

Toughening Sustainable Thermoplastics with Poly(ester-*alt*-ethers): Catalyst Development, Polymer Blends and Recycling

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January 2025

A thesis submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy in Chemistry

“We can be the first generation to achieve a sustainable world... If you are living today, you are in a truly unique position to achieve something that was unthinkable to our ancestors: to deliver a sustainable future. I believe that we can be the first generation that meets the needs of everyone while leaving the environment in a better state than we found it.”

- Hannah Ritchie - Not the End of the World

Declaration

The work described in this thesis was conducted between April 2021 and January 2025 at the University of Oxford. This is the work of the author unless otherwise stated.

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A handwritten signature in black ink, appearing to read 'Alexander Craze', with a stylized, cursive script.

Alexander Craze

Abstract

Strong, tough and chemically resistant plastic materials, that are derived from petroleum, are responsible for a significant amount of CO₂ emissions, and break down to form nano and micro-plastics, which are now pervasive in the environment. A more sustainable future for plastics relies on the development of high-performance materials that are renewably sourced, recycled without suffering losses in performance, and which are, ultimately, degradable to small molecules. This thesis aims to develop simple, low-cost strategies to improve the mechanical properties of the sustainable thermoplastics poly(L-lactide) (PLLA, from starch-rich biomass) and poly(cyclopentene carbonate) (PCPC, derived from CO₂), as alternatives to current commercial petrochemically-sourced plastics. The goal is to improve the material's toughness and ductility, without compromising their thermal properties, mechanical strength or sustainability. The strategy is to use block polymers—employing elastomeric, (bio)degradable poly(ester-*alt*-ethers)—in polymer blending, with high molar mass PLLA and PCPC. The blend properties, processing and recycling are explored. The end-of-life options were investigated and include either mechanical or chemical recycling, as well and enzymatic degradation.

Chapter 1 provides an introduction to a circular plastics economy and presents the target alternative thermoplastics, PLLA and PCPC. Prior attempts to use polymer blending to improve mechanical properties are discussed, and, the strategy used in this work to apply amphiphilic block copolymers is outlined. The chemistry of poly(ester-*alt*-ether) materials and opportunities to make them by controlled polymerisation catalysis is described.

Chapter 2 reports upon an innovative and controlled polymerisation catalysis to make poly(ester-*alt*-ethers). The ring-opening copolymerisation of anhydrides (**A**), epoxides (**B**) and cyclic ethers (**C**), using a Zr(IV) catalyst, produces new families of either **ABB** or **ABC** type poly(ester-*alt*-ethers). A range of commercial epoxide and anhydride monomers are used to make poly(ester-*alt*-ethers) with variable compositions and structures. The catalysis is examined for its selectivity for poly(ester-*alt*-ethers) linkages, rate and polymer thermal properties are determined. The aim is to identify candidates for polymer blending studies. Copolymers are synthesised with molar mass values from 4 to 11 kg mol⁻¹ and mostly with narrow and monomodal molecular weight dispersity. The poly(ester-*alt*-ethers) are amorphous, with thermal decomposition temperatures from 270-344 °C and glass transition temperatures

from -50 – 48 °C, depending on their compositions. Post-polymerisation techniques are explored to further expand the properties available.

Chapter 3 reports the synthesis of block polymers comprising poly(ester-*alt*-ethers)-*b*-PLLA as rubber tougheners to improve PLLA ductility. The block polymers are blended with commercial, semi-crystalline PLLA. The best performing material, featuring 15 wt% block polymer (11 wt% poly(ester-*alt*-ether)), has a similar high modulus ($E = 3.1 \pm 0.1$ GPa) and high tensile strength ($\sigma = 48.7 \pm 1.2$ MPa) to PLLA, but, much higher ductility (7 x higher than PLLA, $\epsilon_B = 24.5 \pm 4.6$ %) and greater tensile toughness (8 x higher than PLLA, $U_T = 10.8 \pm 2.2$ MJ m⁻³). Its mechanical properties are improved without compromise to the PLLA thermal properties, as evidenced by very similar glass transition temperatures, crystallinity and melt temperatures. The PLLA/block polymer blend (15 wt%) shows a lower melt viscosity and earlier onset of shear thinning, than PLLA, facilitating its processing. The blends are efficiently chemically recycled, using a solid-state catalysed process, to L-lactide (87% yield, 100 % L-LA selectivity) and the starting poly(ester-*alt*-ethers)-*b*-PLLA. The blend components, including the block polymer, are all enzymatically degraded. The properties of the PLLA materials are compared with current commercial thermoplastics, identifying them as replacements for materials like polystyrene (PS), poly(acrylonitrile butadiene styrene) (ABS) or high impact polystyrene (HIPS).

Chapter 4 examines different catalysts for poly(ester-*alt*-ether) synthesis. A series of $ML_2(O^iPr)_2$ complexes are compared in terms of their rate, selectivity and control of molar mass distribution. Changing the ancillary ligand had only minor effects on catalysis, and, Zr(IV) or Hf(IV) complexes outperform the Ti(IV) analogues. Also, a series of commercial Zirconium(IV) ZrX_4 catalysts are investigated, where $X = (O^iPr)_4(HO^iPr)$, $(OEt)_4$, $(Oct)_4$, $(Cl)_4$, $(NMe_2)_4$, $(Bn)_4$ and $(Bn)_4 + (HOBn)_2$. These catalysts show a range of selectivities for poly(ester-*alt*-ethers) (40-95 %) and are 1-3 times faster than the heteroleptic group (IV) complexes. A non-initiating commercial $Hf(Bn)_4$ is used to make poly(ester-*alt*-ethers) with a variable degrees of polymerisation, functional end-groups and architectures.

Chapter 5 reports upon block copolymers to improve the properties of poly(cyclopentene carbonate) (PCPC). High molar mass PCPC ($M_n = 82.2$ kg mol⁻¹, $\bar{D} = 1.58$) is synthesised from the ROCOP of CO₂ and cyclopentene oxide (CPO). It is toughened with diblock copolymers of the form poly(ester-*alt*-ethers)-*b*-PC (where PC = PCPC or PCHC). With as little as 5 wt% additive, the ductility of the blends improves substantially, with the

elongation at break increasing by 6 times (82.1 ± 10.1 %) and tensile toughness increasing by 5 times (28.1 ± 4.1 MJm⁻³). Importantly, this occurs without changing the thermal properties ($T_g = 88$ °C), or compromising mechanical strength (38.1 ± 2.1 MPa) or modulus (2.6-2.7 GPa). The PCPC blends are mechanically recycled and chemically recycled to epoxides, CO₂ and the poly(ester-*alt*-ether)-*b*-PC. Further, all blend components are enzymatically degraded. The blend thermal-mechanical properties suggest they may replace acrylonitrile–butadiene–styrene (ABS) or high-impact polystyrene (HIPS), which are current petrochemically derived materials that are very hard/impossible to recycle.

Chapter 6 summarises the work, and outlines future directions to build upon it.

Chapter 7 includes experimental details for chapters 2-5.

Chapter 8 is an appendix encompassing all supplementary information (tables, figures and schemes) to support the results discussed in chapters 2-5.

Dedication

I would like to dedicate this work to the life of Ross Bryce Craze. He showed me what it meant to be a gentleman and someone who lived to put smiles on faces. He took every opportunity to make someone else's life better and could turn even the dullest of situations into a treasured memory. His love for life and his constant search for laughter and good times will forever be my moral compass. As will his passion for the environment and doing his bit to make the world a better place.

There was never a single moment that I didn't feel holistically loved, or know that you would support me with everything you had in whatever I chose to do. Thank you for not just letting me chase my dreams, but for giving me the opportunity, support and confidence to do so.

You showed me the true definition of love, joy, compassion and empathy, but also of sacrifice and hard work. More importantly you showed me what's truly important in life, and, what simply isn't.

Nothing that I have achieved, or ever will achieve, would have been possible without you. I never needed to achieve anything to make you proud—that's why I felt so loved and appreciated—but I really hope this would have. It's for you.



Acknowledgements

With every possible meaning of the words, I would not be here without my loved ones. My journey to oxford has been such a team effort, and the list of people I have to thank would need another 180-page appendix (sorry!). I acknowledge from the outset how privileged I am, to lead such a fortunate life, to wake up each day healthy and joyful, to have been so unconditionally loved by such a supporting family/loved ones/friends, the opportunity for an education and to follow my passion to extent I have done.

To my family, Mum, Nicky, Grandma, Amaryllis and all my loved ones, thank you for your unwavering support and love. It means more to me than I could possibly put into words. I will love you always with everything I have.

Mum, through all that has been thrown at us, you have been such an inspiration. You and Dad have been my role models, my support and my inspiration always. Thank you for always inspiring me to follow my passions, to always be curious and have a love for learning, and to use my knowledge to try to make a difference. Thanks for instilling in me a love for family, friends and nature. More than anything thanks for showing me what is truly important in in life.

Nicky, I'm so proud of the person you are. Knowing that I have your love and support has made this possible. I'm in awe of how you've supported mum, Granny, me and everyone in our life while I've been away; thank you for making this possible for me. It's no surprise you've met such an amazing person like Franny, and your love is a model for me. Thank you also to the Daniel family for the love and support you have shown Nicky, Mum and I.

In the course of this thesis, we lost a cherished member our family, Betty Craze. I am so grateful for every cherished moment we shared together. Thank you for loving, caring teaching and supporting me, and always keeping me grounded. You showed me the importance of caring for your family and friends, and for showing up for your loved ones (a 6-hour drive for a family event in her 80's was never going to stop her).

Amaryllis, thank you for helping me build a home away from home. I am so grateful for every moment we've had, every adventure we've shared, and I look forward to making the most of every moment to come. Thank you for the friends, family, love and life we have built together. I love doing life with you. Thank you for keeping me grounded, listening to me rant or tell me I'm being silly. Thank you for supporting me at all times, but especially through

writing this thesis. Thanks to the Hill family for welcoming me so lovingly, sharing so many beautiful moments and giving me another new family. I have loved and cherished the time spent together.

To my family and friends, thank you for your love, for your acceptance of my absence, and for your support over the last three and a half years that have culminated in this thesis. Deciding to do my PhD overseas was one of the most difficult decisions I've made, as I knew it would mean missing birthdays, weddings, births, and three years of the life I loved and was so grateful for. Thank you for always being there for me, even when contact has been so difficult, with an 11-hour time difference. Without the good times away from the confines of the university and the environment of science, this would not have been possible. Your love, time, friendship, laughs and good-times have been a constant reminder of the most important things in life—family, friendship, love and joy. Thank you to Lindsay and Tori, Sue and John, Chris and Chris, Sharon and Russel, Coral, as well as other family and friends for making my time in Oxford a possibility.

To my 'English parents', Michele and Nigel, your generosity, compassion and warmth that you welcomed me with has not only made my time in the UK possible, but you have made it the best time possible. Not only have you helped me chase my dreams, you have given me another family. I am so grateful for the two of you, your family (and the neighbours!) for taking me in and making me family.

To all of English friends and family, moving away from home, from my family, friends and my support network, has been an extremely hard thing to do for me, something I didn't think I would have done, and you have made it such an incredible time that I will always cherish (you can keep the weather though!).

To Aaron, Sadie and Thomas, thank you for always being there, going so far beyond and above to help me in my moments of need, to celebrate the good times and the stressful ones. Your love, friendship and support has meant so much. I will always cherish the time we've had together in Oxford and can't wait for all those to come. Gobble. To Aaron and Sadie, thanks for taking me in on so many occasions and I apologise for the Sandy-size shape in your couch that would have resulted. To Aaron, thanks for always talking when I needed to listen.

Charlotte, thanks for giving me this opportunity, for caring about us like you do, for the time you have given me, for teaching me, for pushing me and for giving me the best scientific

education I could ever have asked for. I hope I've made the most of how privileged we are to study in this group and to have you as a supervisor.

To the entire Williams group (for whom there have literally been too many to thank) – I have been so lucky to have learnt from some of the most brilliant and intelligent people I've ever met. Those who have contributed to the science have been acknowledged in the thesis, but thanks to everyone for always being willing to help, to teach, to support and to laugh. On the technical side thanks to Balazs for making some high quality PCPC, Thom for unzipping my polymers and to Lukas for helping to establish the HPLC protocols used in degradation studies.

List of Publications

Cyclic ether and anhydride ring opening copolymerisation delivering new ABB sequences in poly(ester-alt-ethers)

Alexander R. Craze, Ryan W. F. Kerr and Charlotte K. Williams, *Chemical Science*, 2024, **15**, 11617-11625.

List of Abbreviations

AB	Polyester
AB	A diblock copolymer of polymers A and B
ABB	Representation of poly(ester-alt-ethers)
ABC	Poly(ester-alt-ethers) with cyclic ether incorporation
AB_n	polyester with <i>n</i> ether linkages per ester linkage
ABS	Acrylonitrile-butadiene-styrene
AGE	Allyl Glycidyl Ether
<i>alt</i>	alternating
<i>b</i>	Block
BGE	benzyl glycidyl ether
BO	Butylene oxide
Bn	Benzyl
Cat.	Catalyst
CHO	Cyclohexene oxide
CHD	Cyclohexane diol
CO ₂	Carbon Dioxide
CPO	Cclopentene oxide
CPD	Cyclopentene diol
CRM	Chemical recycling to monomer
COSY	Correlated spectroscopy
CTA	Chain transfer agent
Đ	Molar mass dispersity
DFT	Density functional theory

DGA	Diglycolic anhydride
D-LA	D-lactide
DMPA	2,2-dimethoxy-2-phenylacetophenone
DMTA	Dynamic Mechanical Thermal Analysis
DOSY	Diffusion Ordered Spectroscopy
DP	Degree of polymerisation
DSC	Differential scanning calorimetry
E	Young's modulus
E'	Elastic Storage modulus
E''	Elastic Loss modulus
ESI-MS	Electrospray ionisation mass spectrometry
ED	1,2-epoxydecene
EDD	1,2-epoxydodecane
EHGE	2-ethyl hexyl glycidyl ether
EPS	Expanded polystyrene
FA	Fumaric acid
<i>g</i>	Graft
G'	Shear modulus
ΔG_m	Gibbs free energy of mixing
$\Delta G^\ddagger$	Free energy of the transition-state (activated complex)
GC-MS	Gas chromatography–mass spectrometry
GPC	Gel permeation chromatography
<i>Grad</i>	Gradient
ΔH_{cc}	Enthalpy of cold crystallisation

ΔH_m	Enthalpy of melting
ΔH_m	Enthalpy of mixing
HiC	<i>Humicola insolens</i> Cutinase (Novozym 51032)
HIPS	High impact polystyrene
HMBC	Hetronuclear Multiple-Bond Coherence
HPLC	High-performance liquid chromatography
HSQC	Hetronuclear Single Quantum Coherence
HOBn	Benzyl alcohol
IR	Infrared
ISO	International Organization for Standardization
K_{obs}	Observed (pseudo) rate constant
L	Ligand
L-LA	L-lactic acid
MA	Maleic anhydride
MADLI-ToF	Matrix assisted laser desorption ionization time-of-flight
M_c	Critical molar mass
M_e	Entanglement molar mass
MeTHF	2-methyl tetrahydrofuran
NMR	Nuclear magnetic resonance
M	Metal
M_n	number average molar mass
OO	1,2-Epoxyoctane
OBH	7-oxabicyclol-[2.2.1] heptane
Oct	Octanoate

OEt	Ethoxide
O ⁱ Pr	Iso-propoxide
PA	Phthalic anhydride
PB	Polybutadiene
PBAT	Polybutylene adipate terephthalate
PBO	Polybutylene oxide
PBS	Poly(butylene succinate)
PC	polycarbonate
PCHC	Poly(cyclohexene carbonate)
PCPC	Poly(cyclopentene carbonate)
PCL	Poly(caprolactone)
PDA	Photo diode array
PE	Tetra-functional pentaerythritol ethoxylate
PE	Polyethylene
PeCHC	Poly(ethyl-cyclohexene carbonate)
PEO	Polyethylene Oxide
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoates
pK_a	Acid dissociation constant
pK_h	Hydrolysis constant
PLC	Poly(limonene carbonate)
PLA	Poly(lactide)
PLLA	Poly(L-lactide)
PP	Polypropylene

ppm	Parts per million
PS	polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinylchloride
PvCHC	Poly(vinyl-cyclohexene carbonate)
PYSD	Post-yield stress drop
<i>ran</i>	random copolymer
RI	Refractive index
ROCOP	Ring opening copolymerisation
ROP	Ring opening polymerisation
ΔS_m	Entropy of mixing
SAN	Styrene-acrylonitrile copolymer
SAXS	Small Angle X-Ray Scattering
SEM	Scanning electron microscopy
SBS	Styrene-butadiene-styrene
SPI	Society of the Plastic Industry
$\tan\delta$	Damping factor
tBuPA	3- <i>tert</i> -butyl-phthalic anhydride
T_{d5}	The temperature at which 5 wt% of a sample has decomposed
T_{d95}	The temperature at which 95 wt% of a sample has decomposed
TEM	Transmission Electron Microscopy
T_g	Glass transition temperature
TGA	Thermal gravimetric analysis

THF	Tetrahydrofuran
T_m	Melting temperature
TMP	1,1,1-tris(hydroxymethyl)propane
TOF	Turn over frequency
TPU	Thermoplastic polyurethane
U_T	Ultimate tensile toughness
UV	Ultraviolet
WAXS	Wide Angle X-Ray Scattering
wt%	Weight percent
ϵ^B	elongation at break
σ	Maximum tensile strength
χ_{12}	Interaction parameter
χ	Crystallinity
η	Viscosity
δ_H	Proton chemical shift (NMR)
θ	Water contact angle
η^*	Complex viscosity

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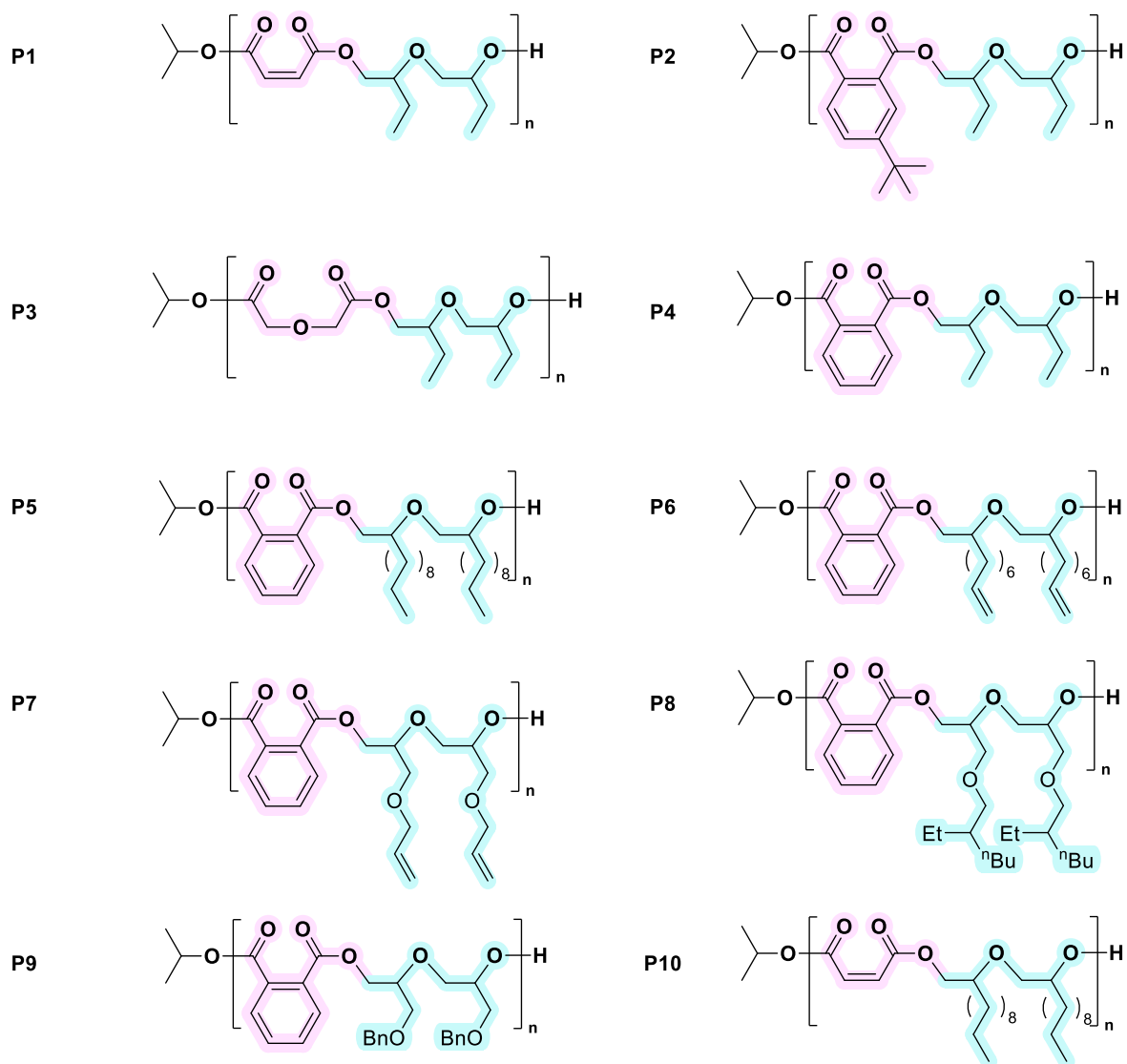
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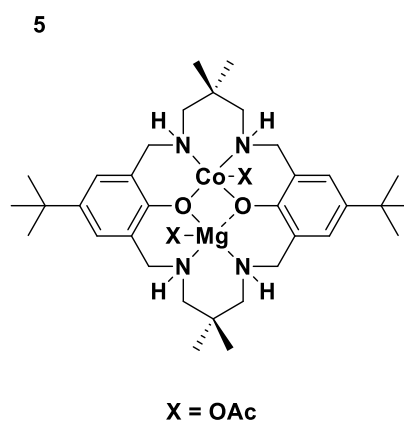
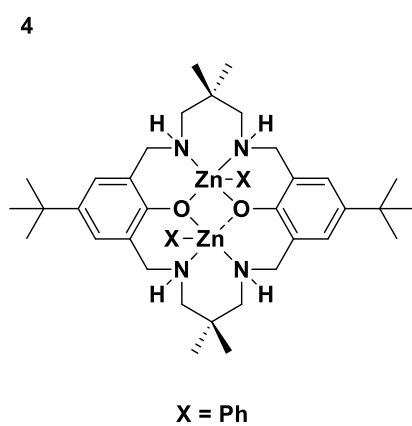
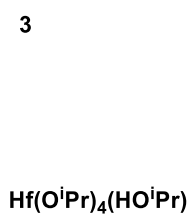
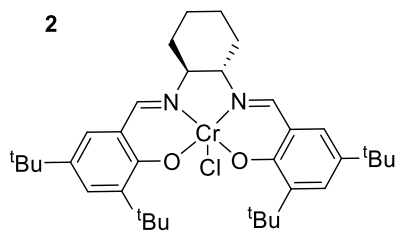
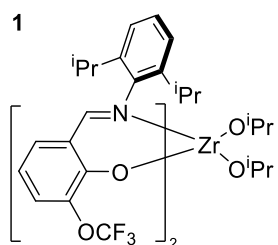
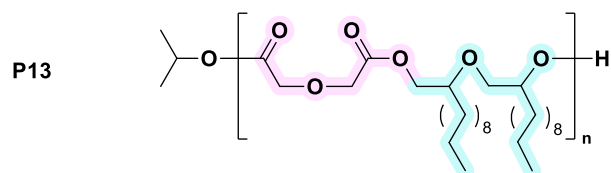
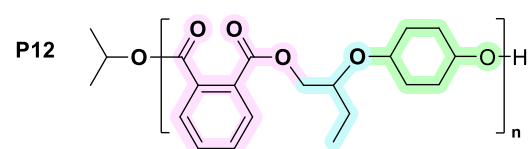
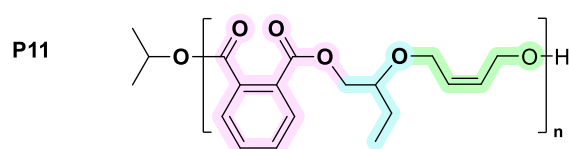
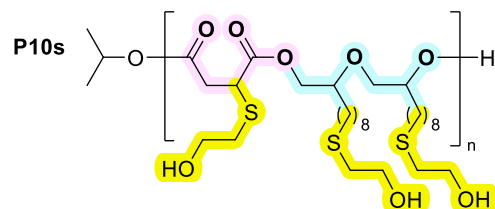
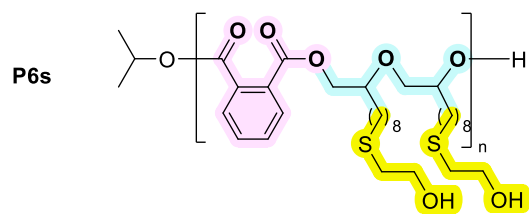
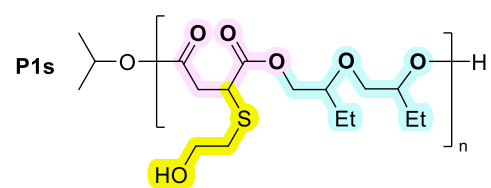
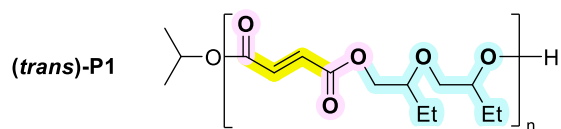
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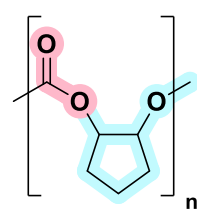
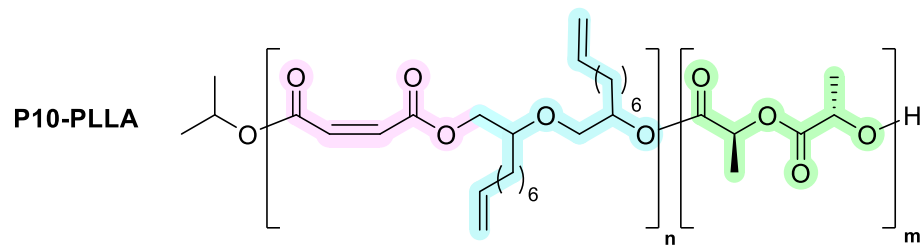
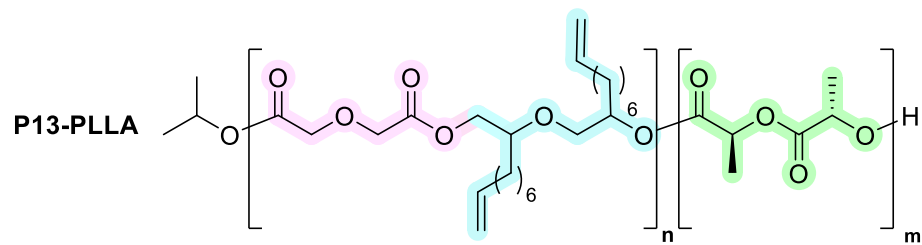
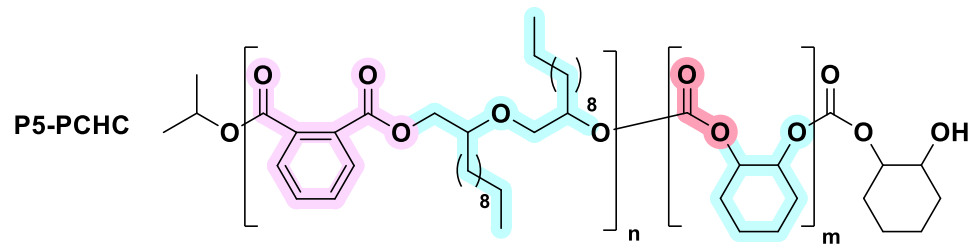
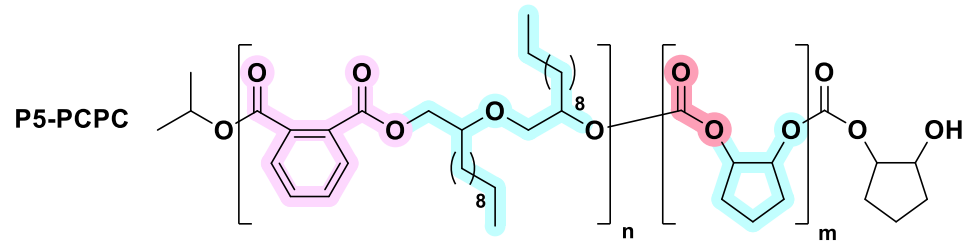
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Polymer and Catalyst Guide

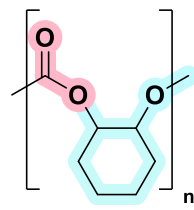
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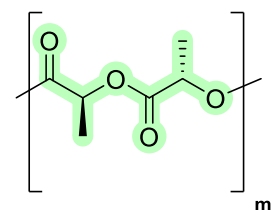




PCPC



PCHC



PLLA

CHAPTER 1

Chapter 1: Introduction

1.1 The Plastic Problem

Plastics have improved our quality life dramatically. They are important in medicine, building, agriculture, house-hold products, and, they are now ubiquitous in modern society.^{1,2} An incredibly wide range of materials have been developed, with excellent properties and extremely low production costs.³ Unfortunately, there are two major problems with the production of plastics today;

- 1) The vast majority are non-renewably resourced, mainly from petrochemicals, giving rise to unacceptable carbon dioxide (CO₂) emissions.
- 2) They do not easily degrade (chemically) and when distributed in the environment they are pervasive.^{3,4}

Polymer manufacturing is an energy and resource intensive industry. For example, in 2017 polymer manufacturing used ~8 % of global oil, emitting 3.8 % (1.8 Gt) of world carbon CO₂.^{5,6} By 2050, the sector could be responsible for more than 6.5 Gt CO₂ emissions per annum and consume 20 % of global fossil fuel.^{7,8} This figure would represent up to 15 % of the worlds annual CO₂ budget in 2050.⁷ The majority of greenhouse gas (GHG) emissions arise during raw material extraction and refining, as well as in polymer production. Addressing these emissions is essential to allow the chemical industry and its customers to achieve net zero emissions.^{1,7}

Many petrochemical-based plastics were designed to be stable, strong and chemically resistant, and consequently, they tend not to be chemically recyclable or biodegradable.² Plastic waste is accumulating world-wide, with estimates of 6 Gt of plastic already in the environment.⁹ In the absence of chemical degradation, plastics can slowly break down, via a combination of ultra violet (UV) and physical abrasion/fragmentation mechanisms, forming micro and nano-plastic pollution.^{2,4,10} These pervasive by-products have entered the environment, waterbodies and food chain, found in places from the arctic to the human body.¹¹ Micro/nano-plastics can accumulate and carry contaminants.¹² The full extent of their health and environmental impacts is not currently well understood.²

One opportunity to try and remediate these issues, is to investigate how to design polymers that can replace fossil-fuel-based feedstocks with renewable ones (either waste-sourced or bio-based materials). These alternative polymers must match or improve upon the properties of existing plastics, and, allow for low energy and efficient recycling or degradation.^{6,13}

1.2 A Circular Plastics Economy

In a circular plastics economy, the aim is to maximise carbon (dioxide) recirculation and material recycling between plastic wastes and feedstocks. This enables the carbon embedded in plastics to more effectively remain in the system, rather than being lost to the environment, reducing overall emissions (Figure 1.1b).^{1,4,14,15} This can be achieved by (in the order of proposed priority); reuse, physical recycling, (bio)chemical recycling (for example by pyrolysis, gasification or depolymerisation to monomer), and as a last resort, by biodegradation (e.g industrial composting or anaerobic digestion) or energy recovery methods (such as incineration) being coupled to CO₂ capture (Figure 1.1b).^{1,16} Although, the first priority should be prevention/reduction, including the drastic reduction in plastic demand and manufacturing.¹ Williams and co-workers suggest that, in order to meet our global climate targets, 50 % of all plastic production will need to be cut, all plastics will need to be renewably sourced (promoting recirculation of carbon), 95 % of plastics will need to be recycled, and, environmental pollutants must be removed/prevented (for example microplastics or toxic additives).¹

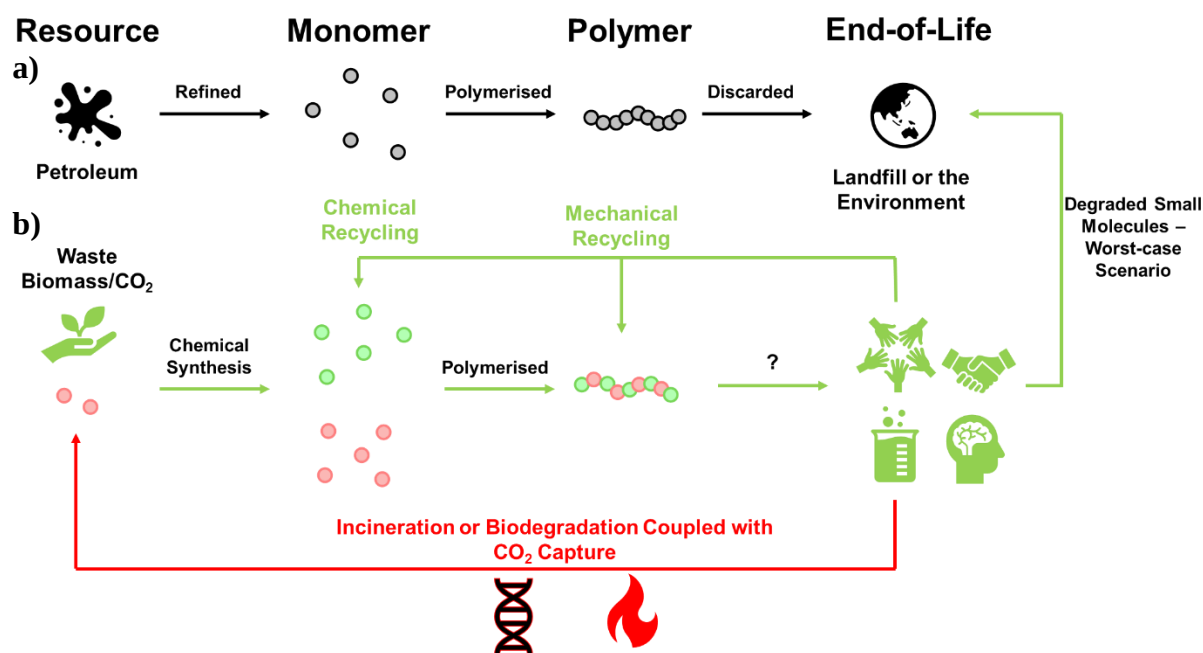


Figure 1.1: Contrasting an example of a) a linear polymer life-cycle, and b) a circular plastics economy.

From the perspective of a polymer chemist, to meet these requirements, a circular design strategy is necessary (Figure 1.2). Monomers should be selected based on current or future ability to be renewably sourced; including bio-based, wastes or CO₂. Atom efficient and controlled polymerisations, with high selectivity and innovative sequence control, can enable production of polymers with useful properties, that can replace existing, pervasive petrochemically-based polymers (points 2 and 3 in Figure 1.2). Finally, polymers should be

designed with end-of-life in mind, being amenable to physical (mechanical) and chemical recycling, or to be biodegradable where environmental dispersal is inevitable (points 4 and 5 Figure 1.2).

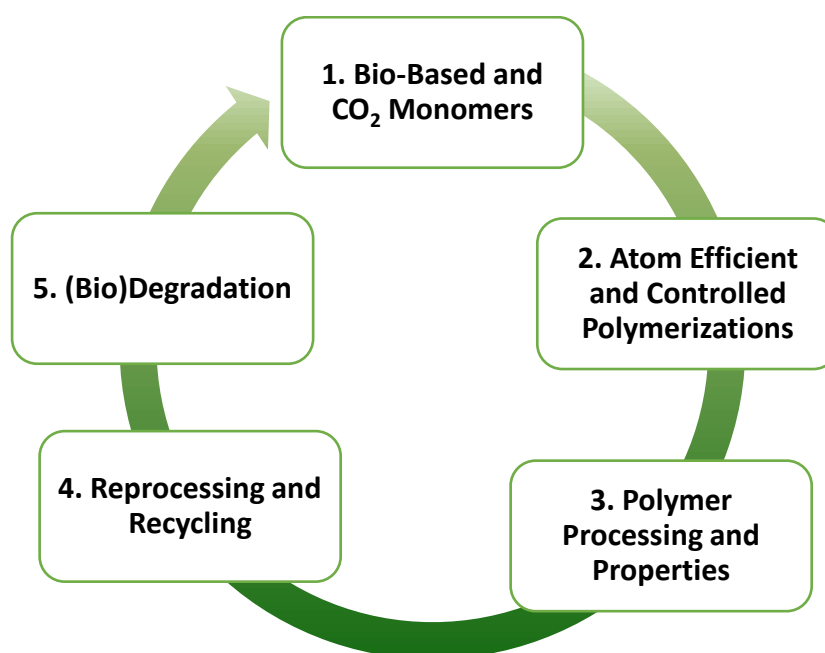


Figure 1.2: An example of a circular polymer design strategy, using circular economy principles.

1.3 Sustainable Alternatives to Thermoplastics

One goal of sustainable polymerisation catalysis is to produce bio-based, sustainable polymers that can replace petrochemically based ones, or even, exhibit functional/performance advantages.^{8,13} For polymers, these improvements can include properties that make manufacture and processing easier, improve application performance—for example strength, adhesion and toughness—as well as end-of-life options and emissions reductions.⁸ This is an extremely difficult task, owing to the impressive properties of existing plastics, as well as the efficiency of established raw material extraction and polymer manufacturing pathways.⁸ The materials that make up the majority of the global plastic wastes include polyethylene (PE, 35 %), polypropylene (PP, 19 %), polyvinylchloride (PVC, 5 %), polyethylene terephthalate (PET, 11 %), polystyrene (PS) and its derivatives (7 %), polyurethane (PU), rubber, acrylics and nylons. Other specialties account for ~4 %.^{6,17}

Many alternative polymers have emerged (Figure 1.3).^{4,8,13} Some are renewably sourced, while some are both renewably sourced and (bio)degradable (Figure 1.3). In 2024, 2.47 Mt of renewably sourced plastics was produced, 56 % of which was also biodegradable.¹⁸ This represents half a percent of the 414 Mt of plastics produced in the same year.¹⁸ The bio-

based, non-renewable polymers included bio-based PE (14 %), PP (1 %), polyamines (PA, 15 %), Poly(trimethylene Terephthalate) (PTT, 13 %) and PET (3 %).¹⁸ Meanwhile, the major bio-based and biodegradable plastics produced were PLA (37 %), starch-based polymers (6 %), PBAT (5 %) and Poly(hydroxyalkanoates) (PHA, 4 %).¹⁸

In this work, we focus specifically on poly(L-lactide) (PLLA) and polycarbonates (PC) derived from CO₂ and epoxides, as possible replacements for PS and its derivatives. While simultaneously meeting physical and chemical recycling requirements, and in some cases biodegradability, possible replacement materials need to meet performance objectives. Many biodegradable plastics (such as PLLA and CO₂-based PC's) often fall short in aspects such as toughness, flexibility/ductility, strength, processability or thermal operating/processing window (Table 1.1).¹³ Therefore, low-cost strategies are required to increase the range of potential applications for these materials. Importantly, these strategies/modifications must not impact the sustainability of these materials, and, studies should focus on such an approach to polymer design, characterisation and testing.¹⁶

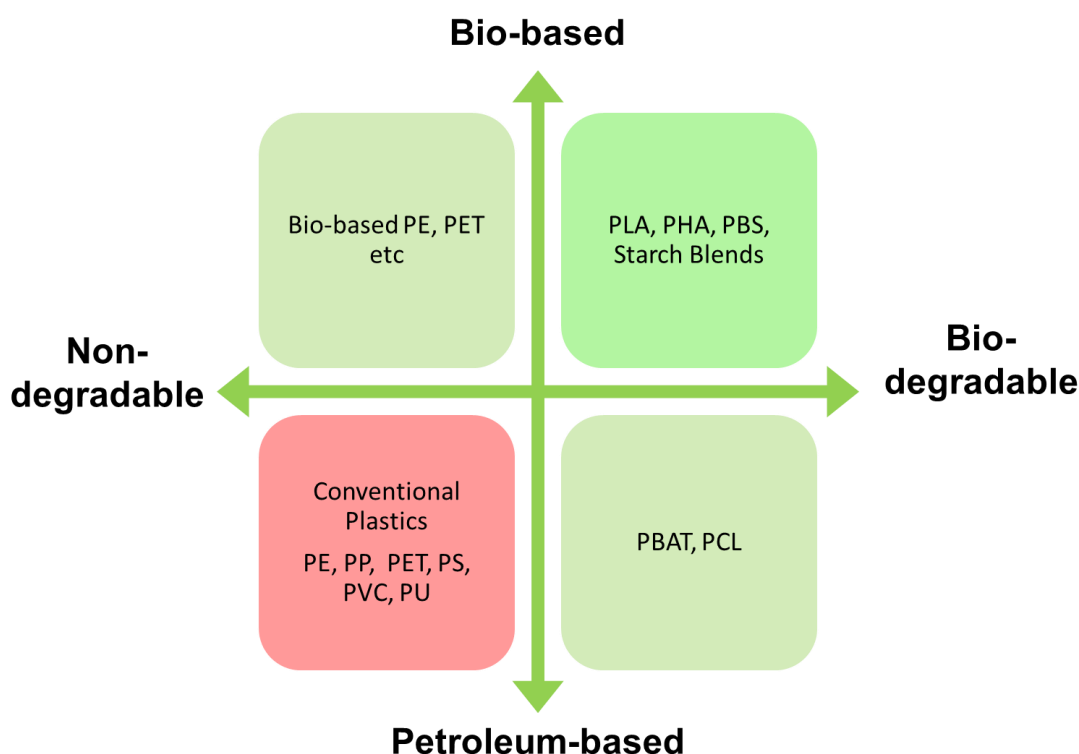


Figure 1.3: Comparison of some conventional plastics and some bio-derived plastics, comparing the sourcing (renewable vs petroleum) and degradability of these materials. PE = polyethylene, PET = polyethylene terephthalate, PP = polypropylene, PS = polystyrene, PVC = polyvinyl chloride, PU = polyurethane, PBAT = polybutylene adipate terephthalate, PCL = polycaprolactone, PLA = polylactide, PHA = Polyhydroxyalkanoate, PBS = polybutylene succinate.

Table 1.1: Comparison of thermal and mechanical properties, as well as end-of-life options available for sustainable thermoplastics PLLA and PCPC with current petrochemical-based thermoplastics PS, ABS and HIPS.

Polymer	T_g (°C)	T_m (°C)	$T_{d,5}$ (°C)	Strength (MPa)	Young's Modulus (GPa)	Elongation (%)	End-of-life
PLLA	65	150-180	321	67	2.9	3	PR, CRM, BD
PCPC	90	-	270	58	2.8	13	PR, CRM, BD*
PS	90-98	-	350	26-46	2.0-3.1	3-15	PR, CR
ABS	107-116	-	340	34-44	1.9-2.4	24-78	PR
HIPS	100	-	350	16-29	0.8-2.2	25-70	PR

PR = physical recycling, CR = chemical recycling, CRM = chemical recycling to monomer, BD = biodegradable. PS, ABS and HIPS data was compiled from commercial data sheets (see section 8.3.6). PLLA and PCPC data are obtained experimentally from chapters 3 and 5 respectively. *= demonstrated in this thesis.

1.3.1 Styrene-based Plastics

1.3.1.1 Properties and Applications of Styrene-based Plastics

Polystyrene (PS) is made from styrene, via a range of manufacturing routes, most-often by means of free radical polymerisation.¹⁹⁻²¹ It is cheap (costing ~2 \$US per kg in 2017),²² strong (tensile strength = 26-46 MPa and Youngs modulus = 2.0-3.1 GPa, Table 1.1), resistant, clear, and, can be processed into a foam (expanded polystyrene, EPS, or known commercially as Styrofoam) with high strength and low weight/density.²¹ PS-based materials are produced at around 30 Mt per year, which equates to ~7 % of global plastic production.^{6,10,19,23} One major shortfall is its brittleness (elongation at break = 3-15 %, Table 1.1), for which there have been many solutions. Of these attempts to impart ductility, two of the most successful and widespread are to make copolymers/blends through acrylonitrile–butadiene–styrene (ABS) and high-impact polystyrene (HIPS).

ABS is a terpolymer, whereby the majority phase consists of styrene/acrylonitrile copolymer (SAN), comprising 40-60 % styrene and 15-35 % acrylonitrile, respectively. Polybutadiene (PB) is dispersed and grafted (5-30 %) to the SAN, forming a dispersed phase. The elastomeric nature of PB, as well as the compatibility provided by grafting, greatly improves the overall ABS toughness (ductility) versus PS.^{19,20,24,25} It shows high strength (tensile strength = 34-44 MPa and Youngs modulus = 1.9-2.4 GPa, Table 1.1) and elongation at break (24-78 %) values. ABS is a bridging material between higher performing, more expensive engineering plastics and commodity plastics. It is commonly used in automotive parts and building materials.^{24,25}

High-impact polystyrene (HIPS) is another modified PS, designed to impart ductility. HIPS makes up 30-40 % of PS manufacture.¹⁹ It comprises a PS continuous phase and a dispersed PB phase, with PB-*g*-PS (or PB-*b*-PS) copolymers being dispersed within the rubbery PB phases. The complex morphology is formed in situ by a phase inversion technique.²⁰ The

sub-structured, or ‘salami’, array of occluded microphases has been credited with the improved material properties such as high strength (16-29 MPa, Table 1.1), elongation at break (25-70 %, Table 1.1) and toughness.^{19,26} HIPS is widely used in transportation and electronics applications.^{19,20,26} HIPS constitutes 42 % of the total waste electrical and electronic equipment world-wide.¹⁹

1.3.1.2 End-of-life Options of Styrene-based Plastics

PS, ABS and HIPS are all derived from petroleum and not biodegradable.¹⁷ PS is extremely difficult to recycle, either physically or chemically. Its low density—particularly when foamed in EPS, which can be up to 95 % air—is extremely hard to separate from mixed wastes and physically recycle.^{10,21,27} As a result, ~1 % of postconsumer PS is recycled.^{21,22} It is therefore given the Society of the Plastic Industry (SPI) code 6, designating that it should not be included in regular recycling programs.²¹ Repeated cycles of mechanical recycling can result in degradation, through chain scission and cross-linking (at higher temperatures), resulting in decreased molecular weight, viscosity and ductility.^{10,21} After 10 reprocessing cycles, PS molecular weight can decrease by half.¹⁰ If PS is mechanically recycled, it is usually downcycled for use in disposable products or building materials.¹⁰ Most commonly, end-of-life management strategies for PS are either incineration or landfilling, and PS-based products make up around 30 % of the plastic in global landfills.^{10,21,22} A further complication, is that only 50 % of PS produced is in its pure/solid form, with 10 % as EPS (Styrofoam) and the rest as either segments in copolymers (e.g SAN, ABS or styrene-butadiene-styrene, SBS) or blends with other materials (e.g. HIPS).²² This creates issues with sorting PS waste.²²

PS can undergo chemical recycling to monomer at 310-350 °C, with styrene yields from 33-80 %.^{17,21,28} Industrially, this process is carried out at temperatures up to 800 °C.²¹ The selectivity of these processes is also an issue, with a range of mono- and poly-aromatic side-products reported.²¹ Chemical recycling is even more problematic for ABS and HIPS, with styrene yields well below 50 %.¹⁹ The PB particles are damaged (charred) during recycling, which is another disbenefit.¹⁹ Potential lower energy chemical recycling methods have been reported, including alternatives to thermal methods, such as photoexcitation/oxidisation, producing oxidised aromatic products with yields of 23-71 %.²⁹⁻³¹

These recycling limitations motivate investigation of alternatives, that meet the properties of PS, but with better end-of-life options. Herein, we explore two lead materials: PLLA made from starch-rich biomass and poly(cyclopentene carbonate) (PCPC) produced from CO₂ and cyclopentene oxide.

1.3.2 Poly(L-lactide) PLLA

1.3.2.1 Production of PLLA

PLA is currently the most widely produced bio-derived plastic.^{3,32} The global PLA market in 2024 was approximately 0.9 Mt, comprising 37 % of the global bioplastics production capacity.¹⁸ This is predicted to reach 2.5 Mt by 2029, with application mainly in flexible and rigid packaging, but also to a smaller extent in fibres, consumer goods and agriculture.¹⁸ Lactic acid, which is a fermentation product of starch rich biomass, like sugarcane, undergoes condensation polymerisation producing an oligomer, which is subsequently depolymerised to L-lactide (L-LA, the cyclic dimer of lactic acid) (Figure 1.4).^{32,33} PLLA is produced by the ring-opening polymerisation (ROP) of L-LA (Figure 1.4).¹³ Heterocycle ROP is an efficient method for other polyester and polycarbonate synthesis (Figure 1.5).^{3,34} It is a chain growth polymerisation, whereby the initiator ring opens the cyclic monomer, which produces a reactive nucleophile, that can then ring-open other cyclic monomers to form a polymer chain (Figure 1.5).¹³ L-LA ROP tends to be high yielding, and typically operates in neat monomer at temperatures of 130-160 °C. L-LA ROP provides control over the PLLA molecular weight and dispersity, end-group control/fidelity and stereo-selectivity. ROP of L-LA can be performed with a variety of catalysts, and the field has been extensively reviewed.^{3,13,35-42} The catalyst can be metal based,⁴³⁻⁴⁶ organic⁴⁷⁻⁴⁹ or enzymatic.³³ Industrially, Tin(II) octoate ($\text{Sn}(\text{Oct})_2$) is often used for L-LA ROP, as it is stable and has high activity.³³

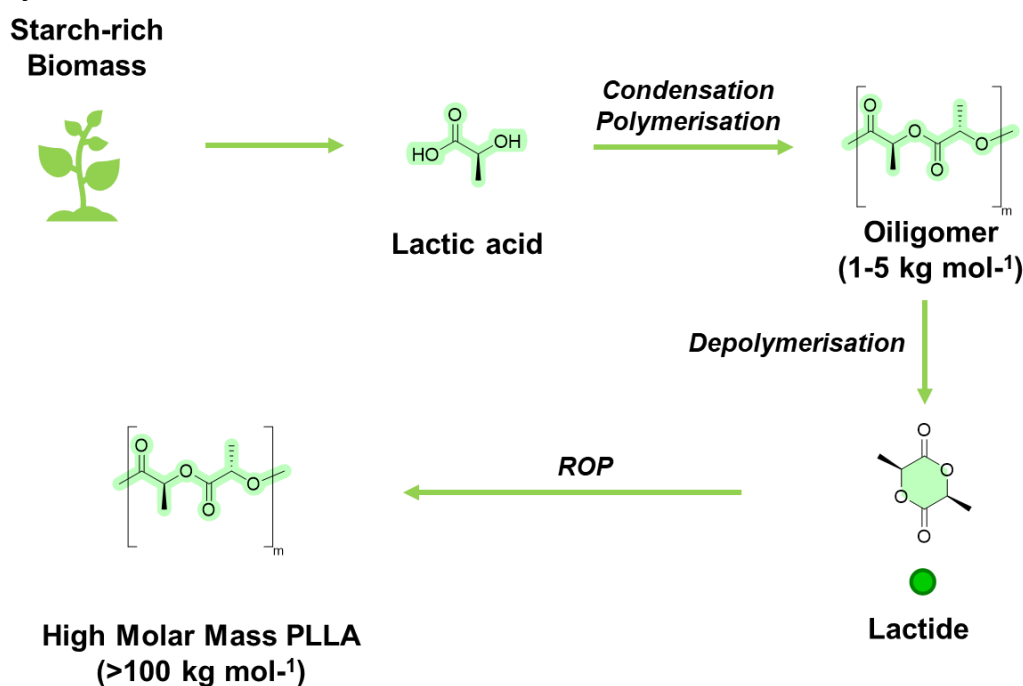


Figure 1.4: Production of lactide from starch-rich biomass.

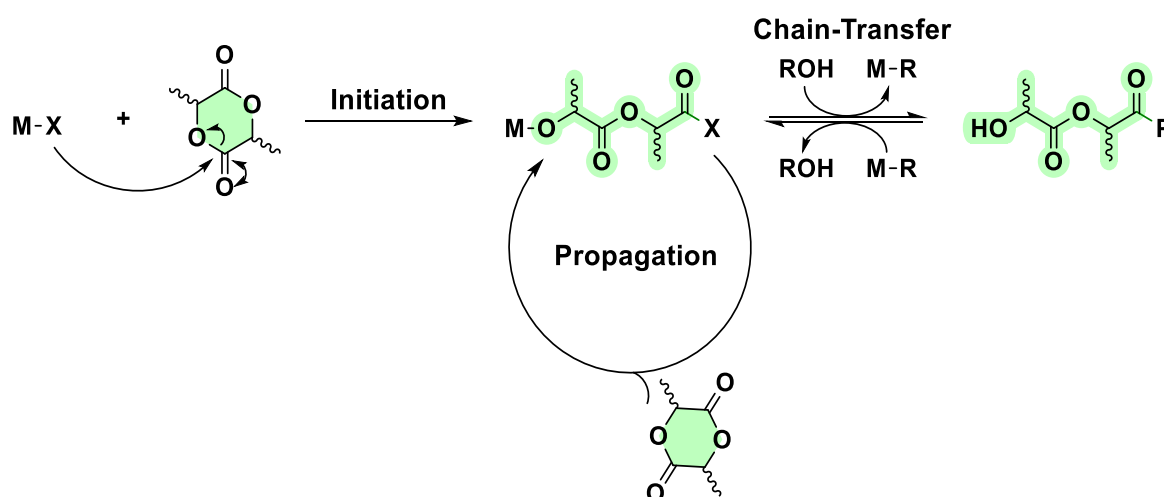


Figure 1.5: General ring opening polymerisation (ROP) of LA with a metal catalyst M and nucleophile X . P = the growing polymer chain.

1.3.2.2 Properties of PLLA

L-LA has two stereo-centres (the pendant methyl groups), resulting in either the L-, D- or meso-lactide stereoisomers (Figure 1.6).³² The properties of the resulting polymer—such as crystallinity, rheology, thermal properties, operating temperature window, mechanical strength and degradability—are highly dependent on its stereochemistry.⁵⁰ Commercial polylactide can be made amorphous (when synthesised from racemic-lactide, a combination of both L- and D-LA, forming PLA) or semi-crystalline (from L-lactide, forming PLLA).^{50–53} This thesis focuses on PLLA, due to its superior strength and higher operating temperature window.^{50–53}

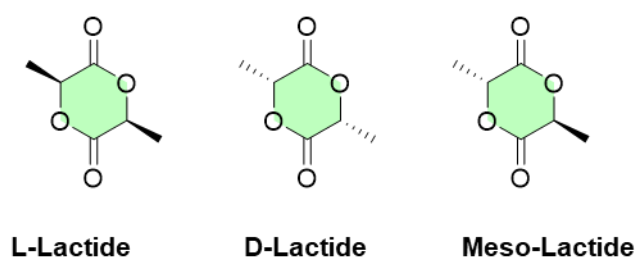


Figure 1.6: Schematic representation of L-, D- and Meso-Lactide monomers.

PLLA is strong, as its semi-crystallinity provides a higher tensile modulus (~ 3.5 GPa) and strength (47–66 MPa, Table 1.1). Its semi-crystallinity also increases the upper service temperature, which may be of interest in uses as an engineering thermoplastic.^{50–53} It has reasonably high thermal stability ($T_{d5\%} = 215$ – 285 °C) and a moderate/high melting point ($T_m = 150$ – 180 °C). One limitation is its low/moderate glass transition temperature ($T_g \sim 60$ °C), which is 40 °C lower than for PS (90 – 98 °C, Table 1.1). In addition to its low T_g , the use of

PLLA is hindered by its brittleness (tensile toughness $<5 \text{ MJ m}^{-3}$ and elongation at break $<5 \%$, Table 1.1).^{52,54} It also shows a relatively slow crystallisation rate, which complicates processing.⁵⁵

PLLA meets targets 1-5 of the circular design strategy used in this thesis (Figure 1.2). Therefore, innovations are required that can improve the ductility of PLLA, without negatively impacting its other properties. A range of approaches to improving its properties include: copolymerisation, adding small-molecule plasticisers, rubber toughening, reactive blending/crosslinking, as well as making composites with organic or inorganic filler materials.^{52,54} These approaches are explored in more detail below.

1.3.2.3 End-of-life Options of PLLA

PLLA can be mechanically and chemically recycled. It is also fully biodegradable and compostable.^{56,57} Life cycle assessment (LCA) against polyethylene, showed that PLLA has 40 % lower greenhouse-gas emissions and 25 % lower non-renewable energy use.^{58,59} The mechanical recycling of PLLA has (similarly to PS) also shown reductions to molar mass, from chain scission, resulting in changes to thermal-mechanical properties.^{33,60} Solutions have included the use of chain extenders during recycling.^{33,61}

PLLA can be chemically recycled by alcoholysis, hydrolysis (producing lactic acid) and chemical recycling to monomer (CRM), which uses a catalyst to yield lactide monomer.³³ Recently, a catalysed PLLA recycling (CRM) technique was reported, allowing for low temperature (130-180 °C) chemical recycling to L-LA, with low loadings of $\text{Sn}(\text{Oct})_2$ as the catalyst (1:1000 cat:PLLA).⁵⁶ Under these conditions, the L-LA monomer was formed selectively (without epimerisation), in very high yield, activity and purity ($>99 \%$ L-LA).⁵⁶ The recycling to monomer occurs at a much lower temperature than PS recycling to styrene.

Potential closed-loop biological recycling pathways have been demonstrated for PLLA.^{33,62} For example, enzymes can be used to degrade PLLA to L-lactic acid, which can then be re-polymerised to form PLLA.⁶³ These processes are interesting as they are conducted at low temperature (°C), although are currently prohibitively expensive for larger scale.³³

1.3.3 Polycarbonates from CO_2 and Cyclic Epoxides

While the ductility of PLLA can be improved, its low T_g cannot be addressed. Polycarbonates formed from the ring opening copolymerisation (ROCOP) of CO_2 and cyclic epoxides may be attractive alternatives (Table 1.1).^{34,64,65} The carbonate linkage provides strength, while also being hydrolysable/degradable (important for end-of-life), whereas the

cyclic epoxide provides higher T_g materials (compared to PLLA, Table 1.1). Incorporating CO_2 into the polymer backbone has resulted in a three-fold reduction in carbon dioxide emissions compared to the analogous polyether formed from epoxide homo-polymerisation.^{66–68} CO_2 is a cheap and abundant waste product, and the copolymerisation can be compatible with current commercial plastic production infrastructure. Currently, cyclic epoxides such as cyclohexene oxide (CHO) and cyclopentene oxide (CPO) are petrochemically sourced, although approaches to make them from biomass have been explored.^{69,70}

In the ROCOP of CO_2 and epoxides, the two different monomers are incorporated into the growing polymer chain, in an alternating fashion, to produce the resulting polycarbonates (Figure 1.7).⁶⁵ The wide range of epoxides available, provides a useful means to tune polycarbonate structural diversity and thermal-mechanical properties.³⁴ For example, employing a more flexible (when ring-opened) epoxide such as propene oxide (PO), compared to a cyclic epoxide (CHO), can result in T_g values being 90 °C lower in the former.³⁴ In this project, we are focused on cyclic epoxides, as a higher T_g is desirable to compete with PS.

Various catalysts have been developed for this epoxide/ CO_2 ROCOP, and the catalysis field has been reviewed.^{34,65,71–76} In this work, hetero-dinuclear metal complexes, containing two different metal centres, were selected due their high rates, selectivity and tolerance to impurities.⁷⁷ It has been suggested that the metal centres act synergistically to provide fast and controlled ROCOP catalysis, with each metal having a different role in the catalysis.^{77,78} The catalysis is proposed to occur by epoxide coordination to a metal centre, followed by initiation by either an anionic co-ligand of the catalyst, or a protic species deliberately added (or present as impurities in the monomers) (Figure 1.7). This produces a metal-alkoxide intermediate, which can insert CO_2 , forming a metal-carbonate intermediate. Subsequent repeat cycles of insertion of an epoxide and CO_2 insertion occur during propagation (Figure 1.7). Side reactions include chain-end backbiting (from the alkoxide intermediate) to form cyclic carbonates, the thermodynamically favoured product, consecutive epoxide insertion to form ether linkages, or chain transfer (Figure 1.7).⁷⁴ These side reactions can be controlled or prevented by the right catalyst, as well as by control over reaction conditions.⁷⁴ Termination of the reaction is achieved by the addition of water or acids (cleaving the metal alkoxide), removal of monomer or reducing the reaction temperature.⁷⁴

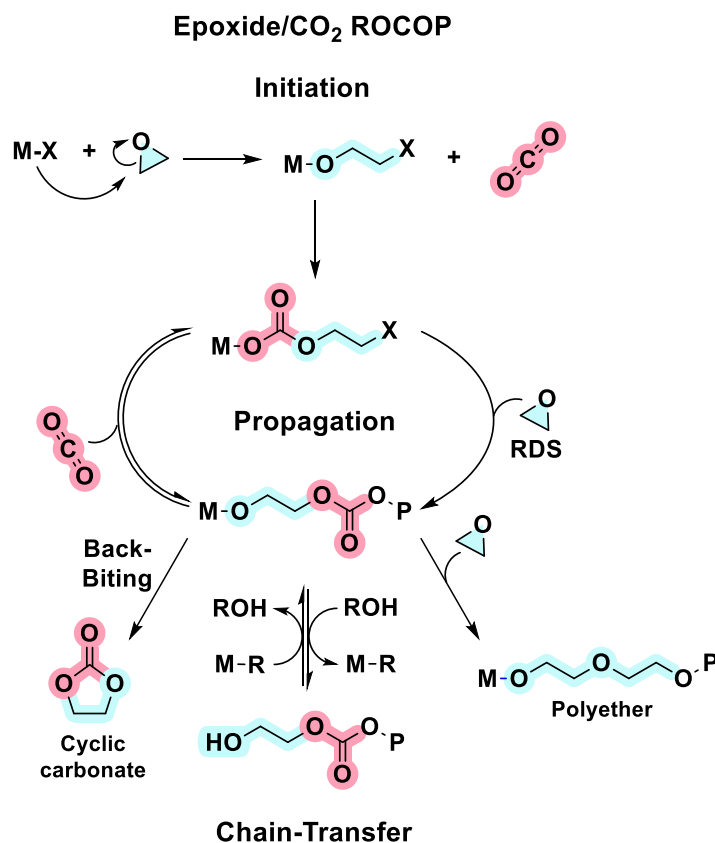


Figure 1.7: General ring opening copolymerisation (ROCOP) of epoxides and CO₂ to form polycarbonates (with side reactions of cyclic carbonate, polyether and chain-transfer shown).

Thermoplastics tend to be high molar mass polymers, since physical properties such as glass transition and strength are optimised when the molar mass of a polymer is 3-6 times higher than its entanglement molar mass (M_e).⁷⁹ The molar mass at which these properties no longer improve is termed the critical molar mass (M_c).⁷⁹ Historically, it has been difficult for CO₂/epoxide ROCOP to access high molar mass polycarbonates, and the M_e was not measured for many materials until very recently. The catalysis is influenced by protic impurities, such as diols from a ring opened epoxide, which serve as chain transfer agents and reduce the achieved polycarbonate molecular weight.⁸⁰ This issue has meant that the field tends to focus on the development of oligo-carbonates or low molar mass polyols (e.g. $M_n < 10 \text{ kg mol}^{-1}$), which are used in polyurethane synthesis, coatings, foams, adhesives and elastomers.^{81–86}

Recent advancements in catalysis have enabled production of higher molar mass polycarbonates from CO₂ and cyclic epoxides (Table 1.2).^{6,68,69–72} Polycarbonates like poly(limonene carbonate) (PLC), poly(cyclohexene carbonate) (PCHC), poly(ethyl-cyclohexene carbonate) (PeCHC), poly(vinyl-cyclohexene carbonate) (PvCHC) and poly(cyclopentene carbonate) (PCPC) have all now been reported with $M_n > 100 \text{ kg mol}^{-1}$.

^{1, 66,68,69–72} Williams and co-workers reported the synthesis of high- M_n (over 100 kg mol⁻¹), narrow dispersity polycarbonates PCHC, PeCHC, PvCHC and PCPC, using an organometallic CoMg catalyst.⁸⁰ This exciting development permitted the first determination of the M_e for these materials, as well as insights into their viscoelastic and thermal-mechanical properties (Table 1.2).⁸⁰

Table 1.2: A Summary of the thermal-mechanical properties of literature high molar mass polycarbonates from CO₂ and cyclic epoxides.

Polymer	T_g (°C)	$T_{d,5}$ (°C)	σ_Y (MPa)	ϵ_B (%)	E (GPa)	U_T (MJm ⁻³)	M_e (kg mol ⁻¹)
PCPC ⁸⁰	85	271	58.5	7.1	1.7	2.9	3.4–4.6
PCHC ⁸⁰	126	265	40.0	3.3	2.1	0.9	56
PLC ⁹⁰	130	240	55.0	15	1.0	-	-
PeCHC ⁸⁰	105	306	46.7	18.7	1.3	7.0	13-18
PvCHC ⁸⁰	118	277	52.2	4.9	1.3	1.6	45-62
PCHC_{0.28-grad-} PCPC_{0.72} ⁹²	96	255	52.0	7.4	1.7	2.8	4.3

In a similar manner to PLLA, CO₂-based polycarbonates from cyclic epoxides are brittle (Table 1.1 and 1.2).⁸⁰ This restricts their application potential. For example, PCHC is one of the most well-studied of the CO₂-based PCs, but is today used only by Empower Materials as a sacrificial binder during electronics manufacture.

1.3.3.1 Poly(cyclopentene carbonate) (PCPC)

A key recent finding, was that PCPC (from cyclopentene oxide, CPO) exhibits a particularly low M_e ($M_e = 4.0$ – 4.9 kg mol⁻¹), which was an order of magnitude lower than the other CO₂/cyclic epoxide derived polycarbonates studied by Williams and co-workers.⁸⁰ Having a low M_e is clearly very desirable in targeting replacements for PS. Also, PCPC (114 kg mol⁻¹) presented promising physical properties, such as a relatively low zero shear viscosity (0.8 MPa s⁻¹), which is important in polymer processing, particularly for melt blending, compounding, extruding and other manufacturing processes.⁸⁰ It exhibited a high glass transition temperature ($T_g = 85$ °C by DSC, 97 °C by rheology) and a high on-set decomposition temperature ($T_{d5} = 271$ °C).⁸⁰ It has a wider operating temperature window than PLLA, and is much closer to that of PS (T_g PLLA = 65 °C, PS = 90-98 °C, Table 1.1). PCPC is strong, with a high tensile strength ($\sigma_Y = 59$ MPa) and Youngs modulus ($E = 1.7$ GPa, Table 1.2). Its elongation at break is 7 %, which is equivalent to the other thermoplastics (for example PLLA = 3 %, PCHC = 3.3 % and PS = 3-15 %, Table 1.1).⁸⁰

The mechanical recycling and chemical recycling to monomer (CRM) of PCPC has also been demonstrated.^{80,88,93} Chemical recycling reforms the CPO and CO₂ monomers.^{80,93} This process preserves some of the embedded energy and material value of the plastic, reducing

the number of chemical steps required for repolymerisation.^{4,7,13,14,57,94,95} Darensbourg and co-workers first demonstrated PCPC CRM in 2013, using a (salen)CrCl/*n*-Bu₄NN₃ catalyst at 110 °C.⁹³ Organoboron catalysts have also been shown to selectively (>99 %) yield CPO monomer at low temperature (140 °C), in 95 % yields and loadings as low as 1.0 kg of PCPC/g of catalyst.⁸⁸ Solid-state CRM was achieved with high selectivity, activity and at low temperatures (e.g for PCPC, TOF = 25,000 h⁻¹, CPO selectivity >99 %, with 0.02 mol % hetero-dinuclear organometallic CoMg catalyst, 1:5000, at 140 °C).⁹⁶ This circumvents the need for large quantities of solvents and separations. In contrast to these methods, chemical recycling of PS occurs at higher temperatures (310-350 °C).^{17,28} Although the enzymatic degradation of poly(propylene carbonate) (PPC) has been demonstrated, PCPC has not yet been explored in this regard.¹³

A major limitation of PCPC, is that it is also brittle. Effective strategies are needed to improve the mechanical properties such as ductility (toughness), without detrimental effects to the thermal properties (stability and operating window). These strategies should also preserve the beneficial recycling options available. One recent strategy has been to copolymerise PCPC and PCHC to form a gradient copolymer.⁹² High molar mass PCHC-*grad*-PCPC terpolymers ($86 < M_n < 164 \text{ kg mol}^{-1}$) produced amorphous polymers, with a single T_g ($96 < T_g < 108 \text{ °C}$), suggesting miscibility between PCHC and PCPC domains (Table 1.2).⁹² The M_e ($4 < M_e < 23 \text{ kg mol}^{-1}$) and mechanical properties were found to be between that of PCPC and PCHC.⁹² So far, there is no literature precedent for PCPC toughening by blending strategies.

1.4 Toughening Sustainable Thermoplastics

This section will outline existing toughening strategies for thermoplastics, focusing specifically on PLA/PLLA, for which there is comprehensive literature.^{52,54} There have not been any studies aiming to toughen PCPC.

1.4.1 Toughening Strategies

Typically, for brittle thermoplastics, the aim is to increase the elongation at break and tensile/impact toughness, without compromising the tensile modulus and strength.⁵² For sustainable thermoplastics, it is also important that the end-of-life options are not affected. There are a variety of strategies to improve the properties of thermoplastics. The molar mass, stereochemistry and crystallinity can all be varied.⁵² Comparing amorphous PLA and semicrystalline PLLA, Perego et al. showed that the tensile strength and notched Izod impact values were higher for the semicrystalline material, while the elongation at break was lower.⁹⁷

For semicrystalline polymers, the processing conditions can be controlled to alter the amount and orientation of crystalline regions. For example, PLLA was processed by melt-stretching from the amorphous state, promoting the formation of nano-crystallites, which produced a semicrystalline form of PLLA that showed vastly improved toughness (tensile strength, σ_Y , ~80 MPa and elongation at break, ϵ_B ~50 %).⁵³

Small molecule plasticisers are extremely effective at increasing elongation at break, although, this comes with a severe loss in mechanical strength and T_g .⁵² McCarthy et al. used 30 wt% triethyl citrate to increase the ϵ_B of PLLA from 7 to 610 %, although, this reduced the σ_Y from 52 to 7 MPa.⁹⁸ In the longer-term, plasticisers may also phase separate or leach, with the samples becoming brittle once more.⁹⁹ Concerns have also been raised over the toxicity of some plasticisers.¹⁰⁰

Copolymerisation is another strategy.^{101,102} Lactide can be copolymerised with a range of cyclic esters, lactones and carbonates, to form block or statistical copolymers, with properties tailored to precise specifications.^{52,101,103} Promising thermoplastic elastomers have been produced, employing PLLA as a hard-block.^{101,104} Although, these polymers would most likely not be suitable replacements for stronger (high tensile strength and modulus) thermoplastics that would look to replace styrenics.¹⁰⁵ Making composites can reinforce the polymer, but often results in compatibility issues and prevents recycling.¹⁰⁶

1.4.2 Polymer Blending

Polymer blending is an efficient, cost-effective method for improving the toughness of brittle polymers.⁵⁴ The aim of Polymer blending is to incorporate desirable properties that are absent in neat polymers. The resulting properties arise from the combination of the intrinsic properties of the polymers used and the resulting phase morphology. The phase morphology is vital to material performance, and is a result of miscibility, viscoelastic properties of the polymers and processing conditions used during blending.

Miscibility is a thermodynamic term, describing the Gibbs free energy of mixing (ΔG_m) for a polymer pair. When the ΔG_m of mixing is negative, a polymer blend will be miscible (Equation 1.1).⁵⁴ This can be effected by temperature, molecular structure, pressure, molecular weight and composition.⁵⁵ The enthalpy change upon mixing (ΔH_m) is a result of interactions between the molecules, while the entropy change (ΔS_m) is determined by the number molecular arrangements (microstates) available.⁵⁵ The enthalpy of mixing for polymers is often positive,

and the entropy of mixing is especially small. This results in very few polymer combinations being thermodynamically miscible.⁵⁵ Instead, they tend to phase separate.

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1.1)$$

The Flory-Huggins formula is a lattice model that can be used to estimate ΔG_m in a polymer blend system (Equation 1.2, for a binary blend). Here, N is the number of sites occupied in the lattice model, X_1 and X_2 are the degrees of polymerisation, Φ_1 and Φ_2 are the volume fractions, and χ_{12} is the interaction parameter (Equation 1.3). The parameter χ_{12} is defined as in Equation 1.3, using the molecular interaction parameters between the two different polymers, w_{12} , and each individual polymer, w_{11} and w_{22} , or estimated by the Hildebrand solubility parameters, δ_1 and δ_2 (Equation 1.4). δ is the square root of the cohesive energy density (the energy to separate molecules to the gas phase) per unit volume. z is the coordination number (the number of nearest neighbours for a coordination site in the lattice model). The components of the blend are more miscible the closer χ_{12} is to 0 (or negative in the case of Equation 1.3).

$$\frac{\Delta G_m}{NK_B T} = \frac{\Phi_1}{X_1} \ln \Phi_1 + \frac{\Phi_2}{X_2} \ln \Phi_2 + \chi_{12} \Phi_1 \Phi_2 \quad (1.2)$$

$$\chi_{12} = \frac{z}{K_B T} \left(w_{12} - \frac{w_{11} + w_{22}}{2} \right) \quad (1.3)$$

$$\chi_{12} = \frac{V}{RT} (\delta_1 - \delta_2)^2 \quad (1.4)$$

In the case of miscible polymers, blending may produce an ‘averaged’ display of polymer properties, dependent on the blending ratio. Conversely, for an immiscible blend, separate phases are observed in the polymer macrostructure.⁵⁵ The blend morphology defines the shape and distribution of the phases present. A variety of polymer blend macro-structures can be achieved, which can be classified into two categories (Figure 1.8);

- 1) Dispersed phase and matrix morphology, such as droplets (emulsion), double emulsions and fibres. These usually occur when one polymer is present in a much higher ratio than the other.
- 2) Co-continuous matrix morphology, including lamella architectures. These are more common when the relative amounts of polymer in the blend are similar.

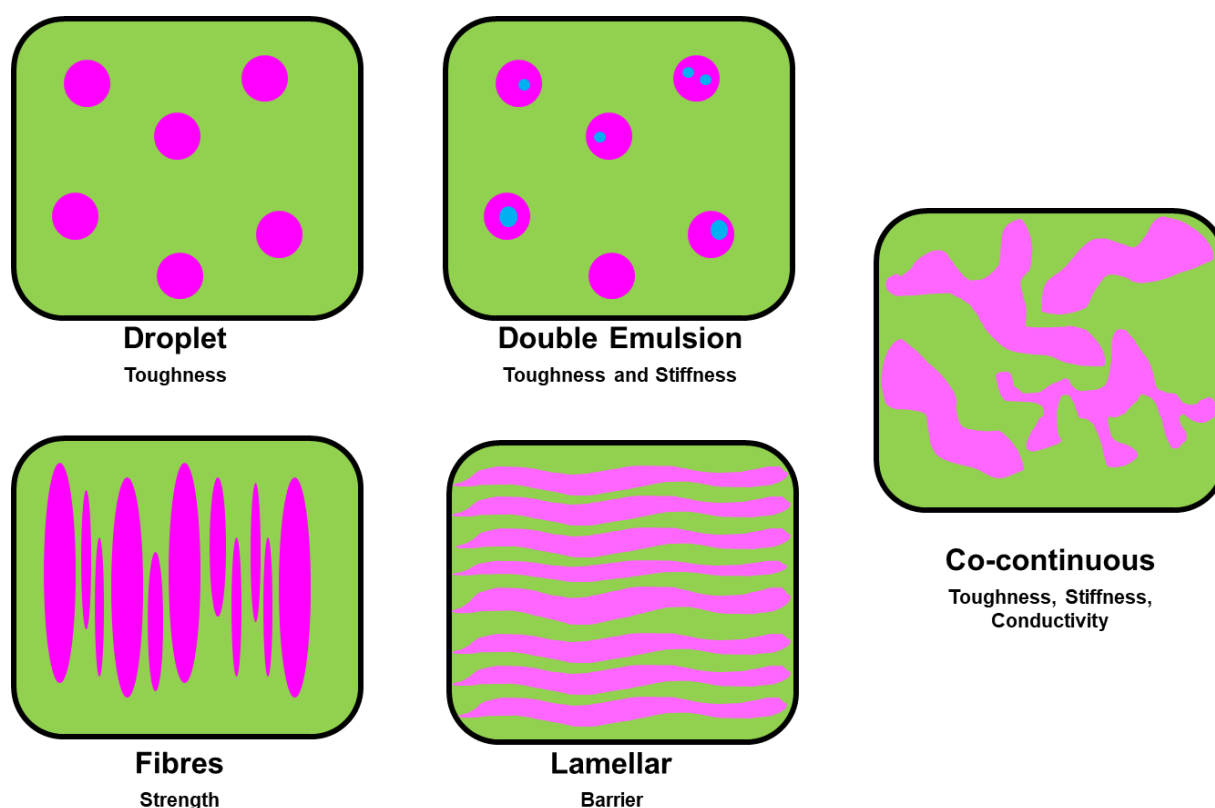


Figure 1.8: A schematic representation of possible morphologies in immiscible blends and their corresponding properties.⁵⁵

The type of morphology can alter the final mechanical, physical and rheological properties of the blend. For example, the lamellar morphology has demonstrated improved barrier properties, while the droplet (emulsion) morphology can result in enhanced toughness (Figure 1.8).⁵⁵ As an example, the double emulsion morphology has worked extremely well in the case of the PS derivative HIPS, providing high impact and tensile toughness.^{19,26}

Compatibility describes the phase morphology and property profile of a blend, usually in regards to a certain application. It refers to the final properties of the blend.⁵⁴ For example, if a partially miscible combination of polymers produces fine phase morphologies, that are uniformly distributed and homogenous, with advantageous combinations of the component polymers, the components are said to be compatible. On the other hand, if blending resulted in coarse phase morphology with poor properties, the components would be said to be incompatible.⁵⁴ Importantly, a polymer combination can be immiscible, but compatible.

The interfacial interactions between two phases can be improved by using a compatibilizer (that has affinity for both phases). Processing parameters, such as the processing methodology, blending ratios, time, shear forces applied, viscosity ratio of the polymers, temperature and annealing can influence the final morphology. The combined implementation

of these strategies can provide control over the phase morphology and properties of the materials.⁵⁴

1.4.2.1 Rubber Toughening

It is sometimes referred to as ‘rubber toughening’, when small amounts of an immiscible, elastomeric (low T_g) polymer is blended into a brittle polymer. The elastomeric polymer phase separates, forming dispersed particles within the plastic matrix (see the droplet morphology in Figure 1.8). The better the interfacial interactions between the two phases, the greater the compatibility and the smaller the dispersed elastomer particles. These particles are proposed to toughen the matrix by cavitating from the interface, during elongation or impact, forming void space that lowers the energy required for matrix shear yielding (Figure 1.9).^{51,105,107} The dispersed phase acts as stress concentrators, which promote matrix deformation and allow the dissipation of more stress before material failure (Figure 1.9).^{54,108} When the particles reach a critical size, and, when they are within a critical interparticle distance (termed the matrix ligament thickness), the stress fields surrounding these stress concentration sites can overlap effectively, preventing the localisation of stress, which greatly improves toughness. The particles can also act as points of craze initiation, acting to disperse energy (Figure 1.9). Although, toughness improvements through simple two-phase polymer blending has proven difficult, as a result of the inherent immiscibility/poor compatibility between most polymers. This often necessitates a compatibiliser, to reduce the energy of the interface and prevent particle coalescence or uneven dispersion.¹⁰⁵

Many early efforts to toughen PLA/PLLA used non-biodegradable elastomeric polymers from petrochemical sources, such as PE, PU and ABS.^{109–111} For example, a thermoplastic polyurethane (TPU) elastomer was blended with PLA (TPU/PLA = 30/70 wt%), demonstrating an increase in the ϵ_B from 13 to 603 %, and a decrease in the σ_Y from 67 to 37 MPa.¹¹² Hillmyer and co-workers pioneered blends of polyethylene (PE) and PLA/PLLA, often requiring PLLA-*b*-PE copolymers as a compatibiliser. One notable example was a PLLA/LLDPE/PLA-*b*-PE (80/20/5 wt%) ternary blend, with an ϵ_B of 62 % and σ_Y of 24 MPa.^{113,114} See table 1.3 for examples of polymer blending to toughen PLA/PLLA.

