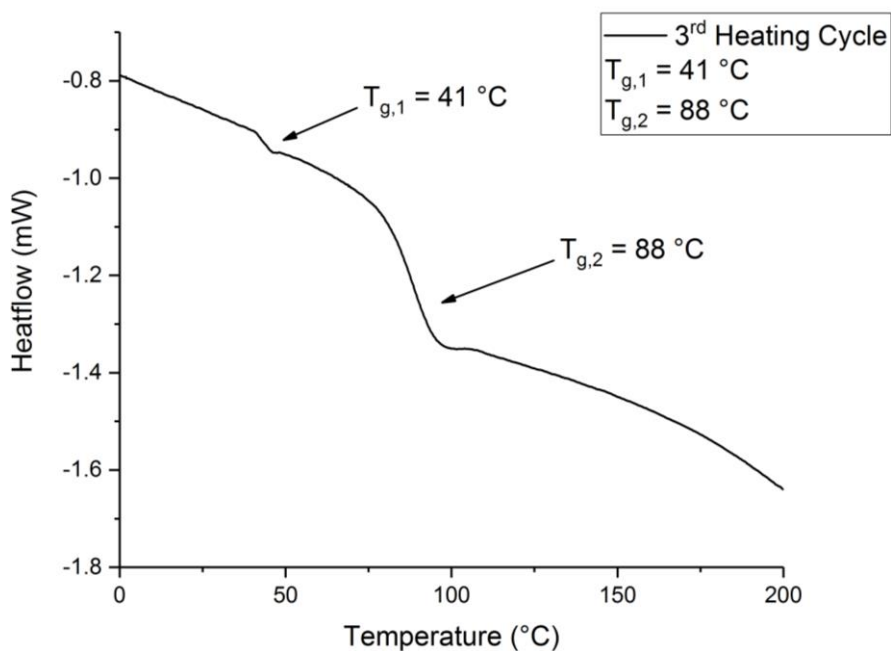


Figure S 3. 77 – DSC Thermogram of polymer obtained from one pot polymerisation of CHO, PA, LA and CO₂.

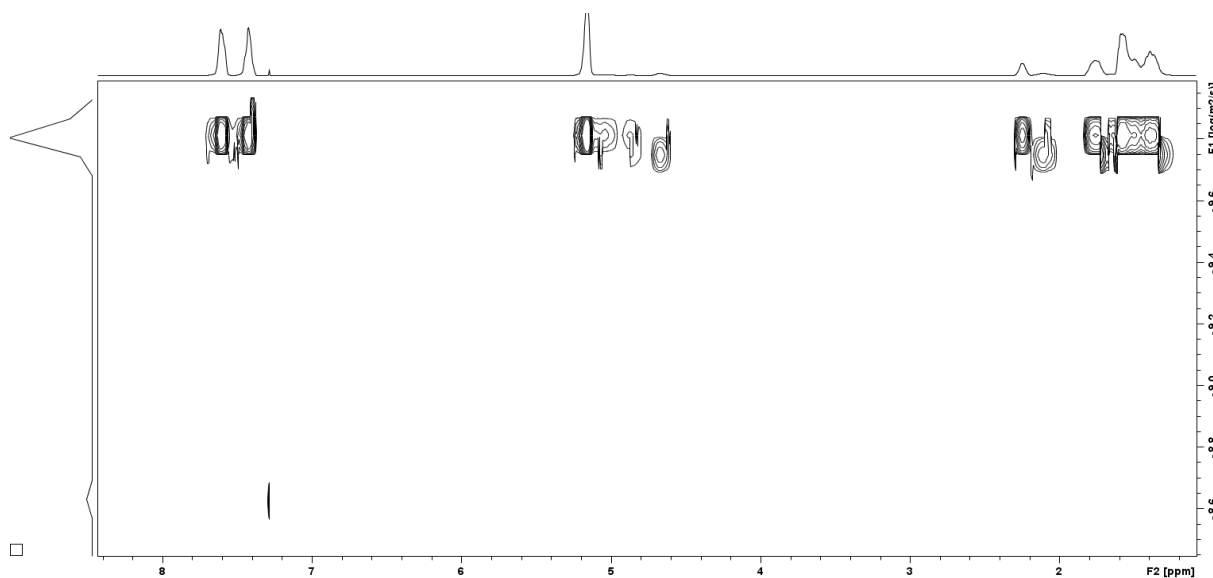


Figure S 3. 78 – DOSY NMR of polymer obtained from one pot polymerisation of CHO, PA, LA and CO₂.

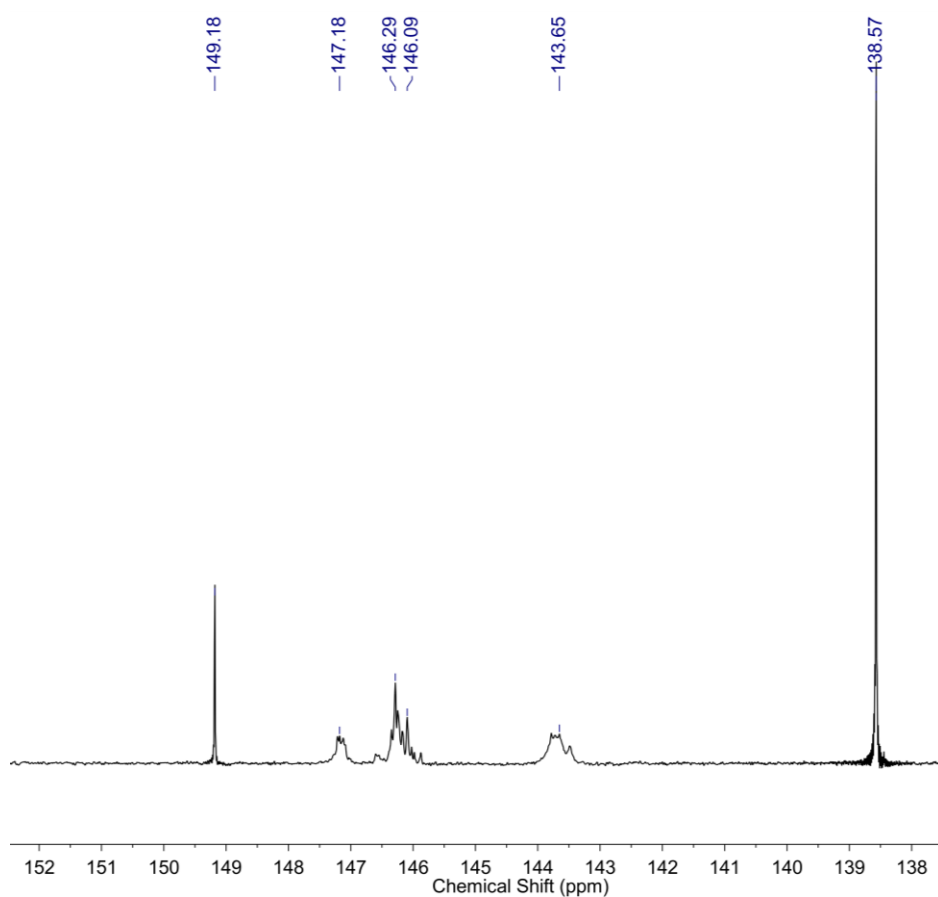


Figure S 3. 79 – ³¹P{¹H} NMR spectrum of polymer obtained from one pot polymerisation of CHO, PA, LA and CO₂ after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane (only region relevant to alcohols shown).

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Chapter 4 - 'Switch' Catalysis with [SalcyCrCl]. Part II – Propylene oxide

^1H NMR Spectra of one-pot polymerisation of TCA1/PO

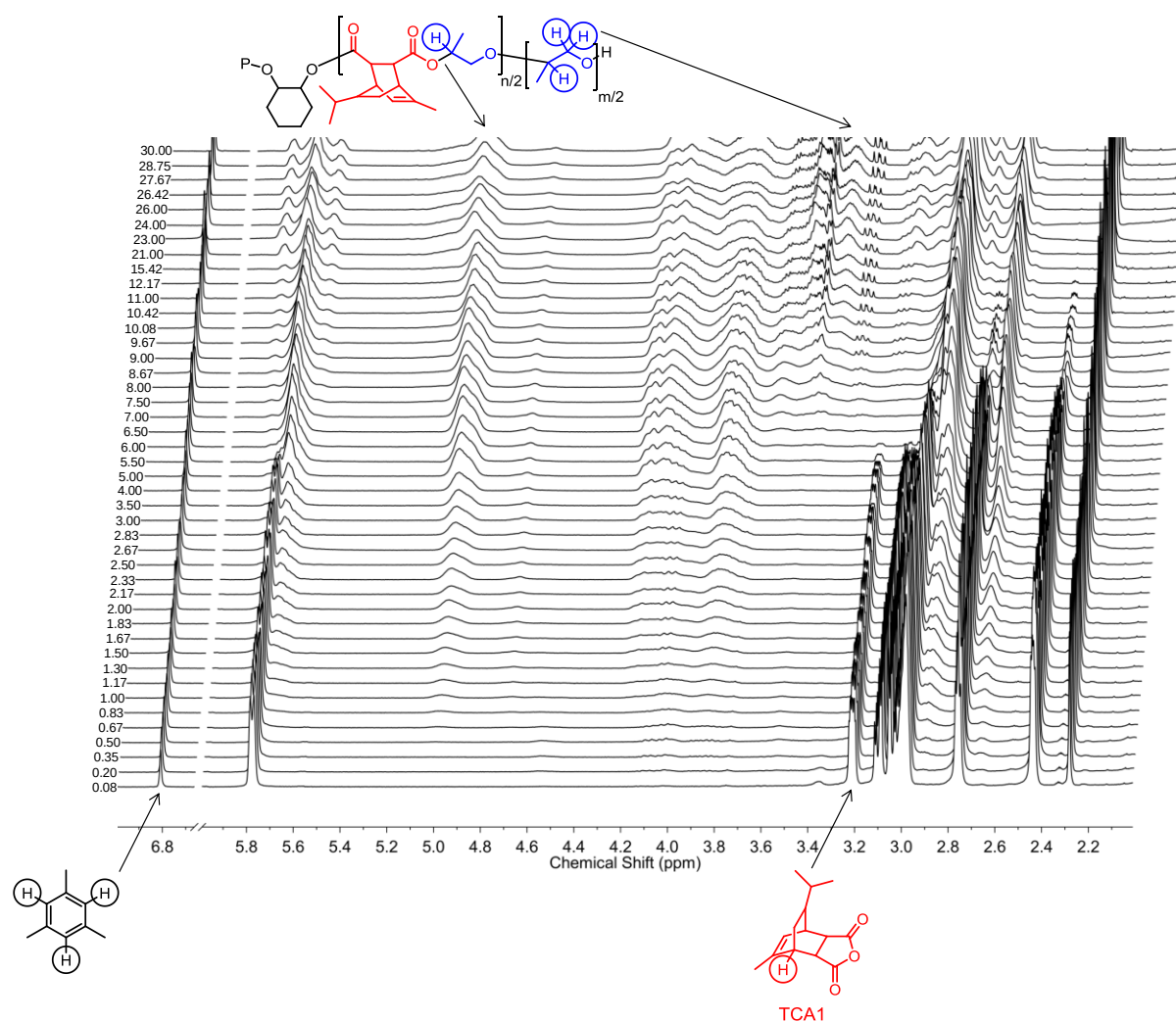
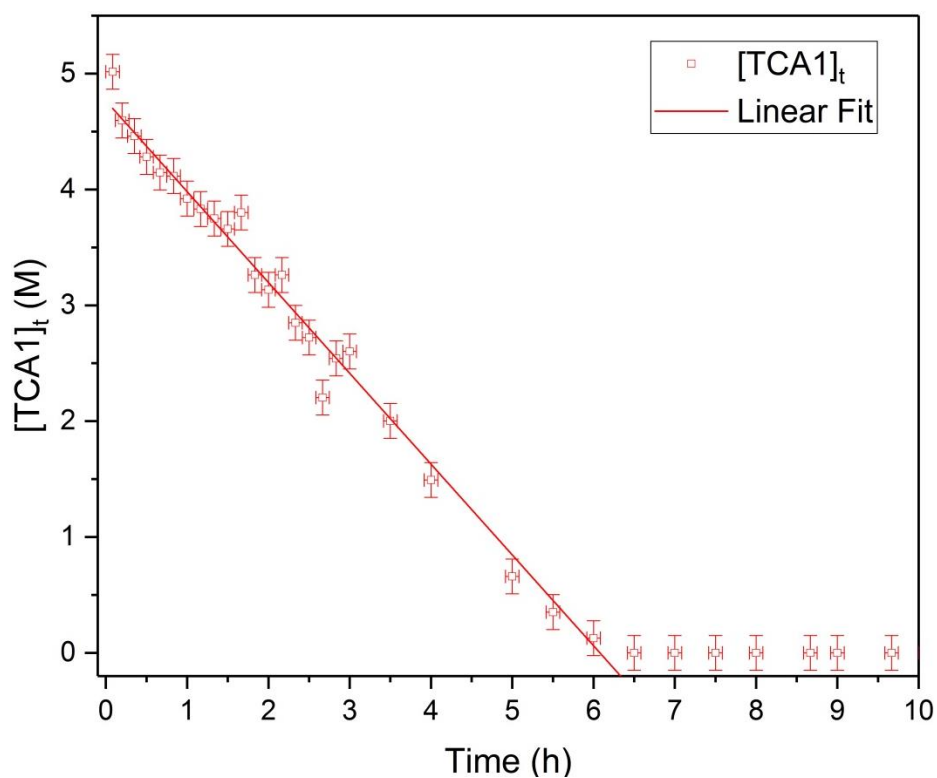


Figure S 4. 1 – ^1H NMR spectra at different times of the one-pot polymerization of TCA1/PO. The arrows indicate the signals used for the conversion vs. time plots.

Table S 4. 1 – Integrals based on ^1H NMR spectroscopy used for conversion vs. time plots

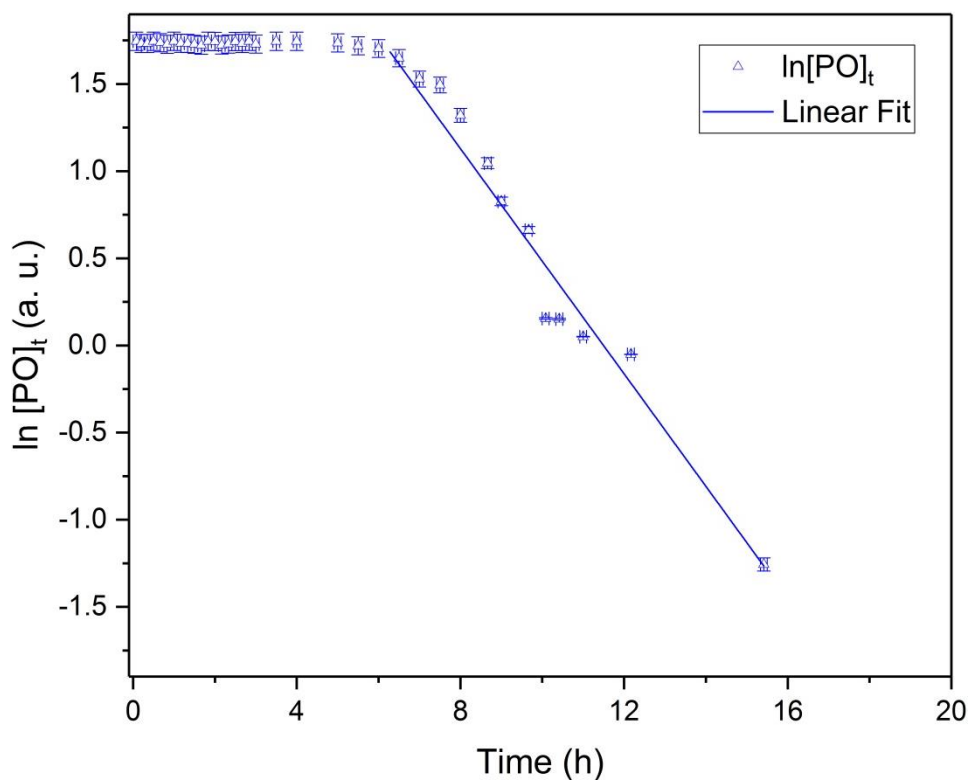
Time (h)	Anhydride (3.27-3.17)	Polyester (5.15-4.83)	Polyether (3.72-3.29)	Normalized Anhydride	Normalized Polyester	Normalized Polyether
0.08	6.69	0.00	0.00	100.00	0.00	0.00
0.20	6.13	0.00	0.15	91.63	0.00	1.20
0.35	5.95	0.00	0.14	88.94	0.00	1.12
0.50	5.71	0.19	0.00	85.35	3.12	0.00
0.67	5.53	0.16	0.09	82.66	2.63	0.72
0.83	5.49	0.37	0.20	82.06	6.08	1.60
1.00	5.23	0.45	0.00	78.18	7.39	0.00
1.17	5.11	0.62	0.13	76.38	10.18	1.04
1.33	5.00	0.85	0.14	74.74	13.96	1.12
1.50	4.88	1.06	0.20	72.94	17.41	1.60
1.67	5.07	1.20	0.26	75.78	19.70	2.08
1.83	4.35	1.42	0.00	65.02	23.32	0.00
2.00	4.18	1.52	0.01	62.48	24.96	0.08
2.17	4.35	1.82	0.25	65.02	29.89	2.00
2.33	3.80	1.90	0.18	56.80	31.20	1.44
2.50	3.63	1.99	0.01	54.26	32.68	0.08
2.67	2.94	2.20	0.14	43.95	36.12	1.12
2.83	3.39	2.38	0.00	50.67	39.08	0.00
3.00	3.47	2.55	0.19	51.87	41.87	1.52
3.50	2.67	3.28	0.00	39.91	53.86	0.00
4.00	1.99	3.46	0.00	29.75	56.81	0.00
5.00	0.88	4.75	0.11	13.15	78.00	0.88
5.50	0.47	5.20	0.30	7.03	85.39	2.40
6.00	0.17	5.63	0.48	2.54	92.45	3.85
6.50	0.00	5.86	1.09	0.00	96.22	8.73
7.00	0.00	5.84	2.31	0.00	95.89	18.51
7.50	0.00	5.84	2.63	0.00	95.89	21.07
8.00	0.00	5.86	4.11	0.00	96.22	32.93
8.67	0.00	5.85	5.97	0.00	96.06	47.84
9.00	0.00	5.74	7.13	0.00	94.25	57.13
9.67	0.00	5.97	7.85	0.00	98.03	62.90
10.08	0.00	5.65	9.45	0.00	92.78	75.72
10.42	0.00	6.00	9.46	0.00	98.52	75.80
11.00	0.00	6.13	9.69	0.00	--*	77.64
12.17	0.00	6.09	9.90	0.00	100.00	79.33
15.42	0.00	5.93	11.28	0.00	97.37	90.38
21.00	0.00	5.56	11.99	0.00	91.30	96.07
23.00	0.00	5.58	12.48	0.00	91.63	100.00
24.00	0.00	6.05	11.51	0.00	99.34	92.23
26.00	0.00	6.06	12.00	0.00	99.51	96.15
26.42	0.00	6.55	13.41	0.00	--*	--*
27.67	0.00	5.93	11.42	0.00	97.37	91.51
28.75	0.00	5.89	11.87	0.00	96.72	95.11
30.00	0.00	5.89	12.55	0.00	96.72	--*

* not considered.



Equation	$y = a + b \cdot x$
Plot	W
Weight	Instrumental
Intercept	4.76 ± 0.06
Slope	-0.78 ± 0.02
Residual Sum of Squares	32.70
Pearson's r	-0.99
R-Square(COD)	0.99
Adj. R-Square	0.98

Figure S 4. 2 – Consumption of TCA1 in one-pot reaction of TCA1/PO. Conversion vs. time data was based on integrals from ^1H NMR spectroscopy after normalizing against mesitylene as an internal standard. The following errors were applied: y-axis ± 0.15 M and x-axis ± 0.08 h.



Equation	$y = a + b \cdot x$
Plot	W
Weight	No Weighting
Intercept	3.71359 ± 0.16158
Slope	-0.32299 ± 0.01714
Residual Sum of Squares	0.33006
Pearson's r	-0.98352
R-Square(COD)	0.96731
Adj. R-Square	0.96459

Figure S 4. 3 – Concentration of PO vs. time data was based on integrals of PPO from ^1H NMR spectroscopy after normalizing against mesitylene as an internal standard. The following errors were applied: y-axis $\pm 3\%$ and x-axis ± 0.08 h.

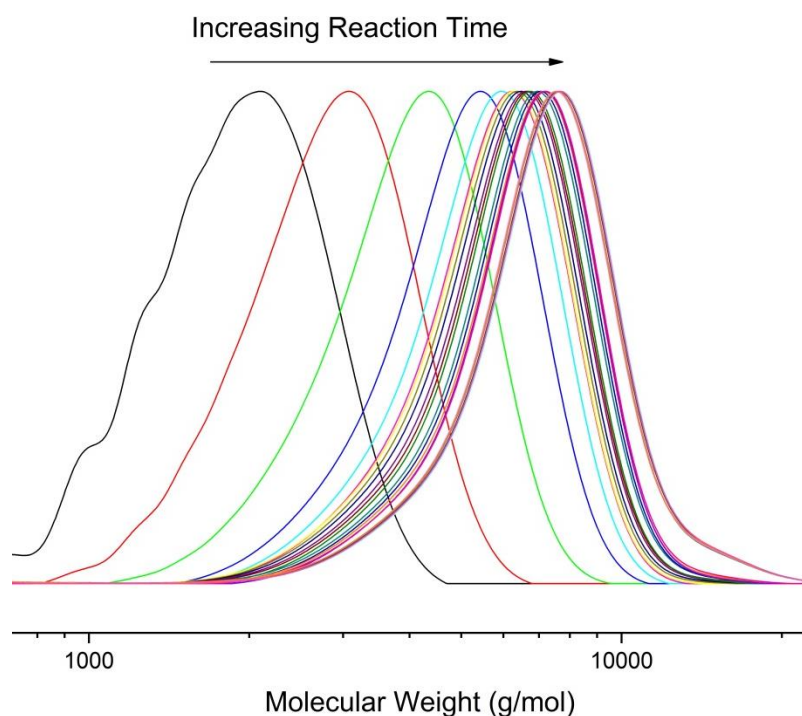


Figure S 4. 4 – GPC traces during the one-pot polymerization of TCA1/PO.

Table S 4. 2 – M_n (g/mol) and $\bar{D}$ values of GPC traces during the one-pot polymerization of TCA1/PO.

Time (h)	M_n (g/mol)	$\bar{D}$
1	950	1.10
2	1,790	1.13
3	2,580	1.13
4	3,670	1.12
5	4,630	1.11
5.5	5,040	1.12
6	5,310	1.11
6.5	5,320	1.11
7	5,430	1.11
7.5	5,540	1.11
8	5,630	1.11
8.67	5,700	1.11
9	5,790	1.11
9.67	5,960	1.11
10	6,070	1.11
10.42	6,150	1.11
12.17	6,220	1.10
15.42	6,184	1.11
21	6,750	1.13
23	6,650	1.12
24	6,770	1.12
26	6,780	1.12
26.25	6,610	1.13
27.67	6,700	1.13
28.75	6,680	1.12
30	6,720	1.13

MALDI Spectrum at Low Conversions

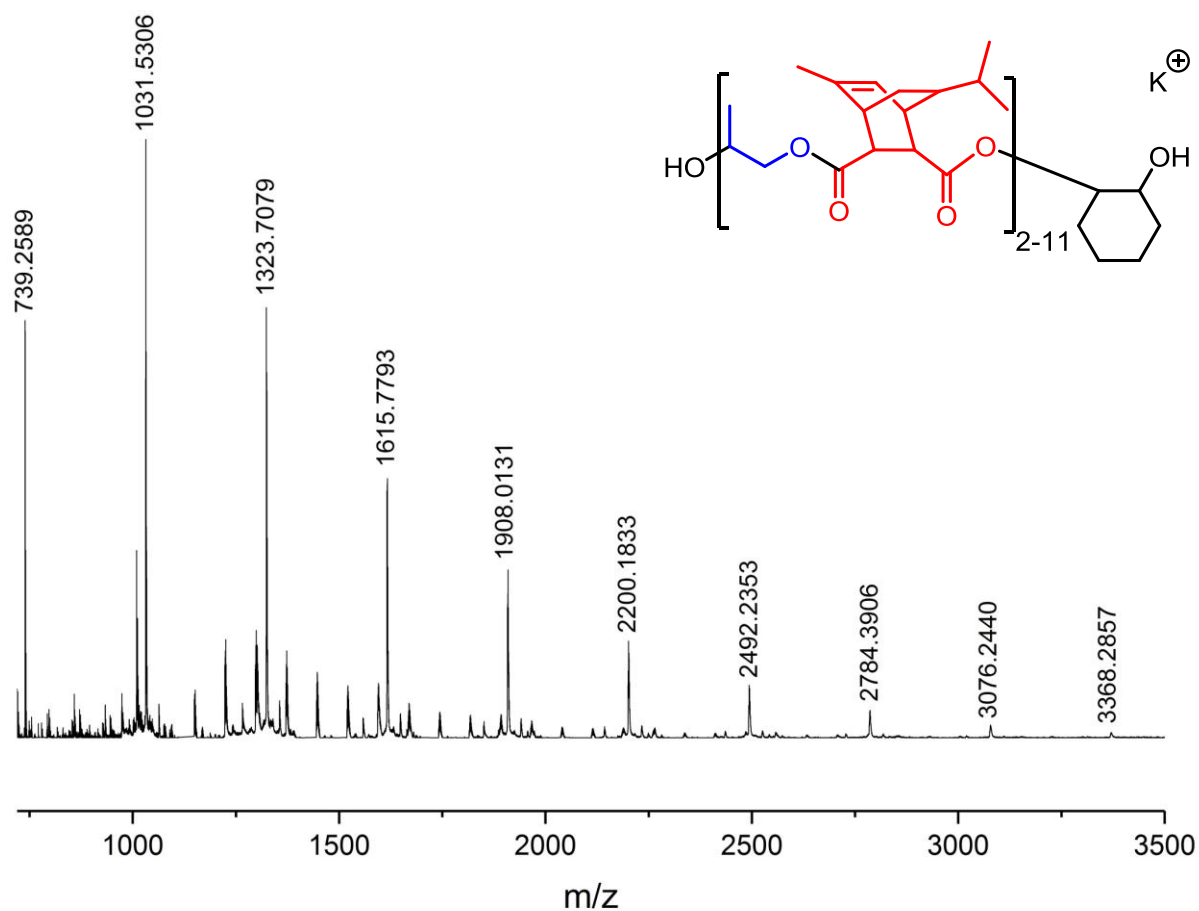


Figure S 4. 5 – MALDI Spectrum of crude sample of one-pot polymerization of TCA1/PO after 2h (25% polyesterformation, < 5% polyether formation, $M_n=1,790$ g/mol ($\text{Đ}=1.13$)). The peaks correspond to a perfectly alternating polyester ($n * 292.167$ with $n=2-11$) + CHD (116.08) + K^+ (38.96). A second distribution with a repeating unit of $m/z=74.00$ was assigned to polysiloxane, a common trace impurity in high-resolution mass spectrometry (not shown).^[4, 5]

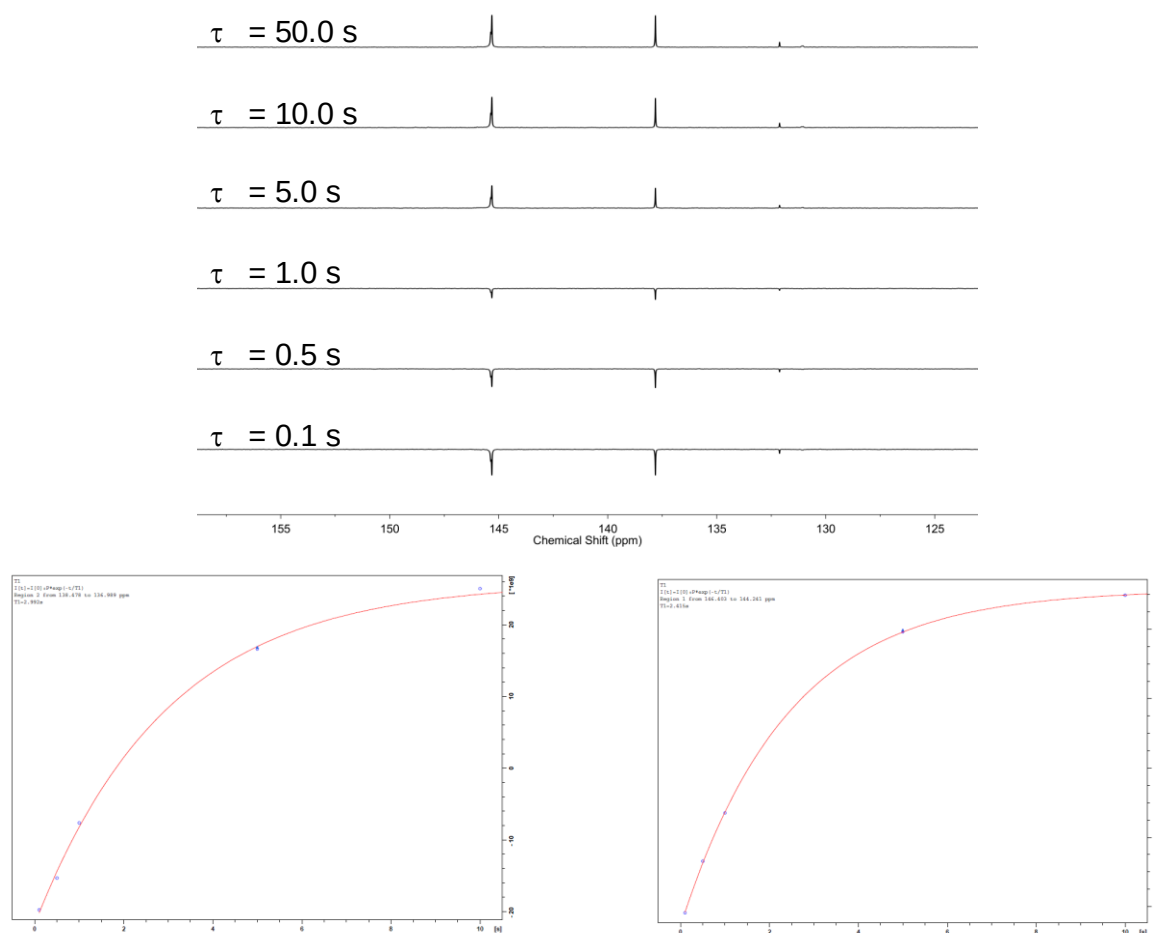


Figure S 4. 6 – T_1 -Inversion recovery experiment for peaks at 138 and 146 ppm in $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum. T_1 values were determined as 2.992 s and 2.415 s after exponential fitting ($I_t = I_0 + P \cdot \exp(-t/T_1)$) for 138 and 144 ppm, respectively.

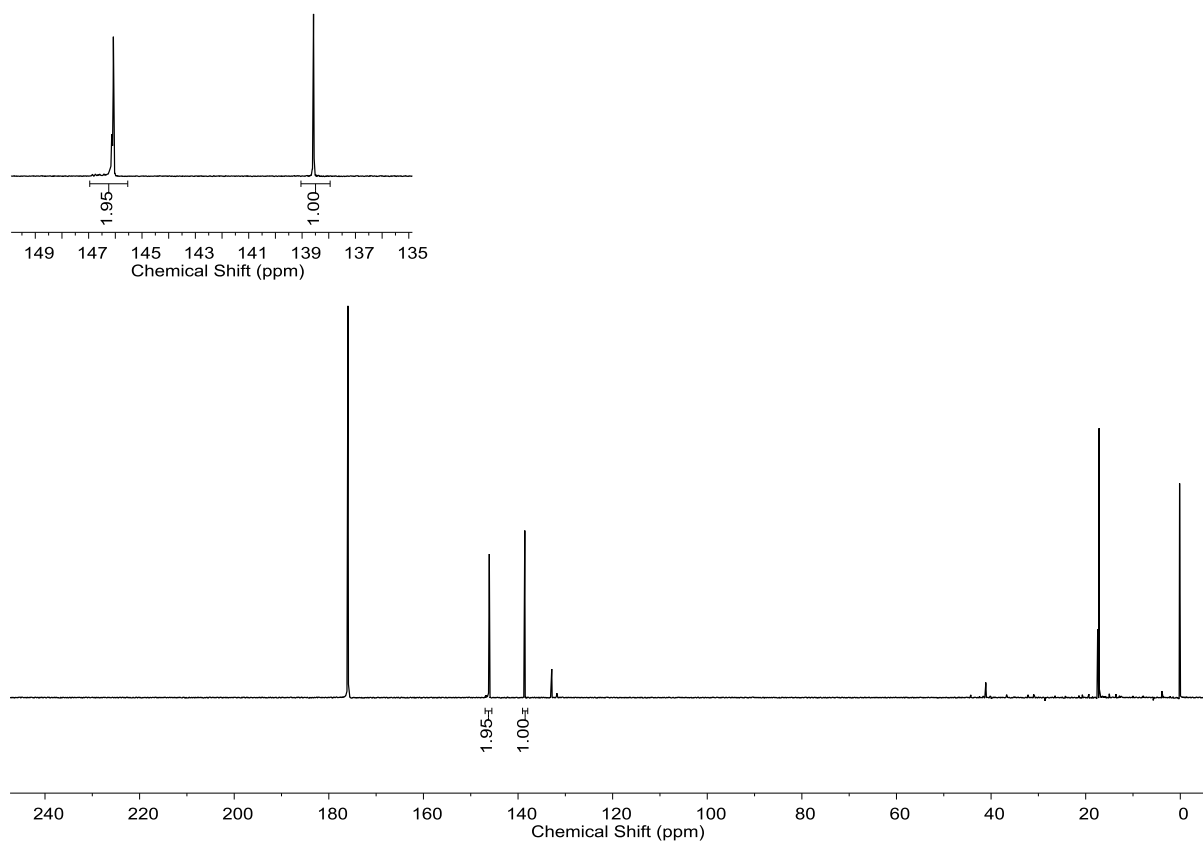


Figure S 4. 7 – $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of block copolymer with $D_1 = 5 * 2.992 \text{ s}$ (as determined above; 128 scans). Based on this integration, $27.3 \text{ } \mu\text{mol [OH]} / 50.0 \text{ mg [Polymer]}$ are present (calculated from standard, the integral 1.00 corresponds to $40 \text{ } \mu\text{L}$ of a stock solution of 40 mg / mL (1.6 mg), which, in turn is equivalent to $14.0 \text{ } \mu\text{mol}$ of $[\text{OH}]$).

NMR Data of Polymer obtained from PO/TCA1

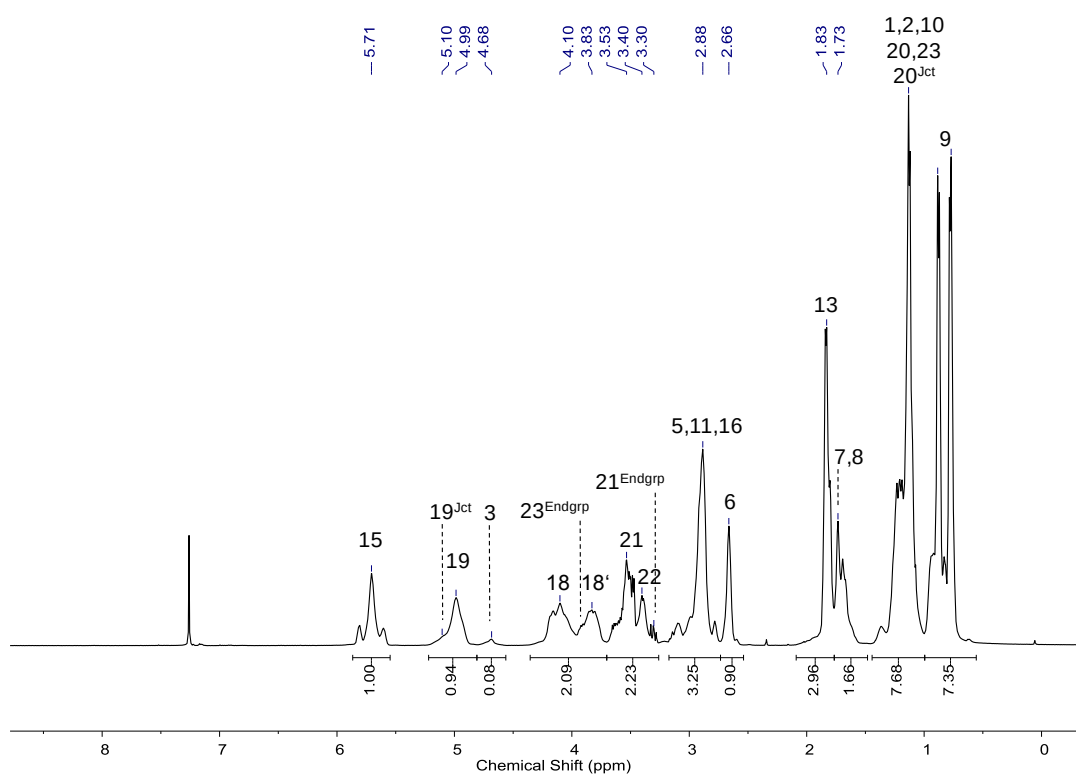


Figure S 4. 8 – ^1H NMR Spectrum of block copolymer.

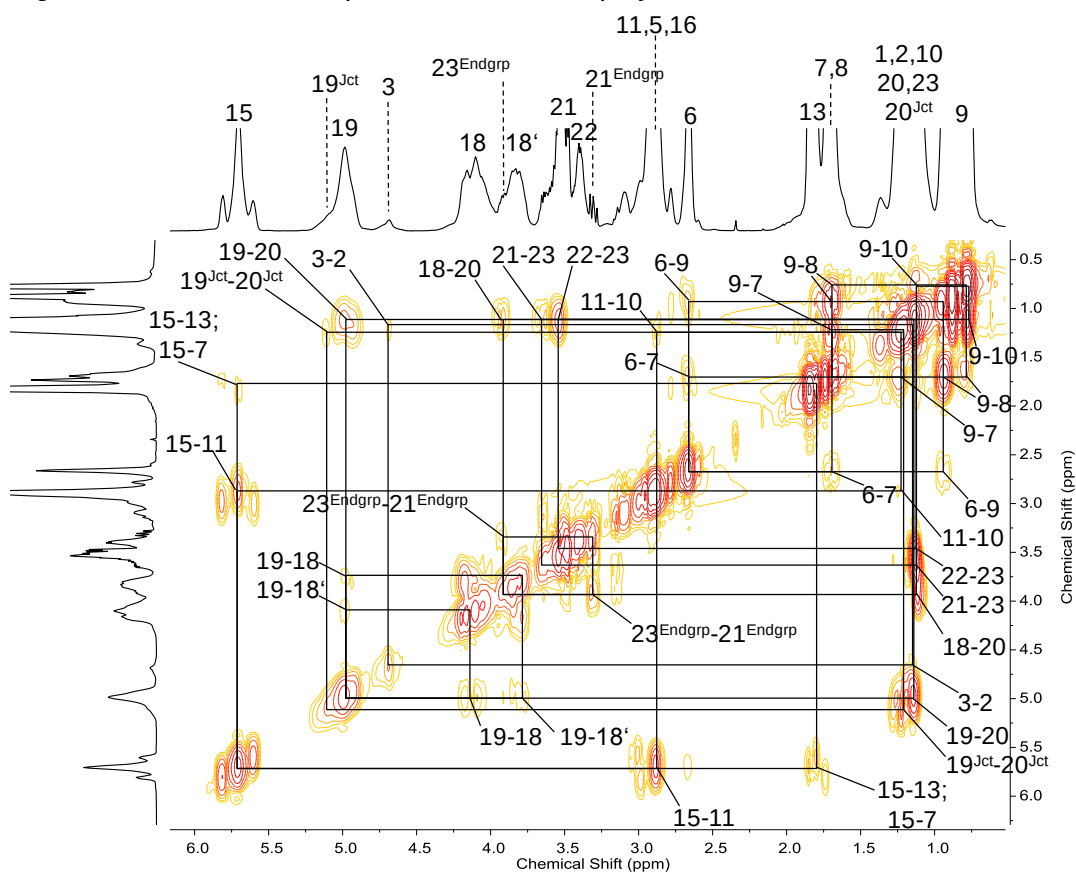


Figure S 4. 9 - H, H COSY NMR Spectrum of block copolymer.

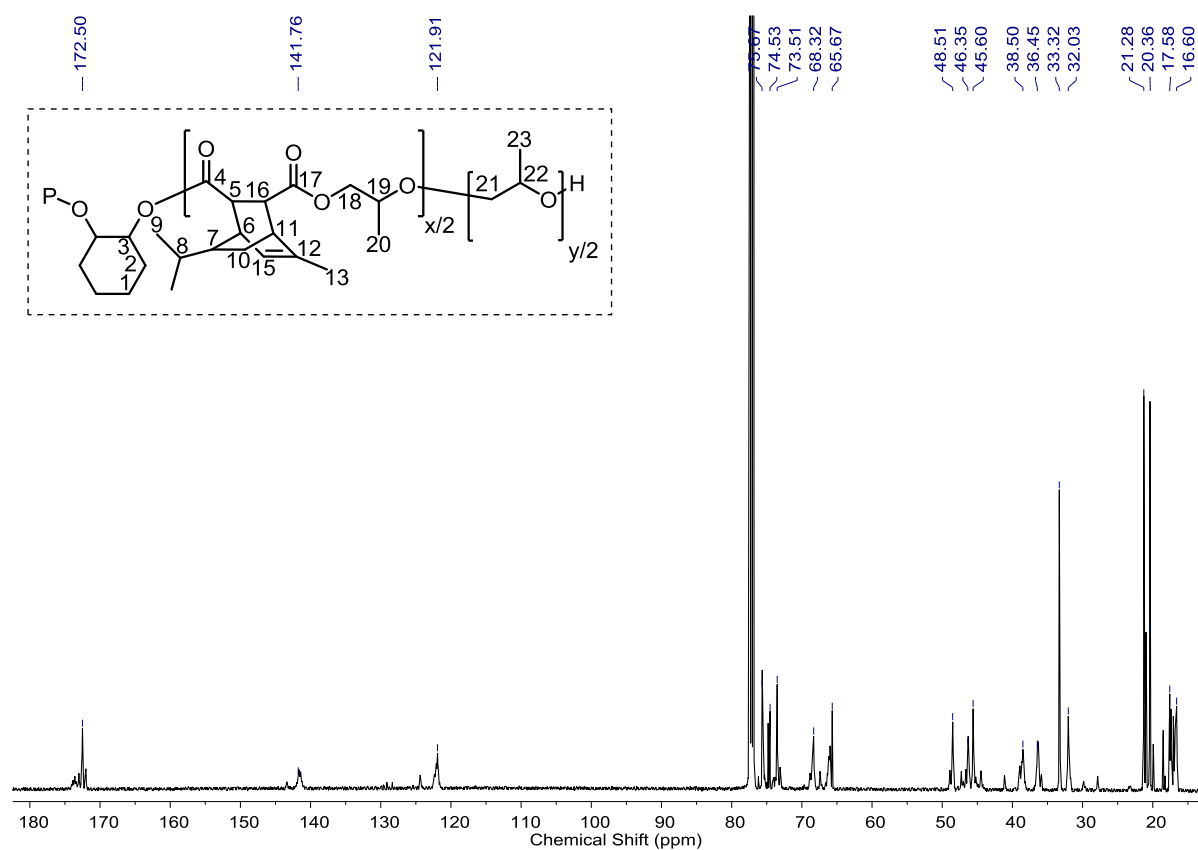


Figure S 4. 10 – $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum of polymer obtained from TCA1/PO.

Kinetic Analysis based on Figure 4.12

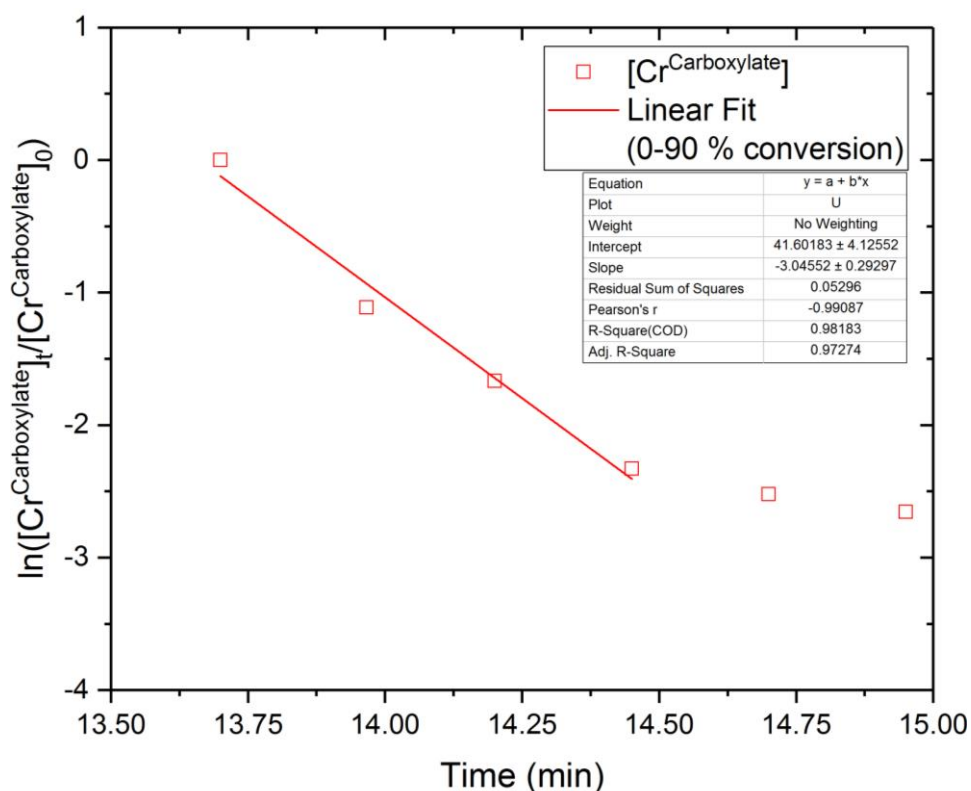


Figure S 4. 11 – $\ln([Cr^{Carboxylate}]_t/[Cr^{Carboxylate}]_0)$ vs. time plot to determine the rate constant. Data based on IR data.

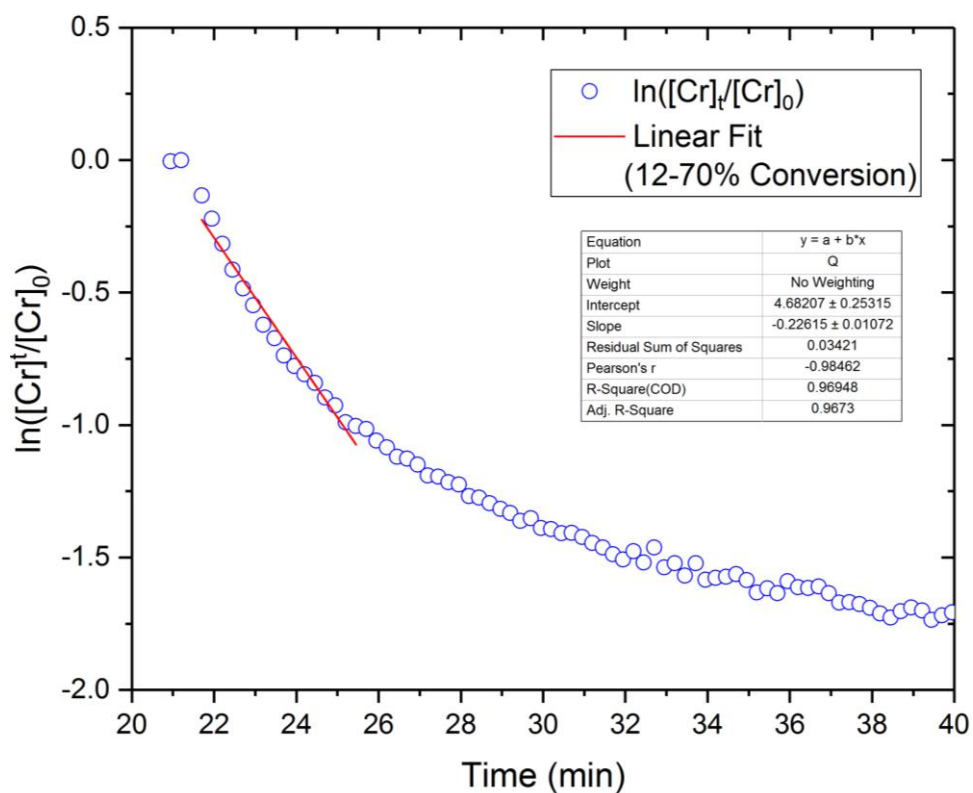


Figure S 4. 12– $\ln([Cr]_t/[Cr]_0)$ vs. time plot to determine the rate constant. Data based on IR data.

DSC Thermograms before and after Chain-Extension

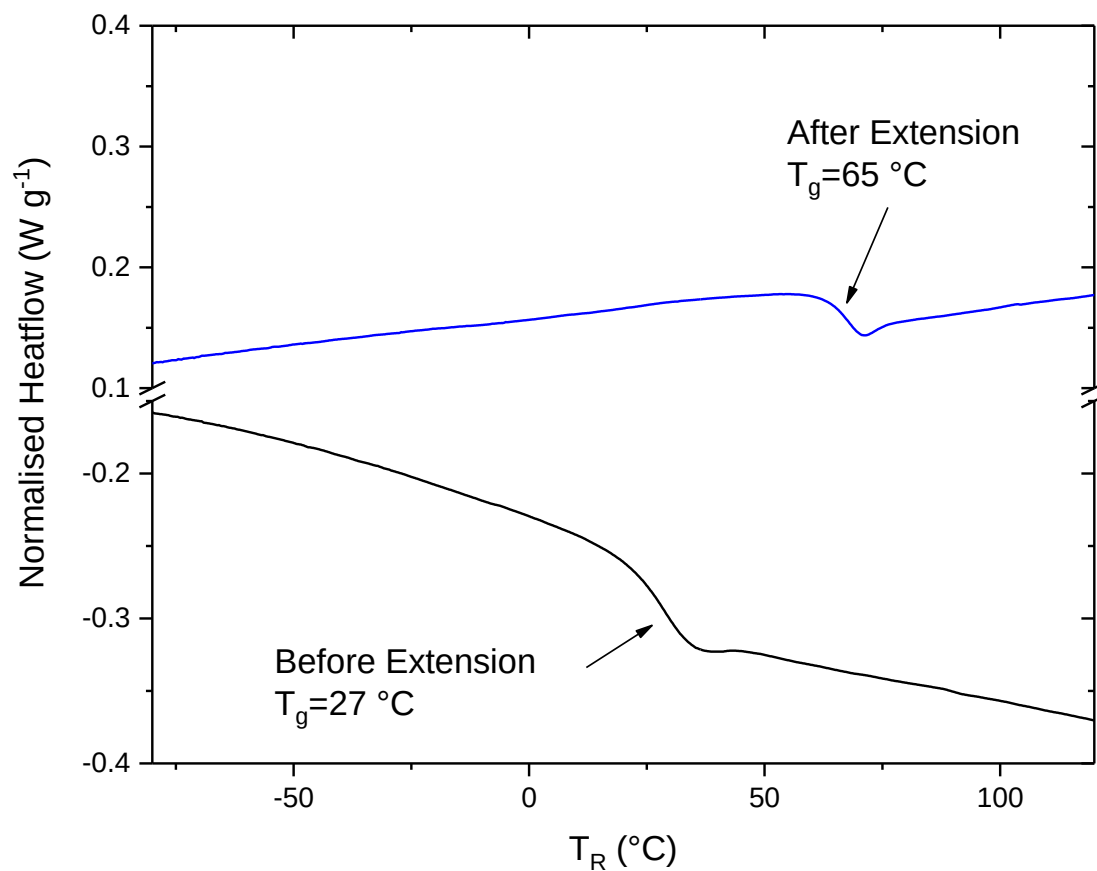
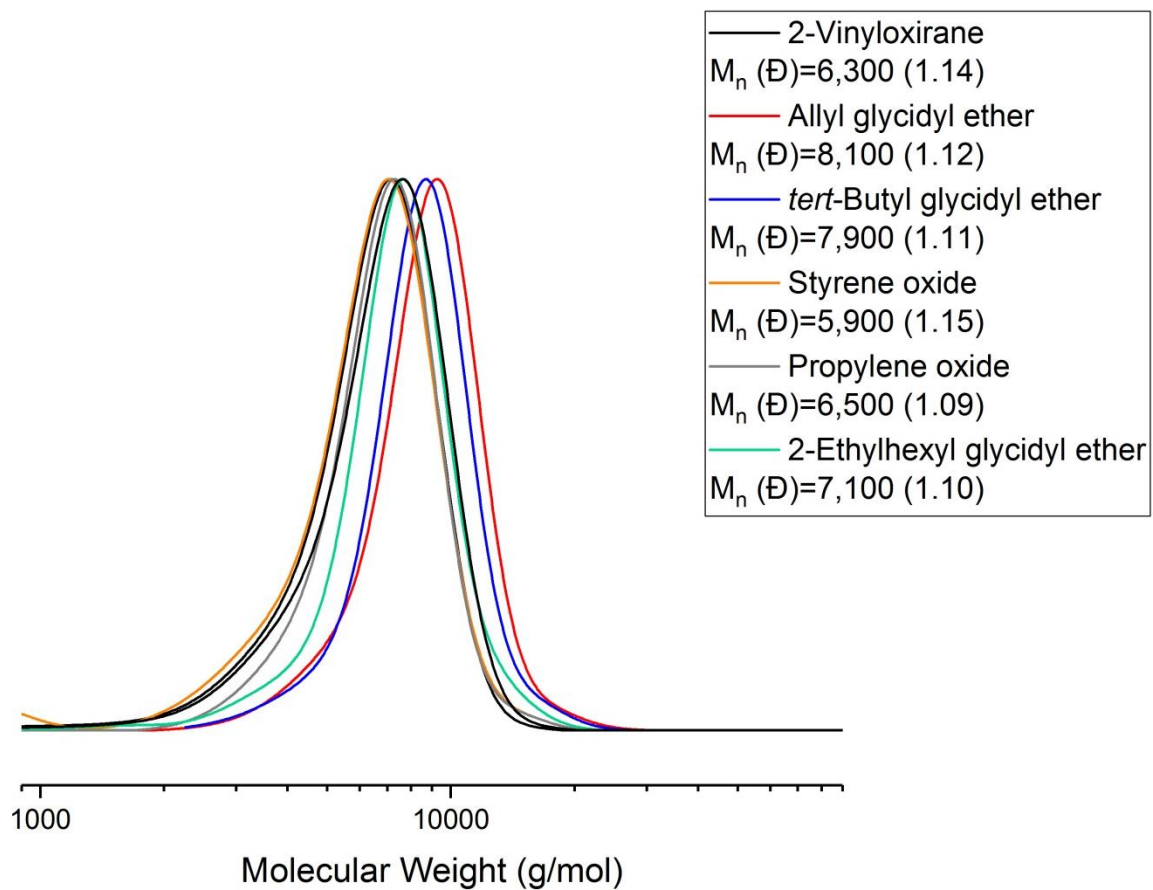


Figure S 4. 13 – DSC Thermograms of polymers before and after chain-extension.