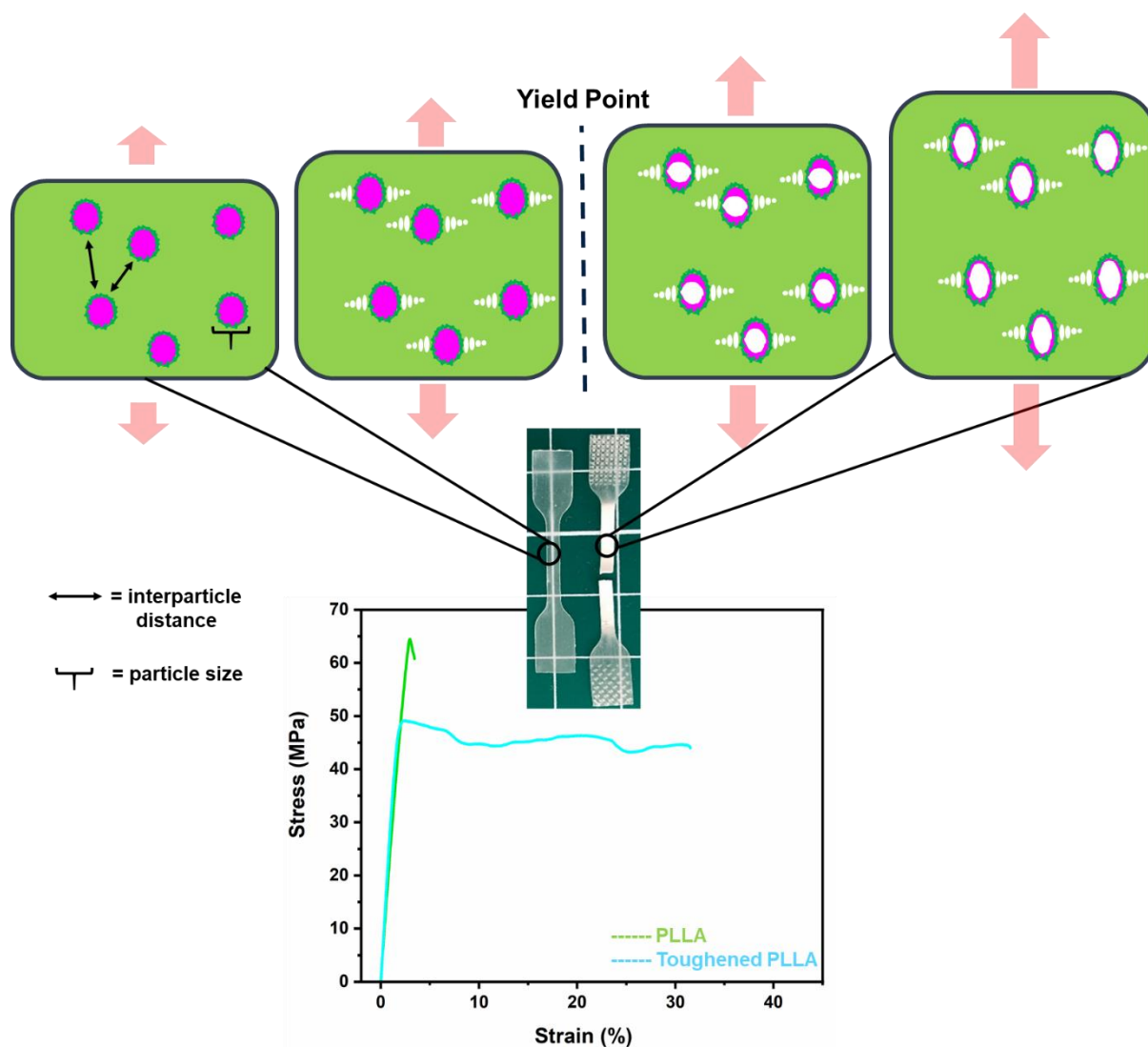


Figure 1.9: Schematic representation of the proposed mechanism of toughening in rubber toughened polymers, through crazing initiated from the dispersed phase and cavitation of the dispersed phase during tensile strain. The images are schematic representations of the tensile polymer bars shown below, as they are stretched uniaxially. The key parameters of interparticle distance and particle size are shown. Below is a representative stress vs strain curve of what PLLA may look like without (green) and with (blue) rubber toughening.

Table 1.3: Some literature examples of the mechanical properties for PLA/PLLA toughened using polymer blending.

Blend	Strength (MPa)	Young's Modulus (GPa)	Elongation (%)	Reference
PLA/TPU (70/30)	36 (67)	-	602 (13)	115
PLA/TPU (80/20)	41 (59)	2.5 (2.3)	350 (5)	116
PLA/PEBA (70/30)	36 (60)	0.9 (1.2)	335 (7)	117
PLA/BE	34 (54)	1.0 (1.2)	179 (7)	118
PLLA/LLDPE/PLA- <i>b</i> -PE (80/20/5)	37 (67)	-	62	113,114

The values in brackets represent the values of neat PLA/PLLA in each study. BE = bio-elastomer, PEBA = poly(ethylene oxide-*b*-amide-12), TPU = thermoplastic poly(urethane).

It is important for end-of-life considerations, that the toughening additives applied to sustainable thermoplastics are themselves open to a variety of recycling options, or are biodegradable. A wide range of biodegradable polymers have been applied to toughening PLLA; for example PCL,^{119–122} PHA,¹²³ PBS¹²⁴ and PBAT.^{125,126} See table 1.4 for examples of

results from biodegradable polymers used to toughen PLLA. Blends of β -hydroxybutyrate-co- β -hydroxyvalerate (PHBV) and PLA (20/80 wt%, respectively), resulted in strong ($\sigma_Y = 42$ MPa, $E = 2.5$ GPa) and tough blends ($\epsilon_B = 230$ %).¹²³ PBS/PLLA (10/90 wt%) blends showed ϵ_B of ~ 100 %, while retaining σ_Y of ~ 60 MPa and E of 2.5 GPa.¹²⁴ PBAT/PLA (20/80 wt%) also showed ϵ_B of up to 200 %, while σ_Y and E remained 47 MPa and 2.6 GPa respectively.¹²⁶ Although not proven in these studies, these examples represent fully biodegradable blends.

Table 1.4: Some literature examples of the mechanical properties for PLA toughened using polymer blending with renewably sourced and biodegradable additives.

Blend	Strength (MPa)	Young's Modulus (GPa)	Elongation (%)	Reference
PLA/PU (70/30)	31 (65)	1.1 (3.6)	363 (4)	127
PLA/PCNL (80/20)	64 (67)	1.8 (2.0)	238 (13)	128
PLA/P(CL-co-LA) (90/10)	48 (58)	1.7 (1.9)	20 (4)	129
PLA/PHBV (80/20)	42 (68)	2.5 (3.5)	230 (4)	123
PLA/PBS (80/20)	40 (66)	1.9 (2.3)	340 (5)	130
PLA/PBAT (80/20)	47 (63)	2.6 (3.4)	200 (4)	126

The values in brackets represent the values of neat PLA in each study. PNCL = poly(1,5-cyclooctadiene-co-5-norbornene-2-methanol-graft-dl-lactide), PU = polyurethane, PBS = poly(butylene succinate), CL = caprolactone, PBAT = polybutylene adipate terephthalate.

Reactive compatibilisation and covalent grafting of a dispersed phase to the matrix have been extremely effective at toughening thermoplastics. For example, a polyurethane (PU) elastomer prepolymer (terminated with an isocyanate group) was blended with PLA. The PU elastomer formed the dispersed phase, and reacted with PLA end-groups to generate copolymers in-situ, which compatibilise the PU in PLA. This produced a PLA/PU (70/30 wt%) blend with σ_Y of ~ 45 MPa and ϵ_B of up to 500 %.¹³¹ See Table 1.5 for more examples of grafted and reactively compatibilised PLA/PLLA blends. While extremely effective, these strategies may compromise on degradability.^{19,54} For example, although this strategy is effective for PS, e.g. ABS and HIPS,^{19,20} it poses severe limitations on recycling.¹⁹

Table 1.5: Some literature examples of the mechanical properties for PLA toughened using reactive compatibilisation and covalent grafting.

Blend	Strength (MPa)	Young's Modulus (GPa)	Elongation (%)	Reference
PLA/UPE-TPV (80/20)	38 (68)	1.5 (1.9)	260 (8)	132
PLA/NR-GMA (80/20)	35	-	136 (4)	133
PLA/ENR (60/40)	28 (81)	-	150 (10)	134
PLA/PU (70/30)	45 (62)	-	500 (15)	131
PLA/MB-g-GMA (75/25)	38 (68)	1.3 (1.8)	200 (6)	135

UPE = Unsaturated aliphatic polyester elastomer, TPV = thermoplastic vulcanizate, NR = natural rubber, ENR = epoxidised natural rubber, PU = polyurethane, GMA = glycidyl methacrylate, MB = methacrylate-butadiene. The values in brackets represent the values of neat PLA in each study.

1.4.2.2 Rubber Toughening Using Amphiphilic Block Copolymers

Building on these concepts, ‘self-compatibilised’ amphiphilic block copolymers could be useful toughening agents (Figure 1.10). These combine an elastomeric, immiscible, matrix-phobic block, with a matrix-philic, compatible (or miscible) block (Figure 1.10). The immiscible block drives phase separation and operates by rubber toughening mechanisms, while the matrix-philic block reduces interfacial interactions with the plastic (Figure 1.10). In this way, a single additive provides both a dispersed rubbery phase and stable interfaces. Using this approach, enhanced control over particle size, as well as smaller particles, can be obtained.^{51,105,107,136–139} Moreover, less additive is often required for effective toughening.^{51,105,107,136–139} This strategy can provide a self-compatibilised dispersed phase, using a simple binary blend.^{51,105,107} Smaller dispersed phase particles (while below the critical interparticle distance) improve the toughening effect, as there is a greater surface area available for stress transition between the two phases.⁵⁵

In regards to PLA/PLLA, this strategy has been pioneered by Bates and coworkers.^{51,105,107,136,137} One seminal report detailed the application of PEO-*b*-PBO (PBO = poly(butylene oxide)) to toughen amorphous PLLA. They demonstrated that these copolymers form micelles within the PLLA matrix, whereby the immiscible, rubbery PBO block forms the core, and the compatible/miscible PEO block is preferentially orientated at the interface with PLLA, forming a corona (Figure 1.10).¹⁰⁵ With just 5 wt% copolymer, the blends exhibited ϵ_B of 175 %, σ_Y of 28 MPa and a E of 2 GPa.¹⁰⁵ After refining the structure of the PEO-*b*-PBO diblock copolymer, with 1.8 wt% PEO-*b*-PBO in PLA, they could retain a σ_Y of 40 MPa and E of 2.8 GPa, while achieving ϵ_B of 221 %.¹⁰⁷

As importantly, they have developed a multifaceted approach to studying the failure mechanisms of these samples, in order to gain a more fundamental understanding of the toughening improvements on the microscopic level. Using a combination of 2D SAXS and TEM at various points along the stress vs strain profile, they could investigate deformation mechanisms such as craze formation, void formation and shear yielding.^{51,107} To compliment this, WAXS provided insights into the effect of strain on crystalline domains, such as strain-induced crystallisation, crystalline slip, partial melting, crystalline morphology transition, as well as crystal orientation, elongation or rotation.⁵¹ By carrying out these experiments at different areas of the stress vs strain curve, insights into the interplay of deformation mechanisms at each point could be obtained, such as when cavitation, crazing and shear yielding (or material flow) are occurring, as well as the role of crystallites.^{51,107}

This provided interesting insights such as;¹⁰⁷

- The void formation, caused by the dispersed particles, occurs at, or slightly beyond, the yield point for the blends, although never before it.
- The dispersed phase can act as craze-initiating sites, from which crazes can grow, in a controlled manner, uniformly throughout the whole material. This permits the dissipation of energy and prevents crack formation and propagation.
- Shear yielding occurred after the cessation of crazing.
- The effects of physical aging of PLA could be reduced by optimum crazing from cavitated dispersed phase particles.

A recent report, using 5 wt% poly(isoprene)-*b*-poly(ethylene oxide) to toughen PLA, provided two important insights to the area.¹³⁶ Firstly, they propose that the greatest toughening effects (ϵ_B of >150 %) were obtained using copolymer molecular weights that bracketed the room temperature order-to-disorder transition temperature ($M_n = 1.7\text{--}3.3$ kg/mol). Secondly, they proposed a mechanism of toughening, whereby the copolymers drain into the advancing crazes, stabilising the craze structures, to improve toughness and reduce aging effects.¹³⁶

In a similar manner, a commercial copolymer of PEO and polyamide-12 (PA12) (PEO-*b*-PA12, commercially known as Pebax 1074), when blended with PLA (10 wt% copolymer), produced blends with σ_Y of 49 MPa and an ϵ_B of 283 %. Although the Young's modulus was 1.1 GPa.¹¹⁷ For a summary of some block copolymers used to toughen PLA/PLLA, see Table 1.6.

Table 1.6: Some literature examples of the mechanical properties for PLA/PLLA toughened using polymer blending with block copolymer additives.

Blend	Strength (MPa)	Young's Modulus (GPa)	Elongation (%)	Reference
PLA/PEO-PBO (98.2/1.8)	40 (51)	2.8 (3.0)	221 (9)	107
PLLA/PEO-PBO (97/3)	38 (51)	2.8 (3.0)	280 (9)	137
PLLA/PEO-PBO (95/5)	49 (61)	2.9 (3.0)	14 (5)	51
PLLA/PEO-PBO (95/5)	31 (50)	2.0 (2.0)	175 (7)	105
PLA/PEO-PPO-PEO (90/10)	31 (50)	1.6 (2.2)	166 (5)	138
PLA/6armstarPCL- <i>b</i> -PLA (90/10)	54 (49)	0.02 (0.02)	24 (9)	140
PLA/PEO-PPO-PEO (90/10)	38 (68)	1.1 (1.5)	72 (5)	141

The values in brackets represent the values of neat PLA/PLLA in each study. PPO = poly(propylene oxide).

These polymer additives are often not themselves biodegradable or recyclable. An important consideration, is to retain the plastic recyclability and/or biodegradability. For example, biodegradable PCL-*b*-PLA copolymers (10 wt%) were blended with PLA, with ϵ_B increasing From 4 to 21 %, although the σ_Y fell from 58 to 10 MPa.¹¹⁹

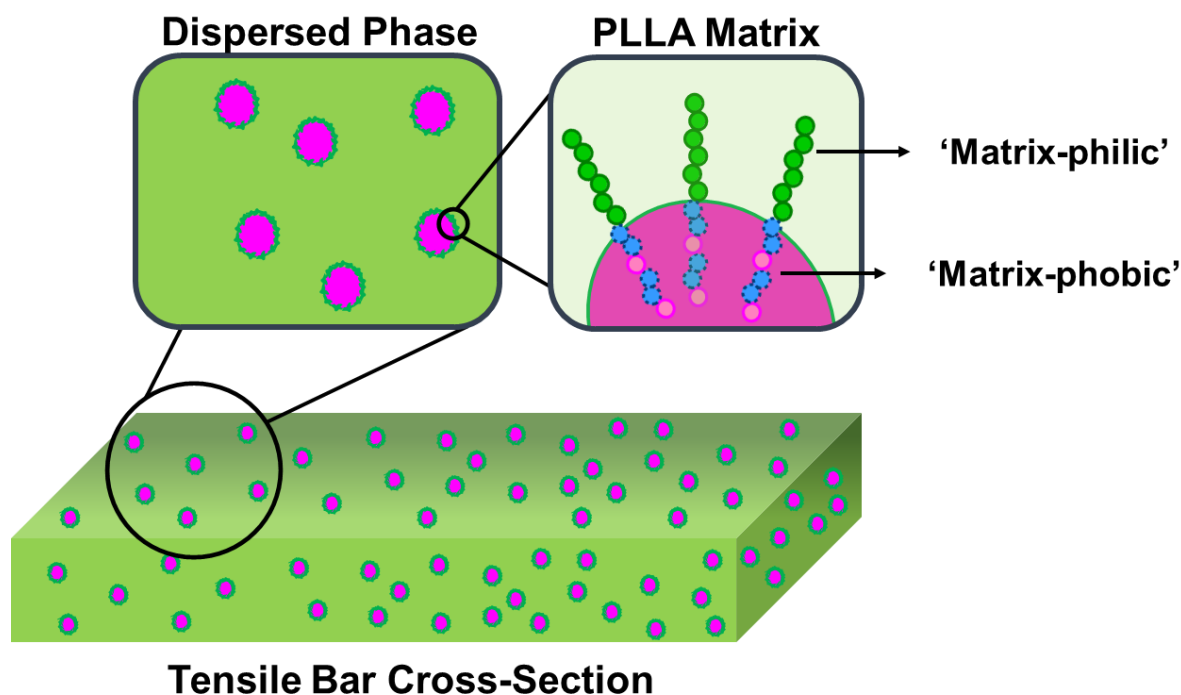


Figure 1.10: Schematic representation of the ‘self-compatibilised’ amphiphilic block copolymer strategy for toughening brittle polymers, using PLLA as an example, proposed by Bates et. al..¹⁰⁵

1.5 Poly(ester-*alt*-ether) Catalysis

To realise these block polymer additives, we targeted as the elastomer, a very new subclass of polymers (first reported in 2022); poly(ester-*alt*-ethers) (Figure 1.11).¹⁴² These polymers contain alternating ester and ether linkages and combine the beneficial properties of polyesters (such as strength and degradability) and polyethers (flexibility and hydrophilicity) (Figure 1.11). Polyethers often have low T_g values, due to the flexibility of the ether linkage, and provide hydrophilicity. Although they are usually not degradable.^{143–146} Polyesters are usually strong and degradable, although are often hydrophobic. Poly(ester-*alt*-ethers) may be able combine the advantageous properties of each linkage, i.e. the flexibility and potential to moderate hydrophilicity or functionality, inherent to ethers, with the degradability of esters.¹⁴⁷ Although, they have been underexplored due to the challenge in accessing the linkage sequence.

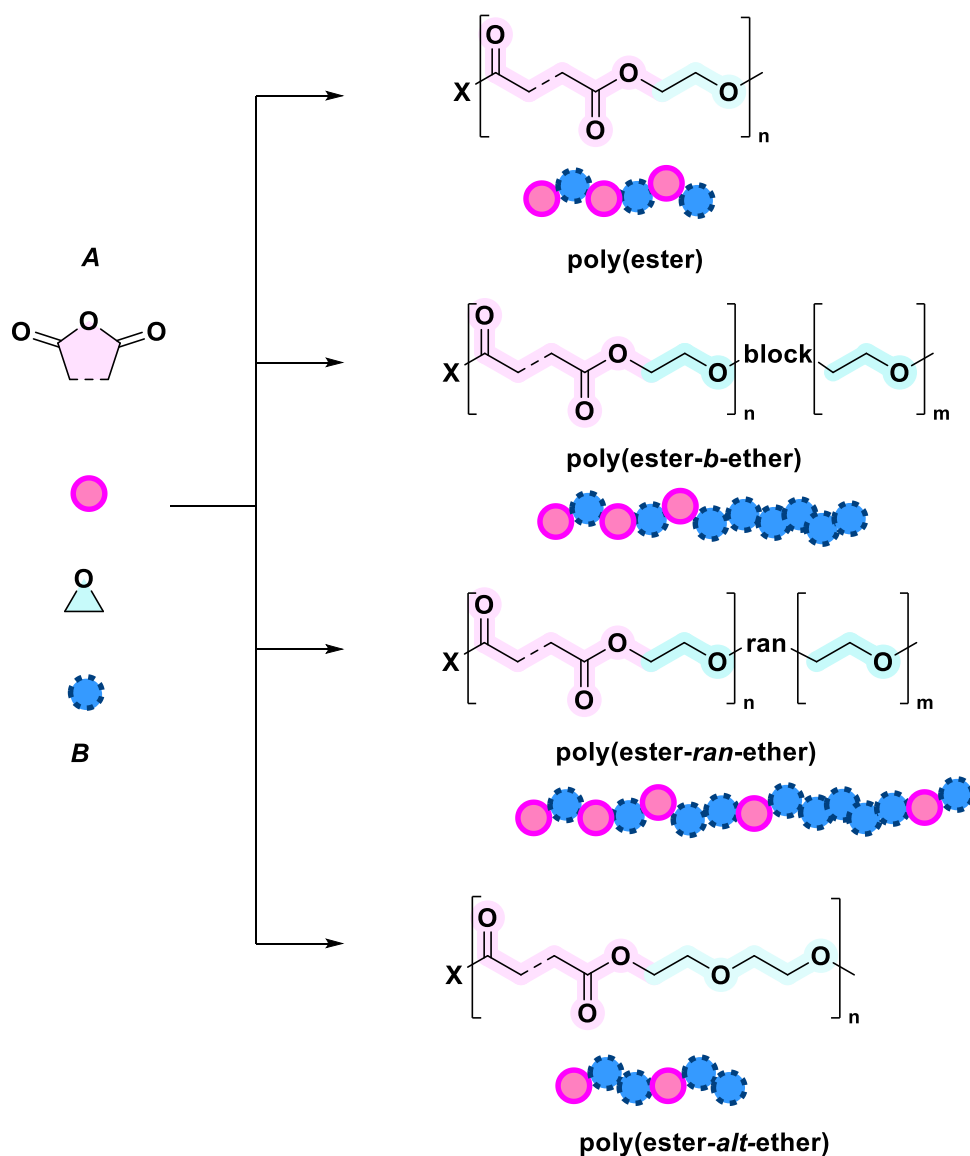


Figure 1.11: Possible selectivity for ROCOP of an anhydride (**A**) and an epoxide (**B**), forming either polyester by the alternating insertion, poly(ester-*b*-ether), poly(ester-*ran*-ether) or poly(ester-*alt*-ethers).

One strategy to make poly(ester-*alt*-ethers) involves the ROP of specialty lactones like 1,4-dioxane-2-one (PDX) or 3-methyl-1,4-dioxane-2-one (MDO).^{148–150} This strategy requires the synthesis of these specialist monomers, and, the reaction may be restricted by low ceiling temperatures of the polymers. Poly(ester-*ran*-ethers) were also formed from a two-step melt polycondensation of 2,5-furandicarboxylic acid and ethylene glycol, using a $\text{Sc}(\text{OTf})_3$ catalyst.¹⁵¹

Commonly, the ring-opening copolymerisation (ROCOP) of anhydrides (**A**) and epoxides (**B**) produces highly alternating polyesters, with **AB** sequences (Figure 1.11).^{34,64,65,152} It has been common-place in the literature to assess the catalytic selectivity by the ratio of ester to ether linkages.³⁴ Incorporation of further epoxide monomer can result in ether linkages,

either randomly, or in blocks, usually after complete reaction of anhydride (Figure 1.11), forming poly(ester-*ran*-ethers) or poly(ester-*b*-ethers) respectively. Previously, our group reported a Sn(II) catalyst that formed poly(ester-*ran*-ethers) with up to 70 % poly(ester-*alt*-ether) (**ABB**) sequence selectivity.¹⁵³ The Sn(octoate)₂/alcohol catalyst system was shown to produce poly(ester-*ran*-ethers), featuring epoxide : anhydride ratios of ~3 : 1.¹⁵⁴

In 2022, the Williams team reported a new route to poly(ester-*alt*-ethers) by the catalysed copolymerisation of an anhydride (**A**) and an epoxide (**B**).¹⁴² The copolymerisation was achieved using a Zr(IV) catalyst (**1**), which was a complex of the form **Zr(L1)₂(OⁱPr)₂** (Figure 1.12). It exerted very unusual selectivity, ensuring that each anhydride insertion is followed by two epoxide insertions.¹⁴² The catalyst formed polymers with **ABB** sequences and poly(ester-*alt*-ether) linkages. The catalysis was established using phthalic anhydride, PA (**A**), and butylene oxide, BO (**B**), yielding poly(ester-*alt*-ethers) with >95 % linkage selectivity. When present, THF (**C**) was also polymerised, affording copolymers with mixtures of **-ABB-** and **-ABC-** sequences (>95 % by ¹H NMR spectroscopy). Kinetic investigations revealed a rate-law that was first order in both epoxide (**B**) and catalyst (**1**) concentrations and zero order in anhydride (**A**) concentration. When present, THF (**C**) was also zero order. This led to the proposal of a novel catalytic mechanism (Figure 1.12). The Zr-alkoxide complex (isopropoxide) initiates the polymerisation by ring opening the anhydride to produce a Zr-carboxylate intermediate (**I**, Figure 1.12), proposed as the catalytic resting state. The subsequent insertion of an epoxide into this carboxylate was proposed as the rate limiting step, to form a Zr-alkoxide intermediate (**II**, Figure 1.12). The Zr-alkoxide then reacts rapidly with either another epoxide (**B**) or a cyclic ether (**C**). This forms another Zr-alkoxide intermediate (species **III**, Figure 1.12), with a longer chain. This species rapidly inserts the anhydride to reform the Zr-carboxylate intermediate, **I**. Control experiments between the anhydride, **A**, and cyclic ether, **C**, revealed no reaction, suggesting that the THF is enchainned only in the second cyclic ether insertion step.¹⁴²

The characterisation of the new linkage selectivity was established using a range of techniques (these will be demonstrated in detail to prove poly(ester-*alt*-ether) sequences in chapter 2 and throughout this work, being only summarised here). The degree of polymerisation of anhydride:epoxide was 1:2, remaining so throughout the reaction. Various NMR spectroscopies were used to establish the selectivity. Furthermore, the products of hydrolytic degradation were analysed to show **ABB** connectivity.¹⁴²

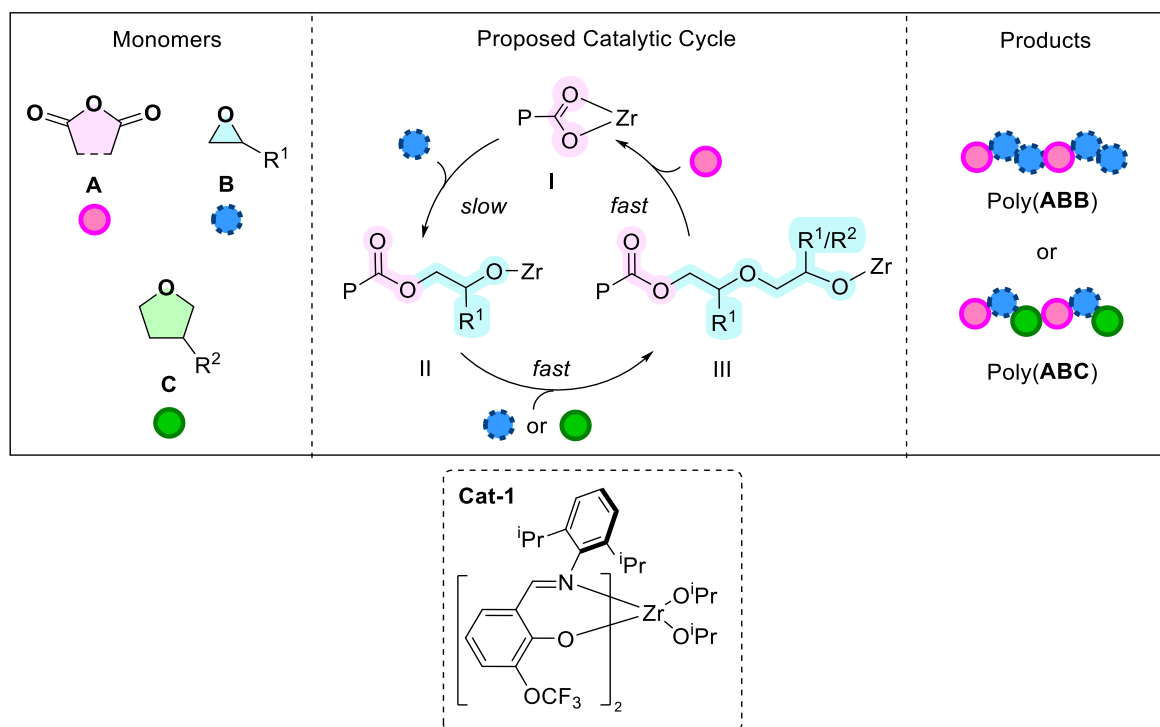


Figure 1.12: Left: The monomer families (anhydride, epoxide/cyclic ether) that can be used for poly(ester-*alt*-ether) ROCOP, Middle: proposed catalytic cycles for poly(ester-*alt*-ether) ROCOP, Right: **ABB** or **ABC** poly(ester-*alt*-ethers) formed by the Zr(IV) catalyst (**1**), P: polymeryl chain; Zr: metal active site. All monomers/polymers represented by the simplest substitution pattern. Bottom: Structure of catalyst **1**, the first and only reported catalyst for poly(ester-*alt*-ethers) synthesis.

Compared to analogous polyesters, the poly(ester-*alt*-ethers) showed lower T_g values, the same thermal stability (equivalent decomposition traces in TGA experiments) and faster degradation in an alkaline aqueous environment.¹⁴² For this reason, poly(ester-*alt*-ethers) were targeted for polymer blending with brittle thermoplastics in this thesis. lower T_g values are desired in an elastomeric toughening agent (see above discussion, section 1.4) and high thermal stability provides a wide processing temperature window. We reasoned that the enhanced hydrolytic degradation may enhance biodegradability. As explored above, Bates and co-workers employed a polyether copolymer, PEO-*b*-PBO diblock copolymer for toughening PLA/PLLA.^{51,105,107} However, these polyethers are not biodegradable. We posit that poly(ester-*alt*-ethers) may provide the toughening effect with enhanced degradability.

So far, only a single catalyst has been reported for poly(ester-*alt*-ether) synthesis from epoxides and anhydrides (catalyst **1**, Figure 1.12). The catalyst synthesis is rather low yielding (22 %). Furthermore, only a limited set of monomers were explored.¹⁴² It is, therefore, essential to establish and test the generality of this catalysis.

1.6 Thesis Aims and Objectives

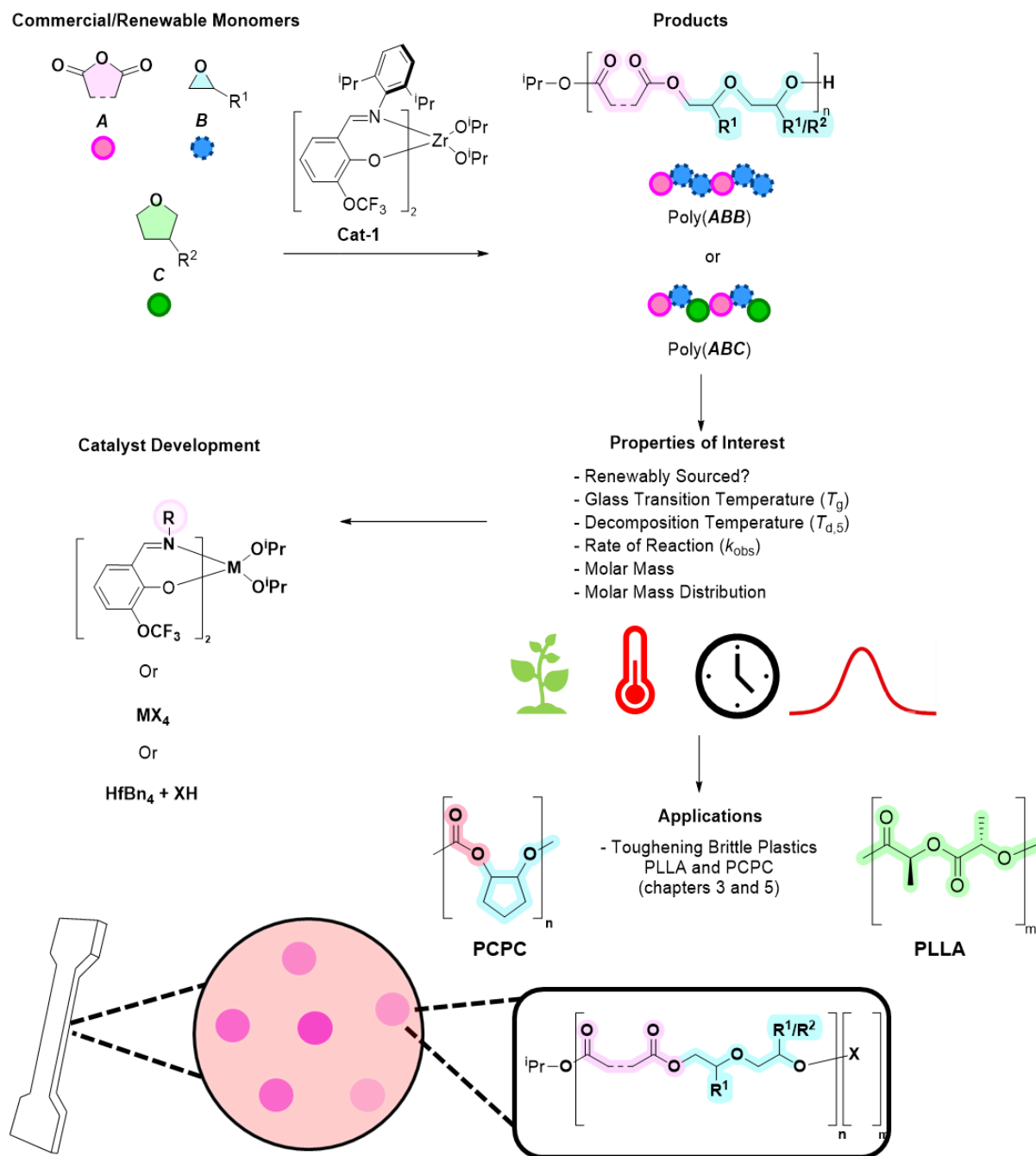
The main objective of this thesis, is to explore blend strategies to toughen two alternative thermoplastic materials, PLLA and PCPC. The goal is to improve their toughness and ductility, without compromising thermal properties, mechanical strength or sustainability (Scheme 1.1). To achieve this, poly(ester-*alt*-ethers) are targeted to make block copolymers of the form poly(ester-*alt*-ether)-*b*-X, where X is either the target plastic or a matrix compatible polymer (Scheme 1.1).

Before this can be achieved, a better understanding of the generality of poly(ester-*alt*-ether) catalysis is required. The key questions being; can this catalysis also be applied to a range of anhydride and epoxide monomers? What are the properties of the polymers, and, specifically, which monomers produce low T_g polymers? This is the focus of chapter 2, where a range of monomers and post-polymerisation chemistries are explored.

There is also need for fundamental understanding of the catalysis. Key questions are; why do two epoxides insert consecutively, and why is it so consistent/selective? Can other catalysts be produced with higher rates and selectivity? For example, can other metals produce poly(ester-*alt*-ethers)? What are the effects of varying the ancillary ligands? What are the effects of the initiating ligands? Chapter 4 aims to investigate these research questions.

The use of poly(ester-*alt*-ethers) to make block copolymers is described in chapter 3 and 5 (with PLLA and PCs). The performance of these polymers as toughening agents in blends with high molar mass PLLA and PCPC are also investigated. Various end-of-life options are explored, reporting any effect the additives may have on the unmodified PLLA and PCPC. Finally, the blends produced should be compared against commercial petrochemically derived plastics (PS, ABS and HIPS)—with a circular plastics economy in mind—to answer the final question, is it possible to bridge the gap in properties between petroleum-derived plastics and alternative materials with a blending strategy? These are the focus of chapters 3 and 5.

Monomers should be selected based on current, or possible methods to be renewably sourced. Polymers should be recyclable and (bio)degradable. Atom efficient polymerisations were selected that would provide controlled polymer sequences, molar masses and molar mass distributions, allowing structure-property (and morphology in some cases) correlation. The blending projects were designed to provide data for future large-scale processing and applications.



Scheme 1.1: A schematic representation of the aims of this thesis; employing commercial monomers, to synthesise a series of poly(ester-*alt*-ethers) and explore their properties (chapter 2), to identify promising polymers for application as toughening agents for PLLA and PCPC (chapters 3 and 5). Chapter 4 explores a range of catalyst development studies.

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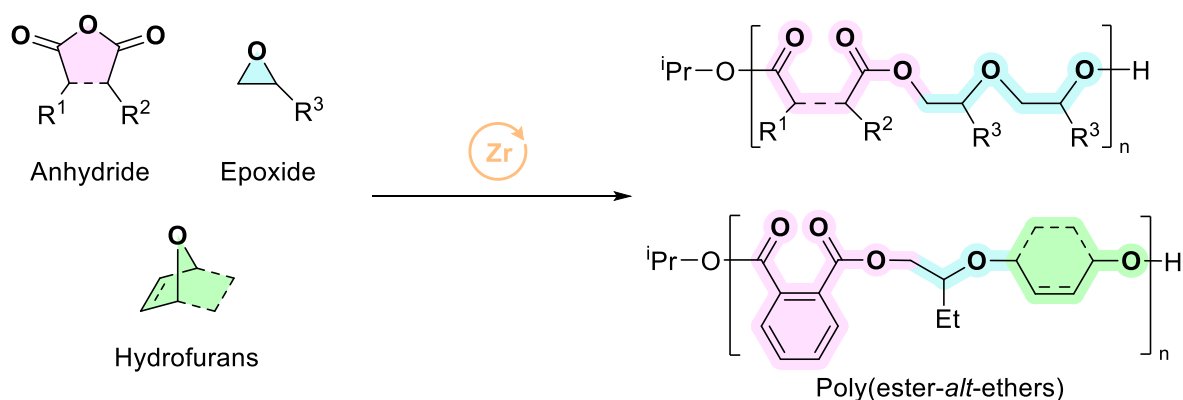
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CHAPTER 2

Chapter 2: Cyclic Ether and Anhydride Ring Opening Copolymerisation Delivering New *ABB* Sequences in Poly(ester-*alt*-ethers)



-
- 16 Examples
 - Commercial Monomers
 - Highly Selective
 - Post-functionalisation

Statement of Contribution to Co-Authored Published Paper

This chapter includes work used in a co-authored paper with the author list;

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Published in the Royal Society of Chemistry's Chemical Science.

Only the author's contributions to the paper are discussed within this chapter.

note: [§] = co-first author

2.1 Introduction

Oligomeric and low molar mass oxygenated copolymers, including polyethers and esters, are useful in formulations for cleaning, beauty, personal care, food, paints, agricultural coatings, energy storage and medicine.^{1–7} They are also widely used to make higher molar mass polymers including gels, resins, polyurethane foams, coatings, elastomers, sealants and adhesives.^{8–10} Since copolymers used in formulations tend to become environmentally dispersed after use, or are highly diluted in mixed wastes, they should be designed to be degradable. Many current formulations and polyols comprise polyethers, but these structures are usually not degradable.^{2,11–13} In contrast, polyesters used in formulations are degradable by hydrolysis and, in some cases, are also biodegradable.⁵ One limitation for aqueous formulation is that most polyesters are generally hydrophobic. Poly(ester-*alt*-ethers) are interesting, since they may be able to combine the beneficial properties of each linkage, i.e. the degradability of esters with the flexibility and potential to moderate hydrophilicity or functionality inherent to ethers.¹⁴ However, these interesting alternating copolymers remain under-explored, perhaps due to challenges in accessing appropriate monomers, or difficulties in controlling sequences.^{15–18}

In 2022, we reported a new route to poly(ester-*alt*-ethers), exploiting the catalytic copolymerisation of an anhydride and an epoxide.¹⁹ These new copolymers feature anhydride-epoxide-epoxide, or **ABB**, sequences (Figure 2.1). The copolymerisation required a specific Zr catalyst (**1**), which exerted very unusual selectivity, ensuring that each anhydride insertion is followed by two epoxide insertions. Usually, the ring-opening copolymerisation (ROCOP) of anhydrides (**A**) and epoxides (**B**) produces perfectly alternating polyesters, i.e., with **AB** sequences (Figure 2.1).^{20–23} There is a need to investigate further, the generality of this synthetic approach to poly(ester-*alt*-ethers), and specifically, to understand the capability to use catalyst **1** with other types of anhydrides and epoxides. In the literature, the only related reports concern epoxide and anhydride copolymerisations which produce mixed polymer sequences, including partial **ABB**-repeats.^{24,25} For example, Phomphrai and co-workers applied Sn(II) catalysts in epoxide/anhydride ROCOP to produce poly(ester-*ran*-ethers) containing up to 70 % **ABB** sequence selectivity.²⁵ Our team also demonstrated that a Sn(octoate)₂/alcohol catalyst system furnished poly(ester-*ran*-ethers), featuring epoxide : anhydride ratios of ~3 : 1, and these were also used to form block copolymers with L-lactide.²⁶ The copolymers were effective as rubber toughening agents for commercial poly(L-Lactide), PLLA.

Previously, catalyst (**1**) was investigated using phthalic anhydride, PA (**A**), and butylene oxide, BO (**B**) in the ROCOP.¹⁹ It yielded poly(ester-*alt*-ethers) with **ABB** sequences in >95 % selectivity (by ¹H NMR spectroscopy). Further, ROCOP using PA (**A**), BO (**B**) and THF (**C**), catalysed by **1**, afforded copolymers with mixtures of -**ABB**- and -**ABC**- sequences (>95 % by ¹H NMR spectroscopy). In comparison to perfectly alternating polyester (**AB**) analogues, the poly(ester-*alt*-ethers) reported similar thermal stability, lower T_g values and faster hydrolytic degradation in aqueous conditions (Figure 2.1).¹⁹

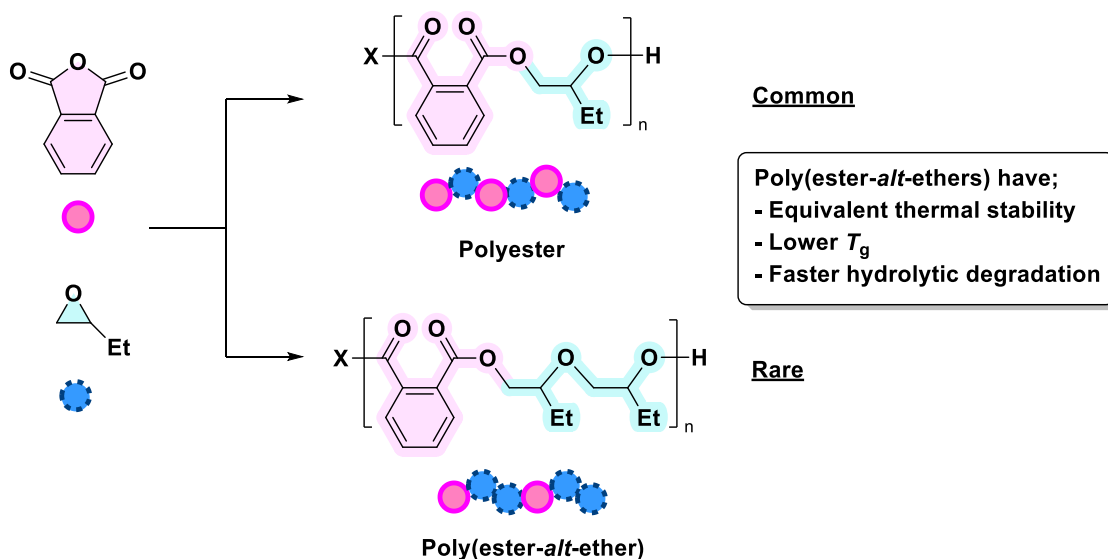
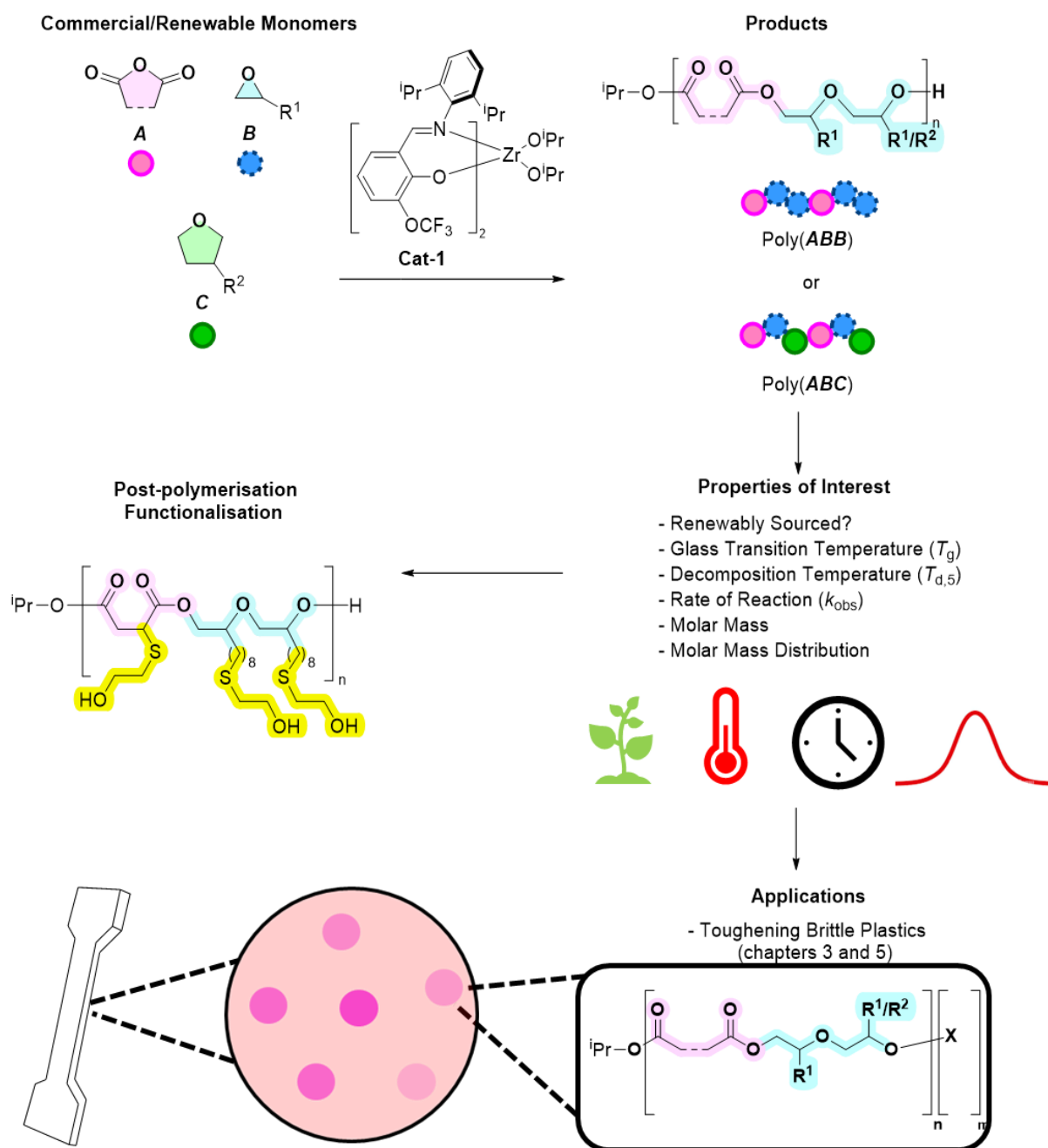


Figure 2.1: A summary of the previously reported property comparison of poly(ester-*alt*-ethers) vs polyesters.¹⁹

2.2 Aims

In addition to delivering useful properties for polymers, it's important to address sustainability concerns throughout the polymer life-cycle. Current trajectories predict that CO₂ emissions from the plastic industries could exceed 6.5 Gt per annum by 2050, threatening global net-zero targets.²⁷ One option to help manage greenhouse gas emissions, is the use of bio-based monomers.²⁸ Anhydrides and epoxides can be made from biomass and those most readily produced should be prioritised as monomers.²⁹ This chapter focused on understanding the generality of this novel catalysis, using a range of different epoxides, anhydrides and cyclic ethers, which have the potential to be sourced from biomass. The objective is to understand whether the copolymerisation operates equivalently with other monomers and, if appropriate, to exploit the sequence selectivity to deliver low molar mass, functionalised **ABB/ABC** poly(ester-*alt*-ethers) for future use in applications (Scheme 2.1).



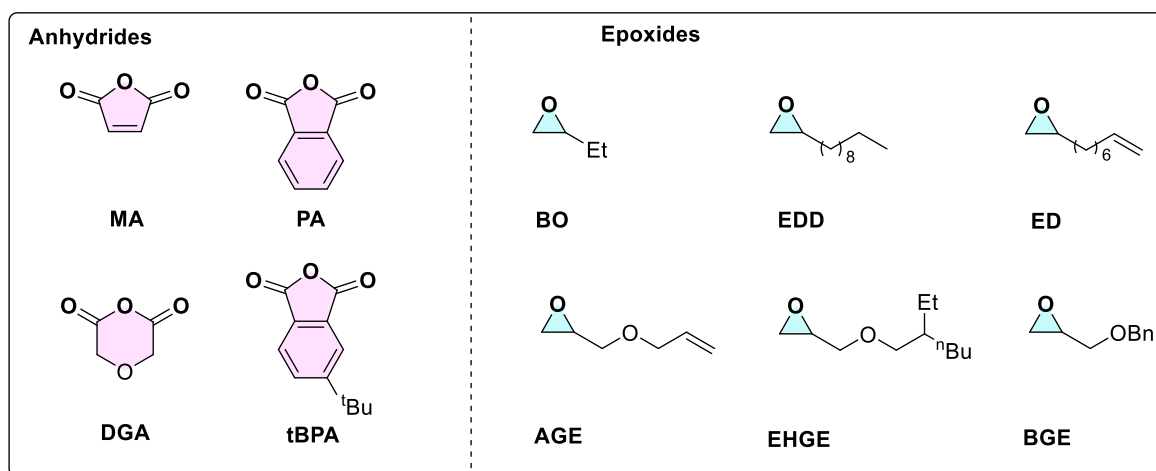
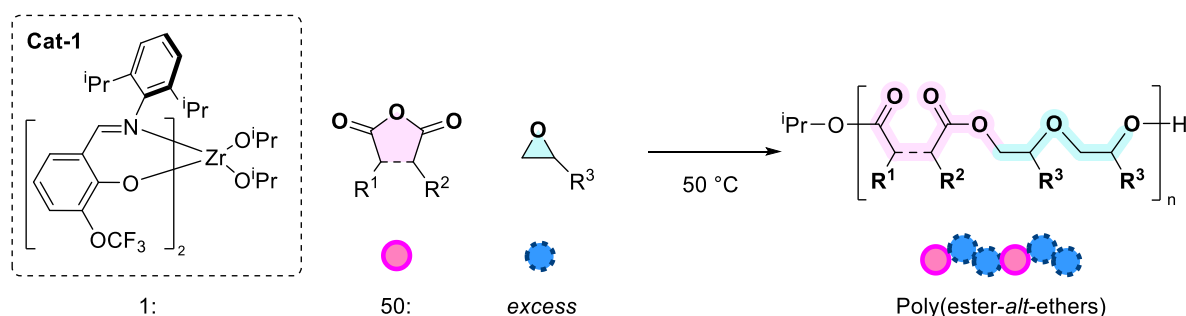
Scheme 2.1: A schematic representation of the aims of this chapter; using bio-based/potentially bio-based commercial monomers, to synthesise a variety of poly(ester-*alt*-ethers) and explore their post-polymerisation chemistries. This was to understand the generality of poly(ester-*alt*-ether) catalysis and to identify polymers with properties suited for application as toughening agents in later chapters.

Of particular interest are polymers that could be used for toughening brittle, sustainable thermoplastics. Polymeric toughening agents are most commonly low T_g , viscoelastic liquids, as this is advantageous when using a dispersed phase toughening strategy (see section 1.4).³⁰ A range of monomers are prioritised to provide polymers showing such low T_g values. The aim is to explore the property space of poly(ester-*alt*-ethers), to identify polymers from potentially renewable monomers, with controlled molar masses/molar mass dispersity and low glass transition temperatures, for application in toughening studies in later chapters (Scheme 2.1).

2.3 Poly(ester-*alt*-ether) Synthesis – Exemplar Characterisation

First, the monomer scope was systematically investigated using a series of 4 anhydrides and 6 epoxides (Table 2.1). Monomer selection was driven by either current commercial availability, by future potential for becoming bio-derived/waste-sourced and by the end goal of application as polymeric toughening agents.²⁹ The copolymerisation reactions were conducted under standard conditions, to allow systematic comparisons between different monomer combinations. For the experiments where the anhydride was varied, butylene oxide (BO) was applied at [1]: [A]: [BO] = 1: 50: 1150, at 50 °C.¹⁹ These conditions are consistent with our earlier report and, given that both the iso-propoxide ligands initiate, should lead to a degree of polymerisation (DP) of 25 at complete anhydride conversion.

To exemplify the methods used to monitor copolymerisation catalysis and characterization of the resulting copolymers, the reaction between maleic anhydride (MA) and BO is discussed here and, subsequently, the equivalent experimental data for all new copolymers is presented in the appendices, chapter 8.2 (Table 2.1, **P1**). The MA/BO copolymerisation was conducted with regular removal of aliquots, which were quenched by exposure to air and the crude product conversion determined. Complete anhydride consumption was observed over 65 minutes. The new copolymer **P1** showed an **ABB** repeat unit composition (Table 2.1, **P1**). For comparison, the perfectly alternating polyester, poly(MA-*alt*-BO) (**P1'**), with **AB** sequence selectivity, was also synthesised (see section S8.2.2 for full characterisation data). The two copolymers showed comparable molar mass values and both featured a degree of polymerisation of 25 (with respect to MA), **P1** $M_n = 8.4 \text{ kg mol}^{-1}$ vs **P1'** $M_n = 5.4 \text{ kg mol}^{-1}$ (Figures S8.2.44 and S8.2.55). It should be noted that the GPC traces for both **P1**, **P1'**, and many of the polymers in this work, show a low intensity high molecular weight series due to trace quantities of diols/diacids present in the monomers (Figures S8.2.44 and S8.2.55). This phenomenon has been discussed in detail for **AB** ROCOP and does not change in **ABB** ROCOP.³¹

Table 2.1: Ring-opening copolymerisation (ROCOP) of anhydrides and epoxides with catalyst **1**^a.

Polymer	Anhy.	Epox.	DP [Anhy.]:[Ep.] ^b	ABB Selectivity (%) ^c	M _n (Đ) [kg mol ⁻¹] ^d	M _n (Theo) ^e	k _{obs} (x10 ⁻⁵ M s ⁻¹) ^f	T _g (°C) ^g
P1	MA	BO	25 : 58	95	8.4 (1.16)	6.6	9.6	-19
P2	tBPA	BO	25 : 58	95	6.8 (1.21)	9.2	6.4	15
P3	DGA	BO	25 : 50	>99	9.3 (1.16)	6.6	6.1	-24
P4	PA	BO	25 : 57	96	6.7 (1.11)	7.9	11.7	4
P5	PA	EDD	25 : 54	98	9.1 (1.18)	13.6	13.5	-37
P6	PA	ED	25 : 58	95	8.4 (1.21)	12.8	7.8	-42
P7	PA	AGE	23 : 50	97	6.0 (1.24)	9.1	0.6	-26
P8	PA	EHGE	25 : 54	98	8.8 (1.33)	13.7	2.1	-44
P9	PA	BGE	25 : 51	>99	10.3 (1.64)	12.1	0.3	0
P10	MA	ED	25 : 56	96	10.5 (1.04)	11.2	13.6	-50

^aROCOP Conditions: [**1**] = 10 mM, [anhydride] = 0.5 M, epoxide = 1 mL, 50 °C. ^bDP of monomer measured by integration of the polymer in the ¹H NMR spectra of purified polymers against 2 isopropoxide initiators. ^cDetermined as the theoretical percentage of perfect **ABB** epoxide selectivity (66.67%) against calculated epoxide selectivity (range = 67–70 %). ^dDetermined by gel permeation chromatography (GPC), using THF as the eluent. **P1–P8** and **P10** calibrated using narrow MW polystyrene standards, **P9** calibrated using triple detection (Figures S8.2.44–45). ^eTheoretical *M_n* are calculated from the monomer conversion data and assume both iso-propoxides initiate. ^fDetermined from the gradient of [PA] vs. time (s), (Figures S8.2.46–47). ^gGlass transition temperature obtained from differential scanning calorimetry (DSC, second heating cycle, 10 °C min⁻¹ heating rate) (Figures S8.2.48–49).

P1 was characterized using ¹H NMR spectroscopy and showed diagnostic methine-ester and methylene-ester resonances at δ_{H} = 4.99 (proton 6) and 4.16 ppm (proton 3), respectively (Figure 2.2b). It also showed signals at δ_{H} = 3.88–3.18 ppm (protons 4 and 5) which are in the expected region for the methylene and methine ether resonances (Figure 2.2b). The ¹H-¹H COSY NMR spectrum showed correlations between these ester and ether protons (Figure 2.2c, correlations 3-4 and 5-6). On the other hand, the ¹H NMR spectrum of **P1'** (**AB**-

sequence) shows only the methine and methylene protons for the ester linkages, without any ether resonances (Figure 2.2d). Its ^1H COSY NMR spectrum shows only correlations between the two ester regions (Figure 2.2e, correlations 3'-6').

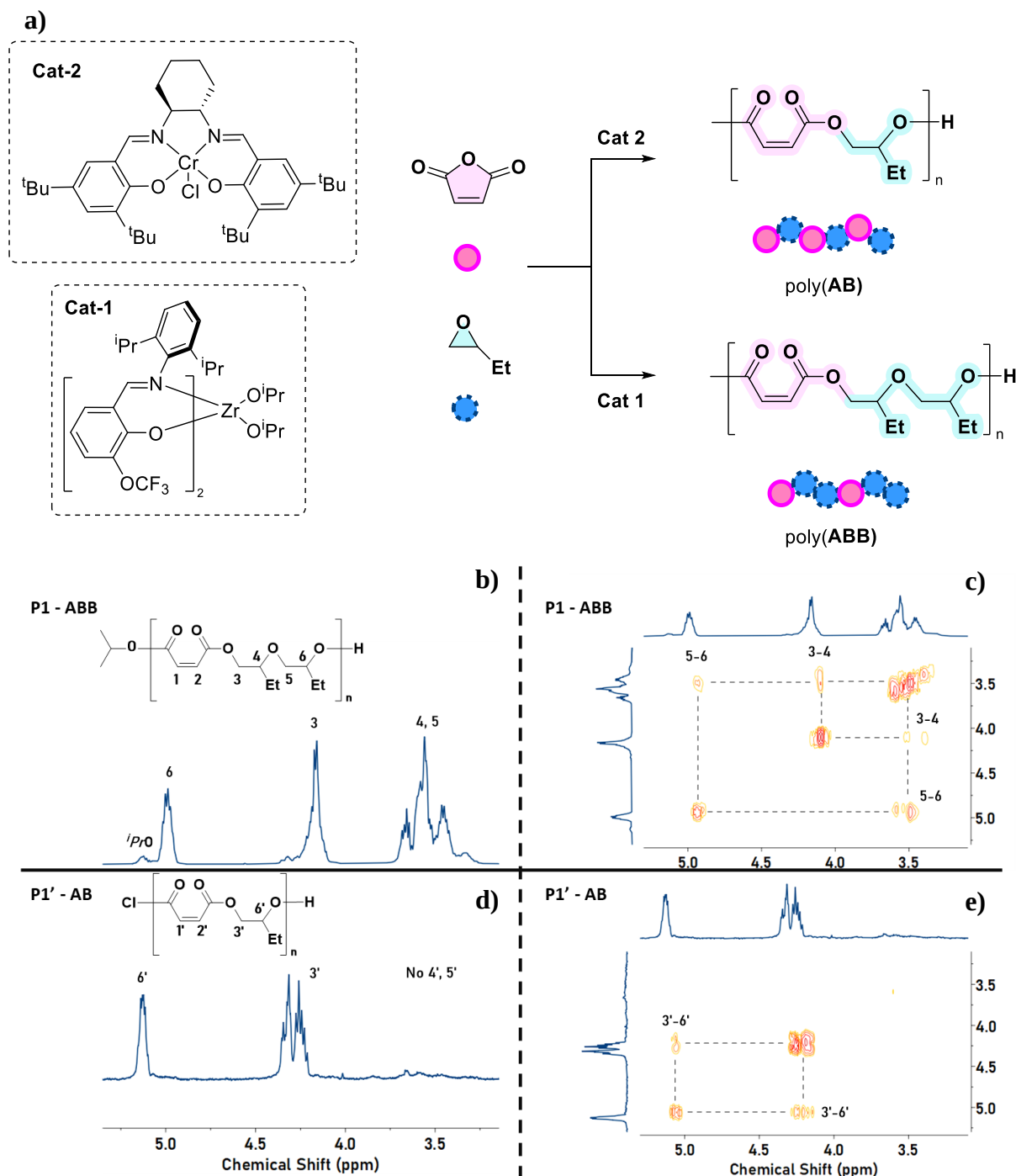


Figure 2.2: Comparison of ^1H and COSY NMR spectra for **P1** (ABB) and **P1'** (AB). Left: selected regions of the ^1H NMR spectra (400 MHz, CDCl_3 referenced at 7.26 ppm), illustrating the methine, methylene and ether regions for **P1** (ABB) and (b) **P1'** (AB) (d). Right: Magnified ^1H COSY NMR spectrum of **P1** (ABB) (c) and **P1'** (AB) (e). Full spectra are available in Figures S8.2.1, S8.2.3-4 and S8.2.52-53.

The ^1H and COSY NMR spectra for **P1** (**ABB**) and **P1'** (**AB**) exemplify how the selectivity for the poly(ester-*alt*-ether) (**ABB**) sequences was determined. The epoxide selectivity was determined, in each case, by comparing integrals for P(MA), $\delta_{\text{H}} = 6.20\text{--}6.30$ vs. protons 3-6 for **P1** or 3' and 6' for **P1'** (Figure 2.2b and d). From these relative integrals (P(MA) vs. P(BO)) the copolymer selectivity for epoxide was calculated to be $\sim 70\%$ for **P1** (and around 50% for **P1'**). The overall poly(ester-*alt*-ether) sequence selectivity was determined by normalising the experimental epoxide selectivity against the theoretical maximum, i.e. 67% for **ABB** polymers and 50% **AB** type polymers, resulting in a sequence selectivity for **ABB** linkages of 95% for **P1**. Selective **ABB** insertions, rather than random formation of ether linkages, were supported by the observation that throughout the reaction the **A** : **B** selectivity was 1 : 2, and, there was no further epoxide conversion after complete anhydride consumption (Figure 2.3). These findings rule out the formation of random or block copolymers. The ^1H DOSY NMR spectrum of **P1** shows a single diffusion coefficient for all resonances, indicative of the formation of a single structure and ruling out the formation of copolymer mixtures (Figure 2.4).

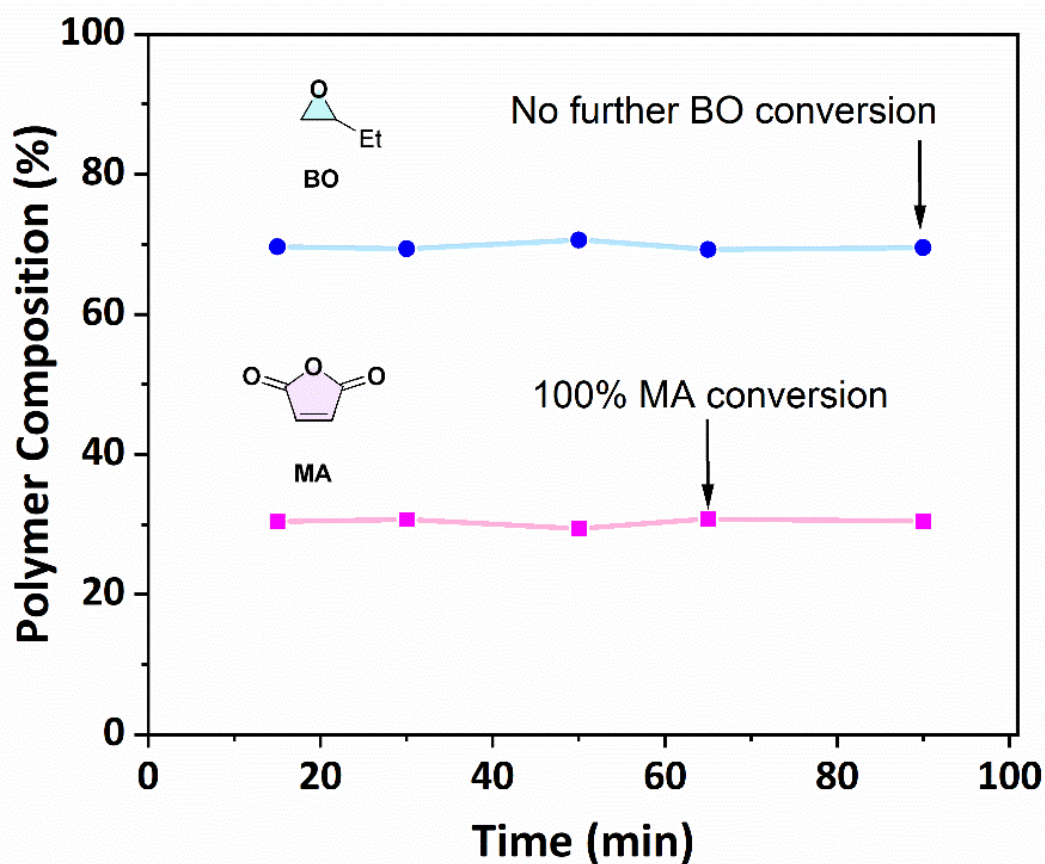


Figure 2.3: Plot of polymer composition vs time (min) from aliquots of the reaction of [1] : [MA] : [BO] = 1: 50 : 1150, from Table 2.1, **P1** (400 MHz, CDCl_3). Plot confirms that the anhydride/epoxide selectivity of the reaction is maintained throughout, and after the complete consumption of MA, no further BO is polymerized.

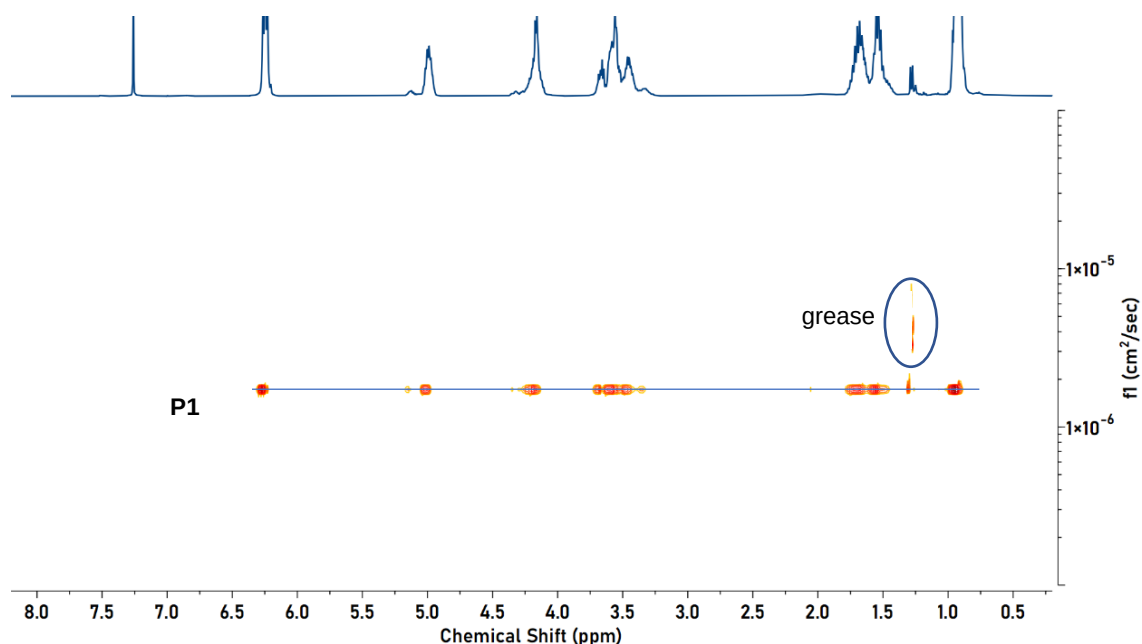


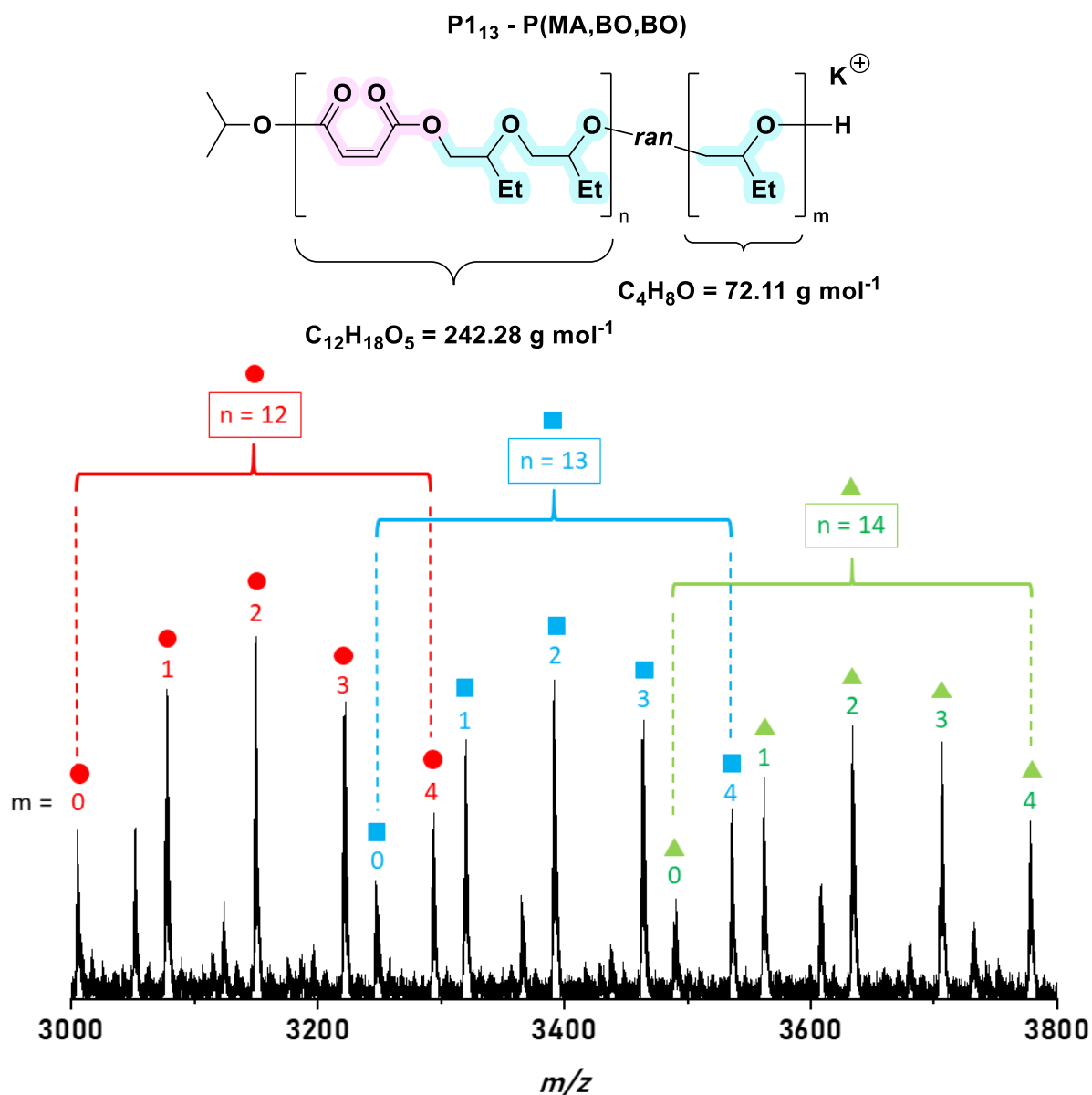
Figure 2.4: ^1H DOSY NMR spectrum from the reaction of $[1] : [\text{MA}] : [\text{BO}] = 1 : 50 : 1150$, from Table 2.1, **P1** (500 MHz, CDCl_3).

GPC analysis of **P1** gives a molar mass of 8.4 kg mol^{-1} , with a molar mass dispersity of 1.16. The calculated molar mass from ^1H NMR spectroscopy is 7.2 kg mol^{-1} (Figure S8.2.1). Assuming that catalyst **1** initiates from both its iso-propoxide ligands, the theoretical molar mass is 6.6 kg mol^{-1} , a value which compares favourably with the experimental results (Table 2.1). $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy was used to characterize the chain-end groups after treatment of **P1** with tetramethylethylene chlorophosphite (Figure S8.2.5). A set of diagnostic resonances for primary and secondary alcohol end-groups were observed. The presence of multiple resonances for both the primary and secondary alcohol is rationalised by the formation regio- and diastereoisomers of the **ABB** chain-end, where both epoxides are opened regio-randomly.

Both copolymers **P1** and **P1'** were analysed by DSC, confirming they both have amorphous structures. **P1** has a lower T_g of -19°C , whereas for **P1'**, the T_g is 5°C (Figure S8.2.48 and S8.2.55). These values are consistent with the expected increase in chain segmental motion (backbone flexibility) for the poly(ester-*alt*-ether), **P1**. This is also a very promising indication, from the outlook of finding low T_g polymers for applications in toughening studies.

Finally, a deliberately low-weight variant of **P1**, produced using **1** ($M_n = 4.4 \text{ kg mol}^{-1}$, see section S8.2.3, polymer **P1**₁₃ for further details, where 13 refers to the DP of anhydride by ^1H NMR spectroscopy), was analysed by matrix assisted laser desorption ionization time-of-flight spectroscopy (MALDI-ToF) (Figure 2.5 and Section S8.2.3). The data is fully consistent with **ABB** polymer sequences and there was no evidence for any **AB** enchainment. Further,

only iso-propoxide chain end initiation was observed. Additional ether linkages were observed, and a series consistent with the composition of $[\text{}^i\text{PrO}-((\text{PA-}i\text{alt-BO}_2)_n\text{-}i\text{ran-}(\text{BO})_m)\text{-H} + \text{K}^+]$ was observed, where m ranged between 0-4 per polymer chain. Analysis of the MALDI-ToF data indicates an approximate **ABB** selectivity of 94-100 %, consistent with the selectivity data from ^1H NMR spectroscopy.



2.4 Anhydrides

Following from MA/BO ROCOP, a series of other anhydrides were selected for investigation: phthalic anhydride (PA), 3-*tert*-butyl-phthalic anhydride (tBPA) and diglycolic anhydride (DGA) (Table 2.1). These were selected either for interesting chemical features (with respect to toughening) or to understand the limits of catalysis and poly(ester-*alt*-ether) properties. MA and PA can be prepared from biomass, and are commonly used monomers in ROCOP, providing unsaturation in the polymer backbone.³² Grafting of the rubbery component in polymer blending, through unsaturation, is a common strategy for improving compatibility of the dispersed phase (see section 1.4). DGA was chosen to install a fully saturated, flexible linkage into the copolymer, and delivers another ether functionality.

The reactions with these different anhydrides were each conducted using the standard conditions established above ([**1**]: [**A**]: [**BO**] = 1: 50: 1150, at 50 °C). Copolymerisations were conducted in neat BO, such that the overall concentration of **1** was 10 mM and the anhydride was 0.5 M. In all cases, the catalysis was selective and furnished copolymers with poly(ester-*alt*-ether) structures (Table 2.1, **P1-P4**). All the new copolymers were fully characterized, including by NMR spectroscopy and GPC (Figures S8.2.1-19 and S8.2.44, respectively). The copolymer molar mass values were in good agreement with theoretical values (Table 2.1). Narrow dispersity, monomodal molar mass distributions were observed for all polymers (**P1-P4**), with slight high weight shoulders (**P1**, **P2** and **P3**) due to trace quantities of diols/diacids present in the monomers (Table 2.1, Figure S8.2.44). ¹H NMR spectroscopy confirmed that, in all cases, the copolymers show poly(ester-*alt*-ether) linkage selectivity of >95 % (Figures S8.2.1, S8.2.6, S8.2.10 and S8.2.14). All the copolymers have amorphous structures, as confirmed by DSC, and show *T_g* values which increase in the order DGA < MA < PA < tBPA, from -24 to 15 °C (Figure 2.6). The thermal stability of **P1-P4**, determined by TGA analysis, show degradation onsets, *T_{d,5}*, from 270-318 °C. These copolymers therefore show relatively high thermal stabilities and broad processing temperature ranges (Figure S8.2.50 and Table S8.2.1). This is an important consideration in polymer blending applications.

Pseudo zero order rate constants were determined as the gradients of linear fits to anhydride concentration vs. time plots (Figure S8.2.46). The anhydride conversions were determined by NMR spectroscopy of crude reaction aliquots. All copolymerisations showed a linear decrease in anhydride concentration over time, consistent with its zero-order dependence in the rate law. Linear fits to the data gave rate constants, *k_{obs}*, which allowed for understanding

of the influences on catalytic activity using the different monomers. For the series of anhydrides, the rates decrease in the order MA > tBPA $\approx$ PA $\approx$ DGA (Figure 2.7).

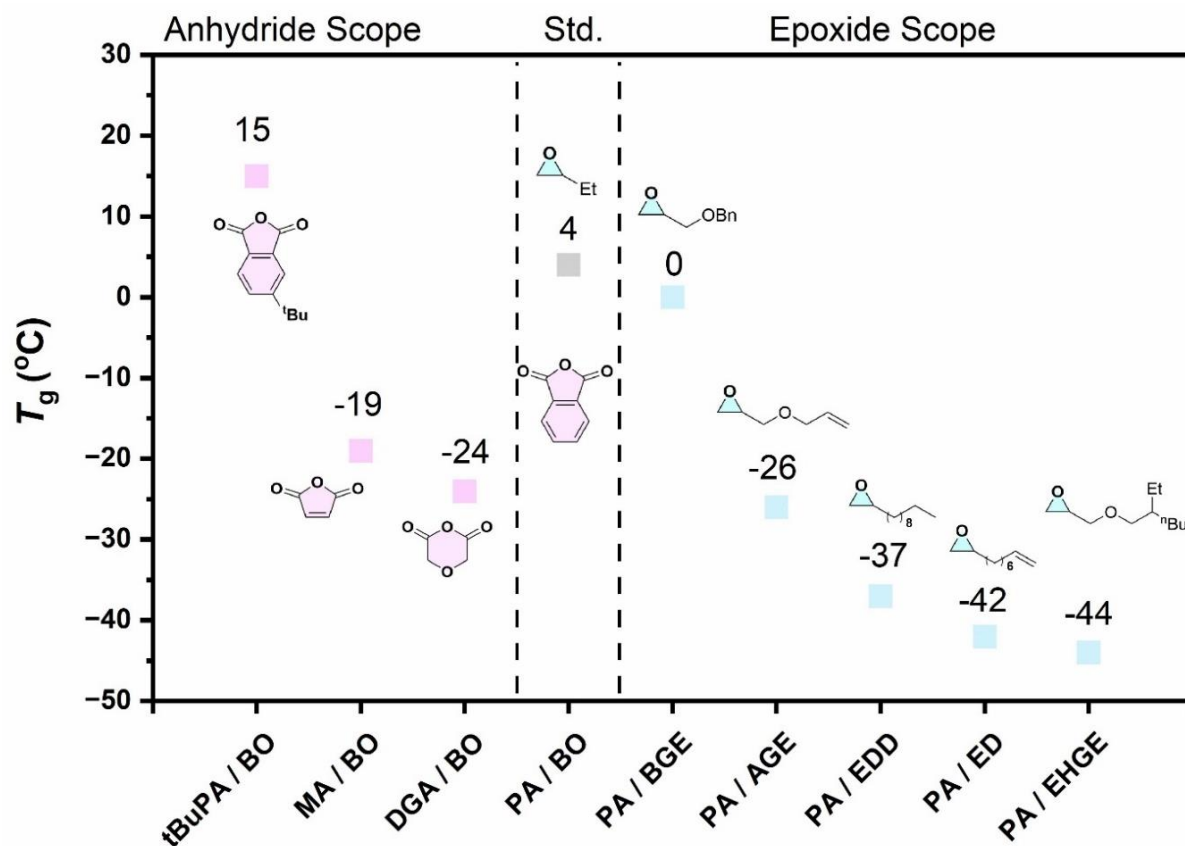


Figure 2.6: Comparison of the T_g values for the poly(ester-*alt*-ethers) **P1-9** synthesised in this work. This property is an important parameter for polymer blending applications. Glass transition temperatures obtained from differential scanning calorimetry (DSC, second heating cycle, 10 °C min⁻¹ heating rate) (Figures S8.2.48-49).

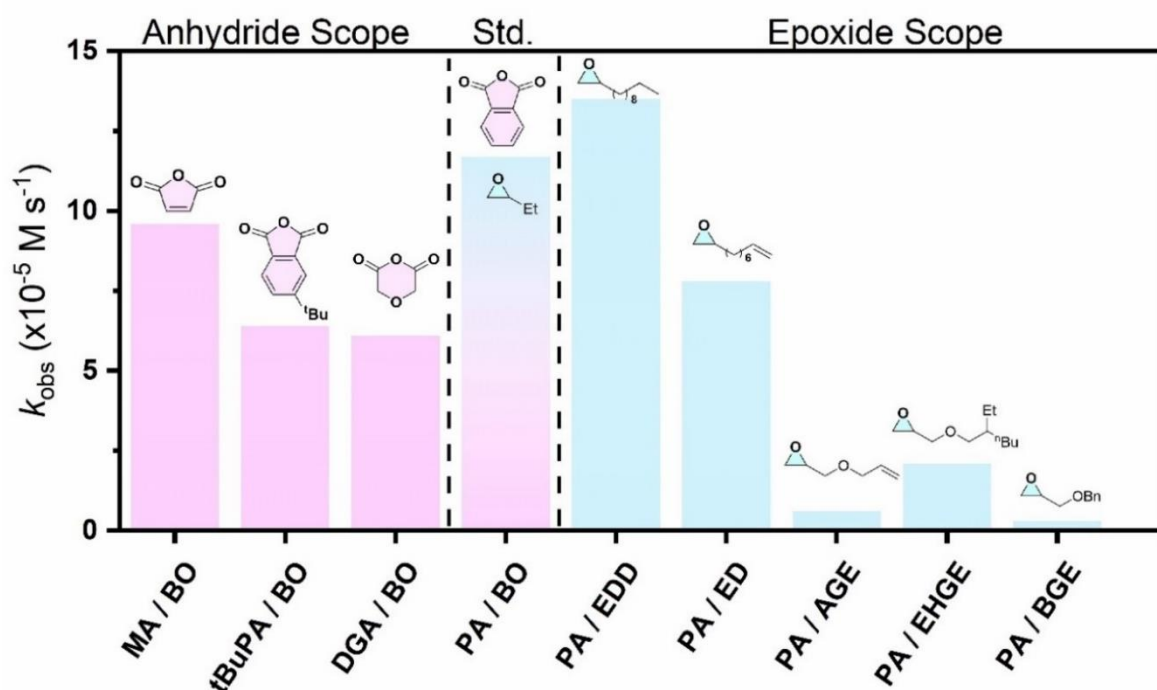


Figure 2.7: The pseudo rate coefficients, k_{obs} (M s⁻¹), for the the poly(ester-*alt*-ethers) **P1-9**. These values were determined from the gradient of [anhydride] vs. time (s) (Figures S8.2.46-47).

2.5 Epoxides

In comparing the influence of the epoxides, 6 representative monomers were evaluated: butylene oxide (BO),¹⁹ 1,2-epoxydodecane (EDD), 1,2-epoxydecene (ED), allyl glycidyl ether (AGE), 2-ethyl hexyl glycidyl ether (EHGE) and benzyl glycidyl ether (BGE) (Table 2.1, **P4-P9**). Experiments were again conducted using the standard conditions outlined earlier, and, with phthalic anhydride (PA) as the co-monomer. The epoxides were selected to deliver copolymers with aliphatic and flexible backbones, targeting materials with low glass transition temperatures to identify promising candidates for use in toughening studies. Further, to deliver functionalised copolymers, monomers featuring alkene substituents were targeted (ED and AGE). Monomers with potentially very different miscibility/solubility were chosen, such as a short alkyl chain (BO), long alkyl chain (EDD) and glycidyl groups with an ether moiety (AGE and EHGE). Although at present the epoxides employed in this study are all petrochemicals, there are routes to produce them from renewables in future.²⁹

In all cases, anhydride (**A**) and epoxide (**B**) ROCOP yielded copolymers with poly(ester-*alt*-ether) sequences (>95 % by ¹H NMR spectroscopy, Figures S8.2.20, S8.2.24, S8.2.28, S8.2.32, S8.2.36, and S8.2.40). The copolymers showed consistent degrees of copolymerisation of 25, with molar mass values from 6.0-10.5 kg mol⁻¹. Within the series of poly(ester-*alt*-ethers) prepared from different epoxides (with PA as anhydride), all materials were amorphous, the *T_g* values increase in the order EHGE ≈ EDD ≈ ED < AGE < BO ≈ BGE (-44 to 4 °C, Figure 2.6 and Table 2.1). In addition, all of the polymers showed *T_{d,5}* values from 283-344 °C (Table S8.2.1, Fig. S8.2.51). This again provides a wide operating window for all poly(ester-*alt*-ethers) explored in this work, affording flexibility in polymer blending strategies, since the polymeric additive can be taken to high temperatures. ROCOP of the aliphatic epoxides with PA (**P4-6**) produced monomodal molecular weight distributions with low dispersity (*Đ* = 1.11-1.21, Figure S8.2.45). In contrast, the glycidyl ethers (**P7-P9**) showed broader dispersity and bimodality (Figure S8.2.45). This is more likely to be the result of residual diols in the monomer (despite triple distillation – see chapter 7.1 for monomer purification protocols).

Comparing the rate constants, *k_{obs}*, for the copolymerisation (determined as gradients of linear fits to anhydride, PA, conversion vs. time data) allowed insight into epoxide structure-activity effects (Table 2.1, Figure 2.7 and Figures S8.2.47). The glycidyl epoxides showed significantly lower rates than the alkylene oxides, with complete conversion requiring 8-96 hours instead of ~2 hours (Figures S8.2.47). For example, **P4** shows a rate which is around

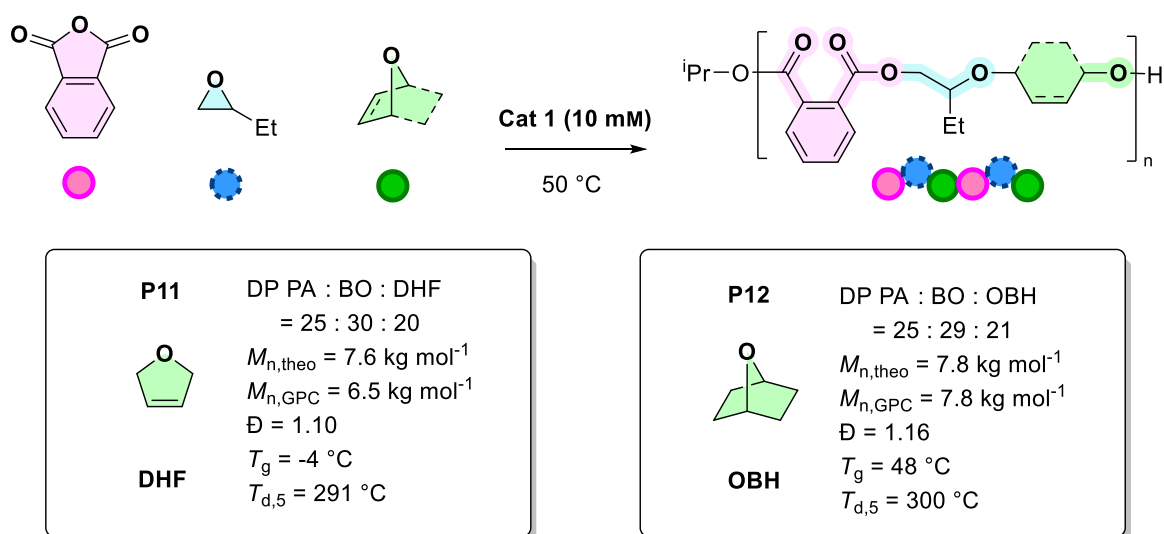
20x higher than AGE (**P4** $k_{\text{obs}} = 11.7 \times 10^{-5} \text{ M s}^{-1}$; **P7** $k_{\text{obs}} = 0.6 \times 10^{-5} \text{ M s}^{-1}$). The slower rates are tentatively attributed to electronic deactivation of the glycidyl epoxide rings vs the aliphatic epoxide, as reported by others.^{33,34} EHGE shows slightly higher rates than both BGE and AGE, but still lower than that of BO, suggesting a potential steric and electronic interplay. Unlike the rest of the series, **P9**, derived from PA and BGE was analysed using a triple-detection GPC to obtain an accurate molar mass ($M_{n,\text{GPC}} = 10.2$, $\text{Đ} = 1.64$, see chapter 7.2.2 for details). It's possible that BGE contains a higher quantity of protic impurities (such as diols) accounting for the broader molecular weight distribution.³⁵

To target poly(ester-*alt*-ether) copolymers featuring alkene substituents on both monomers, MA and ED were polymerized (Table 2.1, **P10**). The copolymer, **P10**, shows the desired **ABB** sequence and has a low T_g of -50°C and $T_{d,5} = 344^\circ\text{C}$ (Table 2.1 and Figure S8.2.51). This would allow functionalisation at each component of the polymer back-bone, as will be explored below. This type of polymer may lend itself to orthogonal functionalisation, whereby the internal and external double bonds can be post-functionalised selectively, providing interesting mixtures of functional groups at sequence selective positions of the polymer.³⁶ This is also an indication of the low T_g values possible for poly(ester-*alt*-ethers).

2.6 Cyclic Ethers

Our prior report demonstrated that catalyst **1** could also enchain some tetrahydrofuran (THF) or bio-derived 2-methyl tetrahydrofuran (MeTHF) into poly(ester-*alt*-ethers).¹⁹ In PA (**A**), BO (**B**) and THF (**C**) ROCOP, the resulting copolymers showed mixtures of **ABB** and **ABC** sequences. Here, the goal is to evaluate the Zr-catalyst in anhydride (**A**)/epoxide (**B**)/cyclic ether (**C**) ROCOP. The copolymerisations were conducted using [**1**] : [PA] : [BO] : [cyclic ether] of 1 : 50 : 288 : 740-992, where catalyst and anhydride concentration were 10 mM and 0.5 M, respectively (BO = 0.25 mL, cyclic ether = 0.75 mL and total volume = 1 mL) (Scheme 2.2). First, 2,5-dihydrofuran (DHF) was targeted, since it has an internal alkene group, which should facilitate post-polymerisation functionalization and can be synthesised from sugars.^{29,37} The copolymerisation of PA, BO and DHF was successful, producing copolymer **P11** with a molar mass value of 6.5 kg mol^{-1} and a narrow dispersity ($\text{Đ} = 1.10$, Figure S8.2.66a). ^1H NMR spectroscopy reveals that the ether linkages comprise 60 % BO and 40 % DHF units (Figure S8.2.58). These ether linkage compositions are similar to those reported for PA, BO and THF ROCOP using the Zr-catalyst.¹⁹ The other spectroscopic data are also fully consistent with the formation of poly(ester-*alt*-ethers) with **ABB/ABC** sequences. The new copolymer, **P11**, is amorphous, with a $T_g = -4^\circ\text{C}$, and shows reasonable thermal stability, with

$T_{d,5}$ of 291 °C (Figure S8.2.69a). Next, 7-oxabicyclo[2.2.1] heptane (OBH), which is a strained bicyclic ether, was investigated (Scheme 2.2). The copolymerisation of PA, BO and OBH yielded the new poly(ester-*alt*-ether) featuring **ABB/ABC** sequences, **P12**. The copolymer shows 58 % BO and 42 % OBH linkages (from ^1H NMR spectroscopy, Figure S8.2.62). It has an amorphous structure with a glass transition temperature of 48 °C (Figure S8.2.68), consistent with the rigidity imparted by the cyclohexane units, as well as good thermal stability, with $T_{d,5}$ of 300 °C (Figure S8.2.69b).



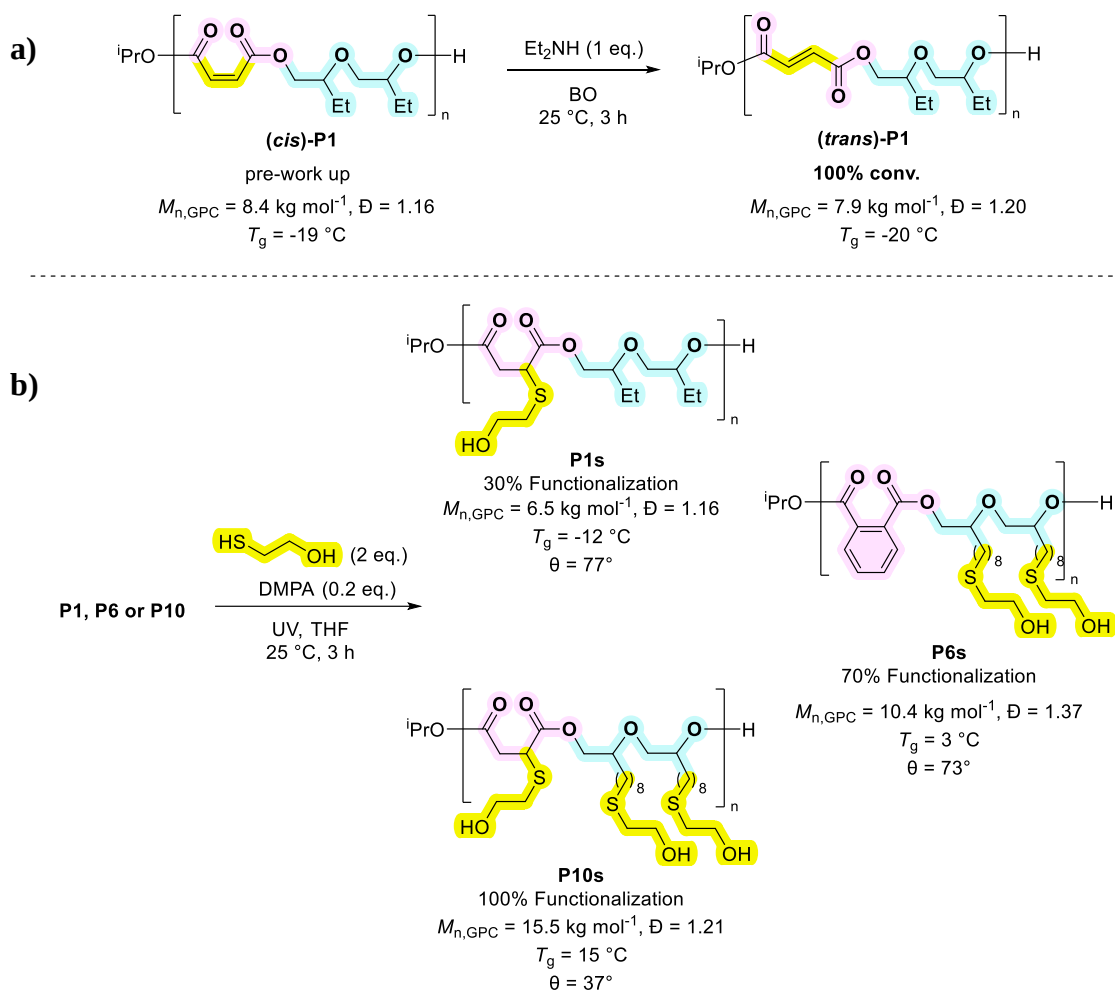
Scheme 2.2: Ring-opening copolymerisation (ROCOP) of PA, BO and cyclic ethers with catalyst **1**. ROCOP conditions for **P11**: [**1**] = 10 mM, [PA] = 0.5 M, BO = 0.25 mL, 2.8 M, DHF = 0.75 mL, 9.9 M, total volume of BO + OBH = 1 mL, 50 °C. ROCOP Conditions for **P12**: [**1**] = 10 mM, [PA] = 0.5 M, BO = 0.25 mL, 2.8 M, OBH = 0.75 mL, 7.4 M, total volume of BO + OBH = 1 mL, 50 °C.

2.7 Functionalised Copolymers

Many applications would benefit from the ability to install functional substituents. For example, to moderate solubility, impart pH or chemical responses, controlling degradation rates or moderating polymer viscoelasticity. As described above, unsaturation also provides the opportunity for polymer grafting in blending applications. The series of poly(ester-*alt*-ethers) feature several polymers with alkene substituents. Copolymers derived from maleic anhydride feature cis-alkene groups in the copolymer backbone. If these are isomerized, they produce repeat units of fumaric acid (FA). Alternatively, copolymers containing FA require the use of step-growth copolymerisations, which are not typically very well controlled.³⁸ Coates and co-workers pioneered the epoxide/maleic anhydride ROCOP, followed by alkene isomerization, to access polyesters featuring FA repeat units.³⁹ In a similar manner, copolymer **P1** was treated

with an equivalent of HNEt₂ (per alkene moiety) to yield FA (*trans*)-**P1** in quantitative yield (Scheme 2.3a).³⁶ The new copolymer showed an amorphous structure and nearly equivalent T_g to **P1** (**P1** = -19 °C, (*trans*)-**P1** = -20 °C, Table 2.2 and Figure S8.2.79). One attraction of fumaric acid repeat units is the future potential for these polymers in biomedical applications. Fumaric acid has a considerably higher lethal dose, when administered orally to rats, than maleic acid (FA, LD₅₀ = 10.1 g kg⁻¹; MA, LD₅₀ = 0.7 g kg⁻¹).^{40,41} Further, poly(ethylene fumarate) was more readily biodegraded than poly(ethylene maleate).⁴²

Alkene groups can also be further reacted, by additions, using high yield thiol-ene reactions to install functional substituents.³⁹ The investigation into this process focused on three copolymers, **P1**, **P6** and **P10**, featuring different numbers of alkenes in the repeat units; 30, 70 and >99 % unsaturation, as defined by the %alkene groups in each repeat unit (Scheme 2.3b). Each copolymer was reacted with 2-mercaptoethanol (2 equivalents per alkene) and with the photo-initiator DMPA (2,2-dimethoxy-2-phenylacetophenone, 0.2 equivalents), in THF at 25 °C and using UV irradiation. The copolymers were all successfully functionalised with alcohol groups, as determined from the ¹H NMR spectra which showed complete alkene resonance consumption ($\delta_H \approx 6.50$ – 5.50 ppm) from MA and/or ED (Figure S8.2.74-76). The spectra also showed new resonances consistent with the thio-ether protons ($\delta_H \approx 2.40$ – 2.75 ppm). GPC analyses showed a slight increase in the molar mass for **P6s** and **P10s**, consistent with the addition of the hydroxyl groups. The T_g values changed from -50 to -12 °C for **P1-P1s**, -42 to 3 °C for **P6-P6s**, and -48 to 15 °C for **P10-P10s** (Table 2.2 and Figure S8.2.78). The functionalised polymers showed reduced water contact angles (θ), by 19, 25 and 51° for **P1s**, **P6s** and **P10s** respectively (Table 2.2). These results demonstrate the expected increase in hydrophilicity as hydroxy functionalisation increases. This property is useful both for surfactant application and to increase degradation rates.



Scheme 2.3: Post-copolymerisation Functionalization of poly(ester-*alt*-ethers) (**ABB**). (a) Isomerization of the alkene moieties in **P1**; (b) Reactions to install hydroxyl groups, using thiol-ene reactions, onto the repeat units. These apply different copolymers, **P1**, **P6**, **P10**, to achieve 30, 70 and 100% hydroxyl substitution (where % refers to the extent of hydroxyl substitution of both **A** and **B** repeat units). Note that the thiol-ene reactions are regio-random. θ = static water contact angle.

Table 2.2: Characterisation data for polymers undergoing post-polymerisation functionalisation (**P1**, **P6** and **P10** compared with (**trans**)-**P1**, **P1s**, **P6s** and **P10s**). **P1**, **P6** and **P10**, reported in Table 2.1, have been reproduced here for comparison.

Polymer	Anhyd.	Epoxide	M_n ($\bar{D}$) [kg mol ⁻¹] ^a	M_n (Theo) ^b	T_g ($^{\circ}\text{C}$) ^c	ΔT_g ($^{\circ}\text{C}$) ^d	Water contact angle ($^{\circ}$) ^e
P1	MA	BO	8.4 (1.16)	6.6	-19	-1	-
(trans)- P1	FA	BO	7.9 (1.20)	6.6	-20		-
P1 ^f	MA	BO	6.7 (1.22)	6.6	-19	+5	96 ± 2
P1s	MA	BO	6.5 (1.16)	8.1	-12		77 ± 1
P6	PA	ED	8.4 (1.21)	12.8	-42	+45	98 ± 4
P6s	PA	ED	10.4 (1.37)	16.1	3		73 ± 3
P10	MA	ED	10.4 (1.04)	11.2	-50	+65	88 ± 3
P10s	MA	ED	15.5 (1.21)	17.5	15		37 ± 1

^aDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards. ^bTheoretical M_n are calculated from the original polymer described in Table 1 after full post-functionalisation measured through ¹H NMR. ^cGlass transition temperature obtained from Differential Scanning Calorimetry (DSC, second heating cycle, 10 $^{\circ}\text{C min}^{-1}$ heating rate). ^dDifference in the glass transition temperature of pre- and post-functionalised polymer. ^eStatic water contact angle measured using a drop shape analysis system. ^fA different batch of **P1** was used, molar mass and thermal properties are consistent with this sample.

2.8 Summary and Future Work

2.8.1 Summary

A Zr(IV) catalyst was able to produce novel poly(ester-*alt*-ethers) from mixtures of several different epoxides, anhydrides and cyclic ethers. This catalysis was used to produce a series of 16 new copolymers which were fully characterised using spectroscopy, GPC and thermal methods. By selecting the various monomer combinations, it was possible to control the copolymer's glass transition temperatures, and, install many chemical moieties such as alkyl chains (from 2-10 carbons long), ether groups, aromatic groups as well as unsaturated double bonds. Through post-functionalisation reactions, pendant hydroxyl groups were installed at regular sites along the copolymer backbone. This not only provides modulation of the polymer's thermal properties, by changing the glass transition temperature by up to 63 °C, but allows future studies into imparting hydrophilicity into a degradable polymer, making it useful in applications such as surfactants. The generally applicable new catalysis should be exploited, in future, to prepare new types of degradable polymers for liquid formulations, electrolytes, elastomers, coatings and adhesives.⁶ Importantly for the focus of this work, the products are anticipated to be highly useful in polymer blends, owing to their thermal properties (lower T_g than the analogous polyester; compare **P1** to **P1'**, **ABB** and **AB**, $T_g = -19$ and 5 °C respectively) and hydrolytic degradability. In this chapter, we have provided a range of poly(ester-*alt*-ethers), with various thermal and chemical properties, from which to select possible candidates to take forward into polymer blending studies with sustainable brittle plastics in the proceeding chapters.

2.8.2 Future Work

Catalyst development: Much can be done to inform/improve catalysis. Exploration of other metals (beyond Zr(IV)) and ligand systems should be performed. Designing a non-initiating catalyst capable of poly(ester-*alt*-ether) ROCOP, a catalyst that did not contain initiating co-ligands, would enable the choice of CTA to be used to match any initiating impurities.⁴³ This would also provide control over the end group functionality, to permit the synthesis of telechelic polyols or a variety of polymer architectures.

End-of-life: The rate of hydrolytic degradation was increased for poly(ester-*alt*-ethers), compared to polyester analogues.¹⁹ It is now necessary to determine whether this family of polymers is able to be chemically recycled, enzymatically degraded or biodegraded. End-of-life considerations are now front and centre of polymer design strategies using circular

economy principles, and this would be an important consideration for potential applications of poly(ester-*alt*-ethers). This is explored in chapters 3 and 5.

Application: The access to low T_g values, chemical diversity and ability functionalise/graft through unsaturation, may warrant further investigation into the adhesive properties of poly(ester-*alt*-ethers). Pressure sensitive adhesives form non-covalent interactions with other surfaces, with contact and brief pressure. These interactions form as a result of the polymer being able to flow under lightly applied pressure, forming sufficient contact area with the substrate surface.⁴⁴ The tack, or ‘stickiness’ of a polymer often reaches a maximum ~40-70 °C above the T_g .⁴⁴ And again, the wide choice of monomers available to poly(ester-*alt*-ether) ROCOP, may permit optimisation of adhesive properties for different applications.

In next generation, safe, solid-state batteries, polymers are of interest as binders in composite cathodes with inorganic solid electrolytes.⁴⁵ Polymers are attracting interest for improving electrode processability and the long-term interfacial stability in the composite cathode.⁴⁵ The life times of these materials are restricted by volume changes in the inorganic components on charge/discharge. Block polymers have been utilised to combine viscoelastic/adhesive properties (improving the binding of inorganic components) with the conductivity of linkages such as ethers (i.e PEO) (oxygenated and polar moieties) and the oxidative stability of linkages such as esters and carbonates.⁴⁵ Poly(ester-*alt*-ethers) may also warrant investigation in solid-state batteries, providing a soft block with suitable thermal properties, and combined ester-*alt*-ether linkages that may impart the conductivity of the polyether linkages with the oxidative stability of polyesters.

Chapters 3 and 5 in this work, explore the application of poly(ester-*alt*-ethers) in toughening sustainable alternative thermoplastics, PLLA (chapter 3) and polycarbonates from the ROCOP of CO₂ and cyclic epoxides (chapter 5).

2.9 References

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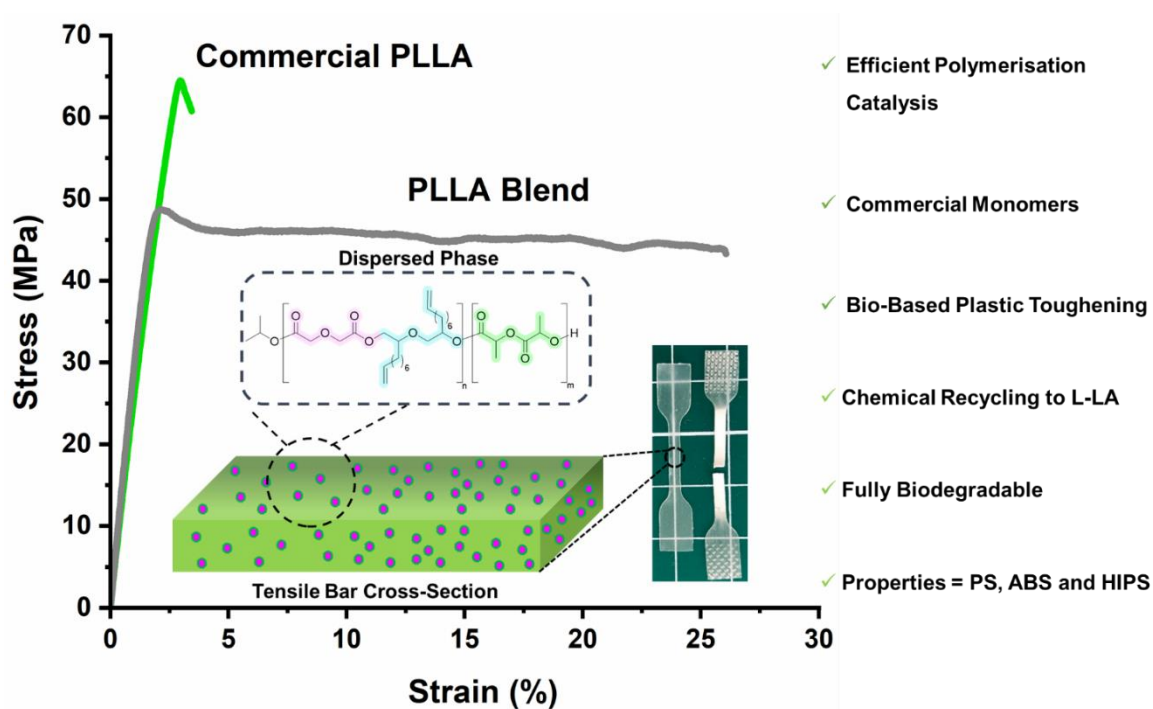
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CHAPTER 3

Chapter 3: Toughened Commercial Poly(L-Lactide) (PLLA) Using Degradable and Recyclable Poly(ester-*alt*-ether)-*b*-PLLA

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Submitted to the Royal Society of Chemistry's Green Chemistry

Statement of Contribution to Co-Authored Work

This chapter includes work performed by other co-authors on this study.

T. M. McGuire; performed chemical recycling experiments

All other work is that of the author.

3.1 Introduction

Poly(L-lactide) (PLLA), is the largest scale commercial bio-derived plastic.¹⁻² It is made by the fermentation of starch-rich biomass, such as sugarcane. After use it is chemically and mechanically recyclable.³ For applications where it is irretrievable after use, it is also fully compostable and biodegradable.⁴ Whilst there are several stereo-chemistries for polylactide, this work focuses only on the major commercial product, PLLA, which derives from L-lactide (L-LA). PLLAs crystalline domains increase tensile modulus (E), strength (σ), moisture barrier properties and significantly increase its upper service temperature.⁵⁻⁷ PLLA has a moderate glass transition temperature ($T_g \sim 60^\circ\text{C}$), but a relatively high melting temperature ($T_m = 150-170^\circ\text{C}$) and reasonable thermal stability ($T_{d5\%} = 215-285^\circ\text{C}$).⁸ PLLA also shows a high tensile strength (47-66 MPa) and Young's modulus (~ 3.8 GPa), as well as high optical clarity and transparency.^{6,8} It is a more sustainable replacement for conventional petrochemicals like polystyrene (PS), high-density polyethylene, polyethylene terephthalate and polypropylene.^{2,9} Nonetheless, some applications are limited by its brittleness, reflected in a very low tensile toughness ($< 5 \text{ MJ m}^{-3}$) and low elongation at break ($< 5\%$).^{6,10} These limitations arise from relatively low crack initiation and propagation energies, which often result in failure by crazing rather than shear yielding.¹¹ Significant research has focused on improving its ductility without loss of advantageous thermal-mechanical properties.^{6,10}

There are a range of toughening chemistries applied to PLLA, including post-polymerisation backbone functionalization, use of nucleating agents, chain orientation strategies, copolymerisation, addition of small-molecule plasticisers, rubber toughening, reactive blending or crosslinking and organic/inorganic fillers.^{6,10} Blending small-molecule plasticizers is often adopted, but whilst this can overcome its brittleness in the short-term, the resulting mixtures may phase separate over time, re-forming brittle samples.^{6,12} Small molecule plasticisers also tend to decrease the blend glass transition temperature and reduce its tensile strength and stiffness (modulus).⁶ It has also been suggested that common plasticizers may leach from PLLA samples under environmental conditions, giving rise to concerns as some plasticizers are believed to be toxic.¹³

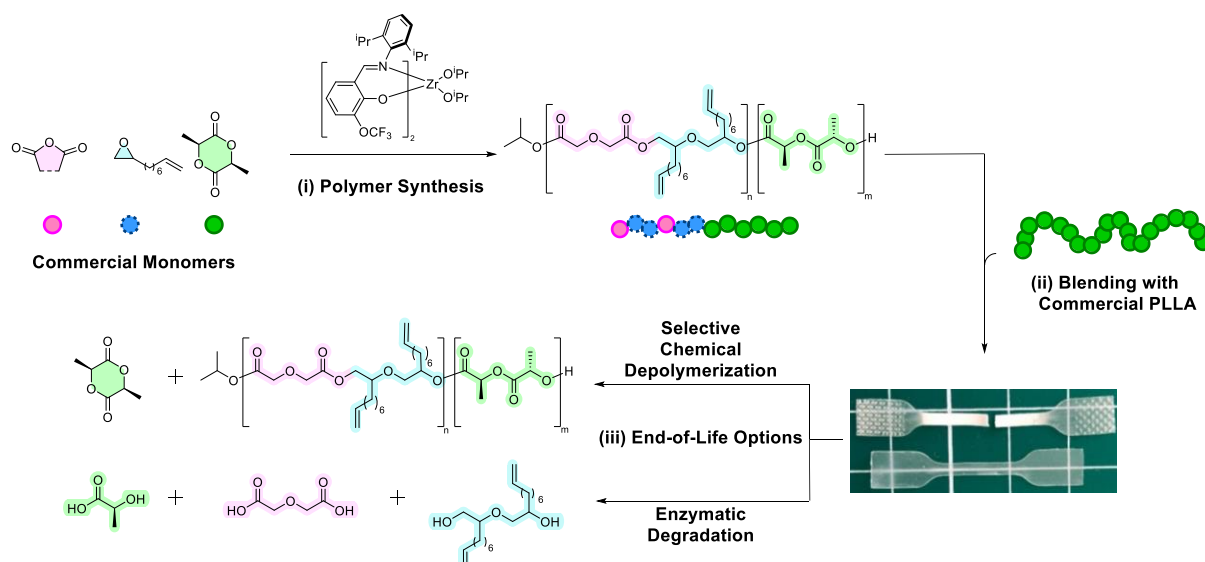
An alternative is to add small quantities of elastomeric polymers into PLLA, known as rubber toughening.^{6,14} When using miscible polymer elastomer/PLLA blends, the elongation at break can increase significantly, but, with the trade-off of compromised strength and decreased glass transition temperature.¹¹ When using immiscible elastomeric polymers, the blends show micron sized elastomer aggregates or particles dispersed in the PLLA. These

particles are believed to function as stress concentrators, promoting plastic deformation and toughening. Optimising the particle sizes and separations helps overlap their stress fields, promoting energy dissipation.^{10,15} Such immiscible blends often also require another additive, a compatibiliser, to stabilise the PLLA-elastomer interface and prevent particle coalescence over time.¹⁶

Amphiphilic block polymers, combining immiscible elastomeric and PLLA miscible blocks, may be useful as toughening agents, providing both dispersed elastomeric phases and stable interfaces. It also provides greater control over dispersed particle sizes; in some cases, it results in ultra-tough PLLA.^{5,16-21} One issue is that most of these amphiphilic blocks feature pervasive polymer chemistries. Given that one of the major benefits of PLLA is its better end-life options, it is important to consider additives which are both recyclable and degradable.

3.2 Aims

Here, we target block polymers comprising elastomeric and PLLA blocks, i.e. poly(ester-*alt*-ether)-*b*-PLLA, for use as rubber toughening additives; both block polymer chemistries feature regular chain ester linkages, potentially delivering (bio)degradability (Scheme 3.1). The block polymer synthesis is proposed following controlled and selective polymerisation catalysis, starting from common commercial monomers: epoxides, anhydrides and L-lactide (L-LA). The poly(ester-*alt*-ether) block is targeted following a recent discovery, from our team, of a Zr(IV) catalyst showing unusual selectivity in the copolymerisation of epoxides and anhydrides, producing polymers whose repeat units feature anhydride-epoxide-epoxide or ester-*alt*-ether sequences.²² In the previous chapter (chapter 2), we demonstrated the application of this controlled polymerisation catalysis using a range of epoxides/anhydrides and used it to make a few poly(ester-*alt*-ethers) that showed the desirable low T_g values needed in an elastomer block ($-60 < T_g < 25$ °C). Proof of concept degradation studies (pH = 14, aqueous conditions) revealed the poly(ester-*alt*-ethers) underwent significantly faster, yet complete, degradation compared with analogous alternating polyesters.^{22,23} Here, the polymerisation catalysis must be developed, to enable production of block polymers combining both the elastomeric poly(ester-*alt*-ethers), with a low molar mass PLLA block, the latter to improve compatibility with the PLLA matrix. End-life options available to the blends are explored by chemical recycling and enzymatic degradation methods.



Scheme 3.1: The strategy for producing poly(ester-*alt*-ethers) used to toughen commercial, semi-crystalline PLLA. The approach in this work includes: i) synthesis of poly(ester-*alt*-ether)-*b*-PLLA block copolymers, ii) blending with commercial PLLA and iii) developing chemical recycling and enzymatic degradation processes.

3.3 Poly(ester-*alt*-ether)-*b*-PLLA Synthesis

A series of block polymers, poly(ester-*alt*-ether)-*b*-PLLA, were synthesised using a Zr(IV) catalyst, **1**, applied in a one-pot, sequential monomer addition process. In the first step, the catalysed ring opening copolymerisation (ROCOP) of either diglycolic anhydride or maleic anhydride (DGA or MA) with racemic 1,2-epoxy-9-decene (ED) produced the poly(ester-*alt*-ether) block, and in the second step, the same catalyst was used for the controlled ring-opening polymerisation (ROP) of L-lactide.²² There are benefits to using commercial monomers and single reactor processes, not least as these syntheses circumvent isolation of intermediates or use of macro-initiators.²⁴ To exemplify the typical conditions used to make the poly(ester-*alt*-ethers), the synthesis of **P10** from MA and ED is described here (full details for other polymers are in chapter S8.3, Figure 3.1).²³ This monomer combination was explored briefly in chapter 2, in the context of providing a polymer with three double bonds per repeat unit. Here, it has been re-synthesised, to make block copolymers and used as an exemplar for polymer characterisation in this chapter. All polymerisations were performed using **[1]** : [Anhydride] : [Epoxide] = 1 : 50 : 546, at 50 °C. As demonstrated in our previous work, both of the iso-propoxide ligands of catalyst **1** initiate the polymerisation, forming a poly(ester-*alt*-ether) with a degree of polymerisation (DP) of 25, after complete anhydride conversion.^{22,23}

The poly(ester-*alt*-ether) sequence was characterised using a combination of NMR, GPC and thermal methods.^{22,23} For example, the ¹H NMR spectrum for **P10** clearly shows resonances assigned to protons adjacent to both ester ($\delta_{\text{H}} = 4.99$ and 4.16 ppm, respectively) and ether ($\delta_{\text{H}} = 3.88$ –3.18 ppm) groups (Figure S8.3.1). In the COSY NMR spectrum, the ester

resonances do not show any correlations to one another, but do correlate with resonances in the ether region (Figure S8.3.3 and S8.3.4). To compare, the alternating polyester prepared from the same monomers, **P10'** (DP = 25, synthesised using catalyst **2**, Figure S8.3.6), did not show any ether signals in its ^1H NMR spectrum (Figure S8.3.6-8). Also, **P10'** shows the methine-ester resonance at higher chemical shift (5.13 ppm) than the equivalent signal for **P10** (4.99 ppm, Figure S8.3.8 and S8.3.4 respectively). For **P10'**, the ^1H COSY NMR spectrum shows clear correlations between the methine-ester and methylene-ester resonances, which is quite different to **P10** (Figures S8.3.7-8, resonances 1-2). The poly(ester-*alt*-ether) **P10** shows a molar mass, determined by GPC, which is consistent with theoretical predictions and a narrow dispersity, monomodal distribution (Table 3.1). **P10** is amorphous, with a glass transition temperature of $-50\text{ }^\circ\text{C}$ (vs. **P10'**, $T_g = -41\text{ }^\circ\text{C}$) consistent with the enhanced segmental motion afforded by the ether linkages (Table 3.1 and Figure S8.3.62). Following the same experimental conditions, a series of new poly(ester-*alt*-ethers) were prepared and all showed NMR spectroscopic characterization data consistent with the repeat unit sequences and experimental M_n values close to theoretical values, with narrow dispersities ($1.12 < \bar{D} < 1.24$) (Table 3.1).

The poly(ester-*alt*-ether)-*b*-PLLA copolymers were all synthesised by a sequential addition process, whereby L-LA was added into the reaction after complete conversion of the anhydride monomers in the ROCOP (Figure 3.1a). For example, **P10**₂₅-**PLLA**₂₇, prepared using the polymerisation conditions outlined above ($[\mathbf{1}] = 0.01\text{ M}$, neat ED, $50\text{ }^\circ\text{C}$), showed rapid MA/ED copolymerisation (complete MA conversion in $< 55\text{ min}$, $k_{\text{obs}} = 54\text{ M min}^{-1}$), forming the **P10** block, with a DP(MA) of 25 and DP(ED) of 59 (Figure 3.1b). The MA:ED ratio stayed at 1:2, throughout the reaction, as expected for selective poly(ester-*alt*-ether) formation (Figure 3.1d). After complete anhydride (MA) consumption, the addition of L-LA initiated a mechanistic switch into L-LA ROP (Figure 3.1b, Figure S8.3.20 illustrates switch catalysis). The ROP of L-LA occurred more slowly ($k_{\text{obs}} = 2.0 \times 10^{-3}\text{ min}^{-1}$), reaching complete conversion, DP(PLLA) = 27, after 30 hours (Figure 3.1b). Conducting the polymerisations with regular aliquot analysis, enabled plots of conversion vs time data. There is a linear increase in poly(ester-*alt*-ether) concentration ($1 - [\text{MA}]$) over time. This data is consistent with rates being zero order in anhydride concentration, as was found in prior kinetic analyses of epoxide/anhydride copolymerisations using catalyst **1**.²² In contrast, the PLLA concentration ($1 - [\text{L-LA}]$) increases exponentially over time, consistent with rates being first order in $[\text{L-LA}]$ (Figure 3.1b).

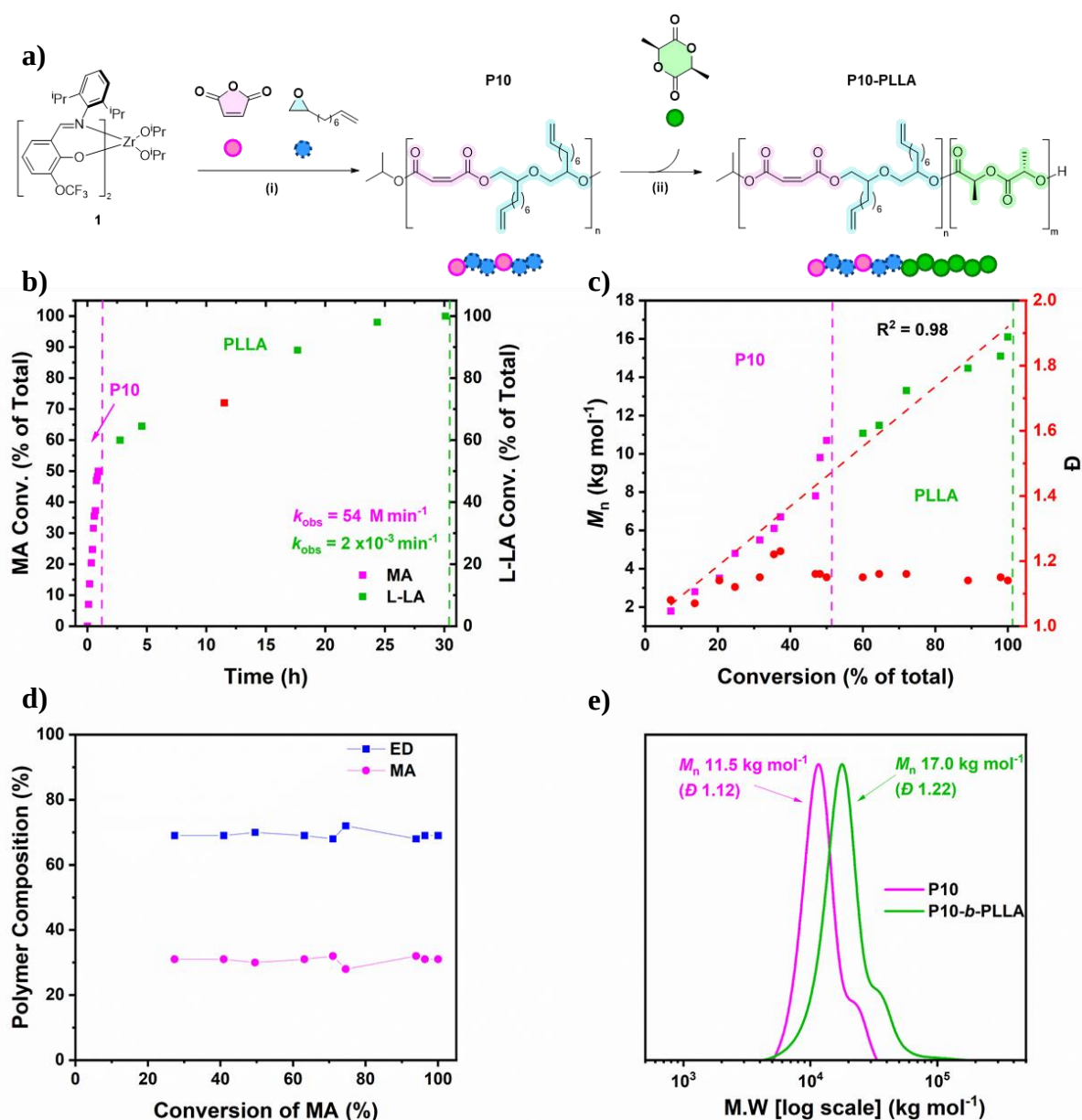


Figure 3.1: Synthesis of poly(ester-*alt*-ether)-*b*-PLLA block polymers using catalyst **1**. a) (i) The copolymerisation of MA/ED, conditions: $[MA]_0 = 0.5$ mM (50 equivalents), 50°C in 1 ml epoxide (546 equivalents for ED), $[1] = 0.01$ mM (one equivalent); (ii) L-LA polymerisation, conditions: the overall monomer stoichiometry is $[1]:[MA]:[ED]:[L-LA] = 1:50:546:50$. b) Conversion vs time data for **P10**₂₅-**PLLA**₂₇ formation, demonstrating MA (pink squares) and L-LA (green squares) conversion (normalised by overall maximum monomer conversion). The pseudo rate coefficients, k_{obs} , were determined as the gradient of the $[MA]$ vs time (min) for MA/ED ROCOP and the gradient of a plot of $\ln([L-LA]/[L-LA]_0)$ vs time (min) for L-LA ROP. c) Plot showing **P10**₂₅-**PLLA**₂₇ M_n and $\bar{D}$ vs monomer conversion. Data for the MA/ED ROCOP (pink), and then L-LA ROP (green). d) Plot showing **P10** composition vs. polymer conversion, with MA (pink) and ED (blue) conversions determined by 1H NMR spectroscopy (Table 3.1). e) GPC data for aliquots collected during **P10**₂₅-**PLLA**₂₇ synthesis. The data show **P10** formation (>99 % conversion, pink) and, later, **P10-b-PLLA**₂₇ formation (>99 % L-LA conversion, green).

Table 3.1: Overview of poly(ester-*alt*-ether)-*b*-PLLA synthesis and characterisation data.^a

DGA MA ED L-LA							
Entry	Polymer	Monomer Stoichiometry [Cat]:[Anhy]: [ED]:[L-LA]	Polymer DP [Anhy]:[ED]: [L-LA] ^b	w _{PLLA} (%) ^c	M _n (<i>D</i>) [kg mol ⁻¹] ^d	M _n (Theo.) ^e	T _g (°C) ^f
1	P10 - P(MA-ED-ED)	1:50:546:0	25:50:0	0	11.5 (1.12)	10.2	-50
2	P10^g - P(MA-ED)	1:25:546:0	24:30:0	0	3.5 (1.52)	7.5	-41
3	P10₂₅-PLLA₂₇	1:50:546:50	25:59:27	0.25	17.0 (1.22)	15.8	-47
4	P10₂₅-PLLA₁₈^{*h}	1:50:546:50	25:60:18	0.18	14.2 (1.13)	14.4	-44
5	P13 - P(DGA-ED-ED)	1:50:546:0	25:54:0	0	10.3 (1.24)	11.3	-51
6	P13₂₅-PLLA₂₃	1:50:546:50	25:56:23	0.26	16.9 (1.28)	14.9	-46
7	P13₂₅-PLLA₆₈	1:50:546:150	25:49:68	0.49	23.6 (1.63)	20.3	-45
8	P13₂₅-PLLA₁₂₅	1:50:546:250	25:53:125	0.62	24.1 (1.48)	29.2	-43, 48
9	P13₈-PLLA₂₆	1:15:546:50	8:18:26	0.55	8.9 (1.27)	7.7	-40
10	P13₁₅-PLLA₂₇	1:30:546:50	15:36:27	0.35	6.9 (1.17)	11.2	-40
11	P13₈-PLLA₉	1:15:546:15	8:16:9	0.30	5.7 (1.17)	4.8	-45
12	P13₁₂-PLLA₁₅	1:25:546:25	12:24:15	0.32	8.5 (1.34)	7.3	-46

^aReaction conditions: [1] = 10 mM in 1 mL epoxide, 50 °C (Figure 3.1a). ^bDP of anhydride was measured by monomer conversion data by integration of the monomer and polymer resonances in the ¹H NMR spectra of purified polymers (e.g. Figure S8.3.1). It is assumed both isopropoxide ligands initiate polymerisation. DP of ED and L-LA were determined by integration of the ¹H NMR spectra of purified polymer against the anhydride polymer resonance. ^cWeight fraction of PLLA blocks (w_{PLLA}) calculated based on monomer DP values from ¹H NMR spectra. ^dDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards. ^eTheoretical M_n were calculated from the monomer conversion data and assume both isopropoxides initiate. ^fObtained from differential scanning calorimetry (DSC, third heating cycle, 10 °C min⁻¹ heating rate). ^gReaction conditions: [2] = 10 mM in neat 1 mL epoxide. ^hOne pot synthesis of monomer mixture (switch polymerisation catalysis).

The block polymers were analysed using a range of techniques, including by ¹H NMR spectroscopy, GPC and DSC methods. For **P10₂₅-PLLA₂₇**, the ¹H and ¹³C{¹H} NMR spectra show resonances for both blocks. In particular, the ¹³C{¹H} NMR spectrum displays carbonyl resonances assigned to **P10** poly(ester-*alt*-ether) at 165 ppm and PLLA at 169 ppm. There are no other carbonyl signals, which is a good indicator of selective block copolymer formation and suggests that any transesterification side-reactions occur more slowly than block propagation (Figure S8.3.13).²⁵ Further evidence for block polymer formation comes from molecular weight (GPC) analyses of reaction aliquots, which show steadily increasing polymer M_n with polymer conversion and narrow dispersity values (*D* < 1.25, Figure 3.1c). The block polymers showed M_n values, by GPC, which were in close agreement with theoretical values (Table 3.1). In a few of the GPC traces, there were low intensity, higher molar mass shoulder peaks which are attributed to block polymers, that, rather than being catalyst initiated, are produced from low quantities of diol/diacid present in the monomers (Figure 3.1e and Figures S8.3.59-61). The DOSY NMR spectra show a single diffusion coefficient, consistent with block polymer formation (Section S8.3.1.1).

3.4 Synthesis of Poly(ester-*alt*-ether)-*b*-PLLA by Switch Catalysis

One-pot polymerisations using monomer mixtures are attractive, in terms of green chemistry, as they prevent additional reaction steps, obviate additional catalysts, solvents and purifications of pre-polymers/macro-initiators. Such processes also simplify larger-scale polymerisation processes. One such route, is a form of switchable catalysis, which selectively enchains mixtures of epoxides, anhydrides and cyclic esters to form block polyesters.^{26,27} The rules for these switchable catalyses are quite generally applicable and predict that from the monomer mixtures, the epoxide/anhydride ROCOP occurs first (forming a polyester) and is followed selectively by lactone ROP (also forming a polyester) only after complete anhydride consumption.²⁴ It is not clear whether catalyst **1**, which forms poly(ester-*alt*-ethers) from epoxides/anhydrides, should follow the same selectivity rules. To investigate its potential in switchable polymerisation catalysis, a mixture of MA/ED/L-LA was reacted with catalyst **1**, under identical conditions to those used above. The polymerisation was monitored by regular removal of aliquots, which were analysed by ¹H NMR spectroscopy (Figure 3.2a and b). Over 2 h, only the anhydride and epoxide were consumed, selectively forming the poly(ester-*alt*-ether). The concentration of [MA] showed a linear decrease with time, once again consistent with rates that are zero order in anhydride concentration ($k_{\text{obs}} = 1.45 \text{ M min}^{-1}$). After 2 h, and once anhydride consumption was >95 %, the ROP of L-LA started and PLLA resonances were observed in the reaction aliquots. PLLA synthesis was significantly slower than the poly(ester-*alt*-ether) block and showed a first order rate dependence on L-LA concentration ($k_{\text{obs}} = 4.6 \times 10^{-4} \text{ min}^{-1}$). The aliquots were also analysed by GPC and showed steady increases to polymer M_n with monomer conversion; throughout the reaction, samples showed monomodal molecular weight distributions and narrow dispersity values ($D < 1.2$). The switchable catalysis resulted in the formation of a very similar/identical block polymer, **P10₂₅-PLLA₁₈***, to the material produced by the sequential addition process. For example, its DOSY NMR spectrum also showed a single diffusion coefficient, indicative of a block polymer (Figure S8.3.19). The thermal properties of the two block polymers, **P10₂₅-PLLA₂₇** and **P10₂₅-PLLA₁₈***, are very similar (e.g. $T_g = -47$ and -44 °C, respectively; $T_{d,5}/T_{d,95} = 237/499$ and $255/500$ °C, respectively, Table 3.1, Figures S8.3.62 and S8.3.65). End-group analysis, using ³¹P{¹H} NMR titration methods, showed only PLLA resonances, consistent with the block polymer structure (Figures S8.3.21-23). The experiment suggests that mixtures of monomers can be enchainned by switchable catalysis to prepare the desired block polymers. The selectivity, from the monomer mixtures, is tentatively attributed to the alkoxide intermediate, formed during catalysis using Zr(IV) catalyst **1**, showing faster and more stable anhydride insertions,

compared with the competitive L-lactide insertions.^{22,24} Although the use of mixtures and switchable catalyses could be useful in future for larger-scale processes, for consistency in this work, all the other block polymers were produced by sequential L-LA addition methods. Accordingly, a series of block polymers were prepared, with focus on polymerisations of DGA/ED (**P13**)/L-LA. By systematically controlling the relative monomer concentrations and conversions, a series of **P13_x-PLLA_y** samples were prepared featuring different block ratios/compositions (DP and weight fraction PLLA) and molecular weights (M_n , Table 3.1).

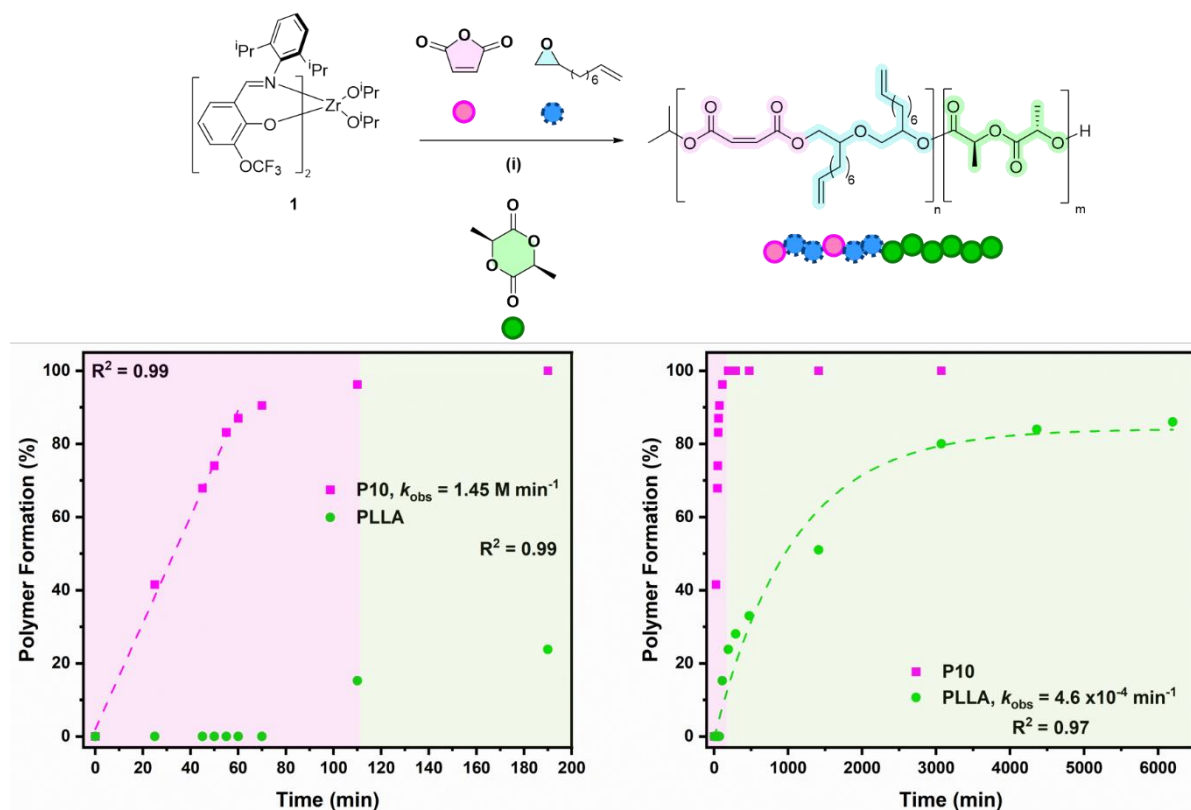


Figure 3.2: Shows conversion vs. time data for the switchable polymerisation catalysis using mixtures of MA, ED and L-LA to form **P10₂₅-PLLA₁₈***. a) Plot showing **P10** formation (% conversion) vs. time, with linear fit to experimental data. Plot also shows that after 110 mins, **PLLA** block formation starts. b) Plot showing block polymer formation (% conversion) vs. time, focussing on the PLLA block formation (110–6000 mins). The experimental data are fit by exponential growth kinetics. Reaction conditions (i): [**1**] = 10 mM (1 equiv.), in neat 1 mL epoxide (546 equiv.), 50 equiv. MA and L-LA, respectively. The pseudo rate coefficients, k_{obs} (min^{-1}), were determined as the gradient of the $[\text{MA}]$ vs time (min) for MA/ED ROCOP and the gradient of a plot of $\ln([\text{L-LA}]/[\text{L-LA}]_0)$ vs time (min) for L-LA ROP.

3.5 PLLA + Block Polymer Blends

The poly(ester-*alt*-ether)-*b*-PLLA were blended into PLLA and the materials' thermal and mechanical properties were compared to the pure PLLA sample (Table 3.2 and Figure 3.3). For these experiments, a commercial, high molecular weight, semi-crystalline PLLA sample was selected, since it should deliver the greatest mechanical strength, and, such samples tend to be more challenging than amorphous PLA to toughen (PLLA, Goodfellow, ME34-GL-

000110, $M_n = 103 \text{ kg mol}^{-1}$, $\bar{D} = 1.81$, from GPC in CHCl_3). The blends were prepared by solvent casting the **P13_x-PLLA_y** samples with commercial PLLA (in CH_2Cl_2). After drying (under vacuum, 60 °C, 2 days), the blends were heated to 180 °C, for 10 minutes (above PLLA melting temperature), and slowly cooled (overnight, see Section S7.3.2.1 for polymer blend procedure). This process formed highly transparent, colourless films. The films were visibly homogeneous, free of air bubbles (Figure S7.1) and processing solvent (Figures S8.3.72-75). The films all showed similar, reproducible thicknesses from 0.15-0.30 mm. Firstly, the blend composition influences over properties was assessed, using systematically increasing quantities of **P13₂₅-PLLA₂₃**: 1, 2, 5, 7.5, 10, 15, 20 and 25 wt% vs. the PLLA matrix (Table 3.2, entries 4-11). Henceforth, these blends will be represented by labels **[P13_x-PLLA_y]_z**, where x = DP **P13**, y = DP PLLA, z = wt% added to the PLLA blend (Table 3.2, entries 4-17).

3.5.1 Thermal Properties

The first series of blends comprise systematically increasing amounts of the 50:50 composition **P13₂₅-PLLA₂₃** block polymer in PLLA (Table 3.2, entries 4-11). The blend thermal properties are all very similar to neat PLLA, which is encouraging since it suggests the elastomeric poly(ester-*alt*-ether) blocks are immiscible in PLLA and may suggest block polymer phase separation in the blend. For the series, the blend materials' glass transition temperature and melting temperature values are very close to those of neat PLLA, with T_g values remaining within 2 °C of PLLA (65 °C) (Table 3.2, entry 1 vs. 4-11). This is important for maintaining a higher operating temperature. Lower T_g values (from the poly(ester-*alt*-ether) block) could be observed between 10-25 wt% blends, although below this, the concentration **P13** is too low to observe a signal in DSC (Figure S8.3.68-71). The PLLA crystallinity (χ), determined by analysis of the DSC melting transitions (S8.3.2.3), shows equivalent or higher values than neat PLLA for most of the blends—important since sample crystallinity is key to providing the beneficial tensile mechanical strength and stiffness. Across the series, PLLA crystallinity values in the range 35-42 % were observed (only the highest additive loading results in decreased crystallinity, Table 3.2, entries 4-11). The maximum crystallinity (42 %) was observed for the 15 wt% blend, **[P13₂₅-PLLA₂₃]₁₅** (Table 3.2, entry 9). The samples all showed similar thermal stability to pure PLLA, with $T_{d5\%}$ values, determined by TGA, in the range 288-317 °C (Table 3.2, entries 1 vs. 4-11, Figures S8.3.72-75).

3.5.2 Tensile Mechanical Properties

Uniaxial tensile extension experiments were performed according to ISO 527 using dumbbell-shaped specimens (ISO 527-2 type 5B, with five technical replicates, see

experimental section S7.2.8). For 1-5 wt% blends of **P13₂₅-PLLA₂₃**, the tensile mechanical properties were nearly identical to PLLA and no toughening was observed (Table 3.2, entries 4-6, Figure 3.3). For blends with >5 wt% block polymer, the elongation at break increased significantly, reaching a maximum at 36% for **[P13₂₅-PLLA₂₃]₂₀** (Table 3.3, entries 7-10). Importantly for samples 5-15 wt%, the elongation at break was increased, but without significant compromise to the high tensile strength and stiffness. The best performing sample was **[P13₂₅-PLLA₂₃]₁₅**, which showed a high strength ($\sigma_Y = 48.7 \pm 1.2$ MPa) and stiffness ($E = 3.1 \pm 0.1$ GPa) together with significantly increased ductility (24.5 ± 4.6 %) vs. neat PLLA (Table 3.2, entry 1 vs. 9). This sample showed the greatest tensile toughness (10.8 ± 2.2 MJ m⁻³, Table 3.2, Figure 3.3a).

Table 3.2: Summary of thermal and mechanical properties of a series of poly(ester-*alt*-ether)-*b*-PLLA and PLLA blends.^a

Entry	Blend	χ (%) ^b	T_g (°C) ^b	T_m (°C) ^b	$T_{d,5}$ (°C) ^c	E (GPa) ^d	σ_Y (MPa) ^d	ϵ_B (%) ^d	U_T (MJm ⁻³) ^d
1	PLLA	34	65	149	321	2.9 ± 0.3	66.7 ± 4.3	3.4 ± 0.5	1.4 ± 0.3
2	[P10₂₅-PLLA₂₇]_{7.5}	46	64	148	279	3.4 ± 0.1	59.2 ± 2.6	6.6 ± 1.5	3.2 ± 0.8
3	[P13]_{7.5}	35	65	150	294	3.2 ± 0.4	52.2 ± 6.2	4.5 ± 1.3	2.0 ± 0.6
4	[P13₂₅-PLLA₂₃]₁	41	64	149	317	3.1 ± 0.3	64.5 ± 5.6	4.2 ± 1.0	2.0 ± 0.6
5	[P13₂₅-PLLA₂₃]₂	39	64	149	308	3.3 ± 0.3	65.0 ± 7.1	3.9 ± 0.9	1.8 ± 0.6
6	[P13₂₅-PLLA₂₃]₅	39	64	152	296	3.3 ± 0.2	63.3 ± 4.3	3.7 ± 1.1	1.7 ± 0.7
7	[P13₂₅-PLLA₂₃]_{7.5}	35	64	149	290	2.9 ± 0.5	59.2 ± 4.8	9.5 ± 1.9	4.6 ± 1.1
8	[P13₂₅-PLLA₂₃]₁₀	40	-46,64	149	288	3.3 ± 0.2	56.4 ± 5.5	9.8 ± 3.0	4.8 ± 1.8
9	[P13₂₅-PLLA₂₃]₁₅	42	-45,63	149	291	3.1 ± 0.1	48.7 ± 1.2	24.5 ± 4.6	10.8 ± 2.2
10	[P13₂₅-PLLA₂₃]₂₀	37	-47,64	151	290	2.4 ± 0.2	35.0 ± 2.1	35.7 ± 3.6	10.8 ± 1.5
11	[P13₂₅-PLLA₂₃]₂₅	22	-45,65	150	292	2.3 ± 0.1	32.0 ± 2.0	20.8 ± 3.9	5.8 ± 0.9
12	[P13₂₅-PLLA₆₈]₁₅	42	-47,63	153	289	3.1 ± 0.3	49.4 ± 4.2	16.5 ± 7.2	6.8 ± 3.1
13	[P13₂₅-PLLA₁₂₅]₁₅	42	-48,64	154	288	3.2 ± 0.2	53.3 ± 2.7	10.7 ± 3.6	4.7 ± 1.8
14	[P13₈-PLLA₂₆]₁₅	43	-46,60	151	278	3.0 ± 0.2	53.1 ± 3.5	4.7 ± 2.5	1.9 ± 1.2
15	[P13₁₅-PLLA₂₇]₁₅	43	-47,60	150	295	2.2 ± 0.2	38.1 ± 2.3	18.5 ± 3.3	5.9 ± 0.9
16	[P13₈-PLLA₉]₁₅	44	-46,60	154	301	2.4 ± 0.2	37.2 ± 2.5	4.3 ± 1.8	1.2 ± 0.5
17	[P13₁₂-PLLA₁₅]₁₅	42	-44,59	158	296	2.7 ± 0.2	42.4 ± 5.2	18.8 ± 7.0	6.7 ± 2.4

^aCommercial PLLA was used in blending, provided by Goodfellow ME34-GL-000110 ($M_n = 103.4(1.81)$ kg mol⁻¹ vs polystyrene standards in CHCl₃). ^bObtained from differential scanning calorimetry (DSC, first heating cycle, 10 °C min⁻¹ heating rate from -80 to 180 °C). The enthalpies of crystallization and melting were determined by the integrated area of the exothermic peak and endothermic peaks respectively, while the crystallization and melting temperatures were obtained from the maximum and minimum of the exo- and endothermic peaks respectively. Crystallinity was calculated by $(\Delta H_m - \Delta H_{cc}) / \Delta H_{m,100} \times 100$, where $\Delta H_{m,100}$ is the enthalpy of melting for 100 % crystalline PLLA and is equal to 93.7 J/g. Below 10 wt% block copolymer, the lower T_g was not able to be observed by DSC. ^cObtained from TGA (Polymer samples were heated from 30 to 700 °C at a rate of 10 °C min⁻¹, under N₂ flow of 12 mL min⁻¹). ^dUniaxial tensile measurements were conducted at 10 mm min⁻¹ extension rate. The mean values and standard deviations are calculated from measurements conducted independently on five separate specimens conforming to dimensions for ISO 527-2 type 5B. Tensile toughness was calculated from the area under the stress-strain plots. Entries 4-11 change the wt% diblock copolymer. Entries 12 and 13 are blends changing PLLA block DP, while fixing **P13** DP (Figure S8.3.79c and d). Entries 14 and 15 are blends changing **P13** block DP, while fixing PLLA block DP (Figure S8.3.79c and d). Entries 16 and 17 are blends changing the overall M_n , fixing DP **P13**: DP PLLA (Figure S8.3.79a and b). The polymer name is contained within square brackets, while the wt% of polymer additive used in the PLLA blend is the subscript on the outside of the square bracket.

To test the importance of the block polymer structure, a PLLA blend containing 7.5 wt% of **P13** was prepared in an identical way (**[P13]_{7.5}**) (Table 3.2, entry 3). The sample behaved very similarly to PLLA and did not show any significant increases to elongation at break ($\epsilon_B = 4.5 \% \pm 1.3$), and low overall tensile toughness ($U_T = 2.0 \pm 0.6 \text{ MJm}^{-3}$). In comparison, the 7.5 wt% block polymer sample showed higher values for tensile strength ($59.2 \pm 4.8 \text{ MPa}$), double the elongation at break ($9.5 \pm 1.9 \%$) and 2x greater tensile toughness ($4.6 \pm 1.1 \text{ MJ m}^{-3}$) than this sample (Table 3.2 Entry 7). These findings indicate that the block polymer structure plays a significant role in delivering the PLLA toughening. A blend of 7.5 wt% **P10₂₅-PLLA₂₇** (**[P10₂₅-PLLA₂₇]_{7.5}**) was also examined (Table 3.2, entry 2), although this copolymer was not explored any further, due to the superior performance of **P13₂₅-PLLA₂₃** as the preferred additive (Table 3.2, entry 7).

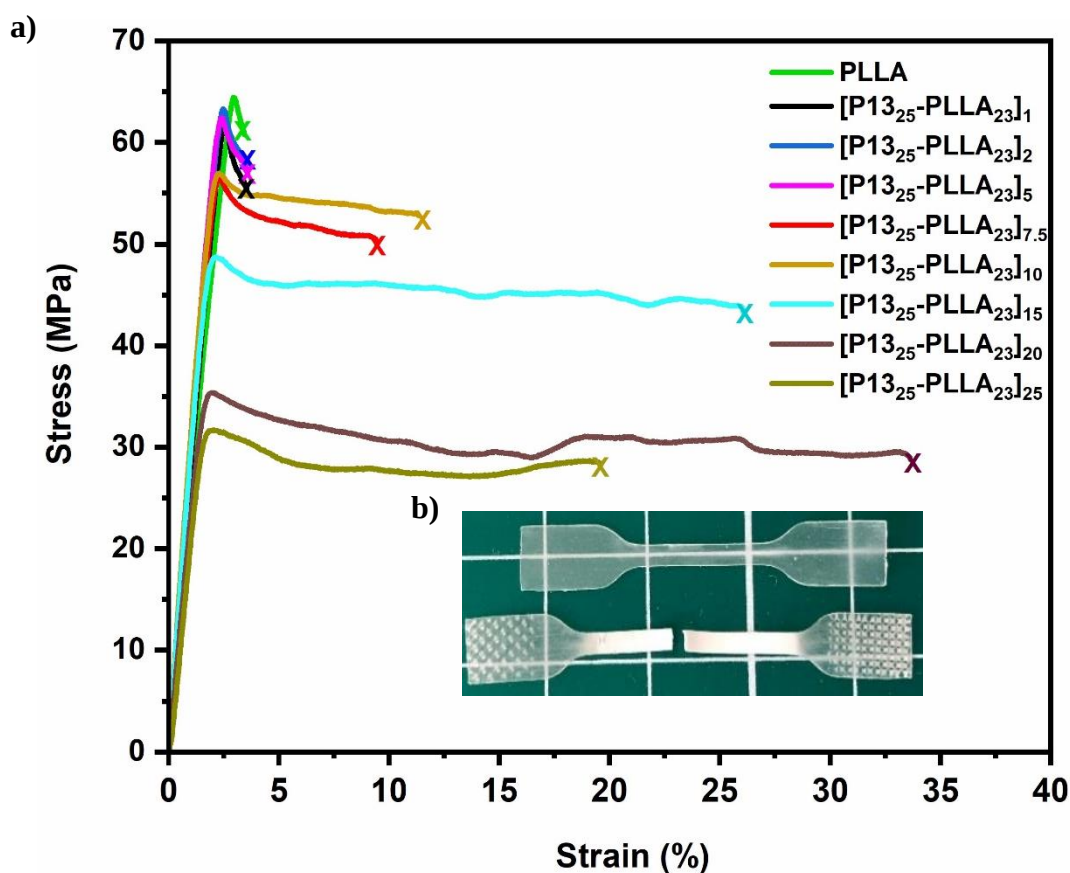


Figure 3.3: Tensile mechanical characterization of **[P13₂₅-PLLA₂₃]_z** series, where $z = 1\text{--}25$ wt%. a) Plot showing sample tensile stress versus strain data for the series of PLLA blends and compared against neat PLLA (see Table 3.2 for numerical values and error analysis). b) Photograph of the tensile specimens (ISO 527–2 type 5B) for **[P13₂₅-PLLA₂₃]₁₅** before (top) and after (bottom) tensile failure.

Commonly, rubber toughened plastics will incur a post yield stress drop (PYSD), as a result of necking behaviour after yielding.^{28,29} This parameter is important in industrial manufacture and commercialisation. The PYSD can often be 10-20 MPa or greater, resulting in a significant sacrifice in practical tensile toughness/strength, from an industrial perspective, irrespective of vast improvements to elongation at break, or any uptick in stress at higher strains in post-yield. Here, semi-crystalline PLLA was chosen to reduce these factors.²⁹ As was demonstrated, adding 7.5 wt% or higher copolymer additive led to PYSD values < 5 MPa, and, for the lead material **[P13₂₅-PLLA₂₃]₁₅**, the PYSD was 3 MPa (Figure 3.3a).

To probe the blend composition, and test whether phase separated block polymer structures were observed, the samples were analysed using scanning electron microscopy (SEM). The SEM measurements were conducted using the fractured surfaces of four tensile specimens (with samples analysed perpendicular to the direction of uniaxial tension stress): neat PLLA, **[P13₂₅-PLLA₂₃]_{7.5}**, **[P13₂₅-PLLA₂₃]₁₅** and **[P13₂₅-PLLA₂₃]₂₅** (Figure 3.4). The neat PLLA sample shows an almost featureless surface, with large microcracks forming. There was no evidence for sample plastic deformation (Figure 3.4a). On the other hand, the blends all showed the formation of evenly distributed micron-sized voids throughout the PLLA matrix, after fracture (Figure 3.4b-d). As the block polymer wt% increases, so do the size of these voids, although they remain well dispersed throughout the fracture surface (Figure 3.4). There was no evidence for any remaining polymer particles in the voids. These data are indicative of mechanical failure by debonding and cavitation of the dispersed block polymer particles within the PLLA matrix. The data also suggest the toughened PLLA samples show shear yielding prior to failure (Figure 3.3a and Figure 3.4).^{10,17} It is proposed that once these samples reach a critical tensile strain, the block polymer particles cavitate from the matrix, which creates voids around them, reducing shear yielding energy and promoting matrix (PLLA) plastic deformation. In this way, the block polymers help prevent strain localisation and mitigate crack propagation and mechanical failure.^{10,17} The blend samples fail by PLLA plastic deformation, which is observed by increases to both sample elongation at break and tensile toughness (Figure 3.3a).^{10,17} Examining photographs of the optimum sample, **[P13₂₅-PLLA₂₃]₁₅**, before and after tensile mechanical testing, shows that the transparent samples (before) turn white in the gauge region upon deformation (after) (Figure 3.3b). This stress whitening observation is consistent with the SEM data and with the formation of micron-sized cavities in PLLA matrix.^{15,16}

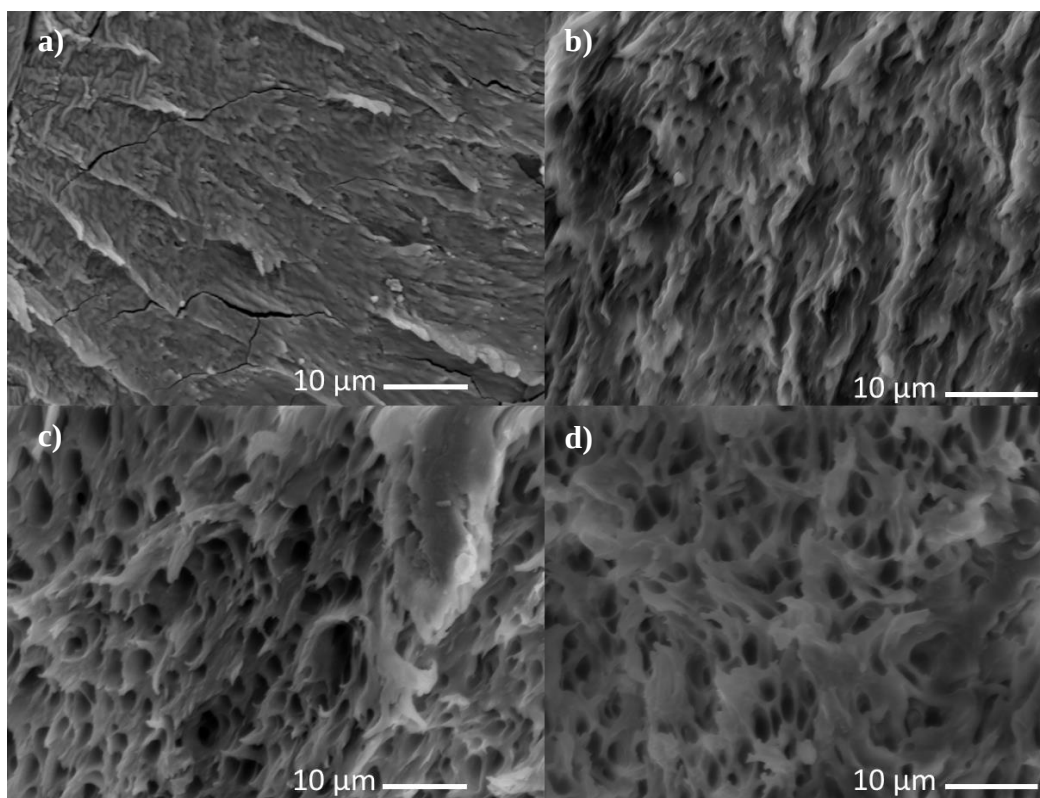


Figure 3.4: SEM images of the fracture surfaces for (a) neat **PLLA**, (b) **[P13₂₅-PLLA₂₃]_{7.5}**, (c) **[P13₂₅-PLLA₂₃]₁₅** and (d) **[P13₂₅-PLLA₂₃]₂₅** after tensile failure (sample magnification illustrated).

As a control experiment, a perfectly alternating (**AB**) polyester-*b*-PLLA (**P13'₂₅-PLLA₂₆**) was prepared using catalyst **2** (**[2]** = 10 mM in neat 1 mL epoxide, **[DGA]** and **[LA]** = 0.25 M) (Section S8.3.2.7). A 15 wt% PLLA blend was prepared (**[P13'₂₅-PLLA₂₆]₁₅**), and compared to the lead poly(ester-*alt*-ether) blend **[P13₂₅-PLLA₂₃]₁₅**. Interestingly, the thermal and mechanical properties of these blends were extremely similar (Table S8.3.6 and Figure S8.3.83). Negligible change was observed in the T_g , T_m or χ . Mechanically, the polyester-based blend was weaker, there was a drop in modulus (0.5 GPa) and strength (9 MPa), although just as ductile, the ϵ_B remained high at 25.1 ± 2.5 %. Subsequently, the U_T decreased from 10.8 ± 2.2 MJ m⁻³ to 9.1 ± 2.5 MJ m⁻³ when using the polyester additive (Table S8.3.6 and Figure S8.3.83).

3.5.3 Other Block Polymer Compositions in PLLA Blends

By exploiting the controlled polymerisation catalysis, two further systematic series of block polymers, **[P13_x-PLLA_y]₁₅** (Table 3.1, entries 6-12), were prepared and used to make PLLA blends (Table 3.2, entries 9, 12-17). Each of the series were designed to be compared against the lead sample from the first series, i.e. **[P13₂₅-PLLA₂₃]₁₅**. In both series, the samples were blended with PLLA at 15 wt% (the optimum additive amount from the first series) and

thermal and tensile mechanical characterisation conducted (Figures S8.3.69-70, 72 and 74 for thermal and Figure S8.3.79 for mechanical data). In the second blend series, the block polymer samples feature either variable **PLLA** DP (from 25-125), with fixed **P13** DP (of 25), or variable **P13** DP (from 8-25), with fixed **PLLA** DP (of 25) (i.e. changing x or y, Table 3.1, entries 6-10; Table 3.2, entries 9, 12-15). The second series was designed to understand the optimum relative chain lengths for the poly(ester-*alt*-ether) or PLLA blocks in the additives. Either increasing the PLLA DP or decreasing the **P13** DP led to blends which showed less effective toughening compared with the lead sample, **[P13₂₅-PLLA₂₃]₁₅** (Table 3.2, entry 9 vs. 12-15). Plots of the tensile toughness vs. the block polymer DP values, help to illustrate these trends (Figure 3.5a). The PLLA blend toughness increases as the DP of the poly(ester-*alt*-ether) increases, reaching a maximum at **P13** DP = 25, and, it decreases as the PLLA block increases, having its maximum also at **PLLA** DP = 23 (Figure 3.5a). These trends highlight the importance of appropriate block polymer design, and, are rationalised by the ability to access the optimum block polymer phase-separated micro-structures in the PLLA matrix, in order to deliver the greatest toughening. This rationale is consistent with the SEM data on the different sample fracture surfaces (Figure 3.6). These showed less prominent matrix deformation and cavitation of the dispersed phase as the relative DP of PLLA increased or the relative DP of **P13** decreased (Figure 3.6).

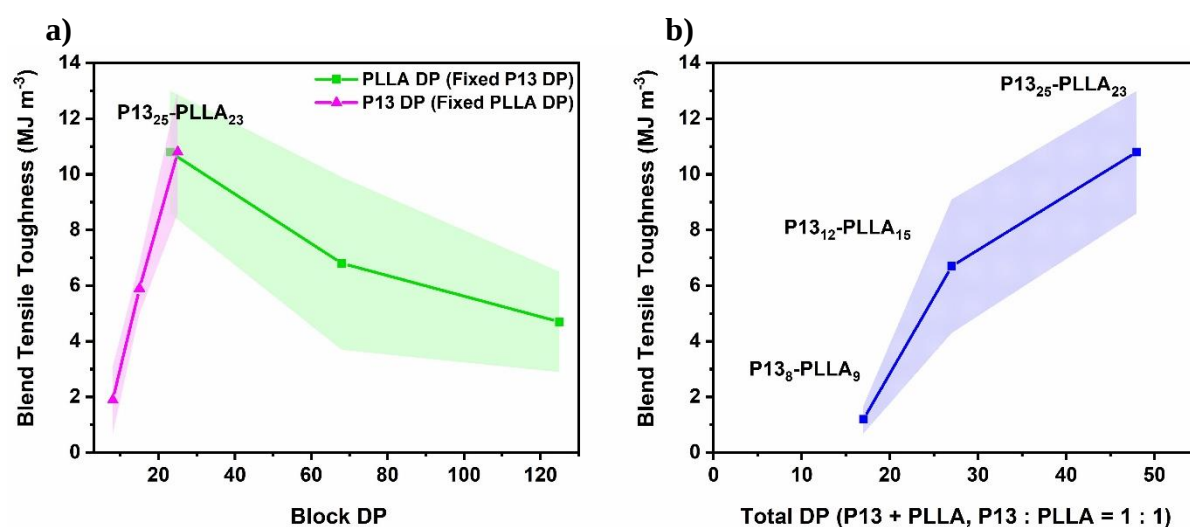


Figure 3.5: Plots to illustrate the influences of block polymer composition (a) and block polymer DP (b) on PLLA toughening (see Table 3.2 for numerical data and errors, and Figure S8.3.79 for stress vs strain data). Blends of the composition **[P13_x-PLLA_y]₁₅** were compared, at a fixed 15 wt% copolymer loading. a) Plot showing tensile toughening vs. block polymer composition for two series of polymers, the first making changes to DP **PLLA** (green squares), while fixing DP **P13**, and the second changing DP **P13** (pink triangles), while fixing DP **PLLA**. b) A plot showing PLLA toughening vs. overall DP of the block polymer (DP of **P13** (x) + DP of **PLLA** (y)), where x : y = 1 : 1, while x + y was increased (each data point is the average of 5 tensile measurements). The error range is shown by the shaded regions.

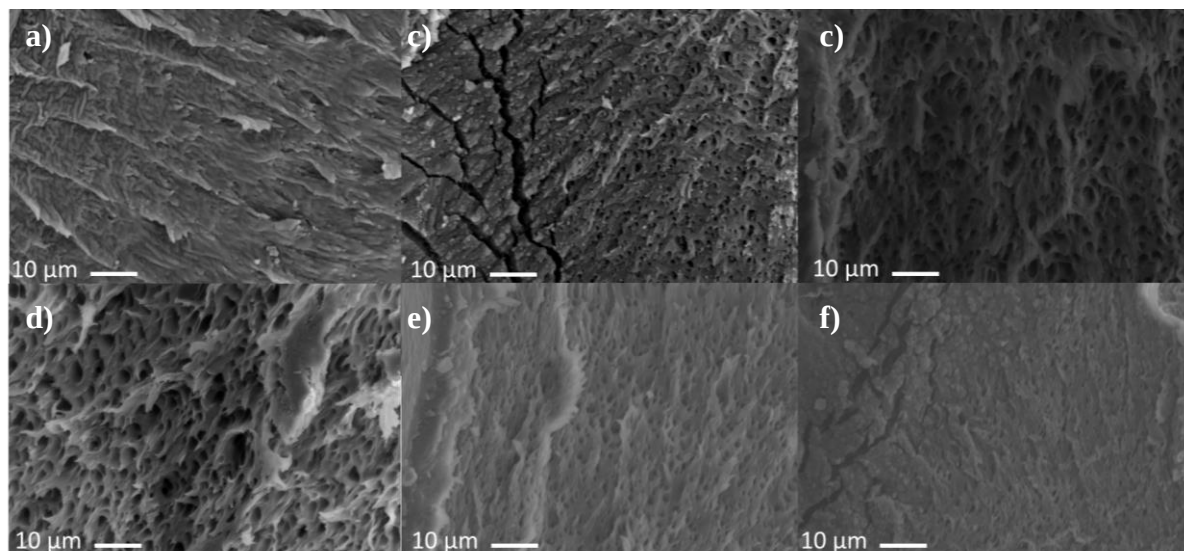


Figure 3.6: SEM images of the fracture surfaces (perpendicular to the direction of uniaxial tension stress) for a) neat PLLA, b) [P138-PLLA₂₆]₁₅, c) [P13₁₅-PLLA₂₇]₁₅, d) [P13₂₅-PLLA₂₃]₁₅, e) [P13₂₅-PLLA₆₈]₁₅ and f) [P13₂₅-PLLA₁₂₅]₁₅, after tensile failure (sample magnification illustrated).