GPC and DSC Data for Polymers obtained from different epoxides and TCA1



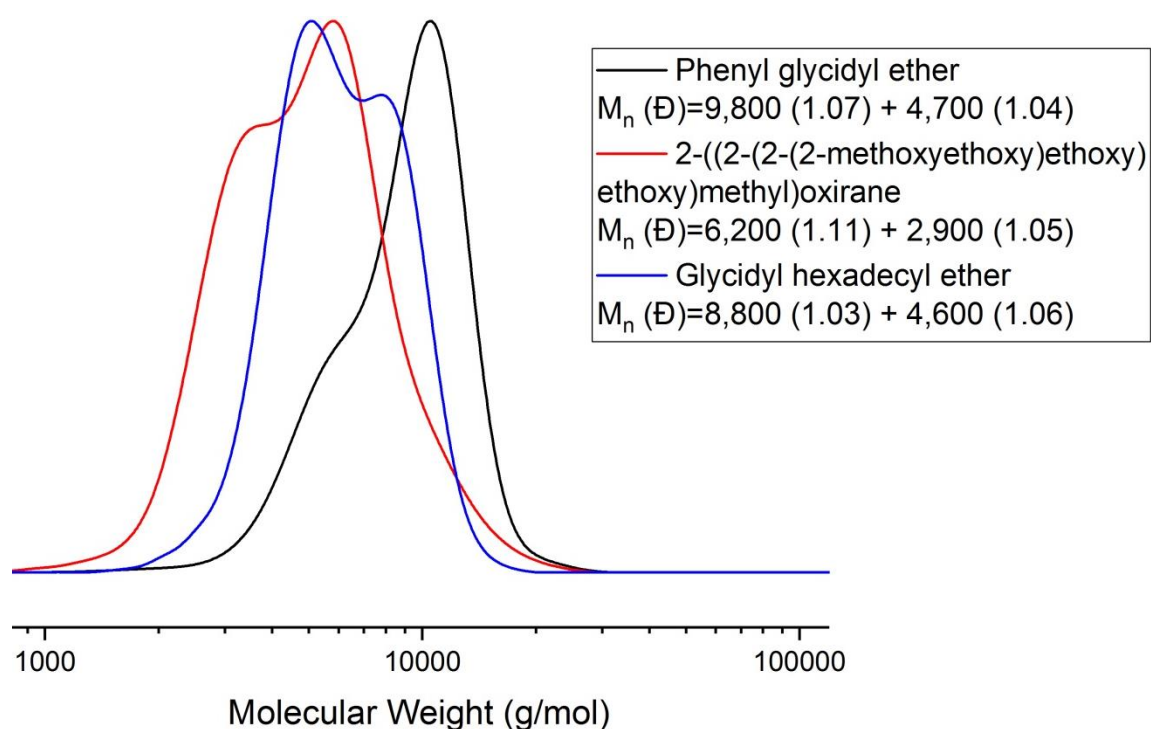


Figure S 4. 14 - Monomodal (top) and bimodal (bottom) GPC traces of substrates shown Table 4.1 after six days.

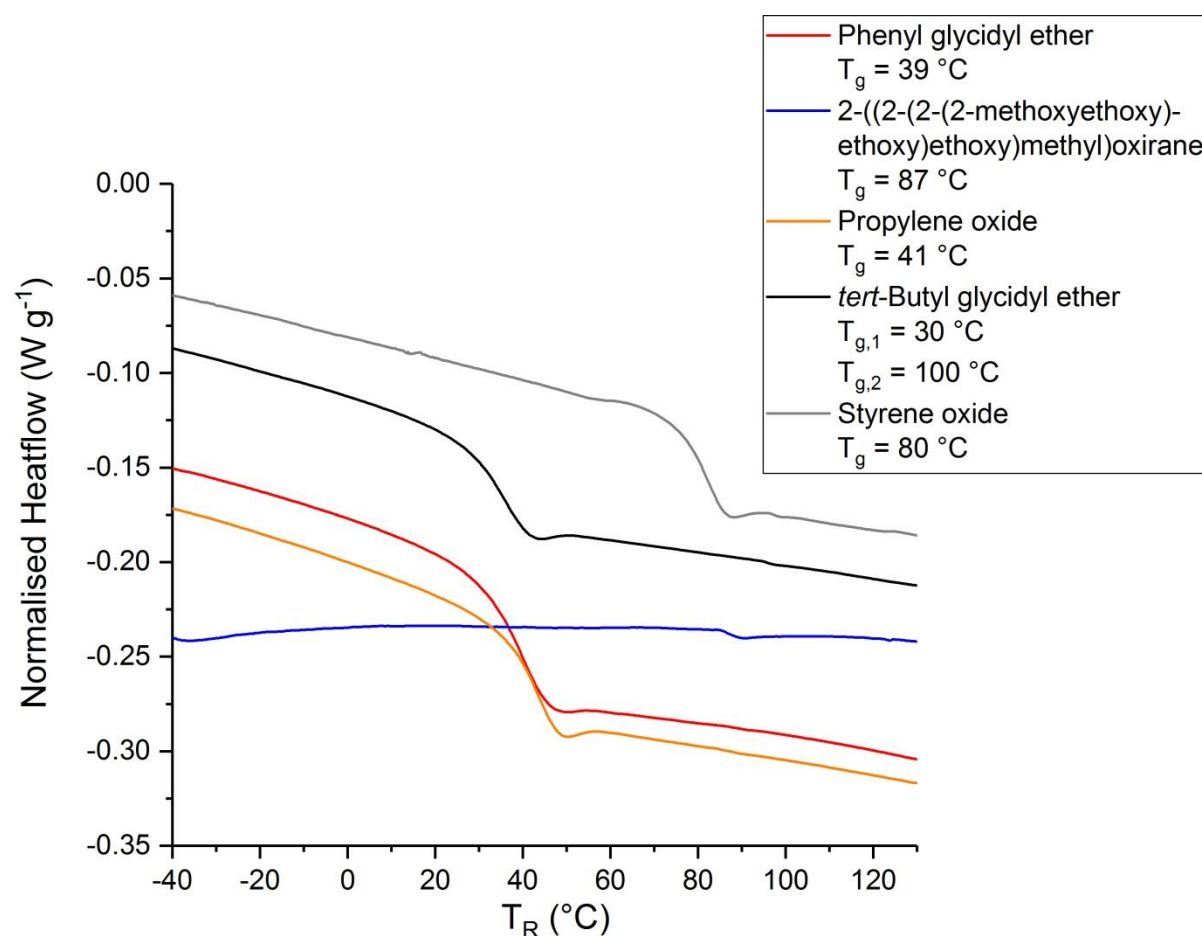


Figure S 4. 15 - DSC Thermograms for substrates shown in Table 4.1.

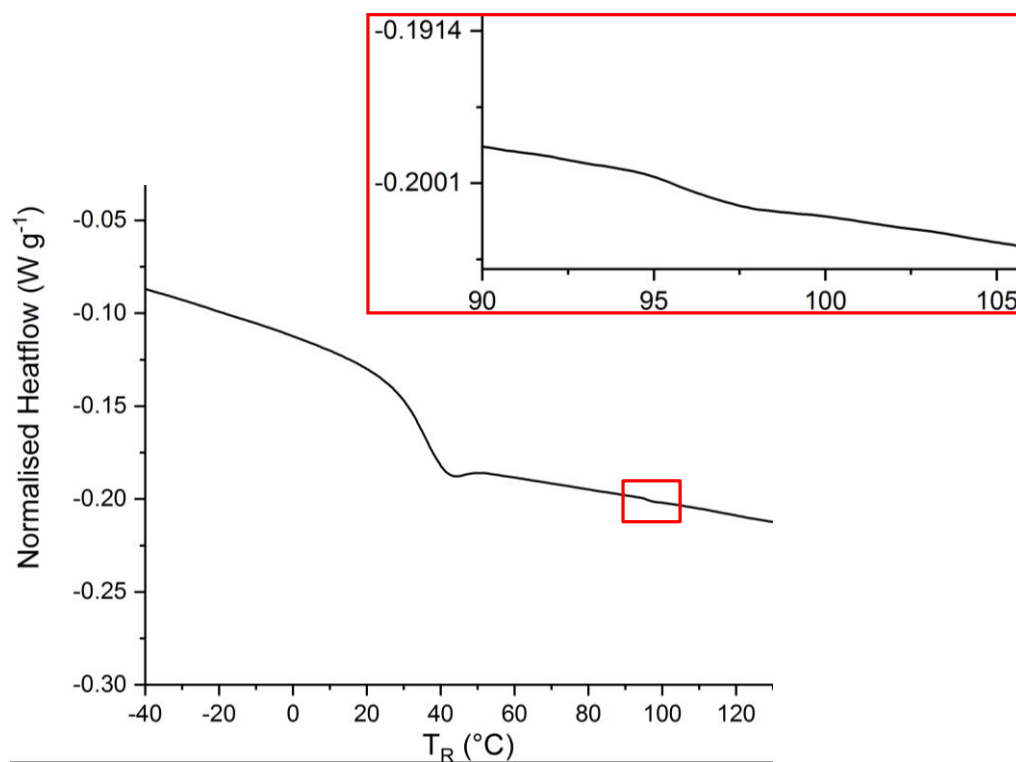


Figure S 4. 16 - DSC Thermograms for polymer based on *tert*-butyl glycidyl ether / TCA1.

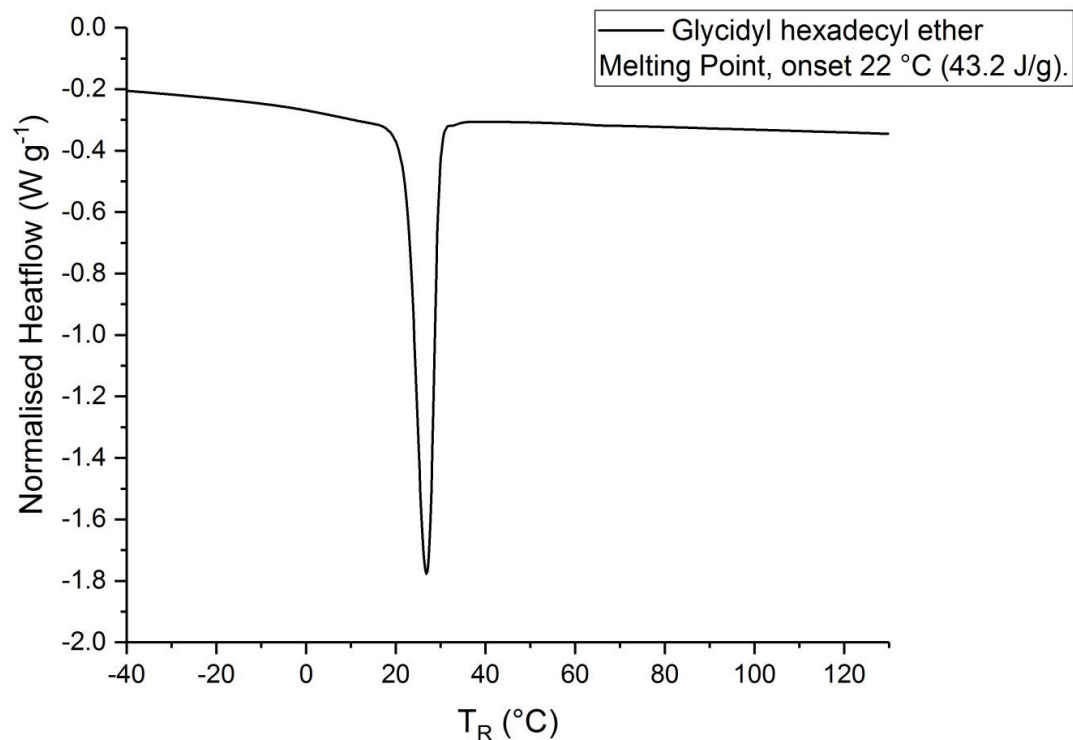


Figure S 4. 17 - DSC Thermogram for polymer based on glycidyl hexadecyl ether / TCA1.

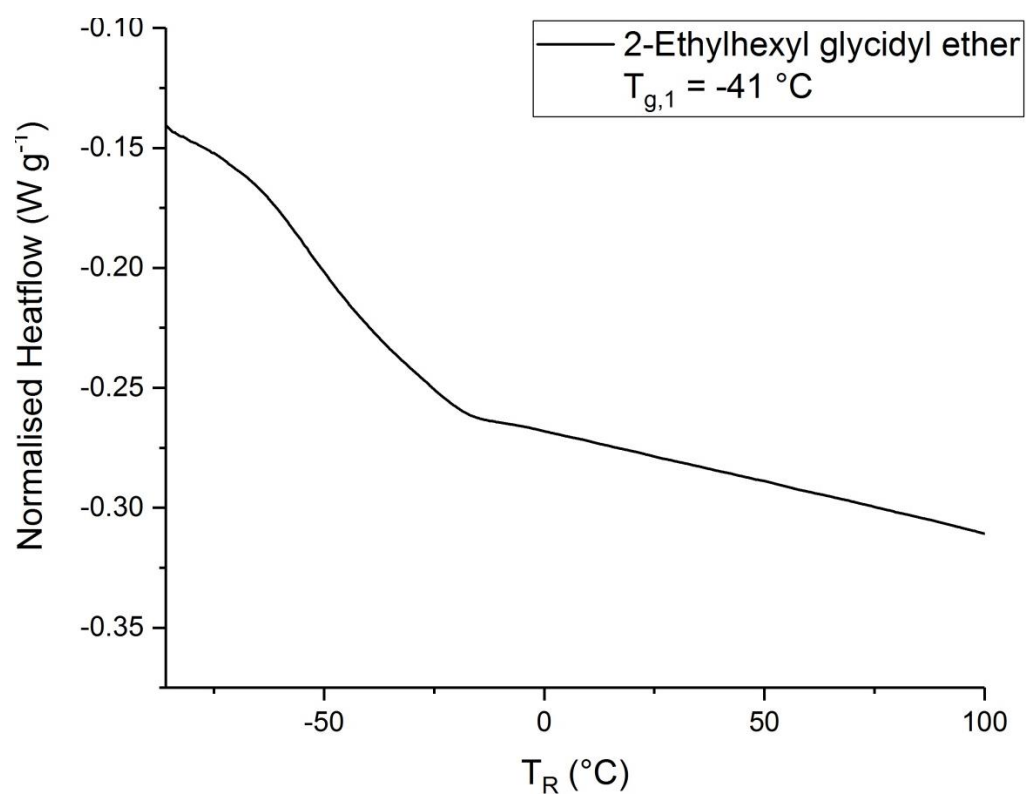
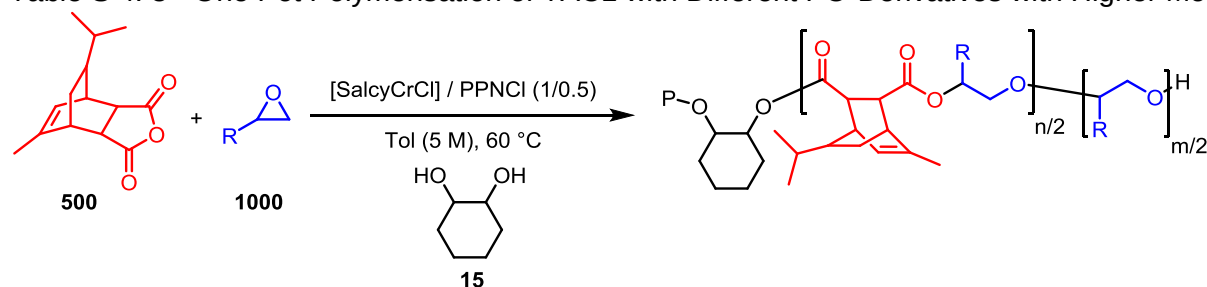


Figure S 4. 18 - DSC Thermogram for polymer based on 2-ethylhexyl glycidyl ether / TCA1.

Table S 4. 3 - One Pot Polymerisation of TAC1 with Different PO-Derivatives with Higher Monomer Loading.



Epoxide	Shift Epoxide Shift TCA1 (¹ H NMR)	Conversion (Epoxide to Homopolymer)	M _n (Đ)	T _g (°C)
 tert-Butyl glycidyl ether	2.64-2.60 (m) 1.04-1.00 (m)	4 d: 31 % 99 % 10 d: 69 % 99 % 15 d: 91 % 99 %	4d: 11,400 (1.10) 15d: 14,300 (1.21)	N. D.
 Styrene oxide	3.16-3.03 (m) 3.07-3.00 (m)	4 d: <5 % 99 % 10 d: 52 % 99 % 15 d: 57 % 99 %	4d: 8,500 (1.11) 15d: 8,300 (1.16)	34 88
 2-6nyloxirane	3.37-3.27 (m) 3.21-3.16 (m)	4 d: 64 % 99 % 15 d: >95 % 99 %	4d: 9,700 (1.10) 15d: 9,800 (1.10)	26 90
 Allyl glycidyl ether	3.45-3.35 (m) 1.04-1.00 (m)	4 d: 80 % 99 % 15 d: >95 % 99 %	4d: 31,600 (1.03) + 13,700 (1.13) 15d: 31,200 (1.05) + 13,200 (1.14)	17 ^s 101 ^s
 2-Ethylhexyl glycidyl ether	2.64-2.59 (dd) or 2.88-2.75 (dd) 1.04-1.00 (m)	4 d: 31 % 99 % 15 d: >95 % 99 %	4d: 13,900 (1.13) 15d: 15,900 (1.20)	N. D.

^s An insoluble material, most likely due to cross-linking, was obtained after 1solation.

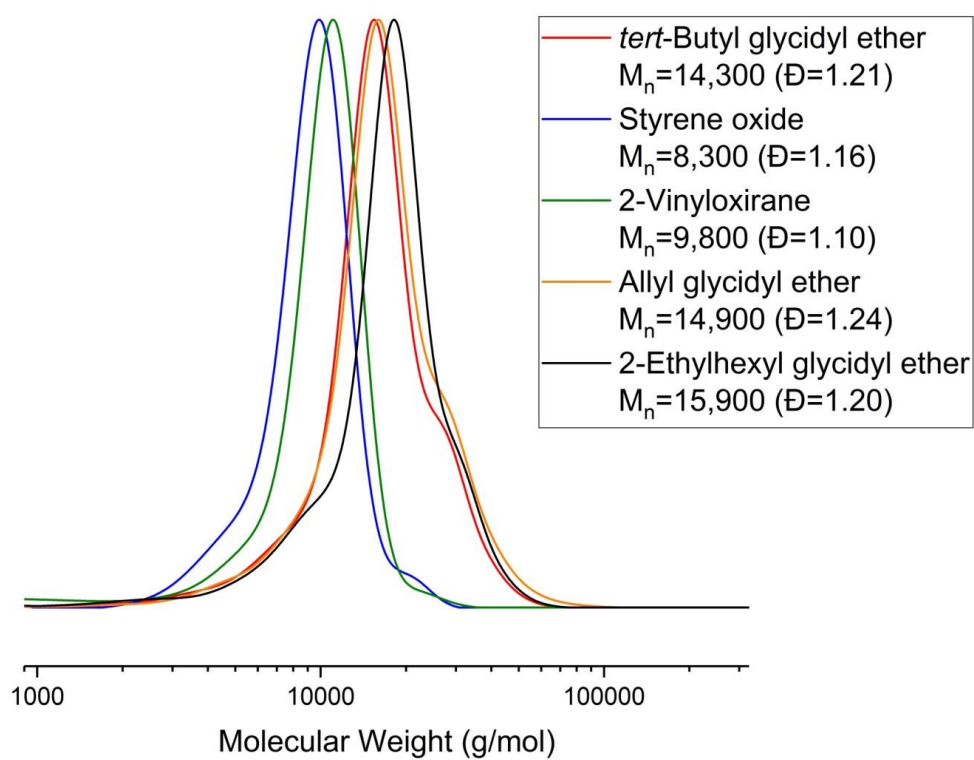
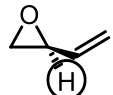
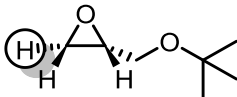
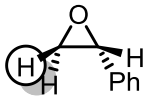
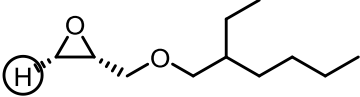
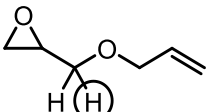


Figure S 4. 19 – GPC traces of one-pot reactions of different epoxides with TCA1.

Table S 4. 4 - Synthesis of Homo- and Blockcopolymers with different Epoxides

Epoxide	Starting Material	Shift Epoxide Shift TCA1 (¹ H NMR)	Conversion (Epoxide Anhydride)	M _n (Đ)
 2-6nyloxirane	vPO (200 equiv.)	3.37-3.27 (m) 2.83-2.56 (m)	99 % (5d)	1,350 (1.17)
	vPO + TCA1 (200 : 200)		> 95 % > 95 % (3d)	4,600 (1.12)
	vPO + TCA1 (400 : 200)		> 95 % > 95 % (3d)	6,000 (1.12)
 tert-Butyl glycidyl ether	BGE (200 equiv.)	2.64-2.60 (m) 1.04-1.00 (m)	83 % (5 d)	1,700 (1.08)
	BGE + TCA1 (200 : 200)		81 % 83 % (3d) UPDATE	5,000 (1.11)
	BGE + TCA1 (400 : 200)		> 95 % > 95 % (5 d)	6,600 (1.10)
 Styrene oxide	SO (200 equiv.)	3.16-3.03 (m) 3.07-3.00 (m)	27 % (5 d)	400 (1.06)
	SO + TCA1 (200 : 200)		95 % 93 % (3 d)	4,800 (1.12)
	SO + TCA1 (400 : 200)		90 % > 95 % (5 d)	5,200 (1.11)
	SO + TCA1 (400 : 200)		> 95 % 50 % (5 d)	5,200 (1.14)
 2-Ethylhexyl glycidyl ether	EHGE (200 equiv.)	2.64-2.59 (dd) or 2.88-2.75 (dd) 1.04-1.00 (m)	> 95 % (5d)	3,000 (1.08)
	EHGE + TCA1 (200 : 200)		> 95 % > 95 % (3d)	6,800 (1.11)
	EHGE + TCA1 (400 : 200)		> 95 % > 95 % (5 d)	10,100 (1.11)
 Allyl glycidyl ether	AGE + TCA1 (200 equiv.)	3.45-3.35 (m) 1.04-1.00 (m)	> 95 % (5d)	2,000 (1.07)
	AGE + TCA1 (200 : 200)		> 95 % > 95 % (3d)	5,000 (1.12)
	AGE + TCA1 (400 : 200)		> 95 % > 95 % (5d)	7,600 (1.11)
PO	PO + TCA1 (200 equiv.)	3.25-3.14 2.79-2.73	> 95 % (5d)	1,400 (1.10)
	PO + TCA1 (200 : 200)		93 % > 95 % (3d)	4,700 (1.10)
	PO + TCA1 (400 :		> 95 % > 95 % (5 d)	6,000 (1.11)

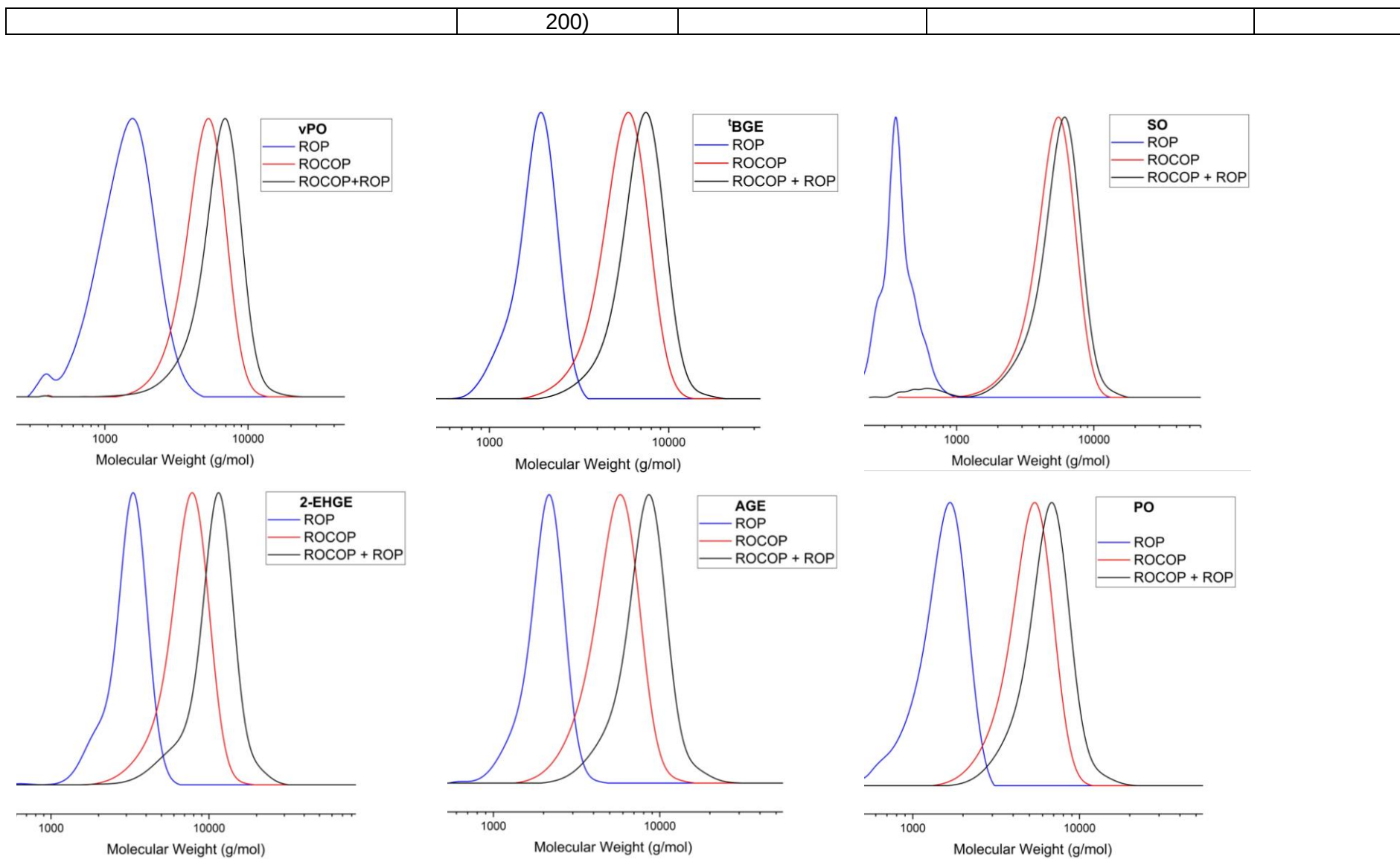
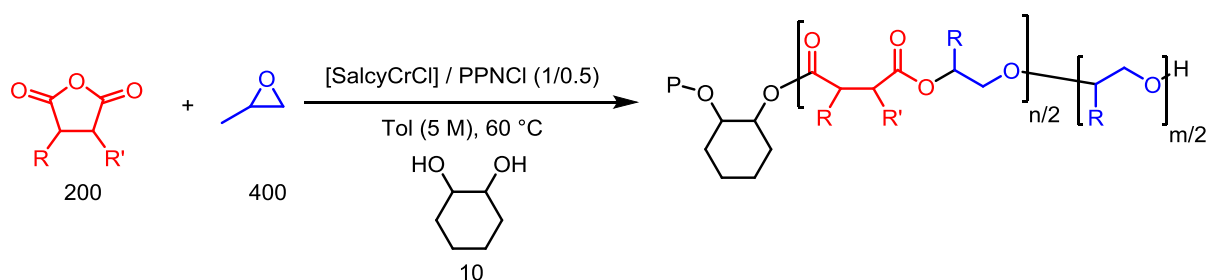
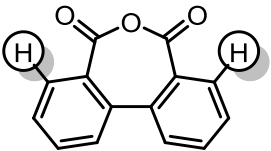


Figure S 4. 20 - GPC Traces of polyethers (blue), polyesters (Red) and polyester-*b*-polyethers (black) with different PO derivatives.

Table S 4. 5 - Anhydride Scope and used ^1H NMR Shifts

Anhydride	Shift Anhydride (^1H NMR)	Time (d)	Conversion		M_n (Đ)
			Anhydride	PO ^[b]	
	7.05 – 6.95 ppm	3 d	99 %	63 %	5,800 (3.11)
		5 d	99 %	67 %	
	3.07 - 2.91 ppm	3 d	99 %	> 95 %	5,400 (1.85)
	2.05 - 2.00 ppm*	3 d	> 95 %	> 95 %	1,700 (1.54)
	4.48 – 4.35 ppm	3 d	99 %	> 95 %	2,100 (2.14)
	1.02 – 0.98 ppm	3 d	82 %	> 95 %	6,100 (1.18)
	8.05 – 7.99 ppm	3 d	99 %	> 95 %	7,800 (1.54)
	6.04 – 5.92 ppm [#]	3 d	99 %	> 95 %	5,100 (1.34)
	1.46 – 1.41 ppm	3 d	> 95 %	> 95 %	5,800 (1.19)

	7.77 – 7.68 ppm [#]	3 d	99 %	> 95 %	5,700 (1.20)
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^[b] Conversion based on integrals in ¹H NMR spectrum at $\delta = 3.03 - 2.97$ ppm of crude mixture and given with respect to the formation of polyether (i. e. $100 * 1 - \text{Integral}(t=x) / (\text{Integral}(t=0) * 0.5)$)

* Partial overlap of anhydride and polyester signals.

[#] Integral between $\delta = 2.80 - 2.73$ ppm used for PO conversion.

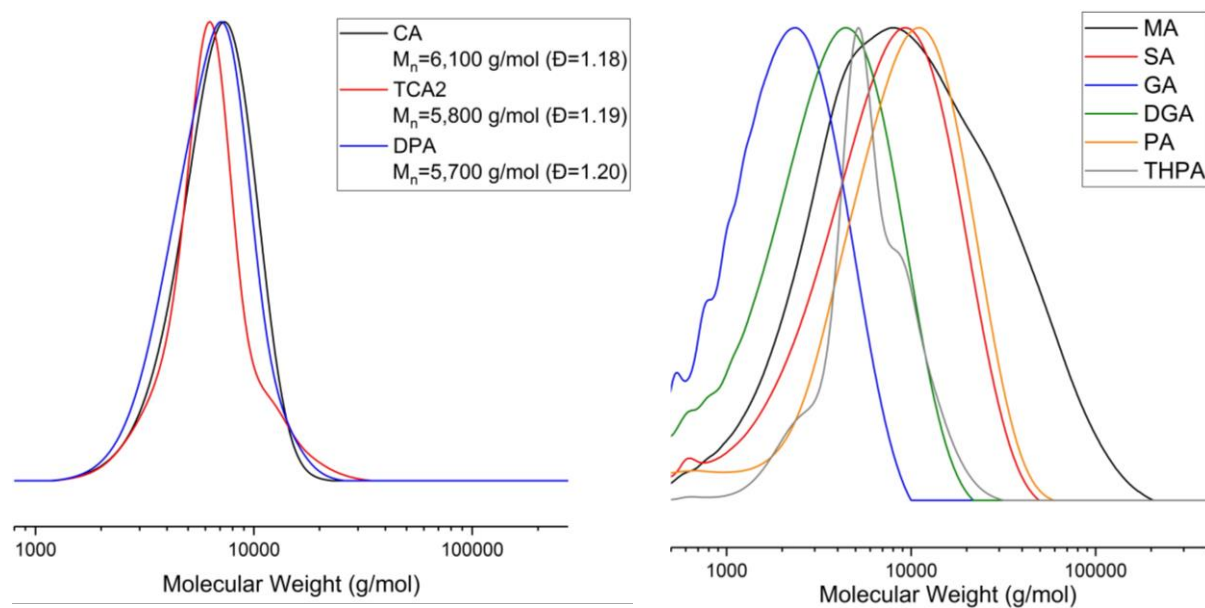
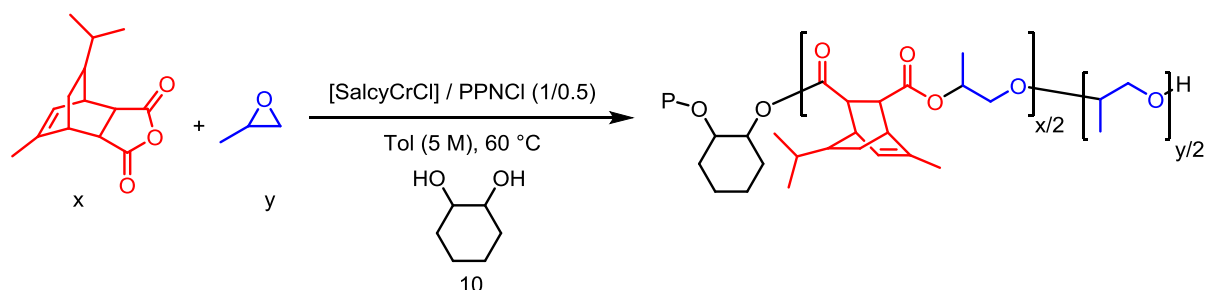


Figure S 4. 21 – GPC Traces of the one-pot polymerization of different anhydrides with PO.

One Pot Polymerisation of TCA1/PO with Increased Monomer Loadings

Table S 4. 6 – Polymerisation of TCA1/PO with different monomer loadings and 10 equiv. of CHD.



TCA1:PO ^[1]	Rct-time	Conversion[%] ^[2] PO TCA1	PE:PPO [mol%] ^[3]	M _n (Đ) [g/mol] ^[4]	T _g [°C] ^[5]
100:200	2d	95 % 99 %	51:49	3,400 (1.12)	N. D. [#]
200:400	5d	90 % 99 %	53:47	6,700 (1.12)	41 °C
300:600	5d	96 % 99 %	51:49	11,100 (1.09)	37 °C
400:800	5d	97 % 99 %	51:49	15,400 (1.14)	39 °C 66 °C
400:800	5d	97 % 99 %	51:49	13,900 (1.14)	38 °C

^[1]Molar ratio with respect to catalyst. ^[2]Based on ¹H NMR spectroscopy. The following chemical shifts were used: 1.04-1.00 ppm (TCA1), 3.72-3.25 ppm (PPO; the conversion was calculated based on the theoretical maximum conversion of PO). ^[3]Based on ¹H NMR spectroscopy of crude sample. PE content was calculated based on shifts for PE (5.85-5.55, HC=C) and PPO (3.72-3.25 ppm), i. e. Integral PE/(Integral PE+Integral PPO/3). ^[4]Measured by GPC (30 °C, THF) with narrow polystyrene standards. ^[5]Measured by DSC, 3rd heating cycle.

* Unsublimed TCA1 used.

Soluble in Pentane (not isolated).

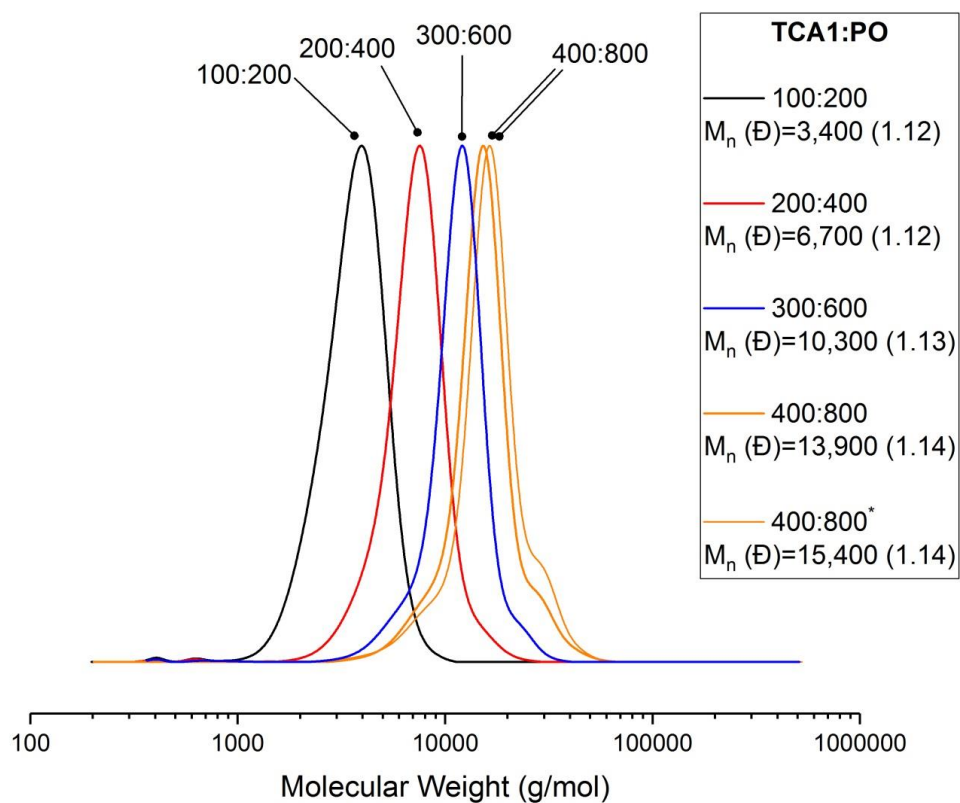


Figure S 4. 22 – TCA1/PO 'Switch' catalysis with different monomer:catalyst loadings.

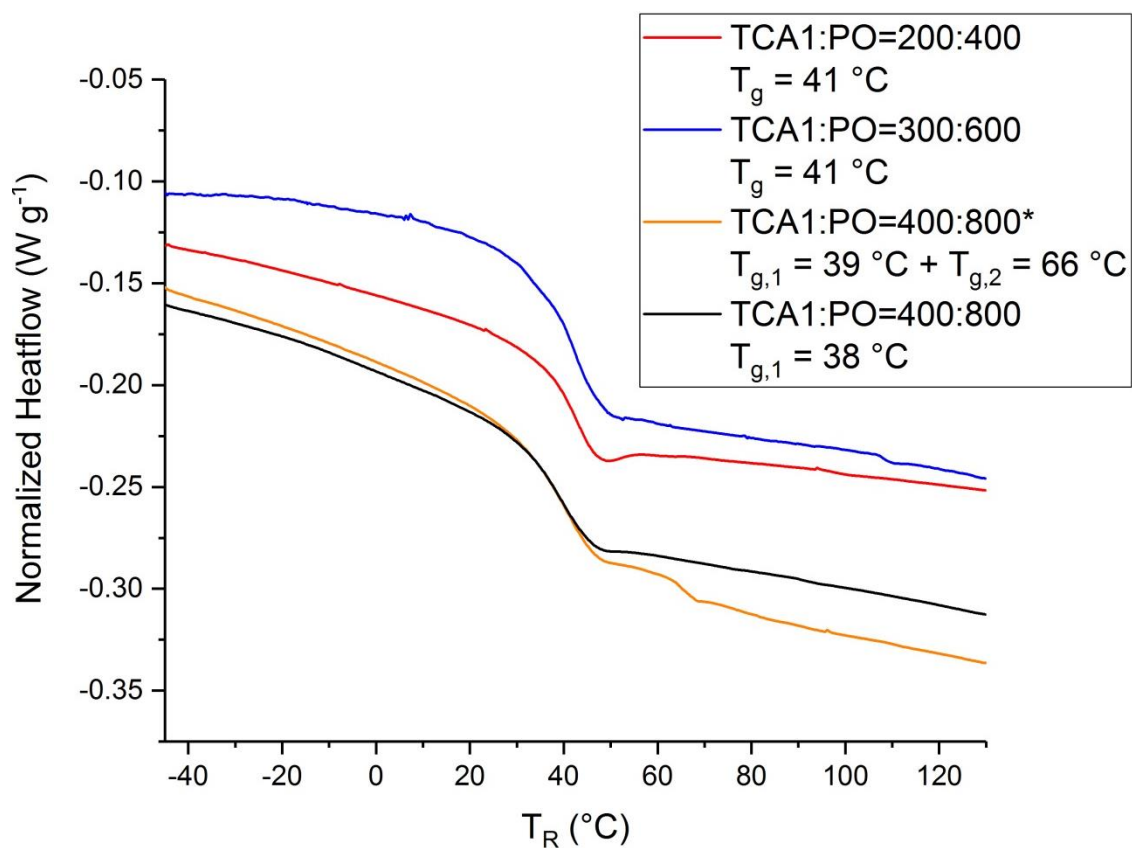


Figure S 4. 23 – DSC Thermograms of polymers based on different TCA1/PO ratios.

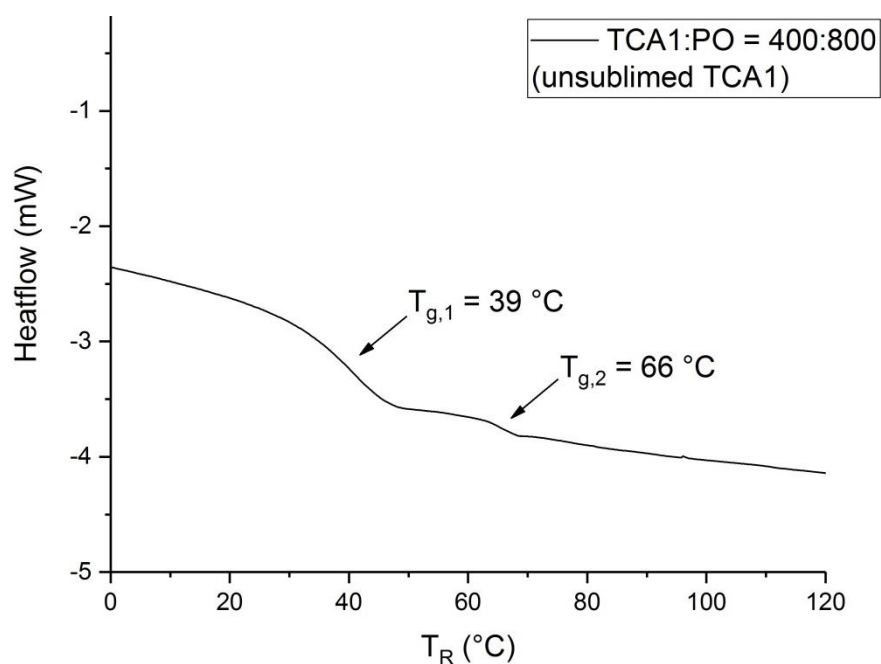
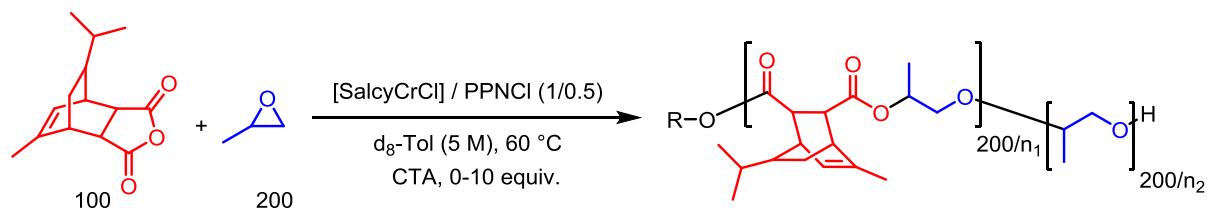


Figure S 4. 24 – DSC Thermogram of polymer obtained from TCA1:PO = 400:800.

Table S 4. 7 – One-pot polymerization of TCA1/PO with various amounts of *iso*-propanol as CTA.

CTA (equiv.)	Rct-time	Conversion[%] ^[2] PO TCA1	M _n (Đ) [g/mol] ^[4]	T _g [°C] ^[5]
0	2d	89 % 99 %	54,900 (1.04) 26,000 (1.04)	N. D.
0	2d	88 % 99 %	48,200 (1.03) 23,200 (1.04)	43 °C 92 °C
2	2d	78 % 99 %	28,700 (1.02) 13,300 (1.04)	45 °C 92 °C
4	2d	85 % 99 %	20,100 (1.01) 8,800 (1.05)	42 °C 92 °C
6	2d	74 % 99 %	5,100 (1.08)	38 °C 93 °C
8	2d	79 % 99 %	4,500 (1.08)	29 °C 89 °C
10	2d	90 % 99 %	3,500 (1.09)	N. D. [#]

* Reaction in absence of 2,6-di-tert-butylpyridine; # highly soluble polymer obtained (not isolated).

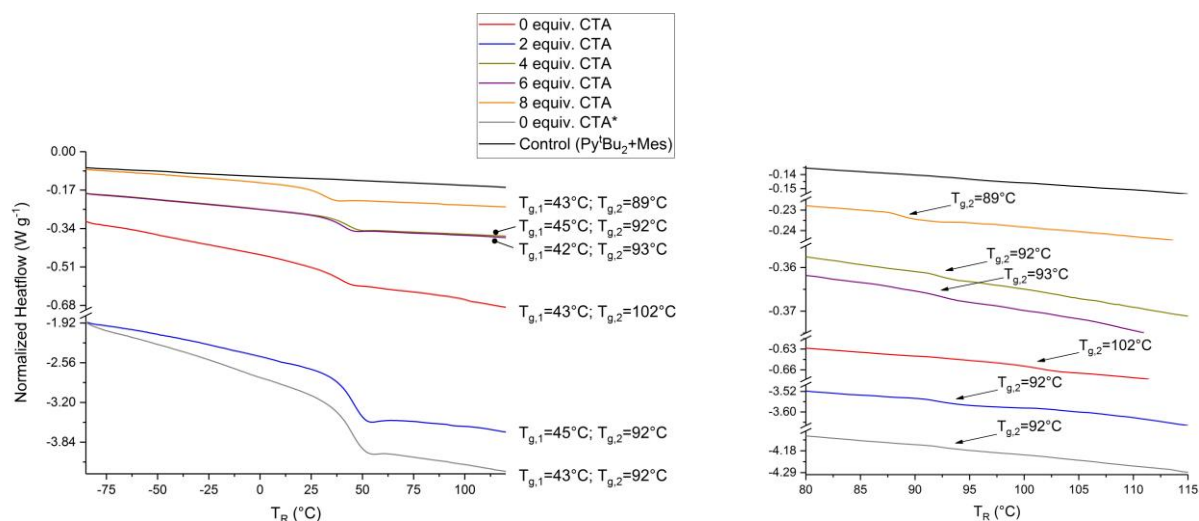


Figure S 4. 25 - DSC Thermograms for polymer obtained from TCA1/PO with different amounts of *iso*-propanol. The transitions at high temperatures were assigned to catalyst residues (see below).

GPC Traces and DSC Thermograms of PPO

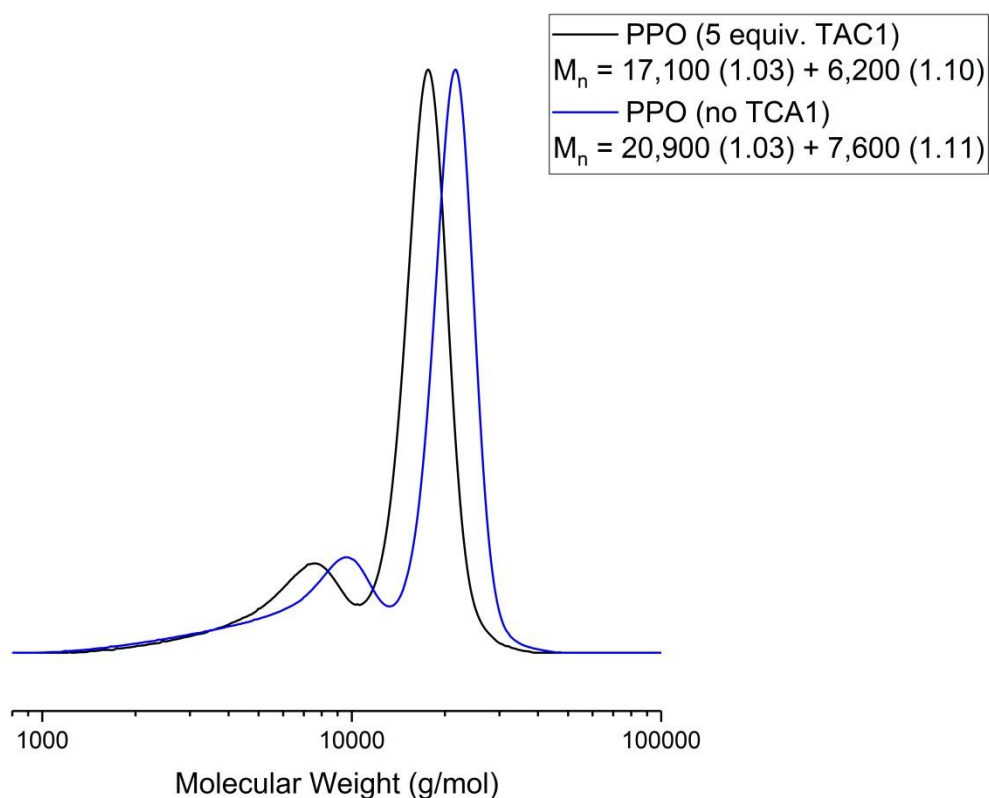


Figure S 4. 26 – GPC Traces of PPO samples in the presence of TCA1 (5 equiv., black) and the absence of TCA1 (blue).

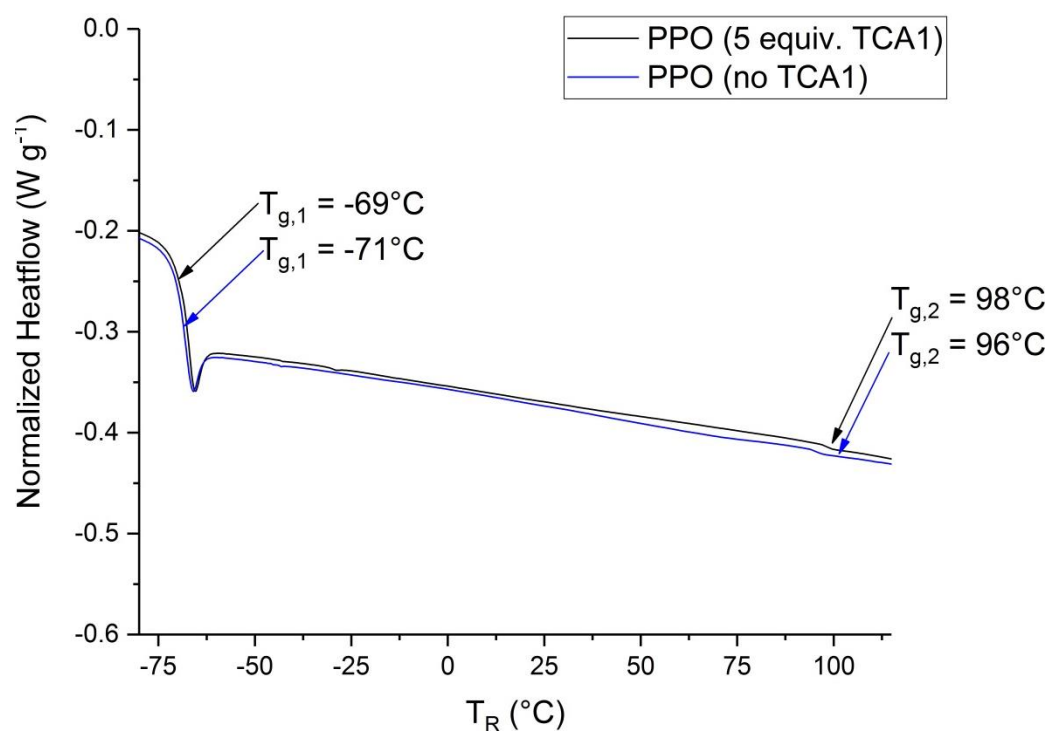


Figure S 4. 27 - DSC Thermograms of PPO samples (with 5 equiv. of TCA1 [black] and in the absence of TCA1 [blue]).

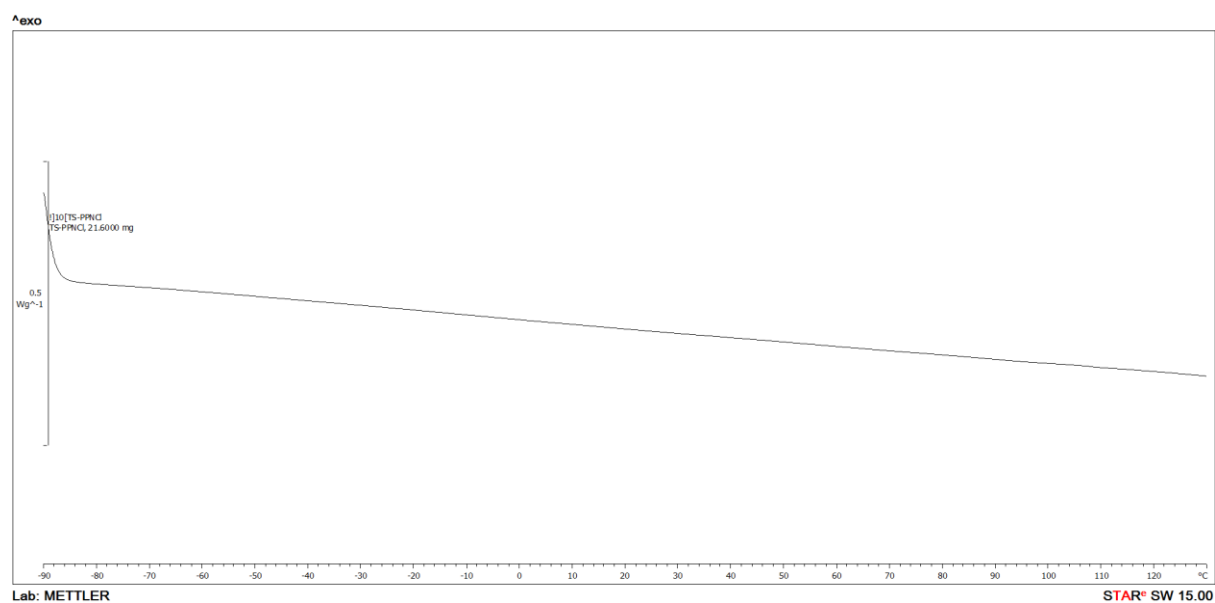


Figure S 4. 28 - DSC Thermogram PPNCI.