In the third series, the two blocks had the same relative (molar) composition (1:1 or $w_{\text{PLLA}} = 0.3$), but variable DP values (for both blocks) from 8-25 (variable $x + y$, Table 3.1, entries 6, 11, 12; Table 3.2, entries 9, 16, 17). In the case of the two block polymers with lower DP values (lower overall molecular weight), the resulting blends showed inferior tensile mechanical properties compared to [P13₂₅-PLLA₂₃]₁₅ (Table 3.2, entries 9, 16, 17, Figure 3.b, Figure S8.3.79). This finding is tentatively attributed to lower molecular weight samples showing partial miscibility, including between the elastomer block (P13) and the PLLA matrix. This notion is supported by the thermal analyses which show lower glass transition temperatures for the blends vs. neat PLLA (Table 3.2, entries 1 vs. 16, 17). Overall, plots of tensile toughness vs block polymer DP showed a maximum for the best sample from series 1, i.e. [P13₂₅-PLLA₂₃]₁₅.

3.5.4 PLLA Blend Dynamic Mechanical Analyses and Melt Rheology

Dynamic Mechanical Thermal Analyses (DMTA) were undertaken to monitor the evolution of the PLLA blend storage modulus (E'), loss modulus (E'') and the damping factor ($\tan \delta$) with temperature (Figure 3.7, Figure S8.3.77, Table S8.3.4). In these experiments the most effective blend, [P13₂₅-PLLA₂₃]₁₅, was compared against the neat PLLA sample, under equivalent conditions (Table 3.2, entry 1 vs. 9). The toughened PLLA blend ([P13₂₅-PLLA₂₃]₁₅) shows a plateau in its storage modulus (E'), from 30-55 °C, at a value which is only slightly higher for neat PLLA (2.9 vs 2.8 GPa, Figure 3.7a). Both samples show similar trends in E' behaviour from 30-120 °C. Over these temperatures the samples are firstly in the glassy region, pass through the glass transition and transform into the rubbery plateau. The

similarity of the data suggests there is broadly equivalent mechanical stability between the toughened PLLA blend and pure PLLA (Figure 3.7a). Considering the trends in $\tan \delta$, the relative magnitude of the damping factor was larger for **[P13₂₅-PLLA₂₃]₁₅** compared with PLLA. Comparing the data for the lead blend sample, against other compositions, show it has the largest magnitude of damping (Figure 3.7b, S8.3.77). It is suggested, in the literature, that the relative magnitude of the $\tan \delta$ peak correlates with the materials' ability to dissipate energy.^{30,31} Thus, the DMA findings further substantiate the experimental evidence that the blend **[P13₂₅-PLLA₂₃]₁₅** shows the optimum balance between tensile strength (48.7 MPa) and elongation (24.5 %).

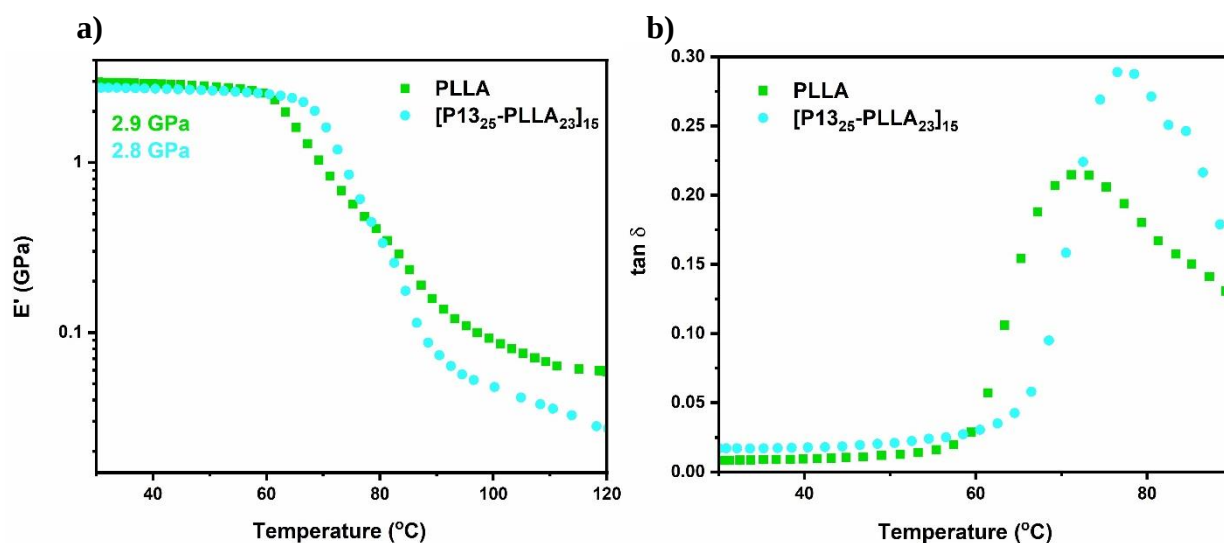


Figure 3.7: Illustrates characterization data for lead sample **[P13₂₅-PLLA₂₃]₁₅** by dynamic thermal mechanical analyses. a and b) Plots contrast Storage modulus and $\tan \delta$ (damping factors), measured by DMTA, vs. temperature for PLLA (green) and **[P13₂₅-PLLA₂₃]₁₅** (blue). Samples were heated from 30-170 °C, at a rate of 2 °C min⁻¹, with a frequency of 1 Hz, 0.001 N pre-load force and 0.015 % strain amplitude.

Rheology frequency sweeps were performed using neat PLLA and **[P13₂₅-PLLA₂₃]₁₅** at 170 °C, i.e. above the PLLA melting temperature (Figure 3.8a, b and Figure S8.3.76). The rheological $\tan \delta$ decreases linearly with frequency for neat PLLA, suggesting it flows as a viscous liquid (Figure 3.8a). On the other hand, **[P13₂₅-PLLA₂₃]₁₅** blend behaves similarly to PLLA at higher frequencies (i.e. it increases steadily with decreasing frequency) but, unlike neat PLLA, it reaches a plateau in $\tan \delta$ at low frequencies (Figure 3.8a). The plateau behaviour arises due to an increase in the elastic component of the shear modulus (G'), compared to neat PLLA, and is tentatively attributed to block polymer-PLLA interfacial interactions.³⁰

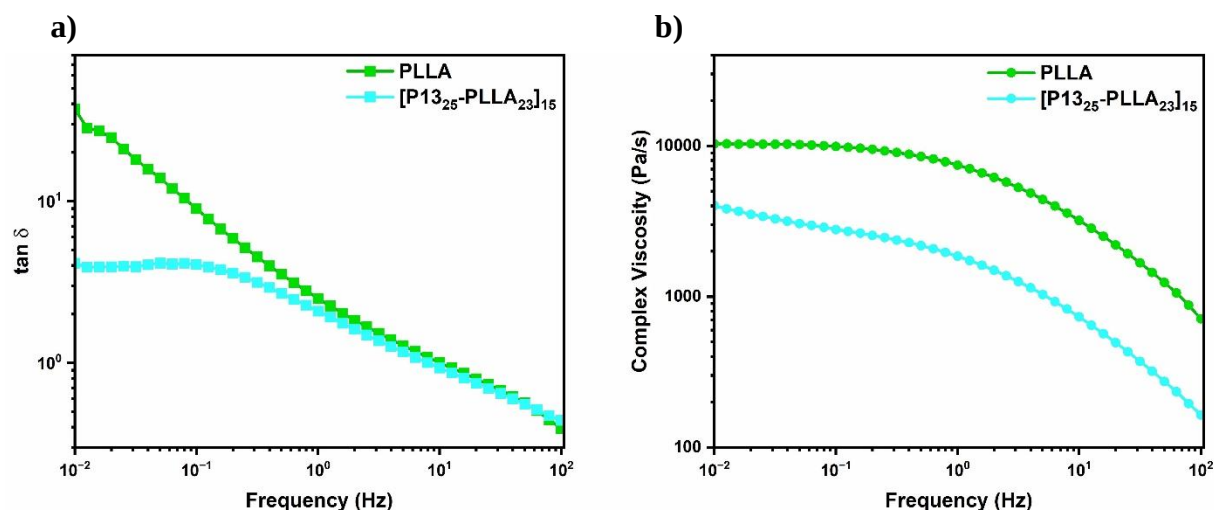


Figure 3.8: Illustrates characterization data for lead sample **[P13₂₅-PLLA₂₃]₁₅** by rheology. a and b) Plots show rheological $\tan \delta$ and complex viscosity (η^*) vs. frequency for PLLA (green) and **[P13₂₅-PLLA₂₃]₁₅** (blue). Samples were analysed by melt rheology (170 °C), conducted in the linear viscoelastic region: 1% amplitude strain, 100-0.01 Hz.

Neat PLLA shows complex viscosity (η^*) vs. frequency behaviour which is indicative of a non-Newtonian fluid; it reaches a plateau at lower frequencies (10,300 Pa s⁻¹ at 10⁻² Hz) and decreases at higher frequency, indicative of shear thinning behaviour (Figure 3.8b).³² **[P13₂₅-PLLA₂₃]₁₅** behaves similarly, but shows lower overall values for the complex viscosity (3,789 Pa s⁻¹ at 10⁻² Hz) and it shows a lower frequency onset of shear-thinning (Figure 3.8b). The blend sample shows both lower melt viscosity and early onset shear thinning vs. neat PLLA, and, these properties may help reduce process energy input, but must be optimised for specific processing and application methods.

3.6 PLLA Blend End-of-Life Options

As well as being bio-sourced, the (bio)degradability of PLLA is a major benefit.¹ There is also growing interest in recycling PLLA, particularly chemically recycling it to its monomer, L-LA, for applications where wastes are retrievable.^{3,34} Given the promising behaviour of the block polymers in toughening commercial PLLA, it's important to establish their influences, if any, over PLLA chemical recycling to monomer and/or biodegradation. Prior development of PLLA toughening agents did not often address experiments to test end-of-life recycling or biodegradation experiments, hence this aspect warrants greater research attention.^{6,10,33}

Chemical recycling of PLLA to L-LA could be important in a future circular plastic economy, helping to reduce greenhouse gas emissions, preserving the L-LA embedded energy and retaining more material value than complete biodegradation.³⁴ Recently, the Williams group reported upon a new type of catalysed PLLA recycling, conducted in the polymer melt

(130-180 °C), with nitrogen flows used to drive monomer evolution, using low loadings of Sn(Oct)₂ as the catalyst (1:1000 molar loading). Under these conditions, only the monomer L-LA was formed in very high yield, activity and purity (>99 % L-LA).³ The recycling was proposed to occur by a Sn(II) alkoxide catalysed depolymerisation process occurring from the PLLA chain-end. Given the success of this methodology using commercial PLLA samples, it was applied to a representative PLLA blend, **[P13₂₅-PLLA₂₃]₁₀** (Section S8.3.4 and chapter S7.2.12-13). First, the Sn(Oct)₂ catalyst was dispersed into the polymer blend (1:1000, solution casting films followed by solvent removal in vacuum oven). The film was heated, in a TGA-IR instrument, at 180 °C with nitrogen flow (25 mL min⁻¹). The sample mass loss vs. time data was collected (Figure 3.9b) and the effluent evaluated using IR spectroscopy (Figure S8.3.90). Over 150 mins, the blend showed 90 % mass loss and IR spectroscopy confirmed the sole product was L-LA (Figure 3.9b, S8.3.90). The sample did not undergo any further mass loss and the residual mass content (10 %) is consistent with the block polymer loading (10 wt%).

Next, the blend was subjected to laboratory scale chemical recycling, using otherwise identical conditions, but with nitrogen flow replaced by dynamic vacuum and a sublimation apparatus to collect L-LA (**[P13₂₅-PLLA₂₃]₁₀** = 128 mg, Section S8.3.4, Figure S8.3.91 and chapter S7.2.13). Once again, at this larger-scale, the highly selective and complete chemical recycling of the blend occurred, with L-LA isolated, as the sole product, in 87% yield (PLLA = 100 mg, Figure S8.3.91). The product ¹H NMR spectrum confirms the formation of 95:5 L-LA:meso-LA, which exactly matches the composition of the commercial PLLA sample (i.e. the commercial material contains ~5% meso-linkages, Figure S8.3.92). Mindful of detection limits using NMR spectroscopy, the L-LA purity, and stereochemistry, was also assessed using GC-MS (Figure S8.3.93). Both monomer characterization data suggest that the blend is efficiently chemically recycled without any L-LA epimerization. Further, in the laboratory scale experiment, the bulk PLLA was efficiently recycled and the **P13₂₅-PLLA₂₃** block copolymer was separated after the reaction, providing a future re-use option.

To test for biodegradation, *in vitro* enzyme catalysed hydrolysis reactions were conducted using (separately) samples of **P13** (poly(ester-*alt*-ether)), **P13₂₅-PLLA₂₃** block copolymer, **[P13₂₅-PLLA₂₃]₁₅** blend or semicrystalline PLLA. The biodegradation experiments all applied an esterase, *Humicola insolens* Cutinase, with samples exposed to the enzyme as a viscous liquid (**P13**), soft solid (**P13₂₅-PLLA₂₃**) or as films (**[P13₂₅-PLLA₂₃]₁₅** and PLLA). The samples were all incubated in the aqueous solutions at 37 °C, with pH controlled at 7.2 by use of phosphate buffer (Section S8.3.5 and Chapter 7.2.14). The enzyme was selected due to its

precedent in PLLA and aliphatic polyester degradations (HiC, trademark name Novozym 51032).^{35,36} Indeed, there is quite a substantial literature detailing PLLA enzymatic degradation, allowing for the commercial sample to serve as an appropriate benchmark when examining degradation chemistry of the new polymers.⁴ The extent of the biodegradations were monitored by regular aliquot analysis by HPLC, equipped with an RI detector, which was calibrated for both diglycolic acid (from **P13**) and L-lactic acid (Figures S8.3.94-96).^{35,37} In addition to the HPLC calibration, the hydrolysis fractions were collected and analysed by ESI-MS to confirm purity (chapter S7.2.14 and Figure S8.3.99).

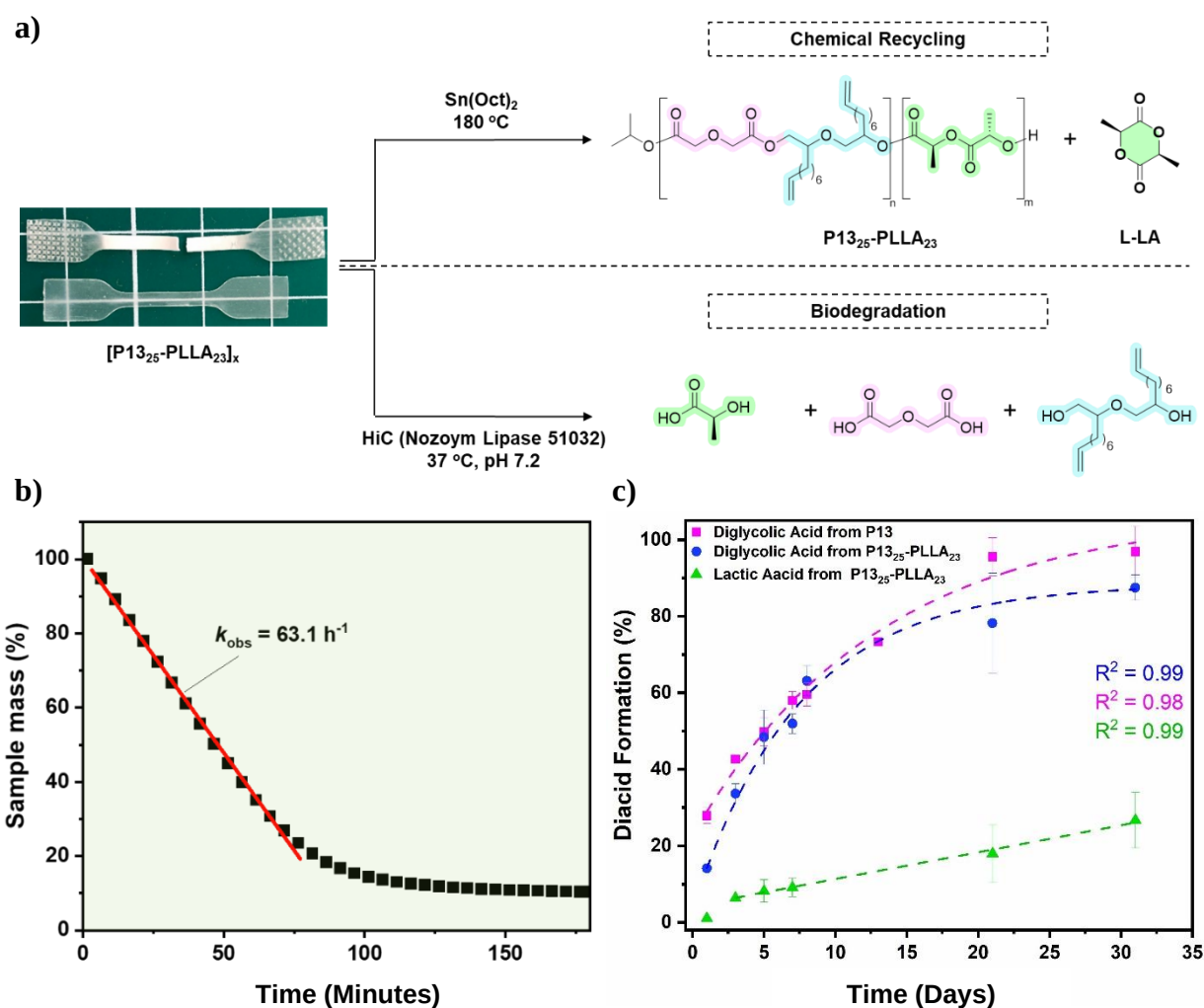


Figure 3.9: Illustrates the chemical recycling and biodegradation routes accessed by the PLLA blends and block polymers. a) Schematic illustration of the two end-of-life options for toughened PLLA; (i) selective chemical recycling to form **P13**₂₅-**PLLA**₂₃ and L-LA and (ii) enzymatic degradation (biodegradation) to form L-lactic and diglycolic acid (and diol). b) Plot showing the chemical recycling of **[P13**₂₅-**PLLA**₂₃]₁₀ by sample mass loss data vs. time. Recycling conditions: Sn(Oct)₂:Polymer, 1:1000, 180 °C, N₂ flow at 25 mL min⁻¹ (L-LA TGA-IR spectrum, Figure S8.3.90). c) Plot showing acid formation, diglycolic acid or lactic acid, vs. time for the biodegradation of **P13** and **P13**₂₅-**PLLA**₂₃. Biodegradation conditions: *Humicola insolens* Cutinase (HiC), polymer:cutinase = 1:2 (by weight), acid formation was measured by HPLC-RI detection calibrated for diglycolic acid (pink squares from **P13** and blue circles from **P13**₂₅-**PLLA**₂₃) and L-lactic acid (green triangles from **P13**₂₅-**PLLA**₂₃). Samples were incubated at 37 °C and pH 7.2, with a 0.05 M phosphate buffer. Degradation rate data are fit to exponentials (diglycolic acid) and linear fits (L-lactic acid).

The biodegradation experiments showed steady increases in the acidic degradation products, allowing for monitoring of polymer conversion vs. time data (Figure 3.9c). Over 31 days, the poly(ester-*alt*-ether) **P13** achieved 97 % degradation and the block polymer **P13**₂₅-**PLLA**₂₃ resulted in 88 % degradation of the **P13** block and 27% degradation of the PLLA block (Figure 3.9c). The presence of the ether-diol, also from the degradation of **P13** (Figure 9a), was confirmed by mass spectrometry (negative ion mode) of the dried degradation reaction (Figure S8.3.102-103). Films of [**P13**₂₅-**PLLA**₂₃]₁₅, and of neat PLLA, incubated with the enzyme under the same conditions, degraded significantly more slowly, as would be expected due to the high molecular weight PLLA, which is the majority component in both cases (Figure S8.3.100 and S8.3.101). It is well-known that PLLA molecular weight, crystallinity and film surface area all influence the relative biodegradation rates.³⁸ Given these constraints, we used the biodegradation experiments for these samples to provide qualitative evidence supporting additive (block polymer) degradability. Over 34 days, the lead blend sample [**P13**₂₅-**PLLA**₂₃]₁₅ showed ~23 % **P13** degradation, demonstrating that blending does not hinder the effective biodegradation of the block polymer additive (Figure S8.3.100).

3.7 Discussion – Comparison to Commercial Thermoplastics

This chapter presents a new series of block polymer rubber toughening additives for commercial, high molar mass PLLA. The block polymers were efficiently synthesised, using single process catalysis, from commercial monomers. They showed effective PLLA toughening, maintaining its high tensile strength, crystallinity, thermal transitions (T_g and T_m) and stiffness, whilst increasing its elongation at break and substantially toughening it. The PLLA blends are all chemically recyclable to L-lactide, with the block polymer being retained after recycling, allowing for its future re-use. The block polymer additives are also biodegradable, forming diacids and diols, as well as L-lactic acid, during enzymatic degradation.

To evaluate and contextualise the performance of these PLLA blends, it's appropriate to compare them against the leading toughend PLLA samples reported in the literature. As outlined in the introduction, there are a range of PLLA toughening approaches, but rubber/elastomer toughening is particularly promising when it delivers stable blends.^{6,10} When making comparisons, it's important to note that most prior toughening studies applied amorphous PLA/PLLA. In these cases, direct comparisons with semicrystalline PLLA are not possible, since the semi-crystalline polymer tends to show much lower elongation at break values.¹⁶ Nonetheless, it is very important to establish toughening strategies for semicrystalline

PLLA, since its commercial applications rely on its greater tensile modulus/strength (than PLA). Furthermore, when considering/evaluating PLLA as a potential substitute for current plastics, e.g. polystyrene (see later), achieving a high temperature melt is important to increase its upper service temperature. An excellent prior investigation into PLLA rubber toughening, by Bates and co-workers, applied semi-crystalline, high molecular weight PLLA, with just 5 wt% of a polyether elastomer, PEO-PBO (PEO = polyethylene oxide; PBO = polybutylene oxide).⁵ The blends showed impressive tensile strength and modulus (49 MPa and 2.9 GPa, respectively) and elongation at break at 14 %.⁵ In our work, the **P13₂₅-PLLA₂₃** block polymer is added at higher (15 wt% diblock polymer, correlating to 11 wt% **P13**) loading into high molecular weight, semi-crystalline PLLA. High strength and modulus was achieved at 48.7 MPa and 3.1 GPa, respectively, and the elongation at break values reached 25 %. In addition, it is useful that the block polymer structure delivers equivalent PLLA crystallinity (42 %), glass transition ($T_g = 63\text{ }^{\circ}\text{C}$), and melt temperatures ($T_m = 149\text{ }^{\circ}\text{C}$) to neat PLLA. Low post yield stress drop ($< 5\%$), relative to the literature (for example, those of Bates and co-workers described above, PYSD = 10-20 MPa for semicrystalline PLLA), is an important factor for potential applications as thermoplastics, maintaining higher tensile strength throughout post yield deformation. Our results are similar to the inspiring work from Bates and co-workers and, as an added benefit, our block polymers are also biodegradable.

There is a major drive to replace current commercial thermoplastics with more sustainable alternatives. PLLA shows high tensile strength and stiffness, but is very brittle; its tensile mechanical properties are perhaps most similar to polystyrene. In terms of thermal properties, PLLA has a lower glass transition temperature ($T_g = 60\text{ }^{\circ}\text{C}$) than polystyrene ($T_g = 83\text{-}104\text{ }^{\circ}\text{C}$), but unlike more common commercial atactic PS, PLLA has a melting temperature ($T_m = 150\text{-}170\text{ }^{\circ}\text{C}$, Figure 3.10).⁸ There are a range of strategies to overcome PS brittleness; amongst these, copolymerisation approaches have delivered two important other commercial polymer classes; poly(acrylonitrile-butadiene-styrene) (ABS) and high-impact polystyrene (HIPS), the latter a blend of PS, poly(butadiene) (PB) and PB-*g*-PS (or PB-*b*-PS).^{39,40} PS is a commodity polymer, produced globally on 30 Mt scale/annum, making it the fourth most produced commodity plastic, serving applications in packaging, automotive, electronics and construction, amongst others.⁴¹ To compare PLLA against various different grades of PS, ABS and HIPS, we collated commercial data-sheets and used them to construct an Ashby plot (Figure 3.11, Section S8.3.6). For example, analyses of these different data-sheets shows that

commercial PS samples show tensile strengths from 23-47 MPa but low elongation at breaks from 3-21 %.

Using the Ashby plots allows for benchmarking and comparison of the toughened PLLA tensile mechanical properties against those of currently used commercial polystyrenes (Figure 3.11a and b). Depending on the quantity of the block polymer additive used, the PLLA blends showed tensile strengths and elongations at break, which fall into the properties exhibited by either pure PS, or toughened samples like ABS/HIPS (Figure 3.11a and b). In these blends, adding 1-10 wt% of the block polymers delivers PLLA samples which are more closely aligned to high strength PS. Whilst, adding more block polymer (15-25 wt%) forms PLLA samples which align with some grades of ABS; the sample with 20 wt% is close to the properties of both ABS and HIPS (Figure 3.11a and b). Similarly, values for the tensile modulus for PLLA blends with between 1-10 wt% block polymer additive, closely matched PS (Figure 3.11b). For 15, 20 and 25 wt%, while the elongation increases to lower/middle ABS and HIPS levels, the modulus remains higher, more comparable to PS or ABS (Figure 3.11b).

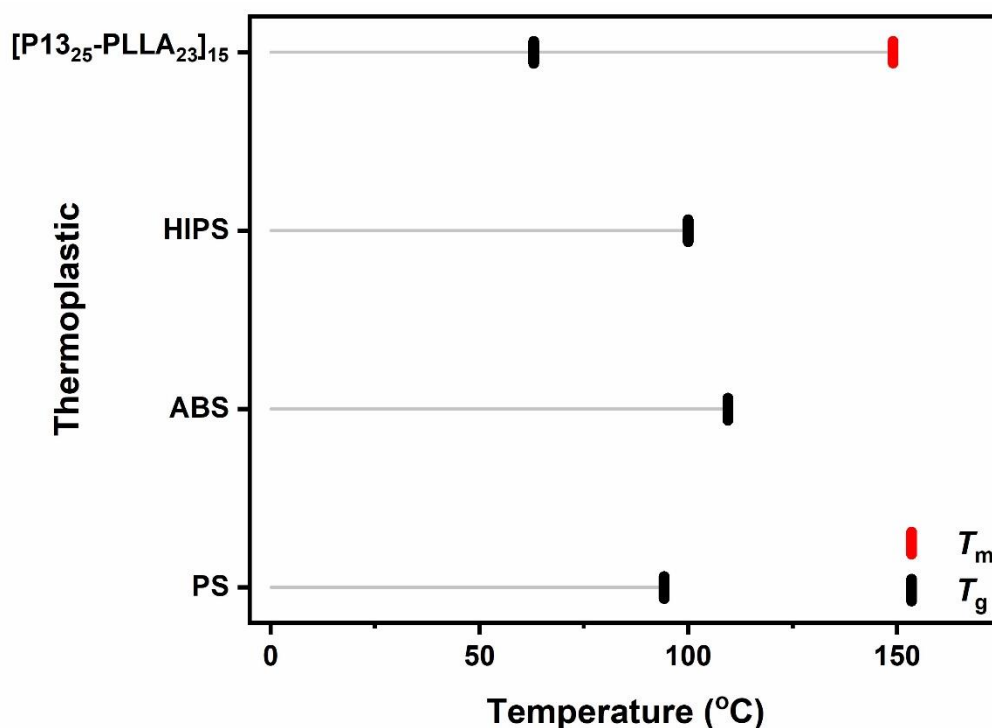


Figure 3.10: Line graph showing the upper temperature limits (service) for commercial polystyrene samples and lead PLLA samples from this work.

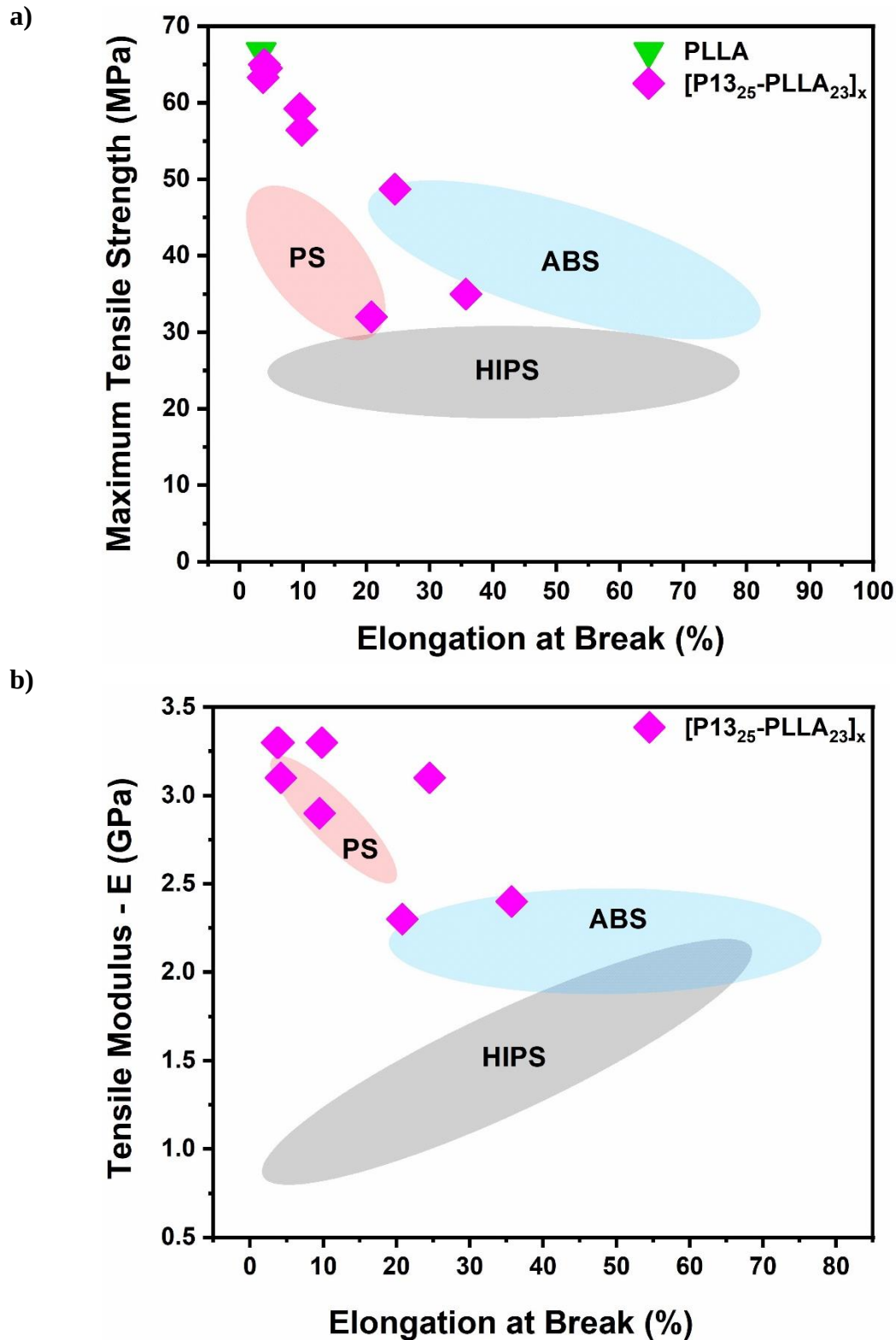


Figure 3.11: Presents plots contextualising PLLA samples in this work, with commercial thermoplastics, specifically polystyrene classes. An Ashby plot showing tensile mechanical property regions for a) tensile strength (MPa) vs. elongation at break (%) and b) Youngs' modulus (GPa) vs elongation at break (%), for polystyrene, PS (red), poly(acrylonitrile-butadiene-styrene), ABS (blue), high-impact polystyrene, HIPS (grey) and PLLA samples in this work (pink diamonds vs. green triangle for pure PLLA).

Whilst Ashby plots are very helpful in providing visual maps of property space, they inevitably risk some over-looking of other critical properties. To allow for a broader evaluation of the toughened PLLA samples, a line graph compares the high temperature service limit for these thermoplastics (Figure 3.10). The diagram helps to illustrate that for some applications, PLLA temperature stability may be an issue, e.g. PLLA T_g (63 °C) is lower than for PS (T_g = 94 °C), ABS (T_g = 110 °C) and HIPS (T_g = 100 °C, see Figure 3.10). On the other-hand, the high temperature melt of PLLA, and the **[P13₂₅-PLLA₂₃]_x** PLLA blends may be helpful in some circumstances.

One important potential future benefit to these toughened PLLA samples is their ability to undergo chemical or biological depolymerisations (biodegradation). Here, we demonstrated that **P13**, **P13₂₅-PLLA₂₃** and blends with PLLA were all enzymatically degradable using a cutinase enzyme, at 37 °C. Also, the blends were efficiently chemically recycled to L-lactide, at 180 °C and in ~2 hours, with retention of the block polymer for future re-use in blends. Naturally, such biodegradation is not feasible using PS, ABS or HIPS, nor are there equivalent low temperature, high selectivity chemical recycling approaches using these commercial plastics (and any recycling is challenging for ABS and HIPS). Therefore, for applications requiring end-life recycling and/or biodegradation, it may be appropriate to substitute existing plastics with these toughened PLLA materials.

In future, other related block polymers to those described here, should be tested to produce new materials and try to map the property (and application) space for current plastics. As shown in chapter 2, the synthetic route to these block polymers should be amenable to other commercial and bio-based monomers, like epoxides, anhydride and/or cyclic esters.²³ Another important priority is to deliver fully bio-based additives, in this regard, there is already literature outlining routes to both DGA and ED from biomass sources, which could be a useful starting point for future optimisations.^{23,42} The block polymer rubber toughening strategy should also be used, in future, to improve ductility for other bio-based (e.g. PHB) and, even, CO₂-derived plastics.

3.9 Summary and Future Work

3.9.1 Summary

Poly(ester-*alt*-ethers)-*b*-PLLA were effective as blend additives for high molecular weight, semi-crystalline, commercial poly(L-lactide) (PLLA). The block polymers were synthesised, using a catalysed one-pot process, from commercial anhydrides, epoxides and L-

lactide. The controlled polymerisations were used to make a series of well-defined block polymers, featuring systematically variable block compositions, degrees of polymerisation and chemistries. These block polymers were blended with commercial PLLA and samples evaluated using a range of thermal, tensile mechanical and rheological methods. The lead PLLA sample featured 15 wt% block polymer (11 wt% poly(ester-*alt*-ether)); it showed both high tensile modulus ($E = 3.1 \pm 0.1$ GPa) and tensile strength (48.7 ± 1.2 MPa). Importantly, it also showed greater ductility (7x higher) and tensile toughness (8x higher) compared to the commercial PLLA alone. The toughened PLLA blend retained equivalent thermal properties (T_g , T_m), crystallinity and thermal stability to PLLA. The PLLA blends were efficiently chemically recycled, using a Sn(II) catalysed process operating in the polymer melt, to produce L-LA in high conversion and selectivity. The chemical recycling process also allowed for collection of the block polymer additive, providing a future pathway for its re-use. The block polymer additive underwent complete enzymatically catalysed hydrolysis over 30 days to form diglycolic acid, diol and L-lactic acid. The PLLA blends showed thermal-mechanical properties which were similar to those of polystyrene, poly(acrylonitrile-butadiene-styrene) or even high-impact polystyrene. The combined synthesis-property-end-life recycling/degradation design approach taken in this work should be more broadly applicable, using other block polymer compositions, to a range of other bio-based and CO₂-derived plastics.

3.9.2 Future Work

Given the thermodynamic immiscibility of the elastomeric dispersed phase in the matrix PLLA, it may easily aggregate and form larger particles during blending. This may be particularly the case with the methodology used in this work, where the PLLA blends were heated above the melt and slowly cooled without stirring, to encourage semi-crystallinity. **P10** and **P13** were designed to include unsaturated moieties. A logical next step would be to graft it to the PLLA matrix, through reactive compatibilisation. In this strategy, the functional groups of the polymer can react at the interface with PLLA. This reduces the interfacial energy, allowing for more efficient dispersion of the immiscible phase, smaller particle sizes and more effective toughening.¹⁰ The cross-linking may exploit the alkene moiety, using a radical initiator to graft it onto the backbone of the PLLA chains. Modification into an epoxide (on the poly(ester-*alt*-ether) backbone) could react with the PLLA alcohol end group to form crosslinks. Installing alcohol or acid functional groups on the poly(ester-*alt*-ether) and using an epoxy end-capped PLLA would also be expected to work.¹⁰

Understanding the mechanism of deformation (crazing, shear banding, cavitation, yielding and combinations of all of these) is vital in finding ways to improve polymer blends. Bates and co-workers have pioneered a series of techniques for analysing the deformation mechanisms in both amorphous or semi-crystalline blends (particularly PLLA). They have employed SEM/TEM (including staining of the dispersed phase), 2D SAXS, WAXS and photographs, all at different points of the stress vs strain curve, to elucidate deformation mechanisms in polymer blends.^{5,16-19} Applying these imaging techniques at different stress vs strain points, e.g (i) in the linear viscoelastic region, (ii) after necking and (iii) post yield, would allow for investigation into deformation mechanisms. TEM provides information on the morphology of individual crazes or shear banding, while SAXS provides analysis of the bulk sample. For in situ 2D SAXS, the equatorial and meridional components of crazes or shear bands give rise to scattering. SAXS provides information on the behaviour of the dispersed phase, such as cavitation.^{28,43} WAXS provides information on the behaviour of crystalline domains throughout tensile measurements. Monitoring the lattice spacing as a function of strain informs upon chain shearing, orientation, rotation, elongation and/or extension of the crystalline lattice.⁵ Understanding the interplay between the dispersed phase, crystalline regions and amorphous matrix upon deformation, would be useful in these PLLA blends to improve their performance.

One important advantage of poly(ester-*alt*-ethers) ROCOP is the facile substitution of monomer combinations to provide many different chemistries (explored in chapter 2). Different anhydride, epoxide and even cyclic ether combinations could be tested to optimise performance in two different roles in this current toughening strategy; as the immiscible block, or the miscible block. It would be interesting to systematically substitute the constituents of the immiscible block, to elucidate the important properties of this in regards to toughening performance, such as viscoelasticity (shear storage and loss moduli as well as complex viscosity) and T_g . Furthermore, it has been demonstrated that the identity of the compatible block is crucial to providing large toughening effects.¹⁶ The chemistry of this block determines the interfacial energy between the dispersed phase and the matrix homopolymer, and consequently, determines the effectiveness of mixing, dispersion of the additive, particle size/shape and interparticle separation. Matrix-miscible polymers, that are not the same as the matrix (i.e. not PLLA in this case), have been shown to provide improved interfacial mixing, smaller particle sizes and enhanced toughening effects in similar PLLA blends, and, should be targeted here.¹⁶

The morphology (size and shape) and distribution of the dispersed particles can be determined by the interfacial tension, viscosity ratios, the ratio of the blend components and the processing strategy/parameters.¹⁰ In this work, on this scale, we were restricted to solvent casting and annealing from the melt. Particularly the second step (heating above the melt to anneal very slowly, without mixing to enhance crystallinity), would most likely cause accumulation of the dispersed phase to a great extent. It would be interesting to optimise the conditions of a technique such as compounding, for example with twin screw extruding and injection moulding, as one would expect much better mixing and particle distribution with controlled shear forces such as in compounders. The mold temperature could also be controlled to still maintain control over crystallinity. With knowledge of the rheological behaviour of the polymers to be blended, blending strategies could be designed to optimise the temperature and shear forces to provide optimal mixing of the blend components. For the same mixtures and quantities as used in this work, much better performing blends could be produced by focusing on the blending conditions, something we intentionally kept constant in this study to reduce the number of variables quickly getting out of hand.

The impact toughness of these samples should be studied, to provide another relevant comparison to industrial data, for which tensile toughness is less commonly reported (this is due to the large quantities of polymer required for these measurements, being more difficult in an academic setting).

PLLA has been shown to undergo physical aging, leading to mechanical embrittlement and limitations to its applications.¹⁷ Physical aging can be measured (as a function of time) by enthalpy relaxation (a T_g ‘overshoot’), creep studies, tensile mechanical studies and the range of techniques explored above.^{17,28} Studying the mechanical properties of our blends over time, would therefore be an important aspect to understand, in regards to applications of thermoplastics, and the effect of the dispersed phase on aging (i.e. vs standard PLLA).

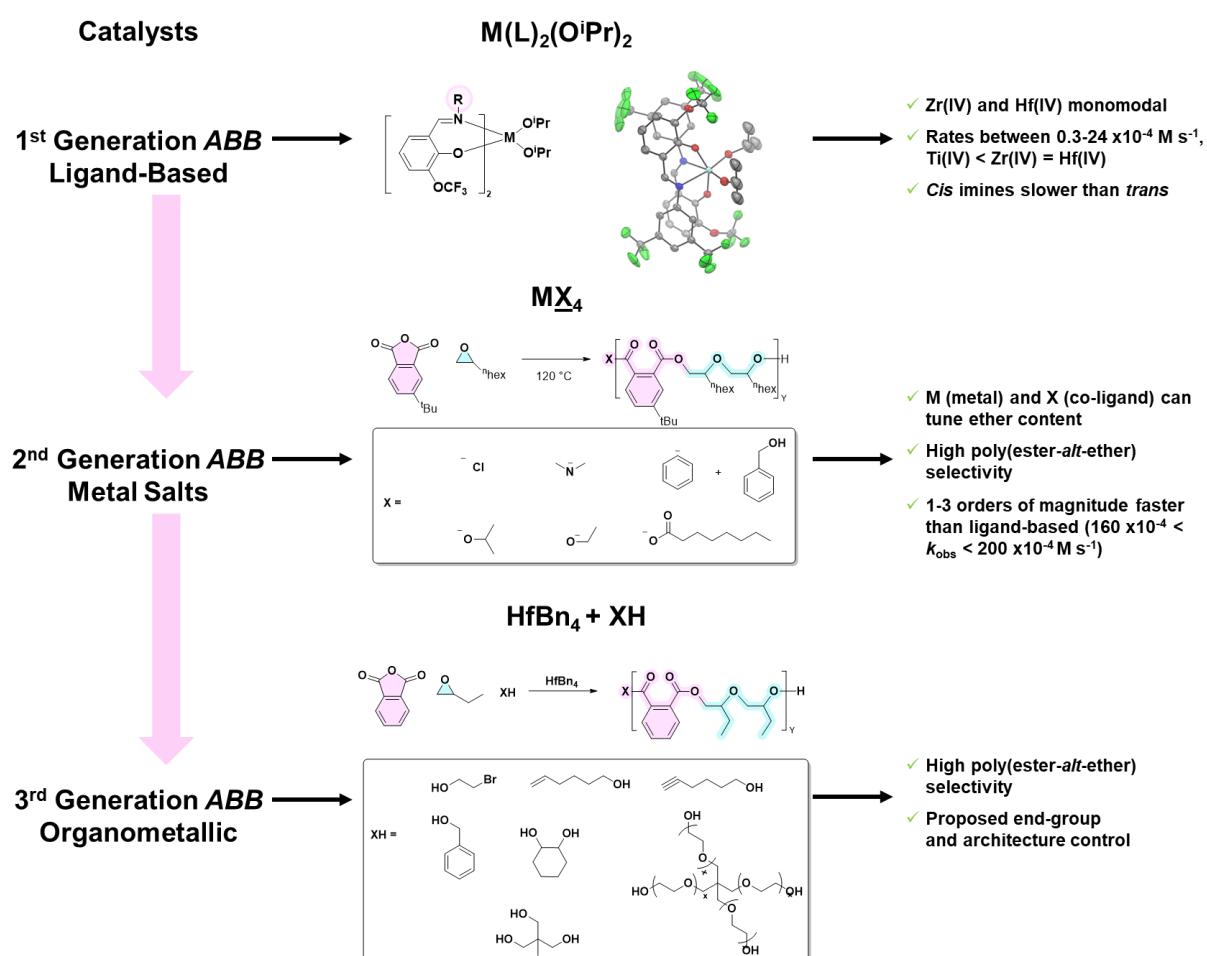
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CHAPTER 4

Chapter 4: Poly(ester-*alt*-ether) Catalysis: Improving Understanding and Scope



4.1 Introduction

To this point, only a single catalyst has been reported for selective poly(ester-*alt*-ether) synthesis (Catalyst **1**, Figure 4.1). Catalyst **1**, with a $\text{Zr}(\text{L1})_2(\text{O}^i\text{Pr})_2$ structure, is highly selective for poly(ester-*alt*-ether) linkage incorporation, can operate selectively with a wide range of monomers (chapter 2) and at acceptable rates (k_{obs} at 50 °C for the PA/BO anhydride/epoxide combination = $11.7 \times 10^{-5} \text{ M s}^{-1}$).^{1,2} Moreover, catalyst **1** can be used to make block copolymers of poly(ester-*alt*-ethers), by either sequential addition or switch catalysis (proven with L-lactide in chapter 3). Although promising, there are currently some important limitations to this catalysis. Firstly, molar masses achieved (M_n) without compromising polymer molar mass distribution (Đ) are restricted to $\sim 10 \text{ kg mol}^{-1}$ (monomer dependant). Synthetic yields of catalyst **1** are also low (22 % with recrystallisation). Furthermore, given the current catalyst framework, $\text{Zr}(\text{L1})_2(\text{O}^i\text{Pr})_2$, the co-ligands (O^iPr) that initiate polymerisation, are coordinated to the catalyst. This can impose restrictions on the molar masses that can be obtained with controlled molar mass distributions. This also restricts the catalyst solubility, the functionality of end-groups and control over polymer architecture, without choice over the initiating species. Selectivity and rate are two fundamentally important aspects of catalysis, although, for commercialisation and up-scaling of chemistries, other important properties of a catalyst to consider are; cost, ease of synthesis (yield), tolerance and ability to provide chemists with functional and creative synthetic options.

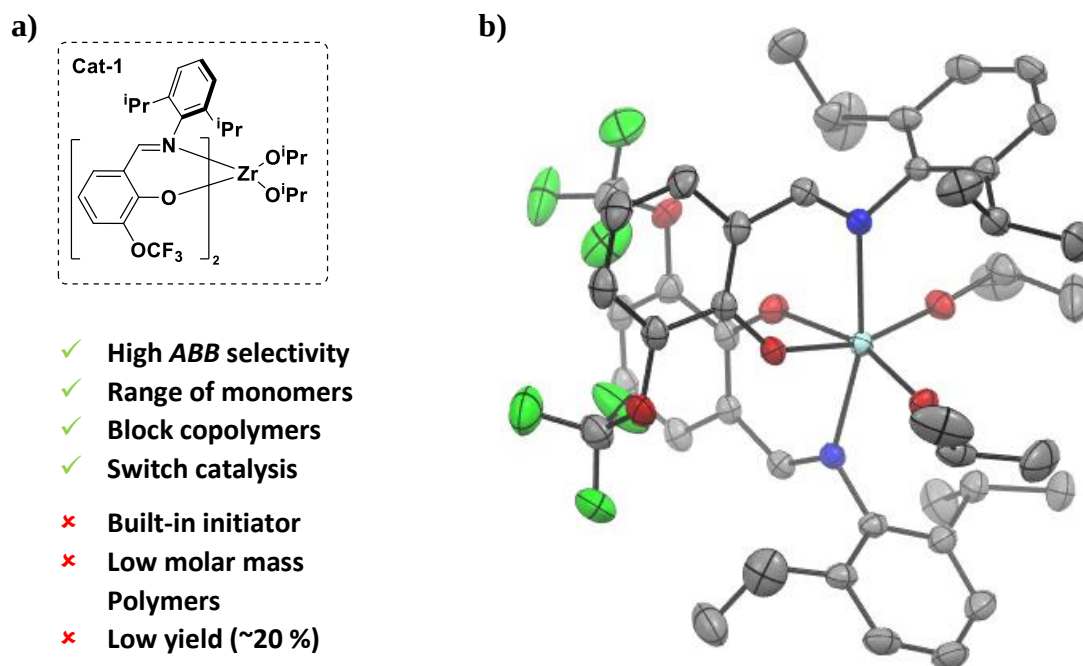


Figure 4.1: Molecular structure of $\text{Zr}(\text{L1})_2(\text{O}^i\text{Pr})_2$ (catalyst **1** from chapters 2 and 3) a) schematic representation and b) from single-crystal X-ray diffraction; thermal ellipsoids presented at 50% probability and H-atoms omitted for clarity (atom colour scheme: Zr (light blue), O (red), N (blue), C (grayscale/black), and F (green)).

The original kinetic investigations conducted using catalyst **1**, PA and BO, found that both the catalyst and epoxide had a first order dependence on concentration, while anhydride was zero order.¹ Iso-propoxide was demonstrated to initiate polymerisation by ring-opening of the anhydride, leading to a proposed Zr-carboxylate species (species I, Figure 4.2) resting state. The first ring opening of epoxide was hypothesised to be rate determining, resulting in a Zr-alkoxide intermediate (species II, Figure 4.2). It was proposed that this Zr-alkoxide intermediate rapidly ring-opened the second equivalent of epoxide (species III, Figure 4.2), which then subsequently rapidly ring-opened the anhydride, reforming the carboxylate intermediate (species I, Figure 4.2).¹

A major question to be answered at this point, was why selectivity for poly(ester-*alt*-ether) linkages, making **ABB** polymers, was so high and so consistent (the ratio of anhydride:epoxide not changing as the reaction progresses)? Why do two epoxides insert consecutively? Recent work from our group, exploring the mechanism through DFT, has suggested that the reaction may proceed through a preorganised oxonium species, coordinated to the Zr(IV), formed from two epoxides (Figure 4.3). These studies found that the activation energy for the insertion of the first alkoxide intermediate (species II, Figure 4.2) into an anhydride, which would form an **AB** polyester linkage, was lower in energy than its insertion into another epoxide (proposed to form species III, Figure 4.2), which would form an **ABB** polymer. It was found that the insertion of the carboxylate intermediate (species I, Figure 4.2) into the epoxide to form an alkoxide intermediate (step 2, Figure 4.2), has a higher energy than its insertion into an oxonium species (step 4, Figure 4.3). Furthermore, the insertion of another epoxide into the oxonium, had a higher activation energy than the insertion of an anhydride into the oxonium (step 1, Figure 4.3). The DFT calculations suggest the oxonium mechanism is more likely to be occurring and are consistent with experimental data. The calculated Gibbs free energy for the transition state ($\Delta G^\ddagger$) is in close agreement with experimentally obtained values.

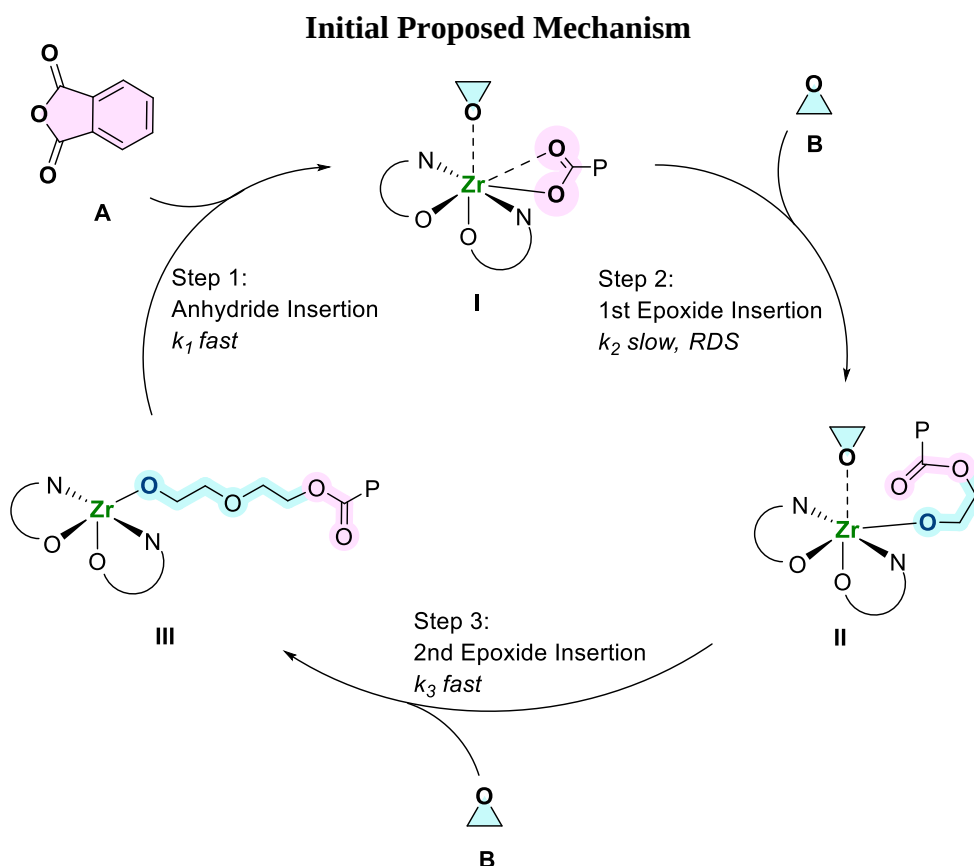


Figure 4.2: Schematic representation of the initial proposed mechanism for poly(ester-*alt*-ether) catalysis, derived from the experimentally obtained rate law.¹ P = the growing polymer chain. RDS = rate determining step.

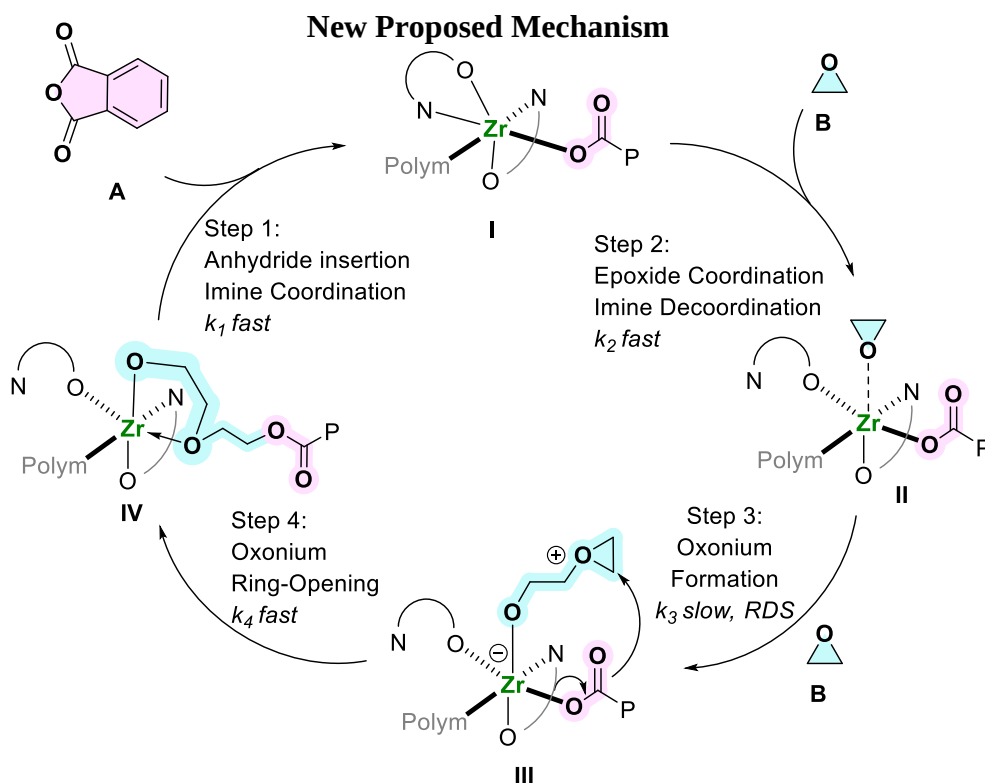


Figure 4.3: Schematic representation of the new proposed mechanism for poly(ester-*alt*-ether) catalysis, following computational work completed in the group. P = the growing polymer chain.

Furthermore, $\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$ (used to make the catalyst) was tested in catalysis with tBuPA and OO. It produced a poly(ester-*alt*-ether), with high selectivity (>90 %) and at rates an order of magnitude faster than catalyst **1**, $\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$ $k_{\text{obs}} = 102.47 \times 10^{-4} \text{ M s}^{-1}$, **1** $k_{\text{obs}} = 24.0 \times 10^{-4} \text{ M s}^{-1}$, at 120 °C, respectively. This exciting result prompted a collaborative investigation into the catalysis, addressed in the second part of this chapter. An evaluation of d^0 metal iso-propoxide/ethoxide salts ($\text{M}(\text{O}^i\text{Pr})_x(\text{OEt})_x$), by Dr Ryan Kerr, showed that $\text{Sc}(\text{O}^i\text{Pr})_3$, $\text{Y}(\text{O}^i\text{Pr})_3$, $\text{La}(\text{O}^i\text{Pr})_3$, $\text{Pr}(\text{O}^i\text{Pr})_3$, $\text{Ti}(\text{O}^i\text{Pr})_4$, $\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$, $\text{Hf}(\text{O}^i\text{Pr})_4(\text{O}^i\text{Pr})$, $\text{Nb}(\text{OEt})_5$ and $\text{Ta}(\text{OEt})_5$ are selective for **ABB** insertion, with selectivity ranging from 10-100 %. The rates are comparable to/faster than catalyst **1** ($k_{\text{obs}} = 0.38 \times 10^{-4}$ to $170.33 \times 10^{-4} \text{ M s}^{-1}$ at 120 °C for tBuPA and OO). A linear trend was observed between the reaction selectivity and the metal ion hydrolysis constant ($\text{p}K_h$) (Figure 4.4). It was rationalised by a lower $\text{p}K_h$ favouring **ABB** selectivity, while higher $\text{p}K_h$ favours **AB** selectivity (esters). This finding may help to explain why poly(ester-*alt*-ethers) have not been seen before, as the metals commonly used for polyester ROCOP tend to have higher $\text{p}K_h$ values (Figure 4.4).^{3,4} The work also provides a means to enable variable ether linkages, providing tuneable polymer thermal and mechanical properties, as well as degradability.

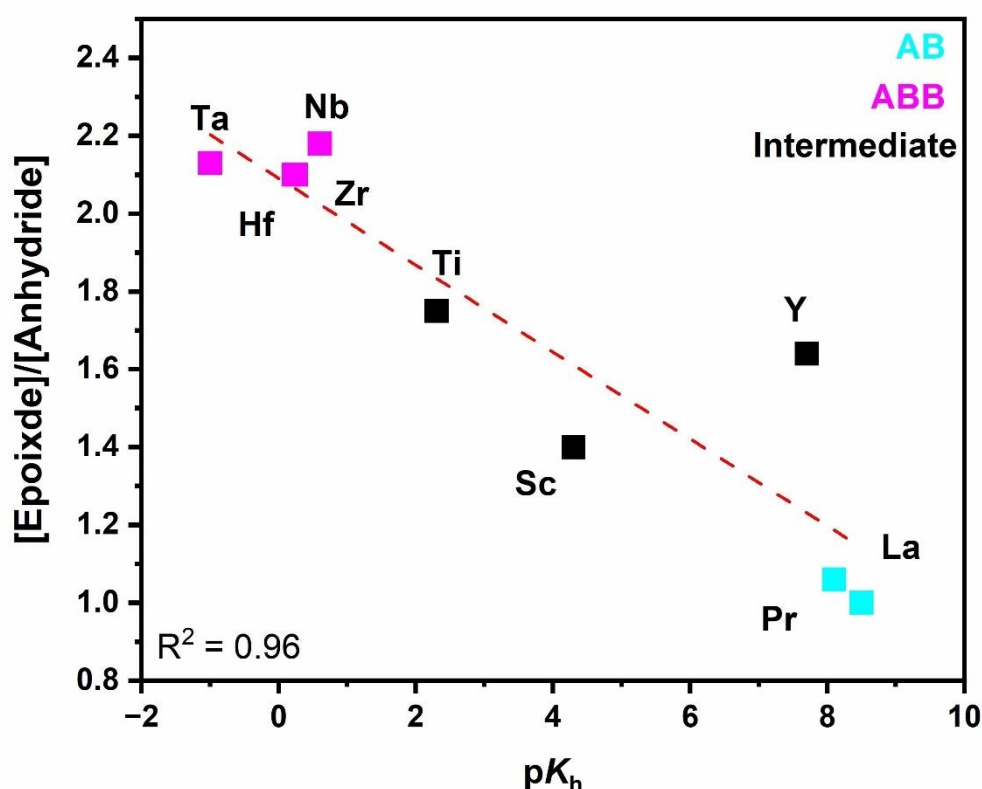


Figure 4.4: Relationship between hydrolysis constant ($\text{p}K_h$) and the epoxide equivalents enchainned per anhydride ($[\text{epoxide}]/[\text{anhydride}]$) by $d^0 \text{M}(\text{O}^i\text{Pr})_x(\text{OEt})_x$ metal salts (not performed by the author). Note that $[\text{epoxide}]/[\text{anhydride}] \sim 2$ for selective poly(ester-*alt*-ether) linkage incorporation (Zr, Hf, Ta, Nb), and, = 1 for polyester (La, Pr).

4.2 Aims

The two key goals addressed here are;

- 1) Improve our understanding of the catalysis; the effects of Group(IV) metals and ligands (and co-ligands) on the **ABB** selectivity and rate.
- 2) Improve the catalysis; widen the functionality of polymers and their potential applications.

The first series of investigations all apply ligand **L2** with Group(IV) metals; Ti(IV), Zr(IV) and Hf(IV), to explore the role of the metal in catalysis. Next, systematic changes to the ligand are undertaken and, in each case, the selectivity, rate and molar mass distributions are determined. The polymerisations in this section are all monitored by DSC, a powerful tool to monitor changes to heat flow, and hence, assess polymerisation rates. All measurements are repeated in triplicate and compared to more conventional methods to ensure reproducibility.

Next, commercially available, un-purified Group(IV) salts are analysed for selectively for **ABB**, rate and control of polymer molar mass distribution. The **Zr(IV)X** salts used are X = (OⁱPr)₄(HOⁱPr), (OEt)₄, (Oct)₄, (Cl)₄, (NMe₂)₄, (Bn)₄ and (Bn)₄ + (HOBn).

Finally, commercially available (un-purified) organometallic catalysts (**Zr/HfBn₄**) are targeted to provide control of the end-group chemistry and polymer architecture.

4.3 ML₂(OⁱPr)₂ Catalyst Structure

Group(IV) metals, with the ligand **L2**, were targeted, forming **Ti(L2)₂(OⁱPr)₂**, **Zr(L2)₂(OⁱPr)₂** and **Hf(L2)₂(OⁱPr)₂**. The cations Ti(IV), Zr(IV) and Hf(IV) were chosen because they are in the same oxidation state, although, differ in their ionic radii and other properties such as pK_a. In this regard, Ti(IV) is markedly different to Hf(IV) and Zr(IV), which are quite similar in these respects. Next, fixing the metal as Zr(IV), a series of three ligand variants were prepared, changing the electronic nature of the 4-position chemical moiety (**L3**, **L4** and **L5**, Figure 4.5), forming the complexes **Zr(L3)₂(OⁱPr)₂**, **Zr(L4)₂(OⁱPr)₂** and **Zr(L5)₂(OⁱPr)₂** (Figure 4.5). The electron withdrawing 4-fluorophenyl variant (**L3**) as well as the electron donating 4-methoxyphenyl (**L4**) and 4-methylphenyl (**L5**) variants were compared. The previously explored **Zr(L1)₂(OⁱPr)₂** (catalyst **1**) was used as a reference (Figure 4.5).^{1,2}

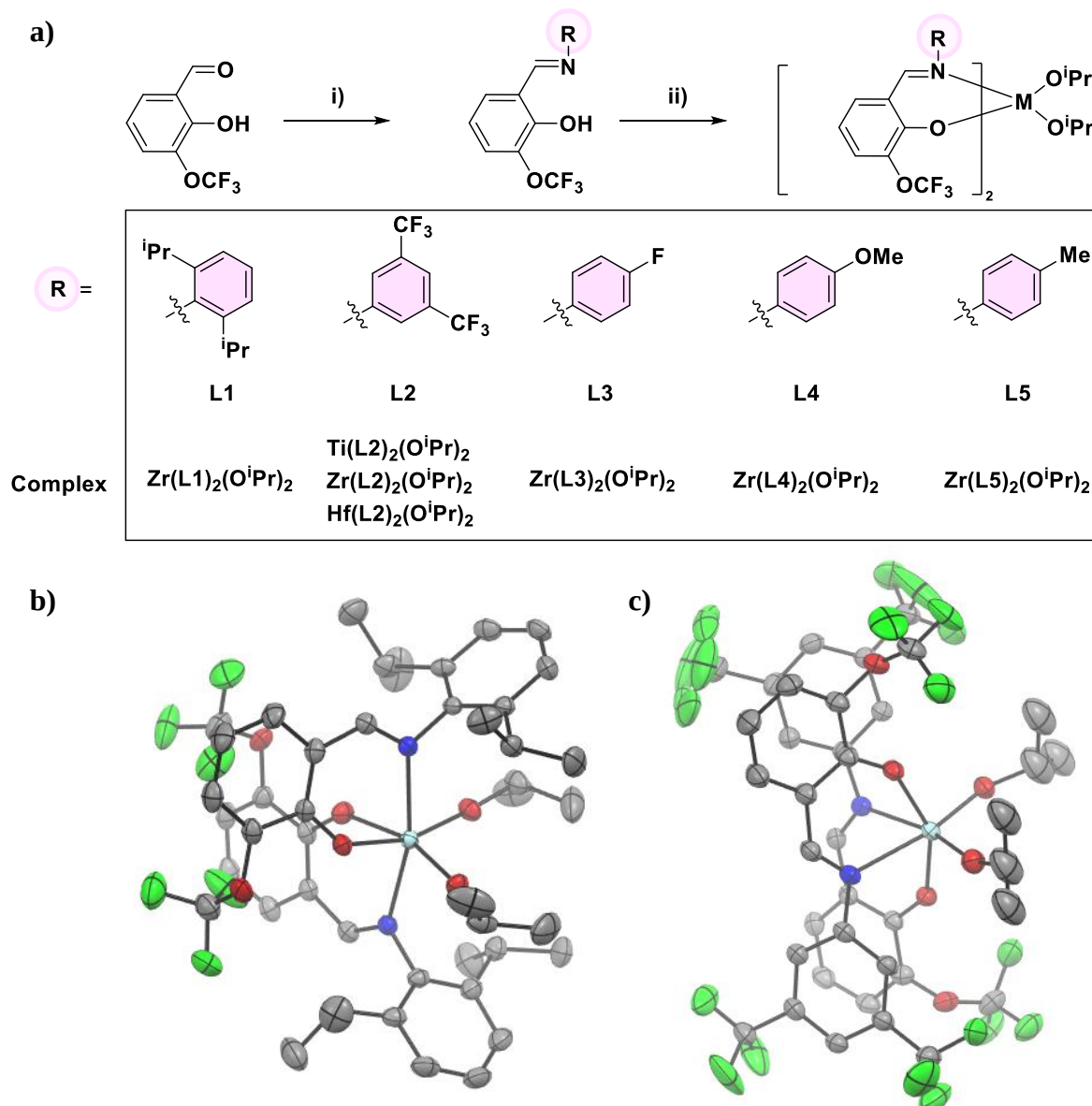


Figure 4.5: a) Synthesis of a range of complexes of the form $M(L)_2(O^iPr)_2$. i) 1 : 1 aldehyde : aniline, formic acid, reflux 18 h. ii) 2 : 1 L : $M(O^iPr)_4$, in toluene, at 40 °C, for 24 h. Molecular structure of b) $Zr(L1)_2(O^iPr)_2$ and c) $Zr(L2)_2(O^iPr)_2$ from single-crystal X-ray diffraction, demonstrating the *trans*- and *cis*-position imine nitrogen coordination respectively; thermal ellipsoids presented at 50% probability and H-atoms omitted for clarity (atom colour scheme: Zr (light blue), O (red), N (blue), C (grayscale/black), and F (green)).

The catalysts were synthesised by analogous procedures to those reported for catalyst **1** (section S7.3.3).¹ As an example, the synthesis and characterisation of $Zr(L2)_2(O^iPr)_2$ will be shown here, while full characterisation of the others can be found in the supplementary chapter (S8.4.1). The ligands were synthesised by the Schiff-base condensation of 2-hydroxy-3-(trifluoromethoxy)benzaldehyde with the corresponding aniline and a catalytic amount of acetic acid (step I in Figure 4.5a, Figure 4.6 for ¹H NMR of **L2**). The metal complexes, bearing alkoxide co-ligands, were synthesised by reacting two equivalents of **L2** with either $[Ti(O^iPr)_4]$, $[Zr(O^iPr)_4(HO^iPr)]$ or $[Hf(O^iPr)_4(HO^iPr)]$, in toluene, at 40 °C, for 24 h. The complexes were

isolated in 22-30% yield, after recrystallisation from a hexane/THF mixture. The catalysts were characterised by ^1H , ^{13}C and ^{19}F NMR spectroscopy (section S8.4.1), and, where possible, by single-crystal X-ray diffraction (section S8.4.8). The complex formation was confirmed by the disappearance of the ligand phenol resonance (δ_{H} : 12.97 ppm) and the shift in the imine resonances (δ_{H} : 8.71 to 8.05 ppm, Figure 4.6 and 4.7). The $\text{Zr}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ structure was further confirmed by 1:1 integration of the isopropoxide methine resonance to the imine resonance (Figure 4.7, signals 14 and 7 respectively). ^{19}F NMR spectroscopy showed two signals (59 ppm, $-\text{OCF}_3$ and 63 ppm, $-\text{CF}_3$), corresponding to two F environments (Figure 4.8). The $-\text{OCF}_3$ group is important in producing bis-ligand complexes.¹

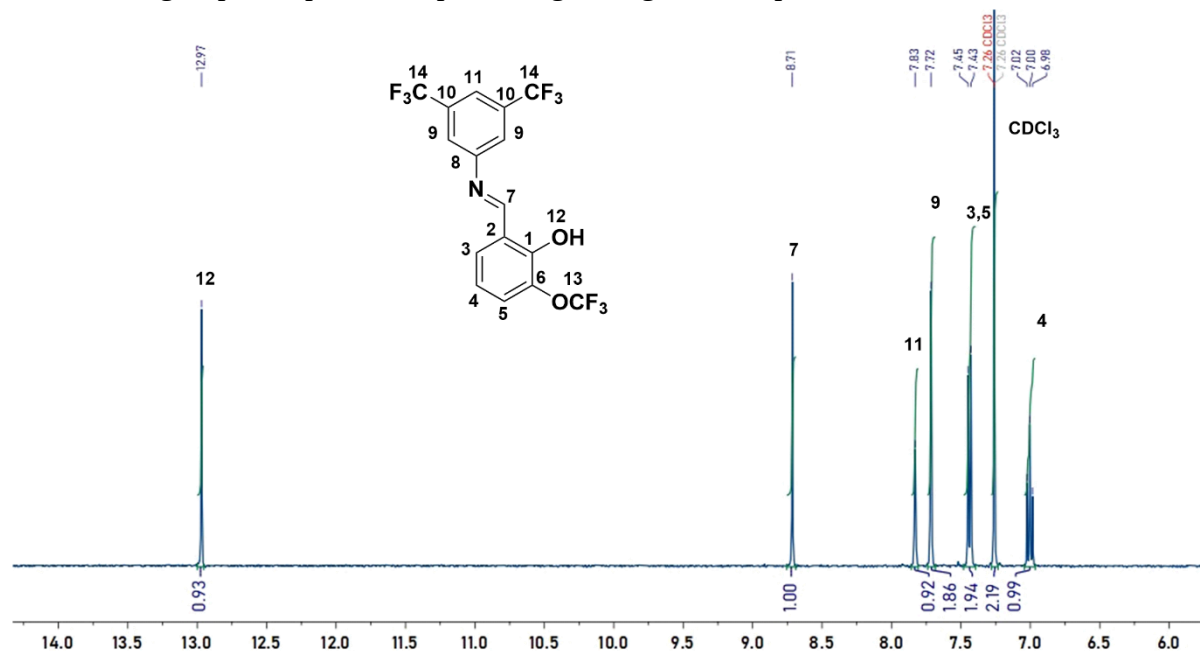


Figure 4.6: ^1H NMR spectrum of **L2** (400 MHz, CDCl_3 , with assignments).

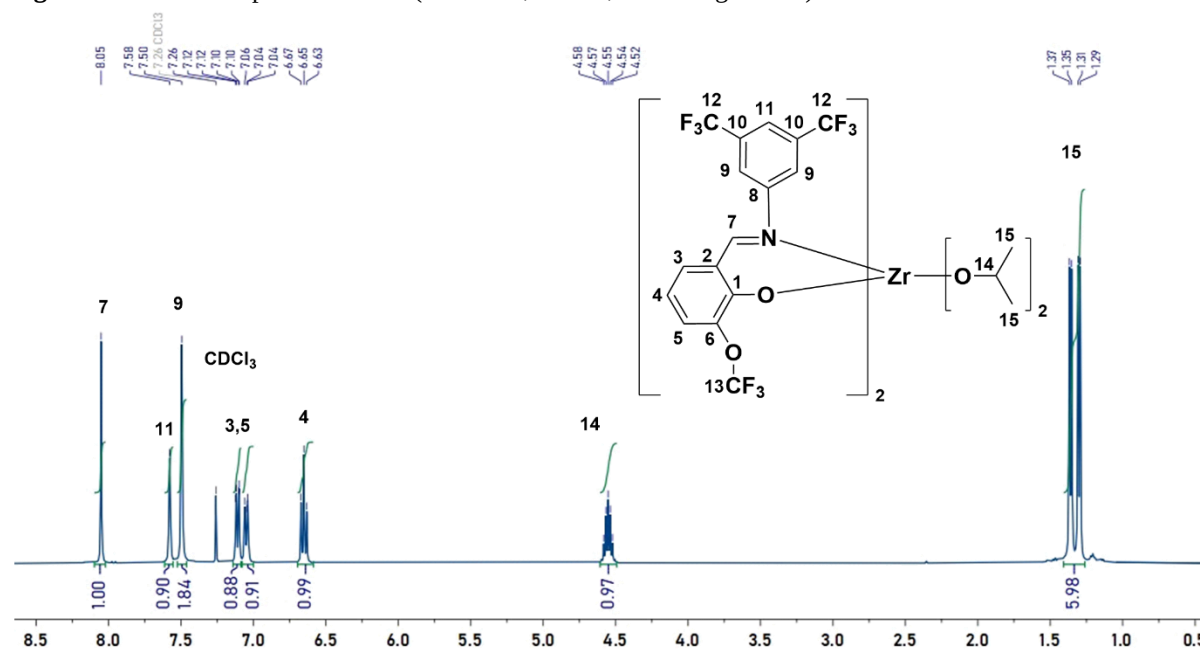


Figure 4.7: ^1H NMR spectrum of $\text{Zr}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3 , with assignments).

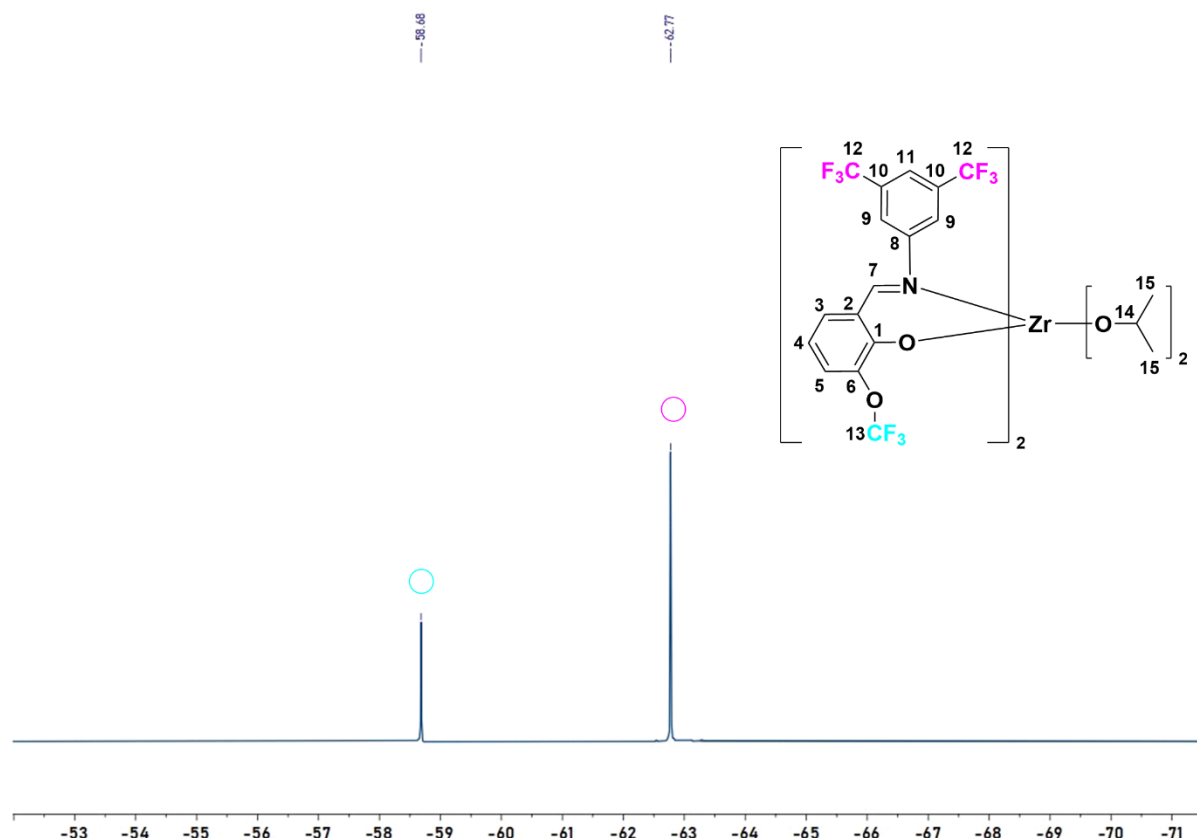


Figure 4.8: ^{19}F NMR spectrum of $\text{Zr}(\text{L2})_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3 , with assignments).

Single crystals for analysis were grown by recrystallisation in a THF/hexane mixture, at $-30\text{ }^\circ\text{C}$, to produce pale-yellow crystals (see section S7.2.16 and S7.3.3 for experimental details and Tables S8.4.1 for crystallographic details). The crystal structures demonstrated an important difference between the new catalysts (Figure 4.5b and c). The previously reported structure of $\text{Zr}(\text{L1})_2(\text{O}^i\text{Pr})_2$ (catalyst **1**), contains two imine nitrogens *trans* to one another (N-M-N angle of 167.02 ° , Figure 4.5b).¹ The isopropoxide co-ligands occupied mutually *cis* coordination sites ($\text{O-Zr-O} = 98.5\text{ }^\circ$). These alkoxide groups are the sites occupied by the growing polymer(s). Crystal structures were obtained for $\text{Ti}(\text{L2})_2(\text{O}^i\text{Pr})_2$, $\text{Zr}(\text{L2})_2(\text{O}^i\text{Pr})_2$, $\text{Hf}(\text{L2})_2(\text{O}^i\text{Pr})_2$ and $\text{Zr}(\text{L4})_2(\text{O}^i\text{Pr})_2$. All complexes show *cis*-coordinated nitrogens (N-M-N angle of $76\text{--}84\text{ }^\circ$, Figure 4.5c).

Poly(ester-*alt*-ether) (**ABB**) linkages are a special condition of the case AB_n , an ester-ether linkage, for which $n = 2$. So far, in this thesis, n has been ~ 2 , as 1 : 2 anhydride : epoxide selectivity (**ABB**) has been almost perfect to this point. It is this ester-ether linkage that is quantified by ^1H NMR spectroscopy, using the methine ester protons (Figure 4.9b and c). The value of n is then determined by the equivalents of DP anhydride : epoxide. In this chapter, to aid the discussion different catalysts, some of which have poor selectivity for ester-ether over

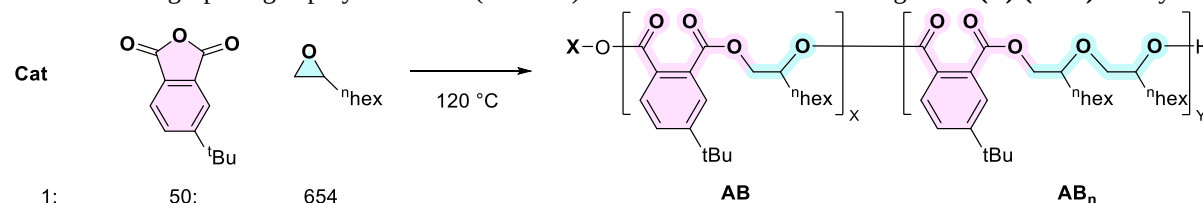
polyester, what has been often referred to as **ABB** selectivity (poly(ester-*alt*-ether), may be described as **AB_n**. This is to allow the discussion of different amounts of polyether linkages for different catalysts (although, the additional epoxide content still remains constant throughout reaction). The ratio of **AB** polyester linkages (X in Figure 4.9c) and **AB_n** poly(ester-ether) linkages (Y in figure 4.9c) were assessed by ¹H NMR (Figure 4.9b and c). This ratio was used as the selectivity for ester-ether insertion (%) vs ester insertion.

The reaction rates in this chapter (where measured) were monitored by DSC. This allowed the reactions to be performed with small sample sizes, in an automated manner and without the need to stop the reaction to take aliquots (as per chapters 2 and 3). Traditional vial method reactions were run simultaneously, from the same stock solution, to ensure consistency between the two methods. For this reason, the anhydride, tBuPA, and epoxide, OO, were selected to ensure sufficient solubility of the anhydride in epoxide (to enable a stock solution to be made for DSC reaction), and, to provide a boiling point high enough to conduct the experiments at higher temperatures (120 °C), allowing for standard conditions to be used to compare multiple samples in a practical time-scale (Table 4.1). As an example, the reaction of **Zr(L2)₂(OⁱPr)₂**, tBuPA and OO will be shown here (Table 4.1, entry 3), and, analogous data can be found in the supplementary chapter 8 (section S8.4.2-7).

The reaction mixture was prepared in the glovebox (**[Zr(L2)₂(OⁱPr)₂]** : [tBuPA] : [OO] = 1 : 50 : 654, 1 mL OO), and kept in the freezer at -30 °C (under inert conditions). A sample (5-10 mg) of the reaction mixture was transferred to a pre-weighed (air-tight) DSC pan, weighed and analysed using DSC kinetics methods (experimental section S7.2.15). The reaction was conducted at 120 °C and the result repeated in triplicate (Figure 4.10). The conversion of monomer to polymer was monitored from the integral of the normalised heat flow (W/g) vs time (s) using the designated kinetics package TRIOS. As expected, the absolute conversion of the anhydride (tBuPA) as a function of time is linear (Figure 4.10). An observed rate constant ($k_{\text{obs}} = 5.0 \times 10^{-4} \text{ M s}^{-1}$, Table 4.1, entry 3) was calculated (between 15-80 % conversion, after conversion was normalised to [tBuPA]). The same reaction stock solution was polymerised in vials at 120 °C, with regular quenching at fixed time points followed by aliquot analysis (NMR and GPC). These methods confirmed the rates and allowed insight into selectivity (**ABB**), molar mass and dispersity as the reaction progressed. The selectivity for ester (**AB**) vs ester-ether (**AB_n**) linkages, was calculated from the ratio of the methine ester resonances (5.35 and 5.10 ppm for **AB**, X, and **AB_n**, Y, respectively, Figure 4.9b and c). The selectivity for poly(ester-*alt*-ether) was high and equivalent in both cases (96 % for the DSC

and vial methods, Table 4.1 entry 3 and Figure 4.9b and c). Molar mass distributions were narrow, with a slight high weight shouldering, and, the GPC traces of polymers produced by the two methods were very similar ($M_n = 8.3 \text{ kg mol}^{-1}$ and $\bar{D} = 1.14$ by DSC, $M_n = 7.9 \text{ kg mol}^{-1}$ and $\bar{D} = 1.18$ by vial method, Figure 4.9a and Table 4.1 entry 3). The DP of the anhydride in the polymer was assessed by ^1H NMR spectroscopy, by comparing the resonances of tBuPA and P(tBuPA) (~ 7.9 vs 7.5 ppm respectively). To measure the DP of OO epoxide, the P(tBuPA) signal was normalised and compared against the integrated ester and ether regions of the epoxide (~ 3.2 - 5.5 ppm respectively). The DP of tBuPA : OO was also equivalent for both methods, 25:50 in both cases, and therefore, $n = 2$ and the polymers had **ABB** sequences. In the subsequent discussion, all values will be determined from DSC polymerisations, unless otherwise stated.

Table 4.1: Ring-opening copolymerisation (ROCOP) of tBuPA and OO with a range of $\text{M}(\text{L})_2(\text{O}^i\text{Pr})_2$ catalysts^a.



Entry	Catalyst	DP [tBuPA] ^b : [OO] ^c	Poly(ester- alt- ether) Selectivity (X : Y) (%) ^d	M_n ($\bar{D}$) [kg mol ⁻¹] ^e	M_n (Theo) ^f	k_{obs} ($\times 10^{-4} \text{ M s}^{-1}$) ^g
1	Zr(L1) ₂ (O ⁱ Pr) ₂	25:55	97	7.7 (1.16)	12.2	24.0
2	Ti(L2) ₂ (O ⁱ Pr) ₂	25:49	89	7.2 (1.32)	11.4	0.3
3	Zr(L2) ₂ (O ⁱ Pr) ₂	25:50	96	8.3 (1.14)	11.6	5.0
4	Hf(L2) ₂ (O ⁱ Pr) ₂	25:49	98	7.1 (1.19)	11.4	5.0
5	Zr(L3) ₂ (O ⁱ Pr) ₂	25:51	94	8.4 (1.41)	11.7	1.2
6	Zr(L4) ₂ (O ⁱ Pr) ₂	25:51	92	7.9 (1.25)	11.7	2.4
7	Zr(L5) ₂ (O ⁱ Pr) ₂	25:51	90	7.0 (1.29)	11.7	3.6

^aROCOP conditions: [Cat] = 10 mM, [tBPA] = 0.5 M, OO = 1 mL, 120 °C, 0.1-6 h. ^bDP of tBPA measured by integration of aromatic resonances of tBPA (7.91-8.01 ppm) and P(tBPA) (7.34-7.84 ppm) in ^1H NMR spectra of the crude polymers (Figure S8.4.26-30, Figure 4.9b and c). ^cDetermined by the integration of ^1H NMR spectra of crude polymers against P(tBPA) (Figure S8.4.26-30, Figure 4.9b and c). ^dDetermined by integration of methine ester resonances (5.35 and 5.10 ppm for ester and ester-ether respectively). ^eDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards (Figure 4.9a). ^fTheoretical M_n are calculated from the monomer conversion data and it is assumed that both iso-propoxides initiate the reaction. ^gRate constant is the gradient of the linear fits to plots of P[tBPA] vs time. The observed rate (k_{obs}) was extracted from 15-80% conversion after normalising conversion to anhydride concentration. Average errors are determined from repeat runs (see S8.4.31 for details).

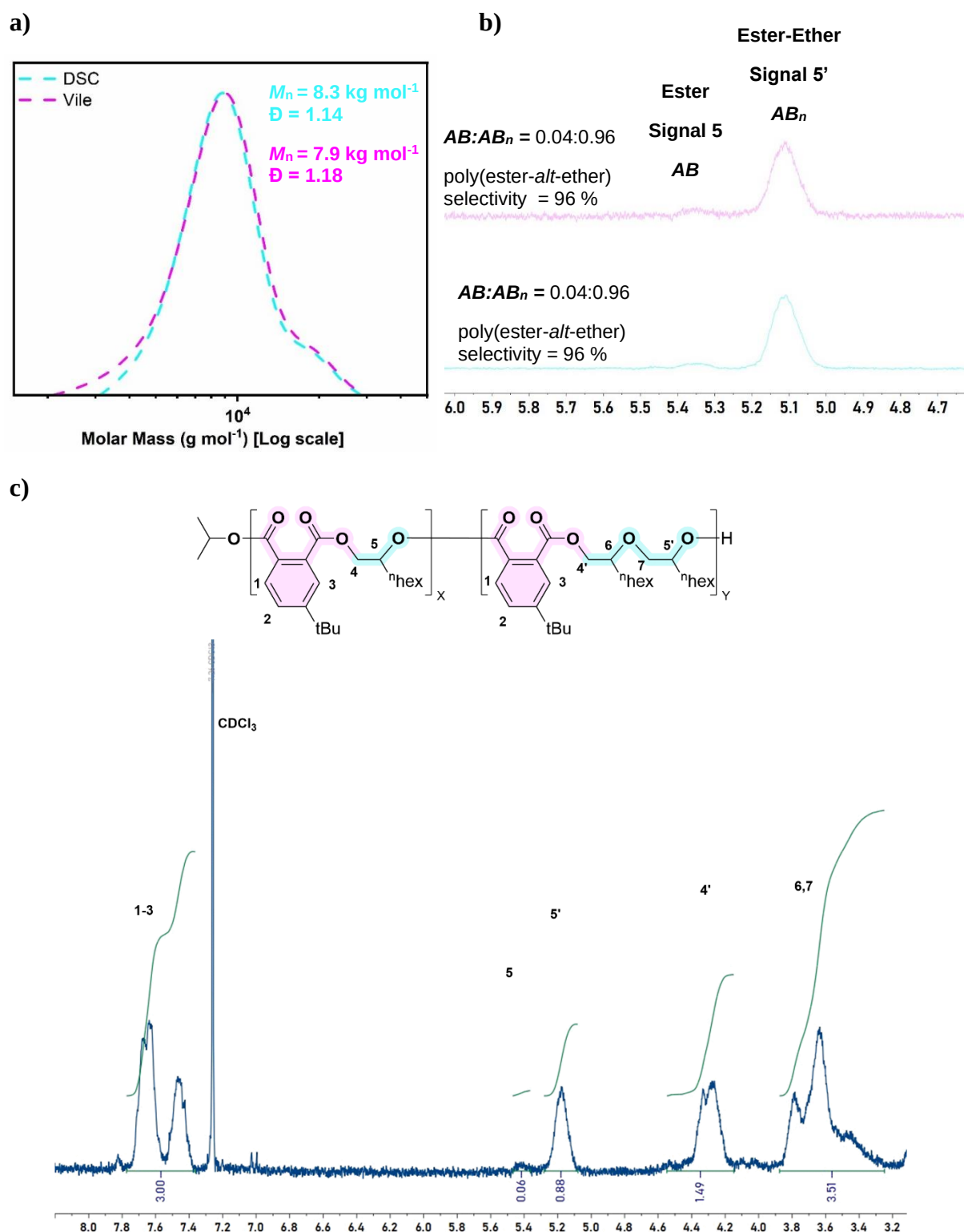


Figure 4.9: Determination of poly(ester-*alt*-ether) selectivity and molar mass distribution for the reaction of $[\text{Zr}(\text{L}2)_2(\text{O}^i\text{Pr})_2] : [\text{tBuPA}] : [\text{OO}] = 1 : 50 : 654$, 1 mL OO, on both a DSC and reaction vial scale. a) GPC chromatograms of DSC scale (blue) and reaction vial scale (pink) reactions (crude due to small DSC scale, 5–10 mg). b) ^1H NMR spectra zoomed into the methine ester region (proton signal 5 at 5.35 ppm for AB , ester, and, signal 5' at 5.10 ppm for AB_n , ester-ether), to calculate poly(ester-*alt*-ether) selectivity. c) ^1H NMR spectra taken from a DSC kinetics pan after complete reaction at 120 °C, demonstrating the integrals used for calculation of DP (from Table 4.1, entry 3, 400 MHz, CDCl_3 , with assignments). For clarity, the alkyl region of the crude spectrum is not shown (see S8.4.2 for full spectra).

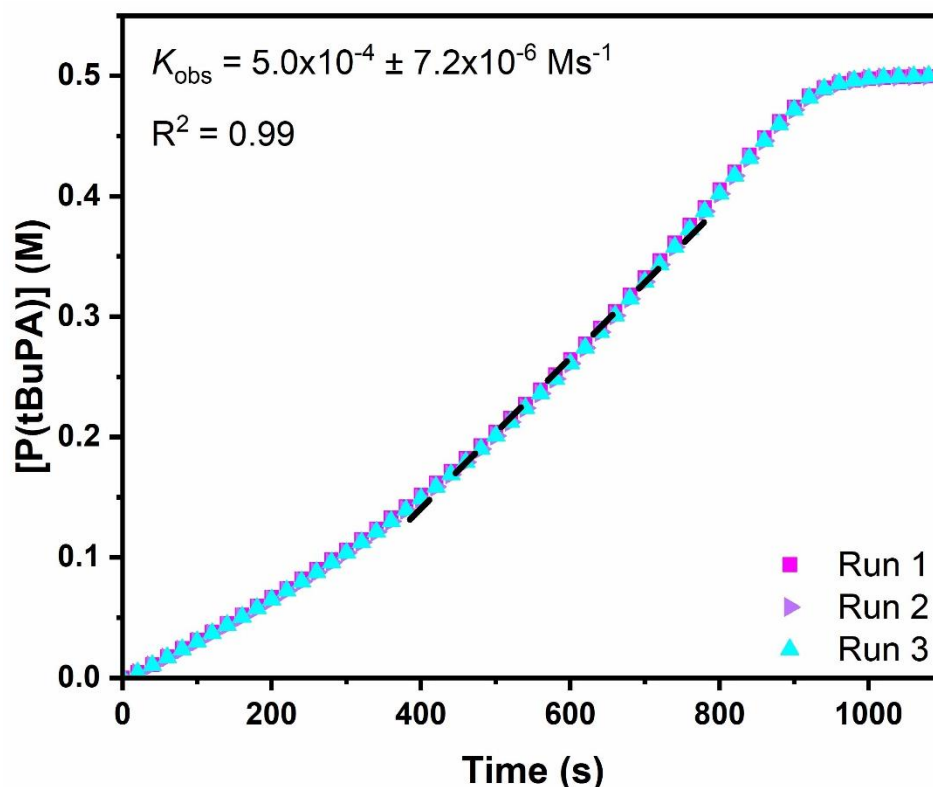


Figure 4.10: Plot of $[P(tBuPA)]$ vs time, obtained via DSC kinetic analysis, for the reaction of $[Zr(L2)_2(O^iPr)_2]$: $[tBuPA]$: $[OO] = 1 : 50 : 654$, 1 mL OO, 120 °C, Table 4.1 entry 3. The reaction was performed in triplicate. The pseudo rate coefficients, k_{obs} (M s^{-1}), were determined as the gradient of the $[tBuPA]$ vs time (s), and the data was fit between 15-80 % conversion.

4.3.1 Influence of Group(IV) Metals

Here, the role of the Group(IV) metal in the catalyst series is explored. The important figures of merit are **ABB** selectivity, poly(ester-*alt*-ether) molar mass and distribution and reaction rate (Table 4.1). Single crystal analysis demonstrated that all three complexes ($Ti(L2)_2(O^iPr)_2$, $Zr(L2)_2(O^iPr)_2$ and $Hf(L2)_2(O^iPr)_2$) are isostructural, allowing for comparison. Although it must be noted that the solid-state and solution structures can differ, and, care must be taken making structure-function conclusions. The reaction of tBuPA and OO (at 120 °C) showed excellent selectivity with the Zr(IV) and Hf(IV) complexes (96 and 98 % for $Zr(L2)_2(O^iPr)_2$ and $Hf(L2)_2(O^iPr)_2$, respectively). The selectivity for the Ti(IV) complex was 89 %. In all cases n (from **ABn**) was 1.96-2.00, resulting in very high selectivity for poly(ester-*alt*-ethers) (**ABB**). Both $Zr(L2)_2(O^iPr)_2$ and $Hf(L2)_2(O^iPr)_2$ produced polymers with narrow molar mass distributions, with $M_n = 8.3$ and 7.1 kg mol^{-1} , while $\mathcal{D} = 1.14$ and 1.19 , respectively (Table 4.1, entries 3 and 4, Figure 4.11a and b). Conversely, polymers produced using $Ti(L2)_2(O^iPr)_2$ possessed bimodal molar mass distributions and with broader dispersity ($M_n = 7.2 \text{ kg mol}^{-1}$ and $\mathcal{D} = 1.32$, Figure 4.11c). The $Zr(L2)_2(O^iPr)_2$ and $Hf(L2)_2(O^iPr)_2$

catalysts operated at almost exactly the same rate, with $k_{\text{obs}} = 5.0 \times 10^{-4} \text{ M s}^{-1}$, in both cases (Table 4.1, entries 3 and 4). This was an order of magnitude slower than the previously reported $\text{Zr}(\text{L1})_2(\text{O}^i\text{Pr})_2$, where $k_{\text{obs}} = 24.0 \times 10^{-4} \text{ M s}^{-1}$ (Table 4.1, entry 1).¹ On the other hand, the rate for $\text{Ti}(\text{L2})_2(\text{O}^i\text{Pr})_2$ is an order of magnitude slower than the Zr(IV) and Hf(IV) complexes, with $k_{\text{obs}} = 0.3 \times 10^{-4} \text{ M s}^{-1}$ (Table 4.1, entry 2).

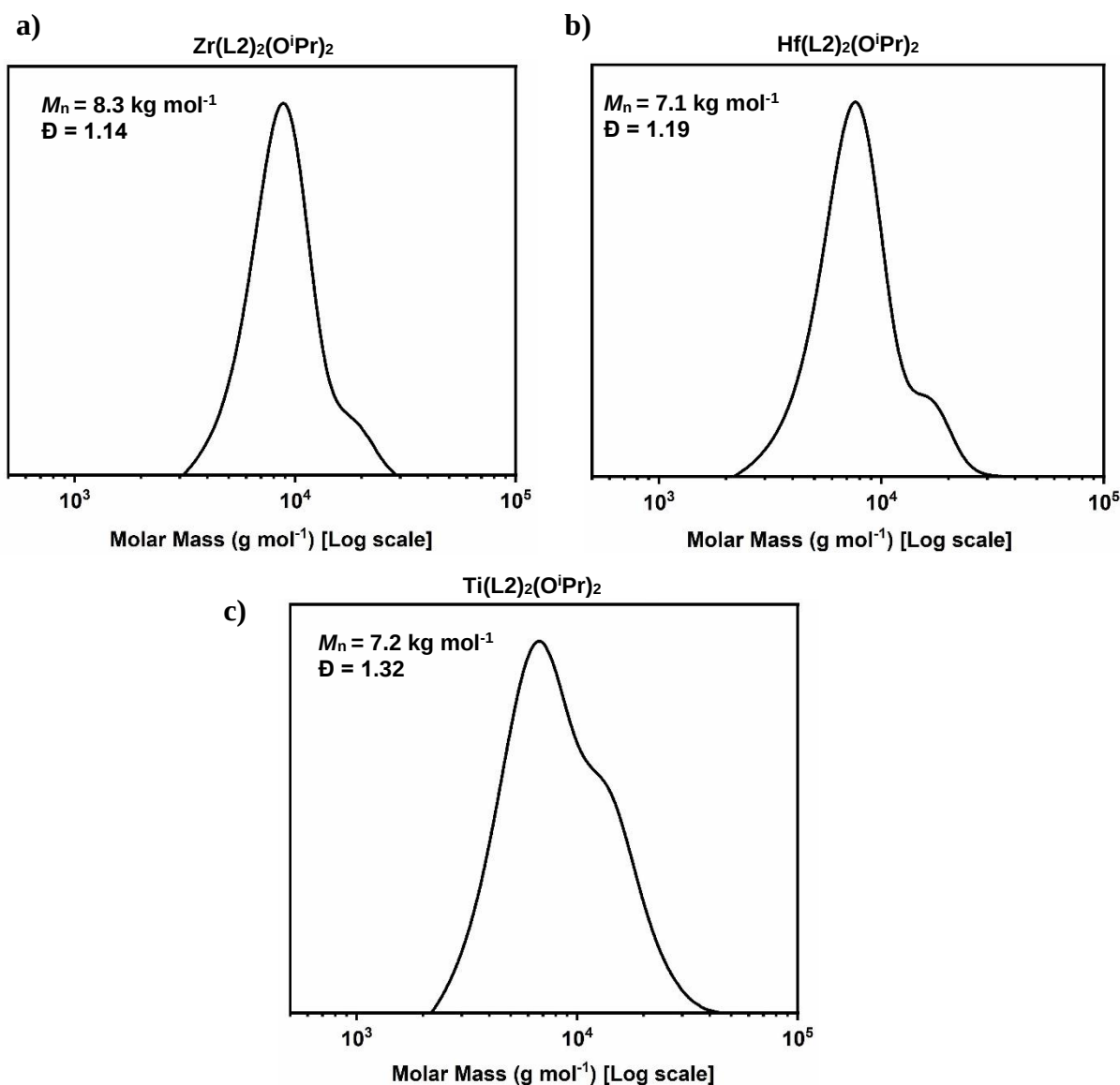


Figure 4.11: GPC chromatograms for polymers described in Table 4.1, from the reaction $[\text{M}(\text{L2})_2(\text{O}^i\text{Pr})_2] : [\text{tBuPA}] : [\text{OO}] = 1 : 50 : 654$, 1 mL OO, 120 °C, where **M** = a) Zr(IV), b) Hf(IV) and c) Ti(IV).

The slower rates observed for **L2** catalysts, could arise from a key difference in catalyst structure. All new catalysts have *cis*-N atom coordination geometries, whereas, **Zr(L1)₂(OⁱPr)₂** shows a *trans*-N geometry. The *trans*-N structure places the two *cis*-(iso-propoxide) initiating co-ligands (and therefore the propagating sites) adjacent to two imine donors (Figure 4.12a). One hypothesis, is that having *cis* propagating sites adjacent to two imine donors, reduces the energy of the transition state in the rate limiting step; the insertion of an epoxide into a carboxylate intermediate I in Figure 4.2, or, the analogous insertion of an oxonium ion, composed of two epoxides, into the carboxylate intermediate III in Figure 4.3.

The results of a series of **M(OⁱPr)_x(OEt)_x** salts (discussed above) indicated that the selectivity for poly(ester-*alt*-ether) insertion correlates strongly to the metal ion hydrolysis constant (pK_h , linearly) and the pK_a (logarithmically), but not to the ionic radii (Figure 4.4). It is proposed that the higher pK_h/pK_a of Ti(IV) may account for its reduced selectivity for poly(ester-*alt*-ether) vs Zr(IV) and Hf(IV) analogues. Further, in the **M(OⁱPr)_x(OEt)_x** series, **Ti(OⁱPr)₄** was two orders of magnitude slower than **Zr(OⁱPr)₄(HOⁱPr)** and **Hf(OⁱPr)₄(HOⁱPr)** ($k_{obs} = 102.5 \times 10^{-4}$ and $170.3 \times 10^{-4} \text{ M s}^{-1}$ for **Zr(OⁱPr)₄(HOⁱPr)** and **Hf(OⁱPr)₄(HOⁱPr)**, respectively), suggesting that the trend is consistent across other complexes.

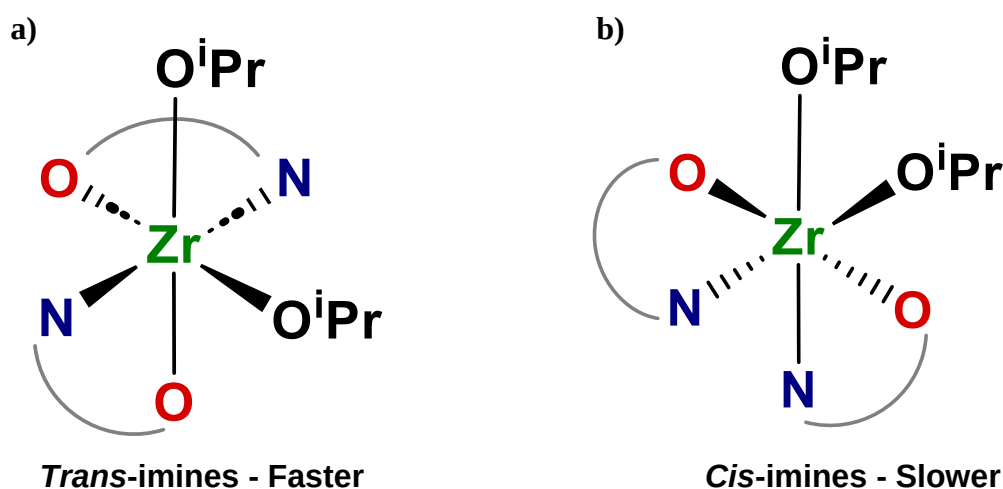


Figure 4.12: Schematic representation of the **M(L)₂(OⁱPr)₂** catalysts with a) *trans*- and b) *cis*-position imine donors.

4.3.2 Ligand Effects in the Catalysis

The effect of **L3**, **L4** and **L5** in catalysis was explored (Figure 13). Varying the electronic nature of the 4-position substituent of the imine portion of the ligand (R- in Figure 4.13), had only minor effects (if any) on selectivity, control over molar mass dispersity or reaction rate. The selectivity values were 94, 92 and 90 % for **Zr(L3)₂(OⁱPr)₂** (4-fluoro), **Zr(L4)₂(OⁱPr)₂** (4-methoxy) and **Zr(L5)₂(OⁱPr)₂** (4-methyl), respectively. The observed rate constants lie between $1.2\text{--}3.6 \times 10^{-4} \text{ M s}^{-1}$ (Table 4.1, entries 5-7). These rates are similar to those for **Zr(L2)₂(OⁱPr)₂** and **Hf(L2)₂(OⁱPr)₂** (3,5-CF₃), and, an order of magnitude slower than **Zr(L1)₂(OⁱPr)₂**. A crystal structure could only be obtained for **Zr(L4)₂(OⁱPr)₂**. This was found to possess a *cis*-N geometry, consistent with the rate hypothesis discussed above. In terms of polymer molar mass, **Zr(L4)₂(OⁱPr)₂** and **Zr(L5)₂(OⁱPr)₂** showed narrow dispersity, with slight high weight shouldering ($M_n = 7.9$ and 7.0 kg mol^{-1} and $\mathcal{D} = 1.25$ and 1.29 for **Zr(L4)₂(OⁱPr)₂** and **Zr(L5)₂(OⁱPr)₂**, respectively, Table 4.1, entries 6 and 7). Only **Zr(L3)₂(OⁱPr)₂** had a broader and more pronounced bimodality ($M_n = 7.9 \text{ kg mol}^{-1}$ and $\mathcal{D} = 1.25$, Figure 4.14). These results suggest that only the change in *cis*- to *trans*-N environments, when using **L1**, significantly effects the catalysis.

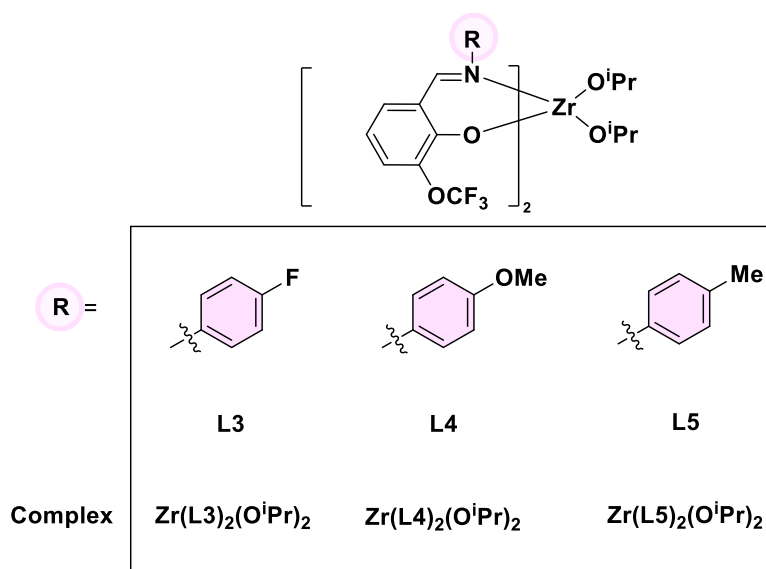


Figure 4.13: The series of complexes used in this section, of the form **Zr(L)₂(OⁱPr)₂**, changing the identity of **L** (the R-group).

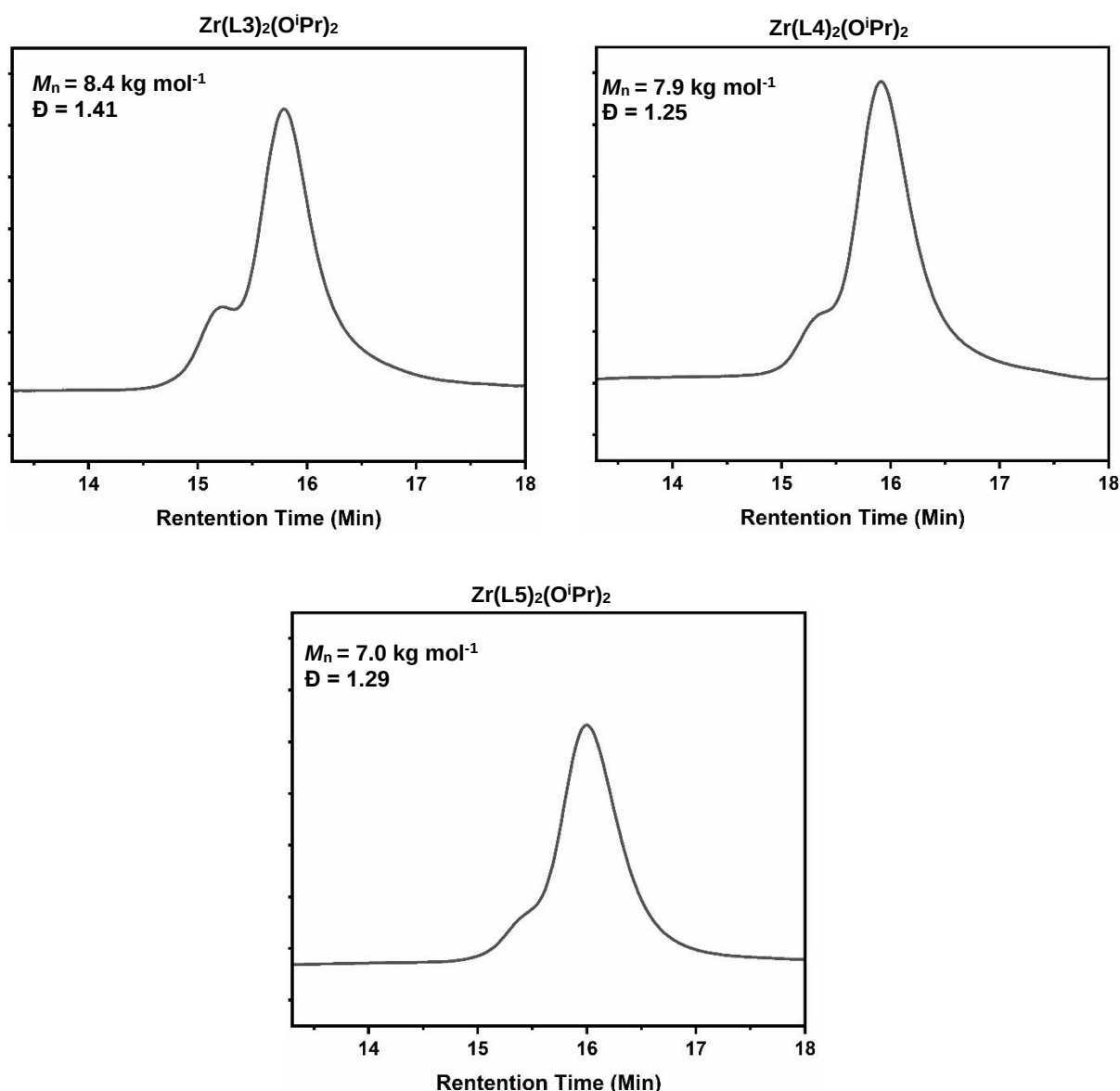


Figure 4.14: GPC chromatograms for polymers described in Table 4.1, from the reaction $[\text{Zr}(\text{L})_2(\text{O}^i\text{Pr})_2] : [\text{tBuPA}] : [\text{OO}] = 1 : 50 : 654$, 1 mL OO, 120 °C, where **L** = a) **L3**, b) **L4** and c) **L5** (Table 4.1, entries 5, 6, 7). The GPCs obtained in this figure were run on a different instrument to those presented elsewhere in this thesis (Agilent LC1260 Infinity II, see S7.2.2 for instrument details).

4.4 Metal Salts as Catalysts

A series of commercial **ZrX₄** samples were selected due to the precedent for Zr(IV) in poly(ester-*alt*-ether) catalysis, with **Zr(OⁱPr)₄(HOⁱPr)** showing excellent rate and selectivity. Again, the reactions were monitored by DSC for kinetics, using the same conditions **[ZrX₄] : [tBuPA] : [OO] = 1 : 50 : 654**, 1 mL OO, with larger scale vial reactions run along-side them to ensure consistency. The reaction of **Zr(OⁱPr)₄(HOⁱPr)** with tBuPA and OO, will be used as an example, to demonstrate the synthesis and characterisation of poly(ester-*alt*-ethers) from metal salts, and, to further show the consistency between DSC and larger vial methods. The reaction of **[Zr(OⁱPr)₄(HOⁱPr)] : [tBuPA] : [OO] = 1 : 50 : 654**, 1 mL OO, was observed to

be zero order in anhydride ($k_{\text{obs}} = 180 \times 10^{-4} \text{ M s}^{-1}$, Table 4.2, entry 1, Figure 4.15). This is 10-1000 times faster than that of the $\text{ML}_2(\text{O}^i\text{Pr})_2$ catalysts explored above ($\sim 0.36\text{--}28.3 \times 10^{-4} \text{ M s}^{-1}$). The selectivity for poly(ester-*alt*-ether) linkages was 96 and 95 % for DSC and vial methods respectively (Table 4.2 entry 1 and Figure 4.16b and c). The molar mass distributions were monomodal, with very little difference between the two methods ($M_n = 4.6 \text{ kg mol}^{-1}$ and $\mathcal{D} = 1.18$ by DSC, $M_n = 4.4 \text{ kg mol}^{-1}$ and $\mathcal{D} = 1.15$ by vial method, Figure 4.16a and Table 4.2 entry 1). The DP of tBuPA : OO showed no difference between methods (10:20 and 10:21 for the DSC and vial methods respectively).

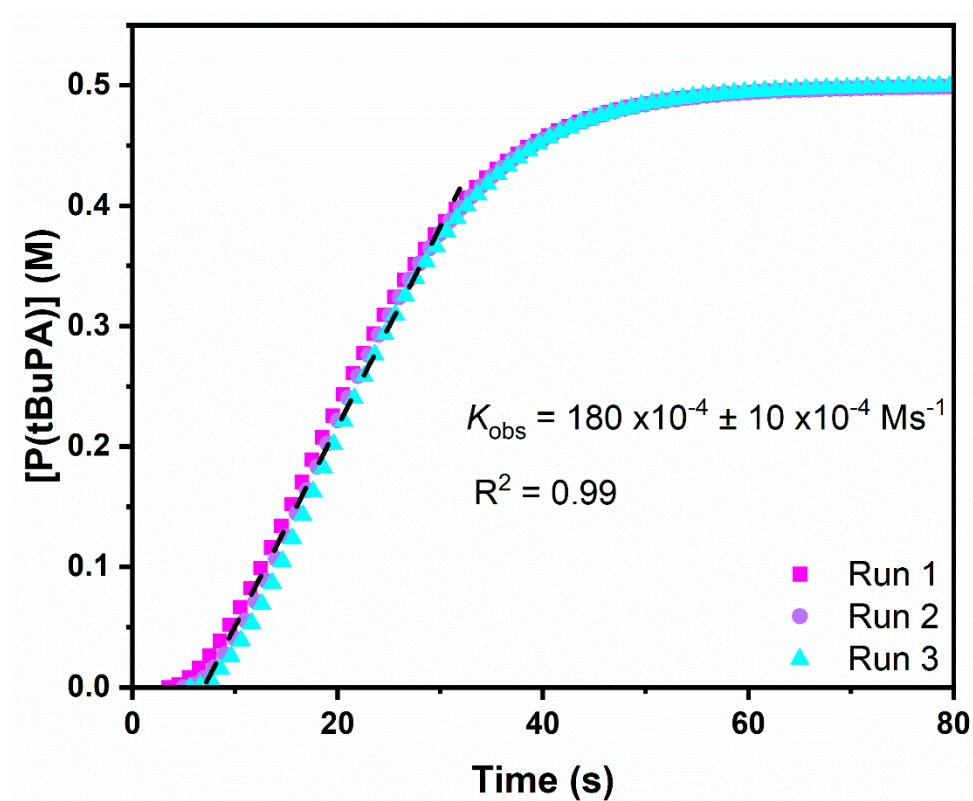


Figure 4.15: Plot of $[\text{P}(\text{tBuPA})]$ vs time, obtained via DSC kinetic analysis, for the reaction of $[\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})] : [\text{tBuPA}] : [\text{OO}] = 1 : 50 : 654$, 1 mL OO, 120 °C, Table 4.2 entry 1. The reaction was performed in triplicate. The pseudo rate coefficients, k_{obs} (M s^{-1}), were determined as the gradient of the $[\text{tBuPA}]$ vs time (s), and the data was fit between 15-80 % conversion.

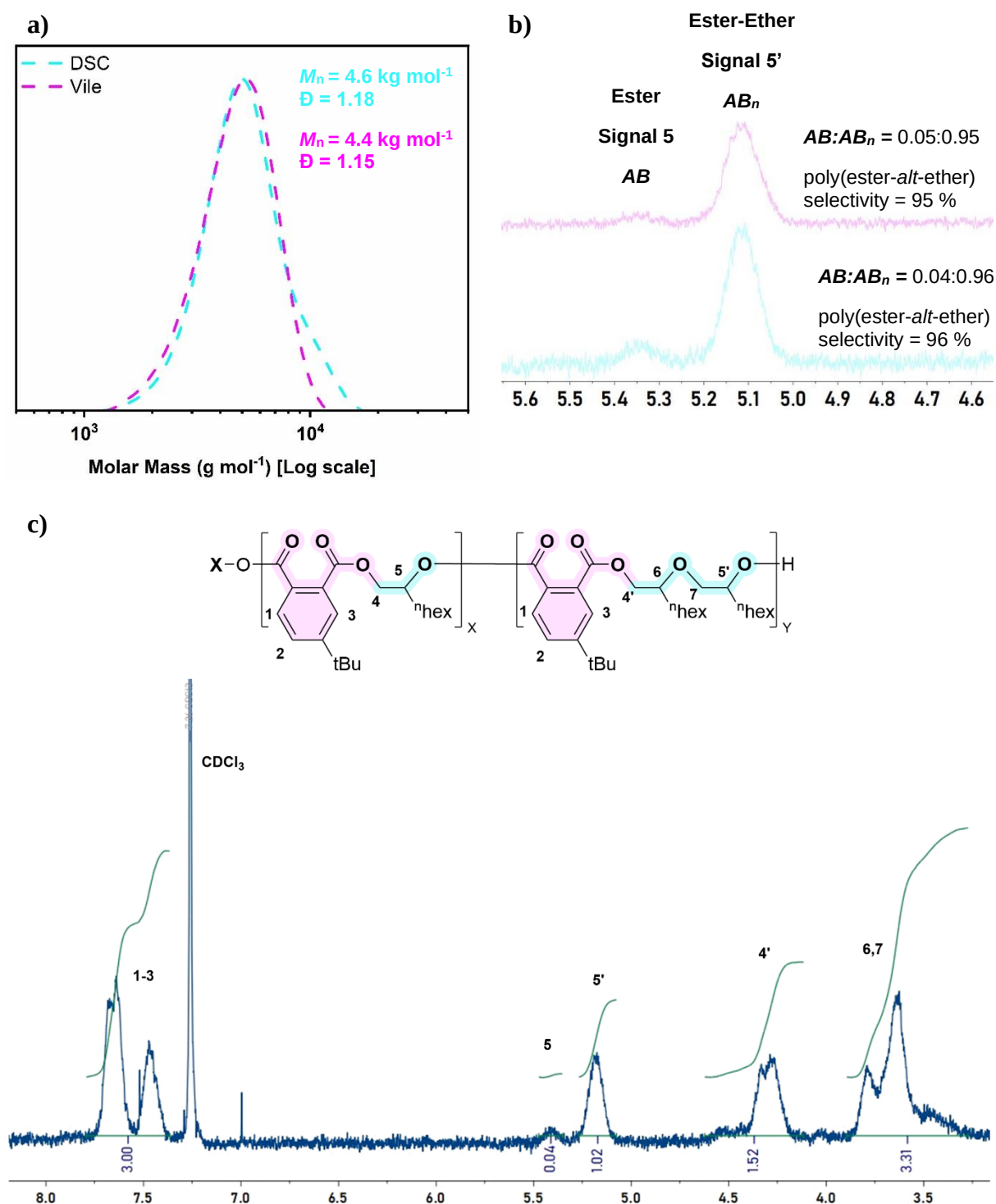
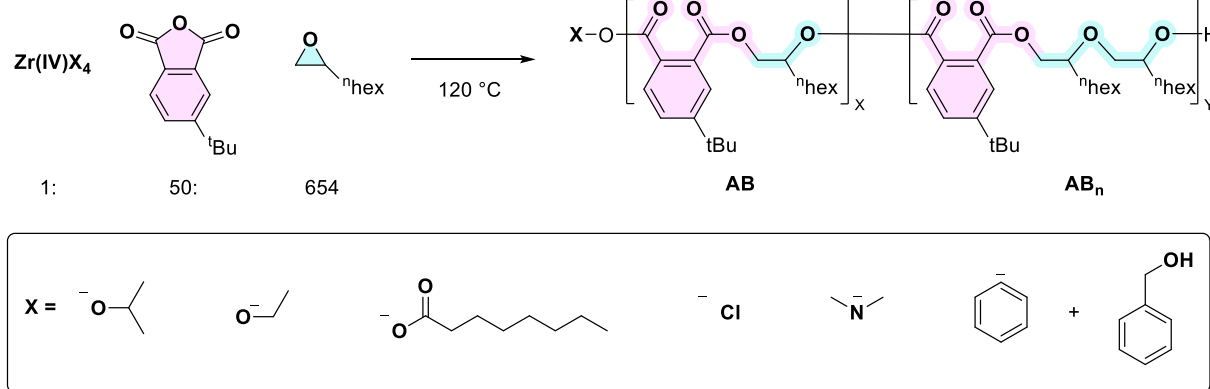


Figure 4.16: Determination of AB vs AB_n selectivity and molar mass distribution for the reaction of $[\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})] : [\text{tBuPA}] : [\text{OO}] = 1 : 50 : 654$, 1 mL OO, on both a DSC and reaction vial scale. a) GPC chromatograms of DSC scale (blue) and reaction vial scale (pink) reactions. b) ^1H NMR spectra zoomed into the methine ester region (proton signal 5 at 5.35 ppm for AB , and, signal 5' at 5.10 ppm for AB_n), to calculate selectivity for ester-ether linkages. c) ^1H NMR spectra taken from a DSC kinetics pan after complete reaction at 120 °C, demonstrating the integrals used for calculation of DP (from Table 4.2, entry 1, 400 MHz, CDCl_3 , with assignments). For clarity, the alkyl region of the crude spectrum is not shown, see section S8.4.3 for full spectra.

4.4.1 Role of the Co-ligand

Various catalysts of the form Zr(IV)X (where $\text{X} = (\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$, $(\text{OEt})_4$, $(\text{Oct})_4$, $(\text{Cl})_4$, $(\text{NMe}_2)_4$, $(\text{Bn})_4$ and $(\text{Bn})_4 + (\text{HOBn})_2$, Table 4.2) were explored. Catalysts containing alkoxide, alcohol or chloride co-ligands ($\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$, $\text{Zr}(\text{OEt})_4$, $\text{Zr}(\text{Cl})_4$ and $\text{Zr}(\text{Bn})_4 + (\text{HOBn})_2$) demonstrated poly(ester-*alt*-ether) selectivity $\geq 95\%$ (Table 4.2, entries 1,2,4 and 7). Furthermore, these catalysts all showed similar rates with $160 \times 10^{-4} < k_{\text{obs}} < 200 \times 10^{-4} \text{ M s}^{-1}$, equating to reaction times of 44-61 s. They produced polymers with monomodal molar mass distributions and $M_n = 4.6\text{-}6.3 \text{ kg mol}^{-1}$, $1.12 < \text{Đ} < 1.23$ (Figure 4.17). These catalysts are both selective, and, provide controlled molar mass distributions, at rates 1-3 orders of magnitude faster than the $\text{ML}_2(\text{O}^i\text{Pr})_2$ catalysts explored above.

Table 4.2: Ring-opening copolymerisation (ROCOP) of tBuPA and OO with a range of Zr(IV)X_4 catalysts^a.



Entry	Catalyst	DP [tBuPA]:[OO] ^d	Poly(ester- <i>alt</i> -ether) Selectivity (%) ^e	M_n (Đ) [kg mol ⁻¹] ^f	M_n (Theo)(No. Initiators) ^g	k_{obs} ($\times 10^{-4} \text{ M s}^{-1}$) ^h
1	$\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$	10:20	96	4.6 (1.18)	4.7 (5)	180
2	$\text{Zr}(\text{OEt})_4$	13:25	97	6.3 (1.23)	6.3 (4)	160
3	$\text{Zr}(\text{Oct})_4$	13:19	40	2.4 (1.23)	2.4 (4)	90
4	$\text{Zr}(\text{Cl})_4$	13:27	95	5.3 (1.12)	5.9 (4)	200
5	$\text{Zr}(\text{NMe}_2)_4$	13:18	43	5.0 (1.29)	5.3 (4)	26
6	$\text{Zr}(\text{Bn})_4$	17:32	87	7.4 (1.36)	7.4 (3)	73
7	$\text{Zr}(\text{Bn})_4 + (\text{HOBn})_2$ ^b	25:52	96	5.2 (1.22)	11.8 (2)	160

^aROCOP conditions: $[\text{ZrX}] = 10 \text{ mM}$, $[\text{tBPA}] = 0.5 \text{ M}$, $\text{OO} = 1 \text{ mL}$ (654 equiv.), 120°C , 40-360 s. ^bROCOP conditions: $[\text{Zr}(\text{Bn})_4] = 10 \text{ mM}$, $[\text{BnOH}] = 20 \text{ mM}$, $[\text{tBPA}] = 0.5 \text{ M}$, $\text{OO} = 1 \text{ mL}$, 120°C . ^cDP of tBPA measured by integration of aromatic resonances of tBPA (7.91-8.01 ppm) and P(tBPA) (7.34-7.84 ppm) in ^1H NMR spectra of the crude polymers (Figures S8.4.32-37). ^dEpoxide DP determined by the integration of ^1H NMR spectra of crude polymers against P(tBPA) (Figures S8.4.32-37). ^eDetermined by integration of the methine ester resonances (5.35 and 5.10 ppm for **AB** and **AB_n** respectively). ^fDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards (Figure 4.17). ^gTheoretical M_n are calculated from the monomer conversion data and it is assumed that all co-ligands or added alcohol (BnOH) initiate the reaction. ^hRate constant is the gradient of the linear fits to plots of $\text{P}[\text{tBPA}]$ vs time (Figure S8.4.38). Average errors are determined from repeat runs. It is expected that Cl^- and Oct^- would initiate by ring-opening of an epoxide.

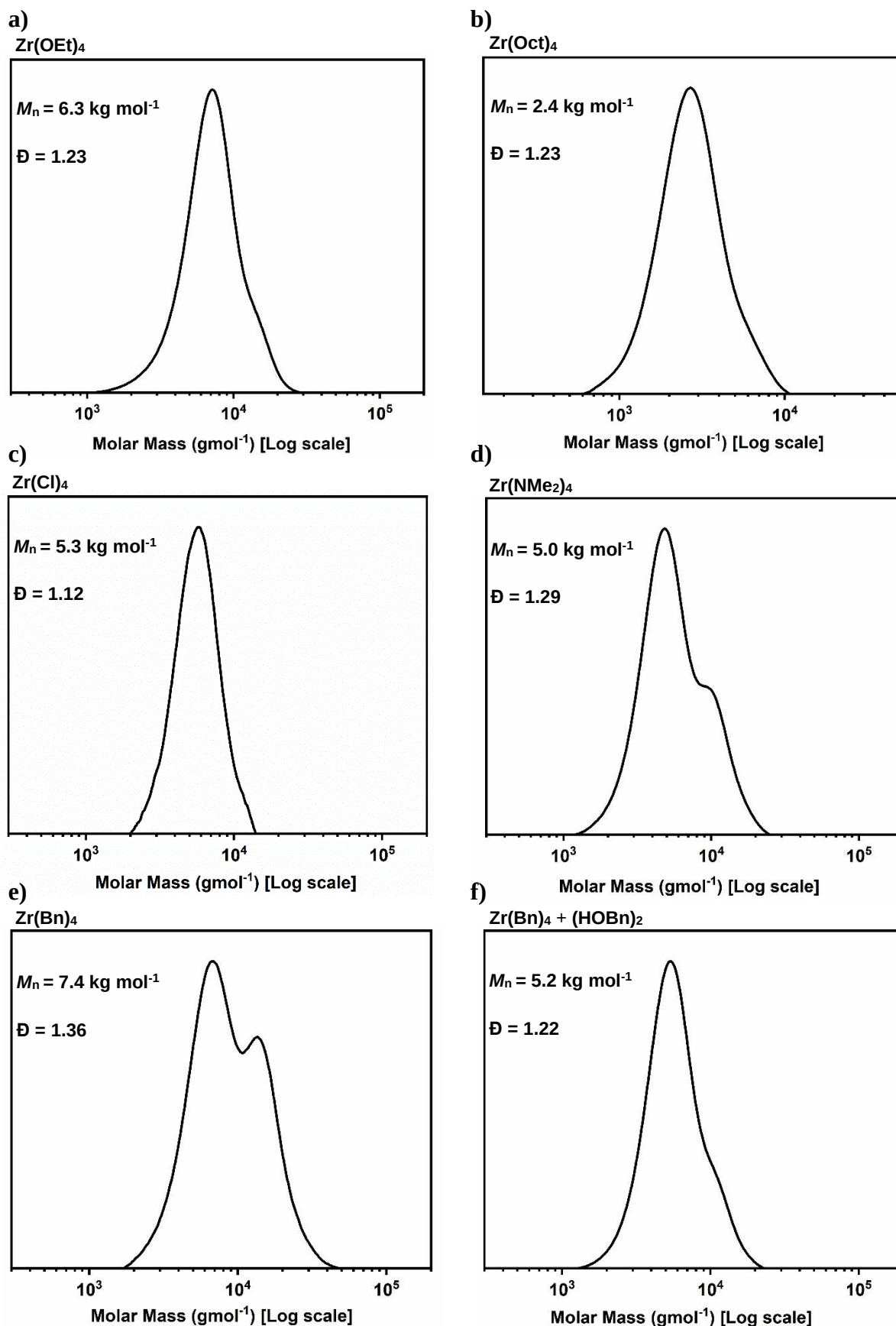


Figure 4.17: GPC traces of tBuPA and OO with $\text{Zr}(\text{IV})\text{X}_4$ (where X = a) $(\text{OEt})_4$, b) $(\text{Oct})_4$, c) $(\text{Cl})_4$, d) $(\text{NMe}_2)_4$, e) $(\text{Bn})_4$ and f) $(\text{Bn})_4 + (\text{HOBn})_2$, (Table 4.2, entries 2-7). ROCOP conditions: $[\text{ZrX}_4] = 10 \text{ mM}$, $[\text{tBPA}] = 0.5 \text{ M}$, $\text{OO} = 1 \text{ mL}$ (654 equiv.), 120°C . The GPC trace for $\text{Zr}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$ can be found in Figure 4.16a.

On the other hand, **Zr(Oct)₄** and **Zr(NMe₂)₄** demonstrated much lower selectivity for poly(ester-*alt*-ether) linkages (40 and 43 %, for **Zr(Oct)₄** and **Zr(NMe₂)₄**, respectively, Table 4.2 entry 3 and 5). Molar masses show monomodal distributions (Figure 4.17). The reactions were also 10 times slower than for the alkoxide/alcohol/chloride complexes ($k_{\text{obs}} = 90 \times 10^{-4}$ and $26 \times 10^{-4} \text{ M s}^{-1}$, reaction time = 263 and 363 s for **Zr(Oct)₄** and **Zr(NMe₂)₄**, respectively). Comparison of the methine ester region for a highly selective catalyst (**Zr(Cl)₄** = 95 %) and a poorly selective catalyst (**Zr(Oct)₄** = 40 %), demonstrates how this region changes in the two cases, for calculating poly(ester-*alt*-ether) linkage selectivity over polyester linkages (Figure 4.18).

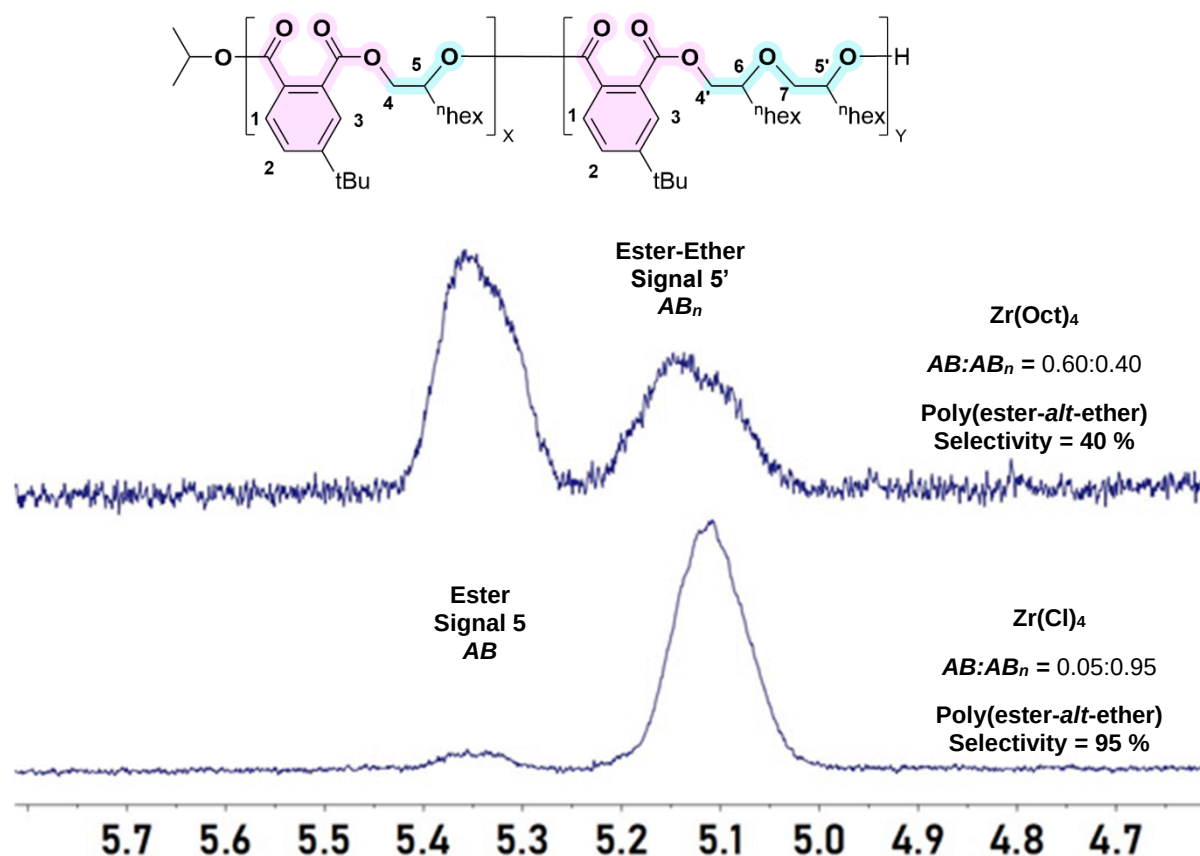


Figure 4.18: ¹H NMR spectra taken from DSC kinetics pans after complete reaction at 120 °C, demonstrating the methine ester signals (signal 5 at 5.35 ppm for ester, **AB**, and, signal 5' at 5.10 ppm for ester-ether, **AB_n**), used for calculation of poly(ester-*alt*-ether) linkage selectivity (400 MHz, CDCl₃, with assignments). The top spectrum is from **Zr(Oct)₄** (Table 4.2, entry 3), showing a larger ester signal (5) and lower poly(ester-*alt*-ether) linkage selectivity (40 %), and the bottom spectrum is from **Zr(Cl)₄** (Table 4.2, entry 4), showing almost perfect poly(ester-*alt*-ether) linkage selectivity (signal 5', 95 %).

Zr(Bn)₄ was an effective catalyst, but the resulting polymer shows a bimodal molar mass distribution (Figure 4.17e). This is likely due to chains initiated from benzyl and diol groups. The catalyst was still highly selective for poly(ester-*alt*-ether) linkages (87 %). The reaction was on the same time scale as the slower catalysts, **Zr(Oct)₄** and **Zr(NMe₂)₄** ($k_{\text{obs}} = 73 \times 10^{-4} \text{ M s}^{-1}$, Table 4.2 entry 6). Adding two equivalents of HOBN produced a monomodal polymer distribution, and improved the selectivity for poly(ester-*alt*-ether) linkages (96 %). It also doubled the rate ($k_{\text{obs}} = 160 \times 10^{-4} \text{ M s}^{-1}$, Table 4.2, entry 7). This is because the alcohol reacts with the benzyl ligands to form a highly effective benzyl alkoxide catalyst in situ.

The best of these simple salt catalysts are between 1-1000 times faster than the **ML₂(OⁱPr)₂** catalysts. Also, by changing the co-ligand, the selectivity for ester-ether (**AB_n** – Y in Figure 4.18) linkages can be altered from 97 % to 40 %. Changing the co-ligand may also offer interesting opportunities for improving catalyst solubility in a wider number of solvents and monomers. It should be noted that co-ligands such as ⁻**Oct** and ⁻**Cl**, would be expected to initiate via ring-opening of an epoxide. The precise initiation mechanisms are not probed here, but could be explored in future.

4.5 Organometallic Catalysts and Chain Transfer with Alcohols

In the **Zr(L1)₂(OⁱPr)₂** catalysts, the alkoxide ligands initiate polymerisation. Most impurities in this catalysis, that can act as initiators, are bifunctional, e.g. diols from ring opened epoxides and diacids from ring opened anhydrides. The mixture of impurity and catalyst initiation leads to bimodality at lower [catalyst]. One solution to this issue, is use a chain transfer agent to control initiation. Another is to employ a non-initiating catalyst (i.e. an organometallic catalyst), and employ alcohols as both initiators and chain transfer agents.^{5,6} Organometallic catalysts also allow better control over end group functionality (which may permit various post-polymerisation chemistries) and polymer architecture. In the previous section, it was demonstrated that commercial (un-purified) **Zr(Bn)₄**, used with 2 equivalents of HOBN, could selectively form poly(ester-*alt*-ethers). Here, **Zr(Bn)₄** and **Hf(Bn)₄** were investigated with various alcohols (as CTA), and, their selectivity and control compared.

First, the loading of alcohol ([CTA]) was investigated, to understand the limits of catalysis. Next, alcohols forming a series of functional end-groups were used, for example bromine, alkene and alkyne containing (Figure 4.19). Finally, alcohols were selected to produce different architectures; linear from a single alcohol, di telechelic from diols, three-arm and four-arm polymers from triols and tetra-ols, respectively (Figure 4.19). The goal is also to

provide a range of low T_g polymers, with different architectures, or, accessibility to post-polymerisation functionalisation (or in situ reactive compatibilisation). In this section, the reactions were no longer performed by DSC, as rather than rate, the selectivity for poly(ester-*alt*-ether) linkages and control of molecular weight dispersity was of particular focus.

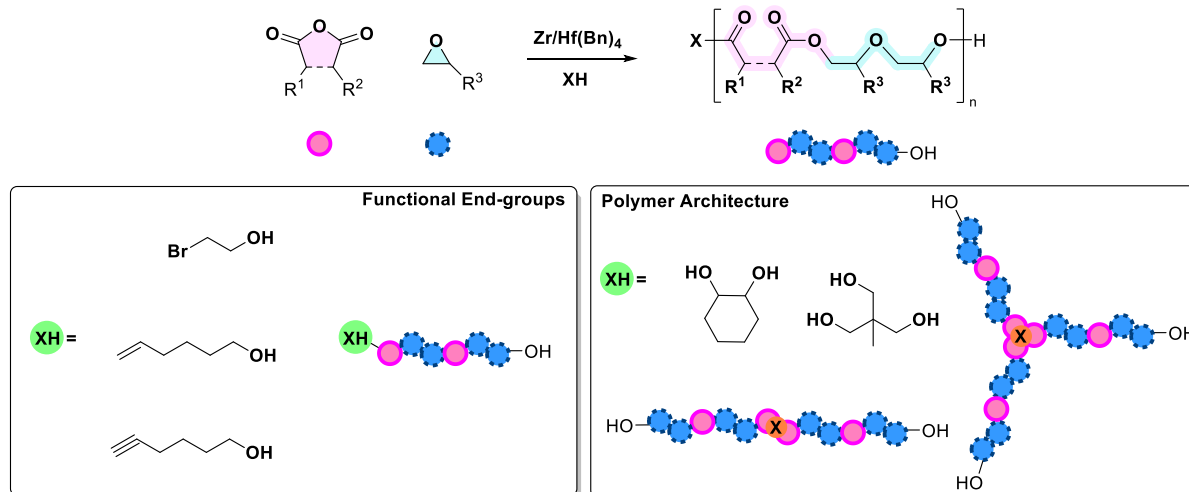


Figure 4.19: Schematic representation of the use of organometallic catalysts with various alcohols.

4.5.1 Alcohol Loading

Zr(Bn)₄ and **Hf(Bn)₄** were explored for poly(ester-*alt*-ether) linkage selectivity and control over molar mass dispersity. The conditions [**Zr/Hf(Bn)₄**] : [PA] : [HOBn] = 1 : 50 : z, in 1 mL EDD at 50 °C, were used to assess the effect of alcohol loading (Table 4.3). When 1-10 equivalents of alcohol were used, in all cases the selectivity for poly(ester-*alt*-ether) was high (85-99 %, Table 4.3). The linkage selectivity decreased with increasing [alcohol]. **Hf(Bn)₄** was more controlled (Table 4.3). The polymer molar masses and dispersity decrease as the [alcohol] increases ($M_n = 13.4\text{--}3.1 \text{ kg mol}^{-1}$ and $1.14 < \bar{D} < 1.52$, Table 4.3). The molar mass distributions remained monomodal throughout the two series (Figure 4.20). At lower [alcohol] (i.e higher molar mass polymers), the molar masses obtained by GPC deviated more dramatically from the theoretical values, while the $M_{n,\text{NMR}}$ was much closer. This is to be expected and arises from poor GPC correlations between these polymers and the PS calibrants.

Given the improved poly(ester-*alt*-ether) linkage selectivity obtained for **Hf(Bn)₄**, this catalyst was selected for further study. The insolubility of some alcohols in EDD, meant that for the proceeding studies, BO was substituted as the epoxide. The PA/BO combination was also used to determine catalyst tolerance to alcohol loading (Table 4.4). Under identical conditions as above ([**Hf(Bn)₄**] : [PA] : [HOBn] = 1 : 50 : z, in 1 mL BO at 50 °C) the value of z was varied between 0.25-10. The results were very similar to those obtained using the PA/EDD monomer combination. With decreasing [HOBn], the polymer molar masses obtained

by GPC and ^1H NMR spectroscopy increased ($M_n = 1.8\text{--}9.0 \text{ kg mol}^{-1}$, $1.21 < \text{Đ} < 1.49$, Table 4.4 and Figure 4.21). Selectivity remained exceptionally high for poly(ester-*alt*-ether) linkages (96–100 %). As a result, the PA/BO combination was selected to examine the possibility to install functional end-groups, or make various polymer architectures.

Table 4.3: Ring opening copolymerisation (ROCOP) of PA and EDD with $\text{Zr}/\text{Hf}(\text{Bn})_4$ catalysts with various amounts of $[\text{HOBn}]$.^a

Entry	Catalyst	HOBn Equiv.	DP [PA] ^b : [EDD] ^c	Poly(ester- <i>alt</i> - ether) Selectivity (%) ^d	M_n (Đ) [kg mol ⁻¹] ^e	M_n (NMR) [kg mol ⁻¹] ^f	M_n (Theo) ^g
1	$\text{Zr}(\text{Bn})_4$	1	50*:102	95	10.7 (1.38)	-	26.3
2	$\text{Zr}(\text{Bn})_4$	2	32:68	94	8.2 (1.24)	17.4	13.8
3	$\text{Zr}(\text{Bn})_4$	5	11:24	90	4.7 (1.16)	6.2	5.6
4	$\text{Zr}(\text{Bn})_4$	10	7:14	85	3.0 (1.14)	3.7	2.7
5	$\text{Hf}(\text{Bn})_4$	1	64:137	99	13.4 (1.52)	34.8	27.3
6	$\text{Hf}(\text{Bn})_4$	2	33:69	95	6.4 (1.27)	17.7	13.4
7	$\text{Hf}(\text{Bn})_4$	5	13:28	95	4.6 (1.23)	7.2	5.6
8	$\text{Hf}(\text{Bn})_4$	10	8:16	92	3.1 (1.17)	4.2	2.7

^aROCOP conditions: $[\text{Zr}/\text{Hf}(\text{Bn})_4] = 10 \text{ mM}$, $[\text{PA}] = 0.5 \text{ M}$, $[\text{HOBn}] = z$, $z = 10\text{--}100 \text{ mM}$, $\text{ED} = 1 \text{ mL}$, 50°C . ^bDP of PA measured by integration of aromatic resonances of PA (7.98 ppm) and P(PA) (7.67 ppm) in ^1H NMR spectra against the end-group OBn methylene resonance (5.32 ppm, Figures S8.4.39–40). ^cEpoxide DP determined by the integration of ^1H NMR spectra of crude polymers against P(PA) (Figures S8.4.39–40). ^dDetermined by integration of methine ester resonances (5.35 and 5.10 ppm for ester and ester-*alt*-ether linkages respectively) against P(PA) anhydride resonances. ^eDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards (Figures 4.20). ^f M_n (NMR) were calculated using the OBn methylene resonance (5.32 ppm). ^gTheoretical M_n are calculated from the monomer conversion data. *HOBn signal was not strong enough, DP was calculated by assuming that all the alcohol initiated.

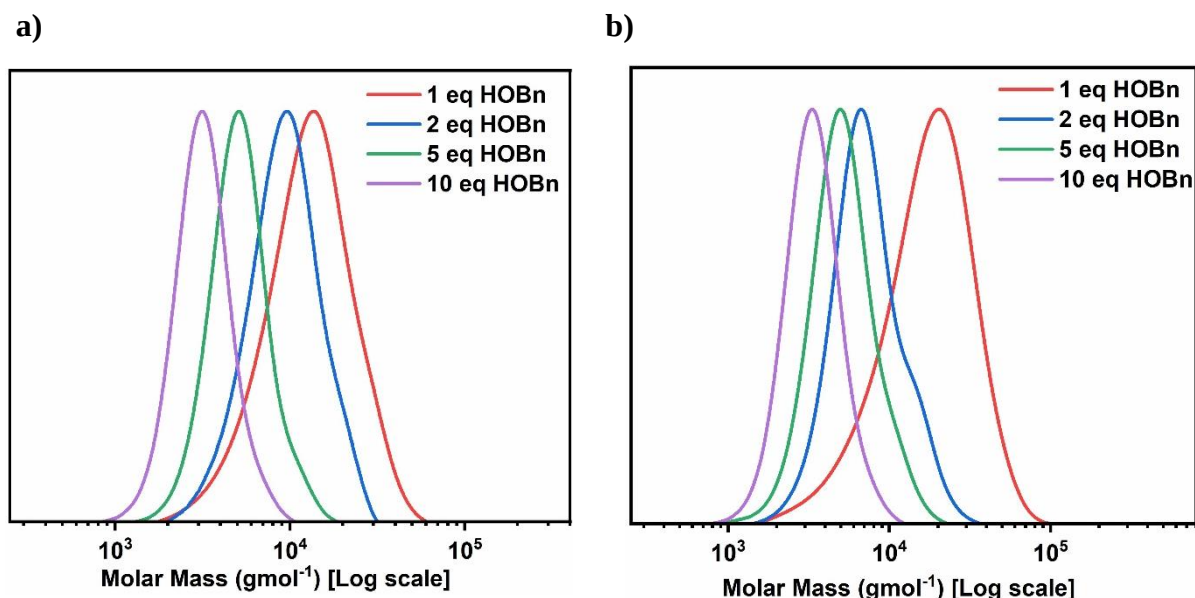


Figure 4.20: GPC traces of the ring-opening copolymerisation (ROCOP) of PA and EDD with a) $\text{Zr}(\text{Bn})_4$ and b) $\text{Hf}(\text{Bn})_4$ catalysts, using various $[\text{HOBn}]$ (^aROCOP conditions: $[\text{Zr}/\text{Hf}(\text{Bn})_4] = 10 \text{ mM}$, $[\text{PA}] = 0.5 \text{ M}$, $[\text{HOBn}] = z$, $z = 10\text{--}100 \text{ mM}$, $\text{ED} = 1 \text{ mL}$, 50°C).

Table 4.4: Ring-opening copolymerisation (ROCOP) of PA and BO with **Hf(Bn)₄** and various [HOBn].^a

Entry	HOBn Equiv. (z)	DP [PA] ^b : [BO] ^c	Poly(ester- <i>alt</i> -ether) Selectivity (%) ^d	<i>M_n</i> (Đ) [kg mol ⁻¹] ^e	<i>M_n</i> (NMR) [kg mol ⁻¹] ^f	<i>M_n</i> (Theo) ^g
1	0.25	94:204	100	9.0 (1.45)	28.7	60.8
2	0.5	95:206	100	7.7 (1.49)	29.0	46.1
3	1	53:116	100	7.0 (1.32)	16.3	15.4
4	2	35:71	97	4.3 (1.21)	10.4	7.5
5	5	12:28	97	3.1 (1.27)	3.9	4.1
6	10	6:14	96	1.8 (1.25)	2.0	1.7

^aROCOP conditions: [**Hf(Bn)₄**] = 10 mM, [PA] = 0.5 M, [HOBn] = 2.5–100 mM, OO = 1 mL, 50 °C. ^bDP of PA measured by integration of aromatic resonances of PA (7.98 ppm) and P(PA) (7.67 ppm) against the end-group OBn methylene resonance (5.32 ppm, Figure S8.4.41). ^cEpoxide DP determined by the integration of methine ester resonances (5.10 ppm) against the end-group OBn methylene resonance (5.32 ppm, Figure S8.4.41). ^dDetermined by integration of methine ester resonances (5.35 and 5.10 ppm for ester and ester-*alt*-ether respectively). ^eDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards (Figures 4.21). ^f*M_n*(NMR) were calculated using the OBn methylene resonance (5.32 ppm). ^gTheoretical *M_n* are calculated from the monomer conversion data.

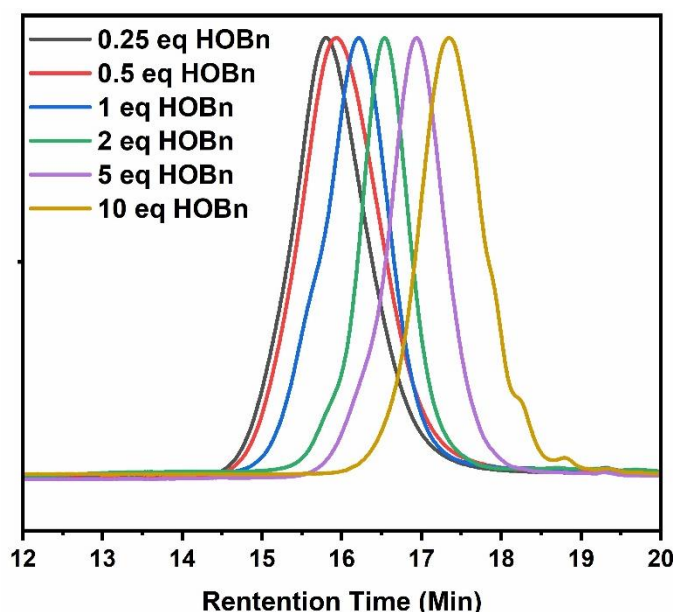


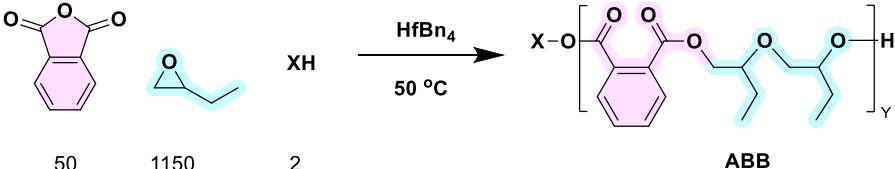
Figure 4.21: GPC traces of the ring-opening copolymerisation (ROCOP) of PA and BO with **Hf(Bn)₄** catalyst, with various [HOBn] (^aROCOP conditions: [**Hf(Bn)₄**] = 10 mM, [PA] = 0.5 M, [HOBn] = 2.5–100 mM, BO = 1 mL, 50 °C). The GPCs obtained in this figure were run on a different instrument to those presented above (Agilent LC1260 Infinity II, see S7.2.2 for instrument details).

4.5.2 Functional End-groups

Polymer chain end-groups can control solubility, surface adsorption, viscoelasticity, reactivity, self-assembly and micro-/macro-phase separation.⁷ Chain end-group modification can influence surface orientations and interfacial interactions.⁷ Low molar mass polymers are also often used to make segmented higher molar mass polymers, and in such cases, control over end-group functionality is vital to allow further reactivity. For example, di-hydroxy telechelic low molar mass polyester and polycarbonate polyols are reacted with di-isocyanates to make polyurethanes.^{3,7}

With the optimum range of [alcohol] identified, the alcohols 2-bromoethanol, 5-hexen-1-ol and 5-hexyn-1-ol were tested, with **Hf(Bn)₄** as the catalyst, to produce chain-end functionalised polymers (Table 4.5). The alcohols were selected because the bromide can undergo nucleophilic substitutions or further polymerisation such as atom transfer radical polymerisation (ATRP).^{7,8} The alkenes can react by high efficiency thiol-ene reactions or undergo further addition polymerisation.^{7,9} Alkynes can undergo azide-alkyne click reactions.⁷ These alcohols were chosen as representative examples, as a proof-of-concept that control over end group functionality can be obtained for the poly(ester-*alt*-ethers). The reactions were all conducted under common conditions [**Hf(Bn)₄**] : [PA] : [CTA] = 1 : 50 : 2, in 1 mL BO at 50 °C. The polymerisations were monitored, as outlined above (Table 4.5).

Table 4.5: Ring-opening copolymerisation (ROCOP) of PA and BO with **Hf(Bn)₄** and various alcohols (2-bromoethanol, 5-hexen-1-ol and 5-hexyn-1-ol) to install functional end-groups.^a

						
2-bromoethanol XH = <chem>HOCH2CH2Br</chem> 5-hexen-1-ol <chem>HO(CH2)5</chem> 5-hexyn-1-ol <chem>HO(CH2)4C#CH</chem>						
Entry	Alcohol	DP [PA] ^b : [BO]	Poly(ester- <i>alt</i> -ether) Selectivity (%) ^c	M _n (D) [kg mol ⁻¹] ^d	M _n (NMR) [kg mol ⁻¹]	M _n (Theo) ^e
1	2-Bromoethanol	25:54	96	4.6 (1.25)	-	7.6
2	5-Hexen-1-ol	27:60	95	4.9 (1.19)	8.2	7.6
3	5-Hexyn-1-ol	29:62	95	4.6 (1.22)	8.9	7.5

^aROCOP conditions: [**Hf(Bn)₄**] = 10 mM, [PA] = 0.5 M, [CTA] = 20 mM, BO = 1 mL (1150 equiv.), 50 °C. ^bDP of PA measured by integration of aromatic resonances of P(PA) (7.67 ppm) against the end-group for 5-hexen-1-ol (at 5.0-4.9 ppm, Figure S8.4.46-47) and 5-hexyn-1-ol (at 2.2 ppm, S8.4.51), while for entry 1 (2-Bromoethanol), the DP was measured by integration of aromatic resonances of PA (7.91-8.01 ppm) and P(PA) (7.34-7.84 ppm). ^cDetermined by integration of methine ester resonances (5.35 and 5.10 ppm for ester and ester-*alt*-ether respectively). ^dDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards (Figure 4.22). ^eTheoretical M_n are calculated from the monomer conversion data.

All three reactions showed high selectivity for poly(ester-*alt*-ether) linkages (95-96 %, Table 4.5). The polymers showed monomodal molar mass distributions and narrow dispersity ($M_n = 4.6\text{--}4.9 \text{ kg mol}^{-1}$, $1.19 < Đ < 1.25$, Table 4.5 and Figure 4.22). The $M_{n\text{NMR}}$ values were in excellent agreement with the theoretical M_n (Table 4.5). The functional end-group signals were observed in the ^1H NMR spectrum for 2-hexen-1-ol (5.0-4.9 ppm, Figures S8.4.46-47) and 2-hexyn-1-ol (methylene protons at 2.2 ppm, Figure S8.4.51).

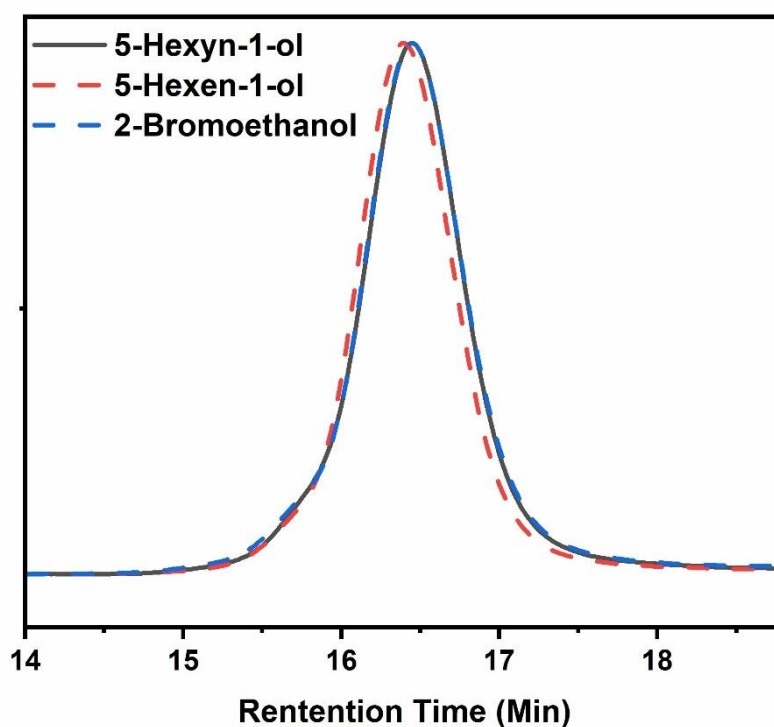


Figure 4.22: GPC traces of the ring-opening copolymerisation (ROCOP) of PA and BO with $\text{Hf}(\text{Bn})_4$ catalyst, with different alcohols (ROCOP conditions: $[\text{Hf}(\text{Bn})_4] = 10 \text{ mM}$, $[\text{PA}] = 0.5 \text{ M}$, $[\text{HOBn}] = 20 \text{ mM}$, $\text{BO} = 1 \text{ mL}$, 50°C). The GPCs were obtained from an Agilent LC1260 Infinity II (see S7.2.2 for instrument details).

4.5.3 Control of Polymer Architecture

In the search for new applications for poly(ester-*alt*-ethers), controlling the polymer architecture would be an important achievement. The architecture of polymers and block copolymers can have an effect over the physical properties, further reactivity as well as possible applications. For example, for use as a soft (low T_g) central block in elastomers or pressure sensitive adhesives, di-hydroxy telechelic poly(ester-*alt*-ethers) would be required.^{10,11} Multi-arm, or star, block copolymers have demonstrated lower melt viscosities and, in some thermoplastic elastomers, they have demonstrated increased tensile strength.¹² Hillmyer and co-workers found that above a certain molar mass, for a constant molar mass of an arm ($M_{n,\text{arm}}$), star architectures showed improved mechanical properties to their linear analogues.¹² It has been hypothesised that improved mechanical properties observed may be a result of the core

of the star architecture, acting to distribute applied stresses more effectively.¹² This was also an important consideration for this work, with the goal of finding effective toughening agents.

The bi-functional cyclohexane diol (CHD), trifunctional 1,1,1-tris(hydroxymethyl)propane (TMP) and tetra-functional pentaerythritol ethoxylate (270 g mol⁻¹, 3/4 EO/OH, PE), were selected to make polymers of different architectures ('two', 'three' and 'four' arm polymers, respectively, Table 4.6). The [alcohol] was targeted so that each 'arm' of the polymer would have the same DP (rather than the polymers each having the same overall DP), by keeping the [OH] constant. In this way, the total DP of the polymer should increase with the number of arms. These polymers were compared against the monofunctional polymer made from adding two equivalents of HOBn (Table 4.6, entry 1). The monomer combinations PA/BO was used to ensure solubility of all the alcohols and the reaction conditions were [Hf(Bn)₄] : [PA] : [CTA] = 1 : 50 : 2/*n*, where *n* = the number of alcohol groups, in 1 mL BO at 50 °C.

Table 4.6: Ring-opening copolymerisation (ROCOP) of PA and BO with Hf(Bn)₄ and various alcohols to produce polymers with different architectures.^a

Abbreviations:

HOBN	CHD	TMP	PE - 270 g mol ⁻¹ 3/4 EO/OH

XH =

Entry	Alcohol	DP [PA] ^b : [BO]	Poly(ester- <i>alt</i> -ether Selectivity) (%) ^c	<i>M_n</i> (Đ) [kg mol ⁻¹] ^d	<i>M_n</i> (Theo) ^e
1	HOBn	35:71	97	4.3 (1.21)	7.5
2	CHD	50:112	96	9.6 (1.31)	15.3
3	TMP	75:165	97	10.7 (1.23)	23.2
4	PE	100:220	97	8.5 (1.32)	30.7

^aROCOP conditions: [Hf(Bn)₄] = 10 mM, [PA] = 0.5 M, [CTA] = 20/*n* mM, where *n* = the number of alcohol groups, BO = 1 mL (1150 equiv.), 50 °C. ^bDP of PA measured by integration of the aromatic resonances of PA (7.91-8.01 ppm) and P(PA) (7.34-7.84 ppm) and it is assumed that all added CTA initiate the reaction (Figures S8.4.55-57). ^cDetermined by integration of methine ester resonances (5.35 and 5.10 ppm for ester and ester-*alt*-ether respectively). ^dDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards (Figure 4.23). ^eTheoretical *M_n* are calculated from the monomer conversion data.

The selectivity for poly(ester-*alt*-ether) linkages was high for all reactions ($\geq 96\%$, Table 4.6), consistent with the alcohol not hindering the formation of **ABB** polymers. The reaction using HOBn went to full PA conversion in 40 s. The polymer molar mass by GPC and ^1H NMR spectroscopy differ, with $M_{n,\text{GPC}} = 4.3 \text{ kg mol}^{-1}$ and $M_{n,\text{NMR}} = 10.4 \text{ kg mol}^{-1}$ (Table 4.6). No end-group signals were observed in the ^1H NMR spectra of polymers initiated from CHD, TMP or PE (Figures S8.4.55-57). When CHD was employed, the $M_{n,\text{GPC}}$ was double that observed with HOBn ($M_{n,\text{GPC}} = 9.6 \text{ kg mol}^{-1}$, Table 4.6 entry 2, Figure 4.23), which is line with keeping the $[\text{OH}]$ groups constant (Table 4.6 entry 2 vs entry 1).