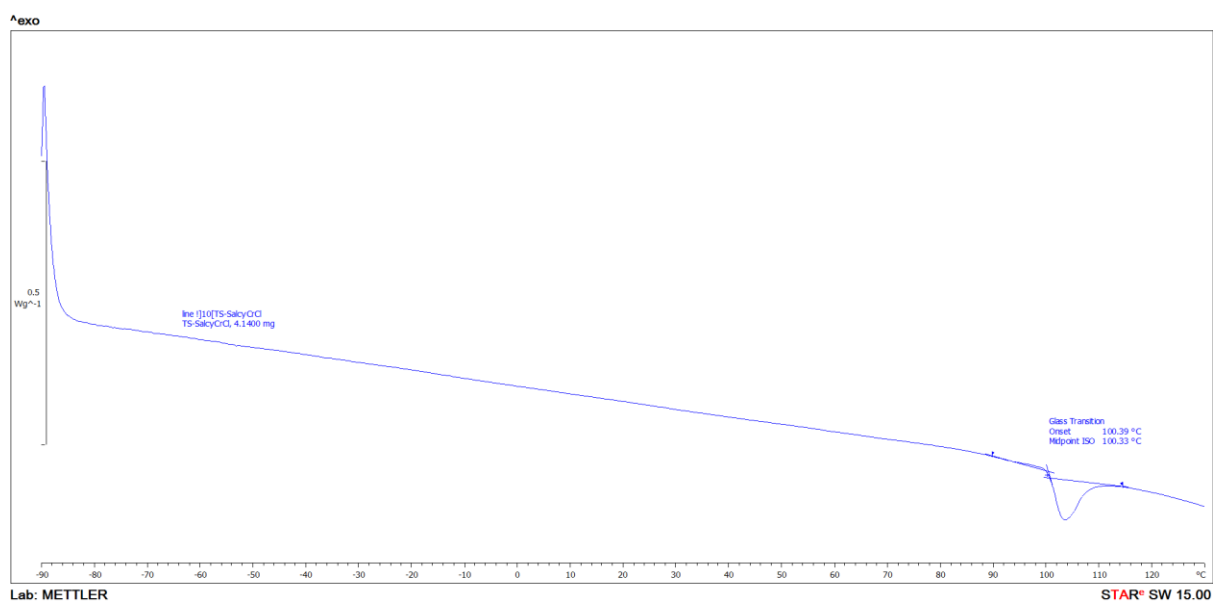


Figure S 4. 29 - DSC Thermogram [SalcyCrCl].

GPC Traces and DSC Thermograms with different alcohols (10 equiv.)

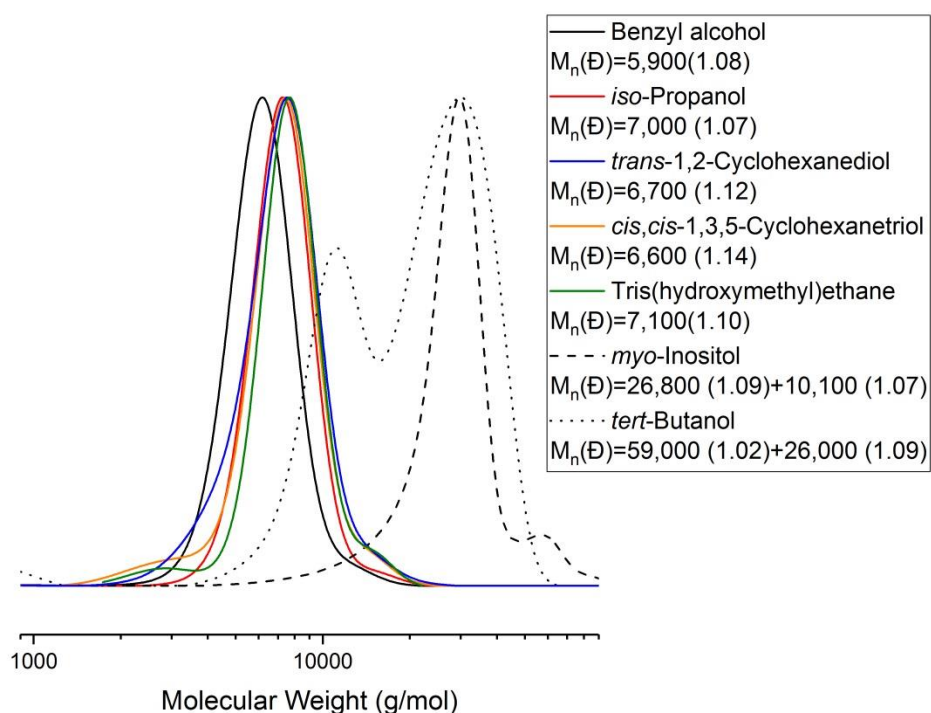


Figure S 4. 30 – GPC traces of TCA1/PO ‘Switch’ catalysis with selected alcohols.

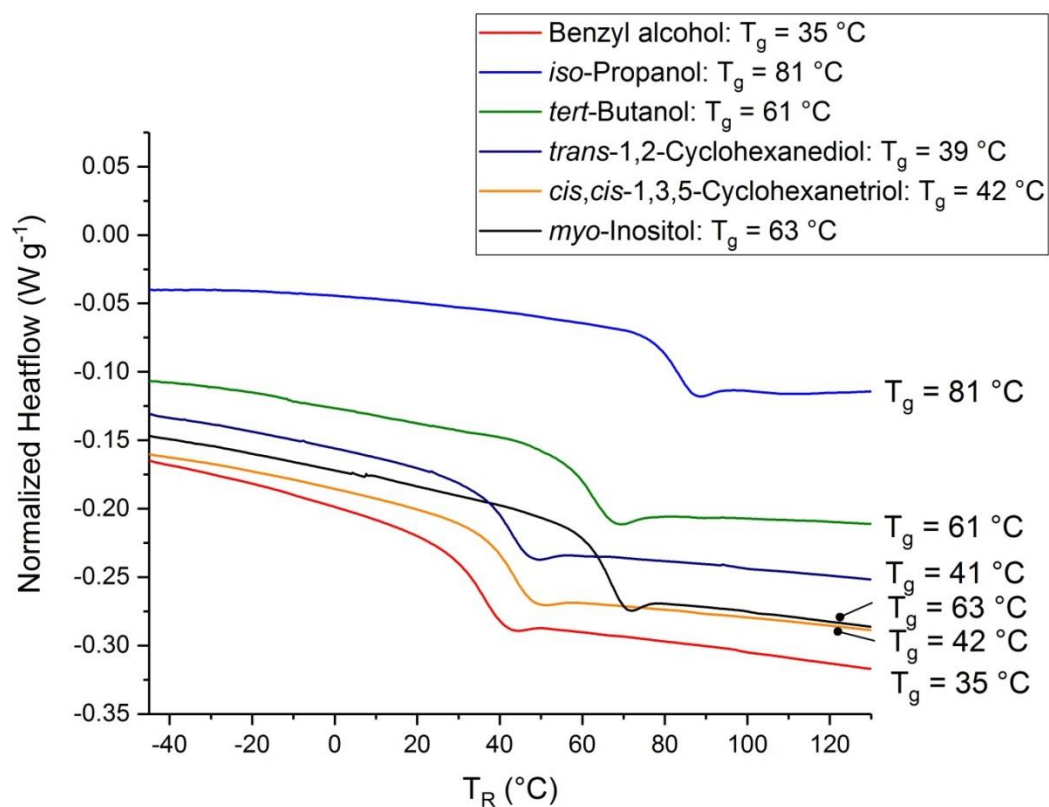
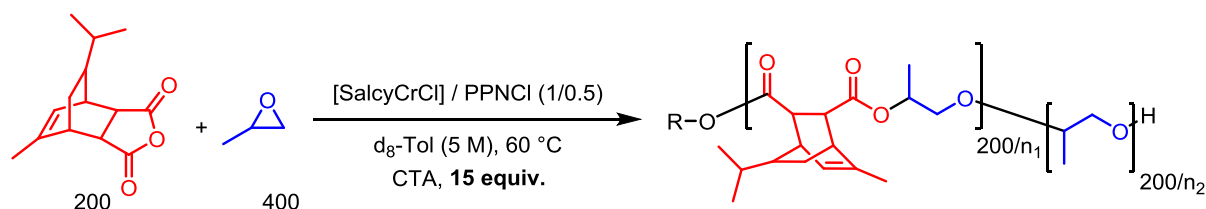
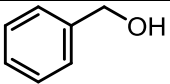
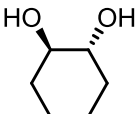
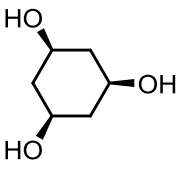
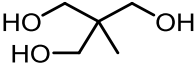


Figure S 4. 31 - DSC thermograms of TCA1/PO 'Switch' catalysis with selected alcohols.

One Pot Polymerisation of TCA1/PO with different alcohols (15 equiv.)

Table S 4. 8 – Polymerisation of TCA1/PO with different alcohols (15 equiv.)



CTA (10 equiv.) ^[1]	Rct-time	Conversion[%] ^[2] PO TCA1	PE:PPO [wt%] ^[3]	M _n (Đ) [g/mol] ^[4]	T _g [°C] ^[5]
 Benzyl alcohol	5d	> 95 99	83	4,500 (1.09)	30 °C 97 °C
 <i>iso</i> -Propanol	5d	> 95 99	83	5,200 (1.08)	28 °C 96 °C
 <i>trans</i> -1,2-Cyclohexanediol	5d	> 95 99	83	4,900 (1.13)	34 °C 94 °C
 <i>cis,cis</i> -1,3,5-Cyclohexanetriol	5d	> 95 99	83	5,700 (1.12)	31 °C 95 °C
 1,1,1-Tris(hydroxymethyl)ethane	5d	94 99	83	5,500 (1.13)	28 °C 92 °C

^[1]Molar ratio with respect to catalyst. ^[2]Based on ¹H NMR spectroscopy. The following chemical shifts were used: 1.04-1.00 ppm (TCA1), 3.72-3.25 ppm (PPO; the conversion was calculated based on the theoretical maximum conversion of PO). ^[3]Based on ¹H NMR spectroscopy of crude sample. PE content was calculated based on shifts for PE (5.85-5.55, HC=C) and PPO (3.72-3.25 ppm), i. e. Integral PE/(Integral PE+Integral PPO/3). ^[4]Measured by GPC (30°C, THF) with narrow polystyrene standards. ^[5]Measured by DSC, 3rd heating cycle.

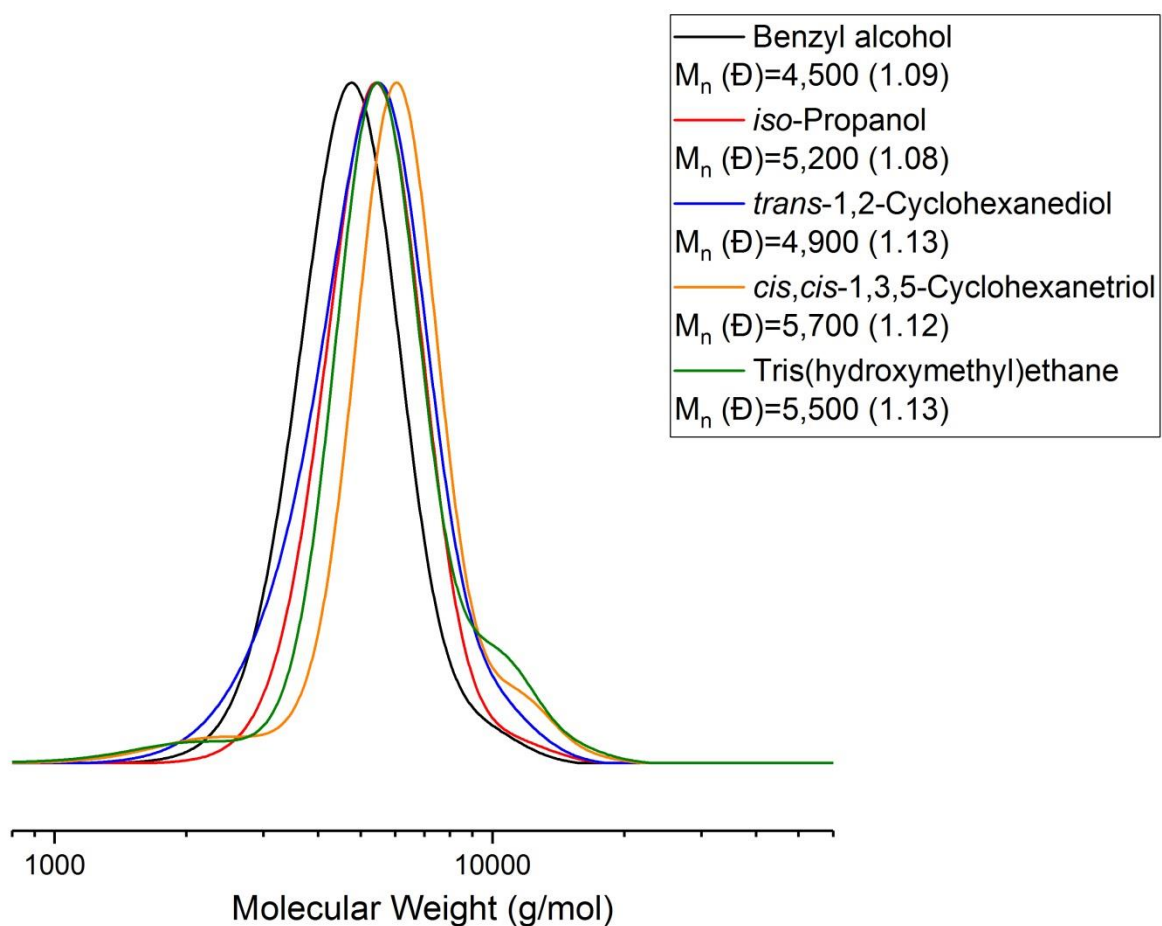


Figure S 4. 32 - GPC traces of TCA1/PO 'Switch' catalysis with selected alcohols.

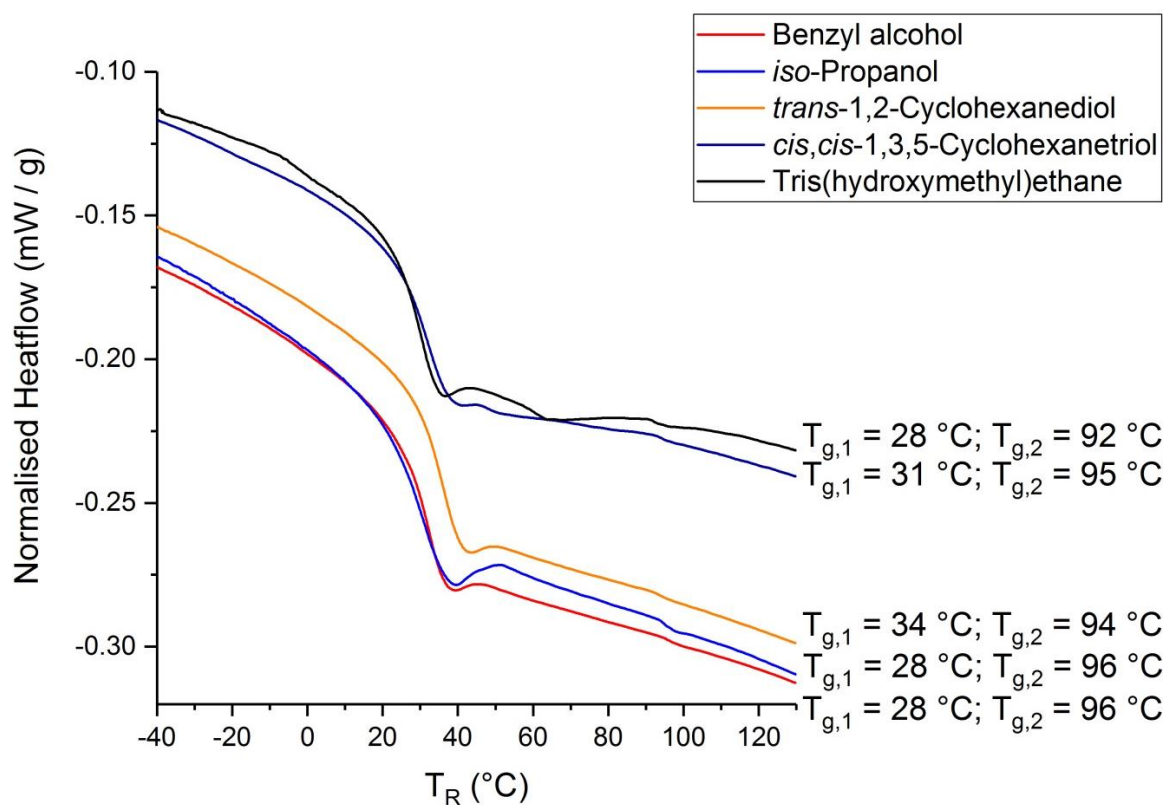
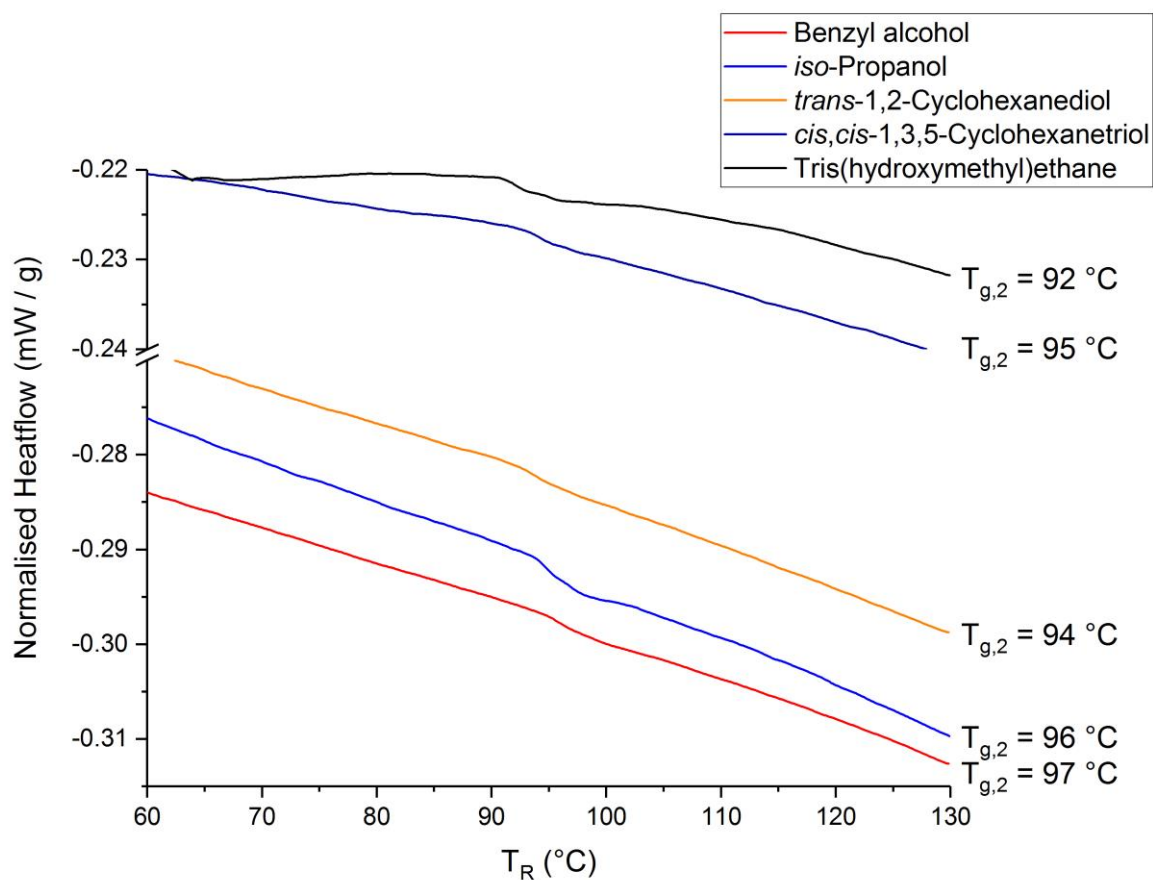
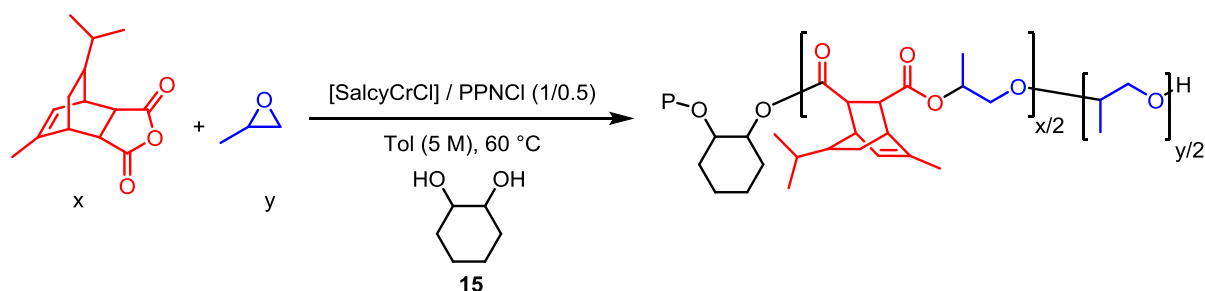


Figure S 4. 33 - DSC thermograms of TCA1/PO 'Switch' catalysis with selected alcohols. The full range is shown on top and the enlarged region (80 – 120 $^{\circ}\text{C}$) is shown on the bottom.

TCA1-PO: Higher LOADINGS 15 EQUIVALENTS CTA



Rct-No	TCA1:PO ^[1]	Rct-time	Conversion[%] ^[2] PO TCA1	PE:PPO [wt%] ^[3]	M _n (Đ) [g/mol] ^[4]	T _g [°C] ^[5]
549-A	100:200	2 d	95 99	51:49	3,400 (1.12)	N. D. [#]
549-B	200:400	5 d	90 99	53:47	6,700 (1.12)	41 °C
559-C	300:600	5 d	> 95 99	83:17	7,600 (1.13)	34 °C 94 °C*
559-D	400:800	5 d	> 95 99	83:17	22,300 (1.05) 9,900 (1.11)	37 °C 78 °C 109 °C
559-E	500:1000	5 d	94 99	83:17	26,200 (1.05) 11,800 (1.10)	34 °C 105 °C
565-A	600:1200	10 d	> 95 99	83:17	38,500 (1.06) 13,700 (1.23)	21 °C 88 °C
565-B	700:1400	10 d	> 95 99	83:17	38,900 (1.06) 14,600 (1.21)	24 °C 90 °C
565-C	800:1600	10 d	> 95 99	83:17	38,500 (1.07) 14,400 (1.21)	35 °C 88 °C
565-D	900:1800	10 d	> 95 99	83:17	21,500 (1.61)	23 °C 49 °C
565-E	1000:2000	10 d	> 95 99	83:17	54,200 (1.09) 18,200 (1.25)	

^[1]Molar ratio with respect to catalyst. ^[2]Based on ¹H NMR spectroscopy. The following chemical shifts were used: 1.04-1.00 ppm (TCA1), 3.72-3.25 ppm (PPO; the conversion was calculated based on the theoretical maximum conversion of PO). ^[3]Based on ¹H NMR spectroscopy of crude sample. PE content was calculated based on shifts for PE (5.85-5.55, HC=C) and PPO (3.72-3.25 ppm), i. e. Integral PE/(Integral PE+Integral PPO/3). ^[4]Measured by GPC (30°C, THF) with narrow polystyrene standards. ^[5]Measured by DSC, 3rd heating cycle.

* Weak Transition.

Soluble in Pentane (not isolated).

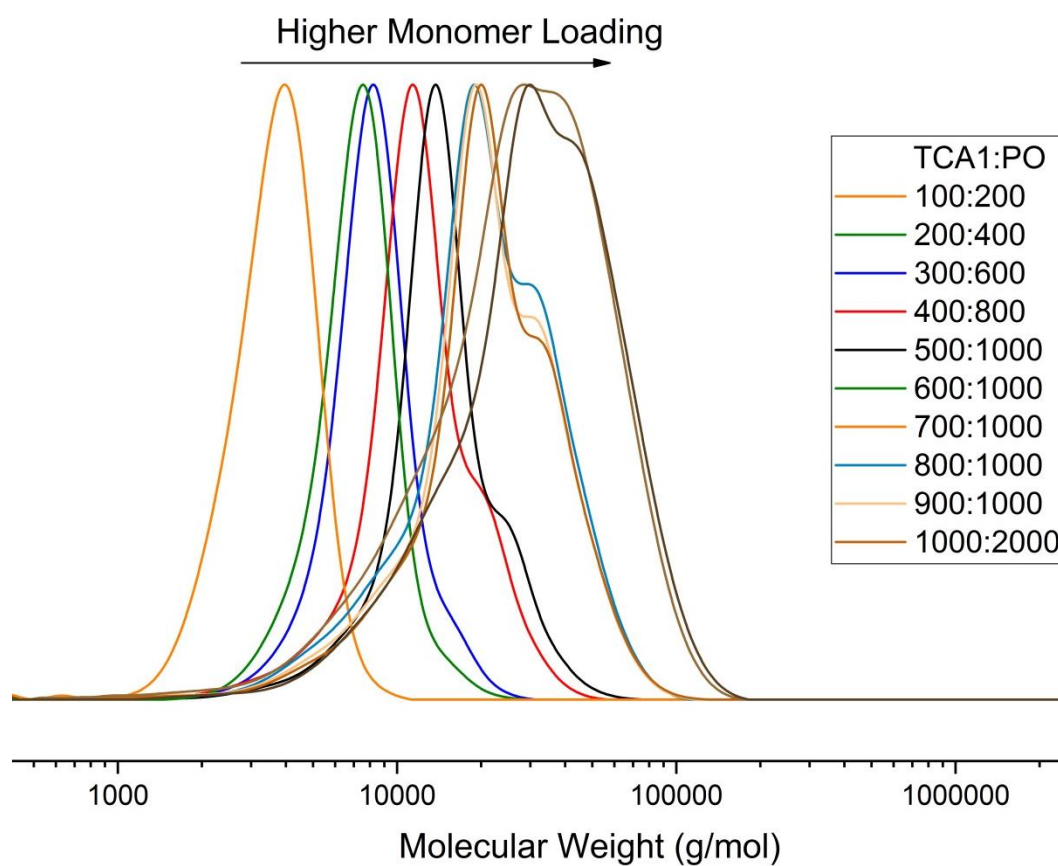


Figure S 4. 34 – GPC traces for Polymers with different monomer loadings.

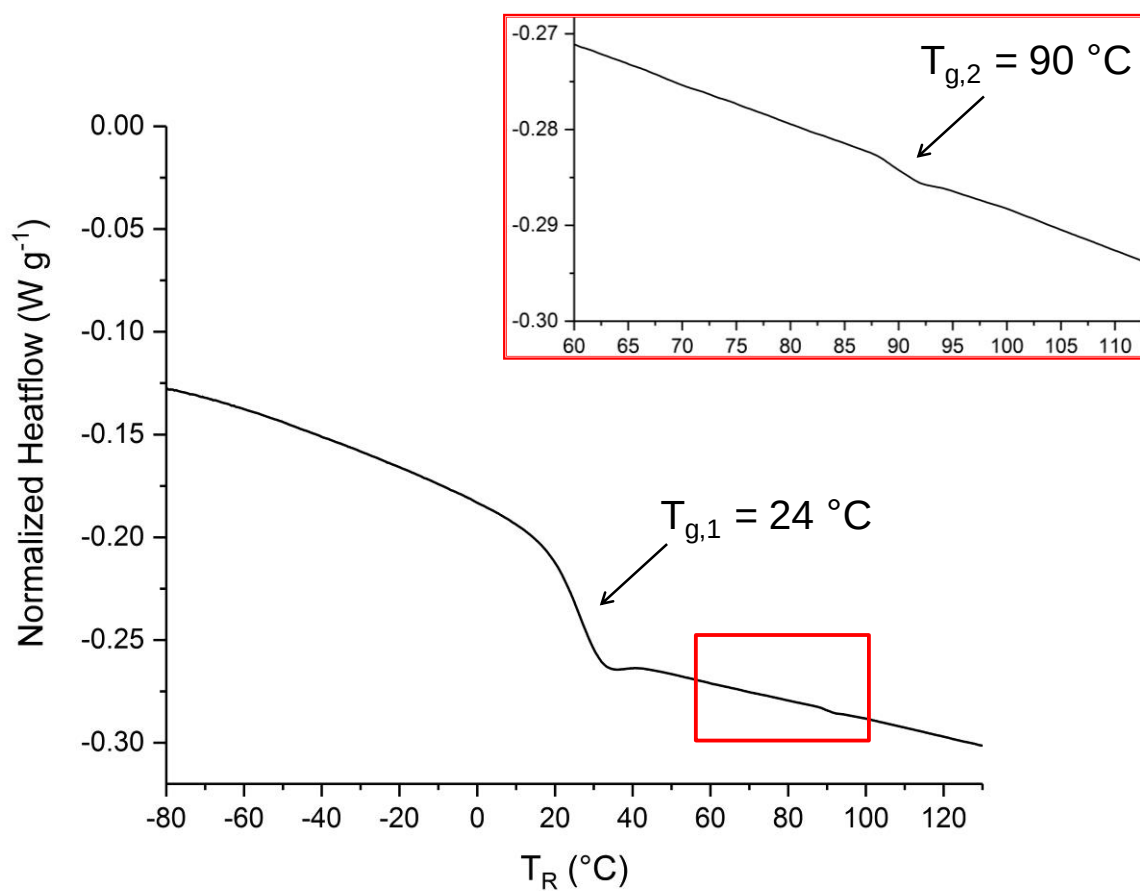
DSC Thermogram of multiblock copolymer based on TCA1/PO.

Figure S 4. 35 – DSC Thermogram of multiblock copolymer based on TCA1/PO. The second transition is ascribed to catalyst residues.

GPC Traces of Block Polymers with different Ratios

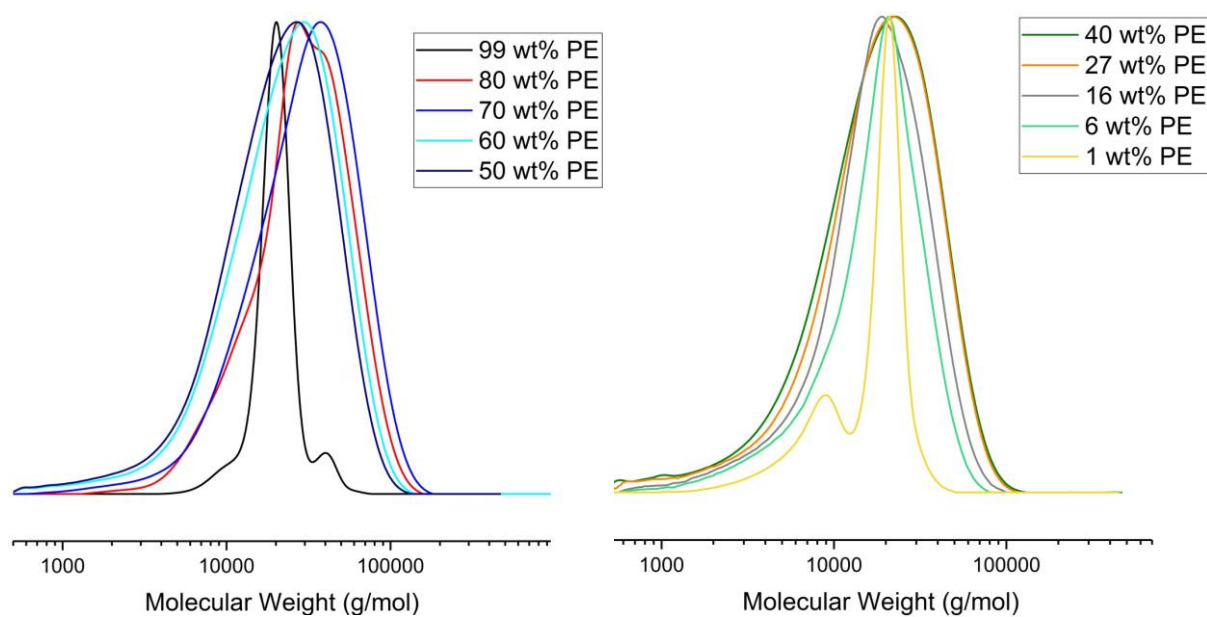


Figure S 4. 36 – GPC traces of polymers based on TCA1/PO with different block ratios.

DSC Thermogram of Polymer obtained from PO/TCA1/DL.

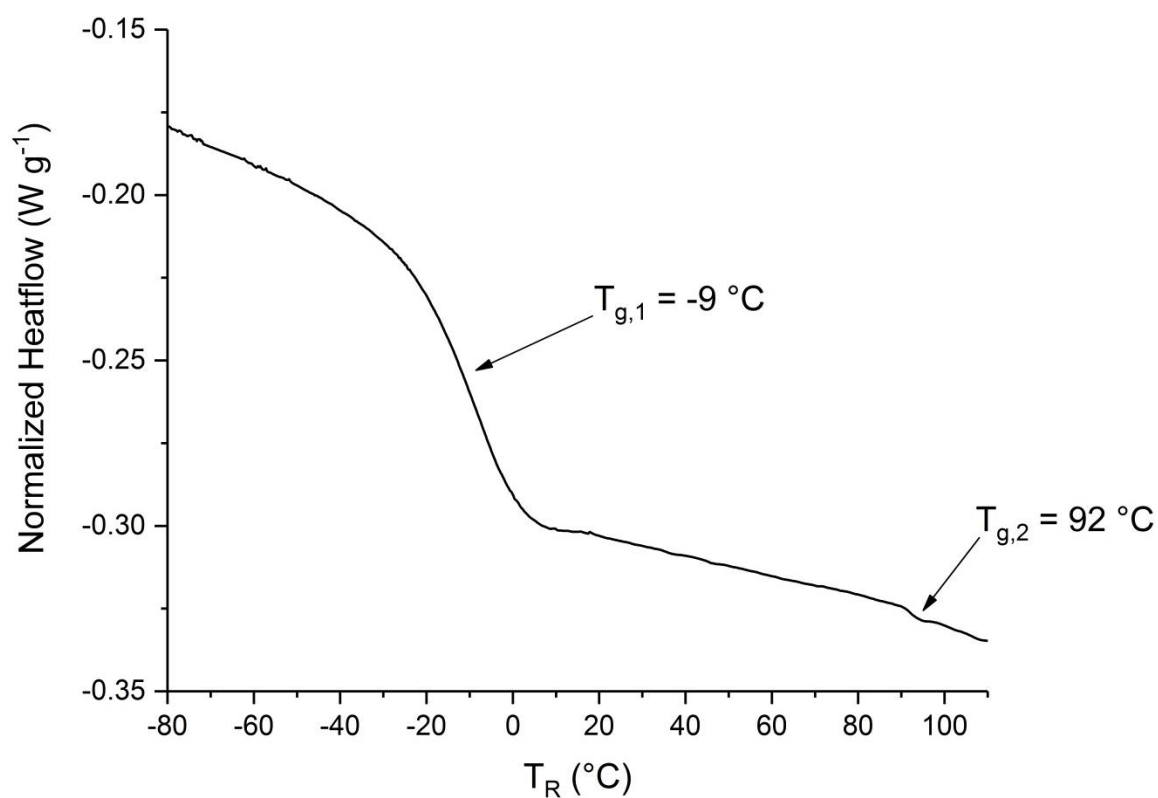


Figure S 4. 37 – DSC Thermogram of polymer obtained from PO/TCA1/DL. The transition at ca. 90 °C is ascribed to catalyst residues

NMR Data for Polymer obtained from PO/TCA1/DL

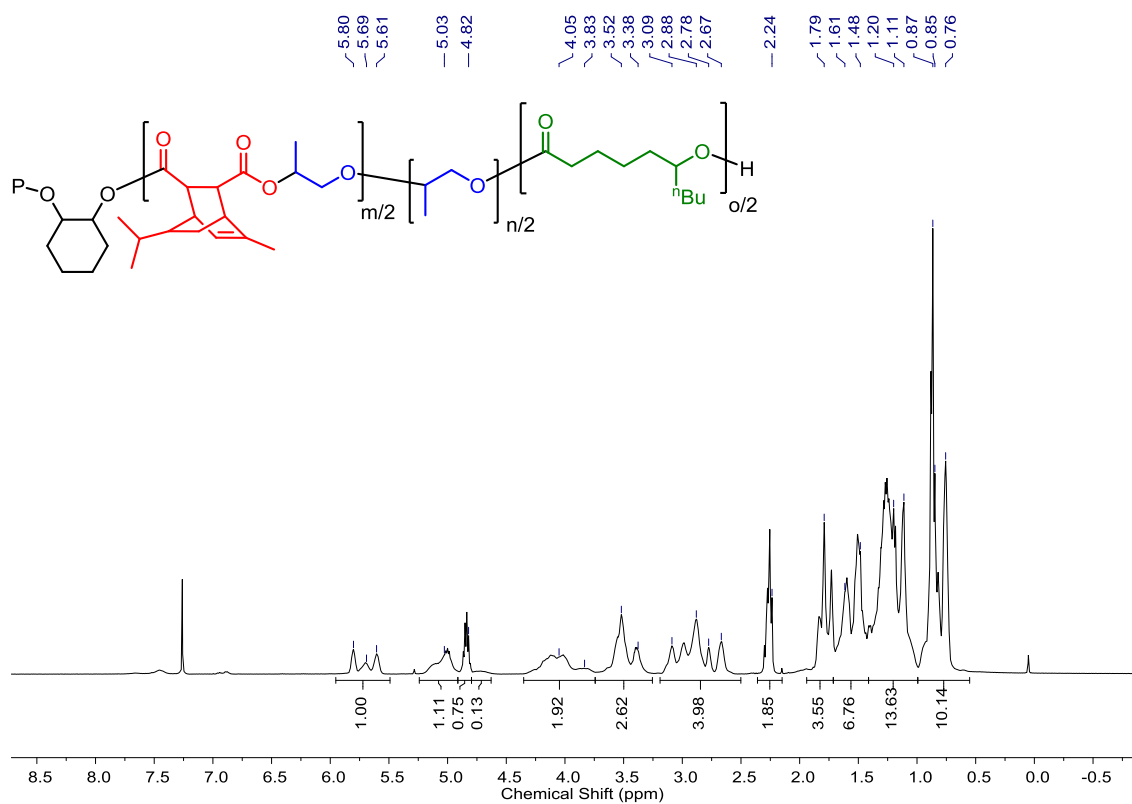


Figure S 4. 38 – ^1H NMR Spectrum for polymer obtained from PO/TCA1/DL.

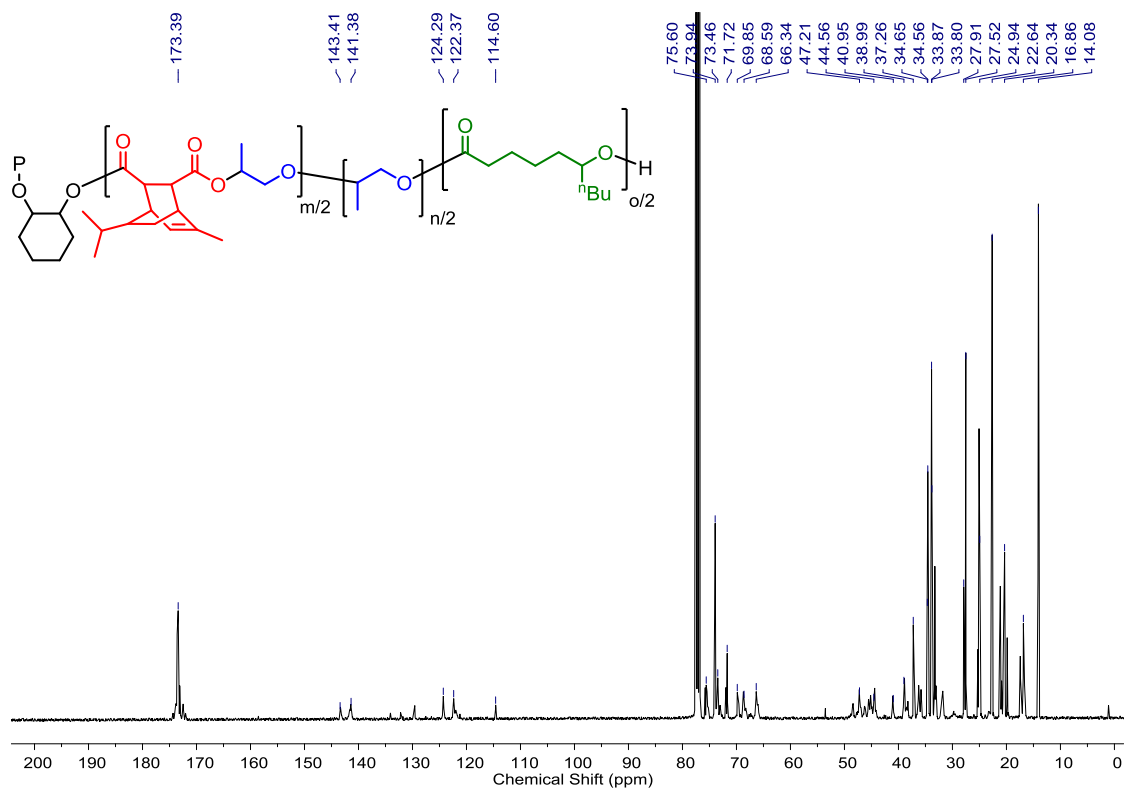
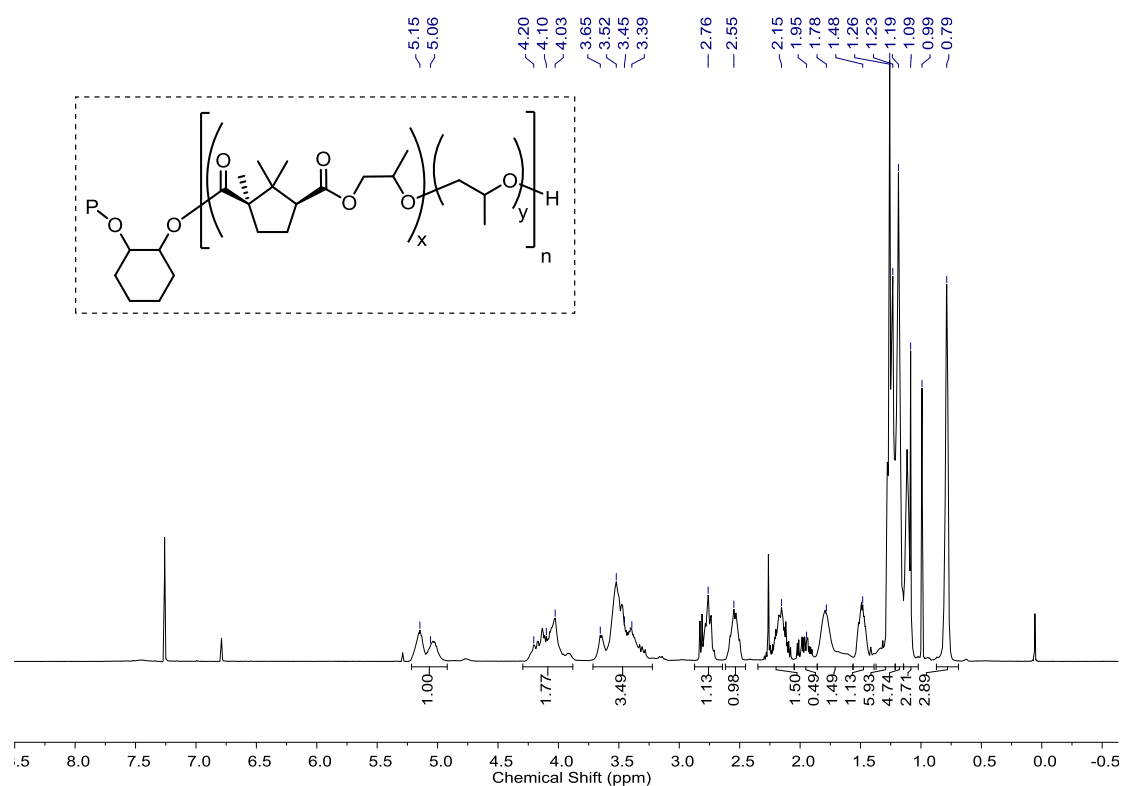
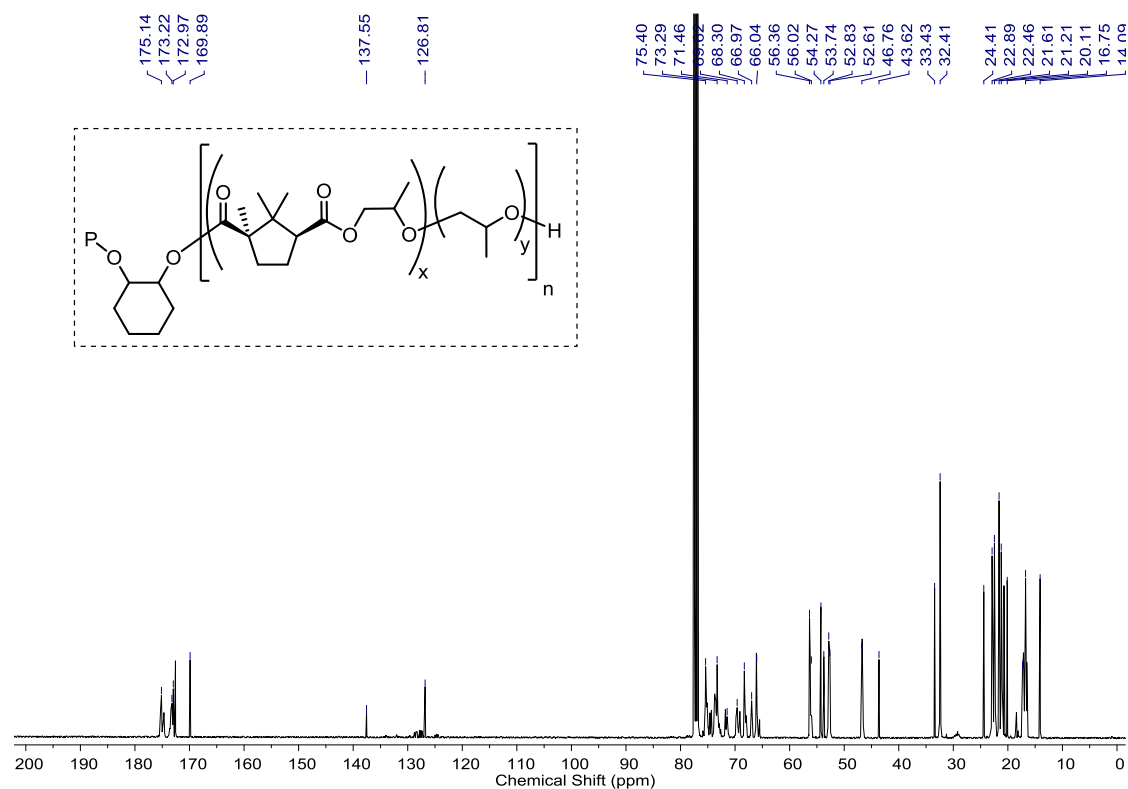
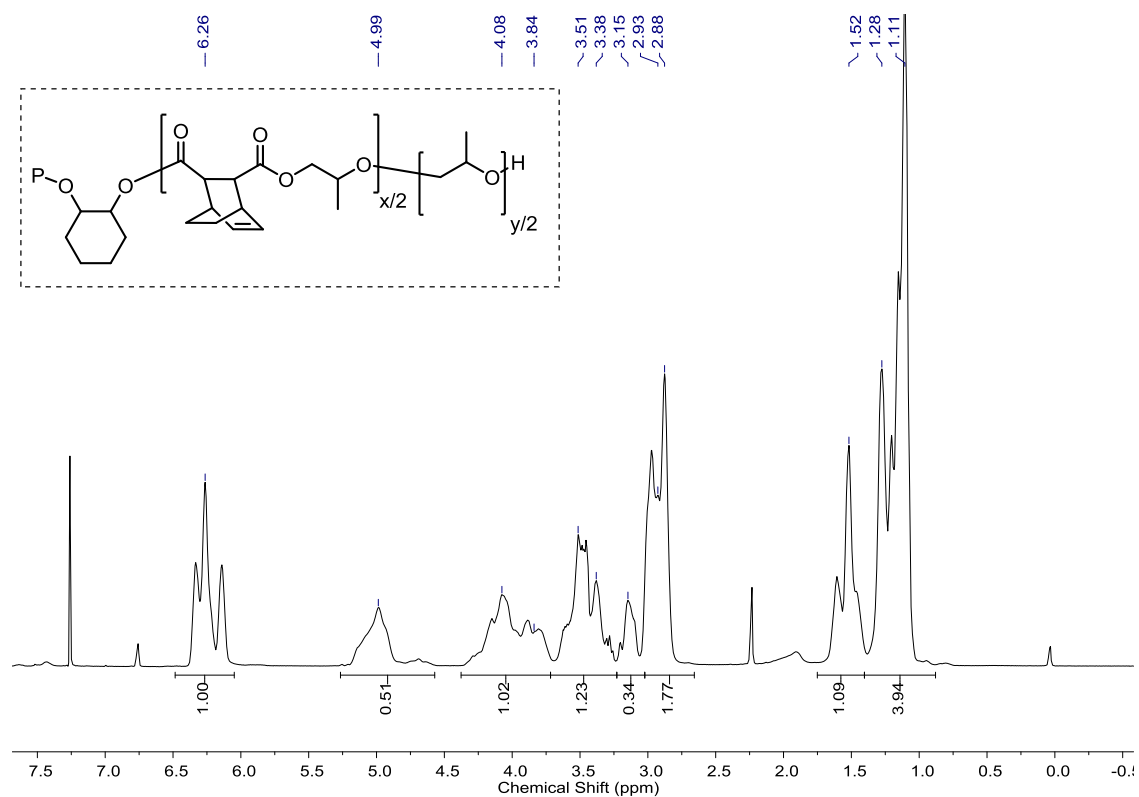


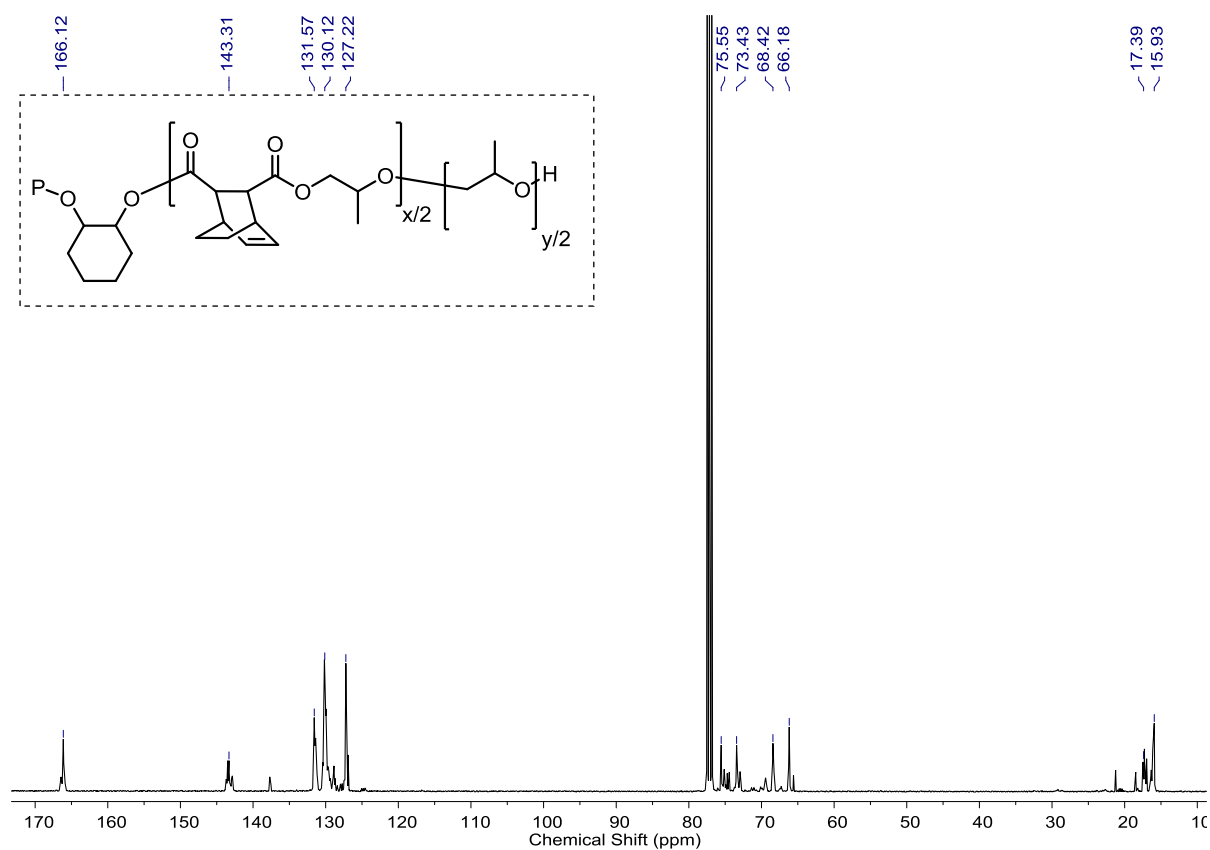
Figure S 4. 39 – $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum for polymer obtained from PO/TCA1/DL.

NMR Data for Polymer obtained from PO/CA

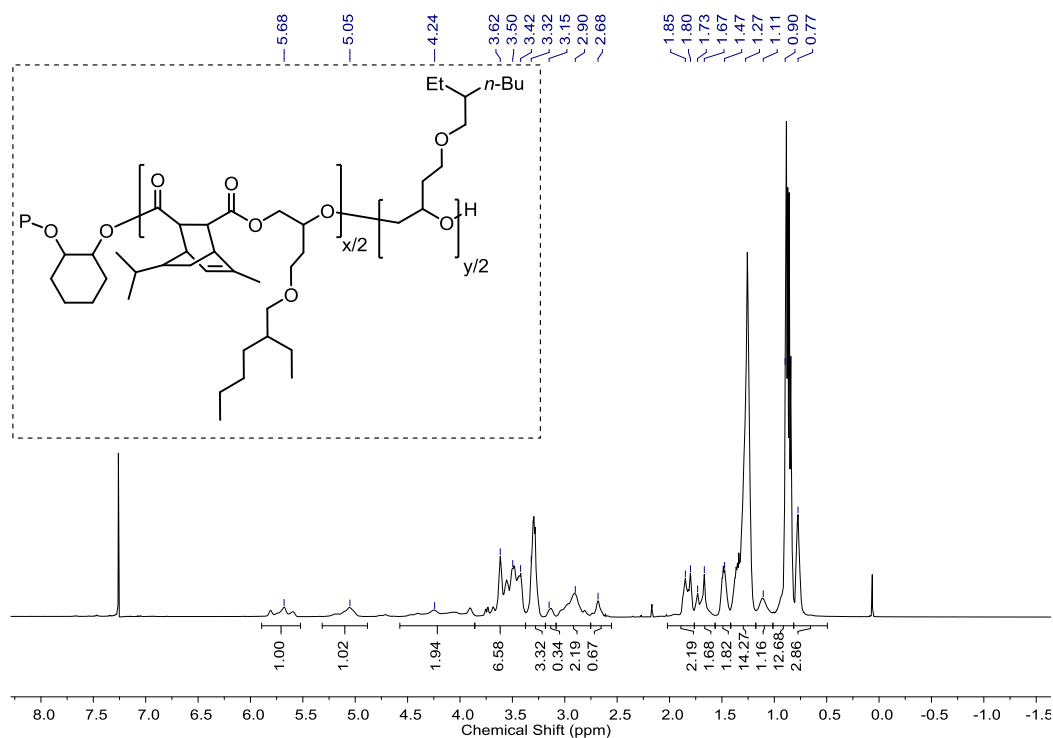
Figure S 4. 40 - ^1H NMR Spectrum for polymer obtained from PO/CA.Figure S 4. 41 - $^{13}\text{C}\{^1\text{H}\}$ NMR Spectrum for polymer obtained from PO/CA.