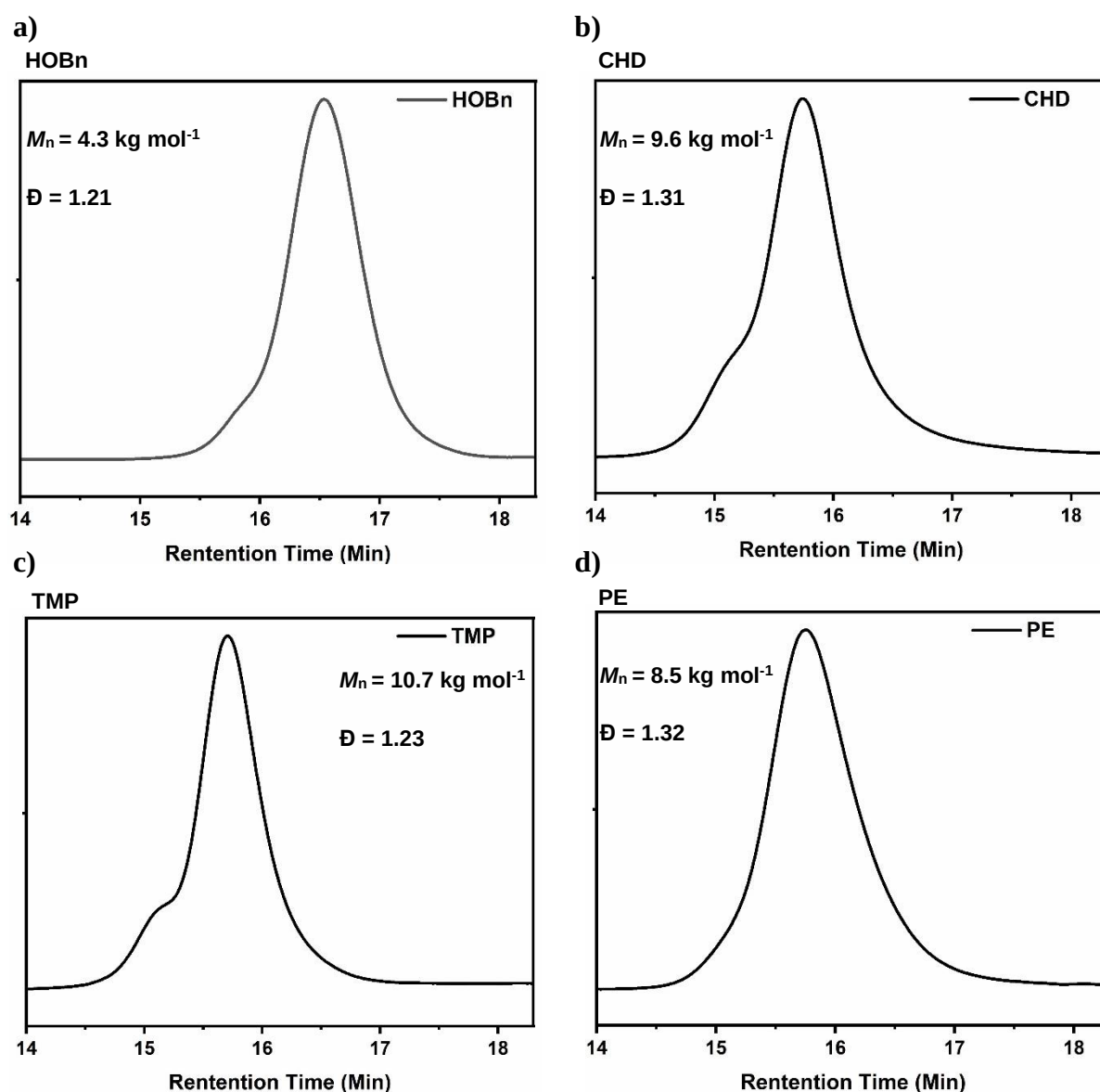


Figure 4.23: GPC traces of the ring-opening copolymerisation (ROCOP) of PA and BO with $\text{Hf}(\text{Bn})_4$ catalyst, with various CTA containing different number of alcohol groups, to create different polymer architectures ($^{\circ}\text{ROCOP}$ conditions: $[\text{Hf}(\text{Bn})_4] = 10 \text{ mM}$, $[\text{PA}] = 0.5 \text{ M}$, $[\text{CTA}] = 20/n \text{ mM}$, where n = the number of alcohol groups, $\text{BO} = 1 \text{ mL}$, $50\text{ }^{\circ}\text{C}$, Table 4.6). CTA = a) HOBn, b) CHD, c) TMP, d) PE (see Table 4.6 for alcohol structure). The GPCs obtained in this figure were run on an Agilent LC1260 Infinity II (see S7.2.2 for instrument details).

The M_n obtained by GPC for the reactions using TMP (three-arm) and PE (four-arm) did not increase in the manner expected for these architectures, $M_{n, GPC} = 10.7$ and 8.5 kg mol^{-1} for TMP and PE respectively (Table 4.6 entries 3 and 4, Figure 4.23), despite all PA being consumed in the reactions. This lack of increase to molar mass could be due interactions of the star polymers (with an increasing number of hydroxyl end groups) with the GPC column, which are calibrated with polystyrene standards. Perhaps, the true molar mass values may be higher for these samples. In future, triple detection GPC experiments should be conducted to determine the K and α values, which are useful to accurately determine molar mass for star polymers (using the Mark-Houwink plot relationship $[\eta] = KM^\alpha$). In all cases, the molar mass distributions were monomodal ($1.21 < Đ < 1.32$, Table 4.6 and Figure 4.23).

4.6 Summary and Future Work

4.6.1 Summary

Three generations of poly(ester-*alt*-ether) catalysts were explored in this work (Figure 4.24). Firstly, ligand-based catalysts of the form $ML_2(O^iPr)_2$, were investigated for the effect of the group(IV) metal and the ligand (**L**). The $Zr(L2)_2(O^iPr)_2$ and $Hf(L2)_2(O^iPr)_2$ catalysts were both highly selective for poly(ester-*alt*-ether) linkages (96 and 98 %, respectively) and produced poly(ester-*alt*-ethers) showing controlled molecular weights. In comparison, the $Ti(L2)_2(O^iPr)_2$ analogue produced bimodal molar mass distributions and was less selective (89 %). The polymerisation rate constants (k_{obs}) were in the order $Ti(IV) < Zr(IV) = Hf(IV)$, which were 10-100 times lower than the previously reported $Zr(L1)_2(O^iPr)_2$ (catalyst **1** in chapters 2 and 3). The ligand (**L**) was found to have only very minor influence on catalysis, unless it produced a change in the complex's coordination environment. Complexes where the two imine nitrogen donors were in *trans*-positions, were an order of magnitude faster than the *cis*-position analogues (e.g all the catalysts synthesised in this study).

Secondly, commercial ZrX_4 catalysts were explored for the influence of co-ligand (**X**). The study of ZrX_4 catalysts showed that a range of co-ligands (**OⁱPr**, **HOⁱPr**, **OEt**, **Cl** and **Bn** + **HOBn**) could be used to make highly selective poly(ester-*alt*-ethers) (≥ 95 %) and with control over molar mass and distributions. Rates were 1-3 orders of magnitude faster than the $ML_2(O^iPr)_2$ catalysts. On the other hand, the $Zr(Oct)_4$, and $Zr(NMe_2)_4$ suffered from reduced selectivity (40 and 43 %, respectively), and in the case of $Zr(NMe_2)_4$, reduced control over molar mass distribution. These results suggest that changing the co-ligand, may offer interesting opportunities to alter the selectivity for poly(ester-*alt*-ether) content (40-97 %), a useful handle in controlling thermal-mechanical properties, solubility and degradability.

Lastly, commercial catalysts of the form $\text{Zr}(\text{Bn})_4$ + alcohol were explored for poly(ester-*alt*-ether) synthesis. A series of PA/EDD and PA/BO monomer combinations showed that both $\text{Zr}(\text{Bn})_4$ and $\text{Hf}(\text{Bn})_4$ can successfully produce poly(ester-*alt*-ethers) with high selectivity and control. The $\text{Hf}(\text{Bn})_4$ was then used to make selective and controlled poly(ester-*alt*-ethers) with functional end-groups (2-bromoethanol, 5-hexen-1-ol and 5-hexyn-1-ol). Alcohols with different numbers of hydroxyl groups were then employed to produce poly(ester-*alt*-ethers) with polymer architectures from linear to star.

In the time this thesis has been produced, poly(ester-*alt*-ether) catalysis has grown from being just one reported catalyst and a limited set of monomers, to being feasible with a range of monomers, catalysts and architectures. Simple, commercial metal salts can be used to alter the amount of polyether (by way of metal or co-ligand specification), as well as decide on end group chemistry and polymer architecture, avoiding low-yielding catalyst synthesis, and, all at faster rates than the original ligand-based complexes.

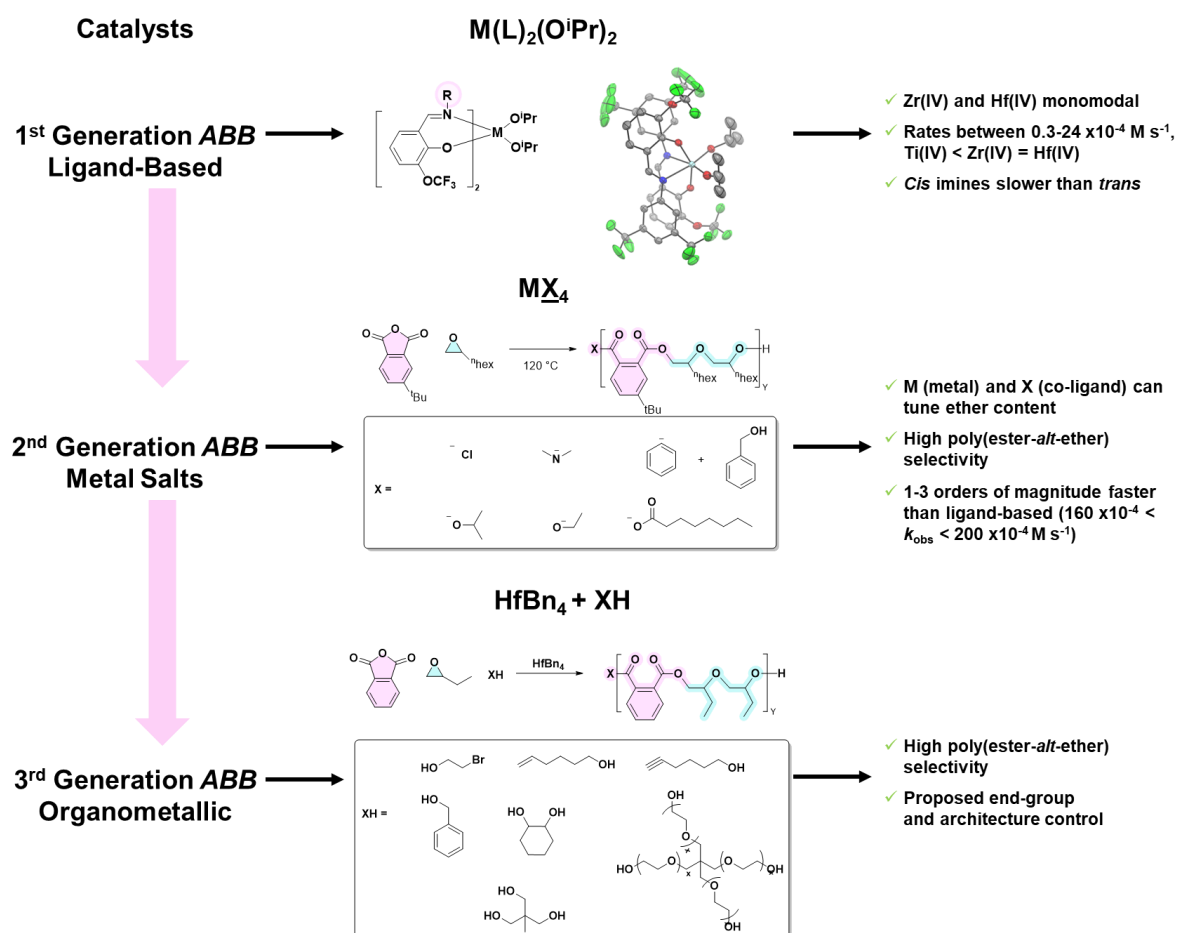


Figure 4.24: An outline of the three ‘generations’ of poly(ester-*alt*-ether) catalysts explored in this work, with a short summary of the conclusions drawn. The ligand-based (1st generation) catalysts were explored in section 4.3, the 2nd generation metal salt-based catalysts were explored in section 4.4, while the non-initiating catalysts (3rd generation) were explored in section 4.5.

4.6.2 Future Work

Further proof of end-group control is required. For example, MALDI-TOF should be utilised to accurately assess the initiation of the polymerisations in sections 4.4.1 to 4.5.3. This has proven a difficult experiment with poly(ester-*alt*-ethers), although would be the most useful here. Furthermore, control experiments, whereby the **ZrX₄** catalysts are stirred with the anhydride or epoxide, separately, and the small molecule products analysed by mass spectrometry and NMR spectroscopy, should be performed to identify if the co-ligand ring opens the monomers, and, whether it first opens an epoxide or anhydride.

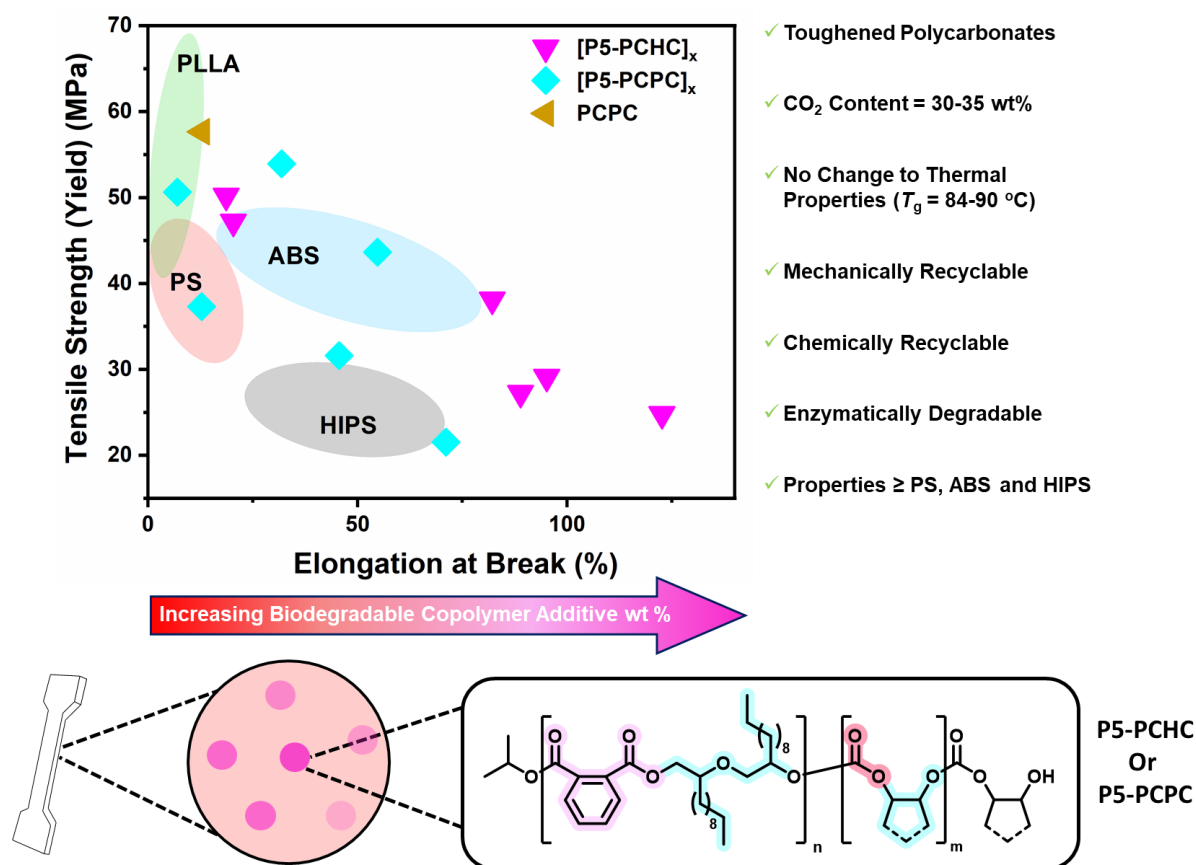
For the polymer architecture study, a useful proof of initiation from the added alcohol (with different number of OH functional groups) would be through triple detection GPC, to get a more accurate molar mass, as well as to ascertain the M_n of each ‘arm’. It could also be useful to synthesise a series of polymers whereby the overall DP is constant (rather than the DP of each arm, as in this work), in order to permit a comparison of viscosities, as polymer architectures with more arms tend to exhibit lower viscosities (for an equivalent overall DP). This work was completed with the intention of producing low T_g polymers for use as tougheners, to compare the effect of architectures on blend performance. Lead (linear) polymer samples from chapters 3 and 5 should be investigated.

4.7 References

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CHAPTER 5

Chapter 5: Degradable, Recyclable and Toughened High Molar Mass Poly(cyclopentene carbonate) (PCPC) Blends for Sustainable Alternative Thermoplastic Materials



Statement of Contribution to Co-Authored Work

This chapter includes work performed by other co-authors on this study.

Balzas Striker; synthesis of the high molar mass PCPC used for toughening.

Dr Thomas M. McGuire; performed the chemical recycling experiments on TGA scale.

Georgios Kalimeris performed tensile experiments utilising digital image correlation (3 samples).

All other work is that of the author.

5.1 Introduction

Plastics have provided many important societal benefits, and, helped improve our quality of life substantially.^{1,2} However, the majority of these plastics, today, are derived from non-renewable sources, such as petrochemicals.^{3,4} In 2017, ~8 % of total annual oil production was consumed in polymer manufacturing, which in 2015, was responsible for 3.8 % (1.8 Gt) of global carbon dioxide (CO₂) emissions.^{2,3,5} Some predictions suggest that this number could exceed 6.5 Gt CO₂ emissions per annum by 2050.⁶ These materials were designed to last, being strong, tough and chemically resistant.² For this reason, they are not typically (bio)degradable, leading to accumulation in waste streams and the environment (potentially 6.0 Gt of plastic waste has accumulated since the 1950s).⁷ Further concerns have been raised over their physical breakdown to micro- and nano-plastics, for which the health and environmental implications of their accumulation are still unfolding.^{2,4,8} It is imperative that the scientific community find alternative materials that are renewably sourced and are amenable to a range of end-of-life options, including mechanical/chemical recycling, as well as biodegradation.^{1,2,9}

One promising set of polymers are those produced directly from CO₂. This is achieved by the ring opening copolymerisation (ROCOP) of CO₂ and heterocycles, most often epoxides.^{10–12} There is a three-fold reduction in green-house gas emissions (relative to the analogous polyether formed by homopolymerisation of the epoxide) when incorporating CO₂ into the polymer backbone, as two molecules of CO₂ are saved per epoxide replaced.^{13–15} As a common waste product, CO₂ is a cheap and abundant feedstock, which can be integrated into current manufacturing infrastructure.¹⁶ Epoxides, such as CHO and CPO, are currently derived from petrochemicals, although more sustainable routes to their preparation from triglycerides have been demonstrated.^{17,18}

Most commercial engineering thermoplastic materials are made with high molar mass polymers, as many properties such as glass transition, processability, strength and toughness, are improved by being 3-6 times above the molar mass of entanglement (M_e), called the critical molar mass (M_c).¹⁹ Traditionally, issues in producing polymers with higher molar masses have restricted the application to polyols, where M_n is less than 10 kg mol⁻¹, for use in coatings, adhesives, foams and elastomers.^{20–25} Recently, improvements in catalysis enabled synthesis of higher molar mass polycarbonates, including poly(cyclohexene carbonate) (PCHC), poly(ethyl-cyclohexene carbonate) (PeCHC), poly(vinyl-cyclohexene carbonate) (PvCHC), poly(limonene carbonate) (PLC) and poly(cyclopentene carbonate) (PCPC).^{24,26–31} Recently, Williams and co-workers investigated the thermal-mechanical and viscoelastic properties of

high- M_n (over 100 kg mol⁻¹), narrowly dispersed polycarbonates PCHC, PeCHC, PvCHC and PCPC.³² Of these, PCPC was particularly promising, with a M_e an order of magnitude below the other CO₂-derived polycarbonates studied ($M_e = 4.0\text{--}4.9$ kg mol⁻¹). The PCPC with $M_n > M_e$ ($M_n = 114$ kg mol⁻¹) demonstrated promise as an engineering thermoplastic, with a relatively low zero shear viscosity (0.8 MPa s⁻¹), important in polymer processing, a high ultimate tensile strength ($\sigma_y = 59$ MPa) and a Young's modulus ($E = 1.7$ GPa), providing the sample with mechanical strength, while also having an elongation at break of 7 %, and, therefore, a tensile toughness of 2.9 MJ m⁻³.³² PCPC can also be mechanically recycled, as well as chemically recycled to monomer (CRM), producing cyclopentane oxide (CPO) and CO₂.^{32,33} Although, its enzymatic degradation has not yet been reported.

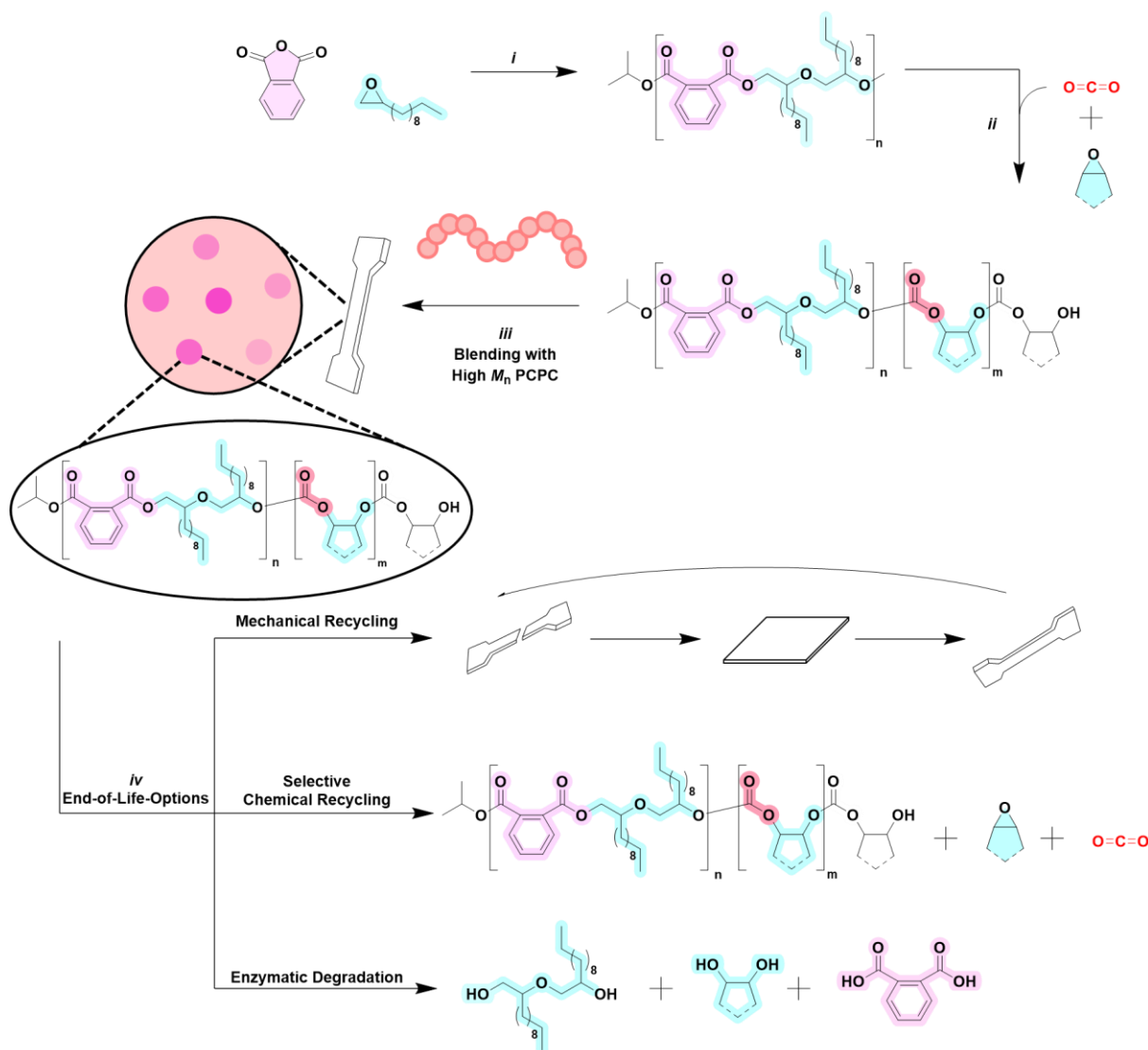
The application of polycarbonates, derived from CO₂, as sustainable replacements for engineering thermoplastics, is still limited by their brittleness.³² Simple strategies are required, to improve material toughness, without compromising the other beneficial thermal-mechanical properties, sustainability, or cost. Rubber toughening is an interesting strategy that has been effective for polyolefins, for example in toughening PS (e.g HIPS), as well as for biorenewable polylactic acid (PLLA). One successful approach has been to blend amphiphilic block copolymers into the polymer matrix.^{34–39} One block is a low T_g ‘matrix-phobic’ polymer, designed to drive phase separation, while the other is ‘matrix-philic’, providing compatibilisation of the dispersed particles within the matrix, enhanced control over their particle size, as well as access to smaller particles.^{39–41} The dispersed phase toughens the polymer matrix by cavitating during elongation (or impact), providing void space that promotes shear yielding within the matrix.^{39–41} When the dispersed phase is of a critical size, and, below a critical interparticle distance (matrix ligament thickness), overlap of stress fields effectively prevents the localisation of stress, which can lead to significant improvements in toughness.^{39–}

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5.2 Aims

The objective of this work, is to toughen high molar mass PCPC, derived from CO₂, in order to provide a possible sustainable alternative for engineering thermoplastics; like PS, HIPS or ABS, which are not recyclable and are petrochemicals. The additives are poly(ester-*alt*-ether)-*b*-PC (**AB** type) copolymers (where PC = PCPC or PCHC). In this work, **A** is a low T_g poly(ester-*alt*-ether) (**P5**, first synthesised in chapter 2), composed of alternating ester and ether linkages, from the selective, consecutive insertion of two epoxides, designed to be the matrix-phobic block.^{42,43} This new class of polymers are enzymatically degradable, and, are very effective in rubber toughening of poly-L-lactide (PLLA), as described in chapter 3. **B** is a low molar mass block of PCPC or PCHC, targeting $M_n = 2.4$ and 2.7 kg mol^{-1} , respectively, to provide compatibility in the matrix. It has been shown previously that PCHC-*grad*-PCPC showed a single T_g , suggesting miscibility of the two polycarbonate domains.⁴⁴ It was also shown for PLLA, that the **B** block is more effective when it is miscible with (i.e a low/negative Flory Huggins interaction parameter, χ_{12}), although not the same species as, the matrix polymer. This miscibility finding was attributed to better ‘wetting’ between the corona formed by the dispersed particles and the chains of the matrix (explored in greater detail below).^{39,45,46} Here, the influences of both low molar mass PCPC and PCHC as **B**-blocks will be targeted (Scheme 5.1).

The strategy is to blend poly(ester-*alt*-ether)-*b*-PC with high molar mass PCPC at various wt%. This should allow the exploration of the effect of loading on the thermal-mechanical properties—to be investigated by DSC, TGA and uniaxial tensile testing—and on morphologies (via SEM). The effect of these blends on the PCPC end-life recycling will also be explored (Scheme 5.1). These will be explored via mechanical recycling, using compression molding, as well as chemical recycling to monomer (CRM). Enzymatic degradation of all polymer components, including the poly(ester-*alt*-ether) (**A**-block), poly(ester-*alt*-ether)-*b*-PC (**AB**), PCPC and the polymer blends will also be explored. In chapter 2, this strategy was successfully applied to toughening PLLA, and here, the aim is to explore whether it can be translated to toughening CO₂-based polycarbonates, as these are also promising sustainable alternatives for PS-based thermoplastics.



Scheme 5.1: The strategy for toughening high molar mass PCPC, derived from CO₂, with (bio)degradable block polymers. The four key parts to this approach are depicted; i) Synthesis of poly(ester-*alt*-ethers), ii) Synthesis of poly(ester-*alt*-ether)-*b*-PC diblock copolymers (where PC = PCPC or PCHC), iii) Blending with high molar mass PCPC and iv) Exploring end-of-life options through mechanical recycling, selective chemical recycling and enzymatic degradation.

5.3 Polymer Synthesis

The objective was to synthesise degradable poly(ester-*alt*-ether)-*b*-PC (**AB**) diblock copolymers (where PC = PCPC or PCHC), for use as toughening agents for high *M_n* PCPC, synthesised from CO₂. Poly(ester-*alt*-ether) synthesis has been previously reported.^{42,43} Here, building on the improved understanding of poly(ester-*alt*-ether) catalysis developed in chapter 4, commercial Hf(O^{*i*}Pr)₄(HO^{*i*}Pr) (referred to here as catalyst **3**, for simplicity) was used for poly(ester-*alt*-ether) ROCOP (Table 5.1 and section S8.5.1).

The polymerisation was performed under the conditions [3] : [PA] : [EDD] = 1 : 125 : 350, at 50 °C in neat epoxide. Aliquots analysed by ¹H NMR spectroscopy, demonstrated complete anhydride consumption within 60 minutes. The polymer was purified by three cycles

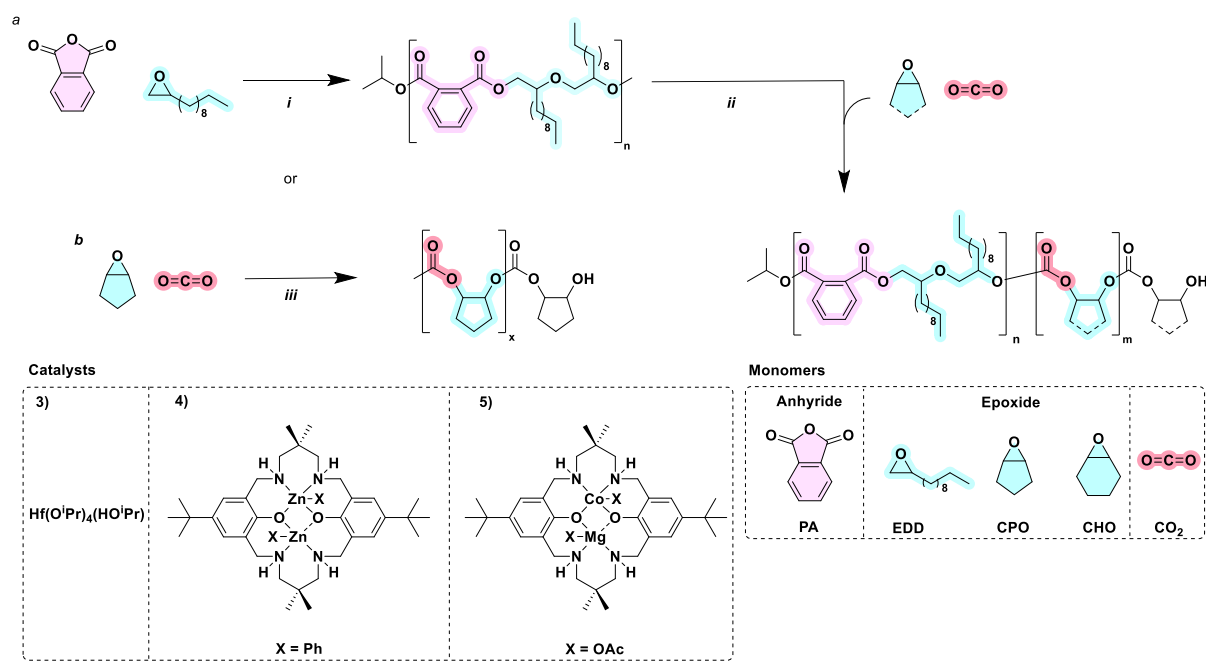
of precipitation (from CH_2Cl_2) in methanol, passing through a PTFE filter. The purified polymer was dried under vacuum, at 60 °C, for 2 days. The resulting **A**-block polymer, **P5**, was comprised of the monomers phthalic anhydride (PA - **A**) and 1,2-epoxy-9-decene (EDD - **B**), enchaind in an **-ABB-** fashion (Table 5.1). The selectivity for ring-opened anhydride : epoxide in the purified polymer was 1 : 2 (DP 24 : 48 for PA : EDD), indicative of a high selectivity for poly(ester-*alt*-ether) linkages. Its ^1H COSY NMR spectrum, showed correlation of the methine ester and methylene ether protons (Figures S8.5.2 and S8.5.3, correlation 19-20) as well as the methine ether and methylene ester protons (Figures S8.5.2 and S8.5.3, correlation 7-8), although not of the ester protons to each other (Figures S8.5.2 and S8.5.3, no correlation 7-20). This has already been demonstrated to be characteristic of the poly(ester-*alt*-ether) linkages.^{42,43} The experimental molar mass ($M_n = 10.9 \text{ kg mol}^{-1}$) was in agreement with theoretical values ($M_{n,\text{theory}} = 12.4 \text{ kg mol}^{-1}$), with a narrow molar mass dispersity ($\mathcal{D} = 1.18$) as determined by size-exclusion chromatography, SEC (Table 5.1 and Figure S8.5.22). Thermal analysis indicated **P5** was amorphous, with a low T_g (-37 °C) and high thermal decomposition ($T_{d,5} = 315 \text{ °C}$, Figure S8.5.24 and S8.5.26).

The poly(ester-*alt*-ether)-*b*-PC samples were synthesised using **P5** as a macroinitiator for the ROCOP of CO_2 and CPO or CHO, using catalyst **4** ([**4**]: [**P5**]: [CPO/CHO] = 1 : 31/19 : 960/1976 at 1 bar CO_2 pressure, 80 °C, see Table 5.1). As an example, the synthesis of **P5-PCPC** will be discussed here, and, the equivalent experimental data for **P5-PCHC** is presented in the supplementary information (S8.5.1). Before use as a macroinitiator, for the synthesis of block polymers, **P5** was dried under vacuum, over P_2O_5 , for 2 days. Full conversion after 136 hours was confirmed by ^1H NMR spectroscopy. The polymer was purified by stirring with 5 mg of benzoic acid for 10 minutes, followed by three cycles of precipitation from minimum CH_2Cl_2 , passing through a PTFE filter into MeOH. The pure polymer was then dried under vacuum, at 60 °C, for 2 days.

The M_n by GPC increased from 10.9 kg mol^{-1} , **P5**, to 13.3 kg mol^{-1} after CO_2 /CPO ROCOP, forming **P5-PCPC**. Furthermore, molar mass dispersity remained low ($\mathcal{D} = 1.11$) and monomodal, evident of block polymer formation (Figures S8.5.22-23 and Table 5.1). The DP of CPO ROCOP, as determined by integration of the alcohol end group signals (vs the main chain) in the ^1H NMR spectrum (Figure S8.5.7), was 20, and, therefore, the DP of PA : EDD : CPO was 24 : 48 : 20. The M_n as estimated by ^1H NMR spectroscopy (13.5 kg mol^{-1}) was in close agreement with the value obtained by GPC. A single diffusion coefficient in DOSY NMR spectra, indicated block polymer formation, rather than mixtures of homopolymers (Figure

S8.5.11). Analysis of polymer end-groups by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, for **P5**, demonstrated a mixture of primary (148.52-148.11 ppm) and secondary (147.13-146.94 ppm) alcohol end group signals, due the regio-random epoxide ring-opening as described in chapters 2 and 3 (Figures S8.5.16-18).⁴³ On the other hand, **P5-PCPC** demonstrated only secondary alcohol resonances in the region typical of PCPC-OH end-groups (146.84 ppm, Figure S8.5.19). No significant change in the poly(ester-*alt*-ether) T_g was observed (from -37 to -34 for **P5** and **P5-PCPC** respectively), which suggests that the two blocks (**AB**) are immiscible (Figure S8.5.24). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showed carbonyl shifts from both **P5** ester and PCPC carbonate linkages (167.0 and 153.7 ppm respectively), with no detectable peaks at intermediate chemical shifts (Figure S8.5.9). This suggests block copolymer formation, without scrambling by transesterification.⁵²

Lastly, high M_n PCPC was synthesised via CO_2/CPO ROCOP, this time using catalyst **5** (ROCOP Conditions; **[5]** : **[CHD]** : **[CPO]** = 1 : 4 : 20 000, diluted with 12 mL toluene, at 20 bar CO_2 and 100 °C, for 164 hr, see experimental section S7.3.1.9 for experimental details and S8.5.1 for full characterisation data of PCPC). The M_n by GPC was 82.2 kg mol⁻¹, approximately 18-24 times the entanglement molecular weight of PCPC (3.4–4.6 kg mol⁻¹),³² with a broad, monomodal molar mass distribution (Đ = 1.58). The thermal properties (T_g and $T_{d,5}$ = 90 and 270 °C respectively) are consistent with previously reported PCPC well above the M_e .³² After the successful synthesis, purification and characterisation, the **AB** polymers, **P5-PCPC** and **P5-PCHC**, were targeted as rubber toughening additives in polymer blends with this high M_n PCPC.

Table 5.1: Overview of polymer synthesis and characterisation data.

Polymer	DP [PA]:[EDD]:[PCPC/PCHC] ^c	$M_n(\text{D})$ [kg mol ⁻¹] ^d	$M_n(\text{Th.})^e$	$T_g(\text{°C})^f$	$T_{d,5}(\text{°C})^g$
P5 P(PA-EDD-EDD) ^a	24:48	10.9 (1.18)	12.4	-37	315
P5-PCPC ^a	24:48:20	13.3 (1.11)	13.5	-33	158
P5-PCHC ^a	24:48:30	13.7 (1.11)	15.2	-34	180
PCPC ^b	0:0:3033	82.2 (1.58)	388.6	90	270

^aROCOP conditions i) [3] = 12.8 mM (1 eq), [PA] = 1.64 M (125 eq), EDD = 25 mL (350 eq), 50 °C. ii) For **P5-PCHC** synthesis, [4] = 5 mM (1 eq), [P5] = 155 mM (31 eq) CHO = 2 mL (1976 eq), 1 bar CO₂ pressure, 80 °C, 124 hrs. For **P5-PCPC** synthesis, [4] = 10 mM (1 eq), [P5] = 190 mM (19 eq), CPO = 1 mL (960 eq), 1 bar CO₂ pressure, 80 °C, 136 hrs. ^bROCOP Conditions: iii) [5] = 0.3 mM (1 eq), CHD = 1.26 mM (4 eq), CPO = 15 mL (172 mol, 20 000 eq), toluene 12 mL, 20 bar CO₂, 100 °C, 164 hr (see appendix section S8.5.1 for full characterisation data). ^cSee section S8.5.1 of the appendix for an explanation of the calculation of DPs. ^dDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards. ^eTheoretical M_n were calculated from the monomer conversion data. ^fObtained from Differential Scanning Calorimetry (DSC, third heating cycle, 10 °C min⁻¹ heating rate). ^gObtained from TGA (polymer samples were heated from 30 to 700 °C at a rate of 10 °C min⁻¹, under N₂ flow 12 mL min⁻¹).

5.4 Blending with high M_n PCPC

The poly(ester-*alt*-ether)-*b*-PC diblock copolymers were then investigated as toughening agents for high M_n PCPC. Their effect on the thermal-mechanical properties of the blends were investigated, in comparison to neat PCPC prepared above (PCPC, M_n = 82.2 kg mol⁻¹, $\bar{D}$ = 1.58). Blended samples were prepared by adding solutions of PCPC and **AB** polymer (from CH₂Cl₂) in teflon moulds, vacuum drying to remove all the solvent at 60 °C (for ~2 days) and compression molding the dry samples above the PCPC glass transition temperature (130 °C for 10 minutes), producing dry, transparent and colourless films (see experimental chapter S7.3.2.2 for blend preparation protocol, Figure S8.5.39 for a representative photograph and section S8.5.2.2 for TGA). Blends of 1, 2, 5, 10, 15 and 20 wt% **P5-PCPC** or **P5-PCHC** in PCPC were prepared, to determine how the blend properties changed with wt% polymer additive. The thermal and mechanical properties were explored by

DSC/TGA (Table 5.2 and sections S8.5.2.1-2) and by uniaxial tensile testing (according to ISO 527 10 mm min⁻¹), respectively (Table 5.2 and Figure 5.1). The PCPC polymer blends described in this work will be represented as **[P5-PCPC]_z**, where the name of the diblock polymer additive is within the square brackets and the wt% used in the PCPC blend is denoted by the subscript on the outside of the square brackets (z).

5.4.1 Thermal-Mechanical Properties

Thermal analysis of PCPC indicated it was amorphous, with a T_g of 90 °C and no observable melt (Table 5.2 and Figure S8.5.27), in-line with previous reports.³² Only minor changes in the T_g occurred throughout the series of **[P5-PCPC]_z** (z = 1-20) and **[P5-PCHC]_z** (z = 1-20) polymer blends, decreasing as wt% polymer additive increased, although remaining within 6 °C of neat PCPC (Table 5.2, Figure S8.5.27-28). Control blends, using systematically increasing quantities of **P5** in PCPC (20, 40, 60 and 80 %), showed no change in T_g at any composition. These results suggest **P5** is completely immiscible in the high molar mass PCPC (Figure S8.5.36).

Table 5.2: Summary of thermal and mechanical properties of a series of poly(ester-*alt*-ether)-*b*-PC)/PCPC polymer blends.^a

Blend	T_g (°C) ^b	$T_{d,5}$ (°C) ^c	E (GPa) ^d	σ_Y (MPa) ^d	ξ_B (%) ^d	U_T (MJ m ⁻³) ^d
PCPC	90	270	1.1 ± 0.1	57.7 ± 5.1	12.8 ± 4.4	5.4 ± 2.6
[P5]₅	87	270	0.9 ± 0.0	43.5 ± 1.0	27.1 ± 12.2	10.1 ± 4.7
[PCHC₂₀]₅	85	230	1.0 ± 0.1	57.7 ± 2.0	8.3 ± 1.3	2.8 ± 0.7
[P5-PCHC]₁	89	269	1.1 ± 0.1	47.2 ± 2.6	20.4 ± 2.9	7.8 ± 1.2
[P5-PCHC]₂	90	268	1.2 ± 0.3	50.2 ± 5.6	18.7 ± 7.6	7.4 ± 3.1
[P5-PCHC]₅	88	265	1.5 ± 0.1	38.1 ± 2.1	82.1 ± 10.1	28.1 ± 4.1
[P5-PCHC]₁₀	87	259	1.3 ± 0.2	29.1 ± 2.6	95.1 ± 23.3	25.8 ± 5.8
[P5-PCHC]₁₅	86	257	1.1 ± 0.1	27.2 ± 2.0	88.9 ± 17.7	20.2 ± 4.6
[P5-PCHC]₂₀	85	252	1.0 ± 0.1	24.8 ± 2.0	122.6 ± 17.4	26.4 ± 3.9
[P5-PCPC]₁	88	267	1.2 ± 0.1	50.6 ± 3.1	7.0 ± 1.7	2.4 ± 0.9
[P5-PCPC]₂	86	267	1.0 ± 0.1	53.9 ± 2.7	31.9 ± 8.9	13.9 ± 3.7
[P5-PCPC]₅	87	247	1.6 ± 0.2	43.6 ± 3.8	54.8 ± 24.4	21.6 ± 8.2
[P5-PCPC]₁₀	87	239	1.6 ± 0.2	31.6 ± 2.2	45.6 ± 6.2	13.6 ± 2.0
[P5-PCPC]₁₅	86	220	1.3 ± 0.1	21.5 ± 4.3	71.1 ± 9.6	13.6 ± 5.6
[P5-PCPC]₂₀	84	220	1.2 ± 0.2	37.3 ± 4.0	12.8 ± 2.1	4.2 ± 1.2

^aPCPC was synthesised as per Table 5.1 and Section S7.3.1.9 (M_n = 82.2, $\bar{D}$ = 1.58). ^bObtained from differential scanning calorimetry (DSC, third heating cycle, 10 °C min⁻¹ heating rate from -80 to 200 °C). ^cObtained from TGA (polymer samples were heated from 30 to 700 °C, at a rate of 10 °C min⁻¹, N₂ flow = 12 mL min⁻¹). ^dUniaxial tensile measurements were conducted at 10 mm min⁻¹ extension rate. The mean values and standard deviations are calculated from measurements conducted independently on five separate specimens, conforming to dimensions for ISO 527-2, type 5B. Tensile toughness was calculated from the area under the stress-strain plots.

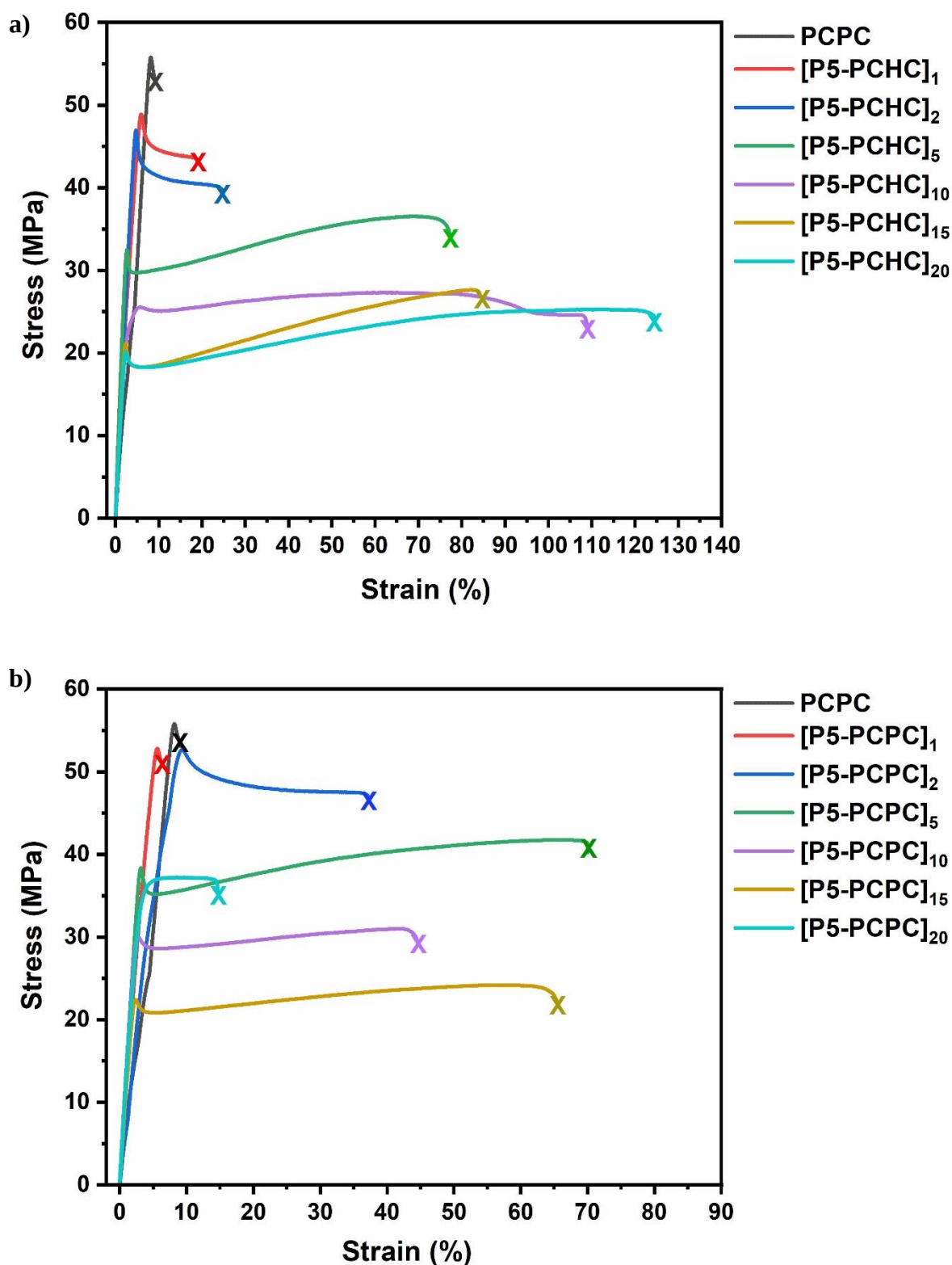


Figure 5.1: Representative stress versus strain data from tensile measurements of a) PCPC/P5-PCHC blends ([P5-PCHC]_z), and b) PCPC/P5-PCPC blends ([P5-PCPC]_z), with between 1-20 wt% polymer additive (z = 1-20).

The wt% of **P5-PCPC** or **P5-PCHC** in PCPC had a substantial effect on the sample mechanical properties. Neat PCPC is a brittle plastic: it is stiff, characterised by a Young's

modulus ($E = 1.1 \pm 0.1$ GPa), strong, with a maximum stress (σ_Y) of 57.7 ± 5.1 MPa, and brittle, failing at an elongation at break (ϵ_B) of 12.8 ± 4.4 % (Table 5.2 and Figure 5.1). All polymer blends showed stress-strain relationships indicative of plastic behaviour, with σ_Y between 54-22 MPa, ϵ_B between 7-123 % and tensile toughness (U_T) between 4.2-28.1 MJ m⁻³. Overall, in most cases, the σ_Y decreased gradually, and the ϵ_B increased dramatically with greater wt% polymer additive. This manifests, in the representative stress-strain curve, as an earlier onset of plastic yielding (necking), followed by plastic (inelastic) deformation and an increased period of elongation, with increased wt% polymer additive (Figure 5.1). The U_T reached a maximum, for both **P5-PCPC** and **P5-PCHC** series, at 5 wt% (**[P5-PCHC]₅** $U_T = 28.1 \pm 4.1$ MJ m⁻³ and **[P5-PCHC]₅** $U_T = 21.6 \pm 8.2$ MJ m⁻³). The blends show toughness values which are 4 (**[P5-PCPC]₅**) and 5 (**[P5-PCHC]₅**) times greater than neat PCPC (5.4 ± 2.6 MJ m⁻³). This is notable, as only small quantities of the polymer additive (5 wt%) are required for effective toughening of the PCPC matrix (a 5 wt% sample means 3.75 % of ‘additive’ for the **P5-PCPC**, as only **P5** is different to the matrix). Also, 2 wt% of **P5-PCPC** (**[P5-PCPC]₂**) increased the elongation and toughness three times ($\epsilon_B = 31.9 \pm 8.9$ and $U_T = 13.9 \pm 3.7$ MJ m⁻³), while maintaining a high tensile strength (53.9 ± 2.7 MPa). The Young’s moduli were analogous for both series of blends, remaining within the range 1.0-1.6 GPa. The E values increase slightly between 1-5 wt%, and reach a maximum of 1.5 ± 0.1 and 1.6 ± 0.2 GPa for **[P5-PCHC]₅** and **[P5-PCPC]₅** respectively. The **P5-PCHC** series showed, overall, larger increases in ϵ_B , and consequently, greater overall U_T compared to the **P5-PCPC** series (Figure 5.1 and Table 5.2).

In order to more accurately determine the Young’s modulus, uniaxial tensile experiments with digital image correlation were undertaken (S7.2.8). These measurements facilitate the measurement of true stress and true strain, as opposed to engineering stress and strain measured on a universal testing system above. The width and thickness of a sample (dog bone) gauge area in a tensile test increase as the sample is elongated, and, these dimensional changes are not determined when calculating engineering stress/strain, but are for true stress/strain. True stress is the ratio of the tensile load/instantaneous area, while true strain is the natural logarithm of the ratio of the instantaneous gauge length and the starting gauge length. These experiments were performed on neat PCPC and the 5 wt% blends (**[P5-PCHC]₅** and **[P5-PCPC]₅**) (Table 5.3 and Figure 5.2). PCPC demonstrated very similar values to the engineering stress and strain ($\sigma_{True} = 49$ MPa and $\epsilon_{True} = 6$ %, Table 5.3 and Figure 5.2). However, the Young’s modulus measured was much higher ($E_{True} = 2.8$ GPa, Table 5.3 and

Figure 5.2). The 5 wt% blends, [P5-PCHC]₅ and [P5-PCPC]₅, again showed high tensile strengths ($\sigma_{\text{True}} = 46$ and 48 MPa, respectively) and improved ductility ($\epsilon_{\text{True}} = 29$ and 30 %, respectively). Importantly, the Young's moduli measured in this manner was also much higher (2.7 GPa, respectively). For application as thermoplastics, this is a promising result (see the discussion of mechanical properties vs PS, ABS and HIPS below, section 5.6). This highlights that the modulus values are highly underestimated for PCPC samples using the universal testing system.

Table 5.3: Summary of the mechanical properties of poly(ester-*alt*-ether)-*b*-PC)/PCPC polymer blends using digital image correlation, calculating the true stress and true strain values.^a

Blend	E (GPa) ^b	σ_{True} (MPa) ^b	ϵ_{True} (%) ^b
PCPC	2.8	49	6
[P5-PCHC] ₅	2.7	46	29
[P5-PCPC] ₅	2.7	48	30

^aPCPC was synthesised as per Table 5.1 and Section S7.3.1.9 ($M_n = 82.2$, $\bar{D} = 1.58$). ^bUniaxial tensile measurements were conducted using specimen of custom dimensions (length= 35 mm, gauge length = 4 mm, gauge width = 4 mm), using an MTS screw driven load frame, a load cell capacity of 1kN and a nominal strain-rate of $\sim 0.001 \text{ S}^{-1}$. For the digital image correlation (DIC), the frames were taken at 5 frames per second, using a point grey camera, with a resolution of 4000x2000 pixels (S7.2.8).

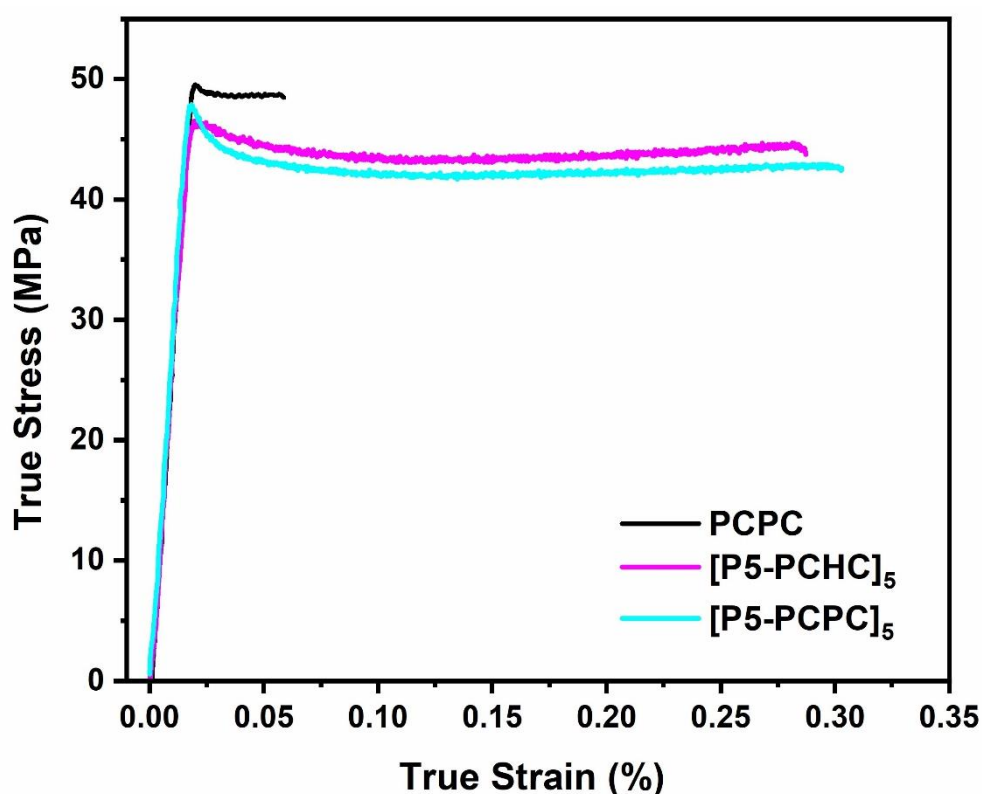


Figure 5.2: Representative true stress versus true strain data from tensile measurements (using digital image correlation) of PCPC and 5 wt% blends ([P5-PCHC]₅ and [P5-PCPC]₅).

To understand the role of the block polymer structure, PCPC blends comprising 5 wt% **P5**, or low molar mass PCHC (**PCHC**₂₀, $M_n = 2.26 \text{ kg mol}^{-1}$, where 20 = DP, see section S8.5.2.3), were prepared. These blends are termed **[P5]₅** and **[PCHC₂₀]₅**, respectively (Table 5.2 and Figure 5.3). The low molar mass PCHC (**[PCHC₂₀]₅**) had no effect on the strength of high molar mass PCPC ($\sigma_Y = 57.7 \pm 2.0 \text{ MPa}$), although it was detrimental to ductility ($\epsilon_B = 8.3 \pm 1.3 \%$ and $U_T = 2.8 \pm 0.7 \text{ MJ m}^{-3}$, the latter 50 % lower than PCPC, Table 5.2 and Figure 5.3). Conversely, the addition of **P5** (**[P5]₅**) caused the ϵ_B and U_T to double ($\epsilon_B = 27.1 \pm 12.2 \%$ and $U_T = 10.1 \pm 4.7 \text{ MJ m}^{-3}$) and the σ_Y to drop ($\sigma_Y = 43.5 \pm 1.0 \text{ MPa}$, Table 5.2 and Figure 5.3). Both blends showed similar modulus values (0.9 ± 0.0 and $1.0 \pm 0.1 \text{ GPa}$ for **[P5]₅** and **[PCHC₂₀]₅**, respectively, Table 5.2). The equivalent 5 wt% copolymer blends, **[P5-PCPC]₅** and **[P5-PCHC]₅**, showed similar tensile strengths (to **[P5]₅**), although elongations and tensile toughness values twice and three times as large for **[P5-PCPC]₅** and **[P5-PCHC]₅**, respectively (Table 5.2 and Figure 5.3). These findings suggest that the block polymer structures are crucial in providing the PCPC toughening effect.

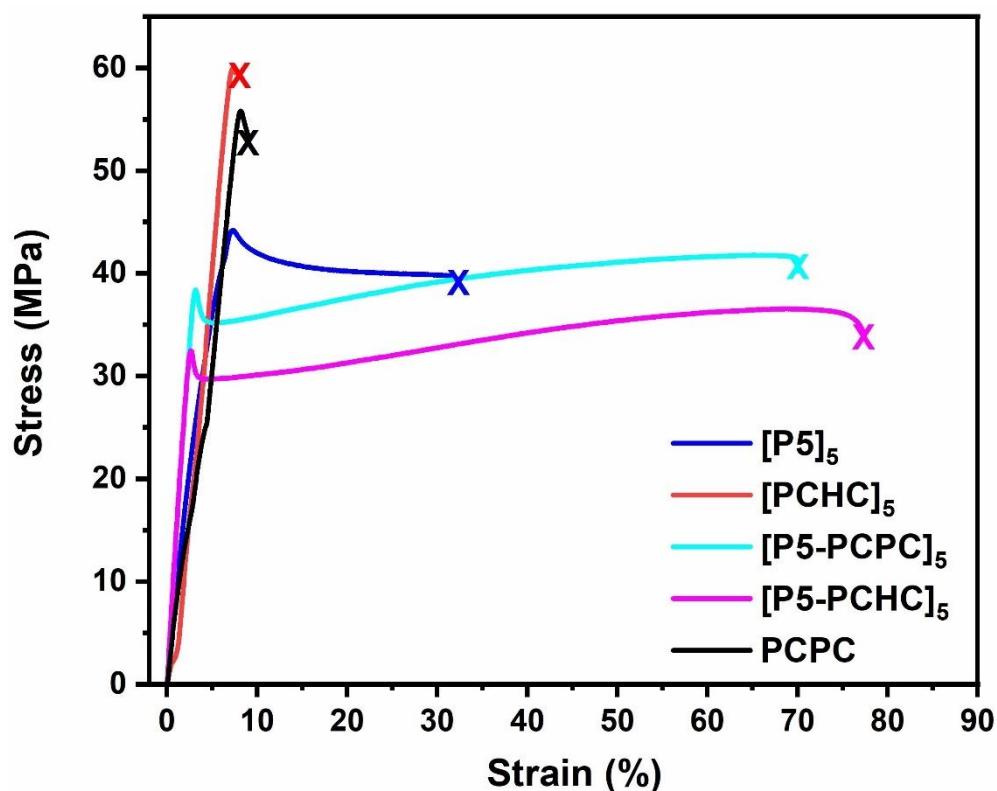


Figure 5.3: Representative stress versus strain data from tensile measurements of 5 wt% PCPC blends with the poly(ester-*alt*-ether) homopolymer **P5** (**[P5]₅**) and a low M_n PCHC (**[PCHC₂₀]₅**), compared against neat PCPC and the two 5 wt% PCPC blends prepared using block copolymers (**[P5-PCPC]₅** and **[P5-PCHC]₅**). This demonstrates the synergistic effect of the diblock copolymers in providing toughening of PCPC.

Rubber toughened thermoplastics, particularly amorphous ones, often exhibit a post yield stress drop (PYSD), manifesting as a necking behaviour after yielding.^{36,47} The decrease in tensile stress after yield can be significant (10-20 MPa or greater in many cases) and results in a loss of the practical tensile strength/toughness of the sample, regardless of large increases to the elongation at break, or stress increases at higher strains in post-yield behaviours (such as strain hardening or strain induced crystallisation).^{36,47} This parameter is important in industrial manufacture and commercialisation of thermoplastics, as it represents the strength the material will have post-yield.^{36,47} Here, the PYSD was < 5 MPa for all samples (Figures 5.1-5.3). Adding 5 wt% or higher block copolymer additive resulted in PYSD values of 2-3 MPa (Figure 5.1). The PYSD for both **[P5-PCPC]₅** and **[P5-PCHC]₅** was 3 MPa (Figure 5.1).

5.4.2 Morphology

SEM was performed on tensile specimen, perpendicular to the direction of stress, before (prepared by ultra-microtome – see S7.2.9) and after tensile fracture. The surface of neat PCPC, before fracture, was smooth and featureless (Figure 5.4a), remaining so after fracture, exhibiting little evidence of extensive plastic deformation or void formation (Figure 5.4b). On the other hand, SEM of polymer blends indicated phase-separated macrostructures (Figure 5.4c, d, e and f). Before fracture, nearly spherical voids/cavities were observed for both **[P5-PCPC]₅** and **[P5-PCHC]₅**, with average particle diameters of 1.92 and 1.46 μm , respectively (Figure 5.4c and e, Figure 5.5a and b and Table S8.5.4). This indicates that the block polymers formed well-dispersed particles throughout the PCPC matrix. It is proposed that unfavourable enthalpic interactions between the poly(ester-*alt*-ether) and PCPC (see Figure S8.5.36, showing immiscibility of **P5**/PCPC blends) drive macrophase separation. The interfacial energy between PCPC and the block polymer is lowered by the PCPC/PCHC (**B**-block) portions, resulting in controlled particles sizes, on a scale suited to toughening the PCPC polymer matrix. After fracture, the voids increased significantly in size (by ~ 5 times), and substantial matrix deformation was observed (Figure 5.4d and f). This is indicative of shear yielding within the polymer matrix (the inelastic deformation of polymer chains by unfolding and conformational change).^{16,35,44,57}

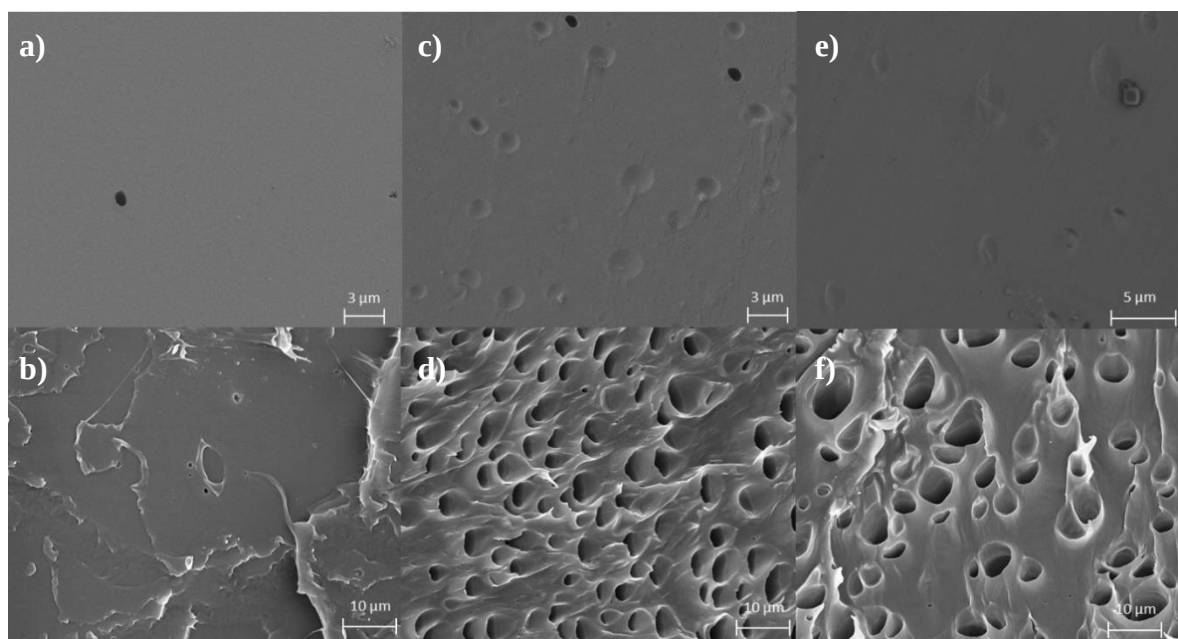


Figure 5.4: Representative SEM images of block copolymer/PCPC blends, before (a, c and e, prepared by microtoming) and after (b, d and f) tensile testing (perpendicular to direction of uniaxial stress). a) and b) control PCPC blend, c) and d) [P5-PCHC]₅, e) and f) [P5-PCPC]₅ (sample magnification illustrated).

As the polymer blend is stretched, it reaches a critical strain, at which point, the lower modulus of the dispersed phase, compared to the PCPC matrix, causes it to cavitate from the matrix. This forms voids within the PCPC matrix, acting as stress concentrators. Overall, the energy required for deformation by shear yielding decreases, promoting plastic deformation. In this way, the dispersed particles prevent the localisation of stress and allow the dissipation of more energy before tensile failure. This causes the matrix to yield at lower stresses, although elongate to much higher strains, leading to, overall, a tougher material (Figure 5.1).⁴⁰ For example, matrix deformation and distortion of the cavities was more extensive for [P5-PCHC]₅ than [P5-PCPC]₅ (Figure 5.4d and f, respectively). This effect may correlate to the greater elongation at break and tensile toughness observed in tensile experiments for [P5-PCHC]₅ (82.1 ± 10.1 % vs 54.8 ± 24.4 %, and 28.1 ± 4.1 MJ m⁻³ vs 21.6 ± 8.2 MJ m⁻³ for [P5-PCHC]₅ and [P5-PCPC]₅ respectively).

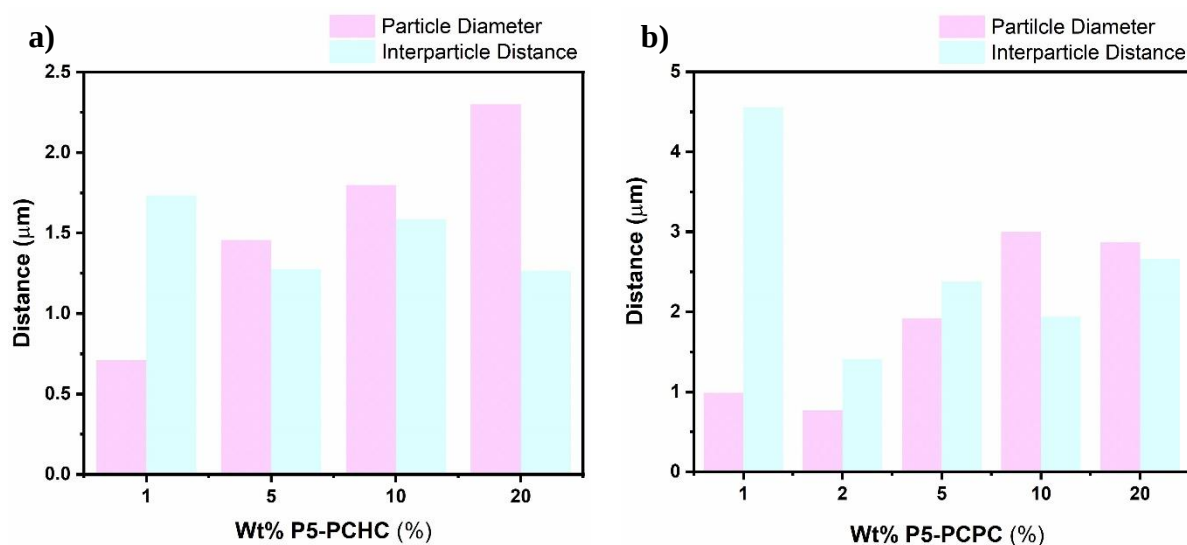


Figure 5.5: Particle diameter and interparticle distances of dispersed **P5-PCHC** or **P5-PCPC** copolymers as a function of wt% for the poly(ester-*alt*-ether)-*b*-PC)/PCPC blends.

The effect of **P5-PCPC** or **P5-PCHC** wt% ($[\text{P5-PCPC/PCHC}]_x$) on the dispersed phase morphology was investigated. The average particle diameter increased with increased wt% in both cases (Figure 5.5). For both series of blends, the tensile strength decreased (almost linearly) with increasing particle diameter (Figure 5.6d and Figure S8.5.37b). The density of stress concentrators also increases as the wt% of dispersed phase increases, promoting matrix yielding at lower stresses, due to the stress required for material flow decreasing as the dispersed particle surface area increases.⁴⁰ In contrast, for the $[\text{P5-PCHC}]_x$ series, elongation at break increased with increasing particle size in a linear fashion (Figure 5.6e).

Each wt% series observed an abrupt increase in tensile toughness, occurring between 2-5 wt% in the $[\text{P5-PCHC}]_x$ series, and, between 1-2 wt% in the $[\text{P5-PCPC}]_x$ series (Figure 5.1 for tensile data and Figure 5.6/Figure S8.5.37 for morphology correlation). As well as particle size, the critical interparticle distance (often termed matrix ligament thickness) has been demonstrated to be an important parameter for rubber toughened thermoplastic materials.⁴⁸ This value is well established for many polymers, but not for PCPC. As the **P5-PCHC** particle diameter increased from $[\text{P5-PCHC}]_1$ (0.71 μm) to $[\text{P5-PCHC}]_5$ (1.46 μm), the tensile toughness increased four-fold (7.8 ± 1.2 to 28.1 ± 4.1 MJ m⁻³) (Figure 5.6b). After this, the tensile toughness remained high as particle size increased further (to a maximum of 2.30 μm, Figure 5.6b). This is indicative of a critical particle diameter between 0.71-1.46 μm. Similarly, the four-fold increase in toughness occurred when the interparticle distance decreased below 1.73-1.59 μm (Figure 5.6c), remaining high as the interparticle distance decreased (as low as 1.27 μm, Figure 5.6c and Table S8.5.4). The $[\text{P5-PCPC}]_x$ blends also showed a sharp increase in tensile toughness, as the particle diameters increased between 0.99-

1.92 μm and the interparticle distances decreased from 4.56-2.66 μm . In both cases, this may be reasoned by more effective overlap of stress fields (that surround the dispersed particles), above the critical particle diameter and below the critical interparticle distance of each dispersed phase. This results in enhanced shear yielding behaviour of the matrix and improved toughness.^{37,48} Identification of these ranges is important, as it may inform future design strategies for PCPC blends. It must be noted that these values will vary between each specific blended material, although, the collection of many toughening studies has shown that they tend to fall into a valuable range for informing future investigations.^{48,49} For example, for toughened amorphous PLA the accepted value for critical interparticle distances is accepted to be below 1 μm .⁵⁰

Hillmyer, Bates and co-workers compared PLLA blends toughened using either poly(butylene oxide)-*b*-PLLA (PBO-*b*-PLLA) or poly(butylene oxide)-*b*-poly(ethylene oxide) (PBO-*b*-PEO) diblock copolymers.³⁹ It had been previously demonstrated, that the Flory–Huggins interaction parameter (χ_{12}) between high molar mass PLLA and short PEO chains was negative.^{39,51,52} Short chains of PEO were a more effective matrix-philic block than short chains of PLLA, leading to smaller, cylindrical particle sizes and enhanced toughening effects. The authors suggested this was due to favourable enthalpic interactions between PEO and large PLLA homopolymer chains, permitting more effective ‘wetting’ of the dispersed phase, facilitating dispersion. Large molar mass differences between the matrix PLLA chains and the small PLLA chains of the dispersed phase, resulted in poor penetration of the ‘corona’ formed by the latter at the interphase of the dispersed particles, forming ‘dry brushes’.^{39,45,46} In this work, the particle sizes and interparticle distances are smaller for the **P5-PCHC** dispersed phase, compared to **P5-PCPC** (Figures 5.4-5.5 and Table S8.5.4). It has been shown previously that PCHC-*grad*-PCPC polymers have a single T_g , suggesting miscibility of the short polymer domains/runs of PCPC and PCHC.⁴⁴ Under identical processing conditions (employed in this study), smaller particle sizes could suggest a lower interfacial energy between the **P5-PCHC** copolymer and the PCPC matrix, resulting in improved compatibility, mixing and superior toughening performance for **P5-PCHC** (compared to **P5-PCPC**).

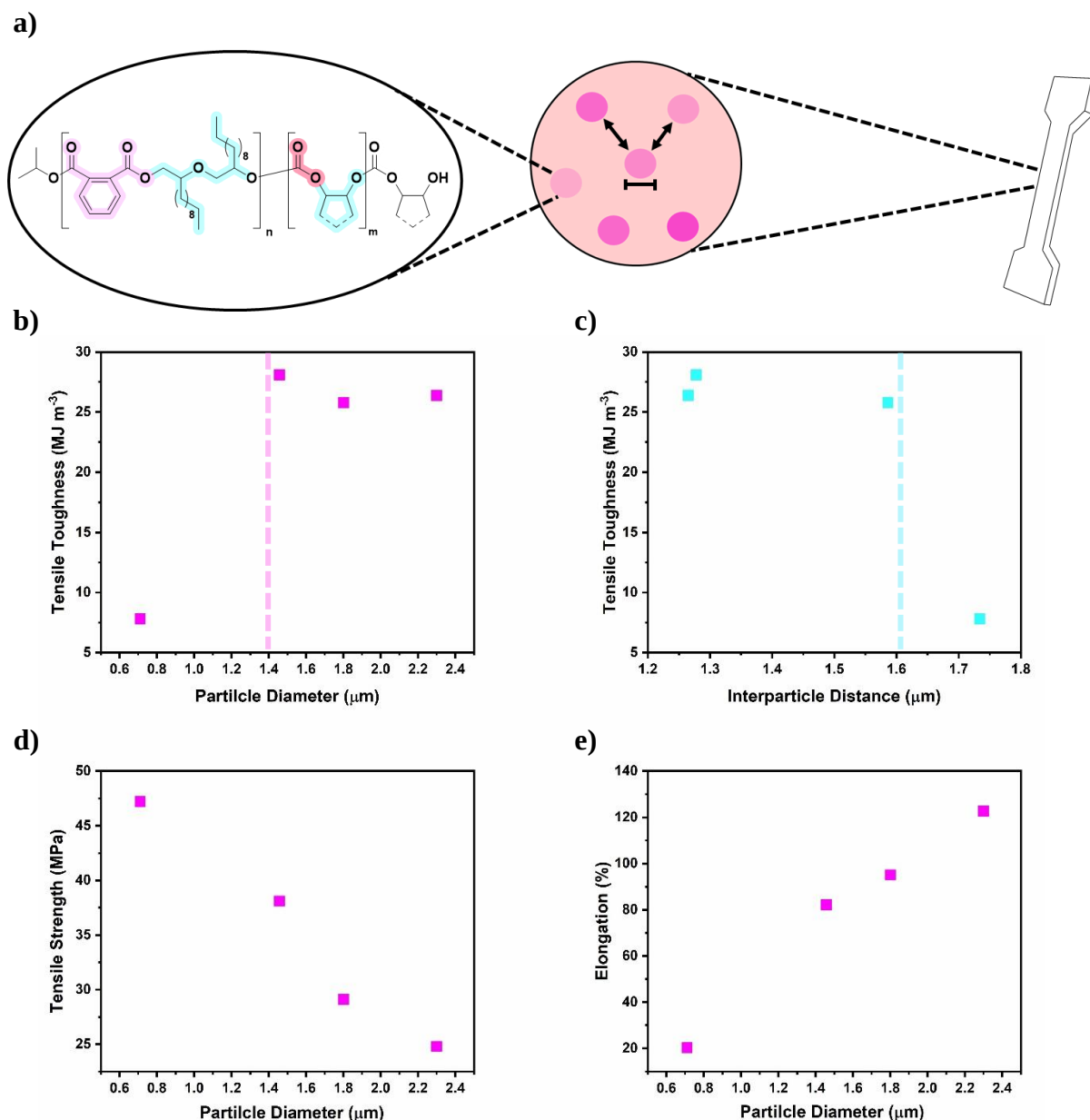


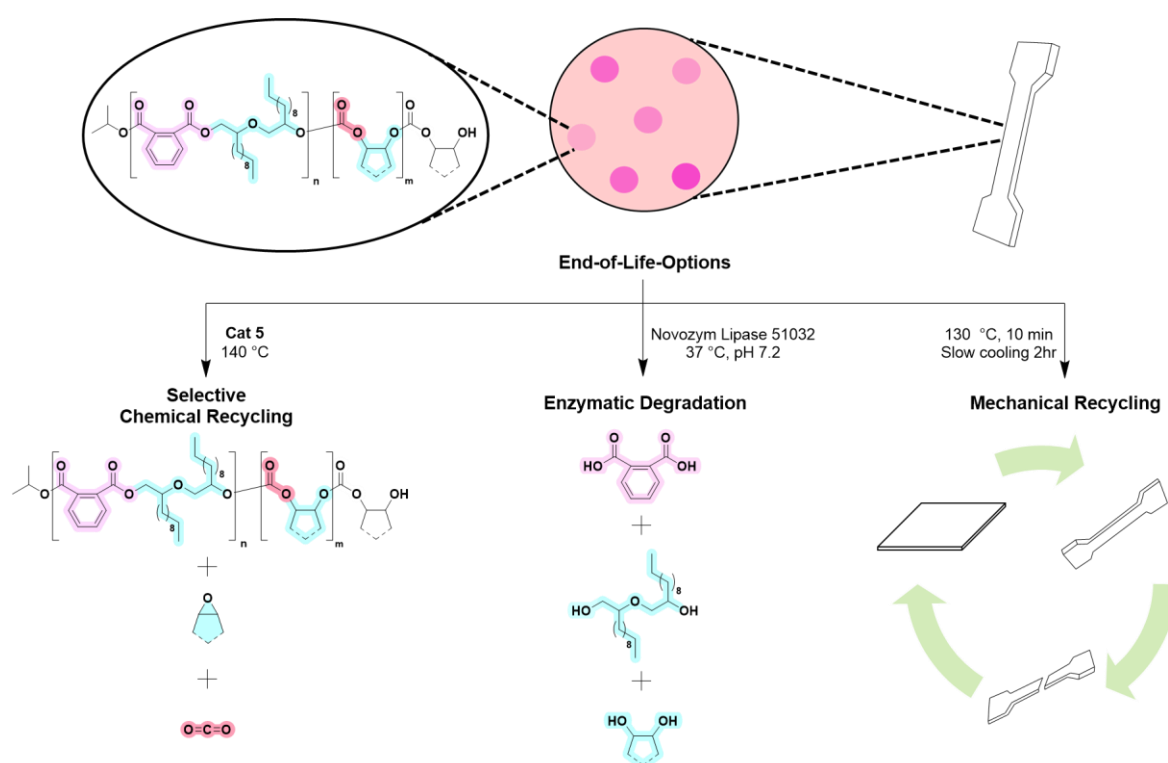
Figure 5.6: A summary of morphological-mechanical property correlations for [P5-PCHC]_x blends. a) Schematic representation of the morphological parameters measured, b) tensile toughness (MJ m⁻³) vs particle diameter (μm), c) tensile toughness (MJ m⁻³) vs interparticle distance (μm), d) tensile strength (MPa) vs particle diameter (μm) and e) elongation at break (%) vs particle diameter (μm). The critical particle size and critical interparticle distance are marked by pink and blue dashed lines in b and c, respectively, and beyond these values the material exhibits vastly improved toughness.

Blends of three PCHC polymers, of increasing molar mass values (2.3, 5.5 and 10.8 kg mol⁻¹, $1.09 < \bar{D} < 1.38$) in high molar mass PCPC, were immiscible (Table S8.5.3). The miscibility of PCHC is obviously improved by being in the same gradient copolymer backbone as PCPC.⁴⁴ The results of blending and SEM studies, suggest that low molar mass PCHC (PCHC DP = 30, $M_{nNMR} = 4.3$ kg mol⁻¹) must be highly compatible with high molar mass PCPC

(more so than low molar mass PCPC), although, DSC experiments indicate they may be immiscible (thermodynamically).

5.5 End-of-life Options

It is important that the end-of-life options available to all new polymers are explored.¹ To minimise the environmental impacts of thermoplastics, it is crucial to consider closed-loop recycling options.^{3,6} PCPC has been effectively recycled, both mechanically and chemically,³² and here, it was important to understand any effect that blending may have on these methods (Scheme 5.2). We were also interested in exploring the enzymatic degradation of PCPC and PCHC, which have not yet been shown.



Scheme 5.2: Schematic representation of the three end-of-life options for PCPC/poly(ester-*alt*-ethers)-*b*-PC polymer blends explored in this study; Mechanical recycling of [P5-PCHC]₅ (using compression molding), selective chemical degradation of [P5-PCHC]₂₀ and [P5-PCPC]₂₀ polymer blends to the diblock copolymer (P5-PCPC) and epoxides (CPO/CHO), as well as enzymatic degradation (monitored via the evolution of phthalic acid, P5, and cyclohexanediol/cyclopentanediol for PCHC and PCPC respectively).

5.5.1 Mechanical Recycling

In order to explore the potential of these materials to be mechanically recycled, **[P5-PCHC]₅** samples, that had been subjected to tensile testing, were reprocessed by compression molding (130 °C for 10 min, followed by 2 h slow cooling), and their mechanical properties remeasured (Figure 5.7). This process was repeated four times (Figure 5.7). Reprocessing resulted in a material that remained transparent and colourless throughout the mechanical recycling (Figure S8.5.39). Analysis by DSC and TGA showed no changes to the recycled samples thermal properties (Table 5.4), and GPC showed the same M_n and dispersity (Figure 5.8).

The Young's modulus, for **[P5-PCHC]₅** (1.5 ± 0.1 GPa), dropped after the 1st mechanical recycling (1.0 ± 0.1 GPa), and remained constant through the rest of the reprocessing cycles (Figure 5.7b). This slight drop may be due to minor contamination by particulate matter (dust), causing defects that reduce the materials stiffness. Such effects can be harder to control on small recycling scales. The maximum tensile strength remained unchanged until the 4th recycling, where it increased substantially to 56.8 ± 1.5 MPa. The material retained ductility (ϵ_B and U_T), also until the 4th cycle of reprocessing, at which point ϵ_B and U_T dropped to 19 ± 7 % and 8.4 ± 3.6 MJ m⁻³ respectively, returning towards the mechanical properties of neat PCPC. This was proposed to be the result of poor mixing of the dispersed phase during compression molding, resulting in poor dispersion or accumulation, and, depletion of the toughening effect afforded by well dispersed particles of **P5-PCHC**. Previous work toughening PLLA, employing a similar amphiphilic diblock copolymer strategy (using PEO-PBO copolymers), found increased tendency for coalescence of the dispersed phase in compression molding in the melt (as opposed to twin-screw extruding), attributed to the limited degree of flow during this process.^{39,40} To test this, the same (fourth recycle) sample was then dissolved (CH₂Cl₂), cast, dried and compression molded (following initial sample preparation procedures, see S7.3.2.2). The Young' modulus and σ_Y returned to **[P5-PCHC]₅** original values (1.6 ± 0.3 GPa and 42.5 ± 4.4 MPa respectively), while ductility returned to the material ($\epsilon_B = 50.9 \pm 22.1$ % and $U_T = 20.4 \pm 11.6$ MJ m⁻³, see Figure 5.7b-e yellow bar 'Re-cast material'). The fluctuation in ϵ_B and U_T values between the virgin **[P5-PCHC]₅** material and the 3rd mechanical recycling (between 82-45 % and 28-17 MJ m⁻³ respectively) was also attributed to poor mixing during compression molding. These results demonstrate the ability to retain the toughness of these materials, when recycling mechanically, for up to three re-cycles, after which point, it is essential to re-cast the material if conducting experiments on a lab-scale.

Recycling on a larger scale, for example with a compounder/extruder, with thorough mixing, would be expected to eliminate any such issues.

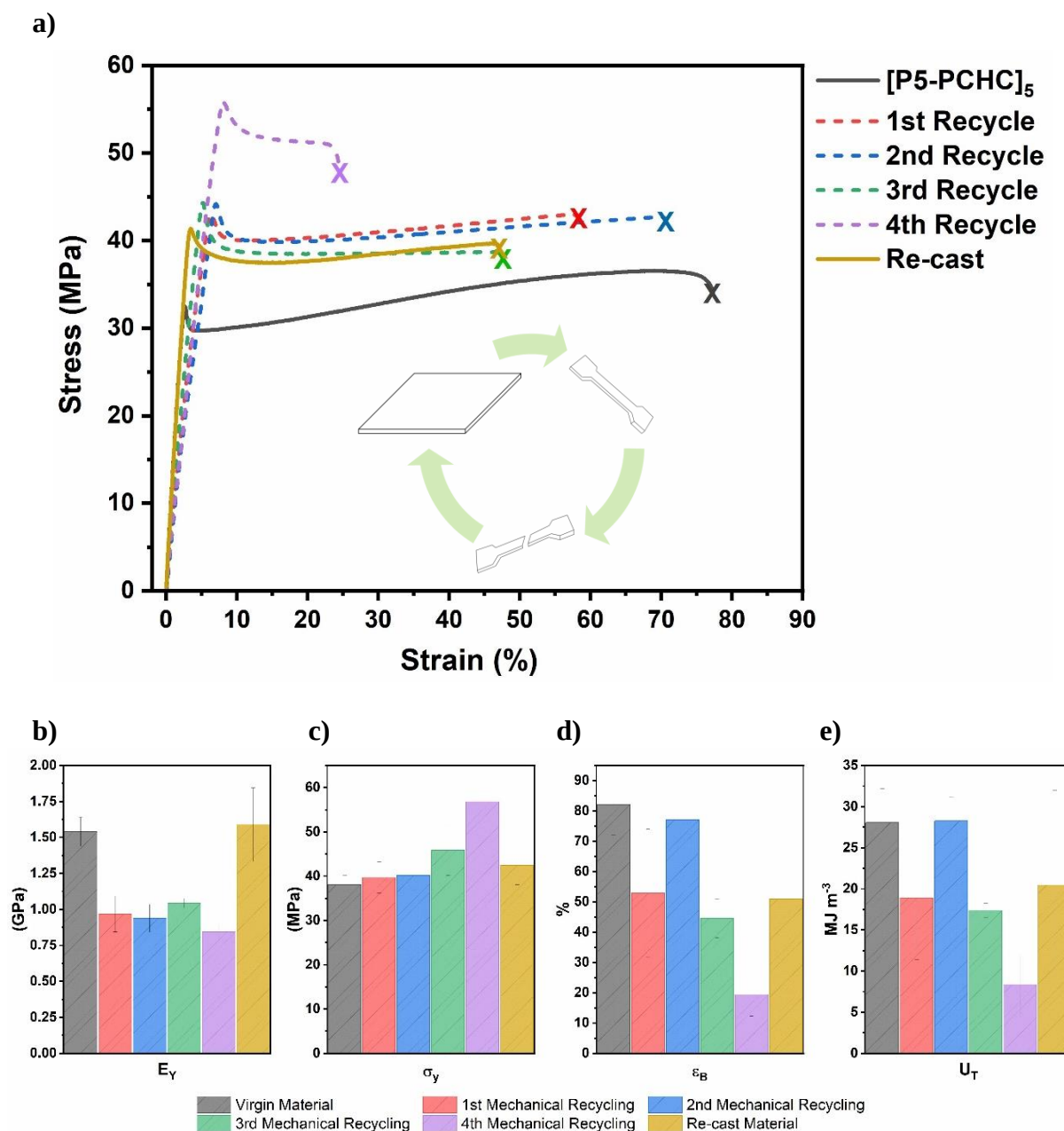
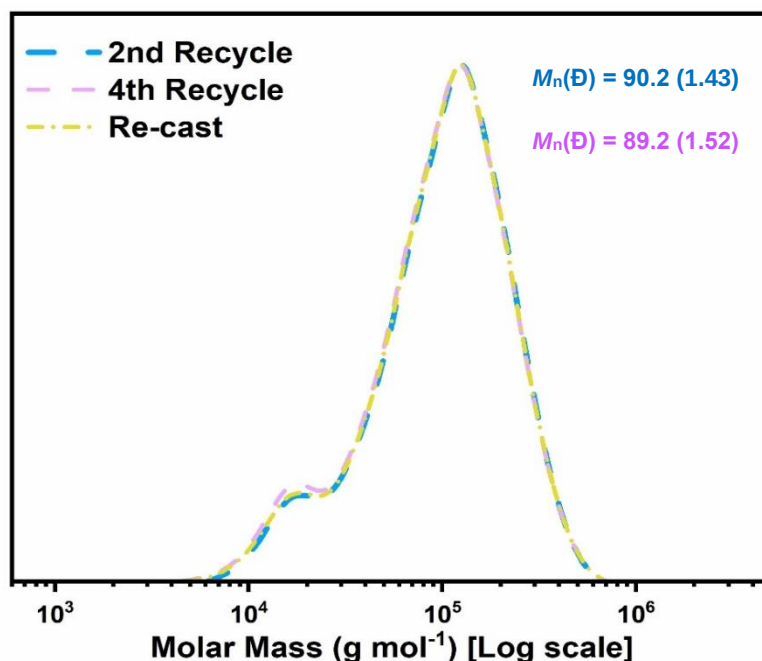


Figure 5.7: The results of mechanical tensile experiments conducted on the PCPC/poly(ester-*alt*-ether)-*b*-PCHC polymer blend ([P5-PCHC]₅) subjected to mechanical recycling. (a) Representative stress–strain curves (10 mm min⁻¹), (b) Young's modulus (E), (c) tensile strength (σ_Y), (d) elongation at break (ϵ_B) and (e) tensile toughness (U_T) for [P5-PCHC]₅ following four mechanical reprocessing cycles. The yellow results are for a sample, solvent cast, dried and compression molded (following initial sample preparation protocols) after 4 cycles of mechanical recycling/testing.

Table 5.4: Summary of thermal-mechanical properties for the blend [P5-PCHC]₅ subjected to four cycles of mechanical recycling, followed by one round of re-solvent casting.

Blend	T_g (°C)	$T_{d,5}$ (°C)	E (GPa)	σ_Y (MPa)	ϵ_B (%)	U_T (MJ m ⁻³)
[P5-PCHC] ₅	88	265	1.5 ± 0.1	38.1 ± 2.1	82.1 ± 10.1	28.1 ± 4.1
1 st Recycle	87	251	1.0 ± 0.1	39.7 ± 3.5	52.8 ± 21.2	18.9 ± 7.5
2 nd Recycle	86	258	0.9 ± 0.1	40.2 ± 3.5	77.1 ± 9.6	28.3 ± 2.9
3 rd Recycle	84	264	1.0 ± 0.0	45.9 ± 5.7	44.5 ± 6.4	17.4 ± 0.9
4 th Recycle	85	263	0.8 ± 0.0	56.8 ± 1.5	19.3 ± 7.1	8.4 ± 3.6
Re-cast	86	260	1.6 ± 0.3	42.5 ± 4.4	50.9 ± 22.1	20.4 ± 11.6

Protocol: Used tensile samples were combined together and compression molded at 130 °C for 10 min, followed by slow cooling for 2 hours. The ‘re-cast’ sample was prepared as per the original blends, by dissolving the polymer and solvent casting in CH₂Cl₂, vacuum oven drying, followed by compression molding.

**Figure 5.8:** GPC chromatogram of the PCPC/poly(ester-*alt*-ether)-*b*-PCHC polymer blend ([P5-PCHC]₅) subjected to mechanical recycling, during various cycles of mechanical recycling (2nd recycle, 4th recycle and after re-solvent casting).

5.5.2 Chemical Recycling

In the attempt to create a circular plastic economy, another promising option is chemical recycling to monomer (CRM). This preserves the energy that is embedded in waste plastic and its material value, with the potential to circulate large quantities of plastic wastes.^{4,6,9,53–56} We have previously demonstrated the solid-state chemical recycling of a range of polycarbonates (including PCPC) to the constituent epoxides and carbon dioxide.^{32,44,57} In this method, polymer films are solvent cast with a dispersed catalyst, and the depolymerisation rates are determined by tracking polymer weight loss with time, at a constant temperature. Under these conditions, CRM occurs with high activity and selectivity, for example, for PCHC, TOF = 25,700 h⁻¹, CHO selectivity >99 %, with 0.02 mol % catalyst, at 140 °C.⁵⁷ The potential for chemical recycling of the polycarbonate blends, **[P5-PCHC]₂₀** and **[P5-PCPC]₂₀** (that is the 20 wt% samples of **P5-PCHC** and **P5-PCPC**), was explored using catalyst 5 (a dinuclear CoMg catalyst, see Table 5.1). The catalyst/polymer blend mixtures were solvent cast into TGA crucibles, at loadings of 1:1000 cat:PCPC. Next, samples were analysed at 140 °C for 50 minutes (see S7.2.12 for full procedures). Depolymerisation occurred quickly and selectively, with a k_{obs} of 8.03 h⁻¹ (**[P5-PCPC]₂₀**) and 6.64 h⁻¹ (**[P5-PCHC]₂₀**), in line with previously reported high molecular weight PCPC or PCHC (Figure 5.9b).³² Depolymerisation formed only CO₂ and the *cis*-epoxide (CHO or CPO), as determined by in situ FTIR of the recylate (Figure 5.9c for **[P5-PCPC]₂₀** and S8.5.40 for **[P5-PCHC]₂₀**). Each reaction resulted in ~20 wt% residue after the 50-minute experiment, with negligible reaction taking place after a further 20 minutes. This is in line with the residue being the block polymer additive (20 wt%), as confirmed by ¹H NMR spectroscopy of the material (Figure S8.5.41). These experiments demonstrate that the toughened PCPC blends can undergo highly efficient and selective chemical recycling to monomer (CHO/CPO and CO₂), and, the **P5-PCPC/P5-PCHC** block polymer additive can be separated for re-use. This strategy could help preserve the chemical complexity and energy embedded in the block polymers.

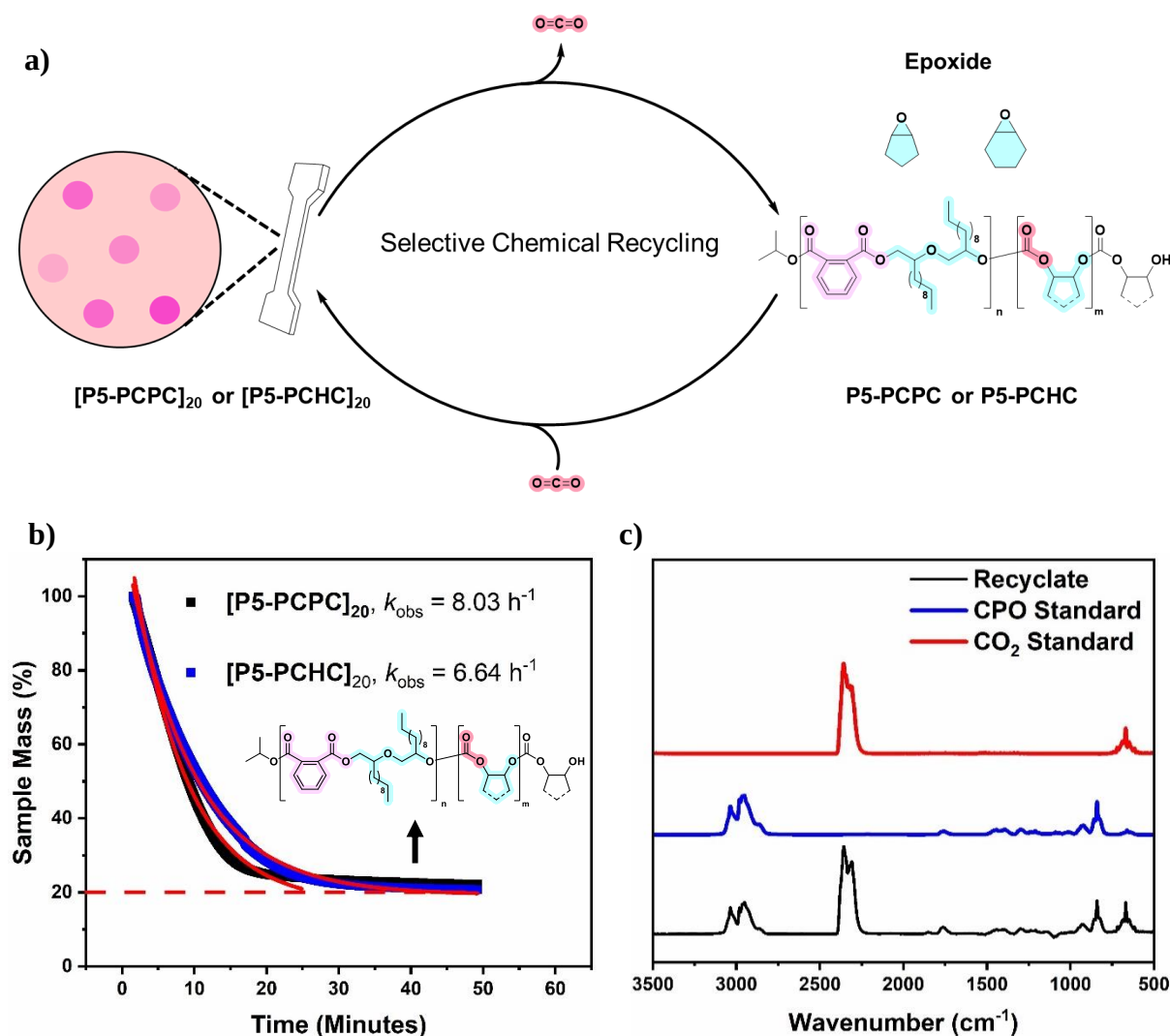


Figure 5.9: a) Schematic representation of the selective chemical recycling for PCPC/poly(ester-*alt*-ethers)-*b*-PC polymer blends in this study ([5] : $[P5-PCPC]_{20}$ = 1 : 1000, 140 °C isotherm, 50 minutes). (b) TGA thermogram of $[P5-PCPC]_{20}$ (black) and $[P5-PCHC]_{20}$ (blue). (c) The corresponding TGA-IR spectrum for $[P5-PCPC]_{20}$, with the recycle (black) and CO₂/CPO standards (red/blue).

5.5.3 Enzymatic degradation

The mechanical and chemical recycling of PCPC (and PCHC) were reported previously, but the propensity of these promising thermoplastics to be biodegraded enzymatically is yet to be explored.^{32,44} Other aliphatic polycarbonates, PPC and PTMC, were enzymatically degradable by lipases.^{9,58,59} In chapter 3, a poly(ester-*alt*-ether) was established to be enzymatically degradable (*Humicola insolens* Cutinase, HiC – Novozym 51032, in 31 days at 37 °C). In this chapter, the monomer combination is different to chapter 3 (chapter 3 was DGA/ED). The enzyme catalysed hydrolysis reactions were performed on (separately) **P5** (poly(ester-*alt*-ether)), **P5-PCPC** and **P5-PCHC**, as well as PCPC. The esterase *Humicola insolens* Cutinase (HiC, Trade name Novozym 51032) was applied in each case (2:1 wt% enzyme to polymer). This enzyme was selected as a result of preliminary screening

experiments using several different enzymes. The samples were exposed to the enzyme as a film (PCPC) or viscous liquid (**P5**, **P5-PCPC** and **P5-PCHC**). The reactions were incubated in pH controlled aqueous solutions, buffered at pH 7.2 by use of phosphate buffer, at 37 °C (S7.2.14). Enzymatic hydrolysis was monitored via aliquot removal and HPLC analysis, using PDA detection (for phthalic acid) and RI detection (for cyclopentane diol and cyclohexane diol), which were calibrated for the relevant acids/diols (Figure 5.10 and Figures S8.5.42-44).

Two PCPC films were examined, of molar mass 82 and 37 kg mol⁻¹, respectively. Both experiments displayed steady increases in the cyclopentane diol degradation products over time (Figure 5.10b). After 103 days, 45 and 92 % degradation conversions were observed for 82 and 37 kg mol⁻¹ PCPC, respectively (Figure 5.10b, Figure S8.5.47). Similarly, for **P5-PCPC**, 45 ± 9 % PCPC degradation was achieved after 140 days (Figure 5.10c, Figure S8.5.48). The degradation of **P5-PCHC** was also monitored by evolution of cyclohexane diol, and, after 140 days, 11 ± 4 % of PCHC was degraded. For **P5**, **P5-PCPC** and **P5-PCHC**, the poly(ester-*alt*-ether) degradation was observed, although significantly more slowly than the rate of polycarbonate degradation of PCPC/PCHC (poly(ester-*alt*-ether) % degradation ~1 % in all cases, Figure S8.5.46). It was also slower than the previously reported poly(ester-*alt*-ether) (chapter 3) comprising DGA-ED. This is expected given the semi-aromatic nature of **P5**, since aromatic esters tend to be much slower to biodegrade. Monitoring of the blend [**P5-PCHC**]₂₀ was also carried out, to observe whether blending had any effect on the degradation of the constituent polymers. After 66 days, ~1 % of **P5** degradation and 15 % of matrix PCPC degradation was observed. The concentration of cyclohexane diol could not be accurately determined in this sample (low [CHD]). The enzyme hydrolysis will continue to be monitored.

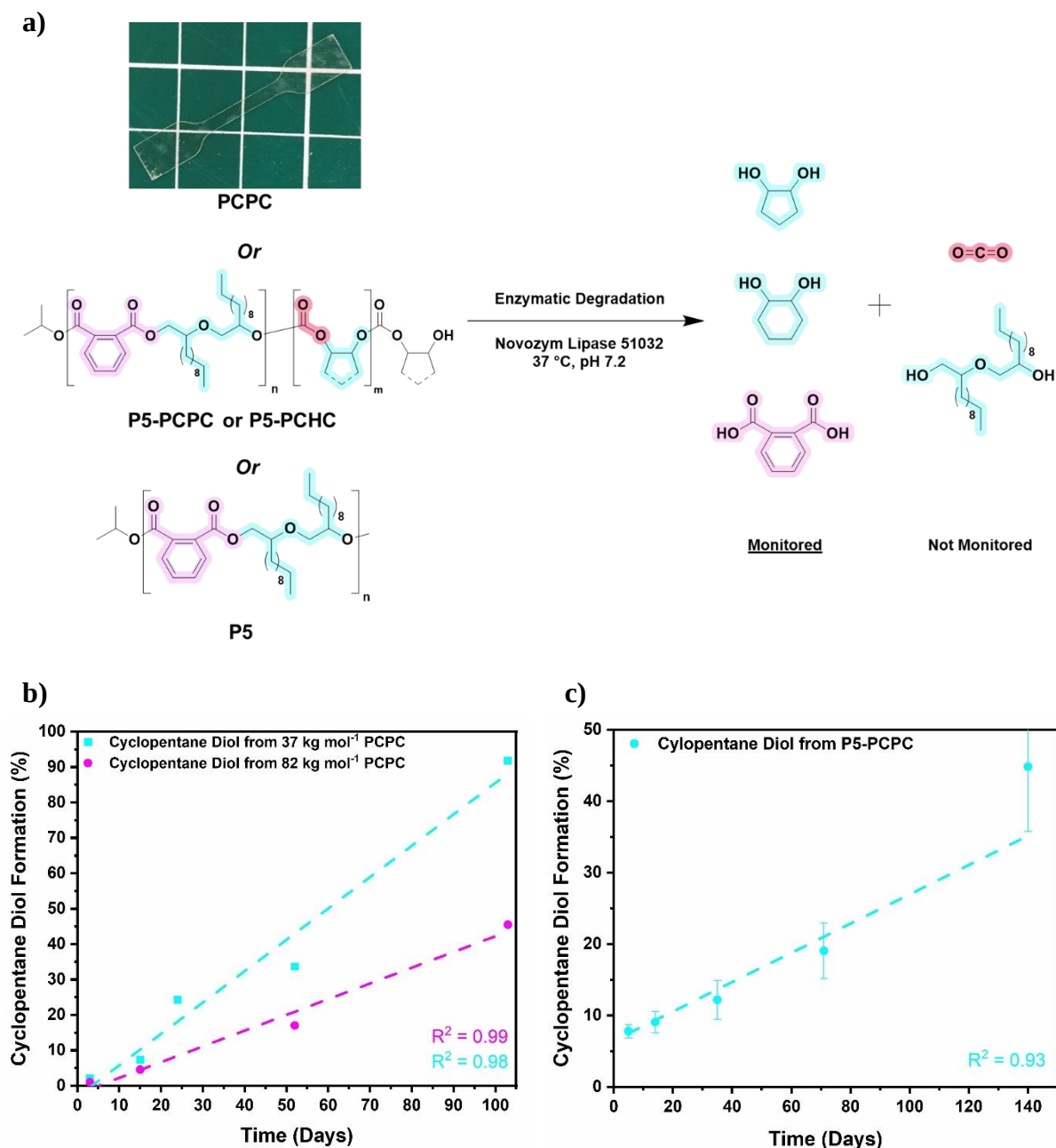


Figure 5.10: a) Schematic representation of the enzymatic hydrolysis for PCPC, poly(ester-*alt*-ethers) (**P5**) and poly(ester-*alt*-ethers)-*b*-PC (**P5-PCPC** and **P5-PCHC**) polymers in this study. Enzymatic degradation (biodegradation) showing diol formation vs. time for the biodegradation of b) PCPC (of two samples, 37 and 82 kg mol⁻¹, the latter was used for blending in this study) and c) **P5-PCPC**, to form cyclopentane diol. Biodegradation conditions: *Humicola insolens* Cutinase (HiC), polymer:cutinase = 1:2 (by weight), diol formation was measured by HPLC-RI detection calibrated for cyclopentane diol. Samples were incubated at 37 °C and pH 7.2, with a 0.05 M phosphate buffer. In b) the pink circles are cyclopentane diol from 82 kg mol⁻¹ PCPC and the blue squares from 37 kg mol⁻¹ PCPC. In c) the blue circles are cyclopentane diol from **P5-PCPC**. Degradation rate data are fit to linear fits.

5.6 Comparison to Commercial Thermoplastics

The plastics industry has developed materials with outstanding properties for use in everyday life, and they are now ubiquitous in society.^{1,2,60} For example, polystyrene (PS) is low cost, strong, chemically resistant and clear, making it of use in applications such as packaging, consumer goods and insulation. PS-based materials account for ~7 % of the world's plastic production, being produced at a 30 Mt scale/annum.^{8,61–63} It is however, limited by its brittleness (Figures 5.11 and 5.12), but there are solutions to this technical limitation. Acrylonitrile–butadiene–styrene (ABS) terpolymers improve on the properties of PS, specifically, increasing ductility. In ABS, the matrix is a styrene/acrylonitrile (40-60/15-35 % respectively) copolymer (SAN), in which an elastomeric polybutadiene (PB, 5-30 %) is dispersed, and grafted, improving compatibility.^{34,35} This strategy improves on the toughness and processibility of PS, making ABS an effective bridging polymer between commodity plastics and higher performing engineering plastics (Figures 5.11 and 5.12). ABS is used in a wide variety of applications where strength and light weight is required, such as automotive parts and building materials.^{64,65} Another modulated form of polystyrene is high-impact polystyrene (HIPS). HIPS is a blend of a PS/PB/ PB-*g*-PS (or PB-*b*-PS). Again, PS forms the continuous phase, while a carefully sub-structured dispersed phase consists of a rubbery PB phase with PB-*g*-PS occlusions.^{34,35} The important improvements in toughness have been attributed to these occluded microphases.^{34,35} HIPS accounts for 30-40 % of PS production and is used extensively in electronics and transportation.^{34,35,63} Figure 5.11 illustrates property comparisons between PS, ABS and HIPS in regards to maximum tensile strength and elongation at break, Figure 5.12 plots elastic modulus vs elongation at break and Figure 5.13 shows the thermal properties (for data tables see section S8.3.6).^{64,65}

Petrochemical-based polymers, such as these styrene-family plastics, show very poor degradability. The stability of these polymers is a major reason for their success, but causes a problem in the environment, as these materials escape waste streams or leach during use.^{1,2,8,66,68,69} Furthermore, the physical abrasion/fragmentation and ultraviolet (UV) light degradation of these plastics, has led to micro- and nano-plastic pollution of water bodies, and ultimately the food chain.^{2,4,8} Microplastics are potentially harmful, due to their particulate nature and propensity to carry contaminants.^{2,4,70} Polystyrenes are also difficult to collect and recycle, as a result of their low densities (for example foamed PS is 95 % air), posing difficulties in collection/separation, transportation and processing.^{8,71} As a result, only ~1 % of post-consumer PS is recycled.⁷¹ This is even more difficult for the more complex blends of

ABS and HIPS. PS-based polymers are most often either land-filled or incinerated.⁷¹ Industrial chemical recycling can show low yields (~33 %) and a range of mono- and poly-aromatic side products.⁷¹

One future solution is to develop plastics that are renewably sourced (this often helps reduce CO₂ emissions), meet the properties of PS plastics, have low-energy closed-loop recycling options and are biodegradable in case of environmental escape.^{1,4,9,72} In this work, the objective was to improve the sustainability of engineered PS family plastics. The toughened CO₂-based polycarbonate blends are mechanically recyclable (Figure 5.7), chemically recyclable (Figure 5.9) and enzymatically degradable (Figure 5.10). Comparison of the mechanical (σ_Y vs ϵ_B) properties of these blends against commercial PS, ABS and HIPS materials, shows that for different wt% of bio-degradable polymer additive, the properties can be tuned (Figure 5.11-12). This allows for polycarbonates showing properties similar to PS, for example neat PCPC or 1-2 wt% additive (Figure 5.11-12). It also allows for materials similar to ABS, as for 5 wt% additive (Figure 5.11-12). As well as similar to HIPS, for example 15 and 20 wt% **P5-b-PCPC** (Figure 5.11). Blends of 10-20 wt% **P5-b-PCHC** additive (**[P5-PCHC]₁₀**, **[P5-PCHC]₁₅** and **[P5-PCHC]₂₀**) have similar strength to HIPS, and, are even more ductile (beneficial) and tough (Figure 5.11). For example, **[P5-PCHC]₅** is as strong and more ductile than ABS (Figure 5.11). It is stronger and more ductile than HIPS, even when adding only 5 wt% block polymer (Figure 5.11 and 5.12).

The tensile modulus (**E**) is an important parameter for many applications of thermoplastics. Comparison of the tensile modulus (**E** vs ϵ_B) also showed that, as for σ_Y vs ϵ_B , neat PCPC (2.8 GPa) is similar to commercial PS (0.8-3.1 GPa) (Figure 5.12). **[P5-PCHC]₅** and **[P5-PCPC]₅** (2.7 GPa, respectively) have similar **E** values to PS, with elongation values more resembling ABS and HIPS (Figure 5.12). These 5 wt% blends are as ductile (ϵ_B) as ABS and HIPS, with the strength of (**E**) of PS (Figure 5.12). This pushes the **[P5-PCHC]₅** and **[P5-PCPC]₅** samples towards the desirable top right-hand corner of the **E** vs ϵ_B property space (Figure 5.12).

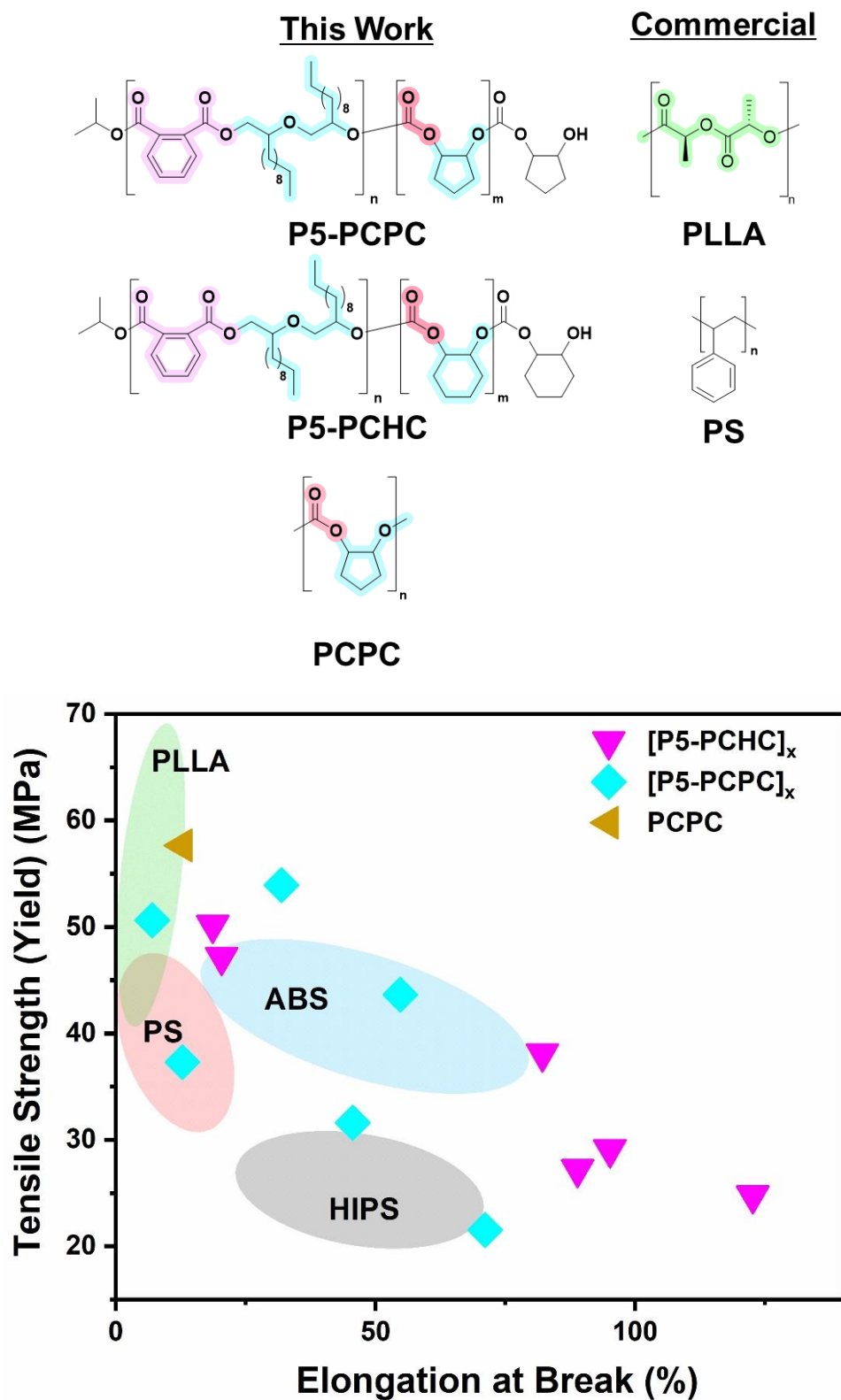


Figure 5.11: A comparison of the mechanical properties, maximum tensile strength (σ_Y) vs elongation at break (ϵ_B), of the poly(ester-*alt*-ether)-*b*-PC/PCPC polymer blends presented in this work, with commercial styrene-based thermoplastics PS, ABS and HIPS, as well as commercial PLLA (poly(L-lactide)). Data was compiled from commercial data sheets (section S8.3.6).

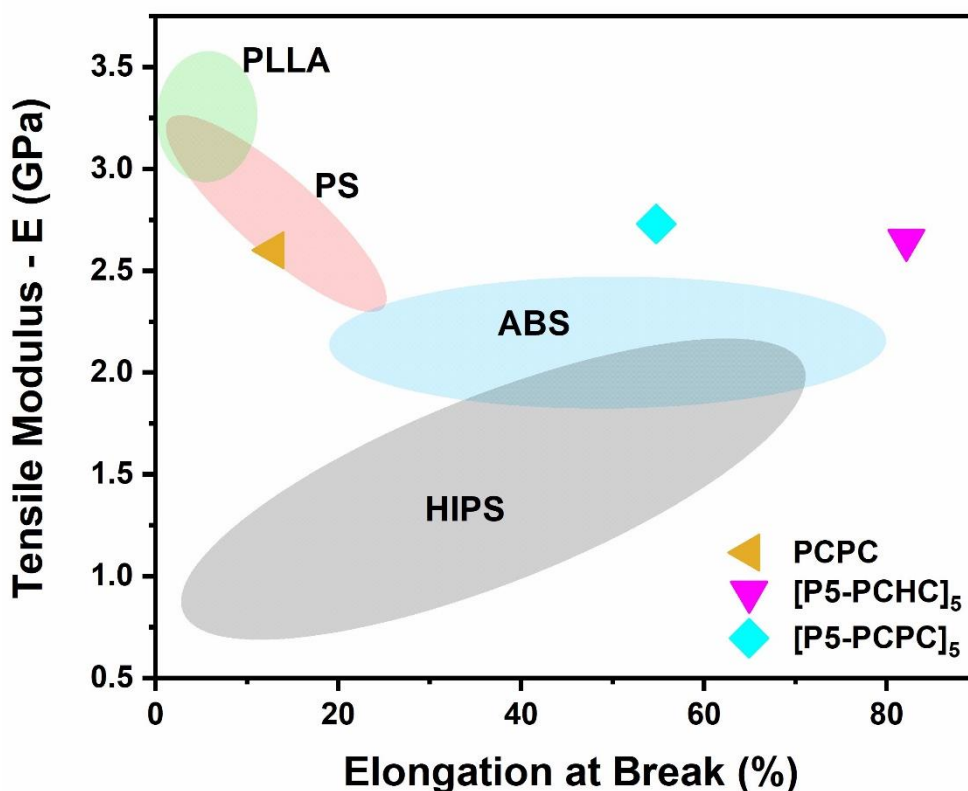


Figure 5.12: A comparison of the mechanical properties, tensile modulus (E - GPa) vs elongation at break (ϵ_B - %), of the poly(ester-*alt*-ether)-*b*-PC/PCPC polymer blends presented in this work, with commercial styrene-based thermoplastics PS, ABS and HIPS, as well as commercial PLLA (poly(L-lactide)). Data was compiled from commercial data sheets (section S8.3.6).

To make comparisons, the thermal properties are also important. All the PCPC blends explored in this work are a close match for the PS based thermoplastics (Figure 5.13). The CO₂-based polycarbonate T_g range is 84-90 °C, which is close to/slightly lower than T_g ranges for PS (90-98 °C), ABS (107-116 °C) and HIPS (100 °C) (Figure 5.13). Other CO₂-based polycarbonates, such as PCHC, PeCHC and PvCHC all showed higher T_g values (105, 118 and 126 °C, respectively, $M_n > 100$ kg mol⁻¹). In future, these may be promising PS-substitutes where higher temperature uses are required (note that PS is also limited by its T_g value for some applications).³²

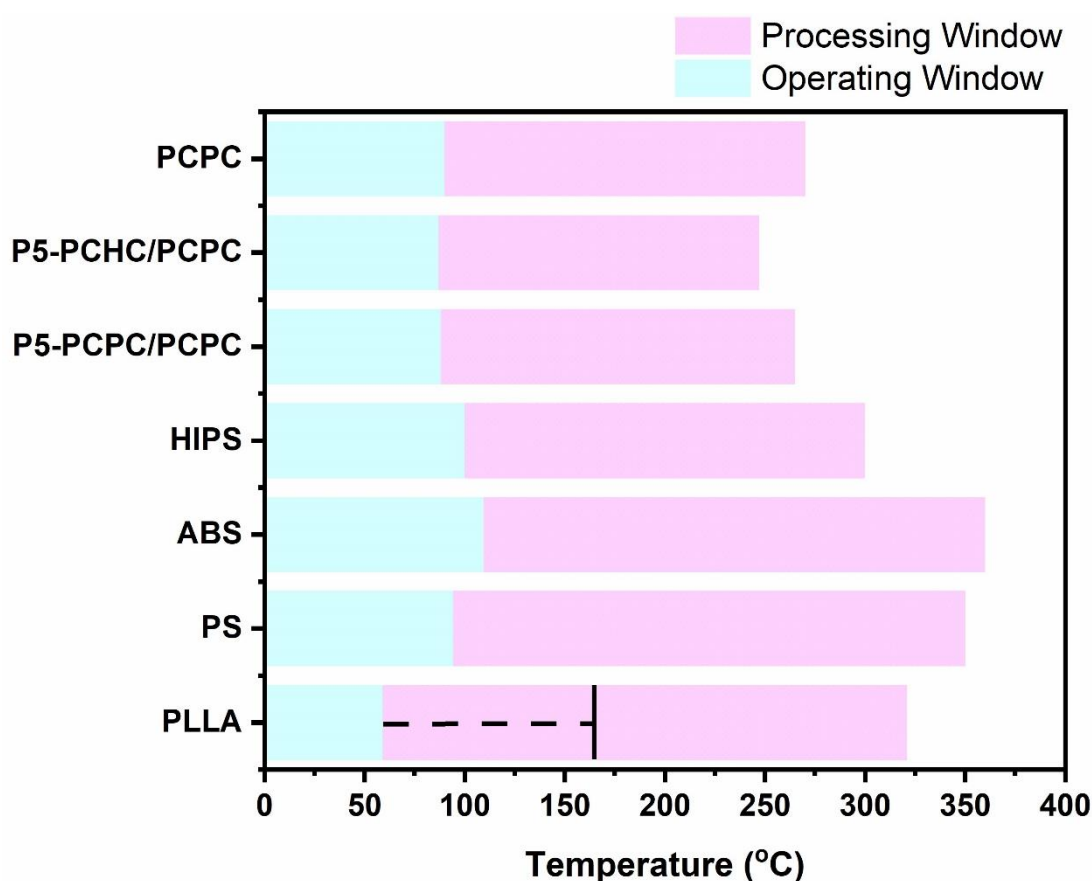


Figure 5.13: Comparing the operating and processing temperature windows for the poly(ester-*alt*-ether)-*b*-PC/PCPC polymer blends presented in this work, with commercial styrene-based thermoplastics PS, ABS and HIPS, as well as commercial PLLA. Where appropriate the melting point is marked by a black line. Data was compiled from commercial data sheets and published sources (section S8.3.6).^{63,73}

ABS and HIPS are very difficult to mechanically or chemically recycle.^{63,71} Mechanical recycling is not possible as they are complex thermosets and blends. In chemical recycling, the PB dispersed phase has a detrimental effect on the styrene yields through side reactions in the thermal decomposition mechanism.^{63,71} For example, the chemical recycling of PS in HIPS by pyrolysis yields < 50%, and, the PB phase undergoes charring and is not recovered.^{63,71} The chemical recycling protocol, presented in this work, allows the PCPC matrix to be completely and selectively recycled only to CPO monomer (Figure 5.9). The block copolymer is isolated for reuse. The PCPC blends can also be mechanically recycled (Figure 5.7). Thus, the major obstacle in the recycling of ABS and HIPS may be addressed by using these CO₂-based polycarbonates.

It is also important to consider the properties of these PCPC blends in relation to other biodegradable, chemically recyclable alternative thermoplastics materials. PLLA is the largest scale commercial, renewably sourced and biodegradable thermoplastic.¹ PLLA is strong (tensile strength = 45-68 MPa and $E = 3-3.45$ GPa), but brittle, akin to PS ($\epsilon_B = 4.8$ %, Figure

5.11 and 5.12). Unmodified PCPC occupies a very similar area of mechanical property space (σ_Y vs ϵ_B) as PLLA (Figure 5.11 and 5.12). Having a higher T_g (PCPC blends = 84-90 °C vs PLA = 55-63 °C), PCPC materials may be sustainable alternatives in higher temperature applications (Figure 5.13). Furthermore, the amorphous nature of PCPC (compared to semi-crystalline PLLA) simplifies polymer processing and recycling.

In summary, unmodified PCPC, or with 1-2 wt% copolymer additive, showed similar stress vs strain and modulus vs strain values to PS (as well as PLLA). Increasing to 5 wt% resulted in blends as ductile (ϵ_B) and strong (σ_Y) as ABS and HIPS, with the modulus of (E) of PS (Figure 5.11 and 5.12). Increasing further to 10-20 wt% produced either HIPS-like materials (using the **P5-PCPC** copolymer additive) or materials as strong (σ_Y) as HIPS, although with larger elastic moduli (E) and elongation at breaks (using the **P5-PCHC** copolymer additive) (Figure 5.11 and 5.12). Further, the toughened PCPC blends reported present potential recyclable (mechanically and chemically) and biodegradable (enzymatically) replacements for PS, ABS and HIPS.

5.7 Summary and Future Work

5.7.1 Summary

An effective method for toughening high molar mass PCPC ($M_n = 82.2 \text{ kg mol}^{-1}$, $D = 1.58$)—a potential sustainable alternative thermoplastic, synthesised from the ROCOP of CO₂ and CPO—was developed using low quantities of diblock copolymers, of the form poly(ester-*alt*-ethers)-*b*-PC (where PC = PCPC or PCHC). For the lead 5 wt% blends, [**P5-PCHC**]₅ (PC = PCHC) and [**P5-PCPC**]₅ (PC = PCPC), ductility increased significantly, the elongation at break (PCPC = 12.8 %) improved by up to 7 times (54.8 and 82.1 %, respectively) and the tensile toughness (PCPC = $5.4 \pm 2.6 \text{ MJ m}^{-3}$) by 5 times (22 and 28 MJ m^{-3} , respectively). Meanwhile, the high tensile strength (PCPC = $57.7 \pm 5.1 \text{ MPa}$, vs 5 wt% blends = 38-44 MPa) and modulus (PCPC = 2.8 GPa vs 5 wt% blends = 2.7 GPa) were retained and there was no detrimental effect to the thermal properties ($T_g = 90 \text{ °C}$ for PCPC, and between 87-88 °C for the 5 wt% blends), which determines the operating window for these materials. These 5 wt% blends are as ductile (ϵ_B) as ABS and HIPS, with the strength of (E and σ_Y) of PS. Spherical dispersed phase morphology was observed, allowing determination of the critical particle sizes and interparticle distances. Dispersed particles formed by **P5-PCHC** were smaller and more closely separated than those formed by **P5-PCPC**. It may be that PCHC shows improved compatibility and a lower interfacial energy in the blends than PCPC (as the **B**-block in **AB** copolymers). The blends were mechanically recycled, by compression molding, up to four

times, with retention of properties. Chemical recycling of the PCPC blends formed the respective monomers (CPO, CHO and CO₂) and the block copolymer, which were selectively isolated. All parts of the blends were enzymatically degraded, to some extent, using *Humicola insolens* Cutinase, HiC, trademark name Novozym 51032, at 37 °C over 51-140 days. The poly(ester-*alt*-ethers) using PA and EDD degraded much more slowly than the DGA/ED combination in chapter 3, most likely due to its semi-aromatic backbone. Comparing the thermal-mechanical properties to various commercial petrochemical styrene-based polymers (PS, ABS and HIPS), demonstrated that PCPC blends present CO₂-derived and recyclable alternatives to these common thermoplastics.

5.7.2 Future Work

As this is the first investigation into additive toughening of high molar mass PCPC, future studies could go in many directions. Section 3.9.2 (Future Work) of Chapter 3, discussed some potential investigations that are also extremely relevant here;

- Investigating physical aging and chemical stability.
- Grafting and other covalent methods of improving the interfacial interactions between the dispersed particles and PCPC matrix.
- Understanding the mechanism of deformation in these samples, to help inform future toughening strategies.
- Here, **AB** diblocks were developed, whereby **A** is immiscible in the PCPC matrix and **B** is compatible with PCPC. Investigating new chemistries for both blocks may provide better toughening and more insights into the toughening mechanisms. The ability of poly(ester-*alt*-ether) ROCOP to readily modify the polymer backbone is an advantage here, with many possible polymers and large area of property space to choose from. Particularly important criteria appear to be miscibility in PCPC for the **B**-block.³⁹ Similarly to chapter 3, the DP of both blocks should be optimised to improve performance.
- Using compounding to prepare larger scale polymer blends should provide evenly distributed, finer particles, to increase performance. The starting point would be to use the same mixtures as in this work.

Furthermore, the degradation experiments should be continued. **P5** demonstrated slower degradation than **P13**, explored in chapter 3 for toughening PLLA (complete degradation in 30 days). Continuing to monitor its enzymatic degradation is important, as if it will not degrade on a realistic time frame, it should be replaced. PCPC polymer blends (for

example [P5-PCPC]₂₀) will also be further examined for degradation, to ensure blending does not affect this end-of-life option.

Lastly, it would be important for any commercial application of PCPC, to understand its flammability, insulative properties, electrical properties (resistivity, dielectric constant etc), creep, impact strength, compressive strength, chemical resistance, moisture absorption and barrier properties. These measurements would aid in future application development. Industrially relevant processing to form foam would also be interesting, particularly as a potential replacement for PS-based materials.

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CHAPTER 6

Chapter 6: Outlook

6.1 Thesis Summary

This thesis has detailed the work completed to improve the mechanical properties of two potential sustainable alternative thermoplastic materials—poly(L-lactide) (PLLA), from starch rich biomass, and poly(cyclopentene carbonate) (PCPC) from CO₂, that both suffer from brittleness—as potential substitutes for petrochemical based commercial plastics. The goal was to improve toughness and ductility without compromising thermal properties, mechanical strength or sustainability. To achieve this, low T_g poly(ester-*alt*-ethers) were targeted to make block copolymers of the form poly(ester-*alt*-ether)-*b*-X, where X was designed to be compatible in the target polymer matrix. Further development of poly(ester-*alt*-ether) catalysis was necessary to realise this.

In chapter 2, a range of monomers were explored for poly(ester-*alt*-ether) catalysis, to understand the generality of this catalysis (with only a single previous report), and, to identify the property space available to these polymers, to be used to toughen PLLA and PCPC. A series of 16 new copolymers were prepared and characterised (Figure 6.1). A range of post-polymerisation functionalisations were carried out to modulate thermal properties and hydrophilicity. This provided an assortment of polymers, as well as an understanding of catalytic boundaries, with which to carry through to polymer blending studies.

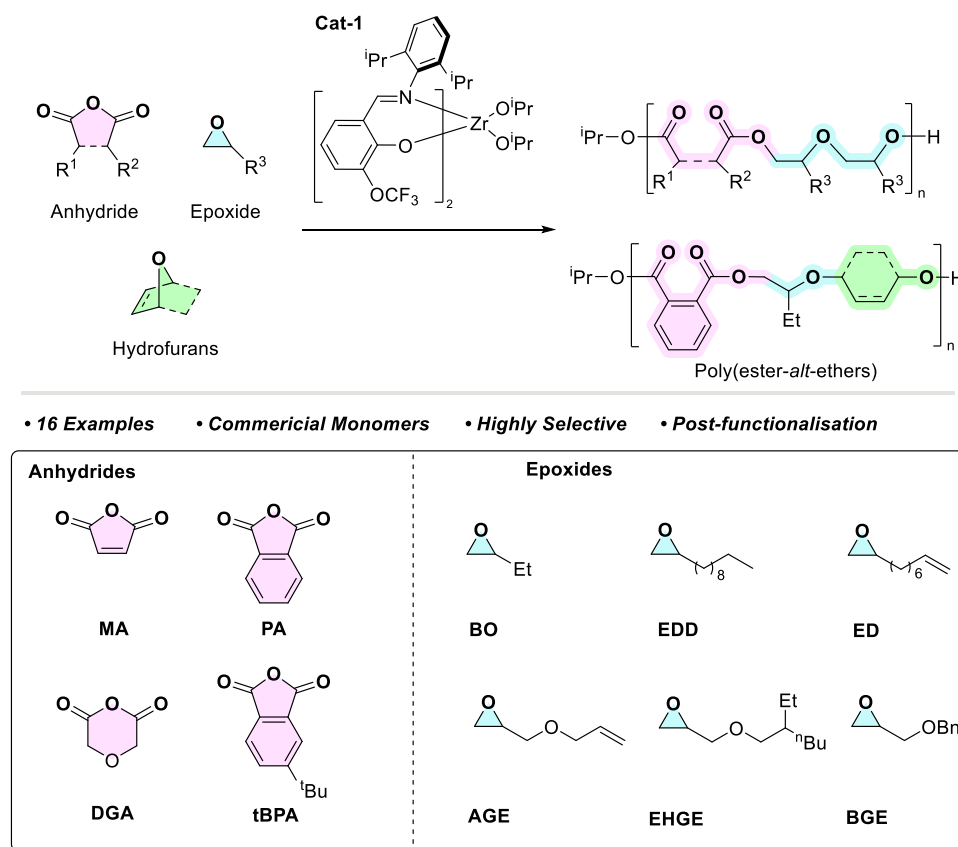


Figure 6.1: An outline of the strategy to form a variety of poly(ester-*alt*-ethers) with catalyst **1** in chapter 2.

In chapter 3, poly(ester-*alt*-ethers) were selected, based on the polymers produced in chapter 2, to make block copolymers of the form poly(ester-*alt*-ethers)-*b*-PLLA. These were used as blend additives to toughen commercial, high molecular weight, semi-crystalline PLLA (Figure 6.2). Blending with 15 wt% copolymer additive improved ductility (elongation at break increased by 700 % and tensile toughness by 800 %), while retaining mechanical strength (tensile modulus = 3.1 ± 0.1 GPa and tensile strength = 48.7 ± 1.2 MPa), and, it did so without effecting thermal properties such as T_g , T_m , crystallinity and thermal stability. The blends could chemically recycled to L-LA and the block copolymer, and, all blend components were also shown to degrade enzymatically.

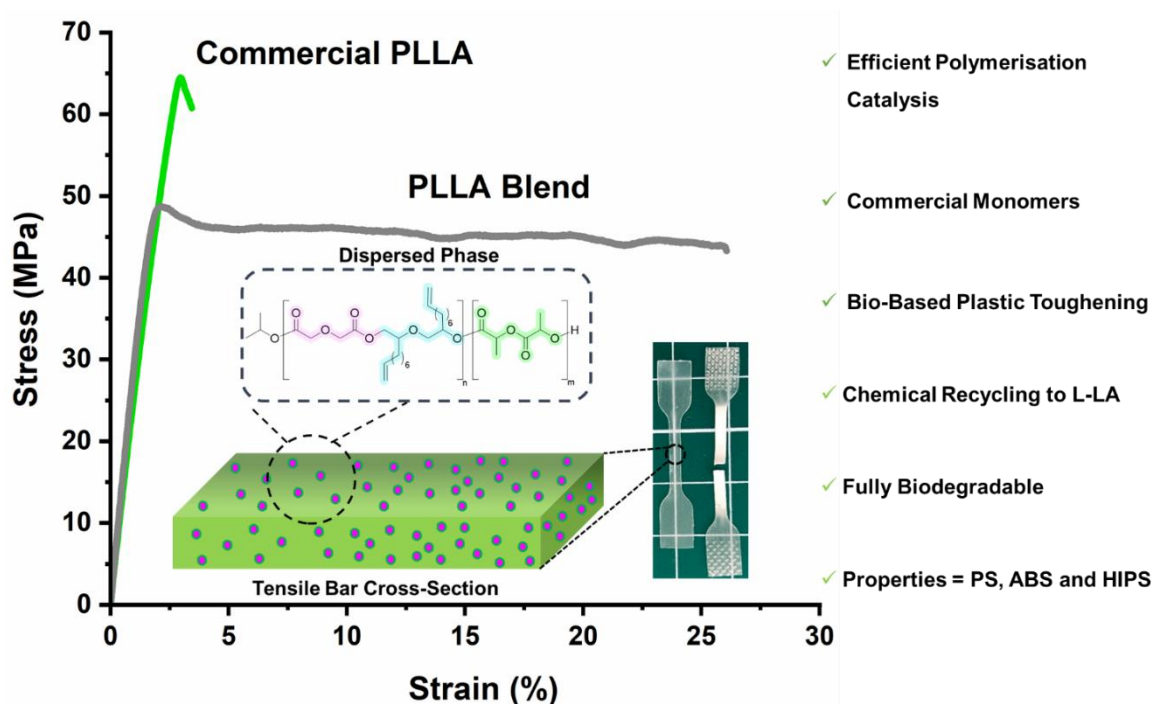


Figure 6.2: An outline of the strategy of using poly(ester-*alt*-ether)-*b*-PLLA copolymers to toughen PLLA in chapter 3 of this work, with a short summary of the conclusions drawn.

In chapter 4, a variety of investigations were performed into poly(ester-*alt*-ether) catalysis (Figure 6.3), exploring three ‘generations’ of catalysts. In the First generation, catalysts of the form $ML_2(O^iPr)_2$, were explored, to understand the effect of the metal (a group IV metal) and ligand on catalysis (rate, selectivity and control of molar mass distribution). Zr(IV) and Hf(IV) catalysts were more selective (96 and 98 % respectively), faster (by an order of magnitude) and displayed more controlled molar mass distributions than Ti(IV). On the other hand, the ligand had only minor effects on catalysis, unless it resulted in a change in the coordination environment. In the second generation catalysts, commercial metal-salt based, ZrX_4 , catalysts, were investigated for the effects of the co-ligand. These catalysts produced

highly selective poly(ester-*alt*-ethers) (95 %) with rates 1-3 orders of magnitude faster than the $\text{ML}_2(\text{O}^i\text{Pr})_2$ catalysts. Lastly, the third generation, commercial catalysts of the form $\text{Hf}(\text{Bn})_4$ + CTA were explored as non-initiating catalysts to make poly(ester-*alt*-ethers) with a variety of DPs, functional end-groups and architectures.

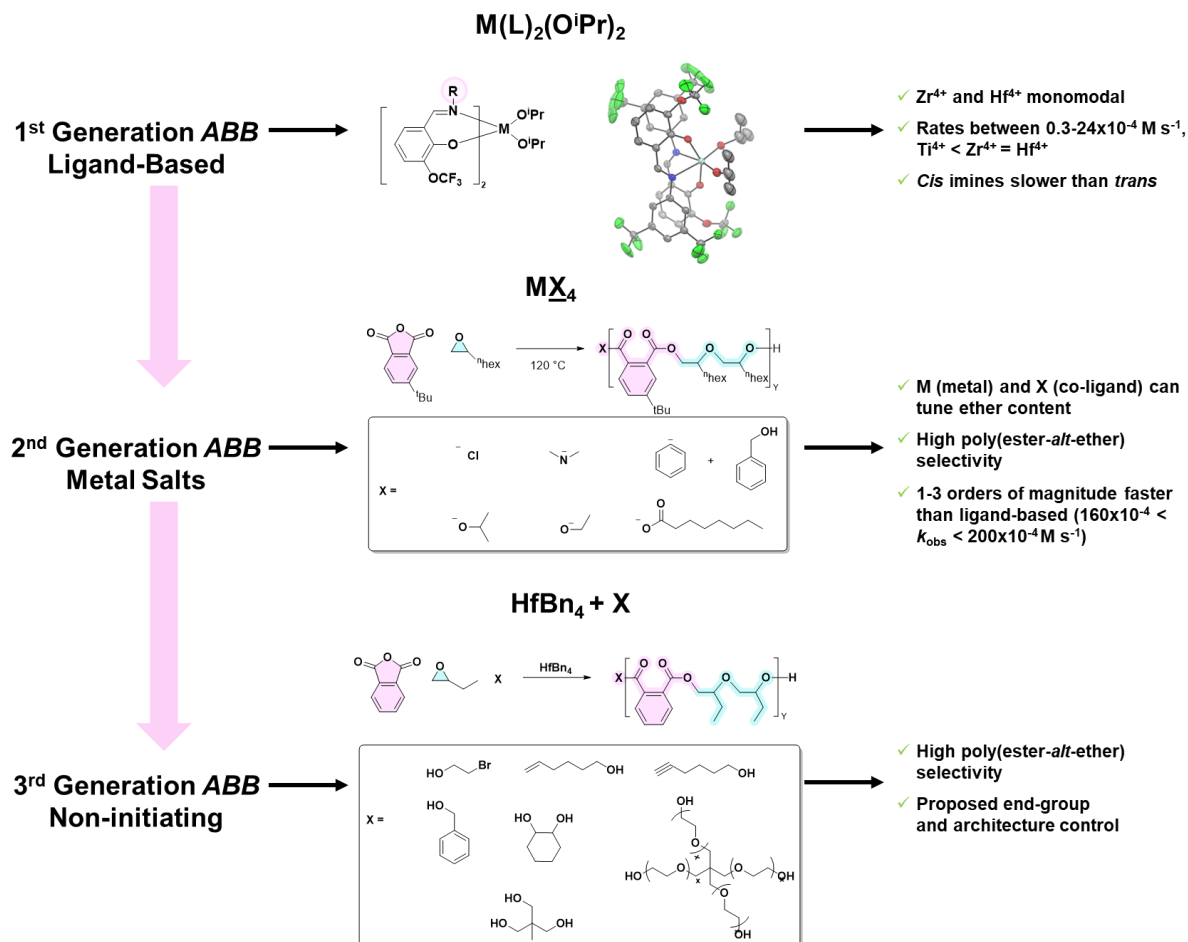


Figure 6.3: An outline of the three ‘generations’ of poly(ester-*alt*-ether) catalysts explored in chapter 4 of this work, with a short summary of the conclusions drawn.

In chapter 5, this improved knowledge of poly(ester-*alt*-ether) catalysis was used to make poly(ester-*alt*-ether)-*b*-PC block copolymers (where PC = PCHC or PCPC), to toughen high molar mass PCPC ($M_n = 82.2 \text{ kg mol}^{-1}$, $\bar{D} = 1.58$). Blending as little as 5 wt% additive, tensile toughness could be improved by 500 % and elongation at break by 650 % (Figure 6.4). Meanwhile the material maintained its strength (tensile strength = $38.1 \pm 2.1 \text{ MPa}$) and modulus (2.7 GPa), without any reduction in thermal properties such as T_g (88 °C) or operating window. The blends could be mechanically recycled, as well as chemically recycled to CPO (and CHO when relevant) and CO_2 monomers, leaving behind the block copolymer (selective isolation). All blend components have demonstrated enzymatic degradation, the PCPC and

PCHC degrading much faster than the semi-aromatic poly(ester-*alt*-ether) employed (under the conditions tested).

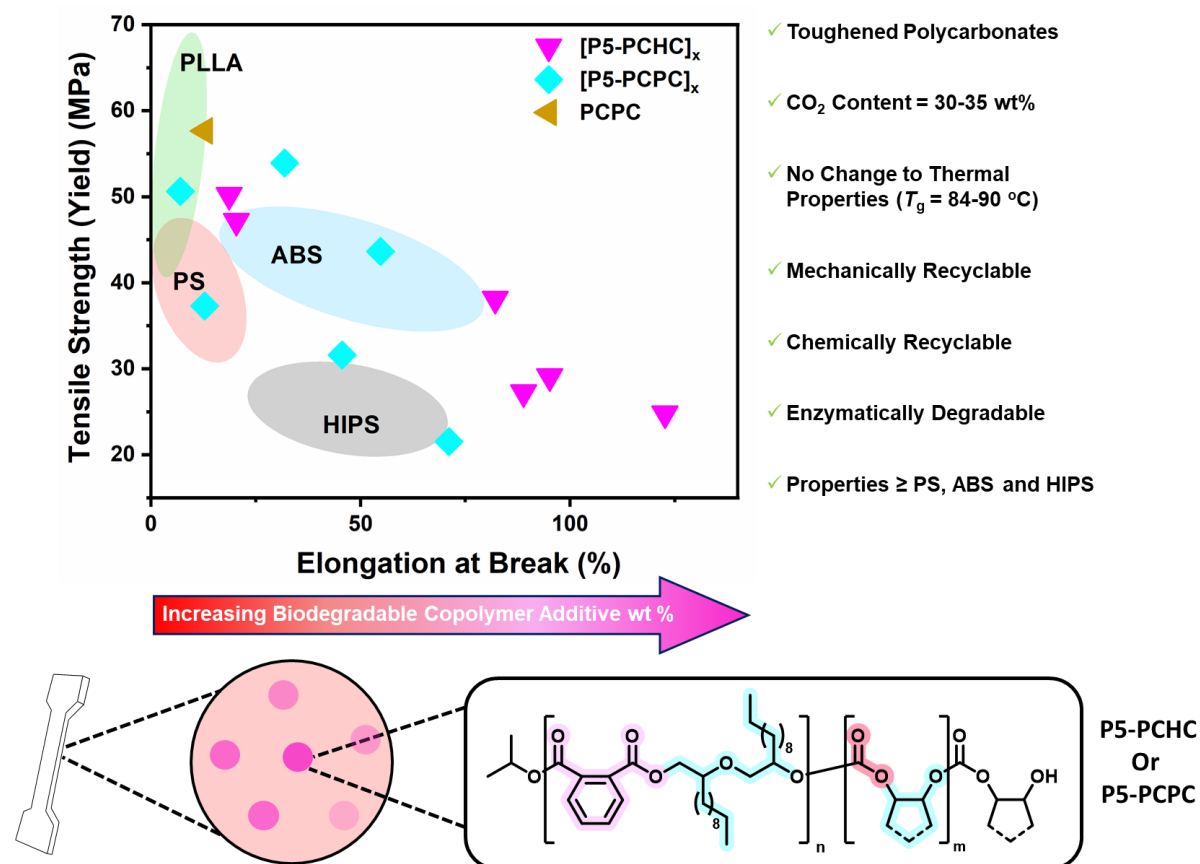


Figure 6.4: An outline of the strategy of using poly(ester-*alt*-ether)-*b*-PC copolymers to toughen PLLA in chapter 5 of this work, with a short summary of the conclusions drawn.

The blends presented in this work cover a range of thermoplastic property space, have multiple end-of-life pathways, and, could be particularly suited for applications of PS, ABS and HIPS, the latter two of which are very difficult to recycle (Figures 6.5 and 6.6). Figures 6.5 and 6.6 below summarise the mechanical properties (tensile strength vs strain and tensile modulus vs strain) of the PLLA and PCPC blends explored in this thesis, demonstrating their potential as replacement materials for these styrene-based polymers.

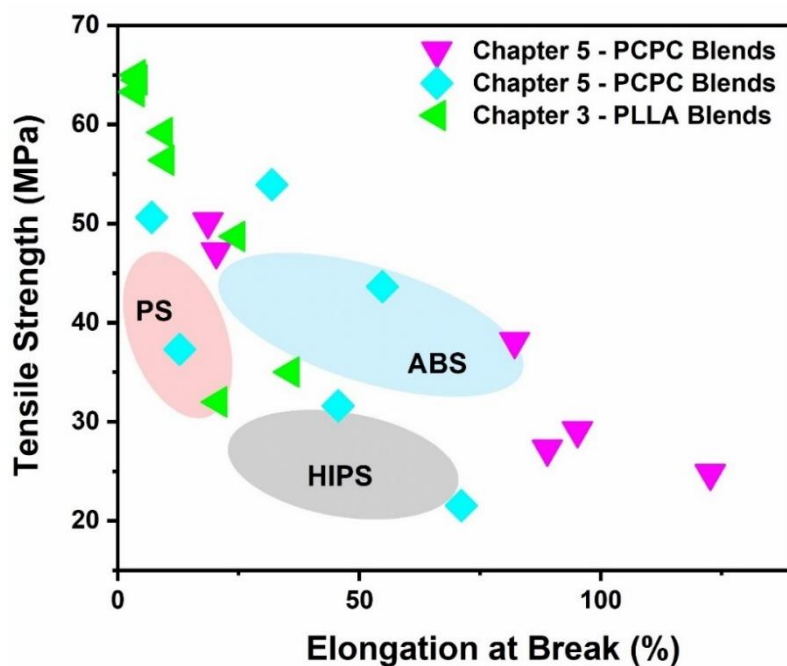


Figure 6.5: A comparison of the mechanical properties, tensile strength (σ_Y) vs elongation at break (ϵ_B), of the PLLA/poly(ester-*alt*-ether)-*b*-PLLA polymer blends presented in chapter 3, the PCPC/poly(ester-*alt*-ether)-*b*-PC polymer blends presented in chapter 5 (where PC = PCHC for pink triangles and PCPC for blue diamonds), with commercial styrene-based thermoplastics PS, ABS and HIPS. Commercial data was compiled from commercial data sheets (section S8.3.6).

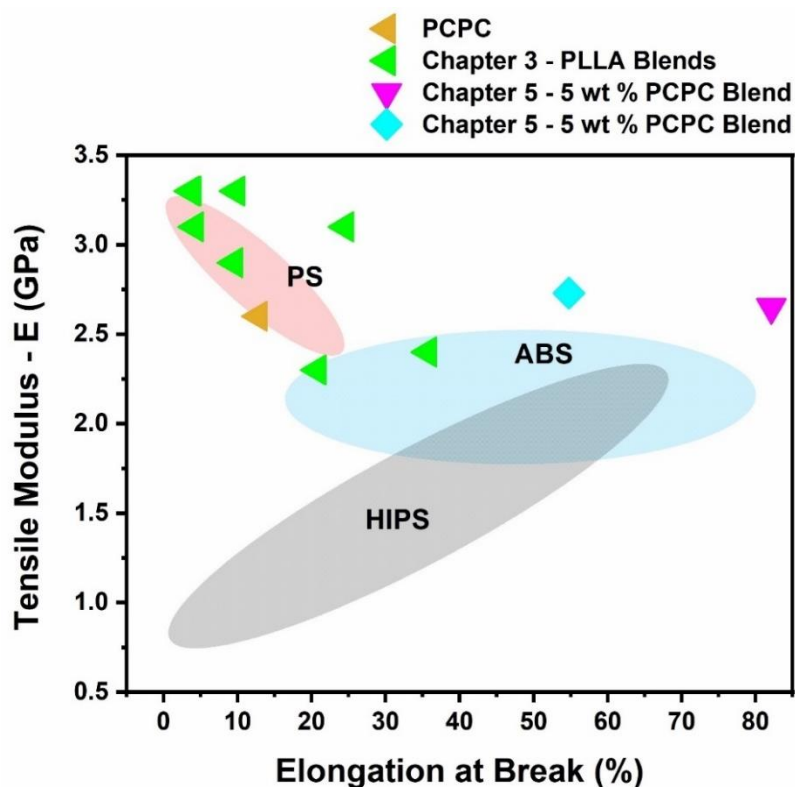


Figure 6.6: A comparison of the mechanical properties, tensile modulus (E) vs elongation at break (ϵ_B), of the PLLA/poly(ester-*alt*-ether)-*b*-PLLA polymer blends presented in chapter 3, PCPC and the PCPC/poly(ester-*alt*-ether)-*b*-PC polymer blends presented in chapter 5 (where PC = PCHC for pink triangles and PCPC for blue diamonds), with commercial styrene-based thermoplastics PS, ABS and HIPS. Commercial data was compiled from commercial data sheets (section S8.3.6).

6.2 Outlook

Future exploration, following the results presented in this thesis, should explore; 1) poly(ester-*alt*-ethers), further improving their catalysis and finding potential applications for these unique materials, and 2) Improving the properties of sustainable thermoplastic materials such as PLLA and polycarbonates from CO₂ and cyclic epoxides (e.g. PCPC).

6.2.1 Poly(ester-*alt*-ether) Catalysis

At the commencement of this thesis, there was yet to be a single report for poly(ester-*alt*-ether) ROCOP. Now, there is an understanding of the generality and limitations of this catalysis. Selective poly(ester-*alt*-ethers) can now be made with commercial (metal salts), for which the polyether content can readily be tuned. There is now also the ability to control end-group chemistry and polymer architecture. There are however, several outstanding research avenues to explore.

These polymerisations are limited by low molar masses (5-16 kg mol⁻¹). This is proposed to be the result of low quantities of initiating impurities. As discussed in chapters 2 and 4, reaching higher polymer molecular weights could broaden applications, for example, in thermoplastic elastomers, coatings, sealants and adhesives.¹⁻³ Maybe, by further exploring the metal salts and non-initiating catalysts, higher molar masses could be realised. Ultimately, this may also require better methods of monomer purification. Alternatively, if polymer bimodality could be accepted, the exploration of the properties of higher molar mass polymers could be achieved more immediately. For now, the application of poly(ester-*alt*-ethers) in a range of (low molar mass) applications should be explored, for example in formulations for cleaning, beauty, personal care, food, paints, agricultural coatings, electrolytes and medicine.

Further investigations into the mechanism of poly(ester-*alt*-ether) catalysis are currently being explored (see chapter 4). A better mechanistic insight may provide opportunities to further improve the catalysis and overcome some of these obstacles.

It would be interesting to explore the possibility of an analogous linkage sequencing for CO₂/epoxide ROCOP—A poly(carbonate-*alt*-ether). Many of the common metals used in catalysis for CO₂/epoxide ROCOP have hydrolysis constants in the wrong regime for poly(ester-*alt*-ethers) (pK_h is too high). Perhaps a good starting point may be catalysts for CO₂/epoxide ROCOP that have been reported to make ~70 % ether, or, catalysts based on lower pK_h metals such as Zr and Hf.

6.2.2 Sustainable Alternatives to Thermoplastics

In attempts to make a net zero plastics industry, performance advantages will most likely need to come from policy and government regulation to speed commercial investment and research in sustainable alternatives, as the set-in infrastructure of petrochemicals makes them much cheaper. Competing on price with plastics such as PE and PP may never be a possibility in such a climate. Metrics (selling points) need to be investigated to establish proposed environmental advantages of these materials. As a priority, future assessments are needed to quantify the overall CO₂ savings from recycling these materials physically or chemically, and subsequently, the saving of extracting raw materials and remaking the polymers. It would be much harder to quantify the advantages given by the biodegradation of the material (given that this carbon is lost to the system), as this refers more to reducing microplastic pollution. Perhaps calculations could be made of the amount of microplastics replaced per tonne of the sustainable alternative?

The blending strategy explored in this work may be broadly applicable to many other brittle sustainable thermoplastics. The many combinations possible for both blocks, also provides the potential for these polymers to be used to target many other sustainable polymers, such as perhaps PHAs and starch-based thermoplastics.

6.2.2.1 PLLA

In this work, using poly(ester-*alt*-ethers)-*b*-PLLA (**AB**) block copolymers to toughen PLLA, the roles of the relative molar masses of the **A** and **B** blocks were explored. A range of poly(ester-*alt*-ethers) should be systematically tested for the **A** block, taking advantage of the wide range of monomers available to poly(ester-*alt*-ethers) ROCOP. This would permit a structure-property analysis to determine the optimum properties for this immiscible block (such as thermal, rheological and solubility). A similar study could be designed to explore the optimum combination for the miscible **B** block, which has shown to be important in reducing interfacial energy between the matrix and dispersed phase to provide compatibility.¹⁶

In order to improve these blends, a more fundamental understanding of the deformation and failure mechanism is required. By applying a combination of WAXS, SAXS and microscopy (SEM and TEM) at deliberately chosen points of strain (such as in the linear viscoelastic region, yield point and post-yield), insight could be gained into the role of crazing, cavitation of the dispersed phase, shear yielding and of crystalline regions, at different points

of straining.^{5,16-19} This would allow a more systematic approach to improving the blend performance.

The blending conditions for this system should be optimised. Compounding and injection molding could be used to improve distribution of the dispersed phase and provide finer particles. This would not only avoid solvent use, but also provide tougher blends.

Future additives for PLLA should be degradable. Many strategies have been shown to produce very high performing PLLA, although many of those use either additives that will not degrade or strategies that may reduce the degradability of PLLA.

6.2.2.2 Polycarbonates from CO₂ and Cyclic Epoxides (PCPC)

PCPC is a promising material due to its impressive mechanical properties, as well as its low entanglement molar mass (M_e). This makes it synthetically more viable to make materials above the critical molar mass (3-6 times M_e), where thermal-mechanical properties are often at a maximum.⁴ Currently, cyclopentene oxide (CPO) is petrochemically derived, although there have been reports of its possible synthesis from more sustainable sources, and, epoxides can often be derived from biomass.⁵⁻⁷ This must become renewably sourced, cheaply, sustainably and ethically. Development in routes to its synthesis from waste biomass should be prioritised. Carbon dioxide is already an industrially relevant monomer, fitting into existing commercial infrastructure, and, with the possibility for utilising waste CO₂ integrated from the co-monomer manufacturing.

The thermal and processing properties of PCPC (amorphous, higher T_g ~90, lower melt viscosity) make it a suitable replacement for thermoplastics such as PS and its derivatives (more so than PLLA). Moreover, it has mechanical strength (59 MPa) and modulus (2.8 GPa) matching these materials. Polymer blending strategies or composite formation should be further investigated. These are cheaper methods to improve particular properties. Perhaps, learning from petrochemical plastics like ABS and HIPS, that utilise more complex three-part blending and grafting to fine-tune properties by better control over microphase separation and interphase stability.

In order to progress applications for PCPC, studies should focus on its impact strength, compression mechanical properties, creep, chemical resistance, moisture absorption and barrier properties, flammability, insulative properties, electrical properties (resistivity, dielectric constant etc), and, its ability to be foamed (a strength of PS). Other commercially relevant

properties should be examined, to understand potential applications of this promising material. By identifying where there are property shortfalls, strategies can be explored to improve these.

Similar to PLLA, understanding the deformation and failure mechanisms in these blends would allow a more rationalised approach to improving performance. Similar studies as outlined above should be explored for these materials. The application of compounding to improve the dispersed phase morphology should also be applied (as outlined above for PLLA).

New elastomers should be identified (particularly for the immiscible **A** block) that are lower cost, bio-sourced, biodegradable and non-toxic. Low T_g polymers that are immiscible in PCPC can be explored here. Alternatively, in the same manner as PLLA above, new poly(ester-*alt*-ethers) could be examined for this also. The toxicity of any degradation products should be determined.

Lastly, another promising high molar mass polycarbonate, explored recently by our group, was PeCHC (poly(ethyl-cyclohexene carbonate)).³² At high molar masses (125 kg mol^{-1}) this polymer showed a low entanglement molecular weight ($13\text{--}18 \text{ kg mol}^{-1}$), as well as impressive elongation ($18.7 \pm 4.2 \%$) without any additives. Importantly PeCHC displayed a higher T_g (105°C), and may be suited for higher temperature applications. This may be another option for future toughening efforts of polycarbonates from CO_2 . Such materials with higher T_g values should be explored, to expand the applications of these materials.

6.3 Conclusion

This thesis has aimed to find strategies to improve the properties of the sustainable thermoplastics poly(L-lactide) (PLLA), from starch rich biomass, and poly(cyclopentene carbonate) (PCPC) from CO_2 , as potential alternatives for petroleum-derived plastics which are now pervasive in the environment. This will be important immediately (for efforts to reach a net-zero plastics industry), particularly if the oil industry is to lean on plastics production on our journey to 2050. These materials will need to have similar (or better) thermal-mechanical properties, be sourced renewably and have a range of end-of-life options available.

This thesis has aimed to increase our understanding of poly(ester-*alt*-ether) catalysis, and, use these interesting polymers in strategies to optimise the thermo-mechanical properties of PLLA and PCPC polymer blends. Morphological studies were used to reason the performance, and, end of life options of the materials were explored.

The success of sustainable materials is dependant on much more than just material development. This is a global, multifaceted challenge requiring cooperative efforts to reduce plastic production, improve material sourcing from renewable sources (ethically), improve recycling and shift from a linear to a circular plastics economy, where materials are designed for end-of-life.

6.4 References

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Chapter 7

Chapter 7: Experimental

7.1 General

All air-sensitive and moisture-sensitive reactions (synthesis of **1**, monomer purifications, and polymerizations) were carried out under inert conditions, using standard Schlenk techniques and in a N₂-filled glovebox. Solvents used for synthesis and polymerization were collected from a solvent purification system (SPS), degassed with three freeze-pump-thaw cycles, and stored over 4 Å molecular sieves, under an inert atmosphere.

Catalyst **1** was synthesised using literature procedures unless otherwise stated.¹ Catalysts **2** and **3** were purchased from STREM, stored in a glove box and used as received. ZrX₄ catalysts explored in chapter 4 (where X = (OⁱPr)₄(HOⁱPr), (OEt)₄, (Oct)₄, (Cl)₄, (NMe₂)₄, (Bn)₄) were purchased from STREM/Merck, stored in a glove box and used as received. Catalysts in chapter 4 were synthesised according to section S7.3.3. The syntheses of catalyst **4** and **5** were performed using literature procedures.^{2,3}

Butylene oxide (BO), 1,2-epoxydodecane (EDD), 1,2-epoxy-9-decene (ED), allyl glycidyl ether (AGE), 2-ethyl hexyl glycidyl ether (EHGE), benzyl glycidyl ether (BGE), 1,2-epoxyoctane (OO), 1,2-cyclopentene oxide (CPO) and 1,2-cyclohexene oxide (CHO) were dried by stirring them over CaH₂, followed by fractional distillation. Next, the epoxides were stirred over BuLi, followed by a second and third series of fractional distillations. Solvents were de-gassed, by freeze-pump-thaw in triplicate, and stored under an inert (N₂) atmosphere. Phthalic anhydride (PA) was purified by extraction using toluene, followed by recrystallization from a chloroform solution and sublimation (three times). It was stored under an inert (N₂) atmosphere. *Tert*-butyl phthalic anhydride (tBPA) was isolated by sublimation and stored under an inert (N₂) atmosphere. Diglycolic anhydride (DGA) was purified by two recrystallizations from acetic anhydride and sublimation in triplicate, and was stored under an inert (N₂) atmosphere. Maleic anhydride (MA) was purified by recrystallization, from chloroform twice, and sublimation, in triplicate, and stored under an inert (N₂) atmosphere. Poly(L-lactide) PLLA (ME346310, M_n = 103 Kg mol⁻¹, D = 1.81 in CHCl₃) was purchased from Goodfellow.

A phosphate buffered solution of 0.05 M was prepared by addition of 0.017 moles Na₂HPO₄, 2.4 g, and 0.008 moles NaH₂PO₄, 0.96 g, in 0.5 L HPLC grade water, making up close to 0.5 L, adjusting pH to 7.2 using phosphoric acid, and then making up to 0.5 L (this buffers pH 5.8-7.4).

Humicola insolens Cutinase (HiC – trade mark name Novozym 51032), purchased from STREM, with activity against glycerol tributyrates of 15 KLU/g (KLU = kilo lipase unit, 1LU is the amount of enzyme activity which liberates 1 μ mol of tritrateable butyric acid from glycerol tributyrates per minute under defined standard conditions).

7.2 Analytical Techniques

7.2.1 NMR Spectroscopy

^1H , ^{13}C , ^{19}F and ^{31}P spectra were obtained using Bruker AV 400 MHz and 500 MHz instruments. ^1H DOSY spectra were obtained using a Bruker NEO600 NMR spectrometer.