NMR Data for Polymer obtained from PO/TCA2

Figure S 4. 42 - ^1H NMR Spectrum for polymer obtained from PO/CA.

Figure S 4. 43 – ^{13}C NMR Spectrum for polymer obtained from PO/CA.

NMR Data for Polymer obtained from 2-EHGE/TCA1

Figure S 4. 44 - ^1H NMR Spectrum for polymer obtained from 2-EHGE/TCA1.

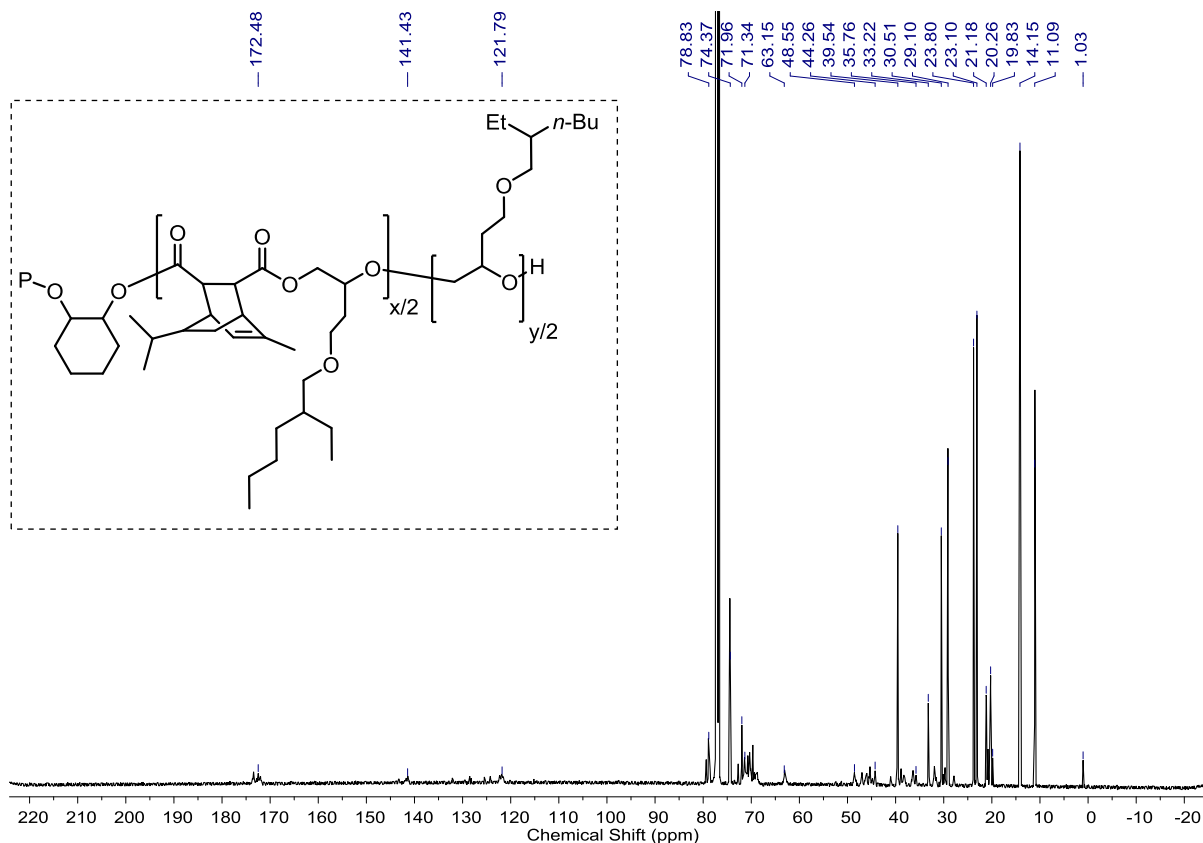


Figure S 4. 45 – ^{13}C NMR Spectrum for polymer obtained from 2-EHGE/TCA1.

NMR Data for Polymer obtained from VPO/TCA1

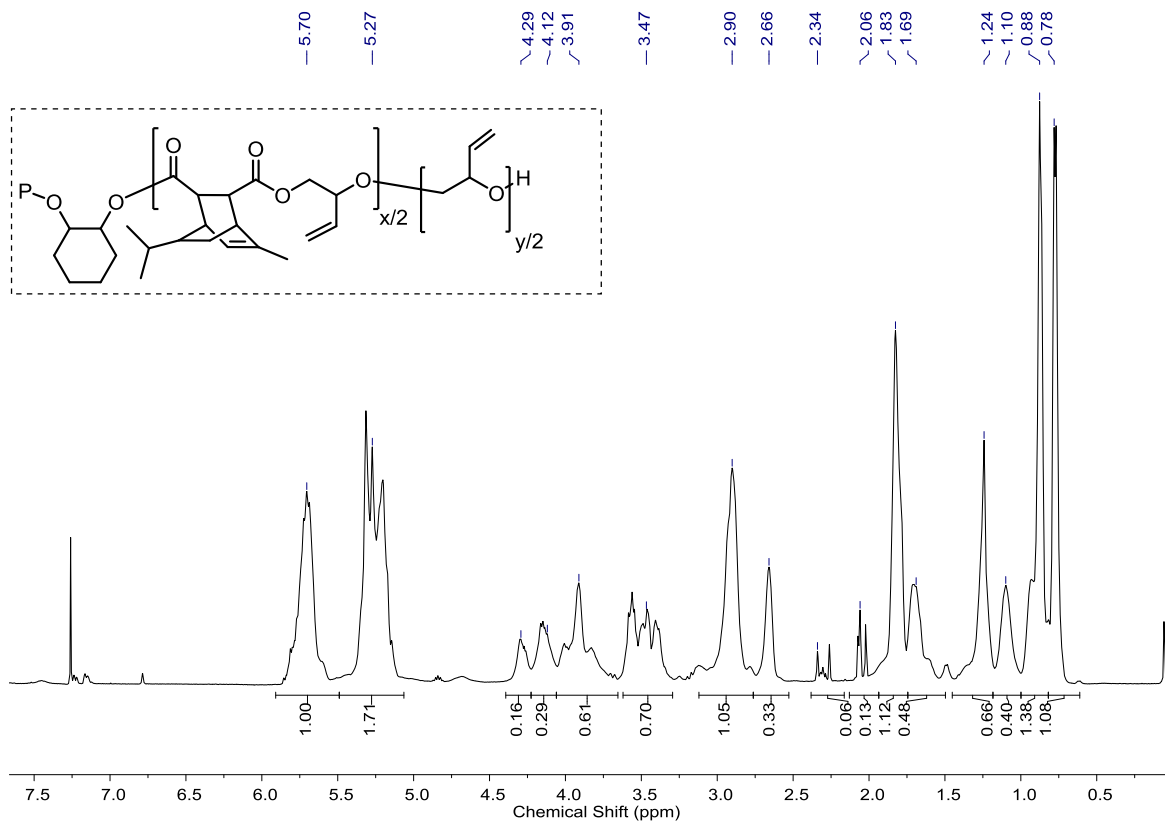


Figure S 4. 46 – ^1H NMR Spectrum for polymer obtained from VPO /TCA1.

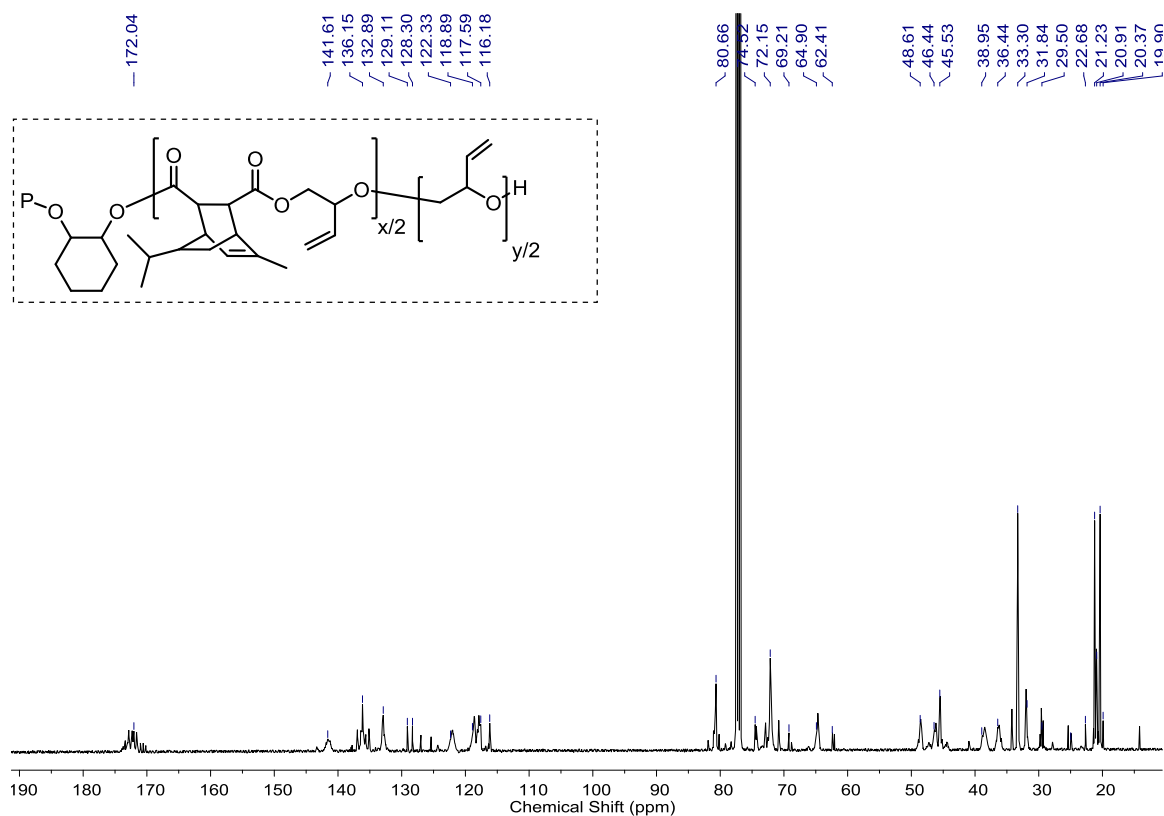


Figure S 4. 47 - ^{13}C NMR Spectrum for polymer obtained from VPO/TCA1.

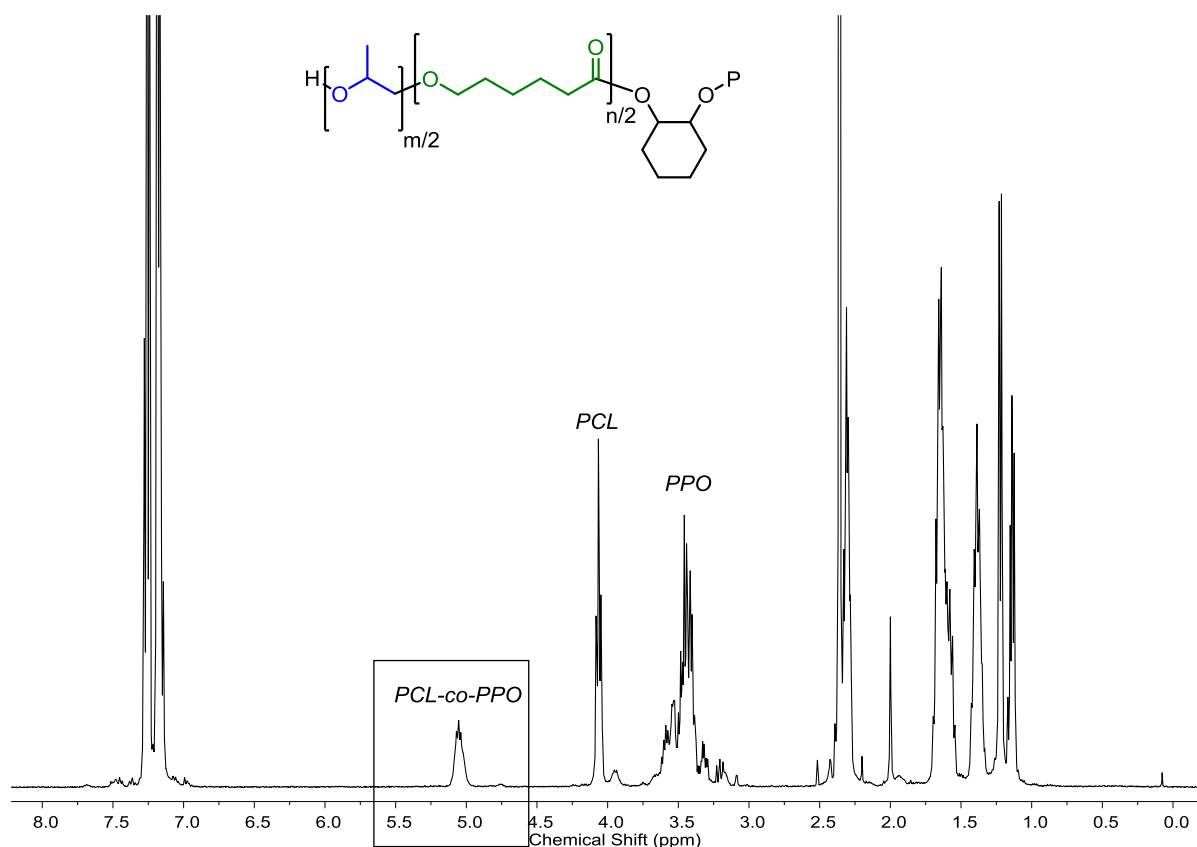


Figure S 4. 48 – ^1H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA and PO. Conditions: $[\text{CL}]:[\text{PO}]:[\text{CHD}]:[\text{SalcyCrCl}]:[\text{PPNCl}] = 200:200:10:1:0.5$, Tol (2.5 M), 60 °C, 20 h.

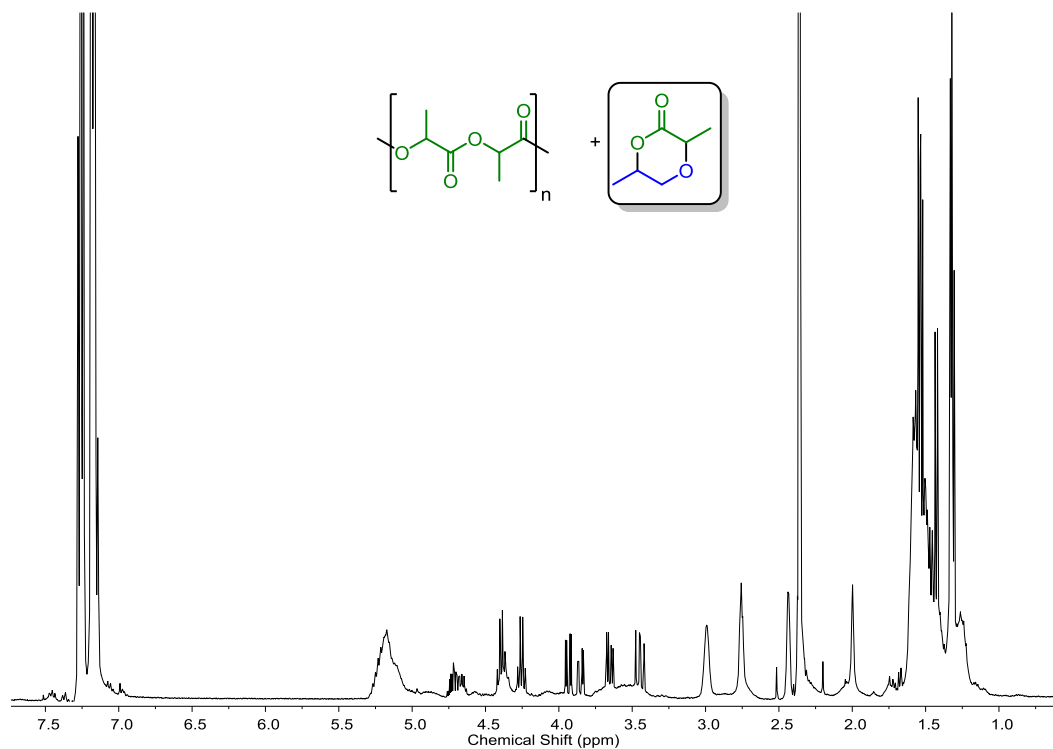


Figure S 4. 49 – ^1H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA and PO. Conditions: $[\text{LA}]:[\text{PO}]:[\text{CHD}]:[\text{SalcyCrCl}]:[\text{PPNCl}] = 200:200:10:1:0.5$, Tol (2.5 M), 60 °C, 20 h. Assignments of the backbiting product are given below.

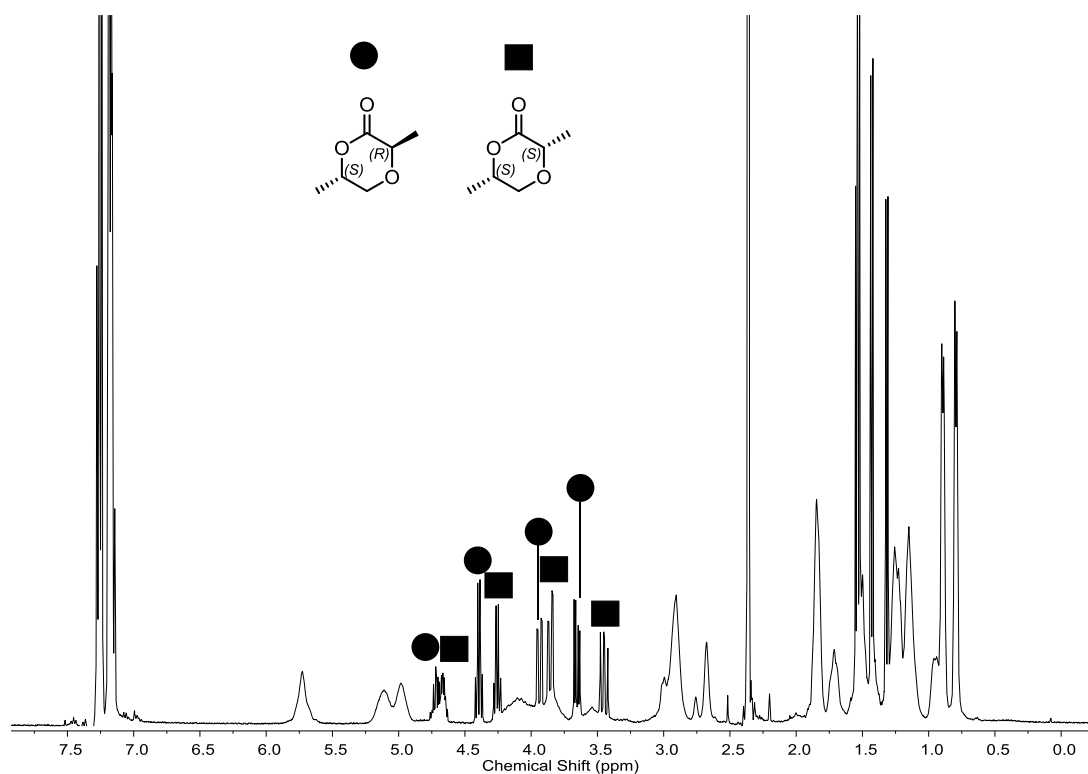


Figure S 4. 50 – ^1H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA, TCA1 and PO. Conditions: $[\text{LA}]:[\text{TCA1}]:[\text{PO}]:[\text{CHD}]:[\text{SalcyCrCl}]:[\text{PPNCl}] = 100:100:200:10:1:0.5$, Tol (2.5 M), 60 °C, 20 h.^[6]

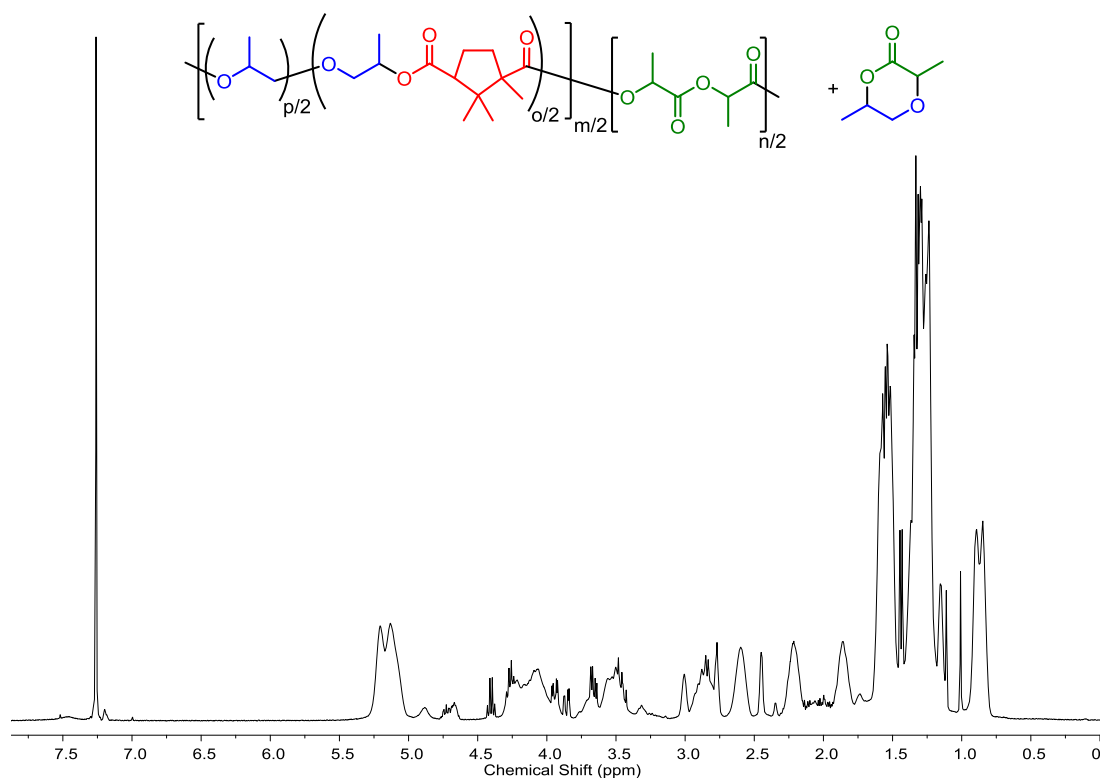


Figure S 4. 51 - ^1H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of LA, CA and PO. Conditions: $[\text{LA}]:[\text{CA}]:[\text{PO}]:[\text{CHD}]:[\text{SalcyCrCl}]:[\text{PPNCl}] = 100:100:200:10:1:0.5$, Tol (2.5 M), 60 °C, 14 h.

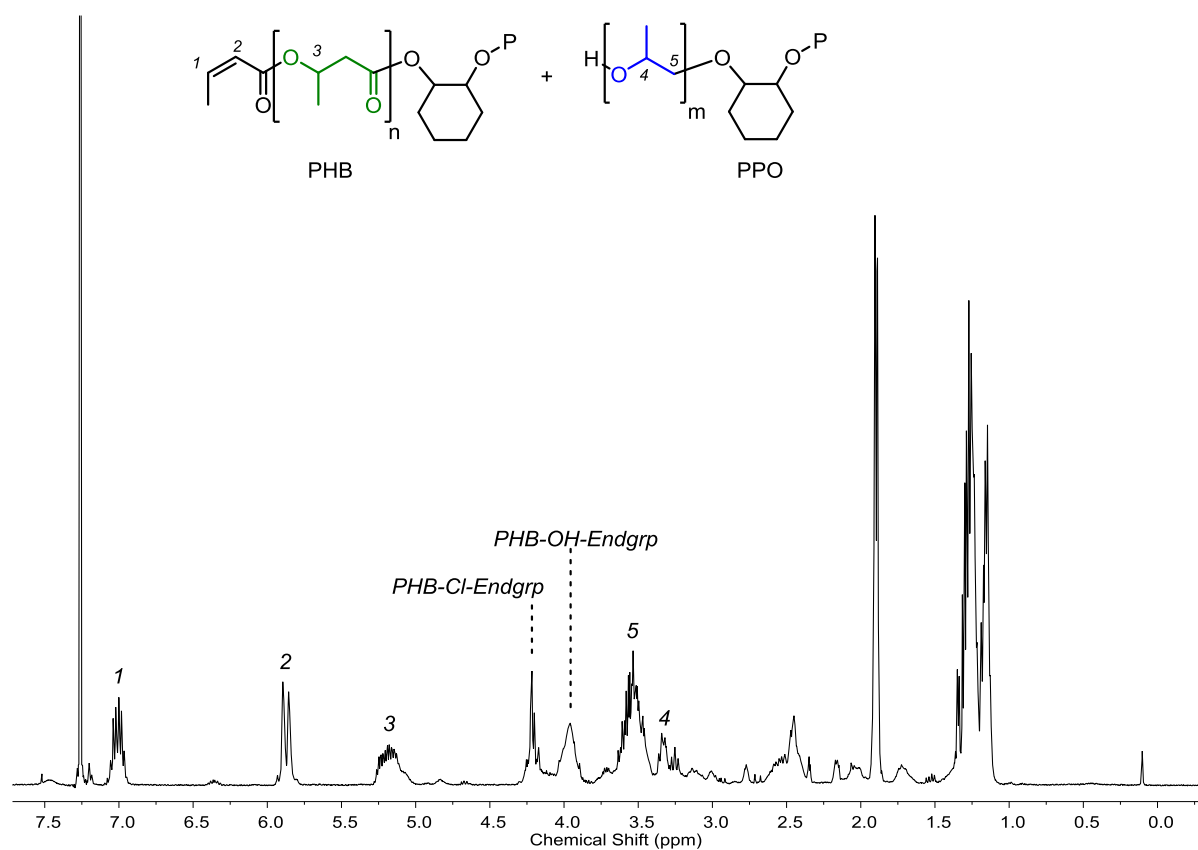


Figure S 4. 52 - ^1H NMR Spectrum of crude reaction mixture after the one-pot polymerisation of BL and PO. Conditions: [BL]:[PO]: [CHD]:[SalcyCrCl]:[PPNCl] = 100:200:10:1:0.5, Tol (2.5 M), 60 °C, 24 h.^[6]

Chapter 5 - 'Switch' Catalysis with [Salphen^FAlCl]. Block Copolyesters from commercially relevant feedstocks

11/28/2018

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Kinetic Analysis based on In Situ IR Plot

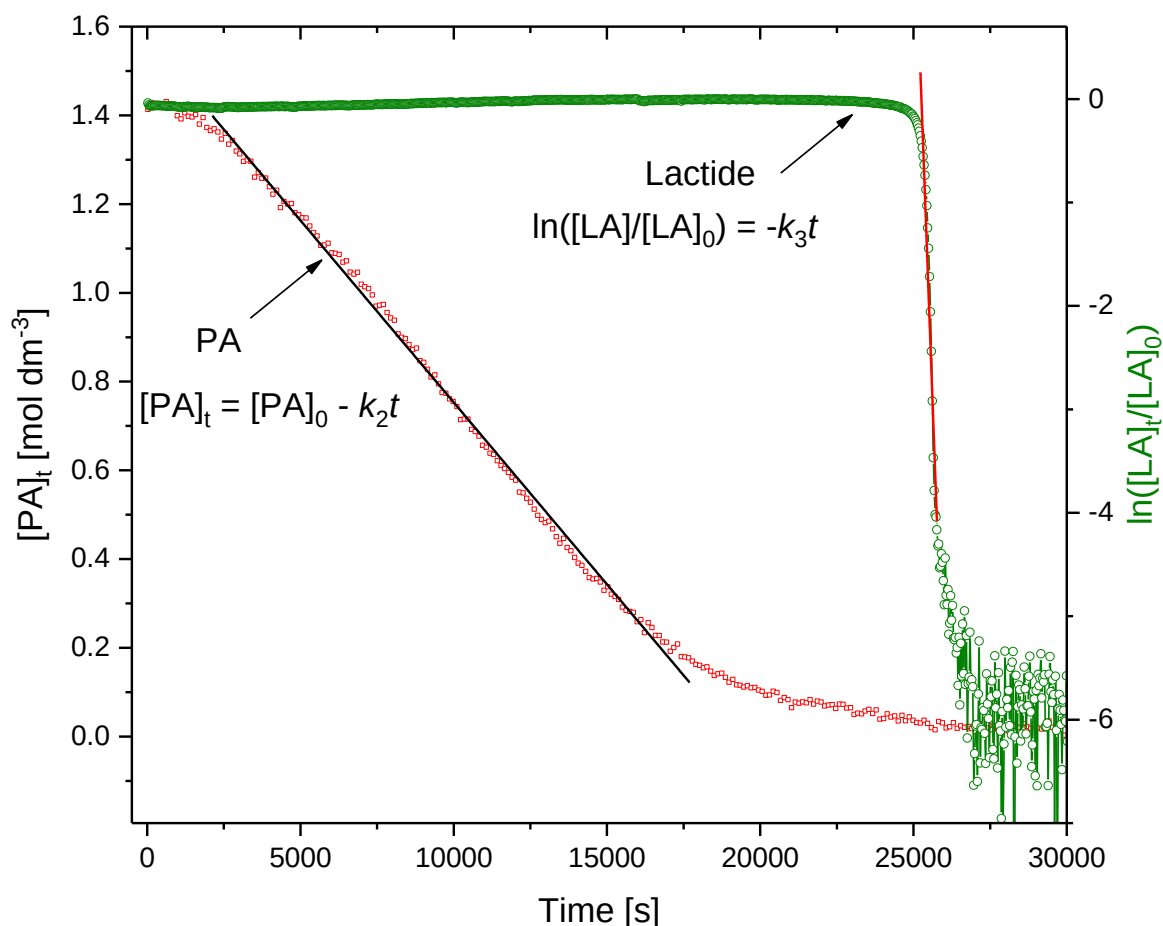


Figure S 5. 2 – Kinetic analysis of *in situ* IR plot (conditions are given in experimental section). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

Table S 5. 1 - Fitting parameters based on Figure S 5. 2. The table (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

Equation	$y = a + b \cdot x$	$y = a + b \cdot x$
Monomer	PA	LA
Weight	No Weighting	No Weighting
Intercept	208.20656 ± 10.55889	1.57331 ± 0.00208
Slope	$-0.00824 \pm 4.13404\text{E-}4$	$-8.20182\text{E-}5 \pm 1.90659\text{E-}7$
Residual Sum of Squares	1.84198	0.19857
Pearson's r	-0.97808	-0.9986
R-Square(COD)	0.95665	0.99721
Adj. R-Square	0.95424	0.9972

MALDI Spectra

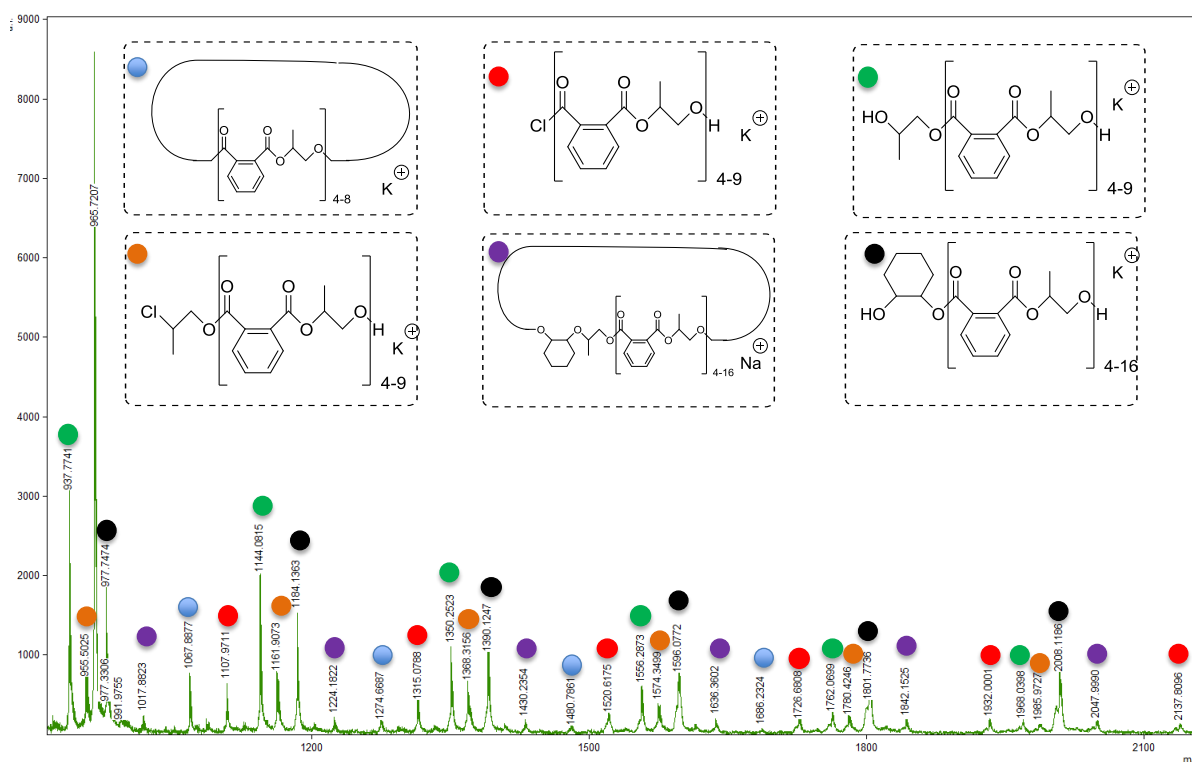
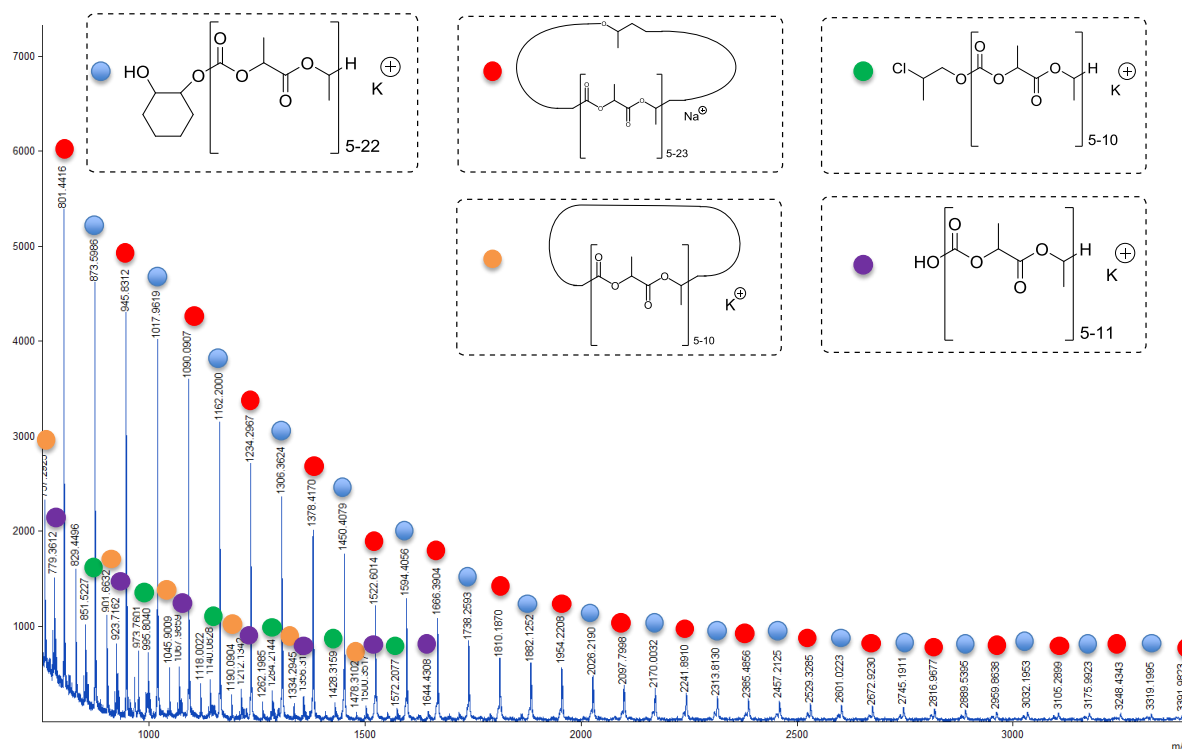


Figure S 5. 3 – MALDI Spectrum of PPE. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.



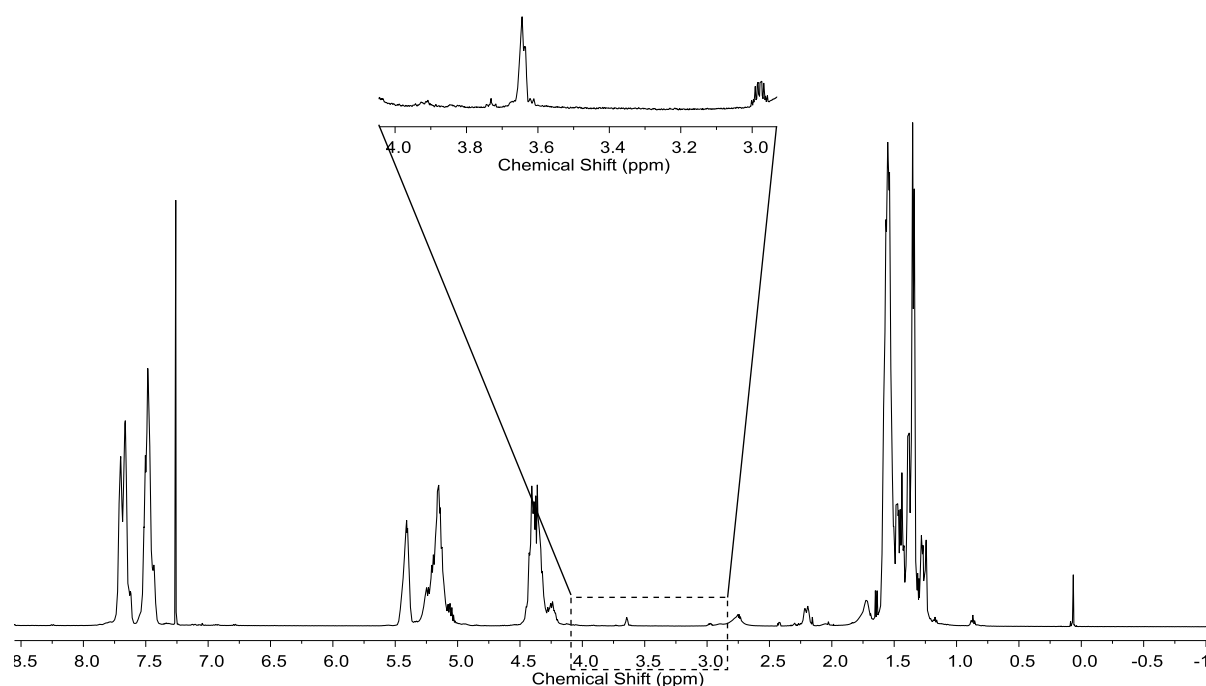


Figure S 5. 5— ^1H NMR spectrum of isolated polyester; the region relevant to the formation of polyether between 3.0 and 4.0 ppm is enlarged (polyether should be observed as broad resonances in this area). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

One-Pot Polymerisation of PO/TAC1/LA with [Salphen^FAlCl]

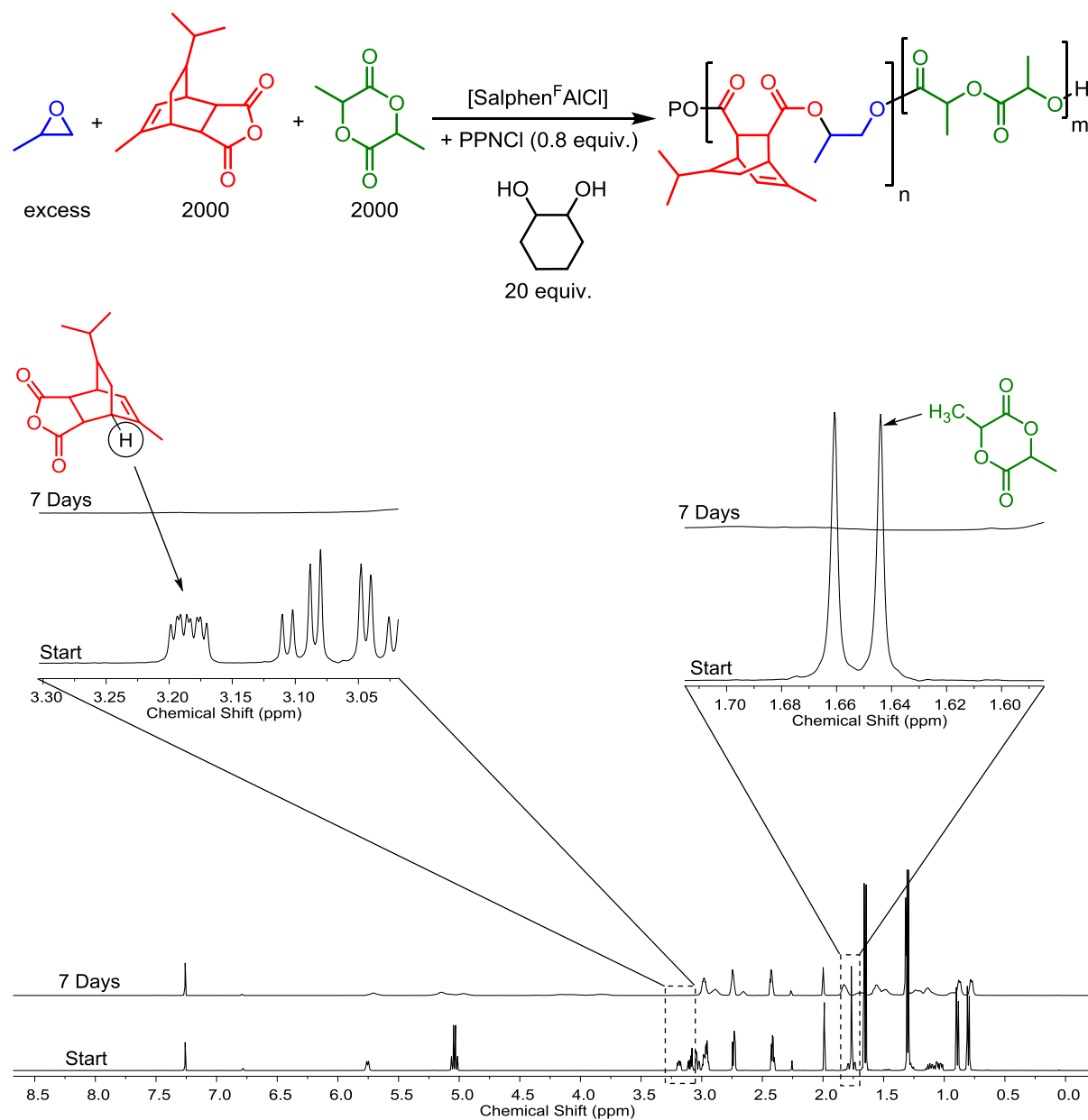


Figure S 5. 6 – ¹H NMR spectrum of the one-pot polymerisation of TCA1/PO/LA. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

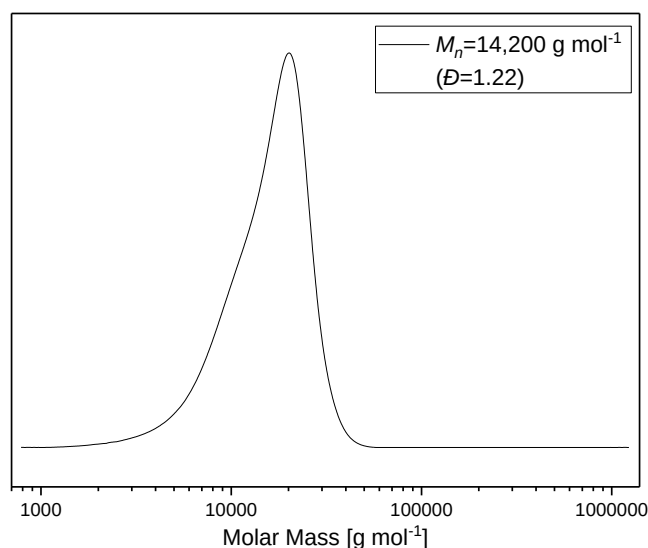


Figure S 5. 7 – GPC trace of polymer obtained from TCA1/PO/LA. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

IR Spectra of Monomers and Polymers

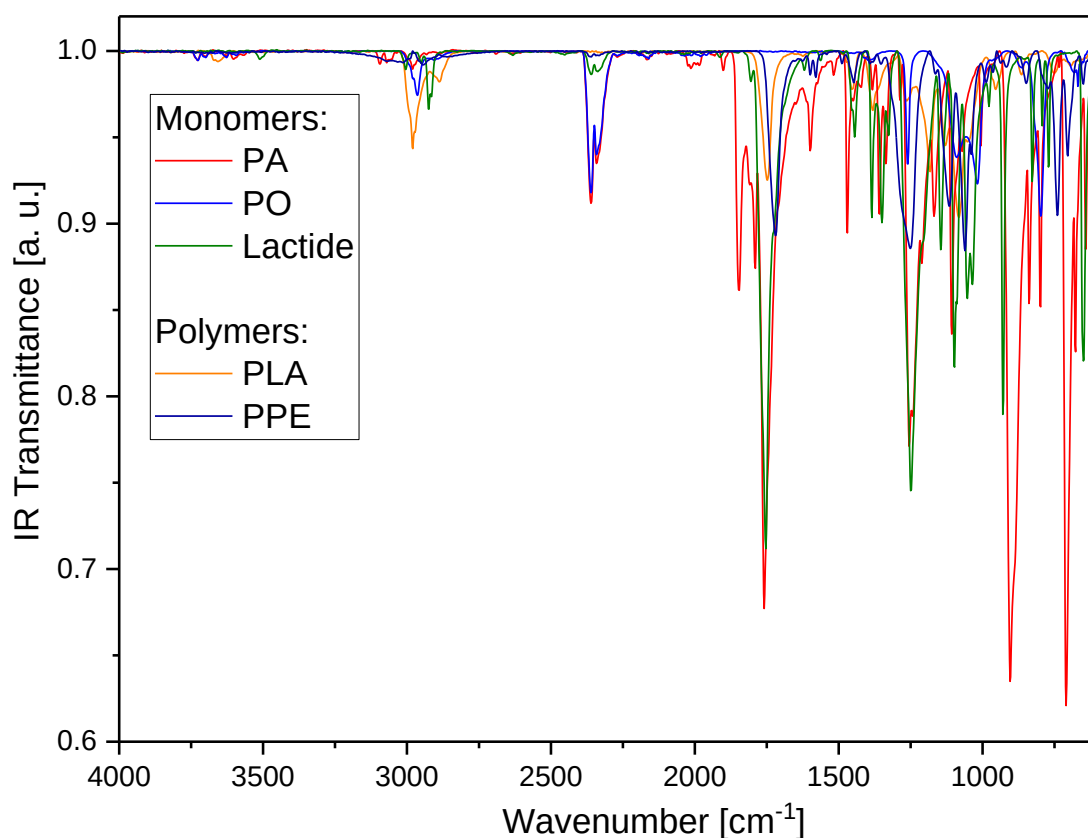


Figure S 5. 8 – IR spectra of monomers and polymers. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

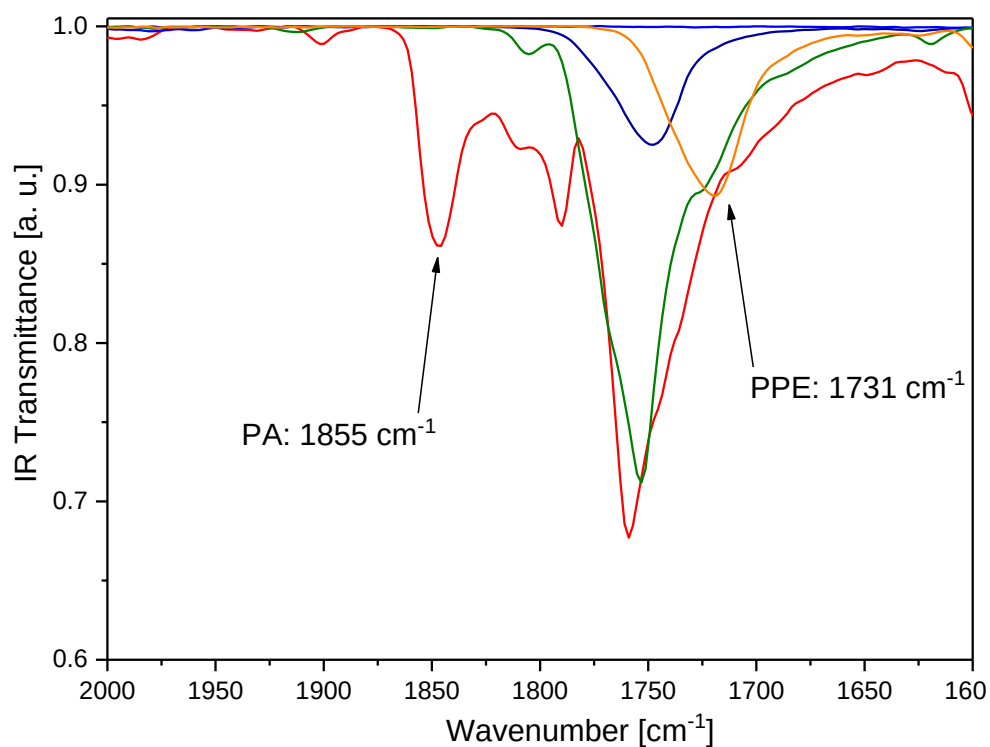


Figure S 5. 9 – Extended region of IR spectra for PA and PPE. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

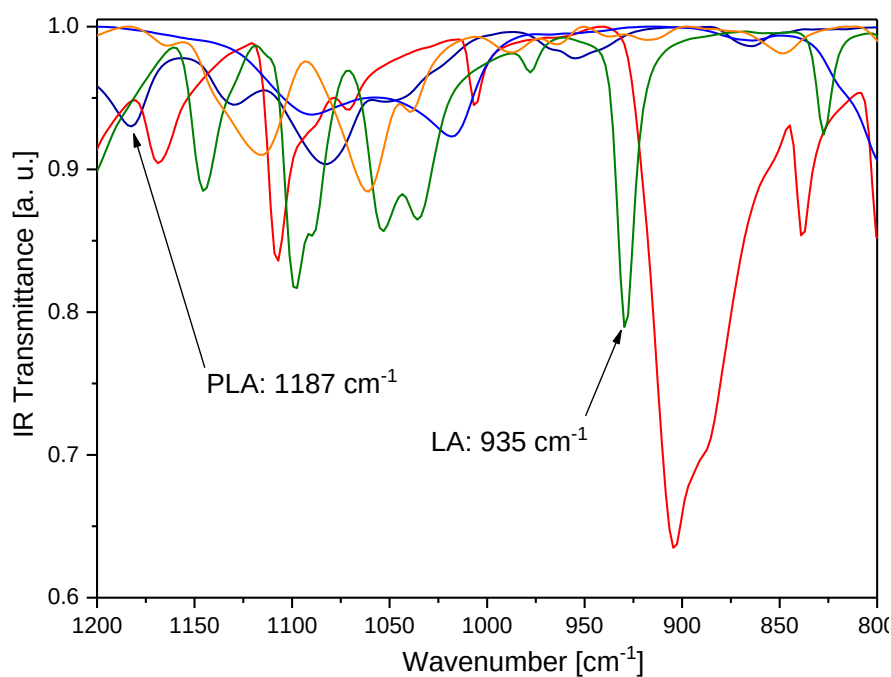


Figure S 5. 10 – Extended region of IR spectra for LA and PLA. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

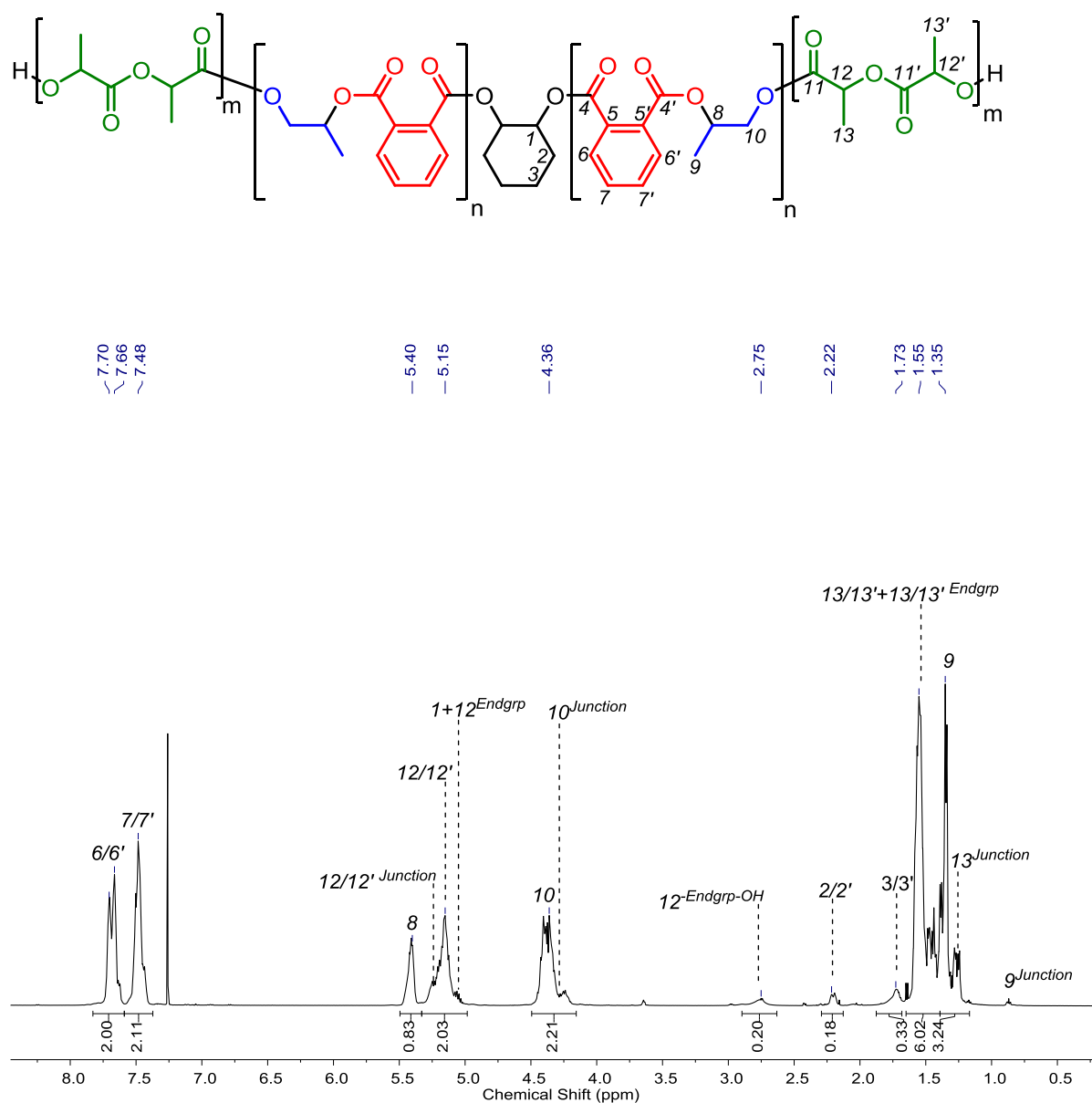
NMR Assignments for PLA-*b*-PPE-*b*-PLA

Figure S 5. 11 – ^1H NMR spectrum of isolated polymer. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

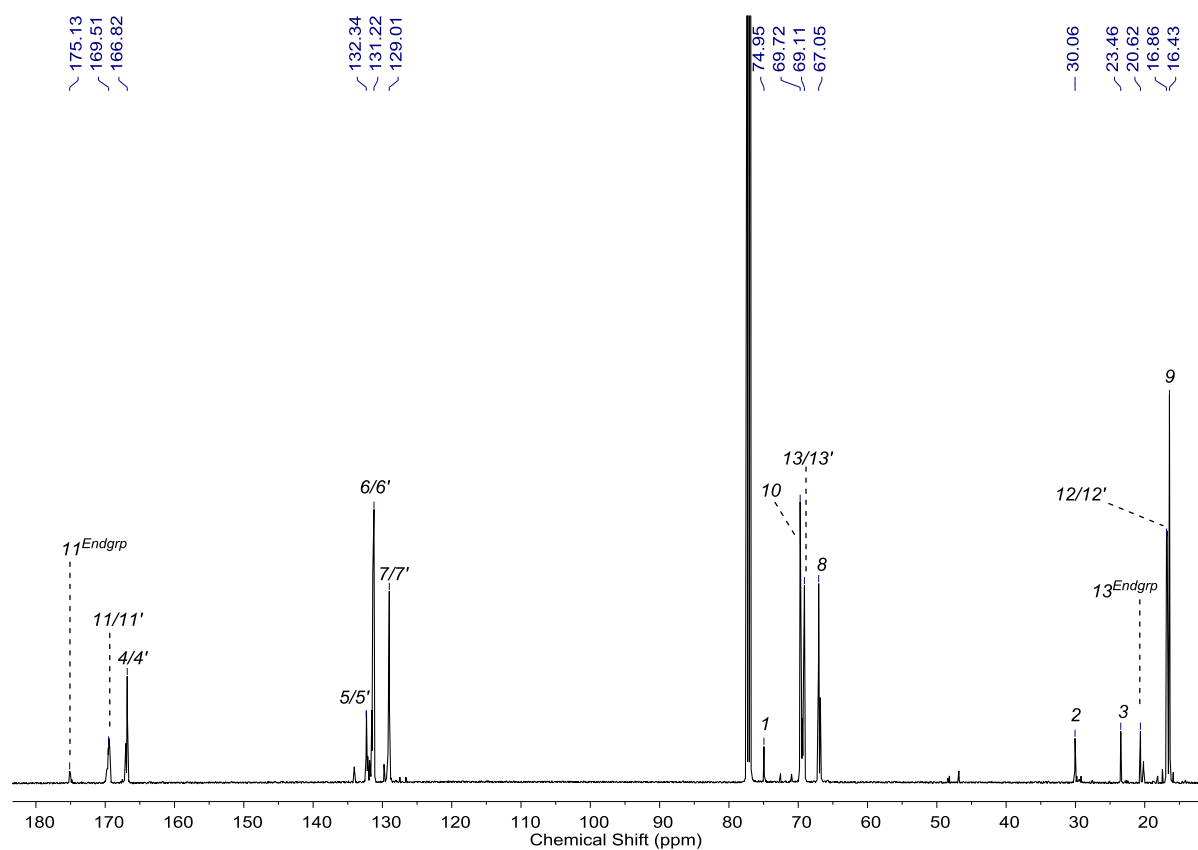


Figure S 5. 12 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of isolated polymer. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

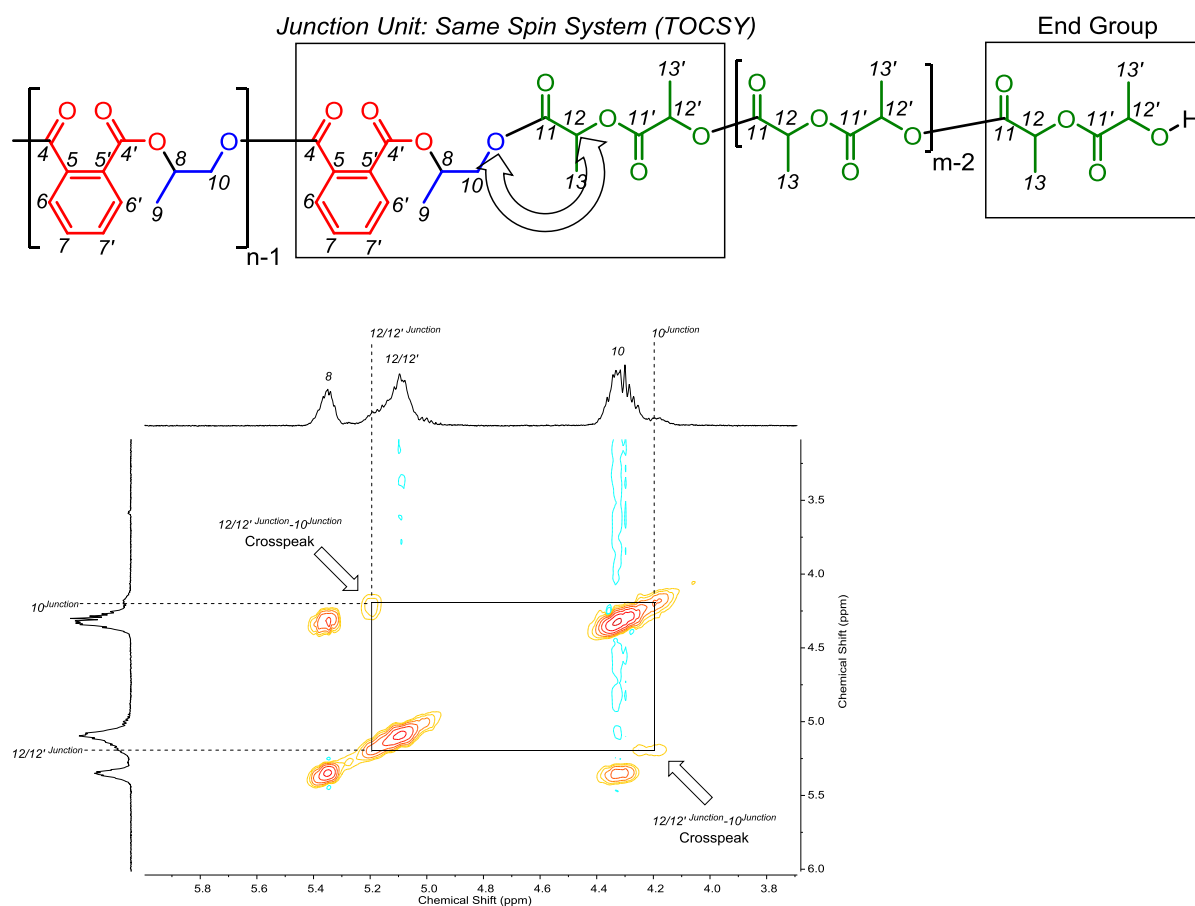


Figure S 5. 13 – ^1H , ^1H TOCSY NMR spectrum (only region relevant to junction unit shown). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

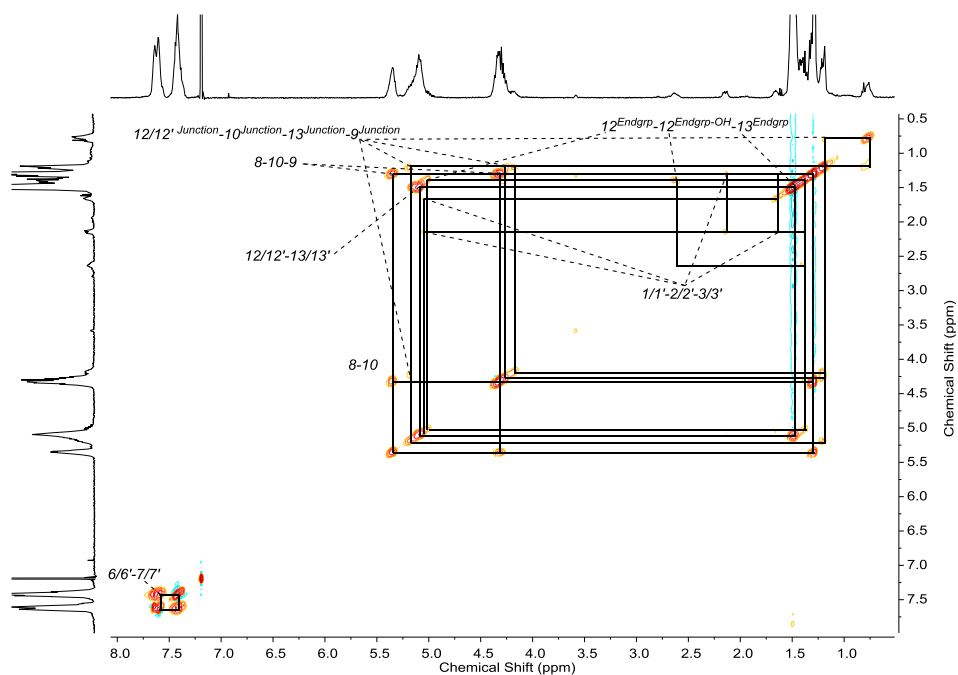


Figure S 5. 14 – ^1H , ^1H TOCSY NMR spectrum (only region relevant to junction unit shown). The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

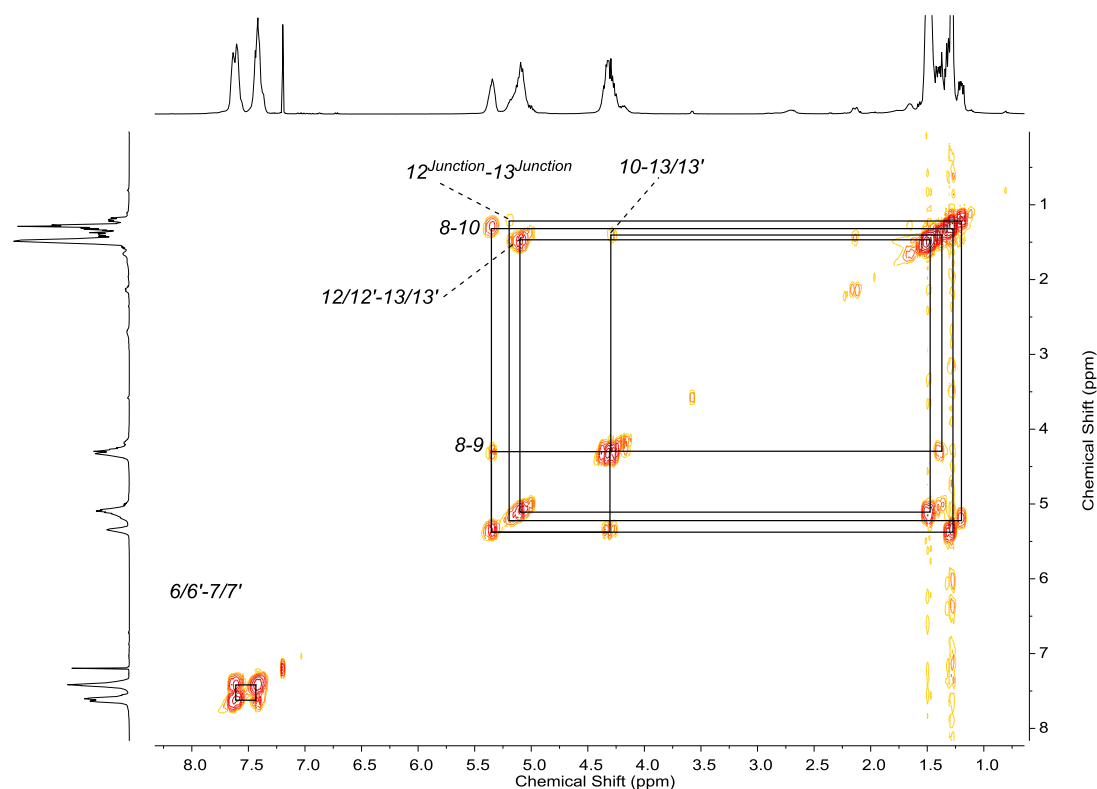


Figure S 5. 15 – $^1\text{H}, ^1\text{H}$ COSY NMR Spectrum of PLA-*b*-PPE-*b*-PLA. The figure (caption) is reprinted (adapted) with permission from *Angew. Chem. Int. Ed.* **2018**, DOI:10.1002/ange.201810245. Copyright (2018) John Wiley and Sons.

DSC Traces for Polyesters with Different Anhydrides

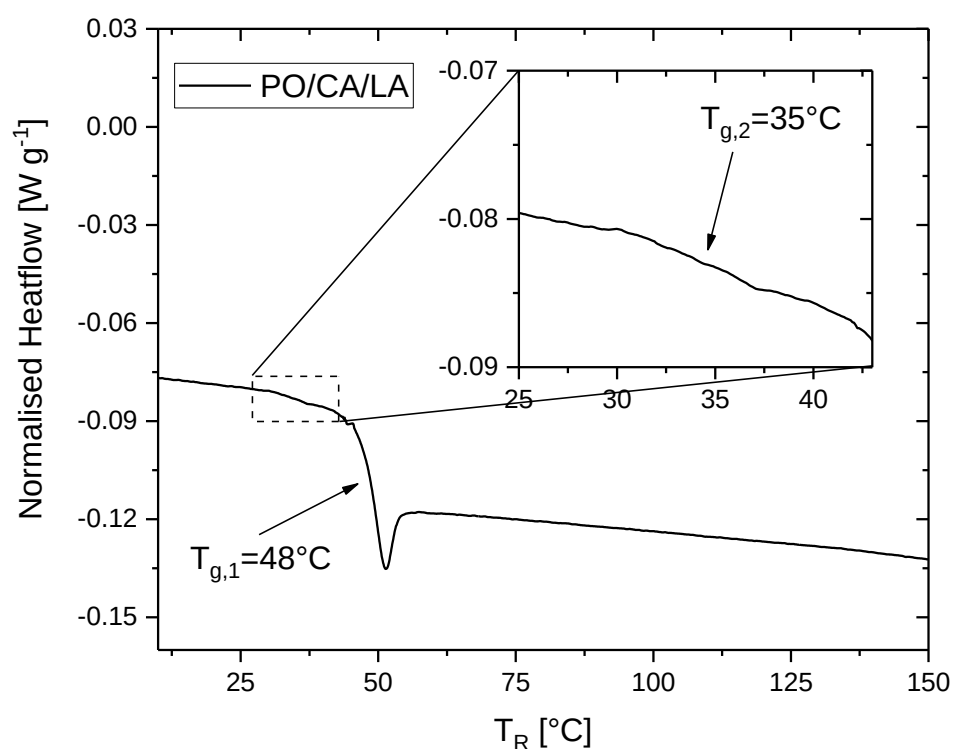


Figure S 5. 16 – DSC Thermogram of Polyester based on PO/CA/LA.

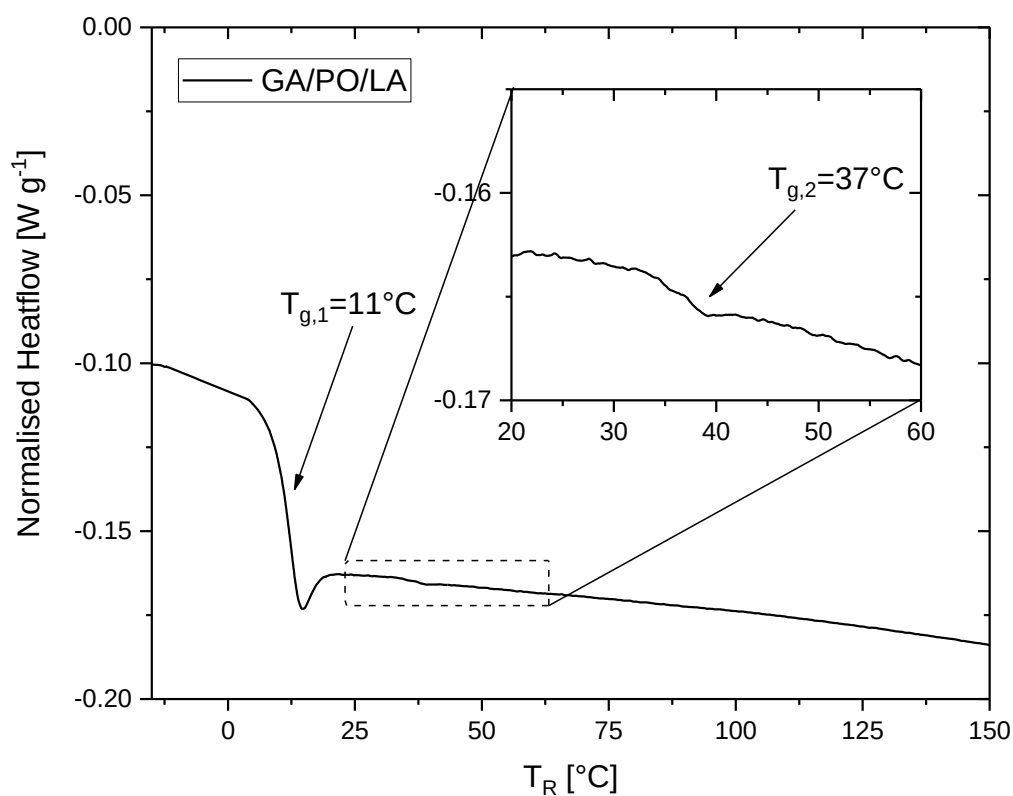


Figure S 5. 17 - DSC Thermogram of Polyester based on PO/CA/LA.

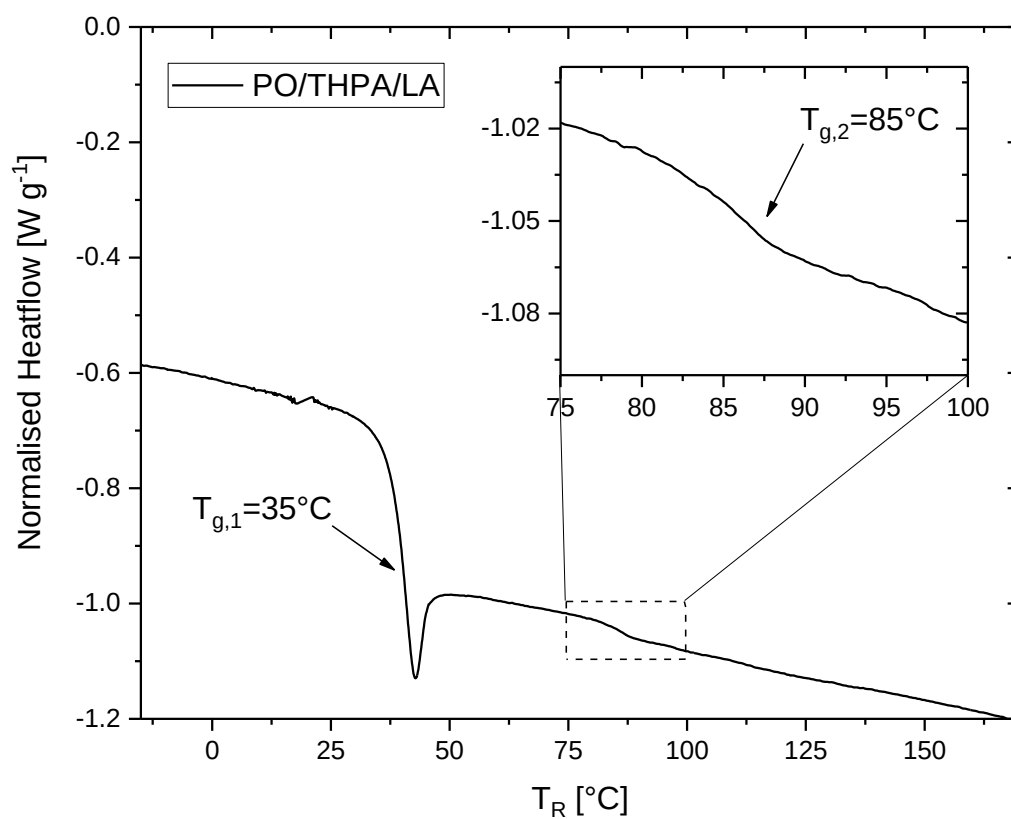


Figure S 5. 18 - DSC Thermogram of Polyester based on PO/CA/LA.

References

- [1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, 29, 2176-2179.
- [2] A. Spyros, D. S. Argyropoulos, R. H. Marchessault, *Macromolecules* **1997**, 30, 327-329.

Chapter 6 - Towards Renewable Coating Materials. A Comparison between Poly(limonene carbonate) and Poly(cyclohexadiene carbonate)

Appendix based on:

T. Stößer, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. Koning, *Polym. Chem.* **2017**, 8, 6099-6105.

GC-MS Spectrum of CHDO

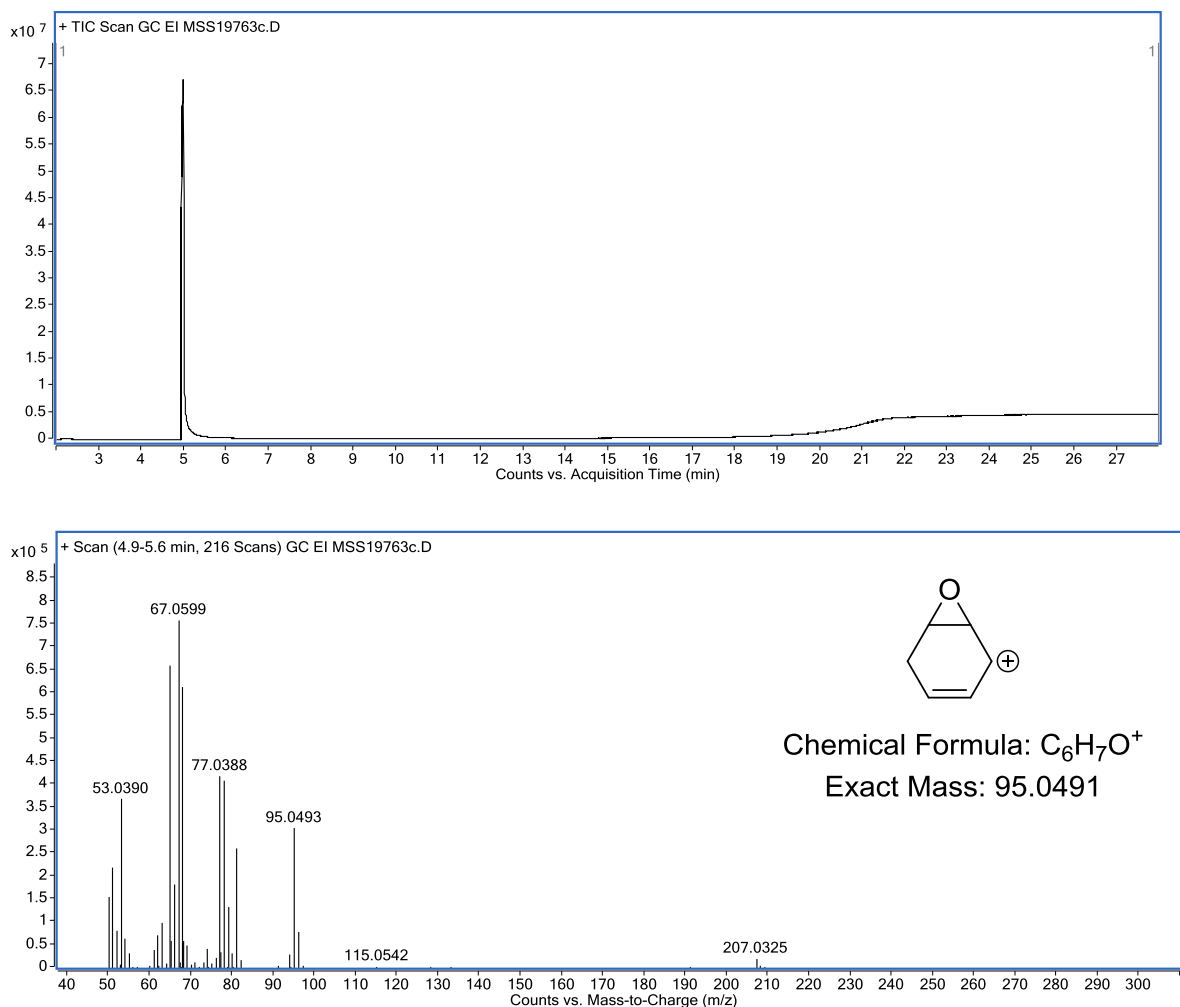
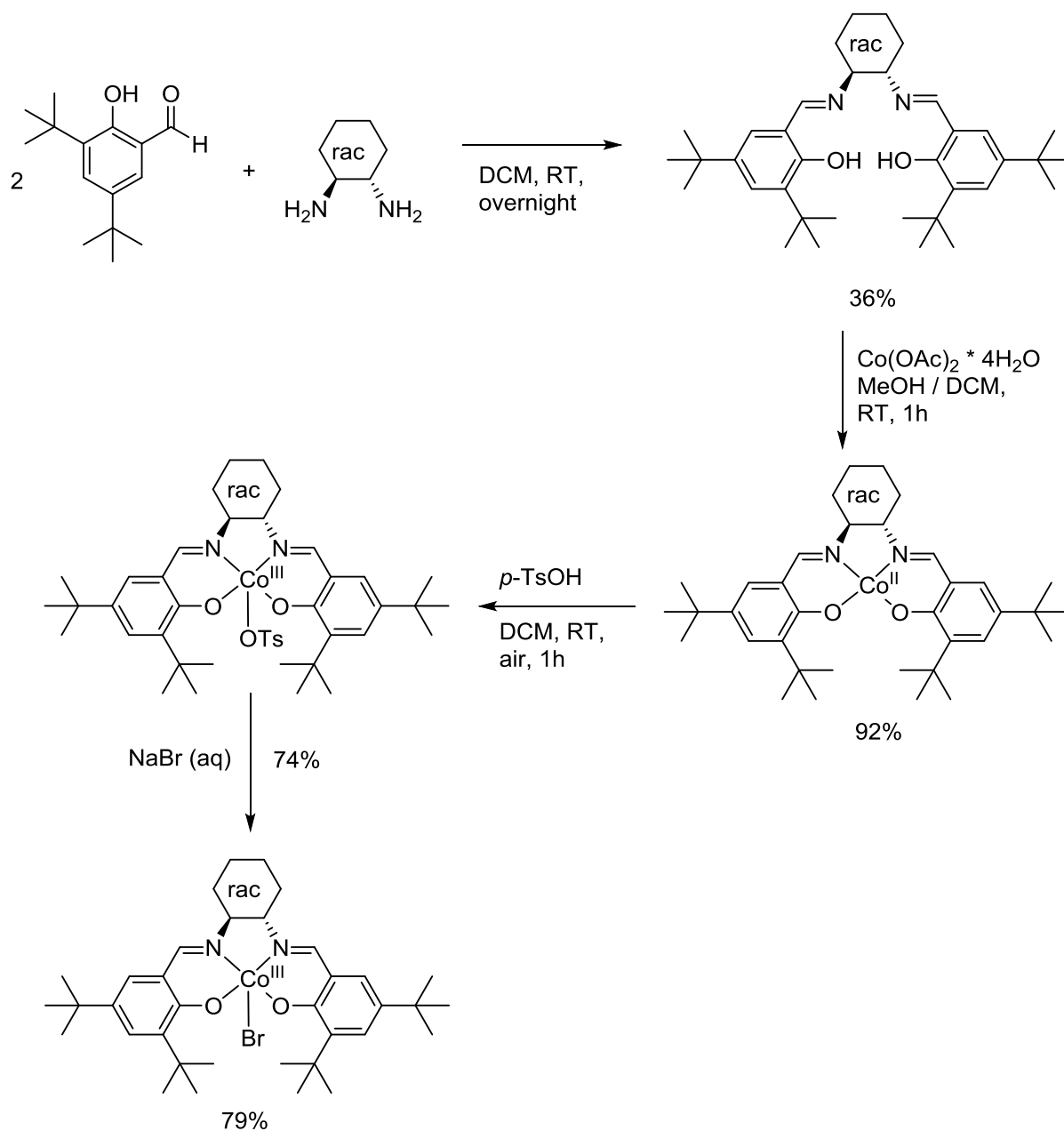


Figure S 6. 1 – GC-MS Spectrum of CHDO. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Synthesis of Cobalt(III)-salen catalyst^[3, 7-9]



Scheme S 6. 1 – Synthesis of [SalcyCoBr]. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

¹H NMR (DMSO-d₆, 400.0 MHz): 7.81 (s, 2H), 7.47 (s, 2H), 7.44 (s, 2H), 2.08-1.79 (m, 6H), 1.74 (s, 18H), 1.65-1.47 (m, 4H), 1.30 (s, 18H) ppm; ¹³C{¹H} NMR (DMSO-d₆, 400.0 MHz): 164.6, 162.0, 141.8, 135.9, 129.2, 128.8, 118.6, 69.3, 35.8, 33.5, 31.5, 30.4, 29.5, 24.3 ppm; MS(ESI-ToF): M⁺(-Br) found (calcd for C₃₆H₅₂CoN₂O₂): 603.3378 (603.3361) m/z; IR (neat): 2865, 2952, 1590, 1521, 1461, 1389, 1359, 1336, 1310, 1251, 1200, 1175, 1033, 916, 876,

834, 812, 782 cm^{-1} ; Elemental Analysis: Calcd. (%): C, 63.25; H, 7.67; N, 4.10. Found (%): C, 63.00; H, 7.62; N, 4.16. Reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Characterisation Data of PCHDC

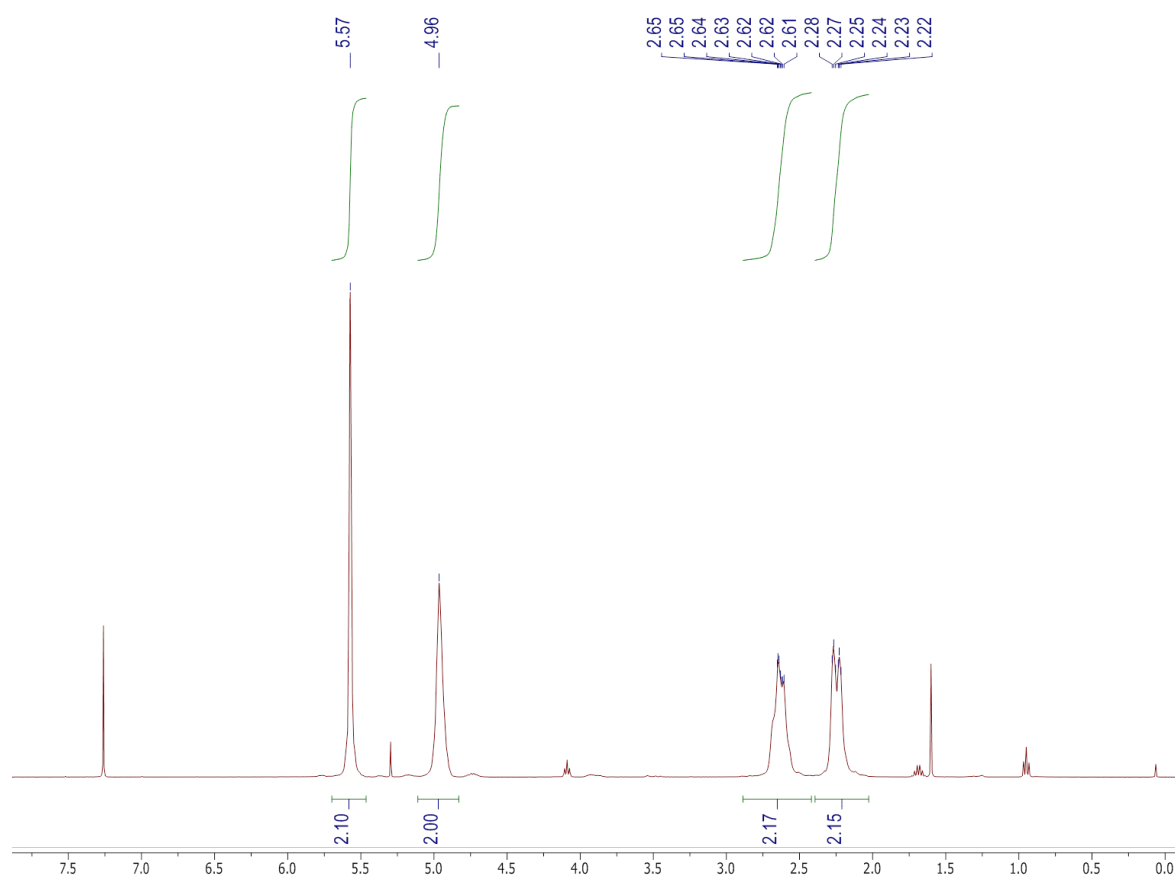


Figure S 6. 2 - ^1H NMR (400 MHz, CDCl_3) of PCHDC. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

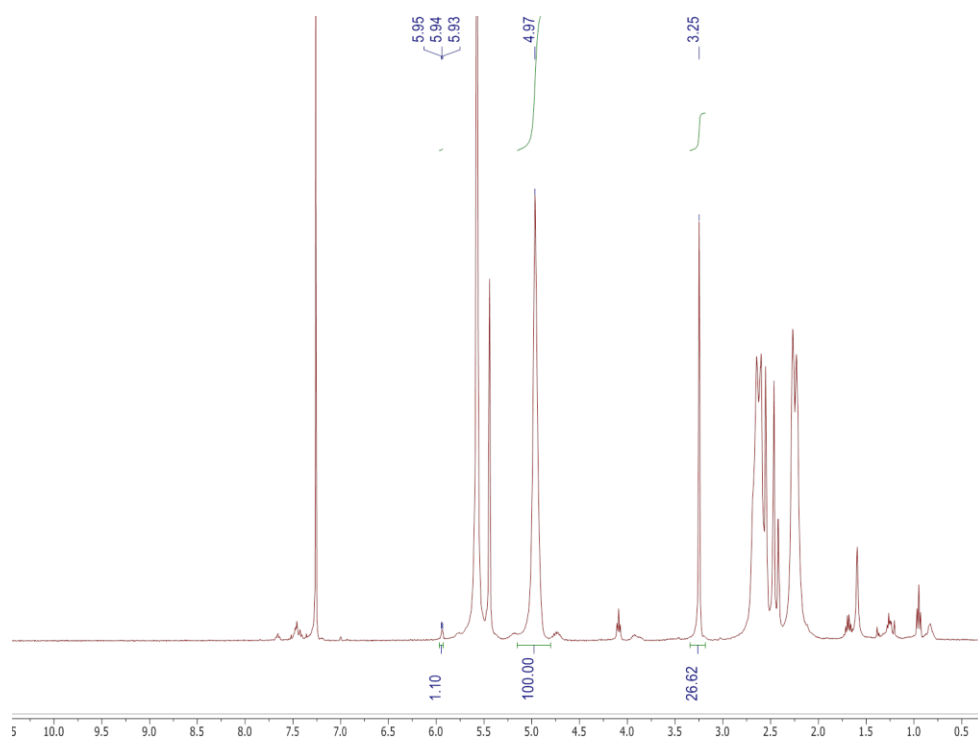


Figure S 6. 3 - ^1H NMR of crude PCHDC (400 MHz, CDCl_3). The signals at 5.94, 4.97, and 3.25 ppm are characteristic of the cyclic carbonate, PCHDC and CHDO, respectively. No signal was found at 3.45 ppm (polyether signal). The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

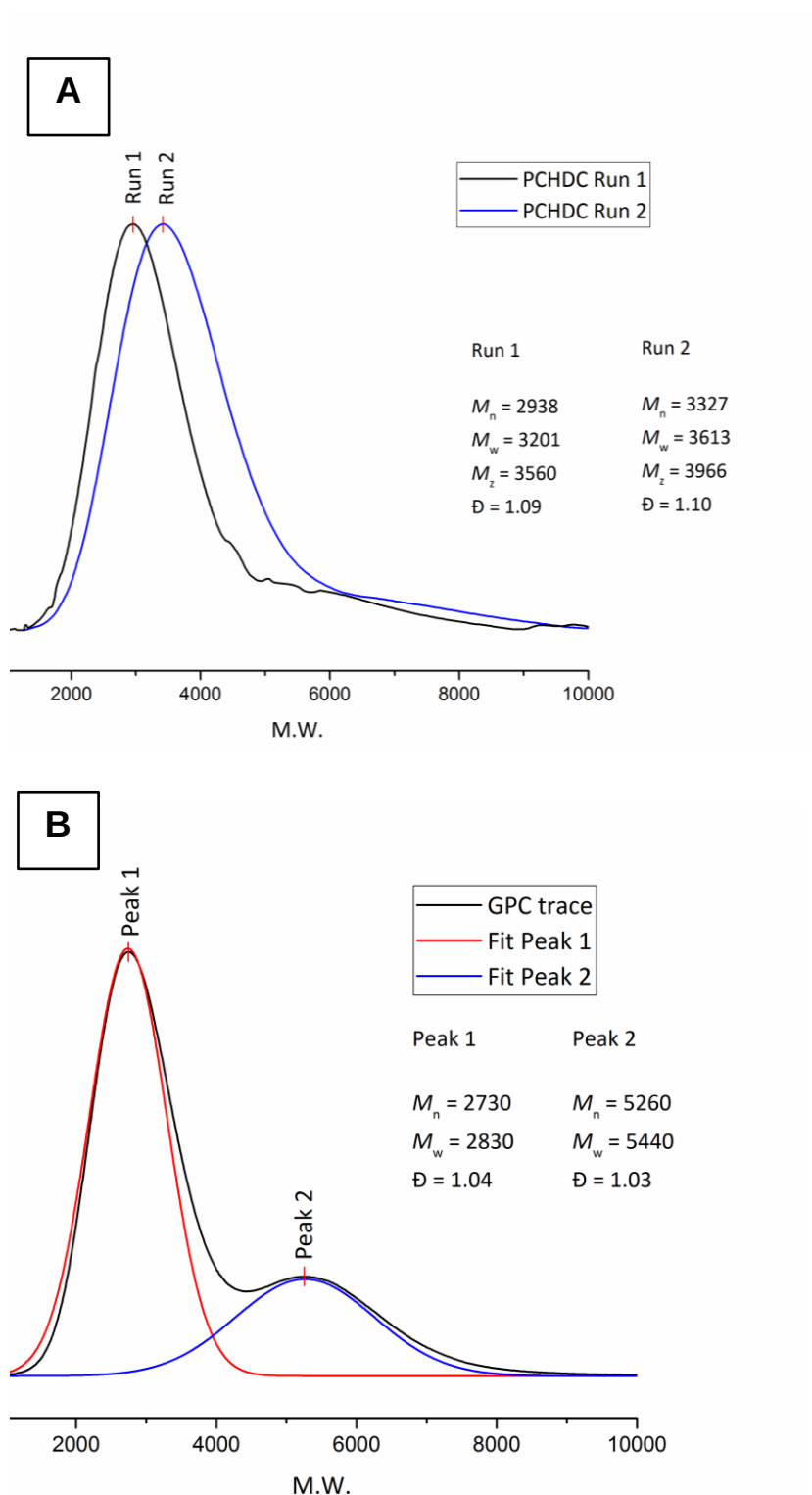


Figure S 6. 4 - (PS)-SEC traces of PCHDC. A: monomodal traces (run 1 and run 2 refer to independently synthesised samples); B: bimodal traces. Fit function for peak 1: $f(x) = -0.03838 + (139830/(1106\sqrt{\pi/2}))\exp(-2((x-2740)/1106)^2)$; peak 2: $f(x) = -0.03838 + (56666/(1981\sqrt{\pi/2}))\exp(-2((x-5265)/1981)^2)$. M_n if both peaks were not considered separately: 2850 g mol^{-1} (1.12). For SEC-MALLS, dn/dc was determined to be 0.0851 mL g^{-1} (not shown). Reported molar masses are relative to polystyrene. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

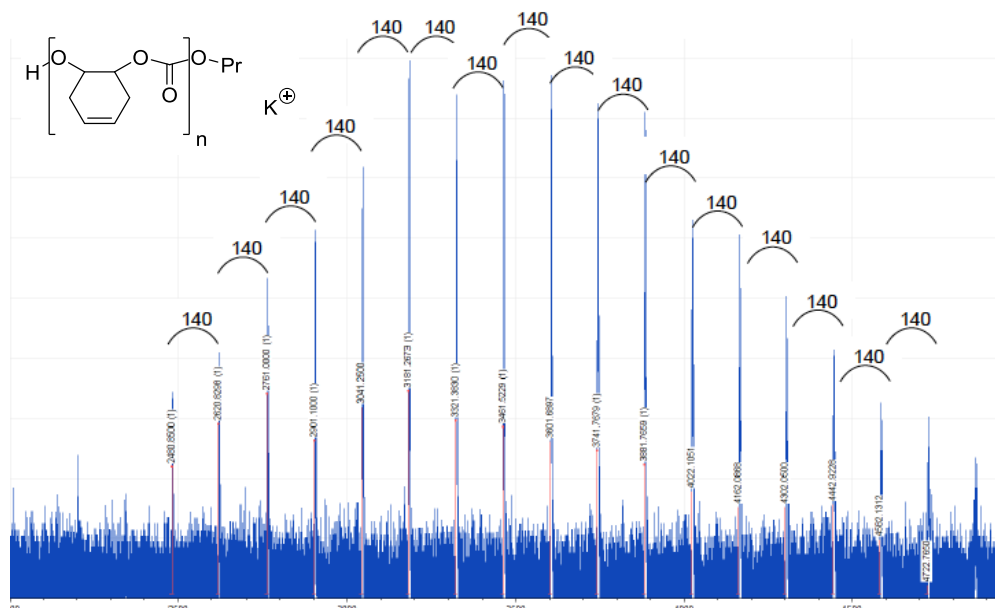


Figure S 6. 5 - MALDI-ToF spectrum of poly(cyclohexadiene carbonate). The series shows $m/z = [60.06 \text{ (propanol)} + (140.05 n) \text{ (PCHDC)} + 38.96 \text{ (K}^+)]$ ($n = 17 \sim 33$). Y-Axis: Intensity (a. u.), x-axis: m/z . The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

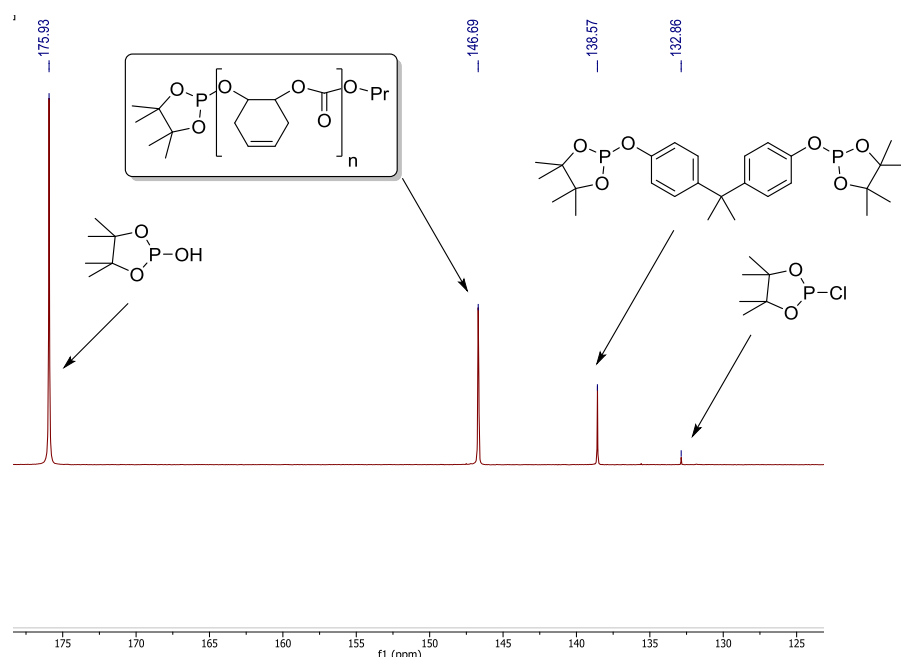


Figure S 6. 6 - $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (400 MHz, CDCl_3) of PCHDC after the reaction with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane (bisphenol A used as an internal standard). The peaks at 175.9, 146.7, 138.6, 132.9 ppm correspond to the phosphorus agent, the OH end-group (after the reaction), bisphenol A and the hydrolysed phosphorus agent, respectively. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

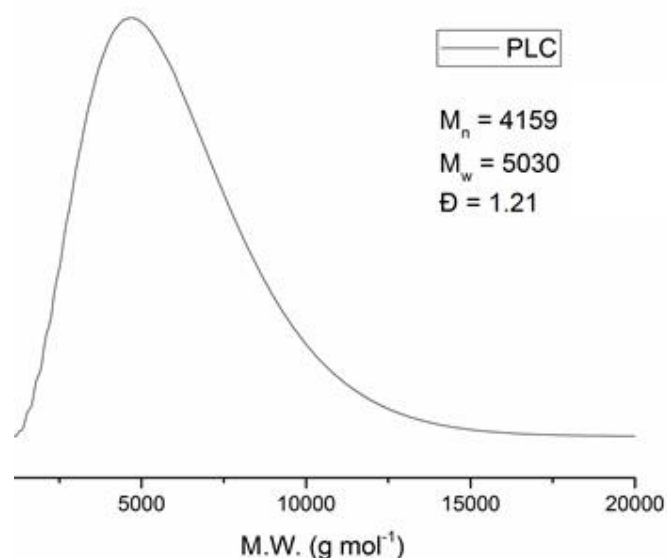


Figure S 6. 7 - (PS)-SEC trace of PLC. For SEC-MALLS, dn/dc was determined to be 0.0804 mL/g (not shown). The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

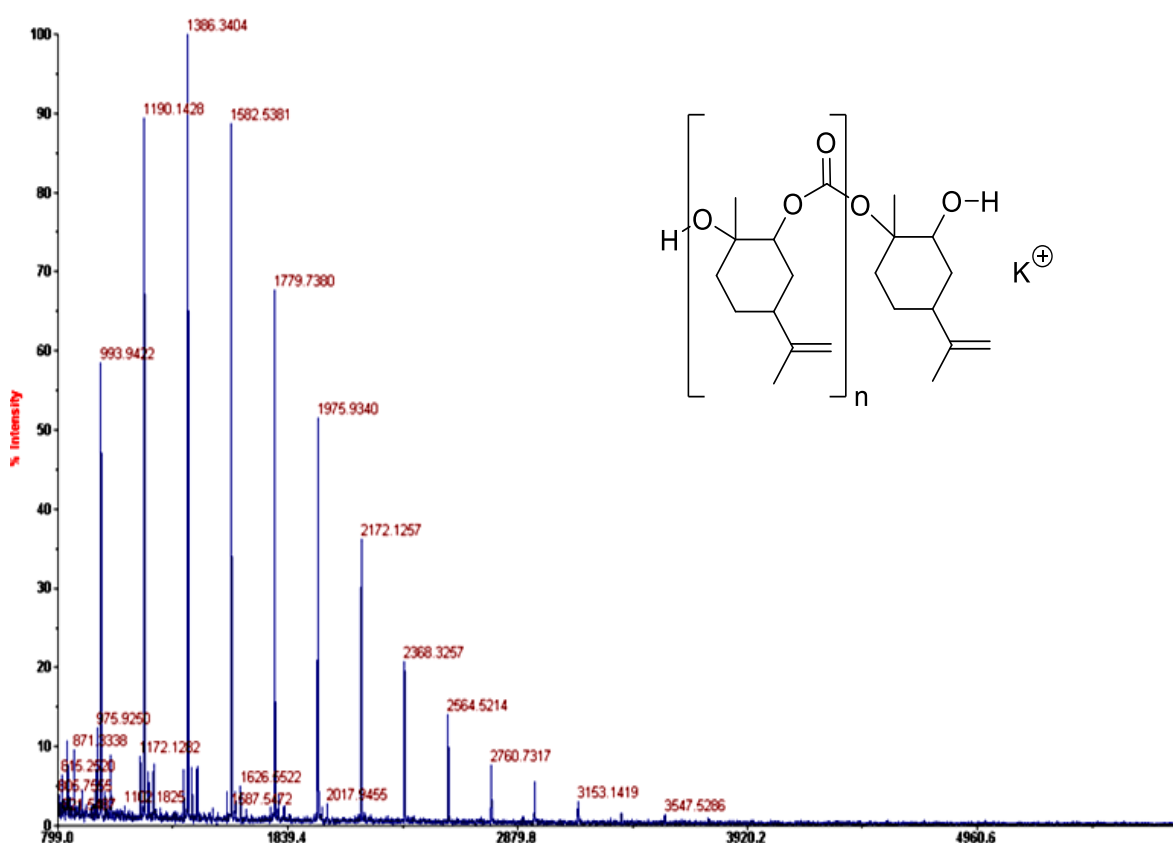


Figure S 6. 8 - MALDI-ToF spectrum of poly(limonene carbonate). The series shows $m/z = [18.01 \text{ (water)} + \text{limonene oxide (152.12)} + (196.11 \times n) \text{ (PLC)} + 38.96 \text{ (K}^+)]$ ($n = 4 \sim 15$). The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

DSC results

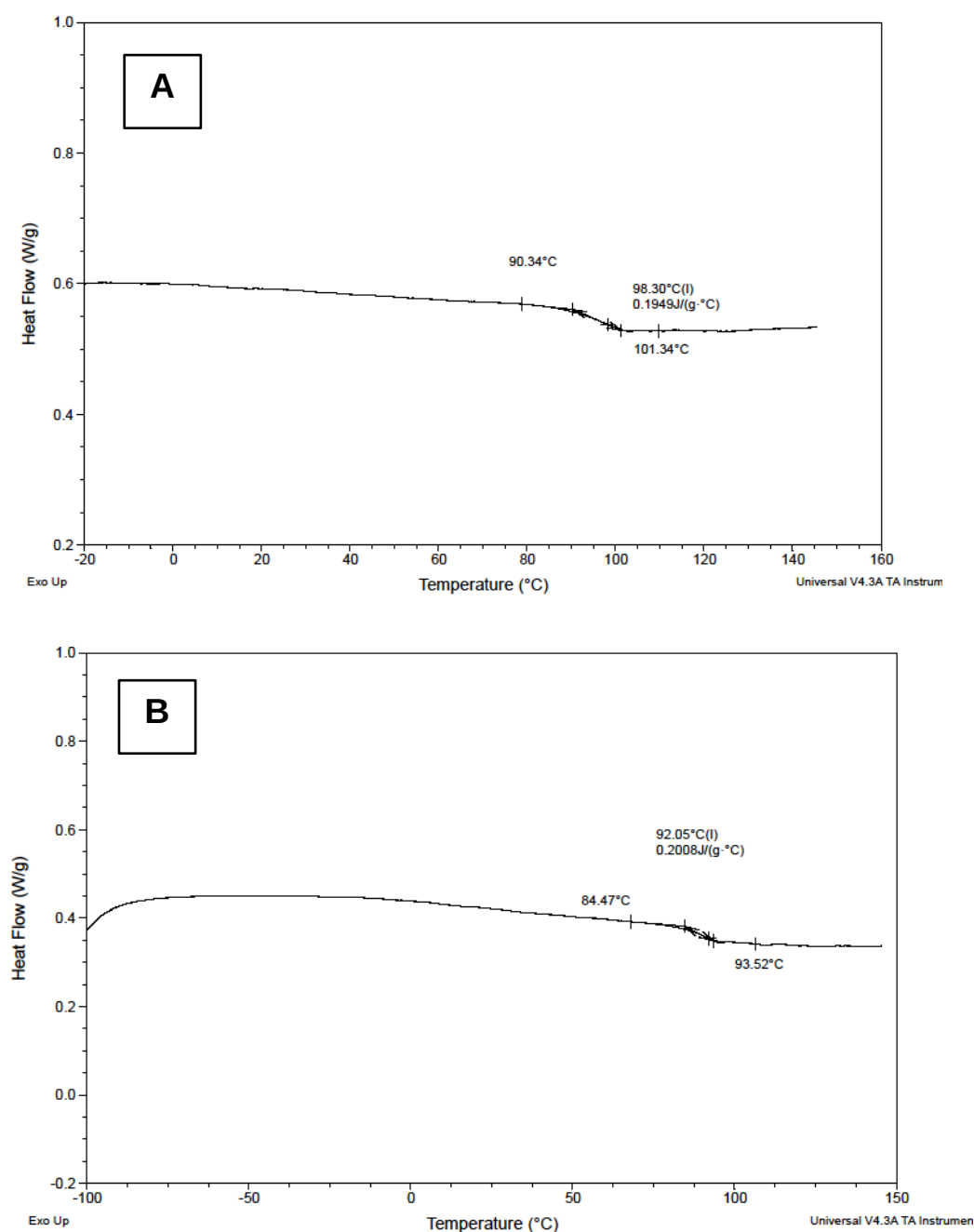


Figure S 6. 9 - DSC thermograms of (A) PCHDC and (B) PLC. All DSC thermograms, the heat flow (W g^{-1} , y-axis) is displayed versus the temperature ($^{\circ}\text{C}$, x-axis). Heating rate: $10^{\circ}\text{C min}^{-1}$. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

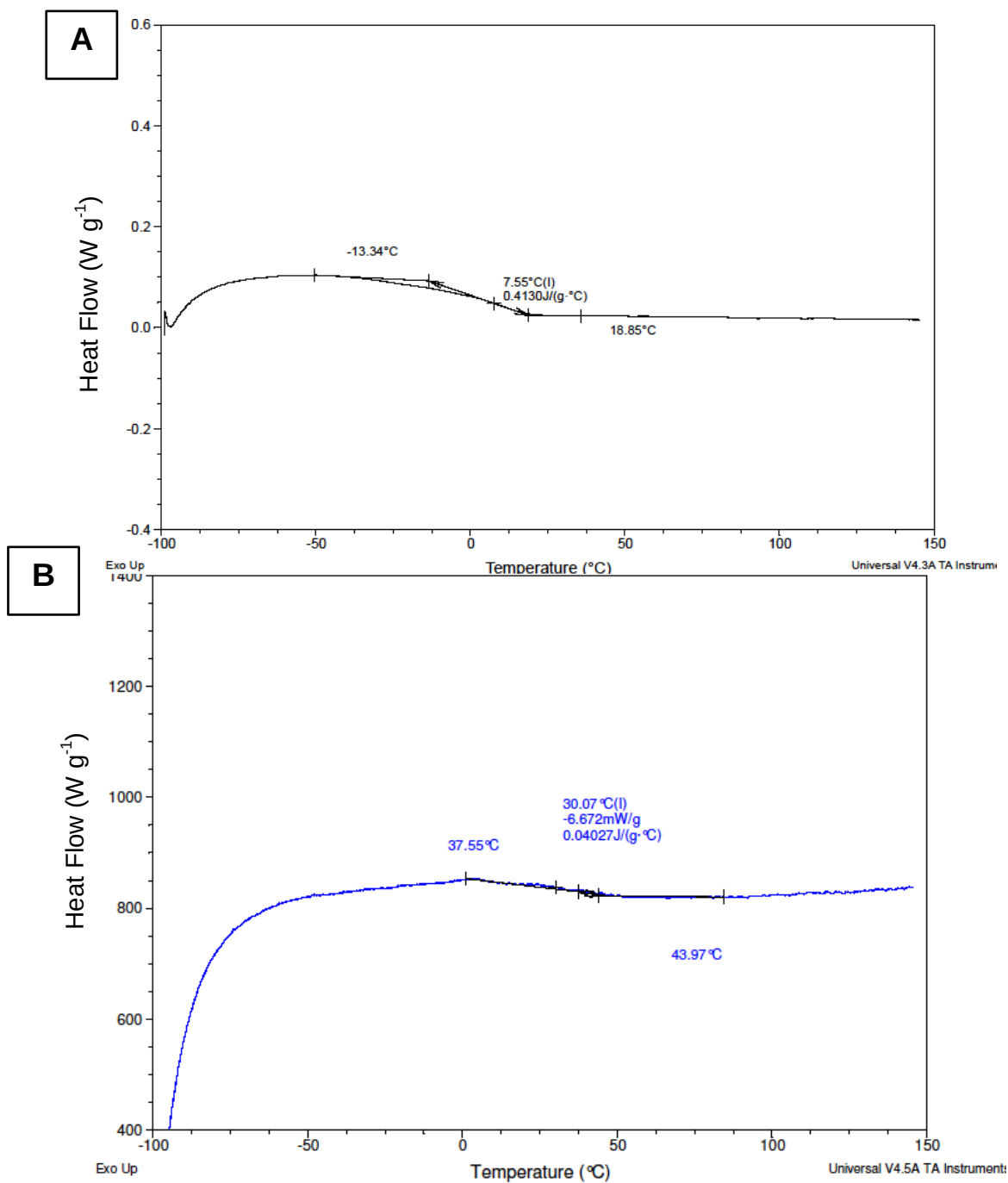


Figure S 6. 10 - DSC thermograms of uncured (C=C):(SH) = 1:1 films for PCHDC (A) and (B) PLC. Heating rate: $10^{\circ}\text{C min}^{-1}$. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

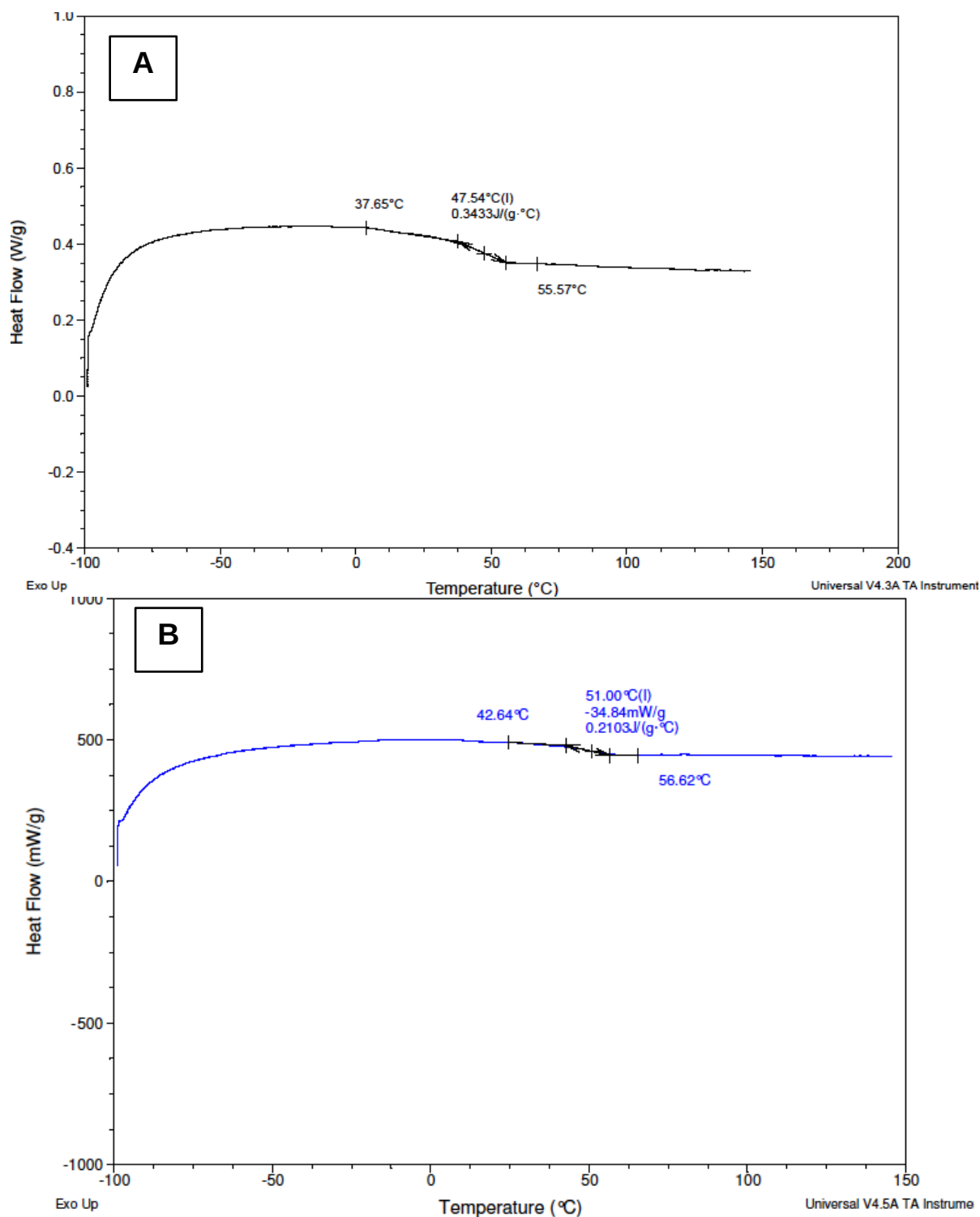


Figure S 6. 11 - DSC thermograms of uncured (C=C):(SH) = 2:1 films for PCHDC (A) and (B) PLC. Heating rate: 10 °C min⁻¹. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

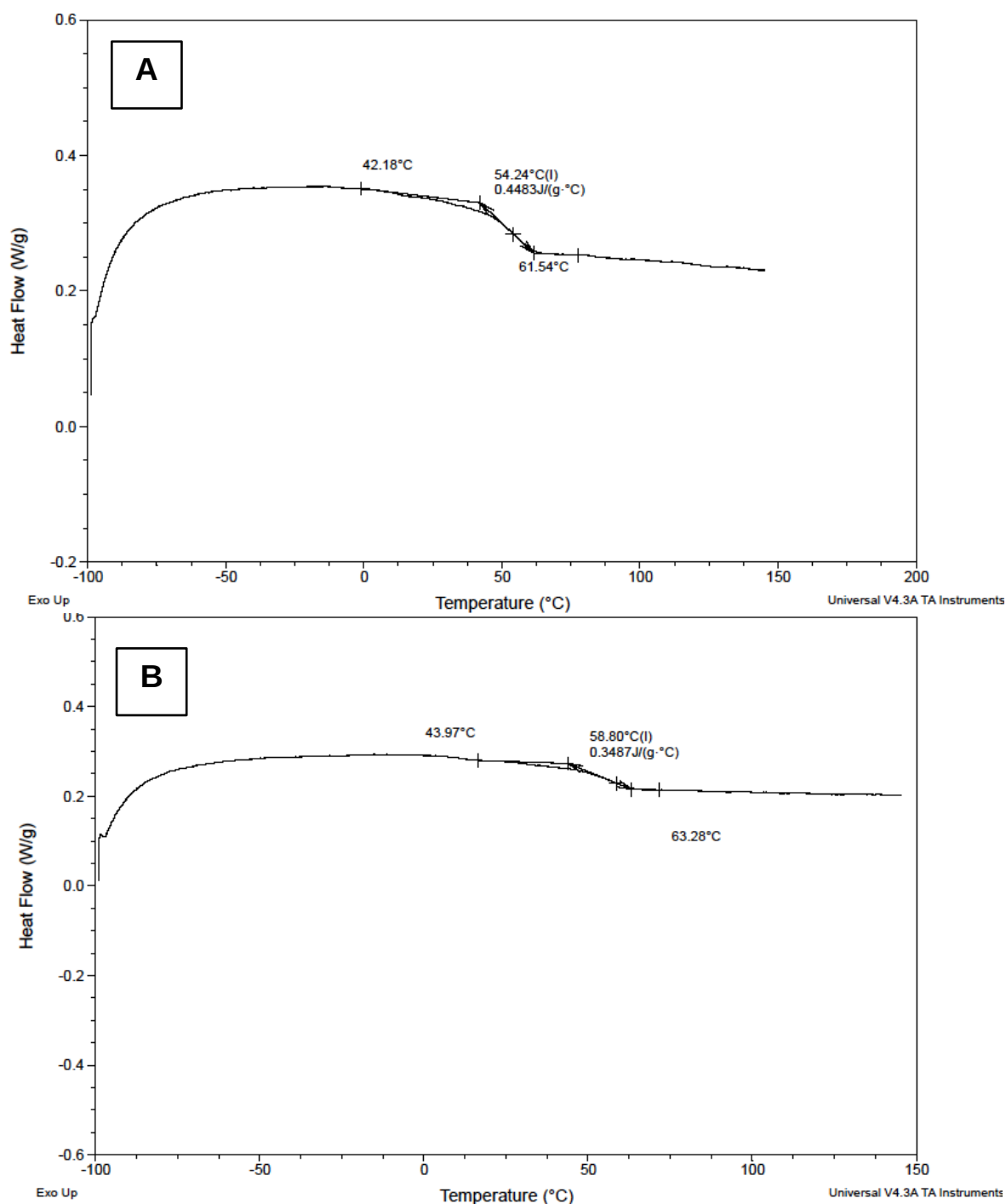


Figure S 6.12 - DSC thermograms of uncured (C=C):(SH) = 4:1 films for PCHDC (A) and (B) PLC films. Heating rate: 10 °C min⁻¹. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Control Experiments

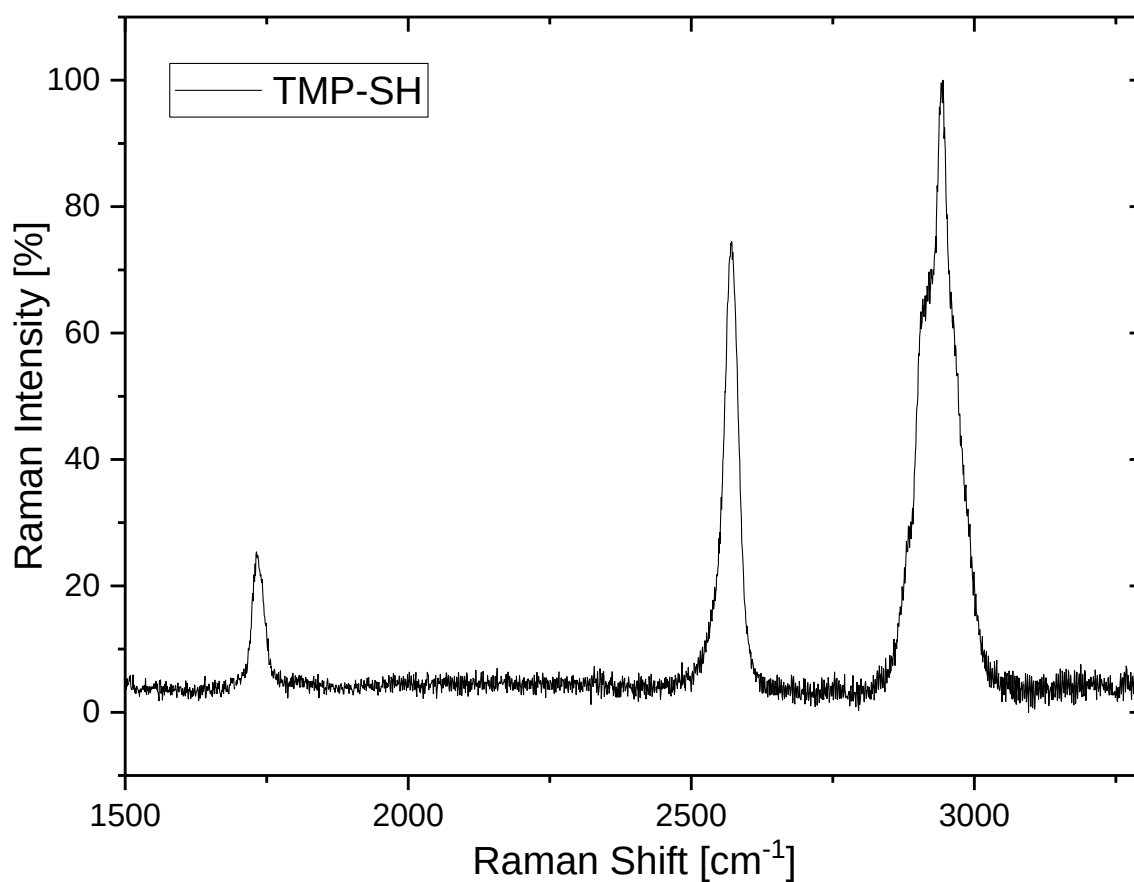


Figure S 6. 13 – Raman Spectrum of TMP-SH. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

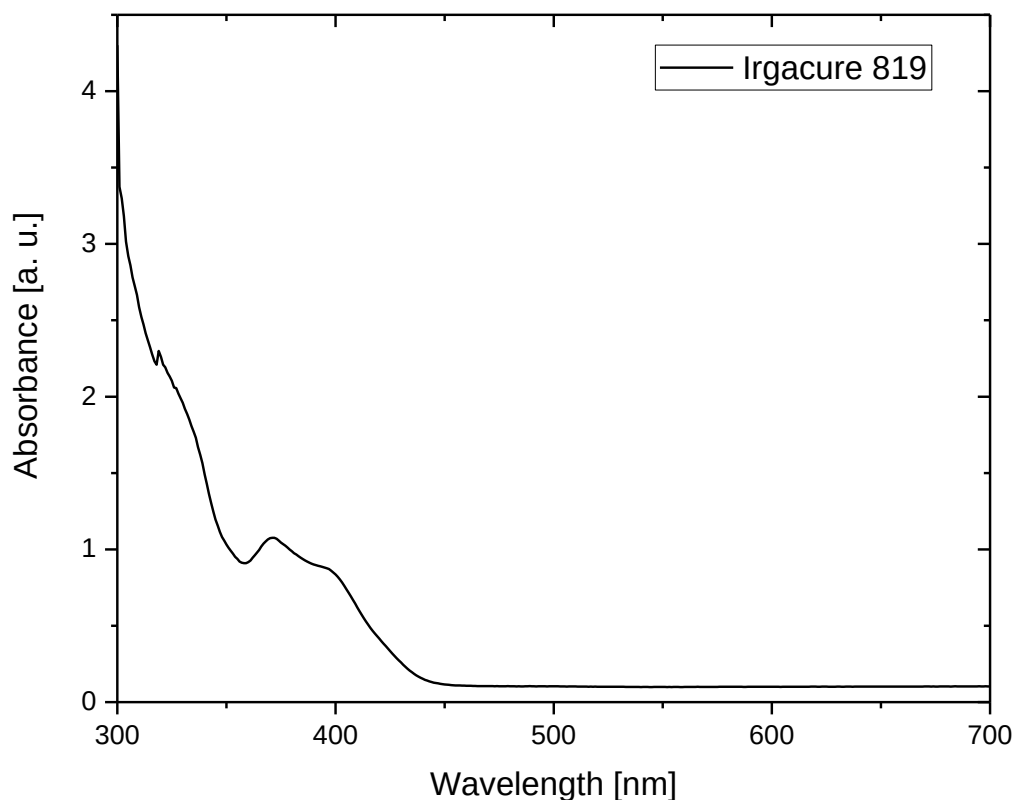


Figure S 6. 14 – UV-6S spectrum of Irgacure 819. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

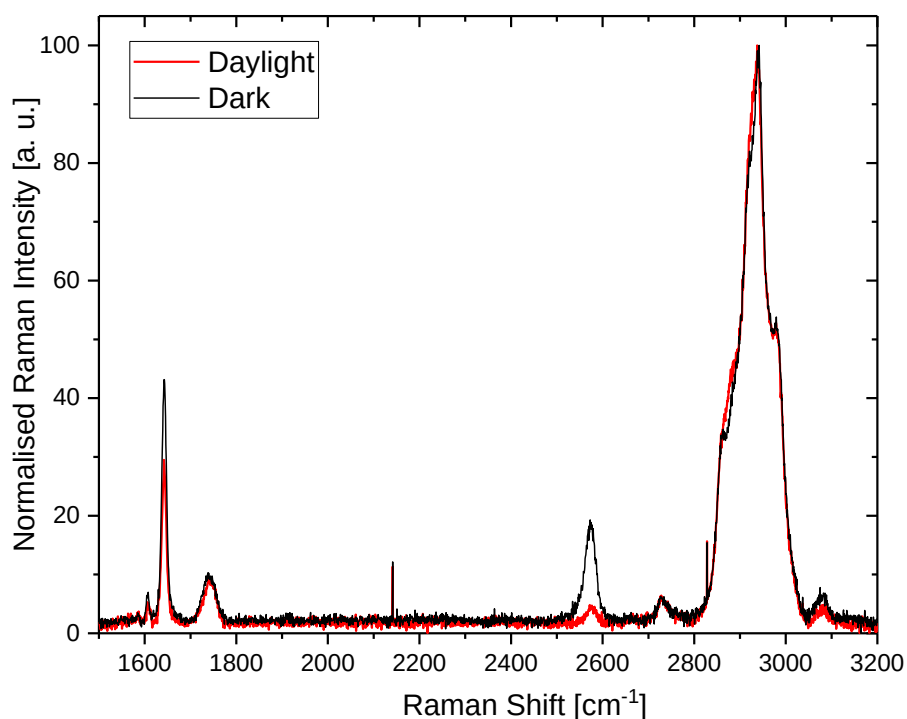


Figure S 6. 15 – Raman spectra of PLC film after casting and curing in the presence of daylight and the exclusion of daylight ((C:C):(SH) = 1:1, 2 mol% irgacure 819). The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

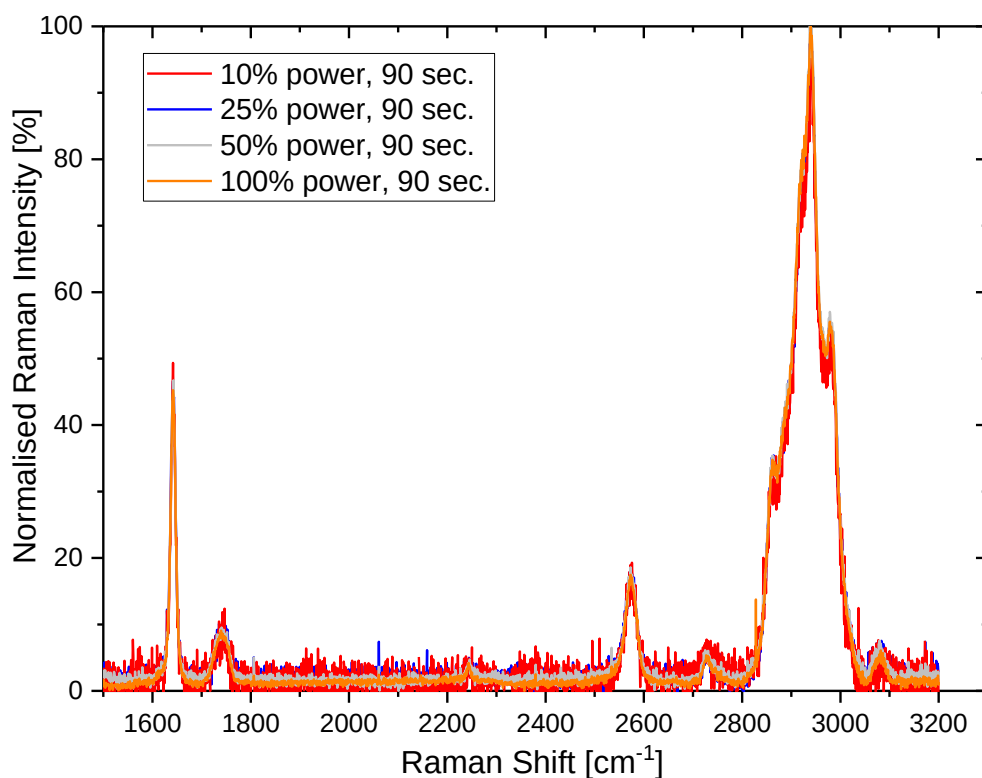


Figure S 6. 16 - Raman spectra of PLC film at different laser power ((C:C):(SH) = 1:1, 2 mol% irgacure 819). The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

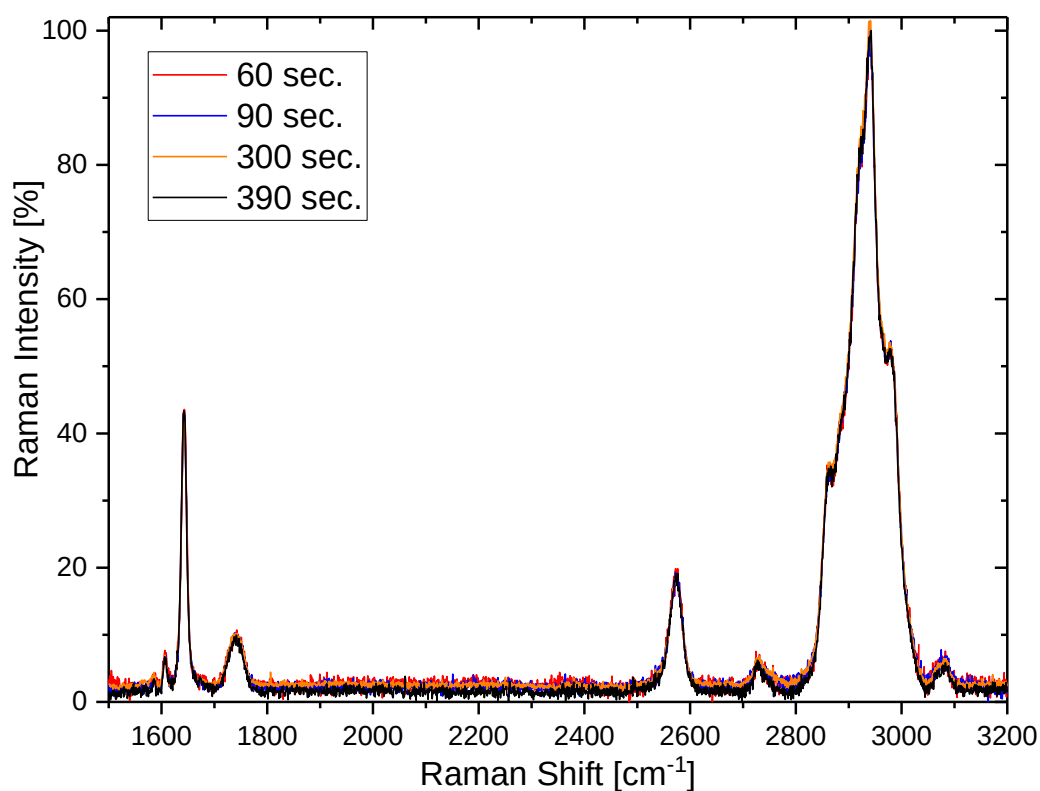


Figure S 6. 17 - Raman spectra of PLC film with different laser exposure times ((C:C):(SH) = 1:1, 2 mol% irgacure 819). The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Individual Raman Spectra for Optimisation of Curing Temperature

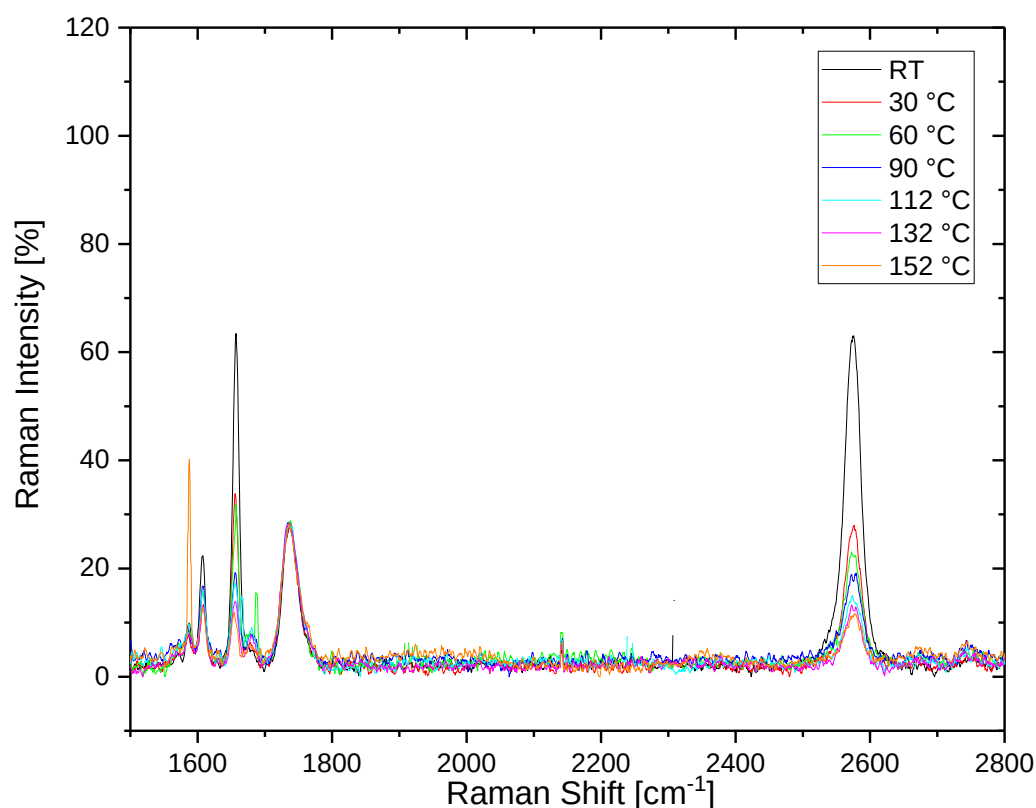


Figure S 6. 18 - Individual Raman spectra for the curing of PCHDC:TMPSH = 1:1 at different temperatures. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

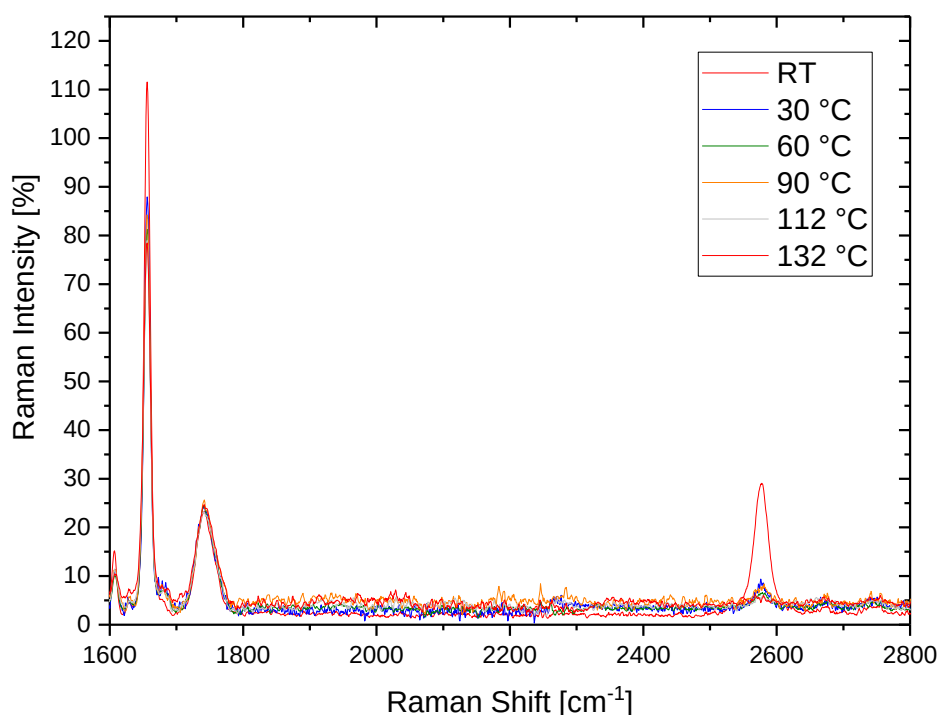


Figure S 6. 19 - Individual Raman spectra for the curing of PCHDC:TMPSH = 4:1 at different temperatures. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

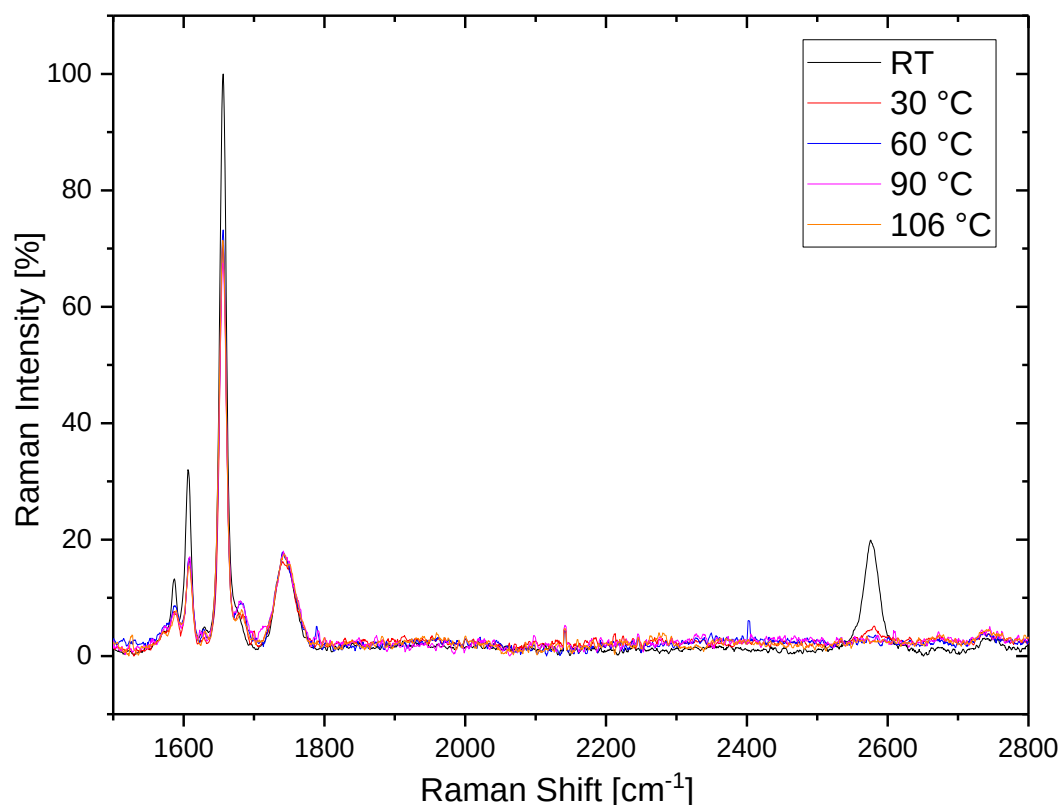


Figure S 6. 20 - Individual Raman spectra for the curing of PCHDC:TMPSH = 4:1 at different temperatures. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

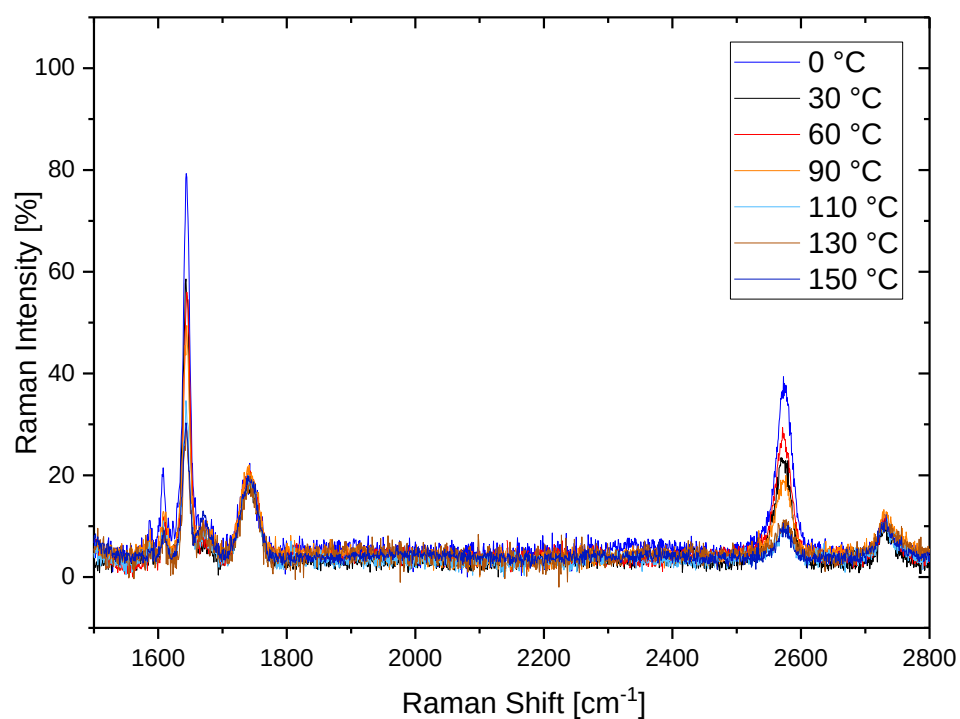


Figure S 6. 21 - Individual Raman spectra for the curing of PLC:TMPSH = 1:1 at different temperatures. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

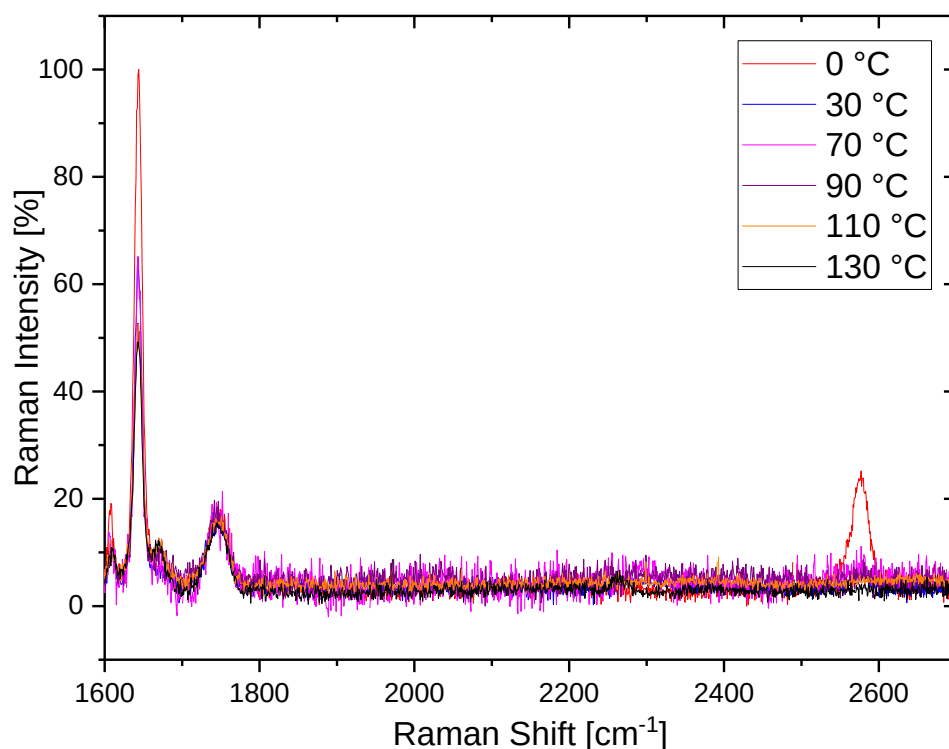


Figure S 6. 22 - Individual Raman spectra for the curing of PLC:TMP SH = 2:1 at different temperatures. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

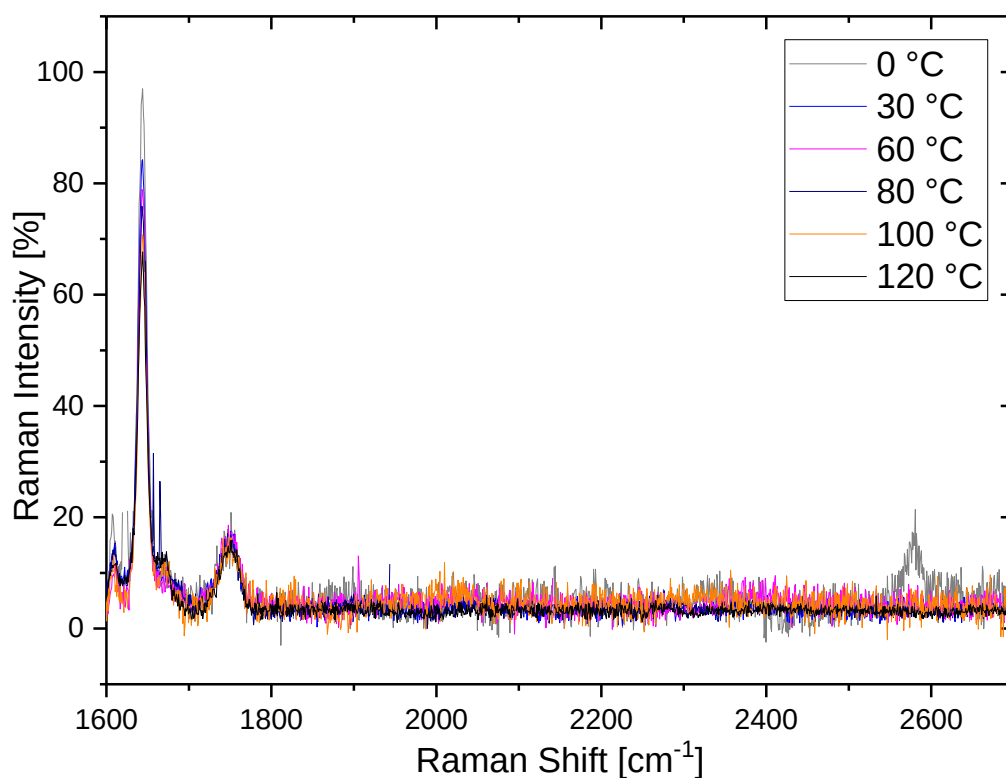


Figure S 6. 23 - Individual Raman spectra for the curing of PLC:TMP SH = 4:1 at different temperatures. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Individual Raman Spectra for Optimisation of Curing Times

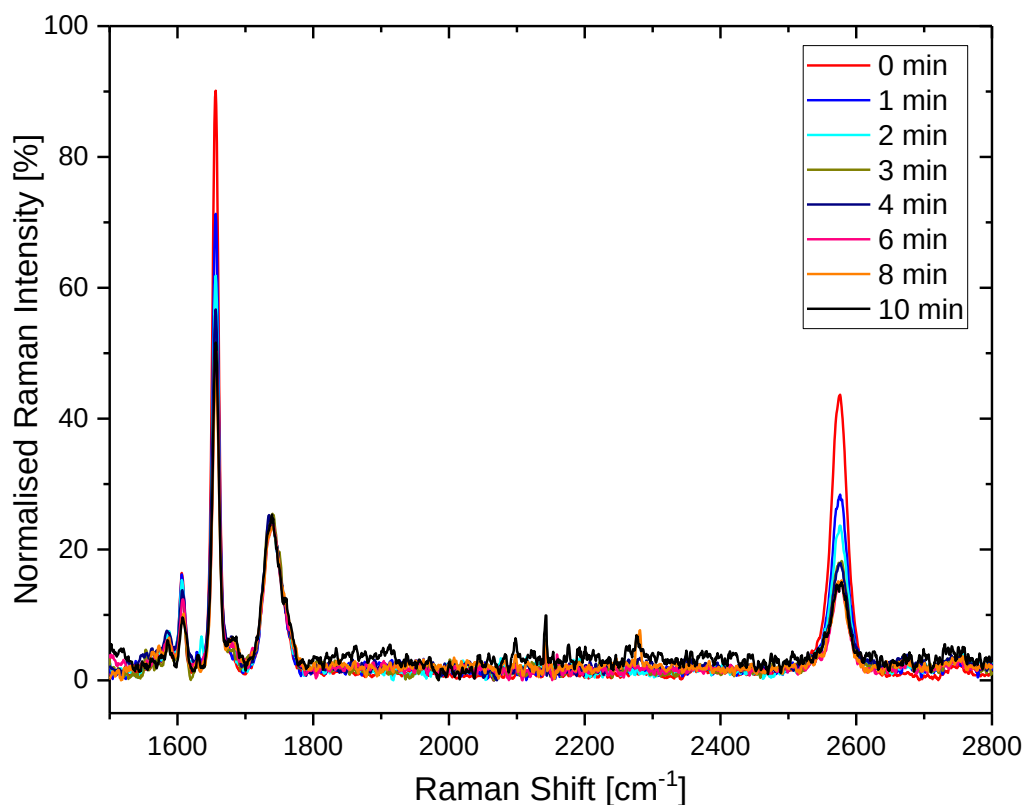


Figure S 6. 24 - Individual Raman spectra for the curing of PCHDC:TMPSH = 4:1 at different times. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

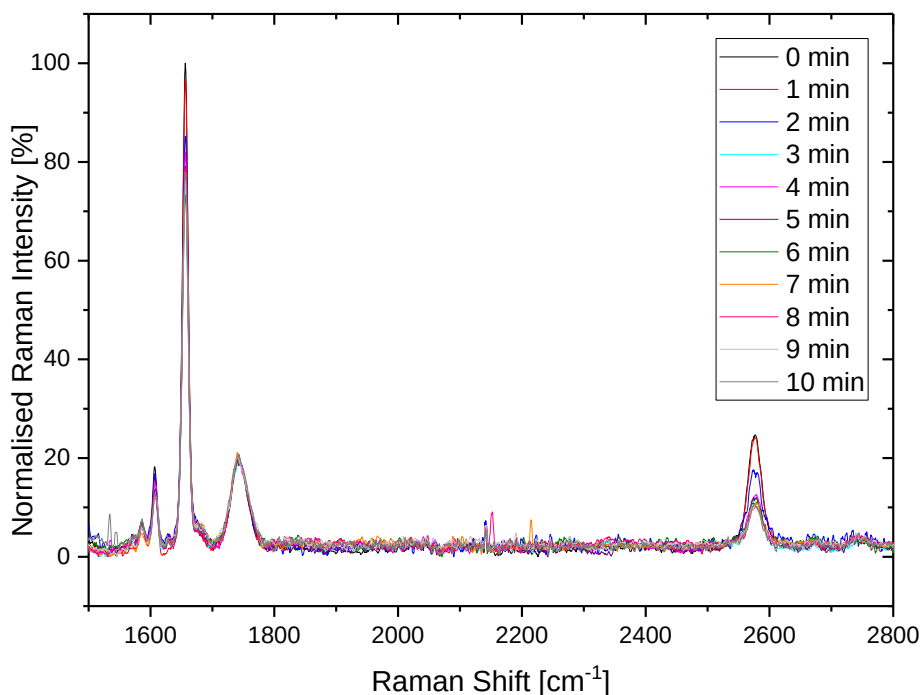


Figure S 6. 25 - Individual Raman spectra for the curing of PCHDC:TMPSH = 2:1 at different times. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

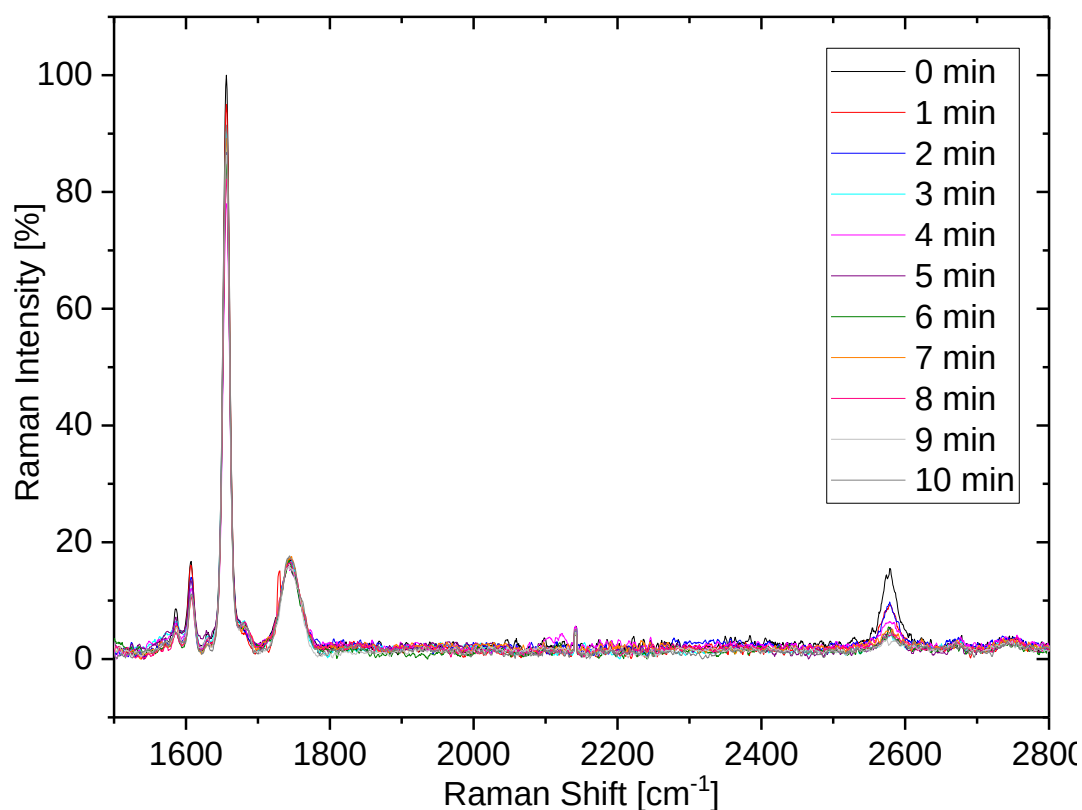


Figure S 6. 26 - Individual Raman spectra for the curing of PCHDC:TMPSH = 4:1 at different times. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

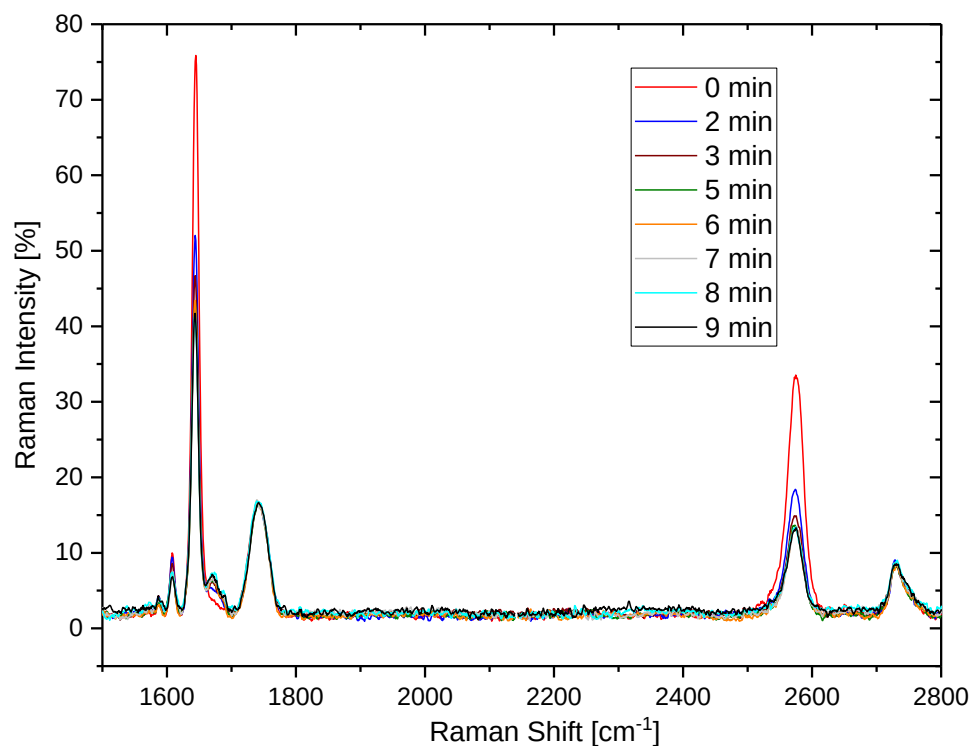


Figure S 6. 27 – Individual Raman spectra for the curing of PLC:TMPSH = 1:1 at different times. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

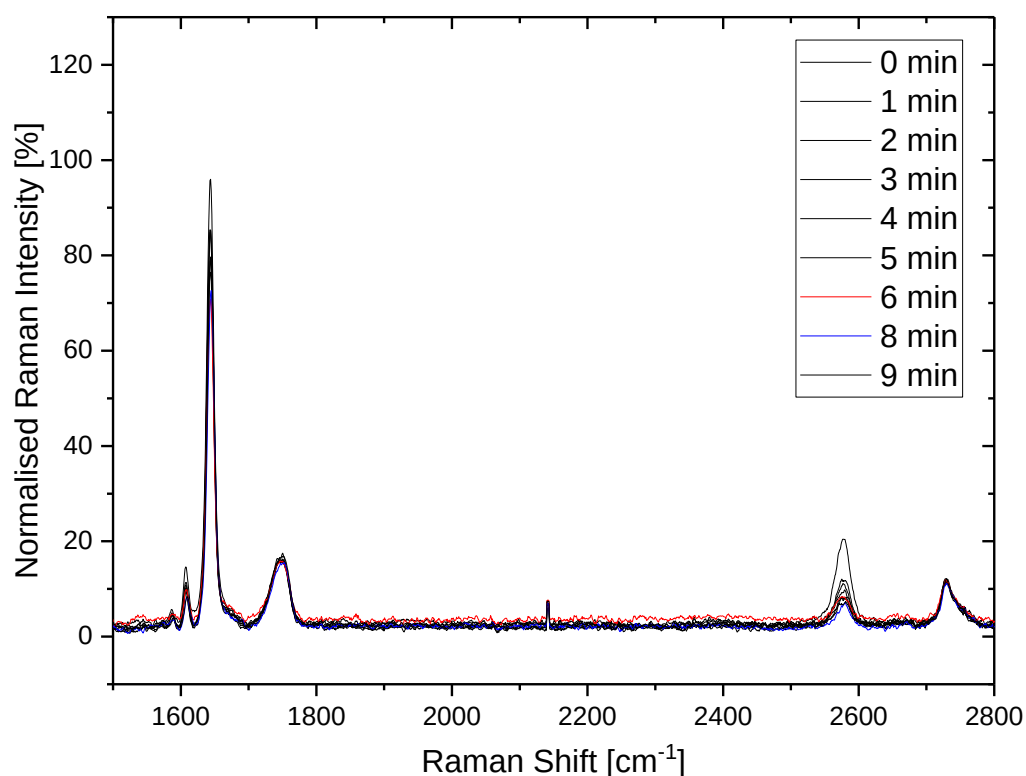


Figure S 6. 28 – Individual Raman spectra for the curing of PLC:TMP SH = 2:1 at different times. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

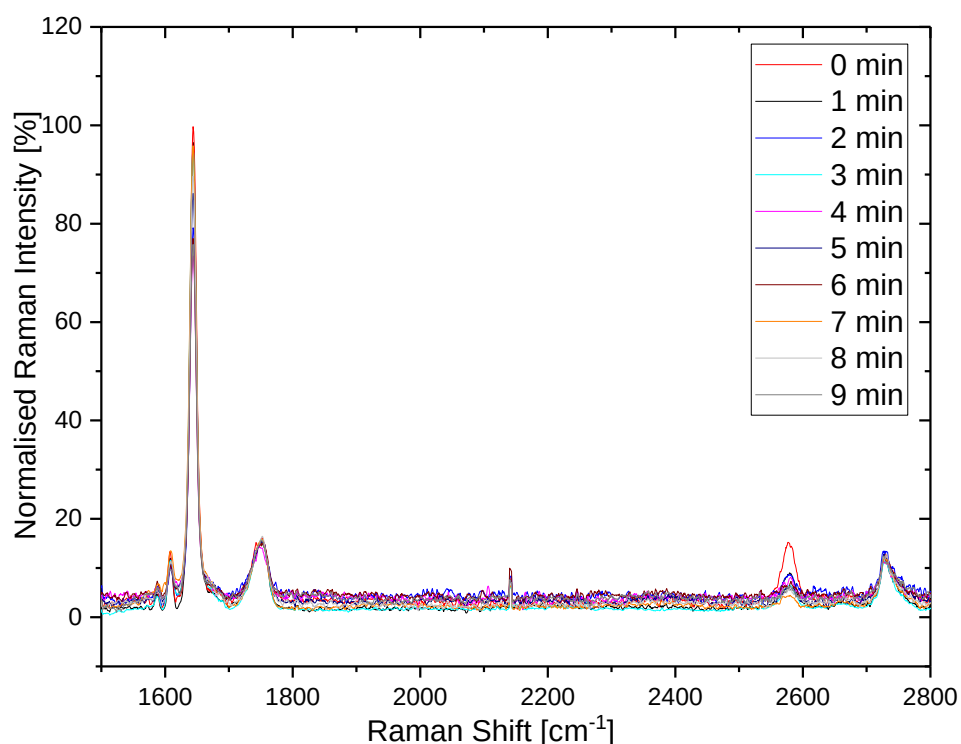


Figure S 6. 29 – Individual Raman spectra for the curing of PLC:TMP SH = 4:1 at different times. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

DMTA Peak Fitting

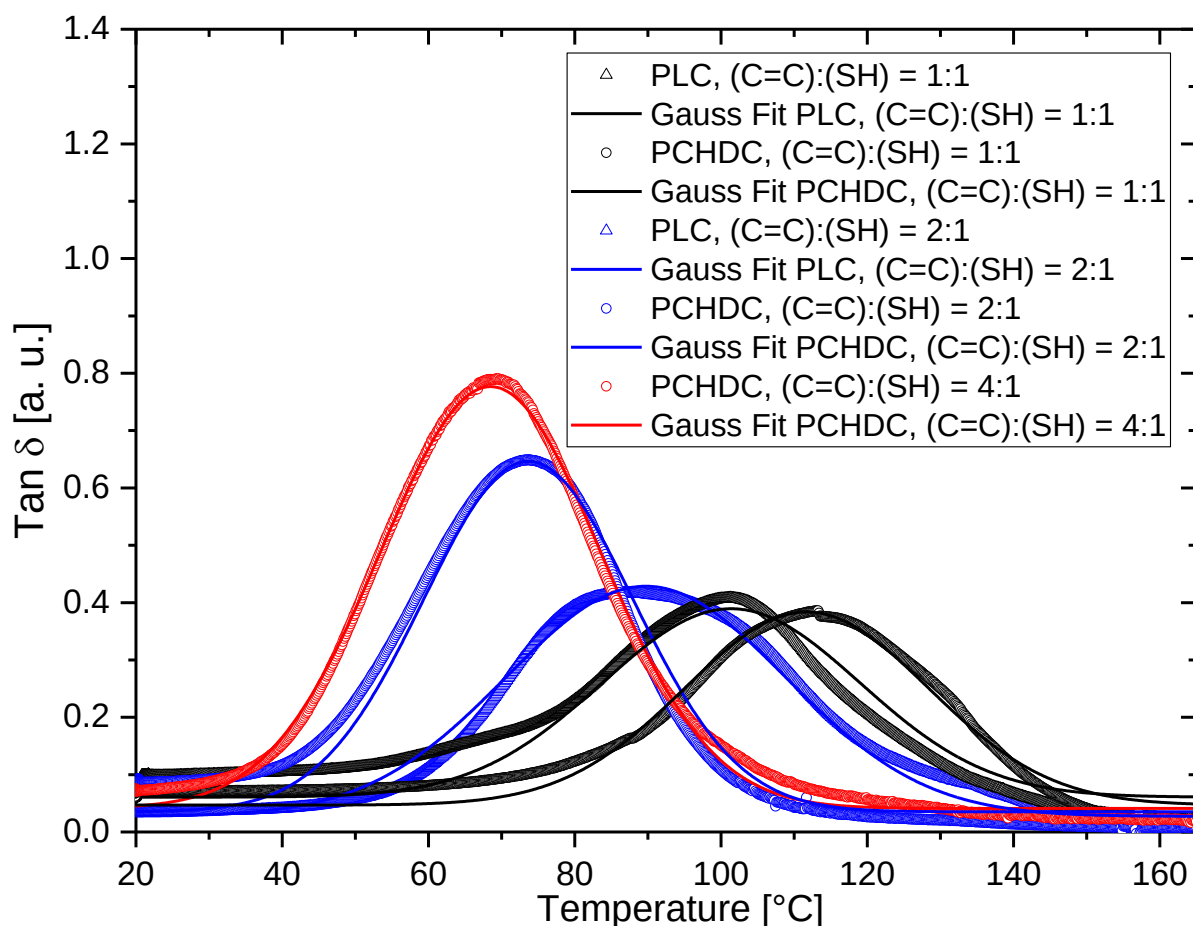


Figure S 6. 30 – Fitting for $\tan \delta$ vs. temperature graphs used to determine FWHM values. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Table S 6. 1 – Data for Fitting with Gauss Model. The table (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Gauss Model: $y = y_0 + (A/(w \cdot \sqrt{\pi/2})) \cdot \exp(-2 \cdot ((x - x_c)/w)^2)$

Reduced Chi-Sqr: 8.56642E-7

Adj. R-Square: 0.99995

	Value	Standard	Error
PLC (C=C):(SH) = 2:1(Tan Delta)	y0	0.0127	8.3924E-4
	xc	63.28342	0.97463
	w	150.09443	5.59044
	A	4.58011	0.29377
	sigma	75.04721	2.79522
	FWHM	176.72268	6.58224
	Height	0.02435	7.55151E-4
PLC (C=C):(SH) = 1:1(Tan Delta)	y0	0.0127	8.3924E-4
	xc	76.88907	0.0273
	w	15.82871	0.08149
	A	1.70945	0.02154

	sigma	7.91436	0.04075
	FWHM	18.63688	0.09595
	Height	0.08617	6.79855E-4
PCHDC (C=C):(SH) = 1:1(Tan Delta)	y0	0.0127	8.3924E-4
	xc	92.91123	0.0365
	w	35.51417	0.04388
	A	16.11067	0.04377
	sigma	17.75709	0.02194
	FWHM	41.81474	0.05166
	Height	0.36195	6.67945E-4
PCHDC (C=C):(SH) = 2:1(Tan Delta)	y0	0.0127	8.3924E-4
	xc	105.03366	0.09272
	w	9.55239	0.24882
	A	0.17821	0.00873
	sigma	4.7762	0.12441
	FWHM	11.24708	0.29296
	Height	0.01489	4.01675E-4
PCHDC (C=C):(SH) = 4:1(Tan Delta)	y0	0.0127	8.3924E-4
	xc	132.69568	0.07299
	w	15.6183	0.15446
	A	0.5785	0.00907
	sigma	7.80915	0.07723
	FWHM	18.38915	0.18186
	Height	0.02955	2.27034E-4

Material Properties obtained from films dried under nitrogen and air

Table S 6. 2 – Material properties for samples dried under nitrogen and air (data collected in collaboration with C. Li, Eindhoven University, The Netherlands). The table (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Dried under	Sample (molar ratio)	Acetone resistance	Thickness (μm)	Pencil hardness	König hardness (s)	Impact
Air	PLC, (C=C):(SH) = 1:1	+	29	2H	109	-
	PLC, (C=C):(SH) = 2:1	+	155	H	96	-
	PLC, (C=C):(SH) = 4:1	-	25	H	102	-
	PCHDC, (C=C):(SH) = 1:1	+	148 and 255	H	113 and 107	-
	PCHDC, (C=C):(SH) = 2:1	-	35	2H	139	-
	PCHDC, (C=C):(SH) = 4:1	-	40	2H	144	-
Nitrogen	PLC, (C=C):(SH) = 1:1	+	40	H	103	-
	PLC, (C=C):(SH) = 2:1	+	36	2H	110	-
	PLC, (C=C):(SH) = 4:1	+/-	32	2H	114	-
	PCHDC, (C=C):(SH) = 1:1	+	60	2H	123	-
	PCHDC, (C=C):(SH) = 2:1	+	40	2H	151	-
	PCHDC, (C=C):(SH) = 4:1	+/-	38	H	159	-

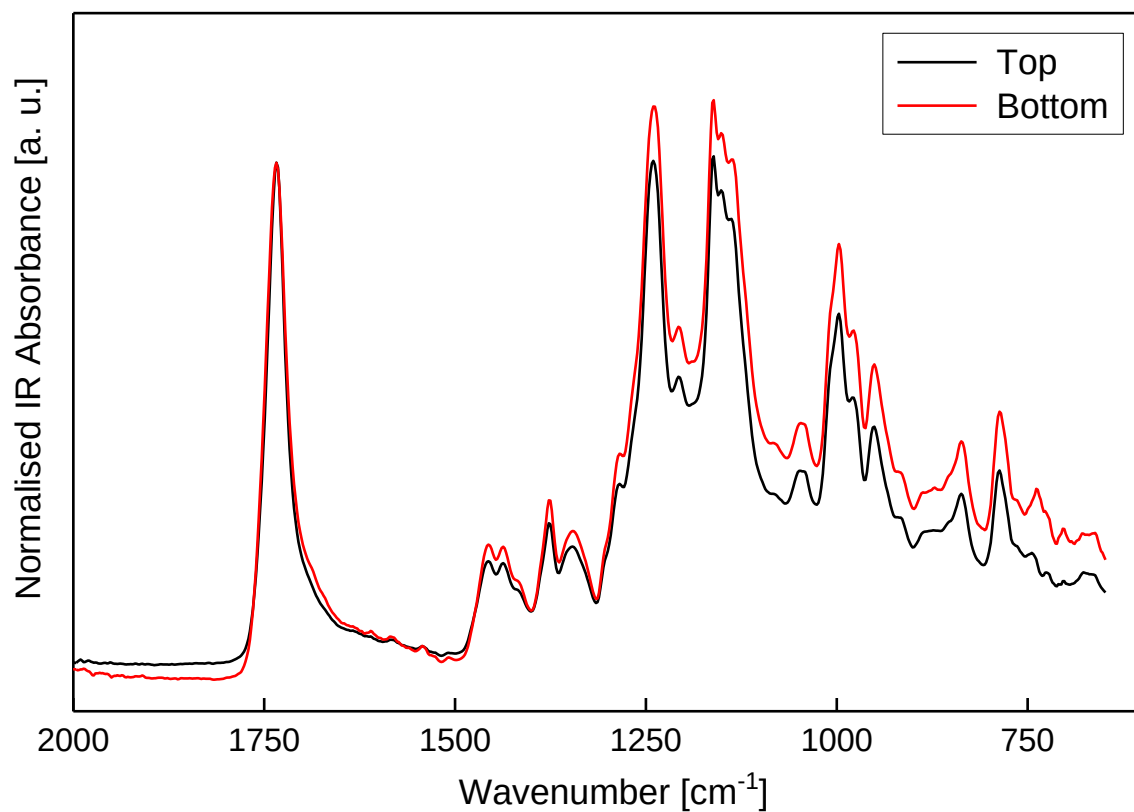


Figure S 6. 31 – ATR-IR spectra of top and bottom of films dried under nitrogen. The figure (caption) is reprinted (adapted) with permission from *Polym. Chem.* **2017**, 8, 6099. Copyright (2018) Royal Society of Chemistry.

Calculation of Crosslink-Density

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The crosslink-density ν_e is defined as the “number of crosslinks per unit volume in a polymer network” (IUPAC).^[10] For cross-linked films, the crosslink-density can be calculated based on the storage modulus E' in the rubbery plateau (measured by DMTA):^[11, 12]

$$E' = 3\nu_e RT,$$

with ν_e as the cross-link density, R as the universal gas constant ($8.314 \frac{J}{mol K}$) and T as the onset temperature of the rubbery plateau in Kelvin. The onset of the rubbery plateau was determined from the Storage Modulus vs. Temperature graph from DMTA once two data points had a difference of less than 0.11% in storage modulus.

Table S 6. 3 - Determination of Crosslink-Density.

Entry	Polymer, Ratio (C=C) : (SH)	$T_{\text{Rubbery}} (^{\circ}C)$	$E'_{\text{Rubbery}} (MPa)$	$\nu_e \left(10^{-3} \frac{\text{mol}}{\text{cm}^3}\right)$
1	PCHDC, 1:1	149.1	27.0	2.5
2	PCHDC, 2:1	131.5	10.8	1.1
3	PCHDC, 4:1	135.5	2.7	0.26
4	PLC, 1:1	136.6	18.0	1.76
5	PLC, 2:1	138.2	6.2	0.6
6 (Reference) ^[12]	Acrylic/MF clearcoat	108	33	3.47

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Chapter 7 - New Polymerisation Catalysts based on *ortho*-Vanillin

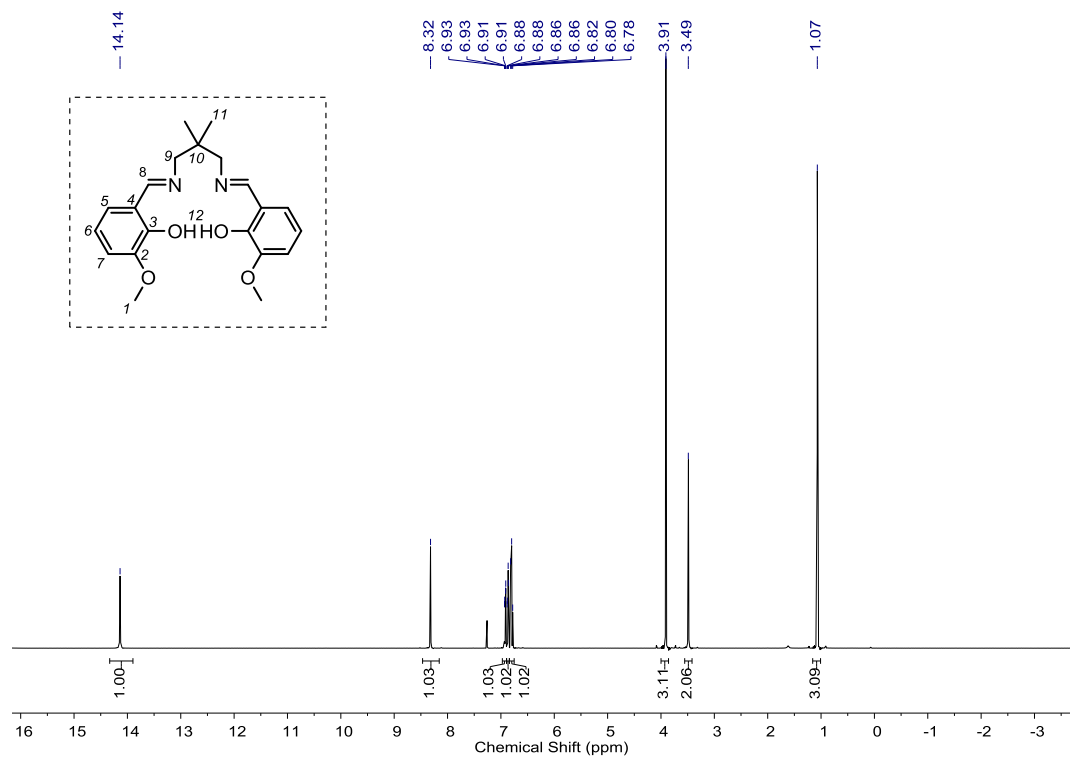


Figure S 7. 1 – ^1H NMR spectrum of **7.4** in CDCl_3 .

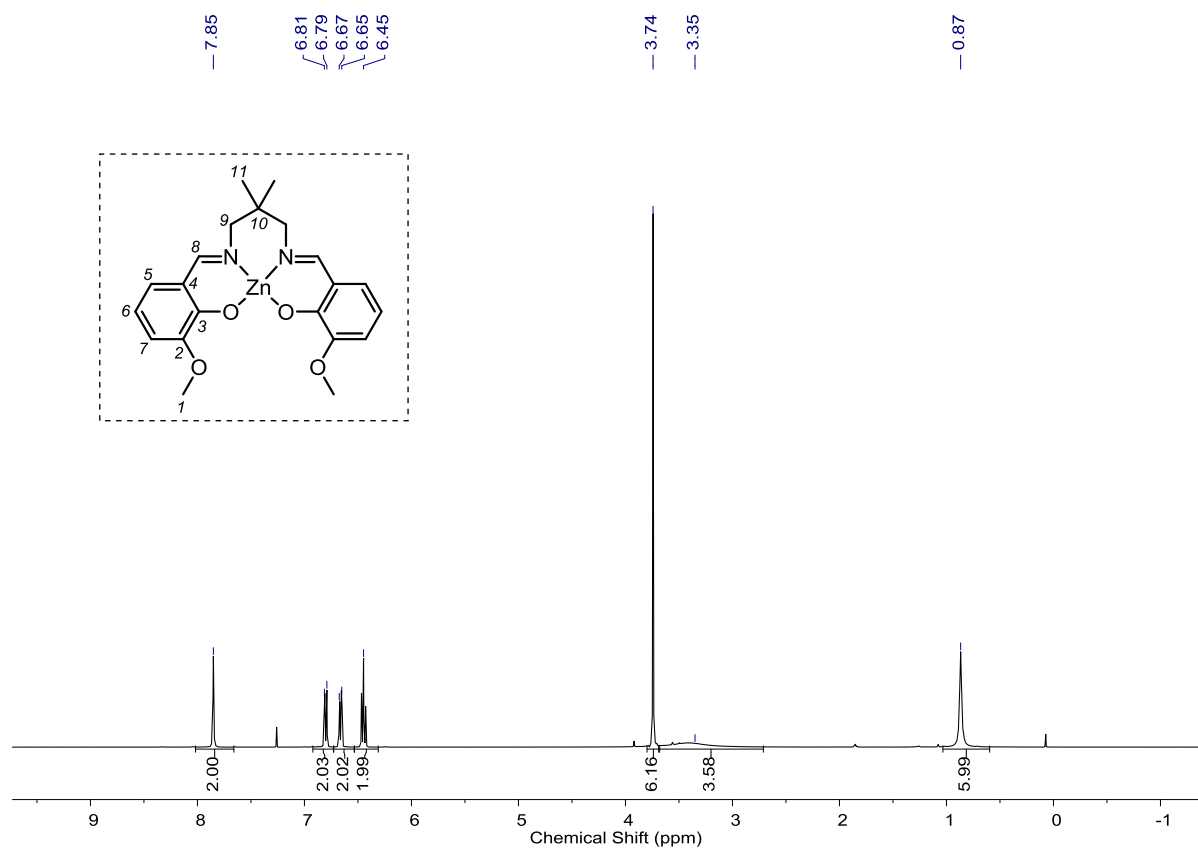
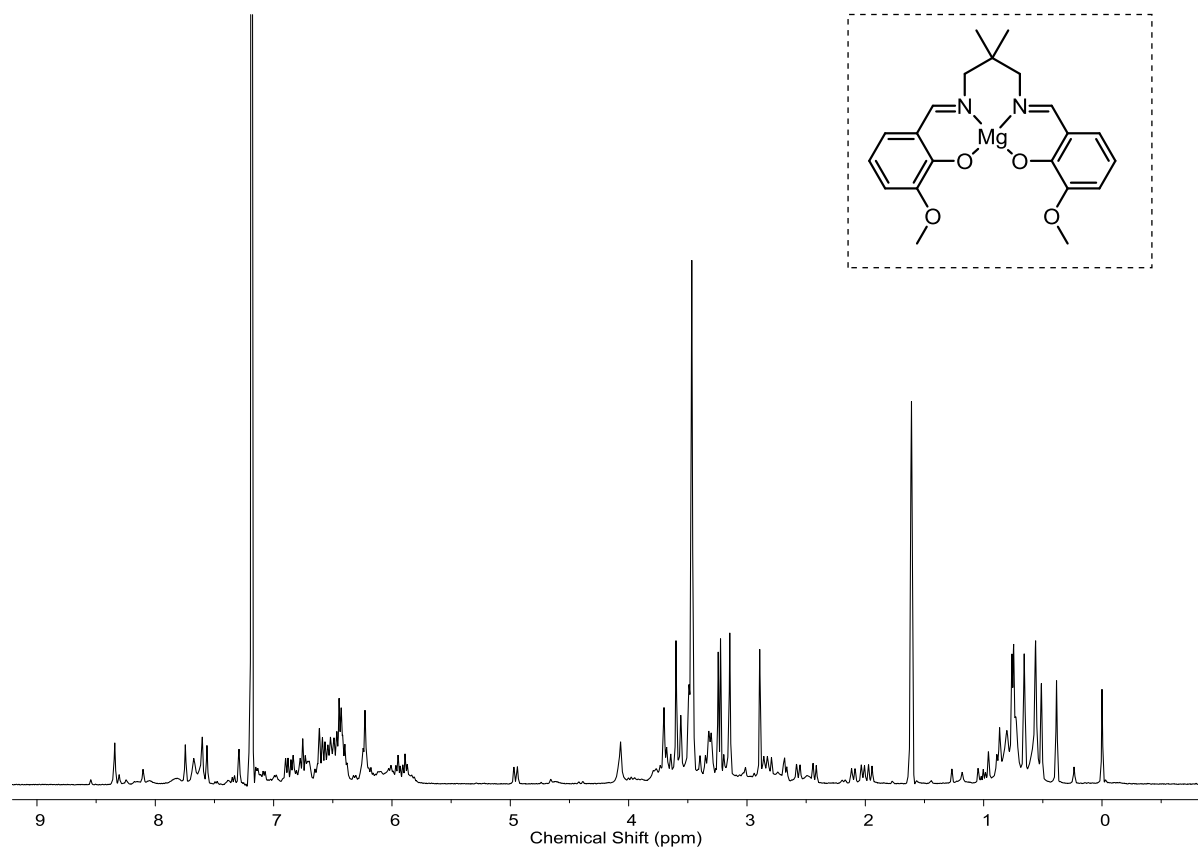
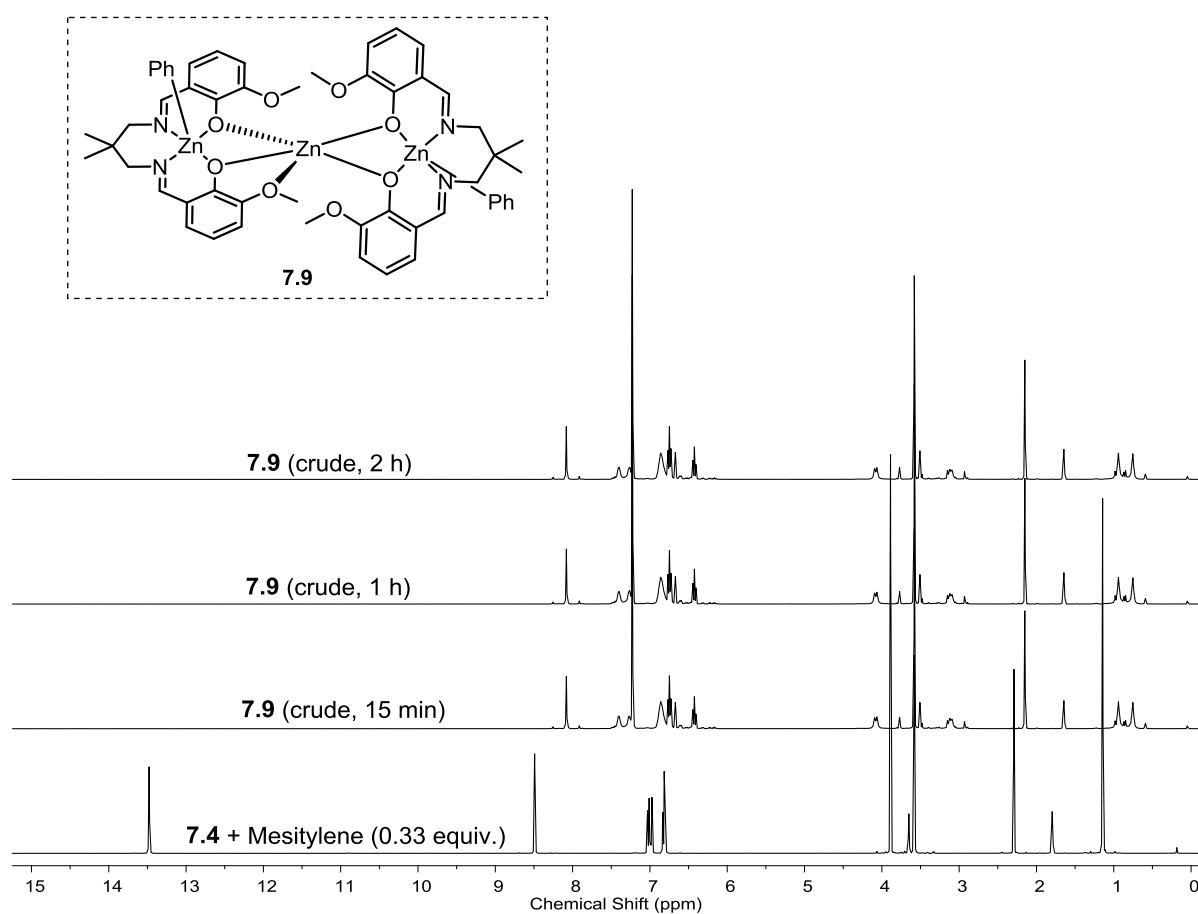
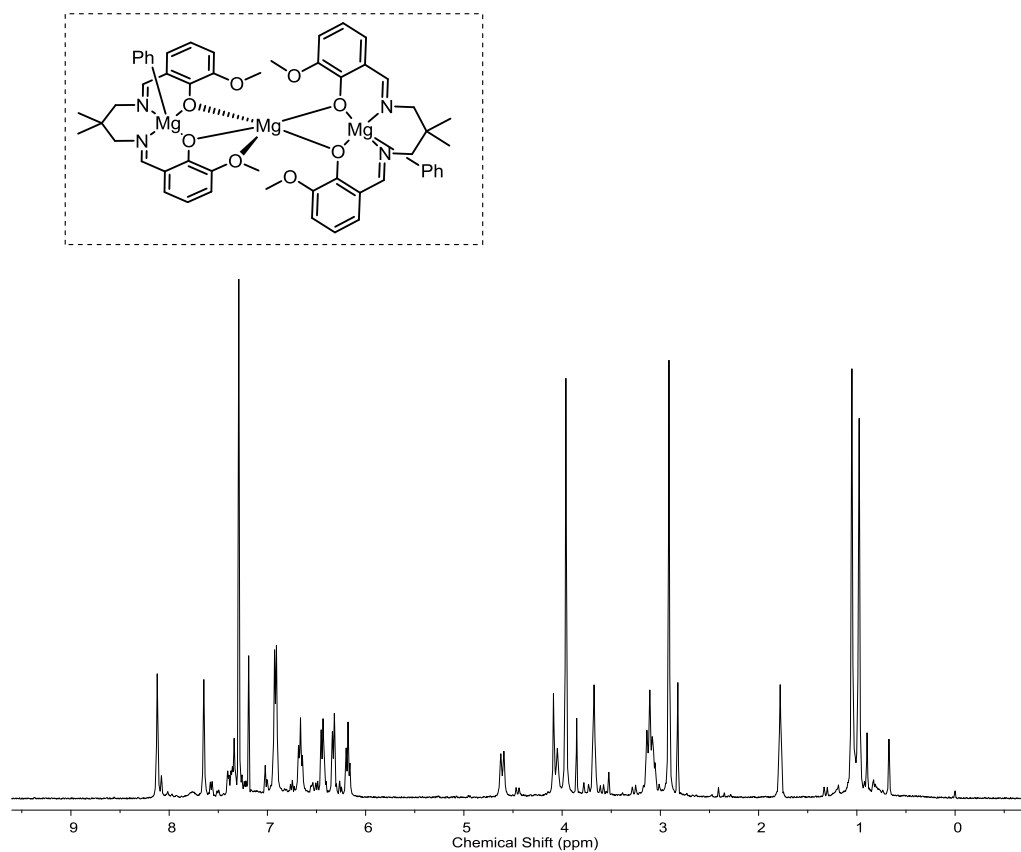
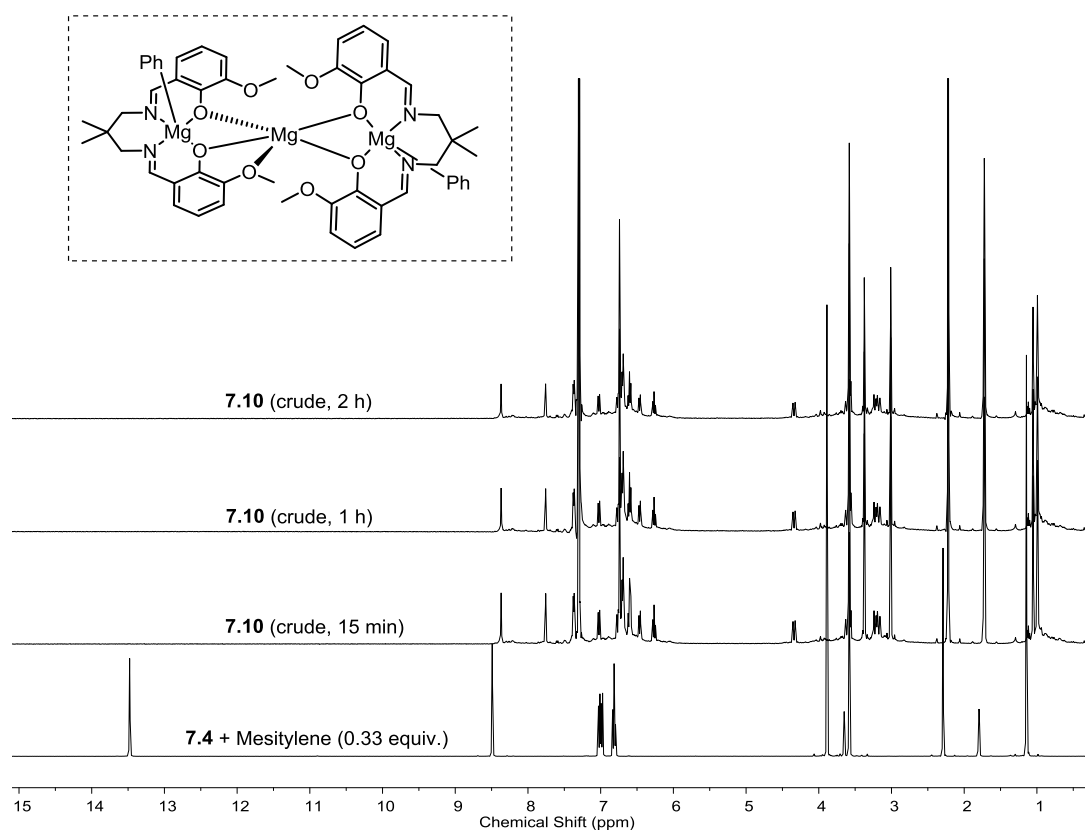
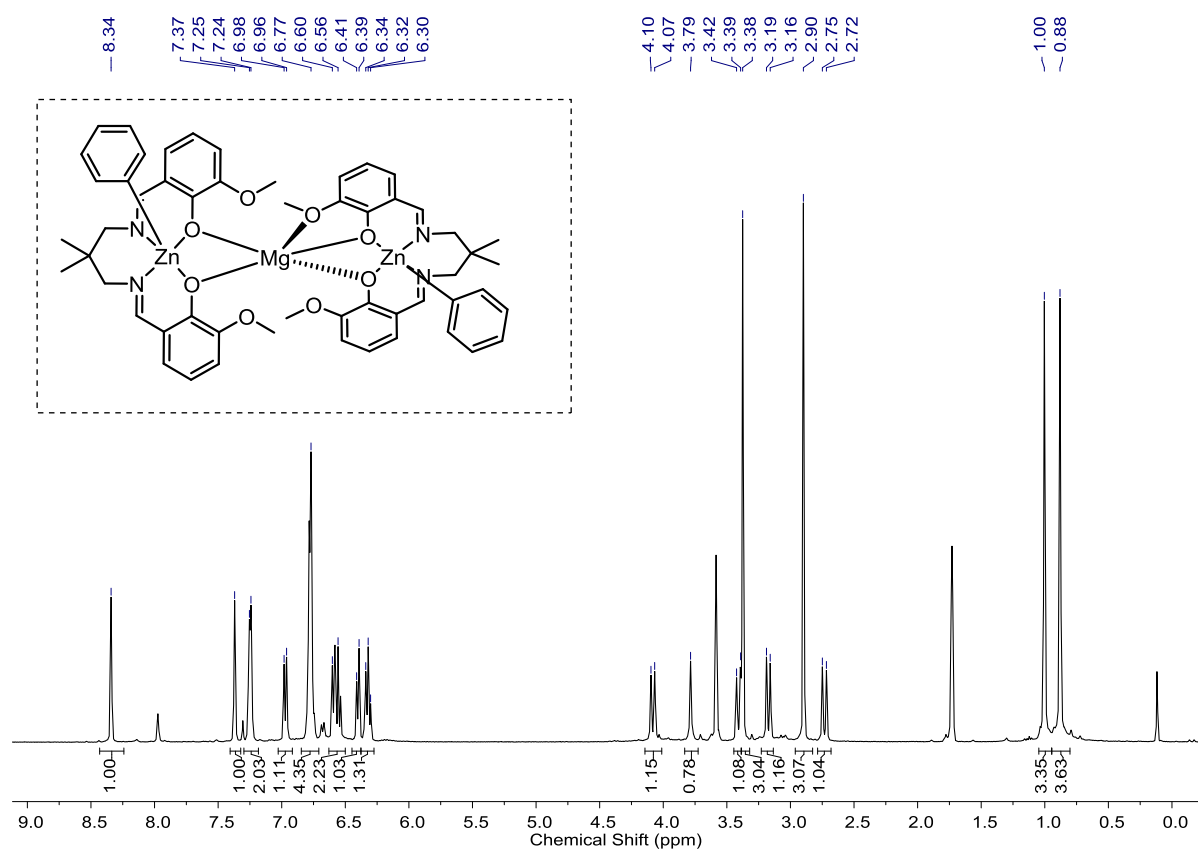
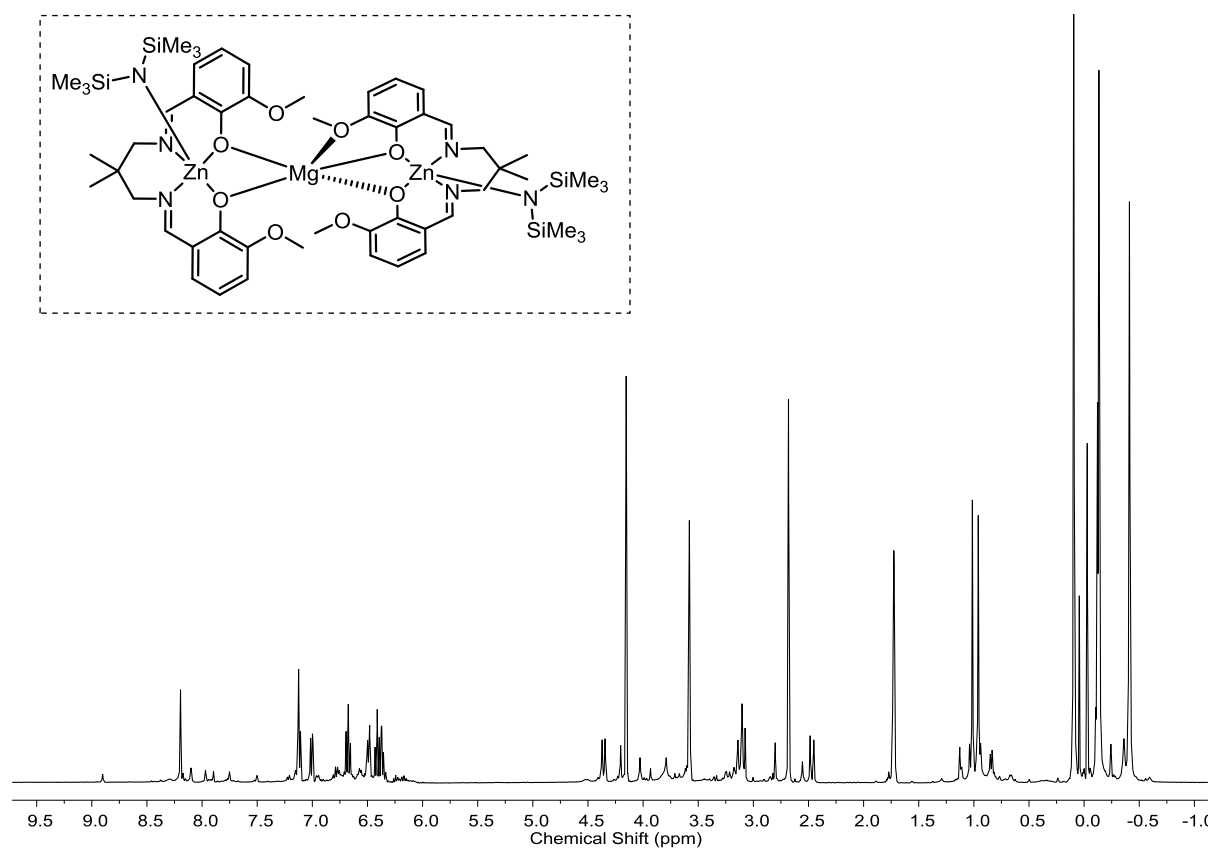
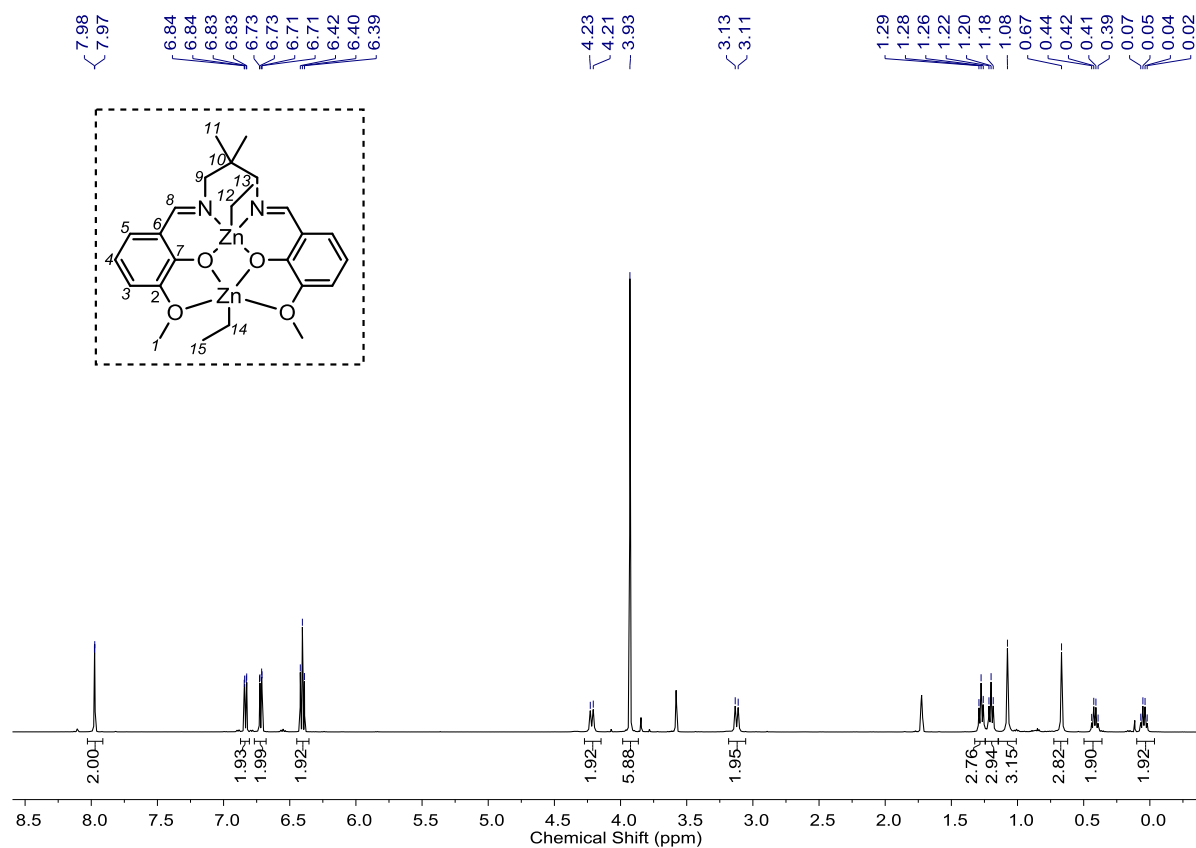
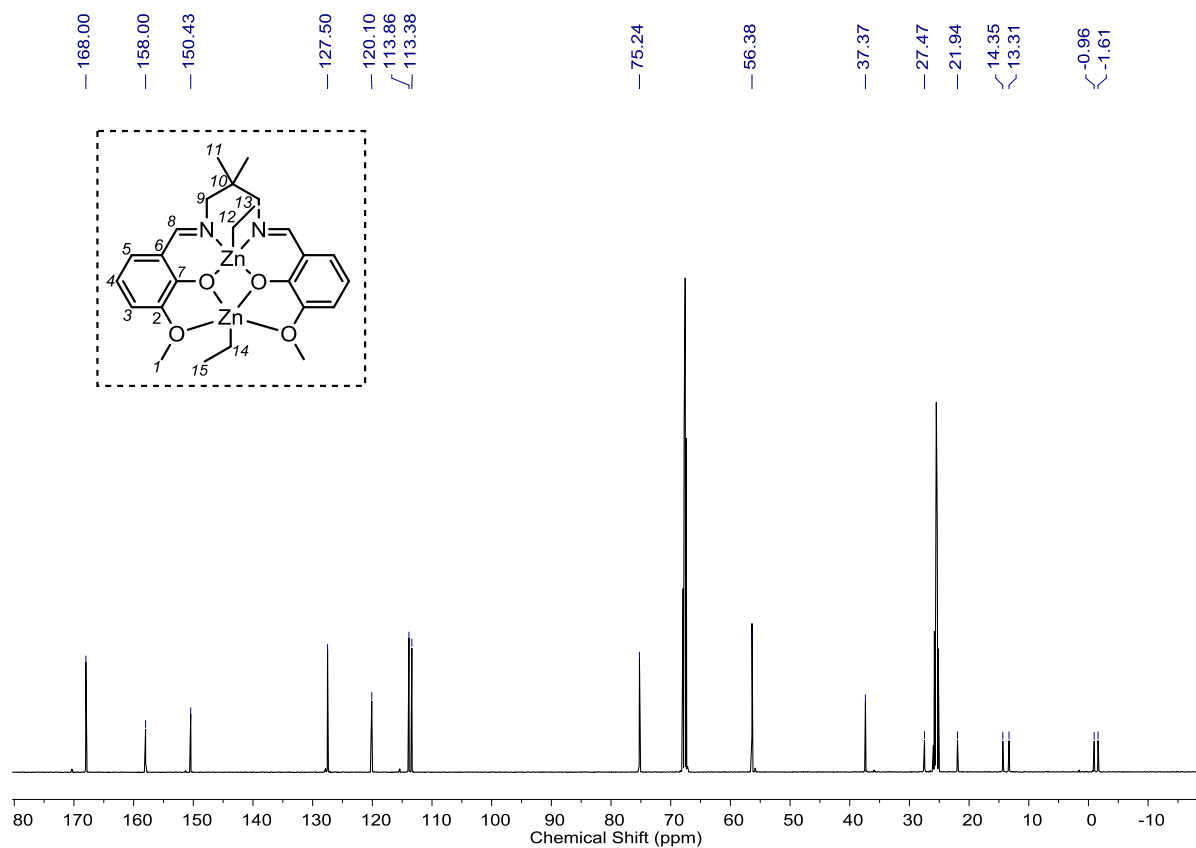


Figure S 7. 2 – ^1H NMR spectrum of **7.5** in CDCl_3 .

Figure S 7. 3 – ^1H NMR spectrum of **7.6** (crude mixture).Figure S 7. 4 – ^1H NMR spectra of crude mixture containing **7.9** in THF-d_8 .

Figure S 7. 5 – ^1H NMR spectrum of isolated **7.10** in CDCl_3 .Figure S 7. 6 - ^1H NMR spectra of crude mixture containing **7.10** in THF-d_8 .

Figure S 7. 7 – ^1H NMR spectrum of **7.9** in THF-d_8 .Figure S 7. 8 - ^1H NMR spectrum of **7.9** in CDCl_3 .

Figure S 7. 9 – ¹H NMR spectrum of **7.13** in THF-d₈.Figure S 7. 10 – ¹³C{¹H} NMR spectrum of **7.13** in THF-d₈.

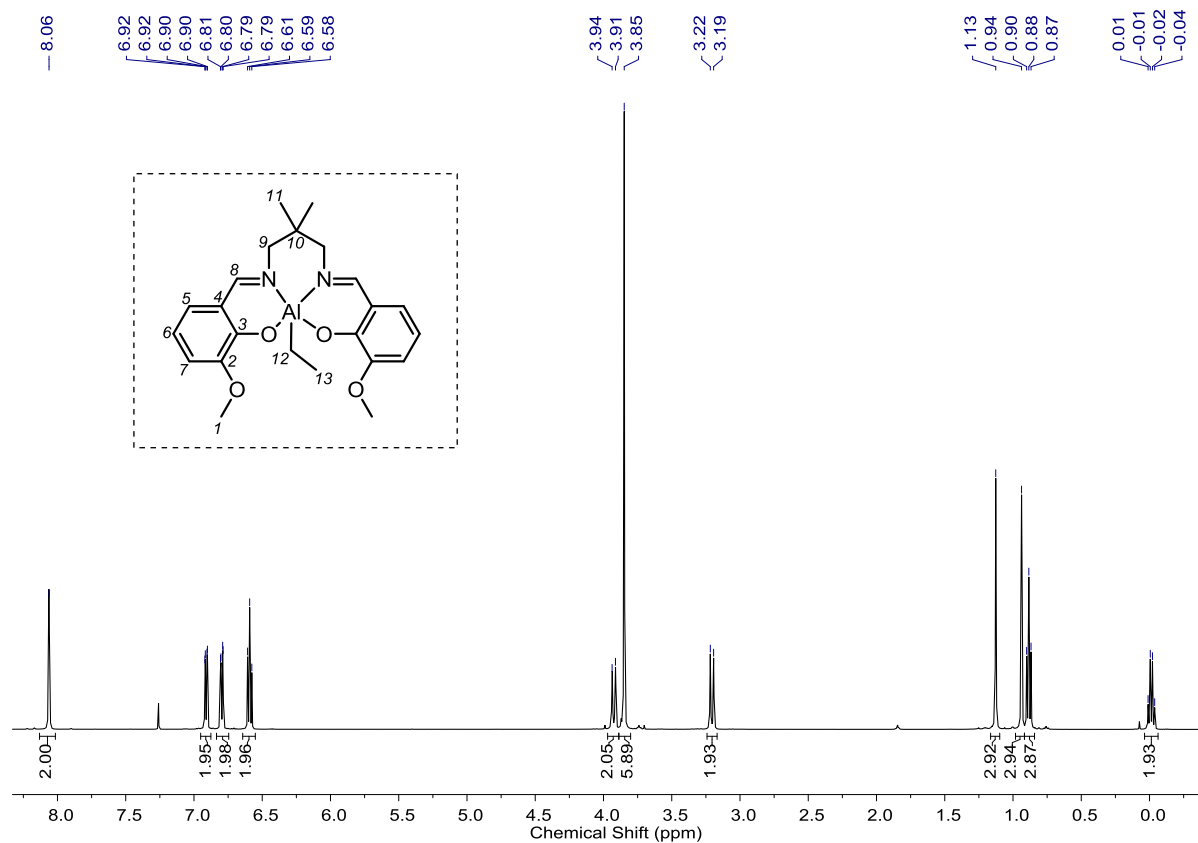


Figure S 7. 11 – ^1H NMR spectrum of **7.16** in CDCl_3 .

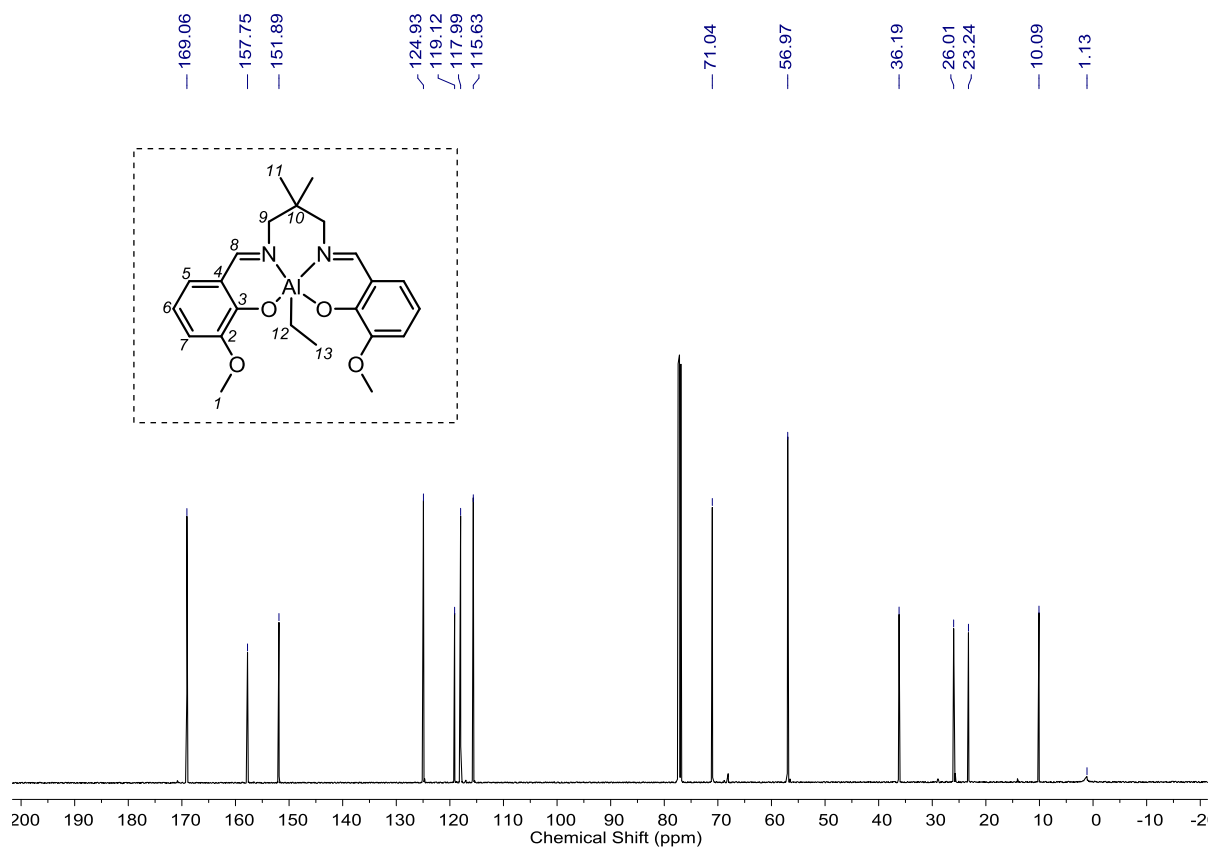
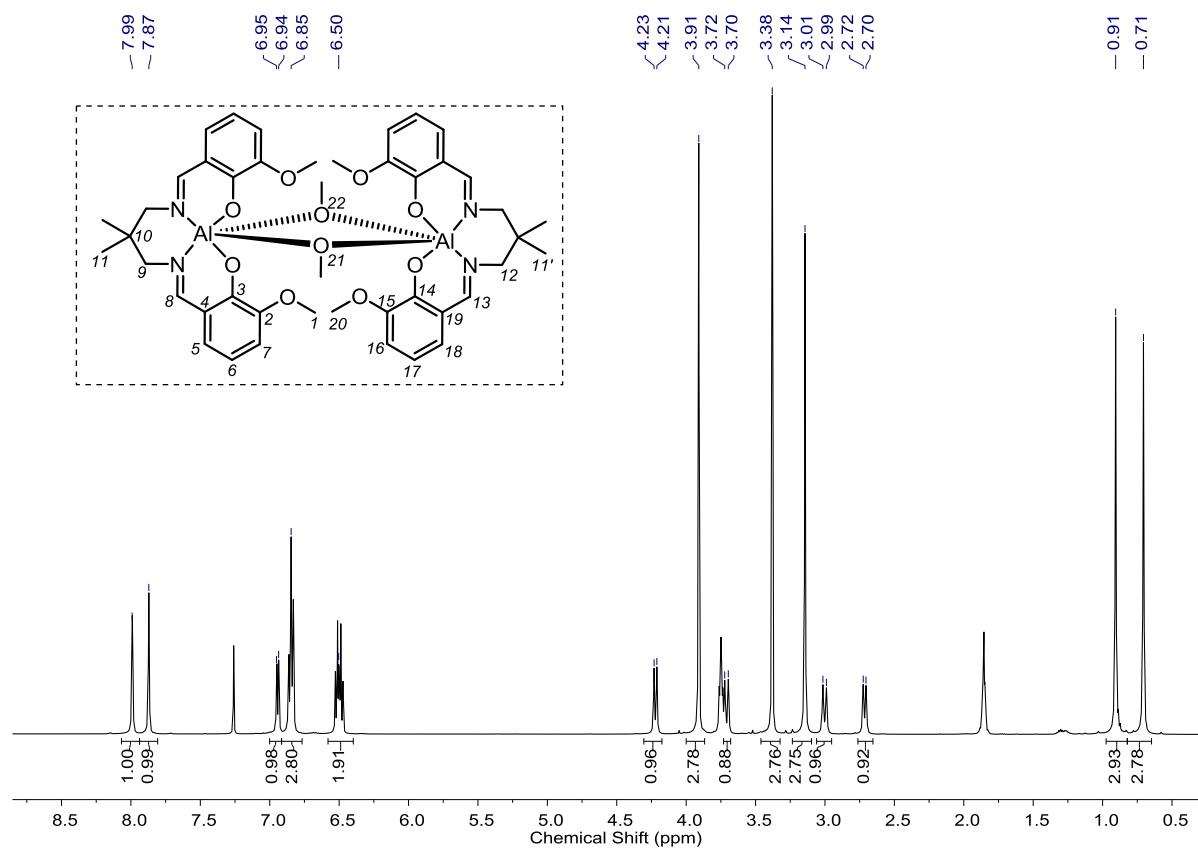
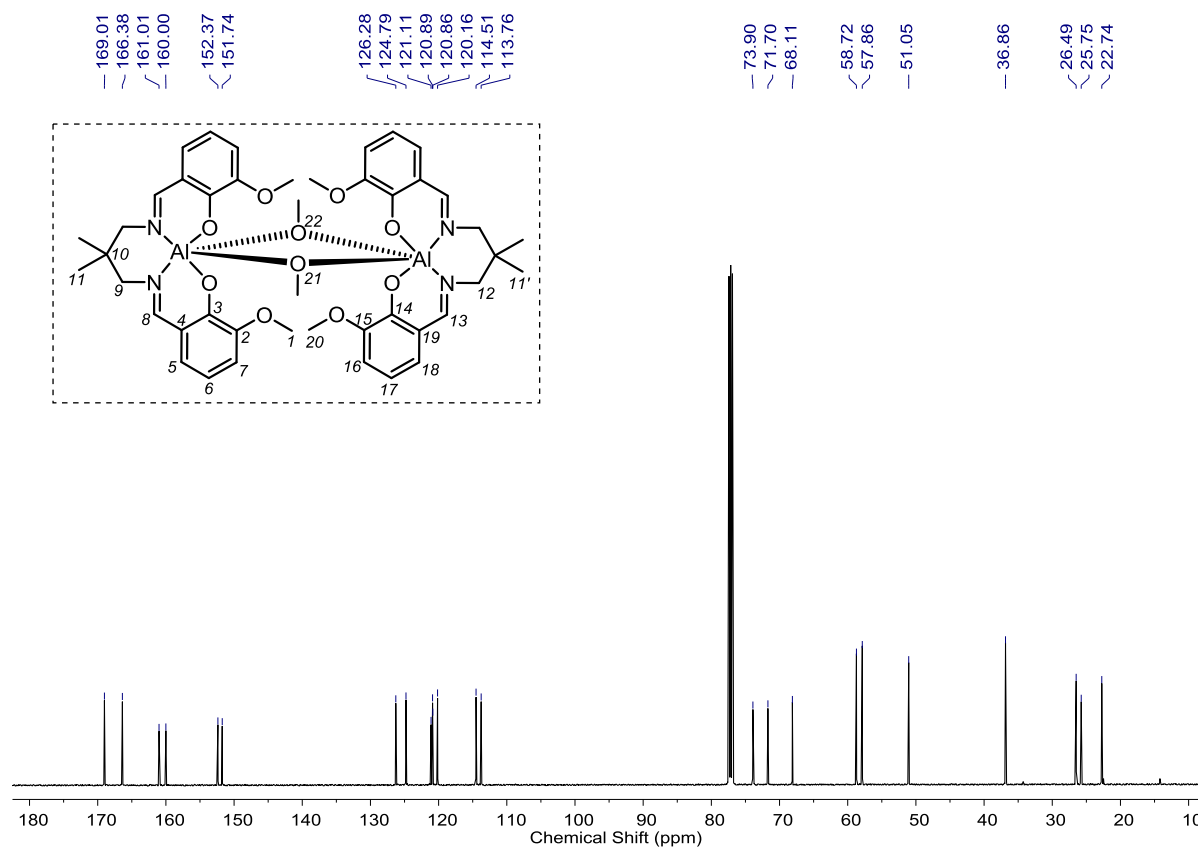
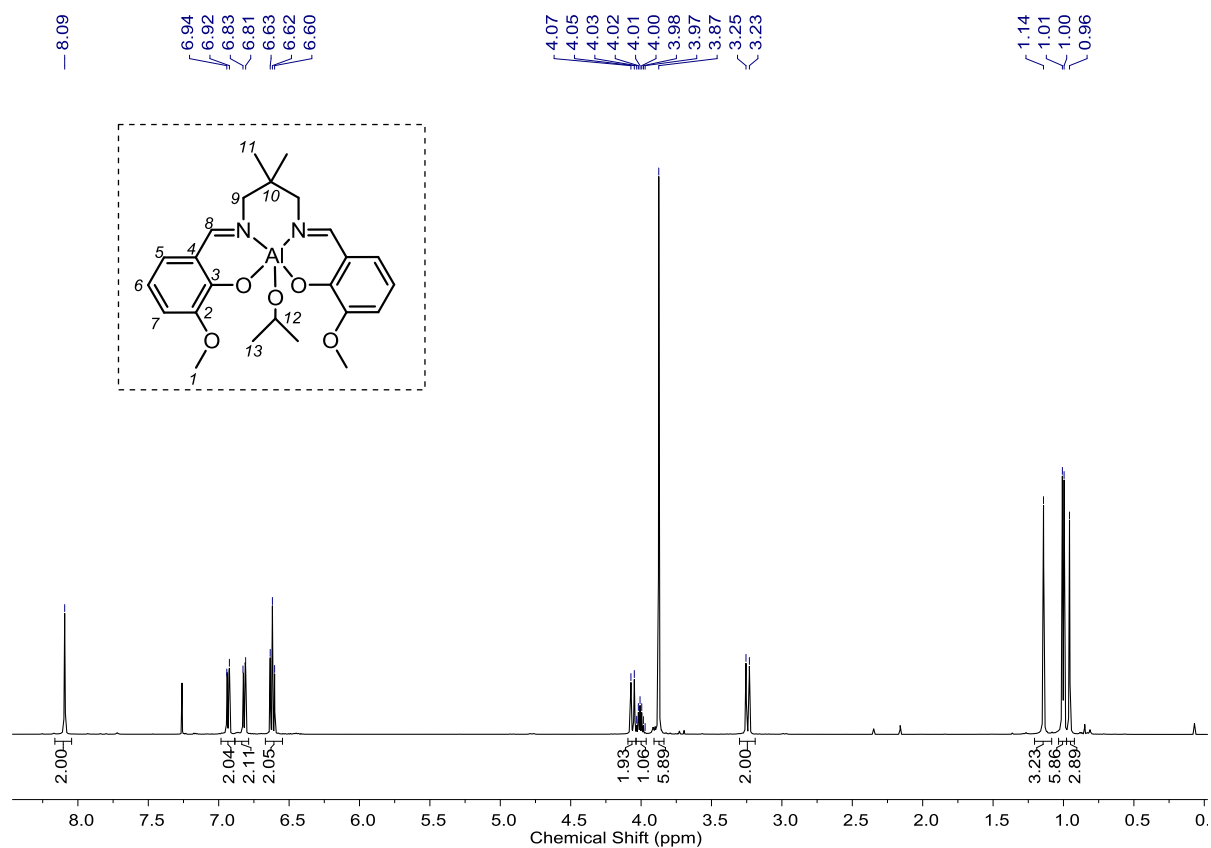
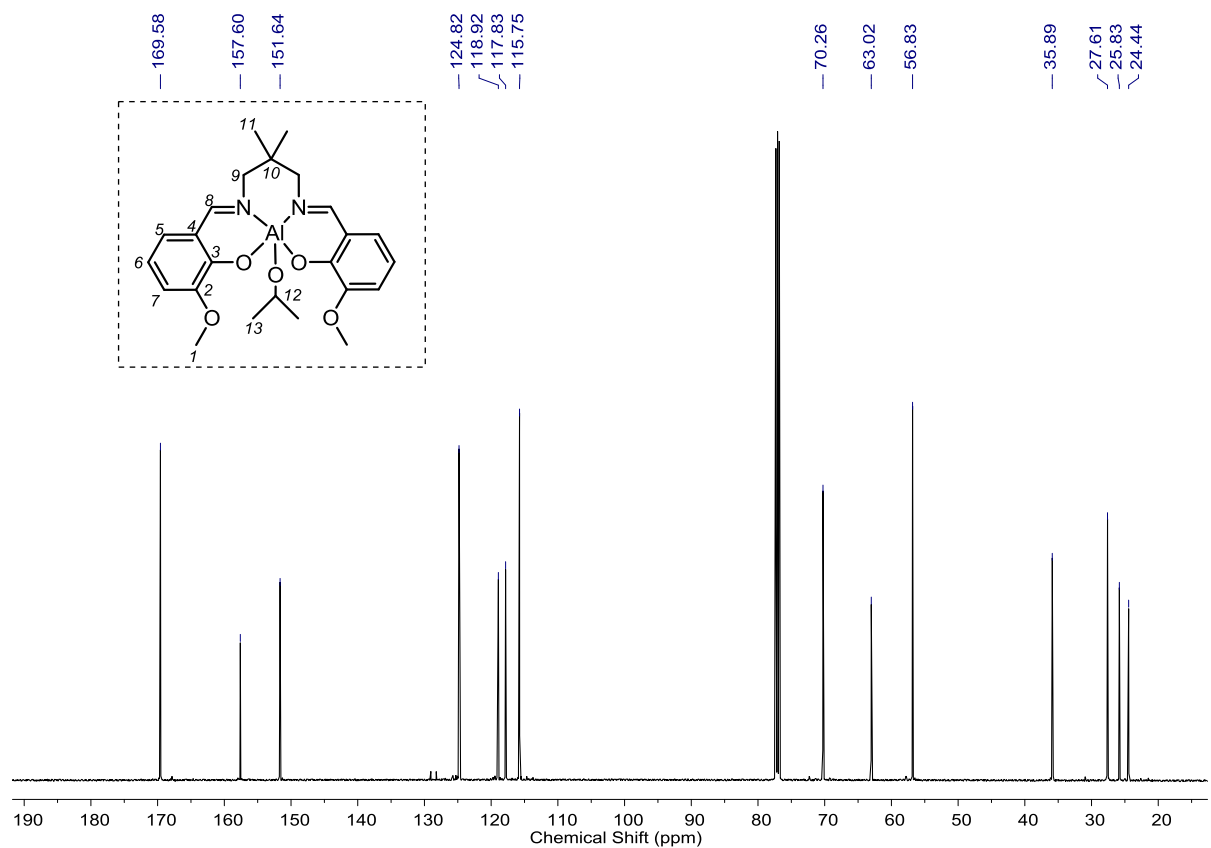
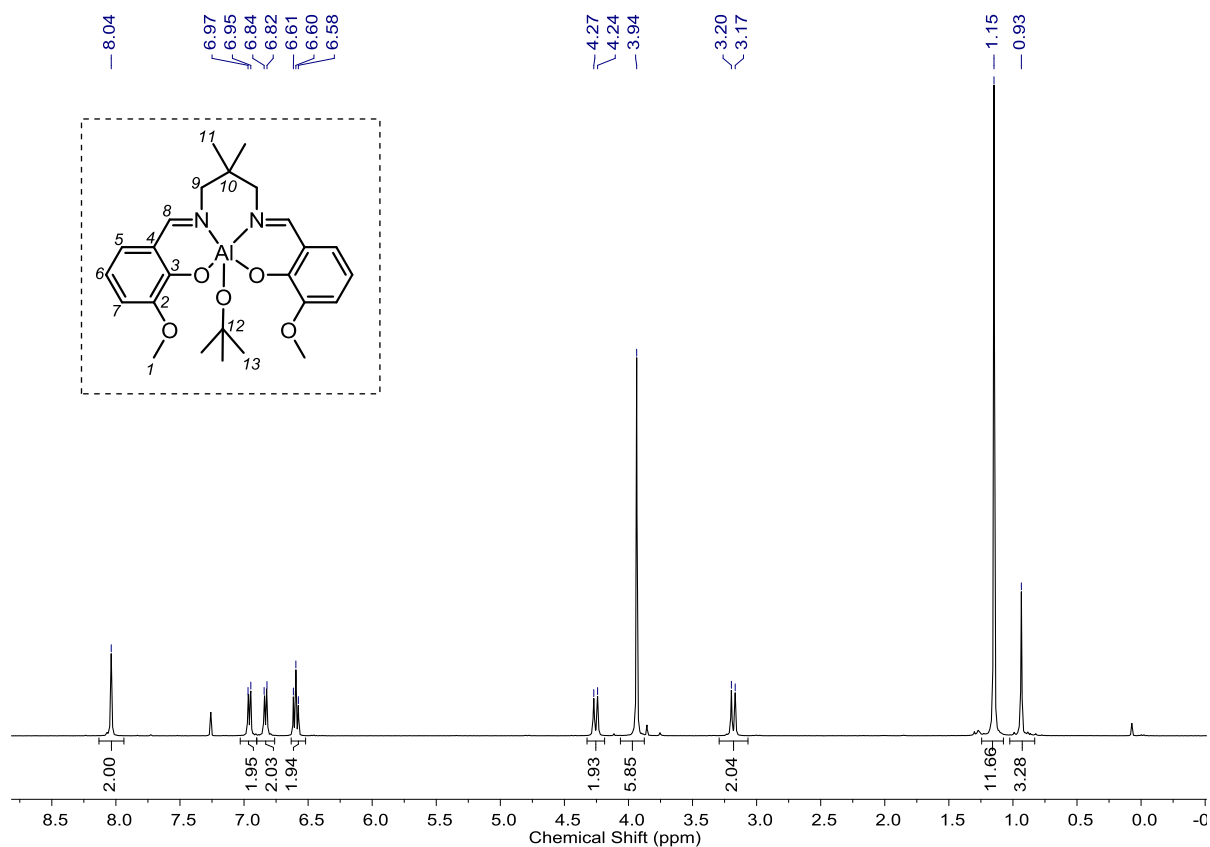
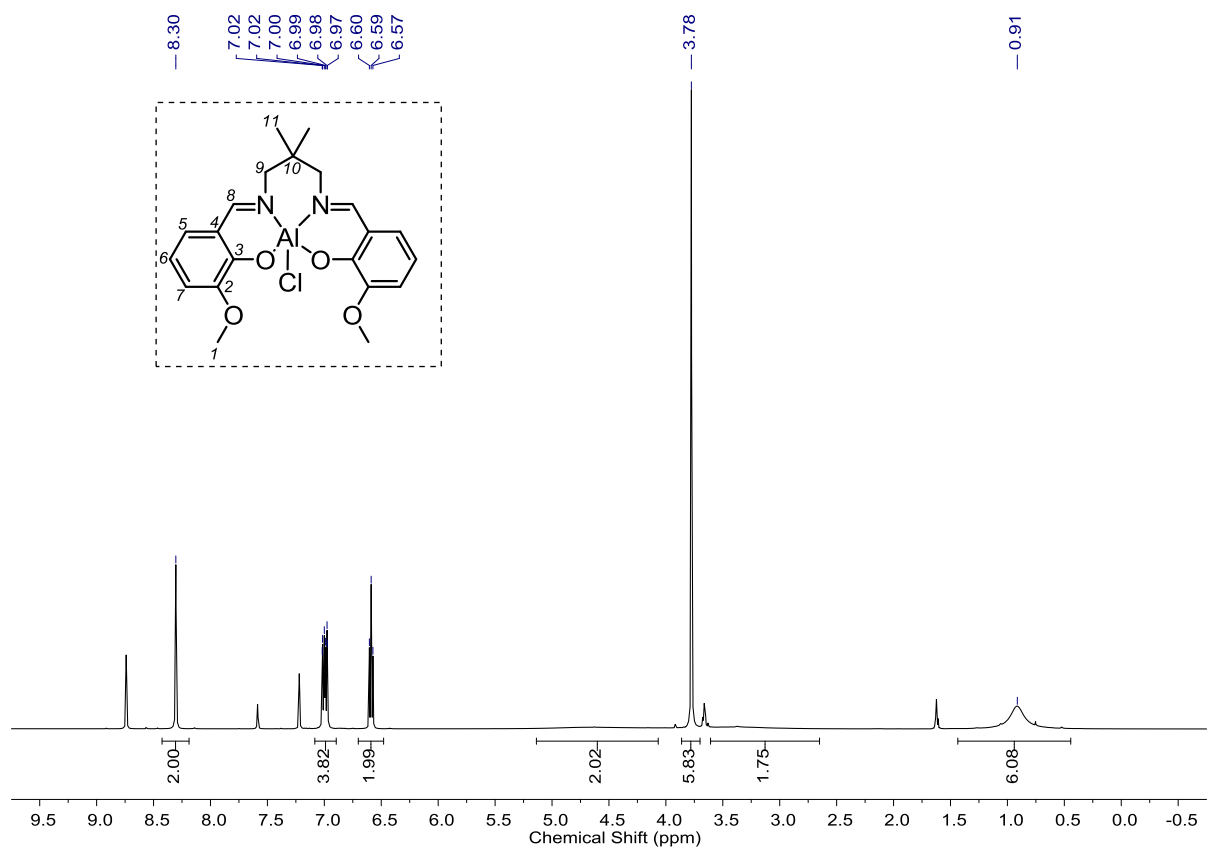
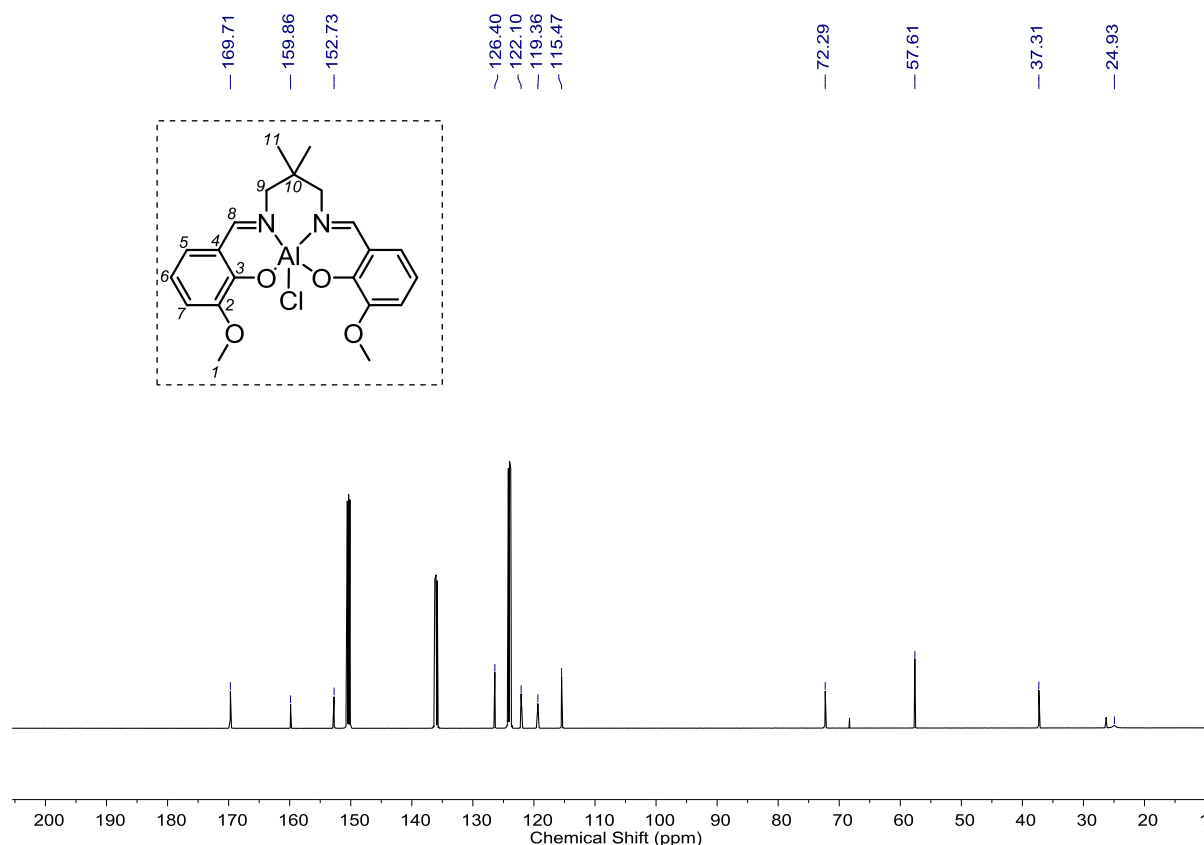


Figure S 7. 12 – ^1H NMR spectrum of **7.16** in CDCl_3 .

Figure S 7. 13 – ¹H NMR spectrum of **7.18** in CDCl₃.Figure S 7. 14 – ¹³C{¹H} NMR spectrum of **7.18** in CDCl₃.

Figure S 7. 15 – ^1H NMR spectrum of **7.17** in CDCl_3 .Figure S 7. 16 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7.17** in CDCl_3 .

Figure S 7. 17 - ^1H NMR spectrum of **7.19** in CDCl_3 .Figure S 7. 18 - ^1H NMR spectrum of **7.20** in pyridine-d_5 .

Figure S 7. 19 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **7.20** in pyridine- d_5 .

Used Search Fragments for Analysis of Bond Lengths

Tabel S 7. 1 - Used search fragments for statistical analysis of bond length (blue distances were analysed; details can be found in the main text).

Complex	Search Fragment	Complex	Search Fragment
7.9, 7.10 7.14, 7.15		7.17	
7.17		7.17	
		7.16	

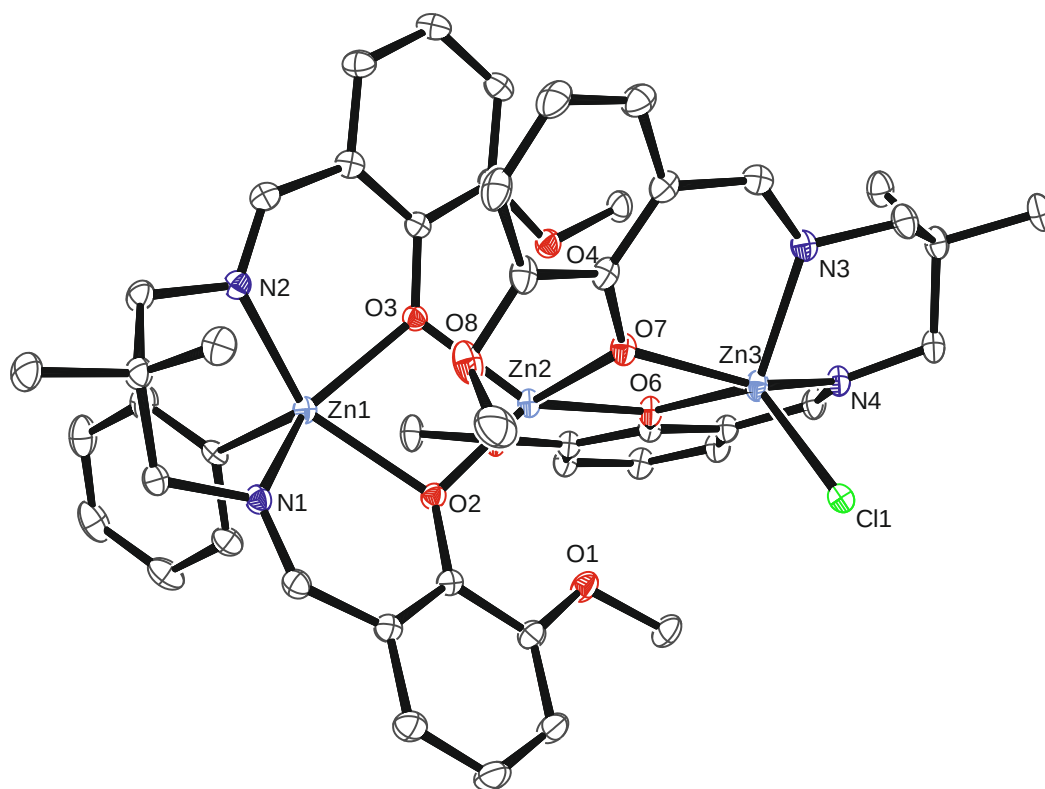


Figure S 7. 20 - Molecular structure of **7.10** with chloro co-ligands with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

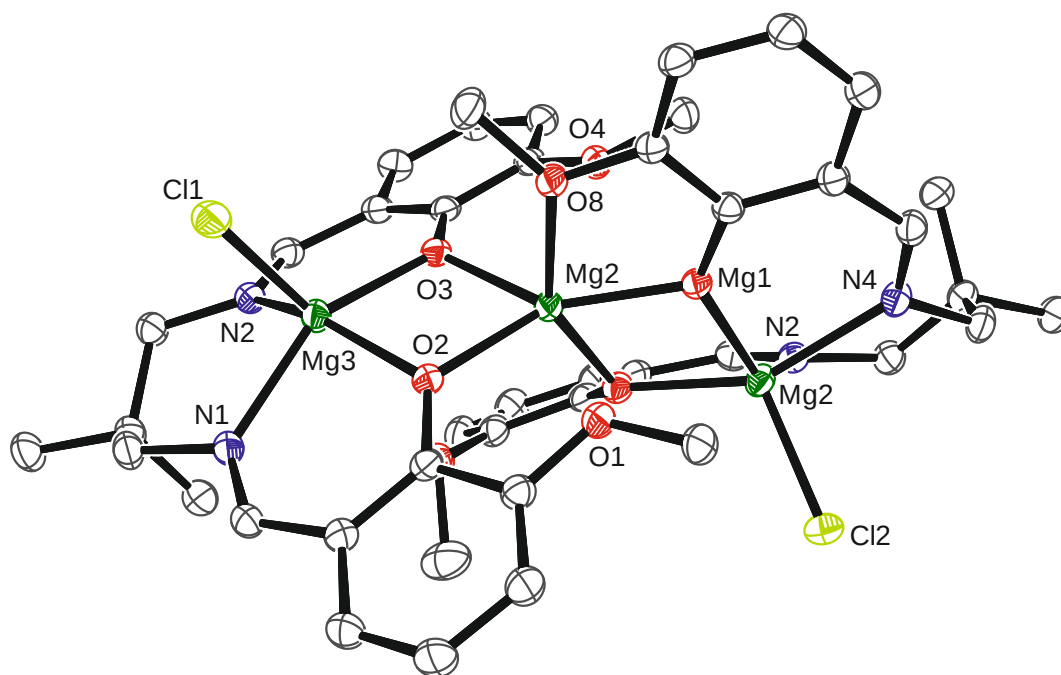
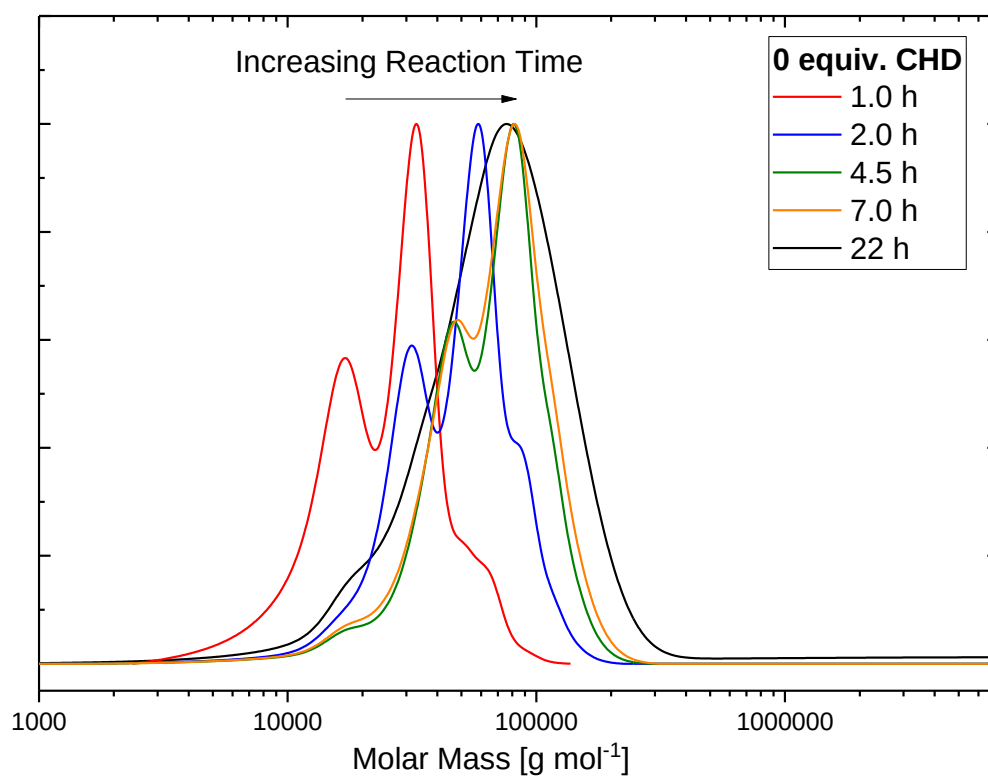
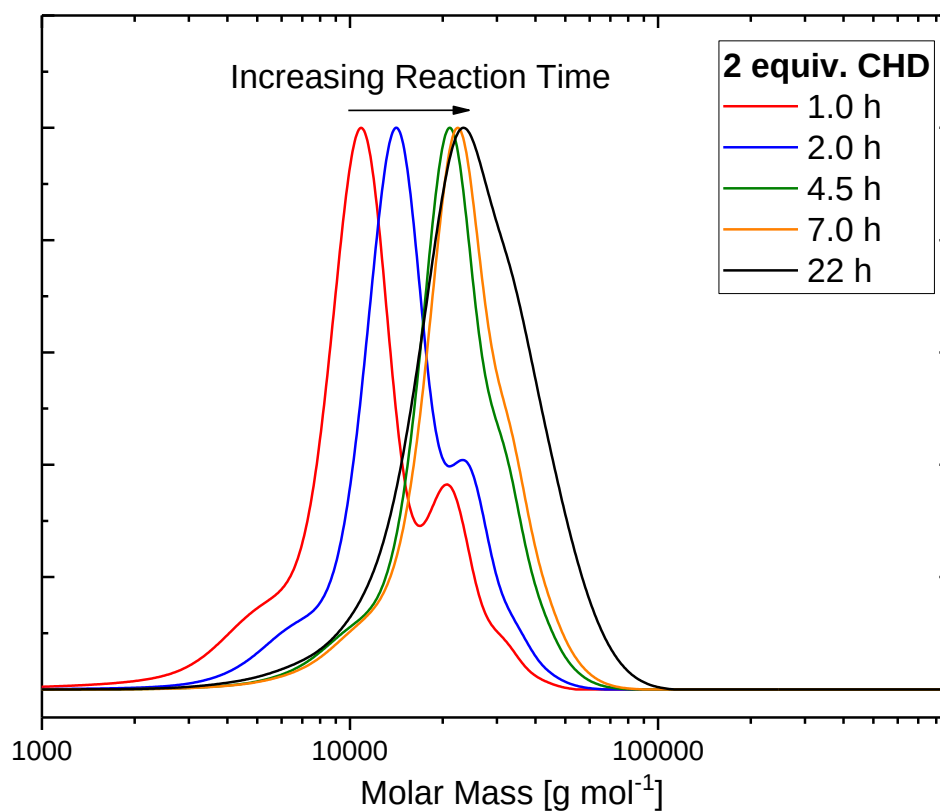
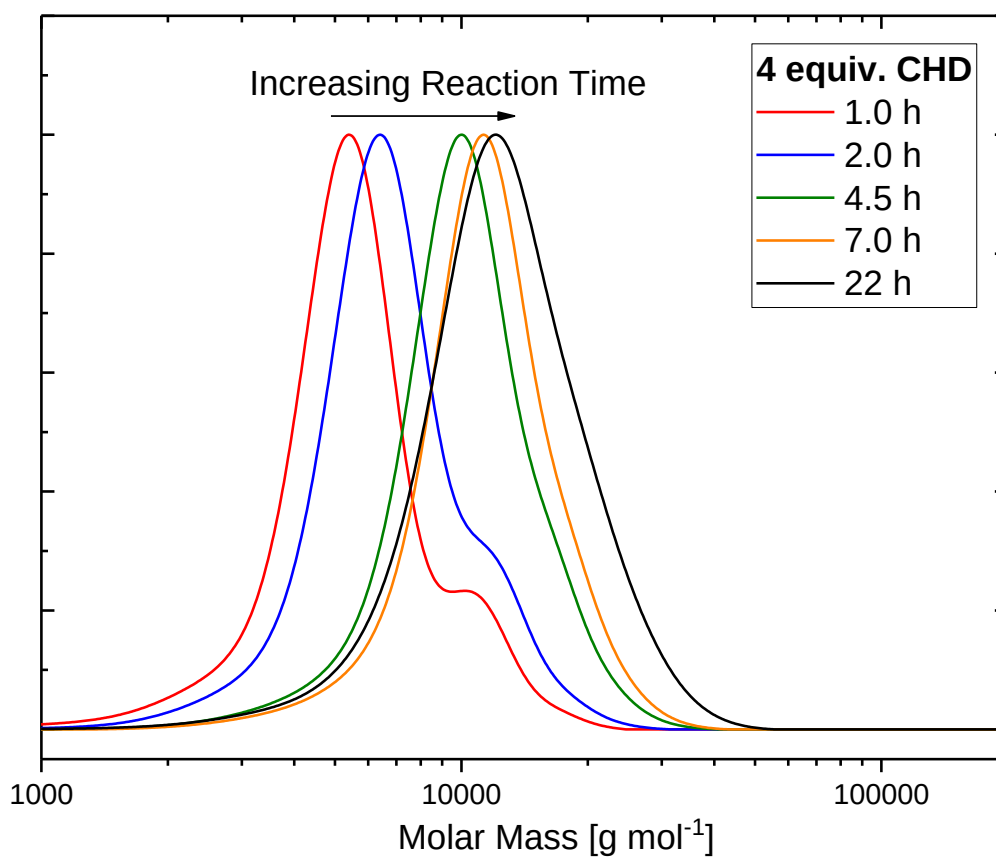
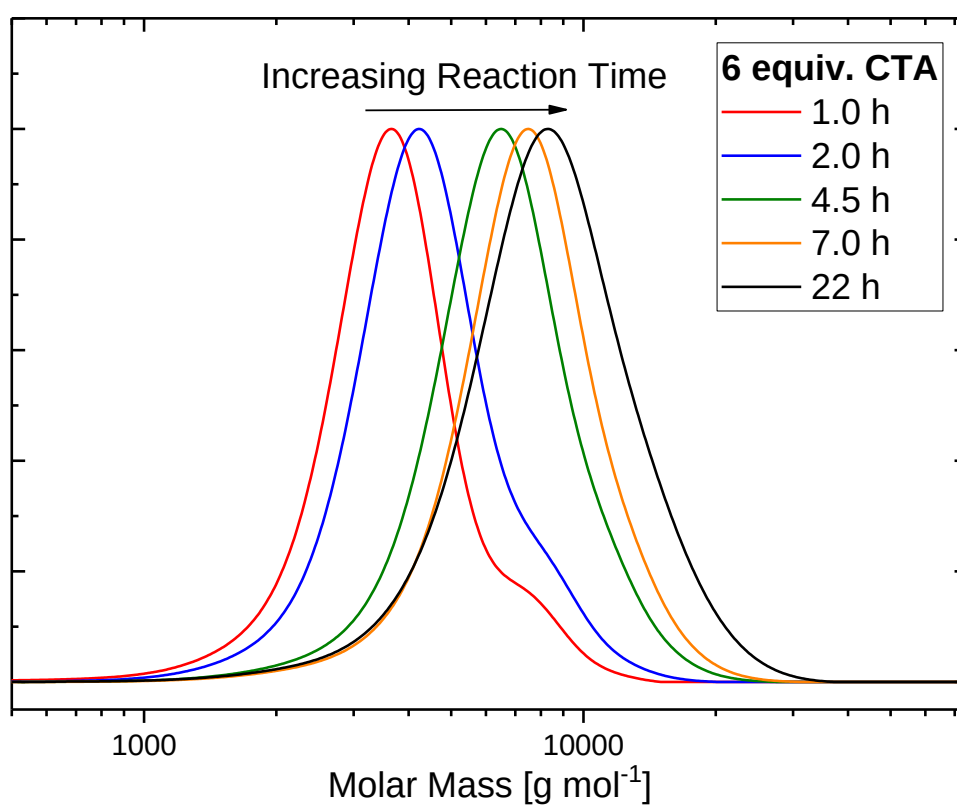
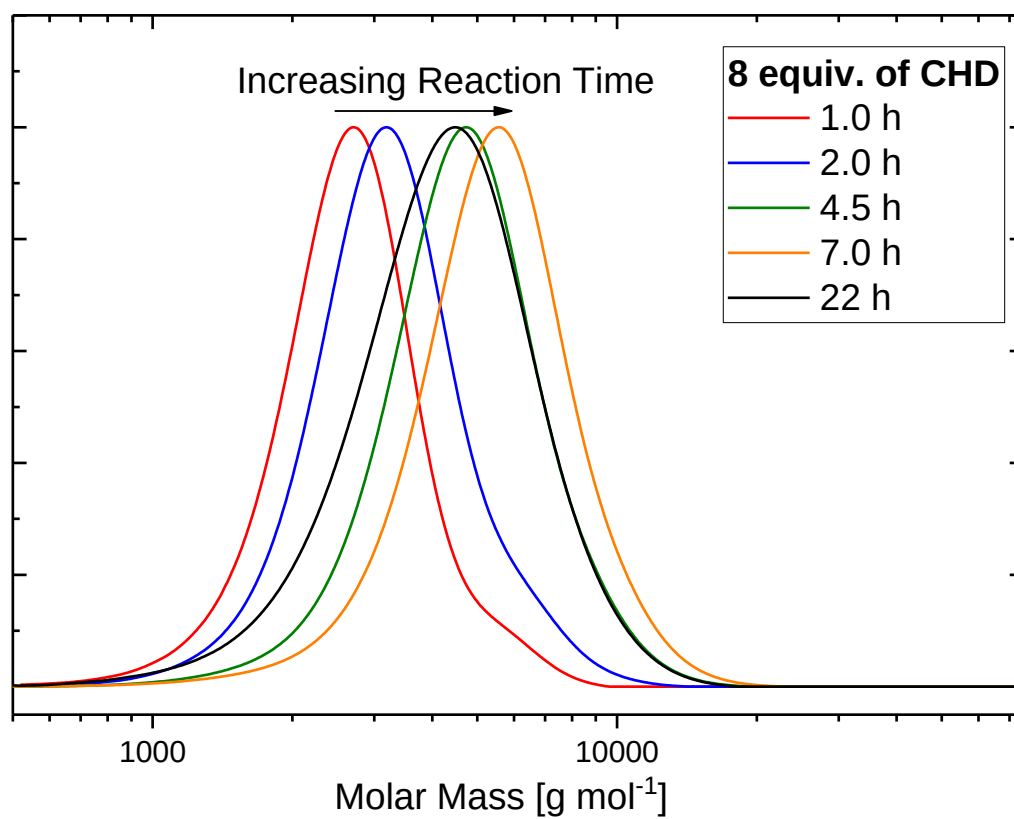
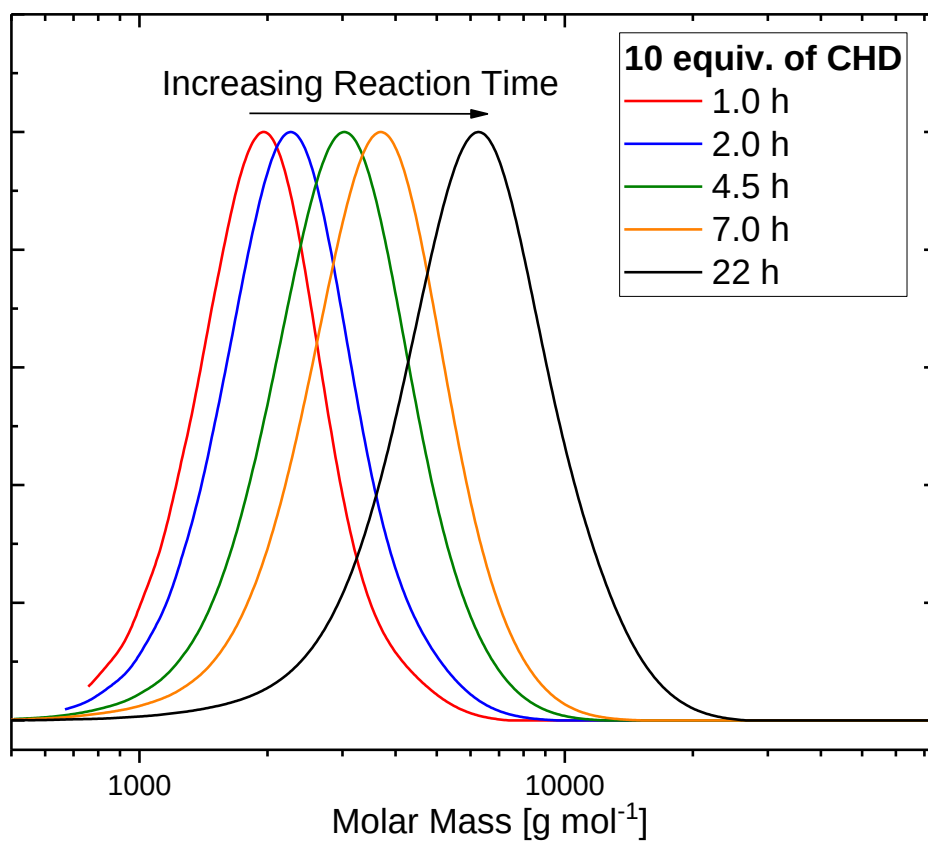


Figure S 7. 21 - Molecular structure of **7.11** with chloro co-ligands with thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

GPC Traces for the one-pot polymerisation of CHO/PA/DL with 7.13 and different amounts of CHD

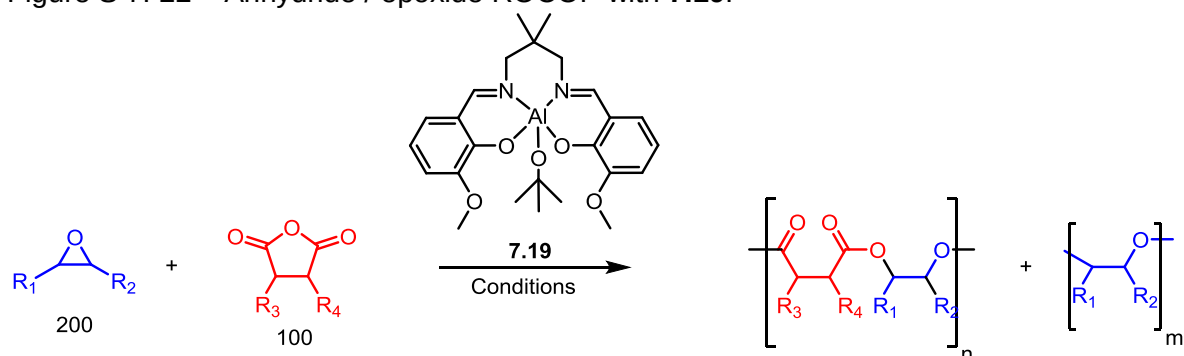






Anhydride/Epoxide ROCOP with 7.19

Figure S 7. 22 – Anhydride / epoxide ROCOP with 7.19.



Epoxide	Anhydride	t [h]	Conversion [%] ^[d]	Selectivity [%] ^[d]
PO	GA	15	< 5	N. D.
	DGA	15	< 5	N. D.
	CA	15	< 5	N. D.
	PA	15	< 5	N. D.
	THPA	15	< 5	N. D.
	NBA	15	< 5	N. D.
	TCA1	15	< 5	N. D.
CHO	GA	15	100	45
	DGA	1.5	78	39
	CA	1.0	36	7
	PA	1.0	87	24
	THPA	1.5	90	26
	NBA	15	100	30
	TCA1	1.0 h	73	19
	 NPA	15	13	4
LO	MA	20	N. D. ^[e]	N. D. ^[e]
	GA	20	80	< 20
	DGA	20	99	< 20
	CA	20	< 5	N. D.
	PA	20	92	14
	THPA	20	99	40
	NBA	20	70	< 20
	TCA1	20	< 5	N. D.
	NPA	20	< 5	N. D.

^[a]Conditions: 40°C, PO (2.5 M), 15 h. ^[b]Conditions: 100 °C, CHO (2.5 M), 1-15 h.

^[c]Conditions: 40°C, LO (1 M), 20 h at 100°C, then 20 h at 160°C. ^[d]Determined by ¹H NMR spectroscopy.

Figure S 7. 23 – Optimisation of conditions for CHO/PA ROCOP with **7.19**.

Concentration ^[a]	t [h]	Conversion ^[b]	Selecti6ty ^[b]
5.0	4.5	45	48
	20	47	50
2.5	4.5	13	40
	20	32	50
1.0	4.5	13	60
	20	62	92
0.5	4.5	< 5	< 5
	20	< 5	< 5
0.25	4.5	< 5	< 5
	20	< 5	< 5

^[a]Given in mol L⁻¹. ^[b]Determined by ¹H NMR spectroscopy.

Table S 7. 1 – ROP with **7.19**.

Anhydride	Conversion [%] ^[a]	Selecti6ty [%] ^[a,b]
CL	95	< 95
DL	85	< 95
Lac	98 ^[c]	< 95

^[a]Determined by ¹H NMR spectroscopy. ^[b]No polyether formation observed. ^[c]P_i = 0.71.

Compound	7.5	7.6	7.9	7.10	7.11	7.12
Empirical formula	C42 H48 N4 O8 Zn2	C63 H72 Mg3 N6 O12	C56.38 H64.65 Cl0.27 N4 O9 Zn3	C50.73 H55.28 Cl0.55 Mg3 N4 O8	C58 H66 Mg N4 O9 Zn2	C54 H84 Mg N6 O8 Si4 Zn2
Formula weight	867.58	1178.19	1148.04	941.27	1118.19	1212.68
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system, space group	Monoclinic, P 21/c	Orthorhombic, P n a 21	Triclinic, P -1	Triclinic, P -1	Triclinic, P -1	Monoclinic, C c
a (Å)	10.70860(10)	26.6385(5)	12.2971(2)	12.2380(4)	12.3665(3)	10.1438(2)
b (Å)	20.5174(2)	12.1506(2)	15.5107(4)	15.4435(5)	15.4098(5)	22.0689(4)
c (Å)	8.98760(10)	18.5863(3)	16.5995(4)	16.4389(4)	16.5339(4)	27.8300(5)
α (°)	90	90	78.587(2)	78.963(3)	78.114(2)	90
β (°)	98.4620(10)	90	75.708(2)	76.295(3)	75.962(2)	96.797(2)
γ (°)	90	90	84.233(2)	84.606(3)	83.094(2)	90
V (Å ³)	1953.19(3)	6015.90(18)	3003.03(12)	2958.77(16)	2982.94(15)	6186.3(2)
Z	2	4	2	2	2	4
Calculated density (Mg/m ³)	1.475	1.301	1.270	1.057	1.245	1.302
Crystal size (mm)	0.250 x 0.250 x 0.150	0.200 x 0.200 x 0.010	0.280 x 0.200 x 0.200	0.280 x 0.200 x 0.080	0.250 x 0.200 x 0.120	0.120 x 0.080 x 0.030
Theta range for data collection (°)	4.174 to 76.205	3.318 to 76.091	3.655 to 76.366	3.682 to 76.273	3.670 to 76.238	3.198 to 76.111

Compound	7.5	7.6	7.9	7.10	7.11	7.12
Limiting indices	-13<=h<=10, - 25<=k<=25, - 11<=l<=11	-33<=h<=32, - 14<=k<=15, - 14<=l<=23	-15<=h<=9, - 19<=k<=19, - 20<=l<=18	-14<=h<=15, - 19<=k<=19, - 20<=l<=20	-15<=h<=14, - 19<=k<=19, - 20<=l<=13	-12<=h<=8, - 24<=k<=27, - 32<=l<=34
Reflections collected / unique	21026 / 4068 [R(int) = 0.0309]	38601 / 10132 [R(int) = 0.0605]	31850 / 12427 [R(int) = 0.0269]	66197 / 12305 [R(int) = 0.0469]	35654 / 12352 [R(int) = 0.0304]	19572 / 8831 [R(int) = 0.0512]
Completeness to theta = 67.684	100.0 %	100.0 %	99.9 %	100.0 %	100.0 %	100.0 %
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	4068 / 0 / 257	10132 / 2 / 767	12427 / 0 / 674	12305 / 1 / 626	12352 / 0 / 675	8831 / 2 / 696
Goodness-of-fit on F ²	1.040	1.031	1.016	1.048	1.027	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0305, wR2 = 0.0833	R1 = 0.0458, wR2 = 0.1158	R1 = 0.0383, wR2 = 0.1051	R1 = 0.0554, wR2 = 0.1625	R1 = 0.0399, wR2 = 0.1008	R1 = 0.0494, wR2 = 0.1236
R indices (all data)	R1 = 0.0323, wR2 = 0.0852	R1 = 0.0524, wR2 = 0.1251	R1 = 0.0433, wR2 = 0.1093	R1 = 0.0663, wR2 = 0.1729	R1 = 0.0499, wR2 = 0.1083	R1 = 0.0553, wR2 = 0.1411
Largest diff. peak and hole	0.318 and -0.338 e.A ⁻³	0.765 and -0.307 e.A ⁻³	0.848 and -0.525 e.A ⁻³	1.160 and -0.375 e.A ⁻³	0.654 and - 0.828 e.A ⁻³	0.573 and - 0.749 e.A ⁻³

Compound	7.13	7.14	7.15	7.16	7.17	7.18
Empirical formula	C ₂₅ H ₃₄ N ₂ O ₄ Zn ₂	C ₄₈ H ₆₂ N ₄ O ₁₀ Zn ₃	C ₅₄ H ₇₄ N ₄ O ₁₀ Zn ₃	C ₂₃ H ₂₉ Al N ₂ O ₄	C ₂₅ H ₃₃ Al Cl ₂ N ₂ O ₅	C ₄₅ H ₅₅ Al ₂ Cl ₃ N ₄ O ₁₀
Formula weight	557.28	1051.12	1135.28	424.46	539.41	972.24
Temperature (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
Wavelength (Å)	1.54184	1.54184	1.54184	1.54184	1.54184	1.54184
Crystal system, space group	Monoclinic, P 21/c	Monoclinic, C 2/c	Monoclinic, C 2/c	Orthorhombic, P 21 21 21	Monoclinic, P 21/n	P c
a (Å)	9.5808(2)	14.01260(10)	19.5987(4)	7.86900(10)	13.0997(2)	10.5314(2)
b (Å)	10.7619(2)	19.5355(2)	15.7744(2)	15.7511(2)	15.9909(2)	11.6531(2)
c (Å)	24.6177(5)	20.3286(2)	23.5232(4)	17.6113(3)	13.3167(2)	19.3484(4)
α (°)	90	90	90	90	90	90
β (°)	95.077(2)	100.8300(10)	118.958(2)	90	103.3660(10)	96.998(2)
γ (°)	90	90	90	90	90	90
V (Å ³)	2528.31(9)	5465.70(9)	6363.1(2)	2182.84(5)	2713.97(7)	2356.81(8)
Z	4	4	4	4	4	2
Calculated density (Mg/m ³)	1.464	1.277	1.185	1.292	1.320	1.370
Crystal size (mm)	0.200 x 0.200 x 0.050	0.200 x 0.200 x 0.150	0.250 x 0.080 x 0.080	0.250 x 0.100 x 0.100	0.250 x 0.200 x 0.150	N. R.
Theta range for data collection (°)	3.605 to 76.184	3.929 to 76.159	3.708 to 76.316	3.765 to 75.942	4.267 to 76.195	Max: 76.155

Compound	7.20	7.14	7.15	7.16	7.17	7.18
Limiting indices	-10<=h<=11, - 13<=k<=12, - 24<=l<=30	-17<=h<=17, - 21<=k<=24, - 25<=l<=23	-24<=h<=24, - 19<=k<=19, - 29<=l<=29	-8<=h<=9, - 15<=k<=19, - 22<=l<=21	-14<=h<=16, - 20<=k<=19, - 16<=l<=13	h<=13, k<=14, l<=24
Reflections collected / unique	14591 / 5219 [R(int) = 0.0302]	41501 / 5688 [R(int) = 0.0350]	78391 / 6642 [R(int) = 0.0392]	9981 / 4245 [R(int) = 0.0340]	23378 / 5620 [R(int) = 0.0344]	9860 / 4937
Completeness to theta = 67.684	100.0 %	100.0 %	100.0 %	100.0 %	100.0 %	1.76 / 0.88
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	5219 / 0 / 304	5688 / 0 / 300	6642 / 19 / 393	4245 / 0 / 276	5620 / 0 / 322	N. R. / N. R. / 587
Goodness-of-fit on F ²	1.036	1.113	1.072	1.110	1.059	1.018
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0767	R1 = 0.0590, wR2 = 0.1475	R1 = 0.0393, wR2 = 0.0976	R1 = 0.0375, wR2 = 0.1009	R1 = 0.0486, wR2 = 0.1307	N. R.
R indices (all data)	R1 = 0.0399, wR2 = 0.0821	R1 = 0.0602, wR2 = 0.1484	R1 = 0.0447, wR2 = 0.1018	R1 = 0.0415, wR2 = 0.1165	R1 = 0.0533, wR2 = 0.1369	R1 = 0.0365, wR2 = 0.0966
Largest diff. peak and hole	0.671 and -0.412 e.A ⁻³	0.851 and -0.761 e.A ⁻³	0.483 and -0.715 e.A ⁻³	0.311 and -0.269 e.A ⁻³	1.098 and -0.816 e.A ⁻³	N. R.

Compound	7.20	7.33
Empirical formula	C69.50 H75.50 Al2 Cl2 N9.50 O8	C52 H55 Al2 N5 O12
Formula weight	1296.75	995.97
Temperature (K)	150(2)	150(2)
Wavelength (Å)	1.54184	1.54184
Crystal system, space group	Triclinic, P -1	Triclinic, P -1
a (Å)	9.6967(3)	12.8883(3)
b (Å)	15.4856(5)	13.7390(5)
c (Å)	23.3812(7)	14.7934(5)
α (°)	74.456(3)	78.650(3)
β (°)	88.902(2)	85.507(2)
γ (°)	76.654(3)	75.123(2)
V (Å ³)	3287.73(19)	2481.11(14)
Z	2	2
Calculated density (Mg/m ³)	1.310	1.333
Crystal size (mm)	0.250 x 0.200 x 0.100	0.250 x 0.250 x 0.100
Theta range for data collection (°)	3.929 to 76.308	3.550 to 76.269

Compound	7.20	7.33
Limiting indices	-11≤h≤12, - 19≤k≤19, - 28≤l≤29	-16≤h≤10, - 16≤k≤17, - 18≤l≤18
Reflections collected / unique	36102 / 13581 [R(int) = 0.0332]	26279 / 10255 [R(int) = 0.0366]
Completeness to theta = 67.684	99.9 %	99.9 %
Refinement method	Full-matrix least- squares on F ²	Full-matrix least- squares on F ²
Data / restraints / parameters	13581 / 156 / 914	10255 / 0 / 649
Goodness-of-fit on F ²	1.020	1.048
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0984	R1 = 0.0377, wR2 = 0.0966
R indices (all data)	R1 = 0.0490, wR2 = 0.1070	R1 = 0.0461, wR2 = 0.1051
Largest diff. peak and hole	0.403 and -0.344 e.Å ⁻³	0.517 and -0.334 e.Å ⁻³

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Chapter 8 – Summary and Outlook

Functions used for Figure 8.5:

1. Monomodal GPC trace. Gauss Function:

$$y = y_0 + \frac{Ae^{\frac{-4 \ln(2) - (x - x_c)^2}{w^2}}}{w \sqrt{\frac{\pi}{4 \ln(2)}}}$$

Table S 8. 1 - Functions used for Figure 8.5 (part 1/2).

Parameter	Meaning	Value
y_0	Base	1
x_c	Centre	100,000
A	Area	50,000
w	FWHM	30,000

2. Bimodal GPC trace. The overall function was plotted in three parts:

Table S 8. 2 - Functions used for Figure 8.5 (part 2/2).

Part	Function	Parameter	Meaning	Values
I: x = 0-84,608	$y = y_0 + \frac{Ae^{\frac{-4 \ln(2) - (x - x_c)^2}{w^2}}}{w \sqrt{\frac{\pi}{4 \ln(2)}}}$	y_0	Base	1
		x_c	Centre	75,000
		A	Area	50,000
		w	FWHM	30,000
II: x = 84,608 – 115,411	$y = a + bx + cx^2$	a	y-offset	1061.81
		b	slope	-0.02
		c	slope	1.04394E-7
III x = 115,411 – 300,000	$y = y_0 + \frac{Ae^{\frac{-4 \ln(2) - (x - x_c)^2}{w^2}}}{w \sqrt{\frac{\pi}{4 \ln(2)}}}$	y_0	Base	1
		x_c	Centre	125,000
		A	Area	50,000
		w	FWHM	30,000

Functions used for Figure 8.6:

Correlation between $\bar{D}$ (x-axis), the relative (y_1) and the absolute standard deviation (y_2).

A data set was generated with equ. 2 for $1.00 < \bar{D} < 2.00$ a polymer with a mass of 100,000 g mol⁻¹ and the resulting points were fitted using the following functions:

Table S 8. 3 - Functions used for Figure 8.6.

Equation	$y = \text{Intercept} + B_1x^1 + B_2x^2 + B_3x^3 + B_4x^4 + B_5x^5 + B_6x^6$	$y = \text{Intercept} + B_1x^1 + B_2x^2 + B_3x^3 + B_4x^4 + B_5x^5 + B_6x^6$
Plot	B	C
Weight	No Weighting	No Weighting
Intercept	-78.18442 ± 6.58807	-7.81844E6 ± 658806.63244
B1	281.10324 ± 25.58861	2.81103E7 ± 2.55886E6
B2	-418.28357 ± 40.78227	-4.18284E7 ± 4.07823E6
B3	330.21819 ± 34.1487	3.30218E7 ± 3.41487E6
B4	-145.32908 ± 15.8512	-1.45329E7 ± 1.58512E6
B5	33.77829 ± 3.86932	3.37783E6 ± 386932.40671
B6	-3.23869 ± 0.38827	-323869.1732 ± 38826.89882
Residual Sum of Squares	0.00694	6.9372E7
R-Square(COD)	0.99931	0.99931
Adj. R-Square	0.99928	0.99928