In order to establish reproducible integrals for the crude and pure polymers by ^1H NMR spectroscopy, sample **P1** was measured with a $D_1 = 1$ s, 15 s and 60 s. No differences between relative aryl/aliphatic integrals were found, therefore $D_1 = 1$ s was used for all further ^1H NMR spectroscopy.

7.2.2 Gel Permeation Chromatography (GPC)

Polymer analysis was carried out using a Shimadzu LC-20AD instrument, equipped with PSS SDV 5 μ m pre-column and two PSS SDV 5 μ m linear M columns and a refractive index (RI) detector. Samples were dissolved in HPLC grade THF, filtered through 0.2 μ m PTFE filters (VWR) and measurements were determined at 1 mL min $^{-1}$ flow rate, at 30 °C. Monodisperse polystyrene standards were used to calibrate the instrument.

Polymer analysis of **P9**, and multiple polymers from chapter 4 (where applicable these are mentioned in the chapter), were carried out using an Agilent LC1260 Infinity II system fitted with a PLgel 5 μ m (50 x 7.5 mm) guard column and two PLgel 5 μ m MIXED-C (300 x 7.5 mm) analytical columns and equipped with a multi-detector suite (MDS) comprising a dual-angle light scattering detector (LS, 15 & 90 degrees), refractive index detector (RI), and viscometer (VS). THF (FisherScientific, GPC grade stabilized with 0.025% BHT) was used as the eluent with a flow rate of 1 mL min $^{-1}$ at 35 °C. The system was calibrated using a set of narrow polystyrene standards (Agilent EasiVial PS-H 2 mL) for standard GPC calibration and a narrow polystyrene standard ($M_p = 29,510$ g/mol, $M_{w,LS} = 29,810$ g/mol, $dn/dc = 0.185$, $M_w/M_n = 1.02$, $[\eta] = 0.1777$ dL/g) for system calibration and triple detection.

7.2.3 Differential Scanning Calorimetry (DSC)

Measurements were performed using a DSC25 (TA Instruments). A sealed, empty crucible was used as a reference, and the instrument was calibrated using zinc and indium samples. Polymer samples were cooled, at 10 °C min $^{-1}$, to -80 °C and under a N $_2$ flow (80 mL

min⁻¹), followed by heating to 200 °C, at the same rate. Each sample was analysed over three heating-cooling cycles, and, it was during the third heating mode that the data was collected. Glass transition temperatures (T_g) are reported as the midpoint of the transition taken from the different heating cycles for different experiments. Note, the minimum and maximum heating temperatures are not the same for every chapter (these are polymer dependant), -80-200 °C is an example, and each chapter will specify the temperature range used.

For PLLA blends (chapter 3); polymer samples were cooled, at 10 °C min⁻¹, to -80 °C and under a N₂ flow (80 mL min⁻¹), followed by heating to 180 °C, at the same rate, and it was during this first heating mode that the data was collected. This was to measure the crystallinity of the annealed PLLA blends, before removing thermal history.

7.2.4 Thermal Gravimetric Analysis (TGA)

Experiments were conducted using a TGA5500 System (TA Instruments), equipped with the TRIOS software package. Polymer samples were heated from 30 to 700 °C, at a rate of 10 °C min⁻¹, under N₂ flow (12 mL min⁻¹).

7.2.5 MALDI-ToF Mass Spectrometry

MALDI-TOF analyse was carried out on a Bruker Autoflex Speed MALDI-TOF.

7.2.6 Water Contact Angle Measurements

Static water contact angles were measured using a Drop Shape Analysis System (Tracker, ITConcept, France). A 5 µL drop of ultra-pure water (MilliQ water, Millipore, MA, USA) was placed on the polymer film surfaces and the static water contact angle was measured. The measurements were performed on multiple different areas of each slide, with the average values calculated and the standard deviation of these measurements determined.

7.2.7 End-group Analysis

Polymer end group analysis was performed according to an established literature procedure.^{4,5} Polymer samples (20 mg) were dissolved in CDCl₃ (0.5 mL) and to this was added a solution (20 µL) containing Cr(acac)₃ (5.5 mg) and internal standard, bisphenol A (400 mg) in pyridine (10 mL), followed by 20 µL of 2-chloro-4,4,5,5-tetramethyl dioxaphospholane. Analysis was performed by ³¹P{¹H} NMR on a Bruker AVIII HD 400 NMR spectrometer.

7.2.8 Tensile Mechanical Experiments

Polymer tensile specimens were cut from the films (0.15-0.45 mm-thick) conforming to dimensions for ISO 527–2 type 5B with a Zwick ZCP020 cutting press (length= 35 mm,

gauge length = 10 mm, width = 2 mm). New specimens were cut for each measurement from the same films and a minimum of five tests were used for each measurement. Uniaxial tensile measurements were conducted on a Instron 8600 series universal testing system according to ISO 527 at 10 mm min⁻¹ extension rate. A minimum of five tests were used for each measurement.

True Stress vs True Strain Measurements: Polymer tensile specimens were cut from the films (0.24-0.33 mm-thick) according to custom dimensions (length= 35 mm, gauge length = 4 mm, gauge width = 4 mm). An MTS screw driven load frame was used to test the specimen with a load cell capacity of 1kN. The tests were performed at ambient temperature (~20 °C) and the loading was quasi-static with a nominal strain-rate of ~0.001 S⁻¹. For the Digital Image Correlation (DIC), the frames were taken at 5 frames per second, using a point grey camera, with a resolution of 4000x2000 pixels. The analysis was performed using the commercial software MatchID.

7.2.9 Scanning Electron Microscopy (SEM)

After fracture: blend morphologies were characterized by SEM (JEOL JSM-6010LV with an accelerating voltage of 15 kV). Images were taken of the blend tensile bar fracture surfaces, sputter-coated in platinum.

Before fracture: samples were mounted and cut in an ultramicrotome (Leica UC7) and the cut edge polished using a freshly cut-glass knife. Polished samples were mounted on SEM stubs (Agar AGG3160) and coated with gold using a Quorum Q150R-ES. Samples were then imaged at 2 kV with a Zeiss Sigma 300 FEG-SEM and SE2 detector.

Particle diameters and interparticle distances were analysed using ImageJ software, analysing 3 images per sample (60-100 particles), and were measured by the diameter of the ‘crater’ left by the particle. For any particles where microtoming may have slightly damaged the shape of the particle ‘crater’, measurements of diameter were taken perpendicular to the direction of slicing.

7.2.10 Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal analysis (DMTA) was carried out using a TA Instruments Q850 RSA-G2 Solids Analyser (TA Instruments), using an ACS III cooling system. Specimens of uniform width (5.3 mm) were cut using two parallel blades. Samples were heated from 30 °C to 170 °C, at a rate of 2 °C min⁻¹, with a frequency of 1 Hz, 0.001 N pre-load force and 0.015 % strain amplitude.

7.2.11 Rheology

Rheological experiments were conducted in the melt on an ARES-G2 (TA Instruments) using polymer samples between 25 mm stainless steel plates. All measurements were conducted in the linear viscoelastic region (as determined by amplitude sweeps). For PLLA blends; 1 % amplitude strain, 100-0.01 Hz, at 170 °C.

7.2.12 Chemical Recycling Method

N.B. The concentration (moles) of blends were calculated as 100 % PLLA. The PLLA molar equivalents were determined from a single lactic acid repeat unit ($M_w = 72.05 \text{ g mol}^{-1}$). E.g. for a sample of 72 mg of 10 wt% blend, the number of moles = $72/72.05 \approx 1 \text{ mmol}$.

PLLA TGA Scale: In the glovebox, stock solutions of **[P13₂₅-PLLA₂₃]₁₀** (1 mmol, 72 mg in 1.0 mL of DCM), Sn(Oct)₂ ($1.00 \times 10^{-2} \text{ M}$, 12.2 mg of Sn(Oct)₂ in 3.00 mL of THF) were prepared. 100 μL of the PLLA (0.1 mmol, 1000.0 equiv.) stock solution was added to a vial containing Sn(Oct)₂ (10.0 μL , $1.00 \times 10^{-4} \text{ mmol}$, 1.0 equiv.). The Sn(Oct)₂-PLLA solution was thoroughly mixed before being drop-cast (*ca* 3 drops) onto Platinum TGA crucibles. The solvent was allowed to evaporate before the crucible was loaded into the TGA instrument for monitoring of the depolymerization. The following TGA method template was used for the reaction: N₂ flow of 25.0 mL min^{-1} , increase temperature from room temperature to 180 °C, hold temperature at 180 °C for 180 minutes.

PCPC TGA Scale: *N.B. Moles of blends were calculated as 100 % PCPC, (PCPC repeat unit $M_w = 128 \text{ g mol}^{-1}$).*

In the glovebox, stock solutions of **[P5-PCPC]₂₀** (1.0 mmol, 128 mg in 1.0 mL of CH₂Cl₂) and cat 5 ($5 \times 10^{-3} \text{ M}$, 15 mg, in 2.00 mL of THF) were prepared. 100 μL of the PCPC (0.1 mmol, 1000.0 equiv.) stock solution was added to a vial containing cat 5 (20.0 μL , $1.00 \times 10^{-4} \text{ mmol}$, 1.0 equiv.). The cat 5-PCPC solution was thoroughly mixed before being drop-cast (*ca* 3 drops) onto platinum TGA crucibles. The solvent was allowed to evaporate before the crucible was loaded into the TGA for monitoring of the depolymerization. The following TGA method template was used for the reaction: N₂ flow of 25.0 mL min^{-1} , increase temperature from room temperature to 180 °C, hold temperature at 150 °C for 50 minutes.

7.2.13 Chemical Recycling of [P13₂₅-PLLA₂₃]₁₀ PLLA Blend to Determine L-Lactide Selectivity

In the glovebox, a stock solution of Sn(Oct)₂ ($1.00 \times 10^{-2} \text{ M}$, 12.2 mg of Sn(Oct)₂ in 3.00 mL of THF) was prepared. The Sn(Oct)₂ (178 μL , $1.78 \times 10^{-3} \text{ mmol}$, 1.0 equiv.) stock

solution was added to a Schlenk, before **[P13₂₅-PLLA₂₃]₁₀** was added (128 mg, 1.78 mmol, 1000.0 equiv.). The mixture was dissolved in a minimum amount of DCM (*approx.* 1 mL) before the solvent was removed *in-vacuo*. A water-cooled cold-finger was connected to the Schlenk, and the reaction mixture was heated to 180 °C, with magnetic stirring, under vacuum (0.1–1 mbar). After 3 h, a white crystalline powder was collected which was determined to be lactide (100 mg, 87 % yield, 95 % *L*-LA as determined by ¹H NMR spectroscopy and GC-MS, Figures S8.3.91 and S8.3.92 respectively). See Figure S8.3.90 for a photograph of the experimental set up.

7.2.14 Enzymatic Degradation

PLLA Enzymatic Degradation (chapter 3): All enzymatic degradation experiments were performed in triplicate. For the detection of diglycolic acid and lactic acid, the hydrolysis products of **P13** and PLLA respectively, the following conditions apply; the polymer sample (20 mg) was suspended in 4 mL (0.05 M, as described in section S7.1) with 10 µL mL⁻¹ HiC (activity of 0.06 KLU mL⁻¹), were added to 5 mL Eppendorf tubes and shaken at 500 rpm at 37 °C. Samples were taken from the degradation experiments using a plastic syringe, filtered with a PTFE filter with a mesh size of 0.45 µm.

The components were separated using a Prevail Organic Acid 5 µm, 250 mm x 4.6 mm reversed phase column (Grace Davison Discovery Sciences). The column was operated with 0.25 mM KH₂PO₄ (pH 2.5) as a mobile phase, at 30 °C and a flow rate of 1 mL min⁻¹.

The concentration of diglycolic acid was quantified using a refractive index detector. The signals obtained were analysed with the Shimadzu Lab Solutions software. Negative control experiments, without any added enzyme, were carried out for each experiment, and showed negligible diglycolic or lactic acid. Figures S8.3.93-95 show the calibration data for diglycolic and lactic acid, Figures S8.3.99-100 show an exemplary chromatogram. The identity of the hydrolysis product was confirmed using the retention time of diglycolic acid standards and via ESI-MS of a collected fraction (Figures S8.3.96-98). Before each set of HPLC experiments, the diglycolic acid and lactic acid standards were run to determine the correct elution times. The **P2** homopolymer and **P2-PLLA** block copolymer were exposed to enzymes in their purified state; a viscous liquid and soft solid, respectively. On the other hand, the **[P2₂₅-PLLA₂₃]₁₅** polymer blend and semicrystalline **PLLA** were used as the semicrystalline films prepared via solvent casting as described in section S3.0.

PCPC Enzymatic Degradation (chapter 5): All enzymatic degradation experiments were performed in triplicate. In a 5 mL Eppendorf tube, the sample (20 mg) was dispersed in the phosphate buffer solution (4 mL of 0.05 M solution, as described in section S7.1) and HiC (10 $\mu\text{L mL}^{-1}$) was added. The mixture was submerged in a sample shaker set to 37 °C and 500 rpm. Samples were taken from the degradation experiments using a plastic syringe, filtered with a PTFE filter with a mesh size of 0.45 μm .

The components were separated using a velox SP-C18 (Shimadzu) column. The column was operated with 95 % H_2O (0.2 % formic acid) and 5 % acetonitrile (0.2 % formic acid) as the mobile phase, at 30 °C and a flow rate of 1 mL min^{-1} and 40 μL injection volume.

The concentration of phthalic acid was quantified using a PDA detector (254 nm), while 1,2-cyclopentanediol and 1,2-cyclohexanediol were quantified using a refractive index detector. The signals obtained were analysed with the Shimadzu Lab Solutions software. Negative control experiments, without any added enzyme showed negligible degradation product. Figures S8.5.43-45 show the calibration data for phthalic acid, 1,2-cyclopentanediol and 1,2-cyclohexanediol standards, and Figures S8.5.46 show an exemplary chromatogram, demonstrating that they can be identified simultaneously under these conditions. The identity of the hydrolysis product was confirmed using the retention times of the standards. Before each set of HPLC experiments, the calibrations using pure phthalic acid, 1,2-cyclopentanediol and 1,2-cyclohexanediol standards were run. The **P5** homopolymer and **P5-PCPC** and **P5-PCHC** block copolymers were exposed to enzymes in their purified states (as viscous liquids). On the other hand, the **[P5-PCHC]₂₀** polymer blend and PCPC were used as the films prepared via compression molding as described in section S7.3.2.2.

7.2.15 Kinetics Experiments (Using DSC to Measure Calorimetry)

In a glovebox, the catalyst (0.01 mol) was weighed into a vial, then dissolved in 1 mL of neat epoxide. The anhydride (0.5 mmol) was added to the reaction mixture until it was fully dissolved. A ~10 mg aliquot was spotted into a DSC pan, sealed and weighed. Samples were prepared and run in triplicate. Samples were analysed at 120 °C. Data was processed using TRIOS software package (kinetics package), and data used to determine k_{obs} was fit between 15-80 % conversion.

7.2.16 Single Crystal X-ray Diffraction

Crystalline samples were isolated in a glovebox, under a pool of fluorinated oil, and mounted on MiTeGen MicroMounts. The crystals were then cooled to 150 K, with an Oxford

Cryosystems nitrogen cooling device. Data collection was carried out with an Oxford Diffraction Supernova diffractometer using Cu K α ($\lambda = 1.5417 \text{ \AA}$) radiation. The resulting raw data was processed using CrysAlisPro and OLEX2. The structures were solved by direct methods and the full-matrix least-squares refinements were carried out using a suite of SHELX programs via the OLEX2 graphical interface. Non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were included in idealised positions and refined using a riding model. Full refinement details can be found in section S8.4.8.

7.3 Experiential Procedures

7.3.1 Polymerisation Procedures

7.3.1.1 ROCOP of Anhydrides and Epoxides - Poly(ester-*alt*-ether) Synthesis

Typical ROCOP procedure: In a glovebox, catalyst **1** (9.4 mg, 0.01 mol) was weighed into a vial, then dissolved/suspended in 1 mL epoxide. The anhydride (0.5 mmol) was added to the reaction mixture, the vial sealed with electric tape, then parafilm, removed from the glovebox and heated to the stipulated temperature (generally 50 °C, or higher for reactions involving TCA and DPA). After the desired time, samples were cooled to 0 °C, taken into the glovebox for removal of aliquots (20 μL), used to determine conversion data, or exposed to air to quench and evaporated to dryness. The crude polymer was characterized at $\sim 10 \text{ mg mL}^{-1}$ (THF solution) for GPC and $\sim 10 \text{ mg mL}^{-1}$ (CDCl_3 solution) for ^1H NMR spectroscopy. The pure polymers were obtained by precipitation from methylene chloride solutions, using methanol or pentane as non-solvents, and by drying under vacuum at 60 °C, overnight.

7.3.1.2 ROCOP of Anhydride, Epoxide and Cyclic Ethers - Poly(ester-*alt*-ether) Synthesis

Typical polymerization procedure: In a glovebox, catalyst **1** (9.4 mg, 0.01 mol) was weighed into a vial, then dissolved/suspended in 0.25 mL butylene oxide and 0.75 mL the selected cyclic ether. Phthalic anhydride (74 mg, 0.5 mmol) was added to the reaction mixture, the vial sealed, removed from the glovebox and heated to 50 °C. After the desired time, samples were cooled to 0 °C, taken into the glovebox for removal of aliquots (20 μL), used for conversion data, or exposed to air to quench and evaporated to dryness. The crude polymer was characterized at $\sim 10 \text{ mg mL}^{-1}$ (THF solution) for GPC and $\sim 10 \text{ mg mL}^{-1}$ (CDCl_3 solution) for ^1H NMR spectroscopy. The pure polymers were obtained by precipitation from methylene chloride solutions, using methanol or pentane as the non-solvents, and after drying under vacuum, at 60 °C, overnight.

7.3.1.3 Procedure for the Synthesis of (*trans*)-P1; *cis-trans* Isomerism of MA

Using a modified general procedure 2.1.1 and literature procedure.⁵⁹ In a glovebox, catalyst **1** (9.4 mg, 0.01 mol) was weighed into a vial, then dissolved in butylene oxide (1 mL, 1.2 mmol). Maleic anhydride (48 mg, 0.5 mmol) was added to the reaction mixture, the vial sealed, removed from the glovebox and heated to 50 °C. After 2 hours, diethyl amine (51 µL, 0.5 mmol) was added and the mixture was stirred for 3 hours. The crude polymer was characterized as ~ 10 mg/mL (THF solution) for GPC and ~ 10 mg/mL (CDCl₃) solution for ¹H NMR spectroscopy. The pure polymer was obtained by precipitation in CH₂Cl₂/MeOH and drying under vacuum at 60 °C, overnight.

7.3.1.4 General Procedure for 2-Mercaptoethanol Functionalization

P1, **P10** or **P14** (0.22 mmol relative to the anhydride linkages), 2-mercaptoethanol (2 equiv. vs alkene groups), and DMPA (0.2 equiv. vs alkene groups) were dissolved in THF (2 mL). The reaction was irradiated with UV light and stirred at room temperature for 1 hour. The crude reaction mixture was exposed to air to quench, filtered through a silica plug and precipitated in pentane (10 mL). The pure polymer was isolated after drying, under vacuum, at 60 °C, overnight.

7.3.1.5 Poly(ester-*alt*-ether)-*b*-PLLA Synthesis

Sequential addition method: In a glovebox, the Zr-catalyst (0.01 mmol, 9.1 mg, 1 equiv.), was weighed into a 4 mL vial and subsequently dissolved in epoxide (1 mL, [catalyst **1**] = 10 mM). The selected anhydride (0.5 mmol, 50 equiv.) was added, the vial was closed and sealed with electrical tape. The reaction mixture was removed from the glovebox and heated to 50 °C, with stirring (1000 rpm). Aliquots were taken, in the glove box, after cooling the reaction in dry ice, and the polymer conversion was assessed by ¹H NMR spectroscopy. After full anhydride conversion, L-LA (0.5 mmol, 1 equiv.) was added to the reaction mixture, and the reaction progress was monitored as above. After full conversion of L-LA, the polymer was purified by three cycles of dissolving in minimum CH₂Cl₂, passing through a PTFE filter and precipitating from MeOH. The pure polymer was then dried under vacuum, at 60 °C, for 2 days.

7.3.1.6 Polymerization by Switch Catalysis - Poly(ester-*alt*-ether)-*b*-PLLA

In a glovebox, the Zr-catalyst (0.01 mmol, 9.1 mg, 1 equiv.), was weighed into a 4 mL vial and subsequently dissolved in epoxide (1 mL, [catalyst **1**] = 10 mM). The selected anhydride (0.5 mmol, 1 equiv.) and L-LA (0.5 mmol, 1 equiv.) were added, the vial was closed

and sealed with electrical tape. The reaction mixture was removed from the glovebox and heated to 50 °C, with stirring (1000 rpm). Aliquots were taken, in the glove box, after cooling the reaction in dry ice, and the polymer conversion was assessed by ^1H NMR spectroscopy. After full conversion of L-LA, the polymer was purified by three cycles of dissolving in minimum CH_2Cl_2 , passing through a PTFE filter and precipitating from MeOH. The pure polymer was then dried under vacuum, at 60 °C, for 2 days.

7.3.1.7 Alternating Polyester Synthesis

For example **P1'**: In a glovebox, Cr(III) catalyst **2** (6 mg, 0.01 mol) was weighed into a vial, then dissolved/suspended in epoxide (1 mL). The maleic anhydride (25 mg, 0.25 mmol) was added to the reaction mixture, the vial was sealed, removed from the glovebox and heated to 50 °C. After the desired time, samples were cooled to 0 °C, taken into the glovebox for removal of aliquots or exposed to air to quench and evaporated to dryness. The pure polymer was obtained by passing through a PTFE filter and precipitating from $\text{CH}_2\text{Cl}_2/\text{MeOH}$, followed by drying under vacuum, at 60 °C.

7.3.1.7 Synthesis of P5 (Poly(ester-*alt*-ether))

In a glovebox, $\text{Hf}(\text{O}^i\text{Pr})_4(\text{HO}^i\text{Pr})$ (catalyst **3**) (0.32 mmol, 133 mg, 1 equiv.), was weighed into a 4 mL vial and subsequently dissolved in EDD (1 mL, [catalyst **3**] = 12.8 mM). The selected anhydride (40.5 mmol, 125 equiv.) was added, the vial was closed and sealed with electrical tape. The reaction mixture was removed from the glovebox and heated to 50 °C, with stirring (1000 rpm). Aliquots were taken, in the glove box, after cooling the reaction in dry ice, and the polymerisation conversion was assessed by ^1H NMR spectroscopy. After full conversion, the polymer was purified by three cycles of dissolving in minimum CH_2Cl_2 , passing through a PTFE filter and precipitating from MeOH. The purified polymer was dried under vacuum, at 60 °C, for 2 days. Before use in the synthesis of **P5-PCPC/P5-PCHC**, it was dried under vacuum, over P_2O_5 , for 2 days.

7.3.1.8 Synthesis of P5 (Poly(ester-*alt*-ether)-*b*-PC

For synthesis of **P5-PCPC**: In a glovebox, **P5** (0.19 mmol, 19 equiv.) was dissolved in CPO (1 mL, 960 equiv. CPO, [**P5**] = 190 mM) in an ampoule. Catalyst **4** (0.01 mmol, 1 equiv.) was added, and the solution stirred for 5 minutes, after which the vial was closed. The ampoule was cycled three times onto a triple manifold CO_2 Schlenk line. The cycling between vacuum and CO_2 , before placing the flask into a pre-heated (80 °C) oil bath, at 1 bar CO_2 pressure, with stirring. As the reaction progressed, aliquots were taken, in the glove box, and the polymer

conversion was assessed by ^1H NMR spectroscopy. After the desired CPO conversion was achieved, the polymer was quenched by adding benzoic acid (5 mg) and stirring for 10 minutes. The sample was purified by three cycles of dissolving in minimum CH_2Cl_2 , passing through a PTFE filter and precipitating from MeOH. The pure polymer was then dried under vacuum, at 60 °C, for 2 days.

For synthesis of **P5-PCHC**: In a glovebox, **P5** (155 mmol, 31 equiv.) was dissolved in CHO (2 mL, 1976 equiv. CHO, [**P5**] = 190 mM, in an ampoule. Catalyst **4** (0.01 mmol, 1 equiv.) was added, and the solution stirred for 5 minutes, after which the vial was closed. All following procedures were identical to **P5-PCPC** described above.

7.3.1.9 Synthesis of High Molar Mass PCPC

Under nitrogen, catalyst **5** (6.4 mg, 0.0085 mmol) and 1,2-cyclohexenediol (3.98 mg, 0.0343 mmol) were dissolved in CPO (15.0 mL, 172 mmol) and toluene (12 mL). The mixture was loaded into a high-pressure reactor, pressurised to 20 bar with CO_2 and heated to 100 °C with stirring (cat : CHD : CPO = 1 : 4 : 20,000). After 164 hours, the reaction was cooled to room temperature and depressurised. The crude mixture was precipitated in MeOH (400 mL), and subsequently re-precipitated from THF/MeOH. The product was then redissolved in THF and filtered through two short columns of silica. The filtrate was then concentrated, solvent cast and air dried overnight. Then it was dried at 113 °C, under vacuum, for 16 hours to yield poly(cyclopentene carbonate) (16.5 g) as a white solid, in 75 % yield. ^1H NMR spectroscopy showed 91 % CPO conversion.

7.3.2 Polymer Blend Preparation

7.3.2.1 PLLA Polymer Blend Preparation

Polymer films were prepared using mixtures of high molecular weight commercial PLLA ($M_n = 103 \text{ kg mol}^{-1}$, $D = 1.81$ in CHCl_3) and various wt% of each block polymer. The block polymers and PLLA were dissolved in CH_2Cl_2 , (1 g in 10 mL), and stirred at room temperature until everything dissolved. The polymer solution was then transferred into a PTFE mould, using a syringe filter. The PTFE mould was covered by a punctured aluminium foil and left to evaporate, at room temperature, overnight. The polymer film was dried, in a vacuum oven, at 60 °C, for 2 days, and at 180 °C, for 10 minutes, followed by slow cooling, overnight, to room temperature, under vacuum. The absence of any residual solvent was checked using DSC and TGA (section 8.3.2.1 and 8.3.2.2).

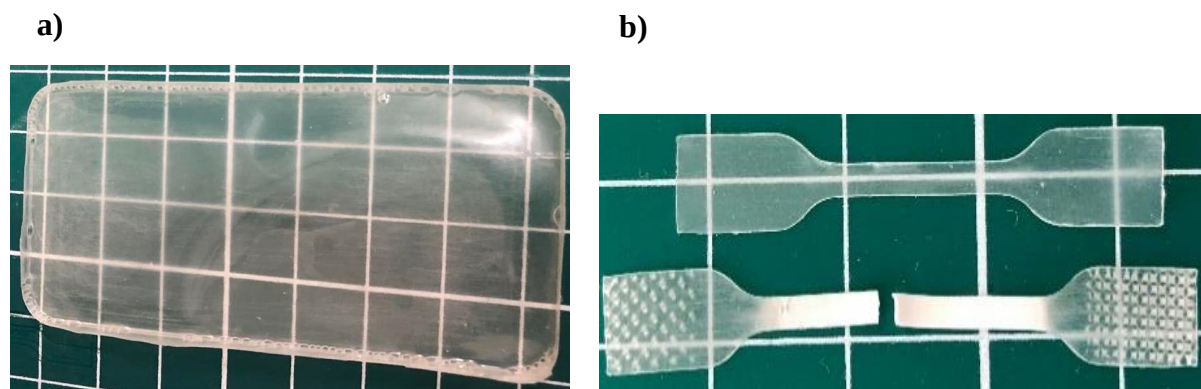


Figure S7.1: Representative photographs illustrating a) film and b) dog bone samples (before, top, and after, bottom, tensile testing) of the polymer PLLA + block polymer blends prepared in chapter 3.

7.3.2.2 PCPC Polymer Blend Preparation

Polymer films were prepared with mixtures of high molecular weight PCPC ($M_n = 82 \text{ kg mol}^{-1}$, $\bar{D} = 1.58$) and various wt% of each block polymer (**P1-PCPC** or **P1-PCHC**). The block polymers and PCPC were dissolved in CH_2Cl_2 , (1 g in 10 mL), and stirred at room temperature until all the sample dissolved. The polymer solution was then transferred into a PTFE mould, using a syringe filter. The PTFE mould was covered by a punctured aluminium foil and left to evaporate, at room temperature, overnight. The polymer film was dried, in a vacuum oven, at 60°C , for 2 days (or until dry). The samples were then compression molded at 130°C for 10 minutes, and cooled slowly (leaving the hot plates together) for 2 h. The absence of any residual solvent was checked using DSC and TGA (section 8.5.2.1 and 8.5.2.2).

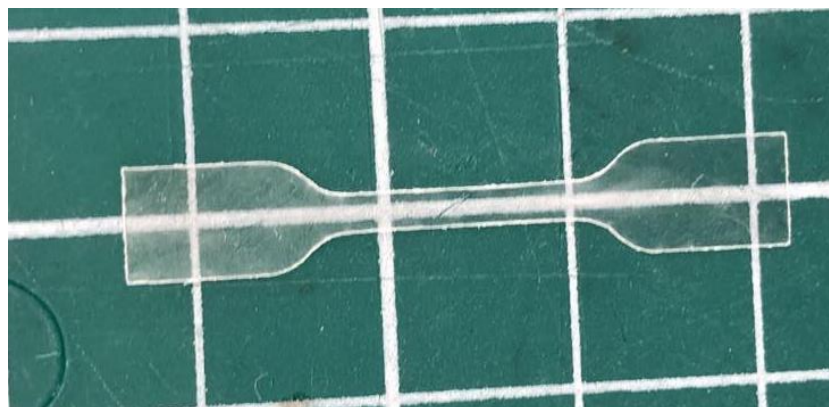


Figure S7.2: Representative photograph illustrating of a dog bone sample of the PCPC + block polymer blends prepared in chapter 5.

7.3.3 Catalyst Synthesis

7.3.3.1 General Ligand (L1-L5) Synthesis

To a round bottom flask charged with aldehyde (1 mmol), dissolved in ethanol (15 mL), was added the respective aniline or amine (1 mmol) and formic acid (0.02 mmol). The reaction

was heated to reflux for 18 h, cooled to RT and concentrated. The pro-ligands were isolated by recrystallization or column chromatography (Figure S7.3).

7.3.3.2 General $(\text{ML}_2(\text{O}^i\text{Pr})_2)$ Catalyst Synthesis

Catalysts $\text{ML}_2(\text{O}^i\text{Pr})_2$ were synthesised from an adapted literature (Figure S7.3).¹ An ampoule was charged with **HL** (1 mmol) dissolved in toluene (10 mL). $[\text{M}(\text{O}^i\text{Pr})_4]$ (0.5 mmol) was added and stirred for 24 h, at 40 °C. The reaction mixture was dried, and recrystallized in a THF/hexane mixture, at –30 °C, overnight, to give pale-yellow crystals and powder (20-30 %, 0.1-0.22 mmol).

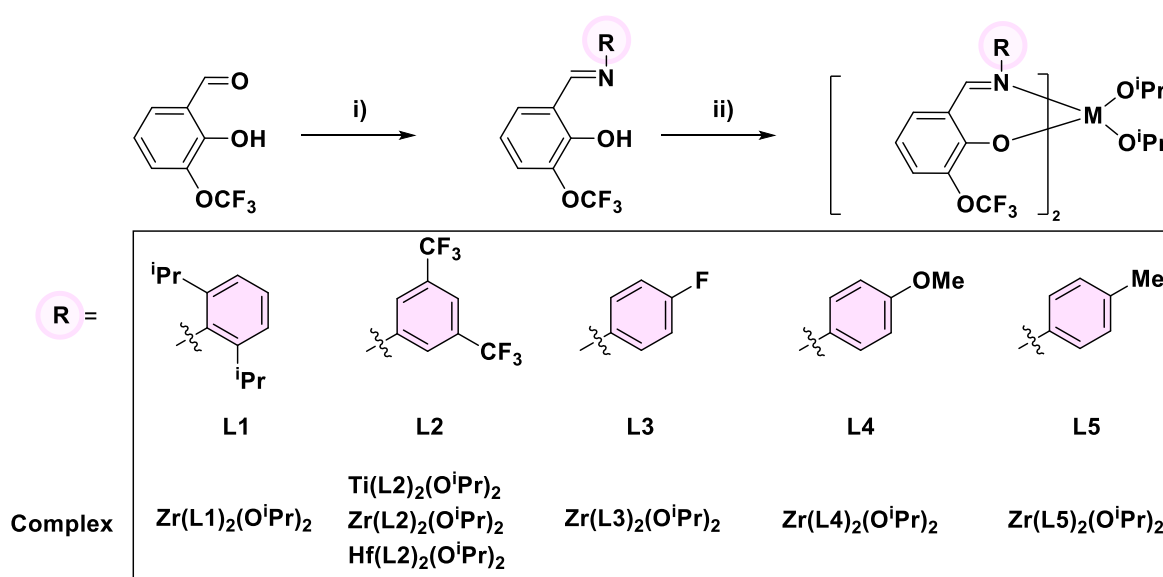


Figure S7.3: Schematic representation of the synthesis of a catalysts of the form $\text{M}(\text{L})_2(\text{O}^i\text{Pr})_2$. i) 1 : 1 aldehyde : aniline, formic acid, reflux 18 h. ii) 2 : 1 **L** : $\text{M}(\text{O}^i\text{Pr})_4$, in toluene, at 40 °C, for 24 h.

7.4 References

1. R. W. F. Kerr and C. K. Williams, *J. Am. Chem. Soc.*, 2022, **144**, 6882–6893.
2. Y. Zhu, C. Romain and C. K. Williams, *J. Am. Chem. Soc.*, 2015, **137**, 12179–12182.
3. A. C. Deacy, A. F. R. Kilpatrick, A. Regoutz and C. K. Williams, *Nat. Chem.*, 2020, **12**, 372–380.
4. A. Spyros, D. S. Argyropoulos and R. H. Marchessault, *Macromolecules*, 1997, **30**, 327–329.
5. T. Stößer, D. Mulryan and C. K. Williams, *Angew. Chem. Int. Edit*, 2018, **57**, 16893–16897.

CHAPTER 8

Chapter 8: Appendices and Supporting Information

8.2: Chapter 2 - Cyclic Ether and Anhydride Ring Opening Copolymerisation Delivering New ABB Sequences in Poly(Ester-*alt*-Ethers)

8.2.1 Characterization Data for Polymers Described in Table 2.1

8.2.1.1 NMR Spectra for Polymers Described in Table 2.1

8.2.1.1.1 NMR Spectra for P1

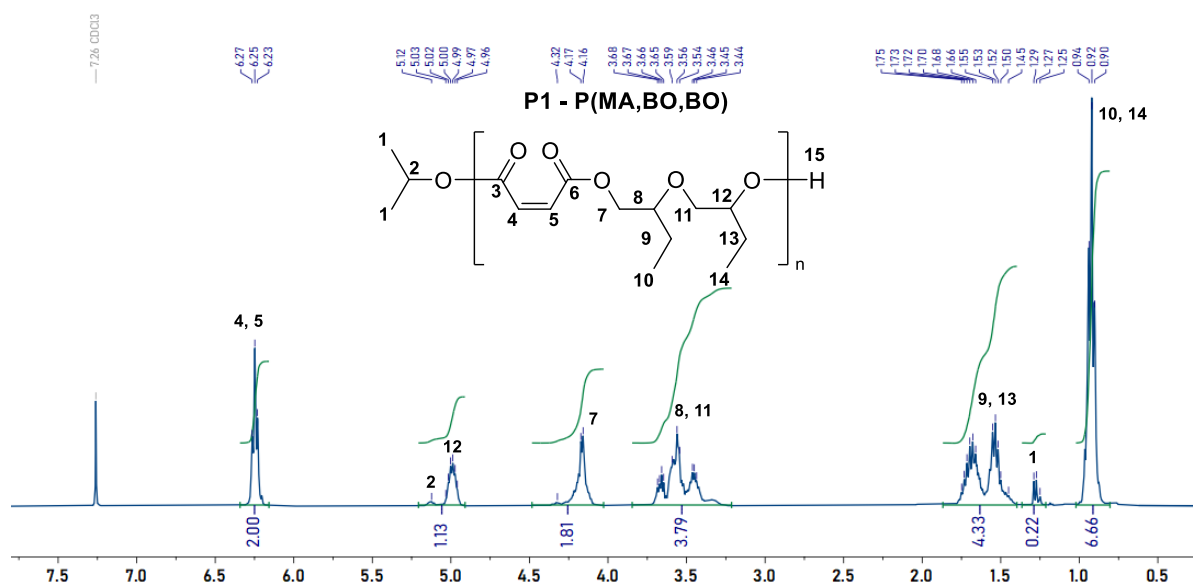


Figure S8.2.1: ^1H NMR spectrum from the reaction of $[1]:[\text{MA}]:[\text{BO}] = 1: 50: 1150$, (work up in $\text{MeOH}/\text{CH}_2\text{Cl}_2$). Spectrum corresponds to Table 2.1, **P1** (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 7.2 \text{ kg mol}^{-1}$.

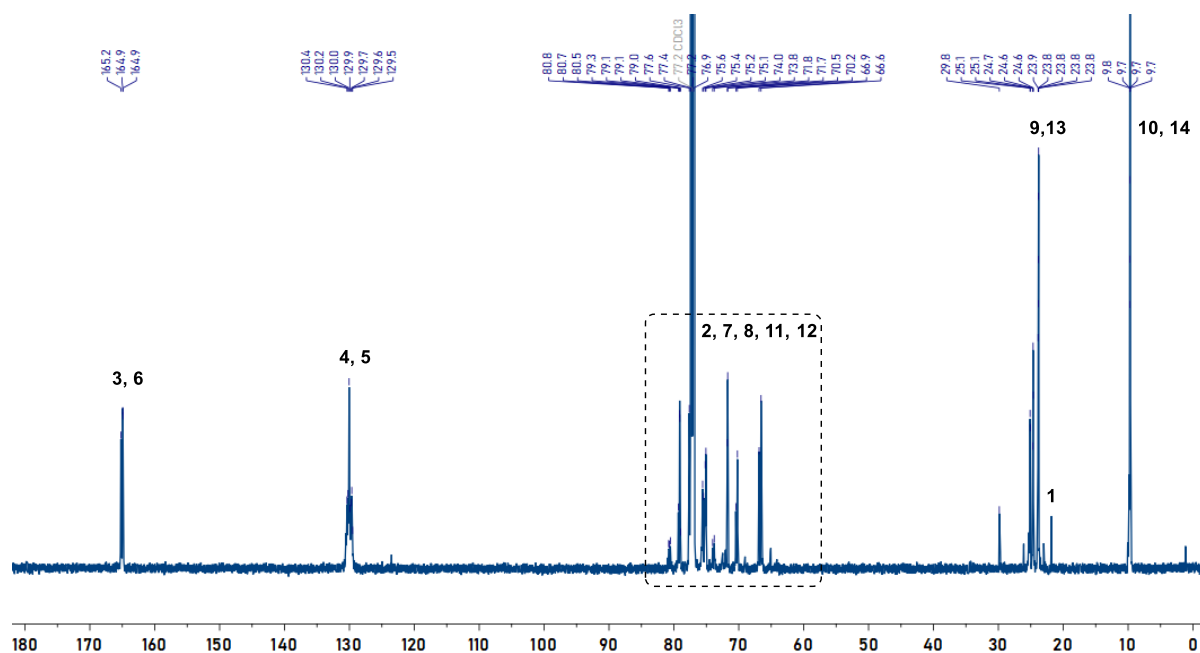


Figure S8.2.2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of $[1]:[\text{MA}]:[\text{BO}] = 1: 50: 1150$. Spectrum corresponds to Table 2.1, **P1** (151 MHz, CDCl_3).

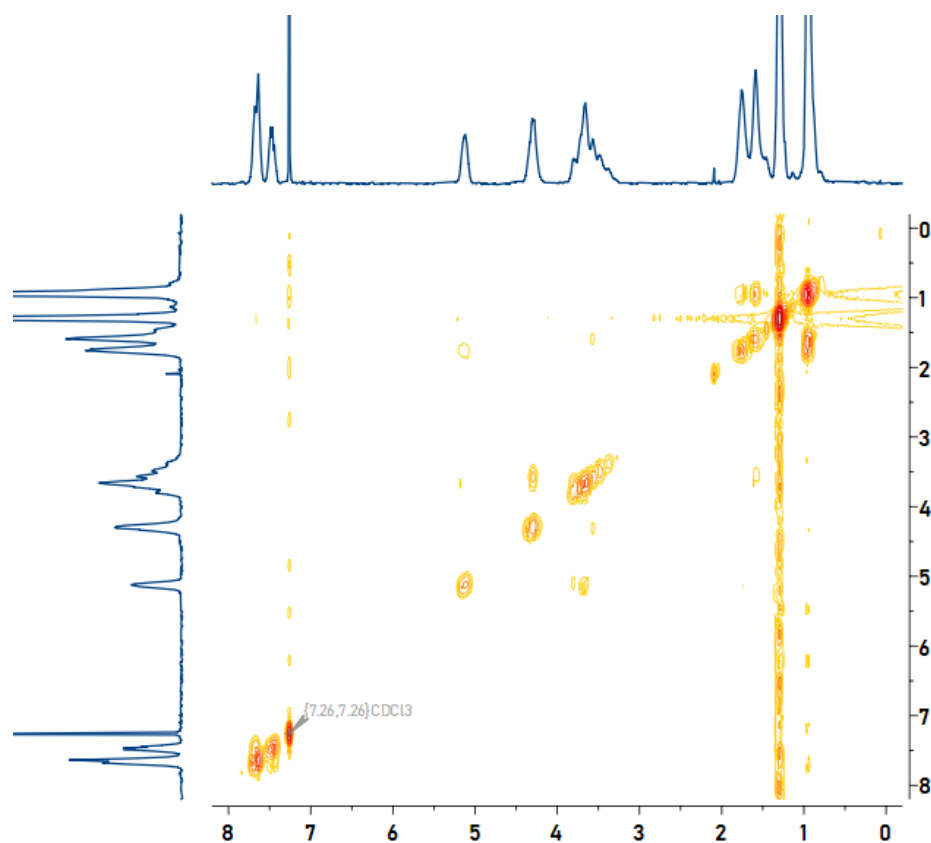


Figure S8.2.3: ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{MA}]:[\text{BO}] = 1: 50: 1150$, from Table 2.1, **P1** (400 MHz, CDCl_3).

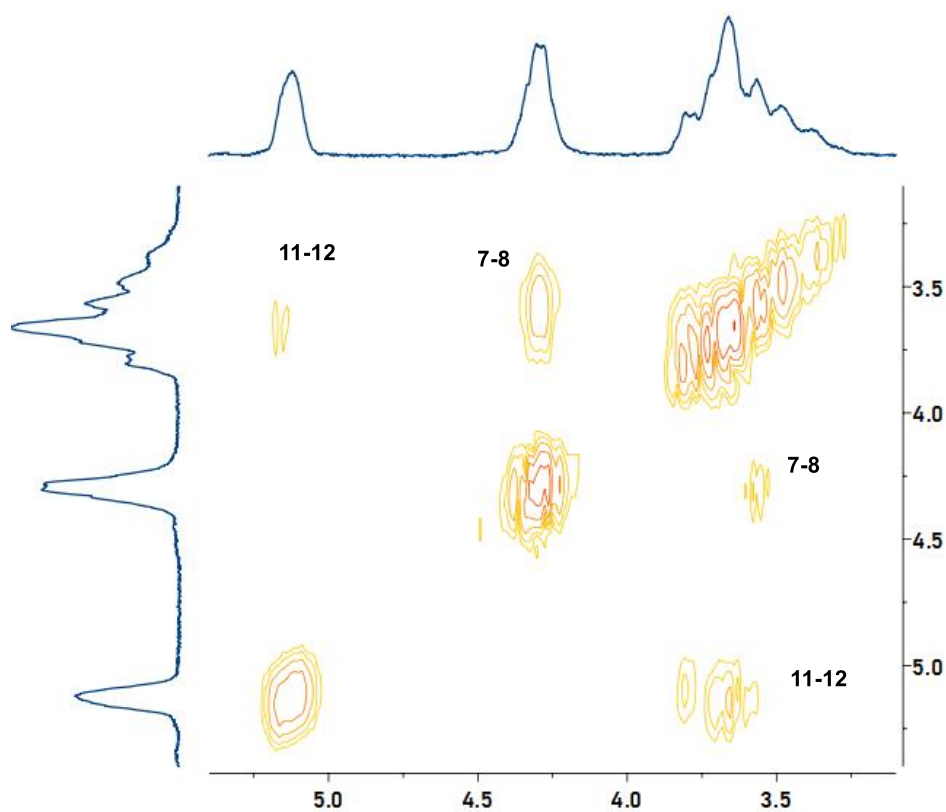
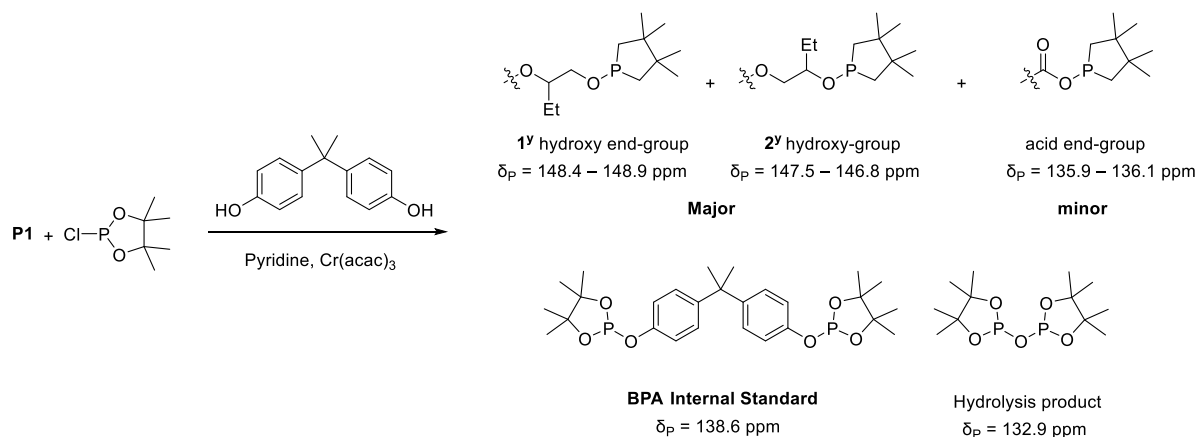


Figure S8.2.4: Magnified ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{MA}]:[\text{BO}] = 1: 50: 1150$, from Table 2.1, **P1** (400 MHz, CDCl_3).

8.2.1.1.1.1 End-group Analysis of P1



Scheme S8.2.1: End group analysis was performed according to literature.¹ **P1** (20 mg) was dissolved in CDCl_3 (0.5 mL) and a solution (40 μL) containing Cr(acac)_3 (5.5 mg) and internal standard, bisphenol A (400 mg) in pyridine (10 mL) was added followed by 40 μL of tetramethylethylene chlorophosphite. The polymer was then analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR.

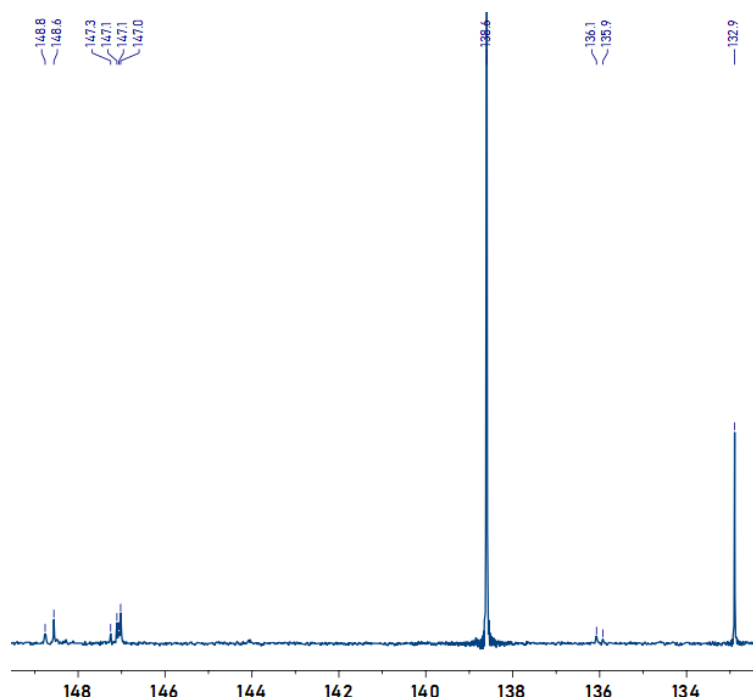


Figure S8.2.5: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum from the reaction **P1** with tetramethylethylene chlorophosphite (162 MHz, CDCl_3). The major polymer resonances at 148.1–148.9 and 147.5–146.8 ppm are characteristic of a mixture of primary and secondary alcohol polymer end-groups, respectively (>90%).² The minor polymer resonances at 135.9–136.1 ppm are characteristic of carboxylic acid end groups (<10%). The standard at 138.6 ppm is Bisphenol-A and the resonance at 132.9 ppm is the hydrolysis product of the chlorophosphite reagent.

8.2.1.1.2 NMR Spectra for P2

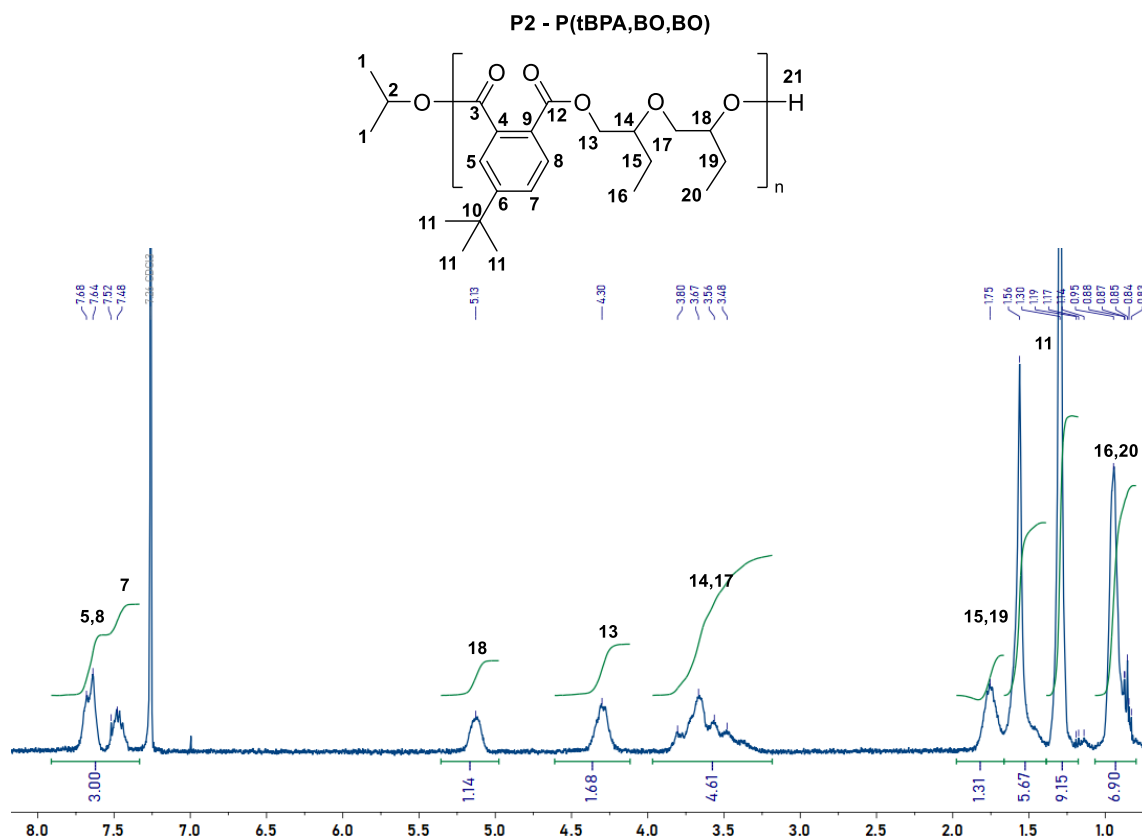


Figure S8.2.6: ¹H NMR spectrum from the reaction of [1]:[tBPA]:[BO] = 1: 50: 1150 (work-up in MeOH/CH₂Cl₂). Spectrum corresponds to Table 2.1, **P2** (400 MHz, CDCl₃).

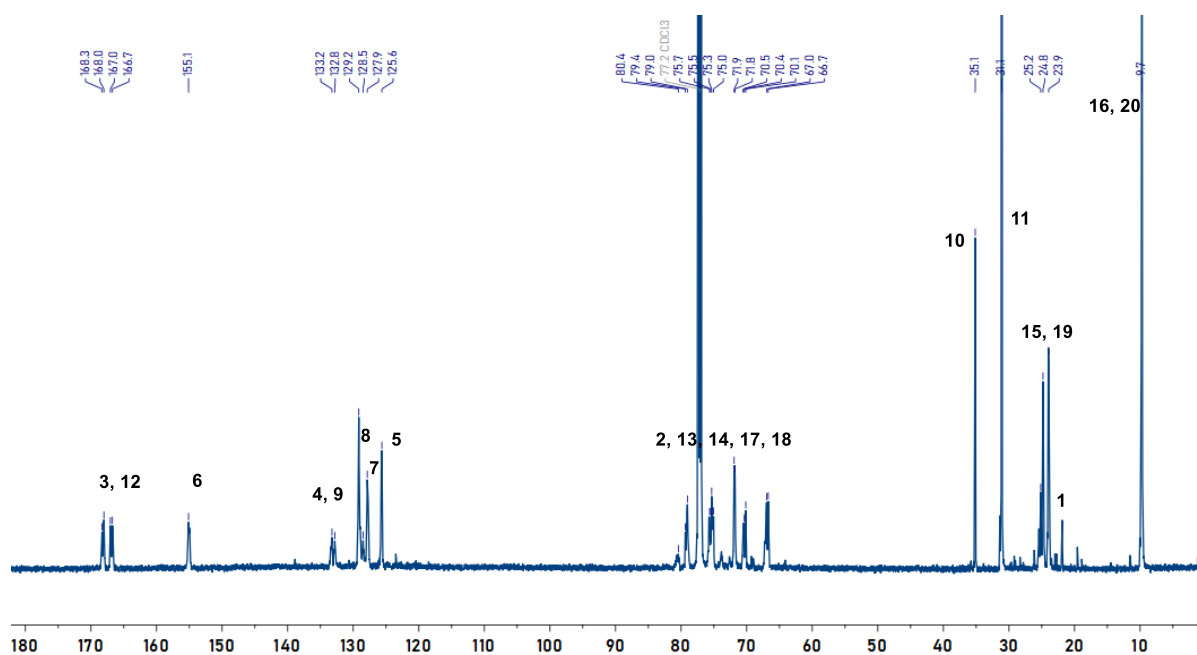


Figure S8.2.7: ¹³C{¹H} NMR spectrum from the reaction of [1]:[MA]:[BO] = 1: 50: 1150, Table 2.1, **P2** (151 MHz, CDCl₃).

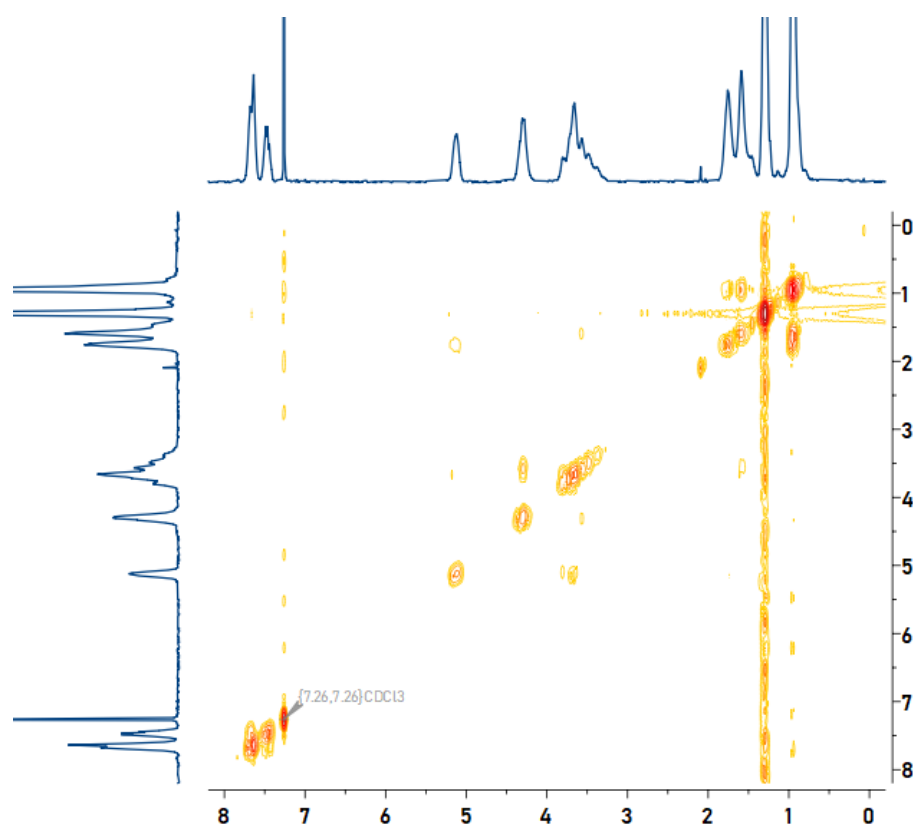


Figure S8.2.8: ^1H COSY NMR spectrum from the reaction of $[1]:[\text{tBPA}]:[\text{BO}] = 1:50:1150$, Table 2.1, **P2** (400 MHz, CDCl_3).

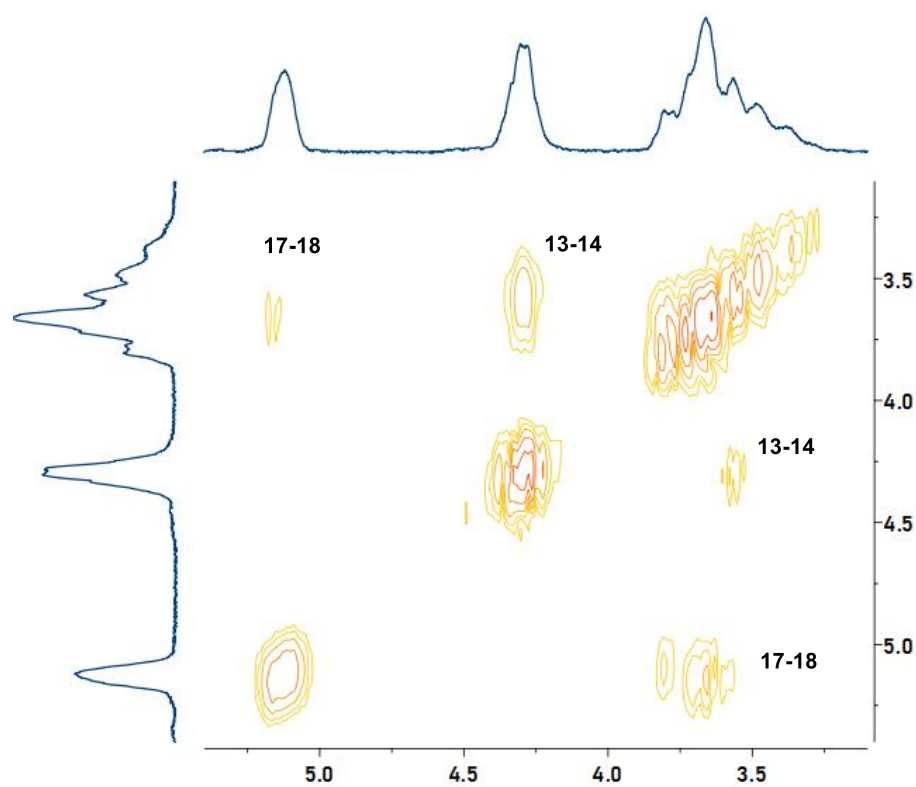


Figure S8.2.9: Magnified ^1H COSY NMR spectrum from the reaction of $[1]:[\text{tBPA}]:[\text{BO}] = 1:50:1150$, Table 2.1, **P2** (400 MHz, CDCl_3).

8.2.1.1.4 NMR Spectra for P3

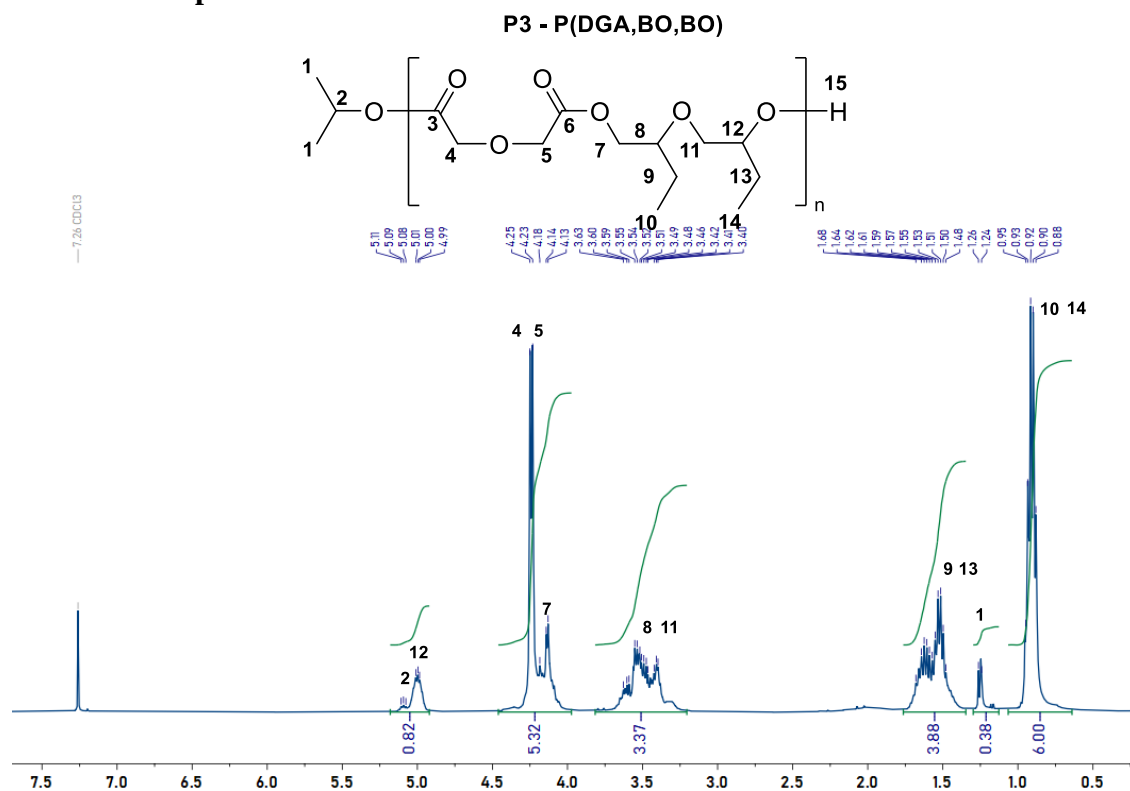


Figure S8.2.10: ^1H NMR spectrum from the reaction of [1]:[DGA]:[BO] = 1: 50: 1150, (work-up in MeOH/Pentane). Spectrum corresponds to Table 2.1, **P43** (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 3.7 \text{ kg mol}^{-1}$.

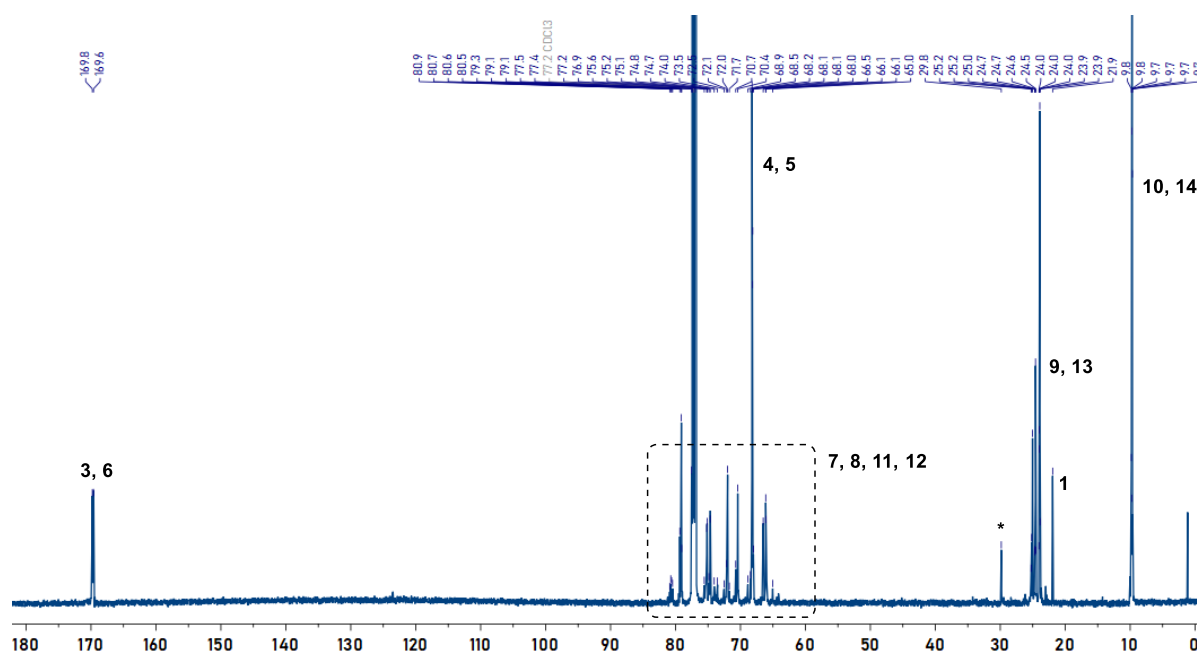


Figure S8.2.11: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of [Cat]:[DGA]:[BO] = 1: 50: 1150, Table 2.1, **P3** (151 MHz, CDCl_3). * = 'H' – grease.

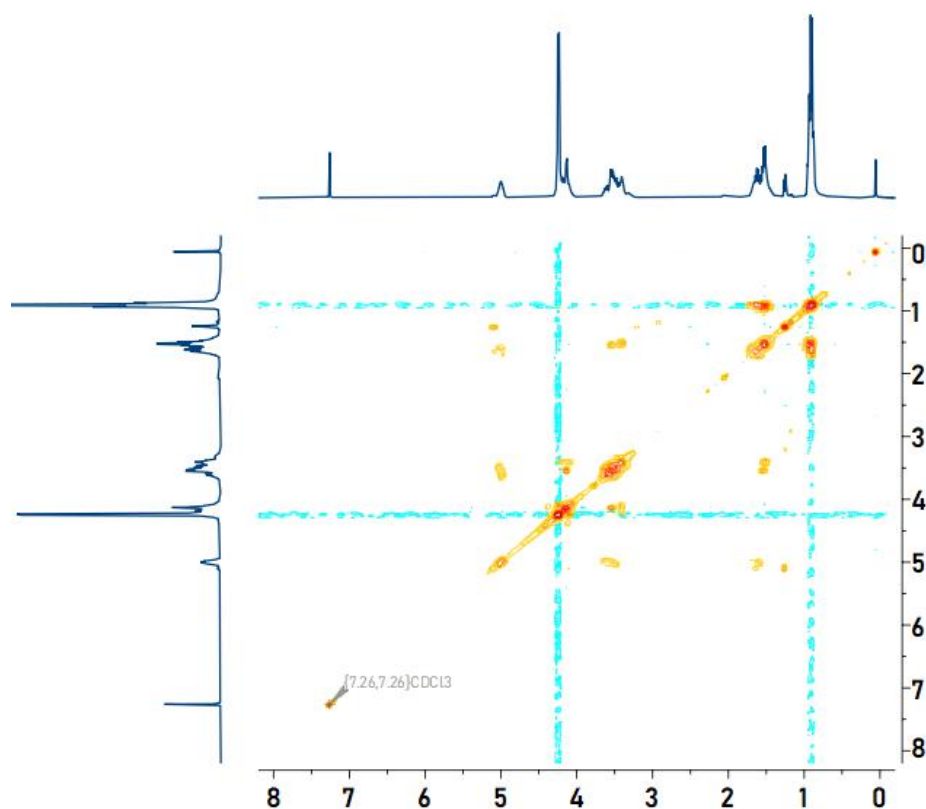


Figure S8.2.12: ^1H COSY NMR spectrum from the reaction of **[1]**:**[DGA]**:**[BO]** = 1: 50: 1150, Table 2.1, **P3** (400 MHz, CDCl_3).

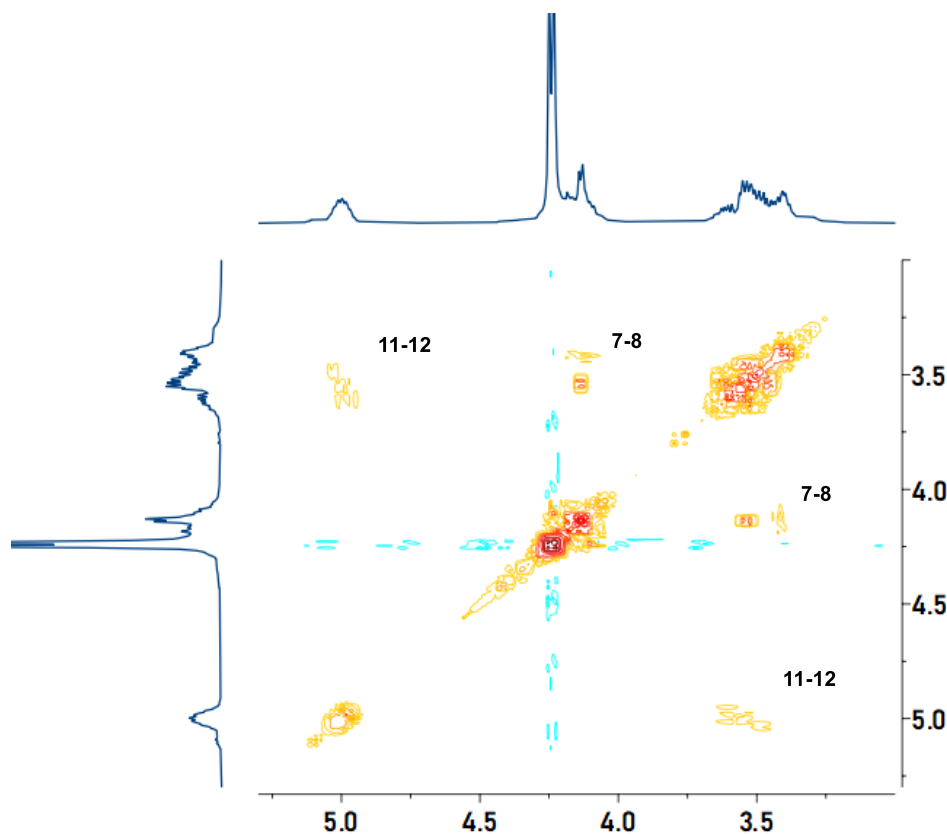


Figure S8.2.13: Magnified ^1H COSY NMR spectrum from the reaction of **[1]**:**[DGA]**:**[BO]** = 1: 50: 1150, Table 2.1, **P3** (400 MHz, CDCl_3).

8.2.1.1.6 NMR Spectra for P4

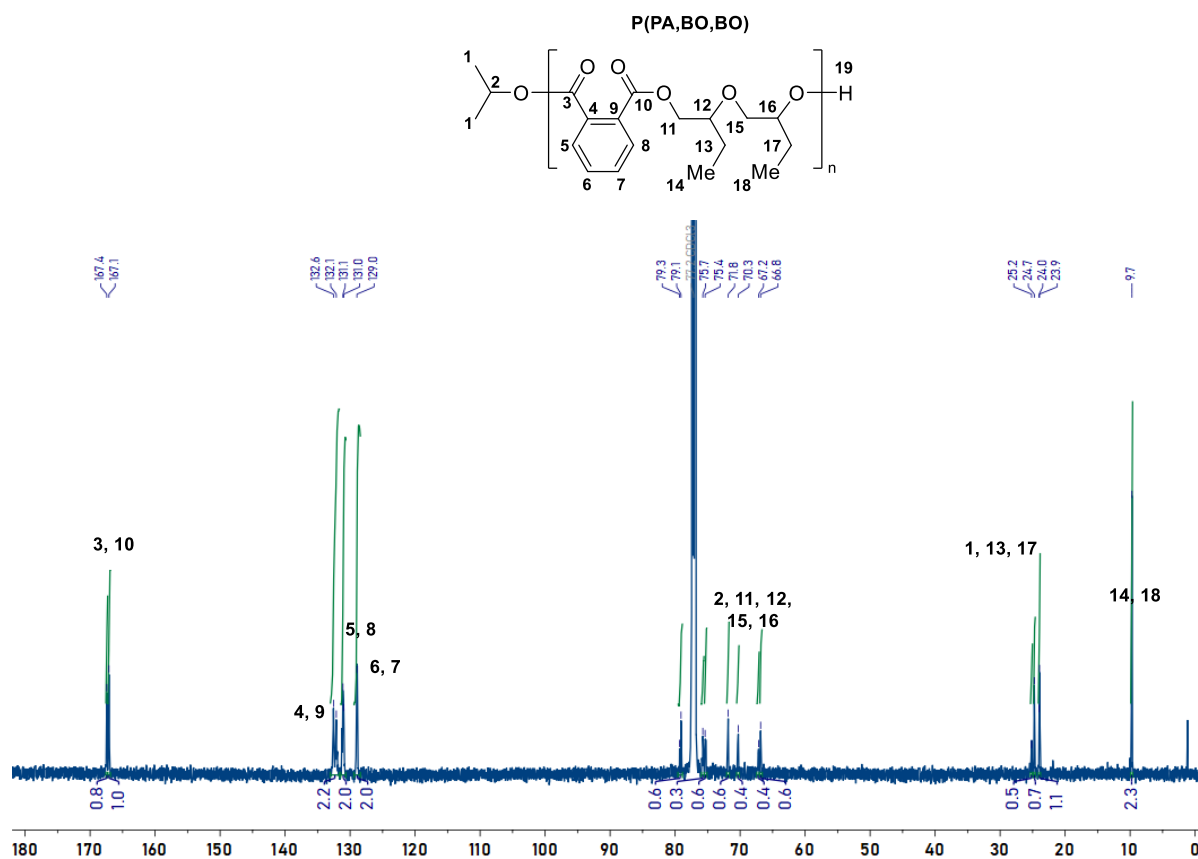


Figure S8.2.14: ^1H NMR spectrum from the reaction of [1]:[PA]:[BO] = 1: 50: 1150, (work-up in MeOH/ CH_2Cl_2). Spectrum corresponds to Table 2.1, **P4** (400 MHz, CDCl_3). * = CH_2Cl_2 .

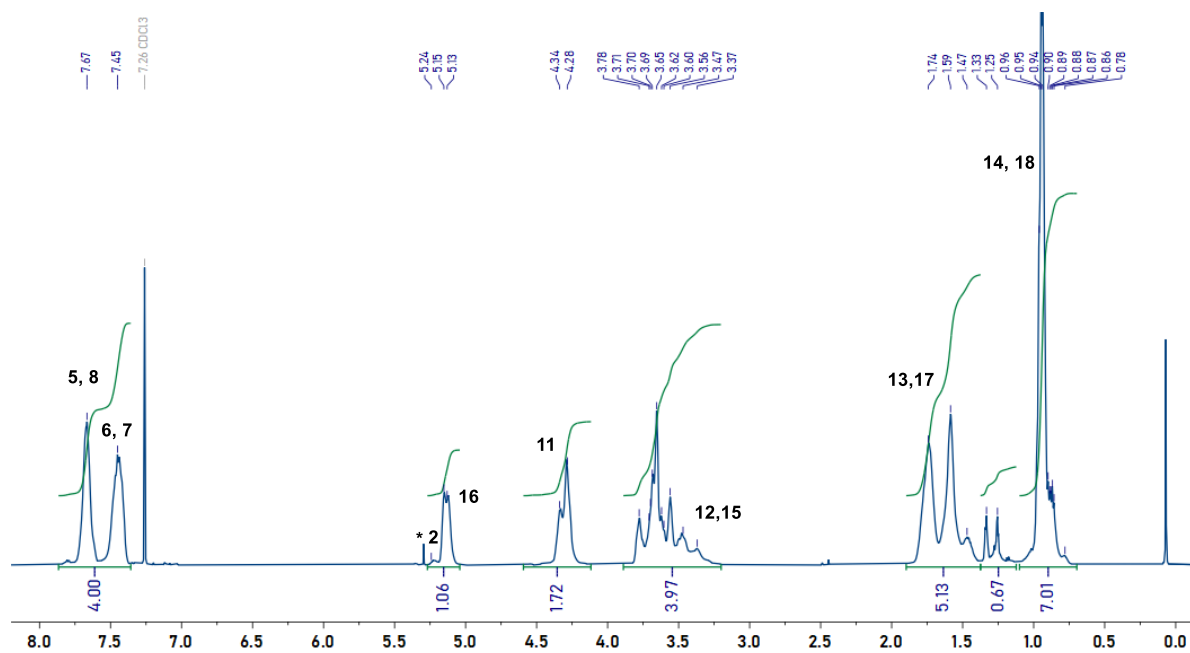


Figure S8.2.15: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of [1]:[PA]:[BO] = 1: 50: 1150, Table 2.1, **P4** (151 MHz, CDCl_3).

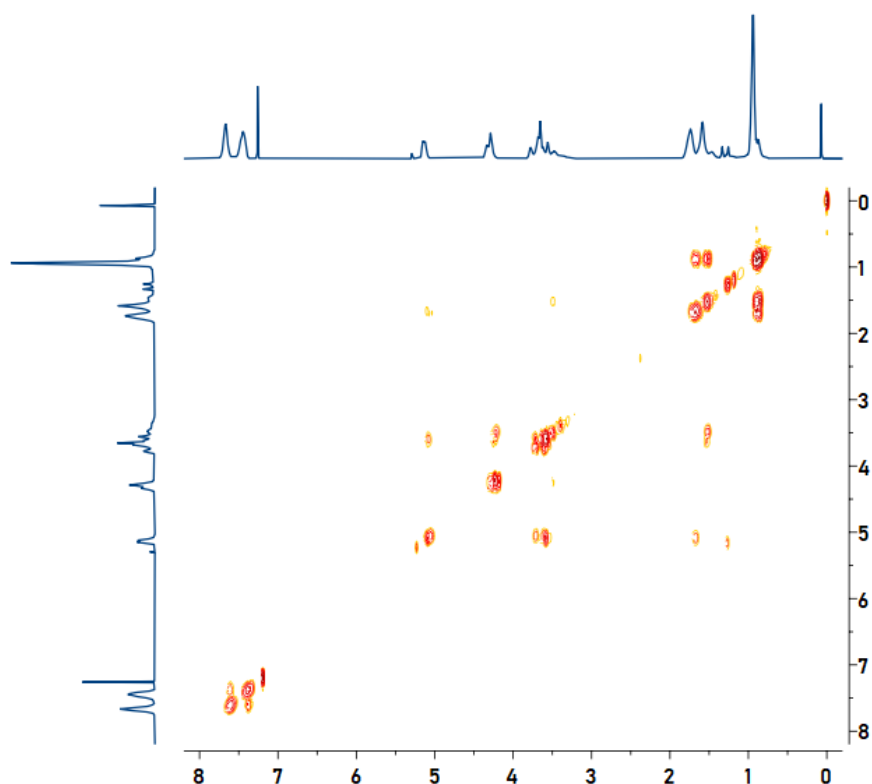


Figure S8.2.16: ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{PA}]:[\text{BO}] = 1: 50: 1150$, Table 2.1, **P4** (400 MHz, CDCl_3).

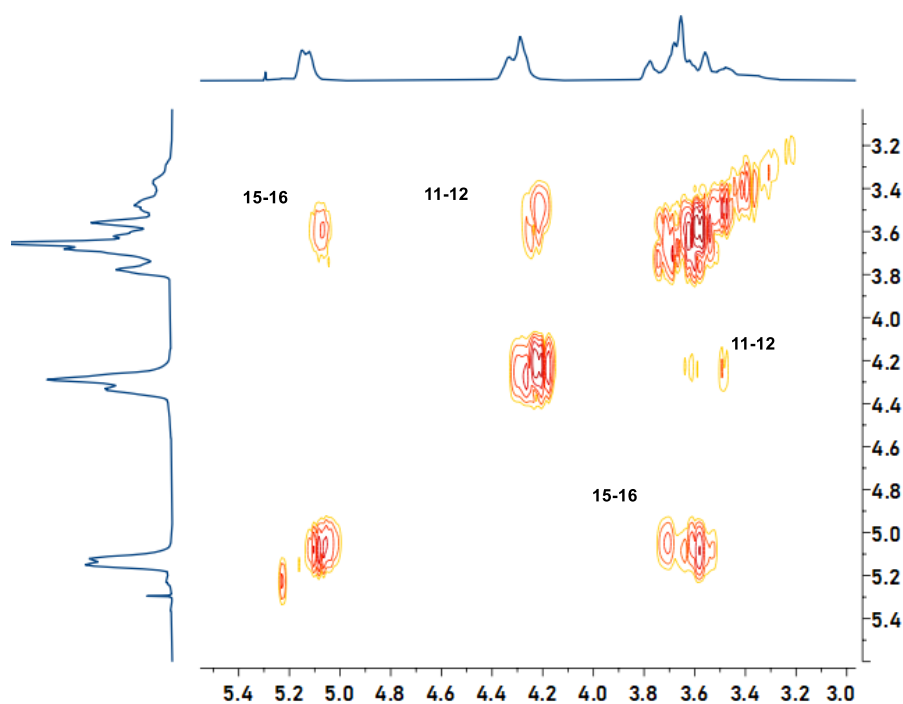


Figure S8.2.17: Magnified ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{PA}]:[\text{BO}] = 1: 50: 1150$, Table 2.1, **P4** (400 MHz, CDCl_3).

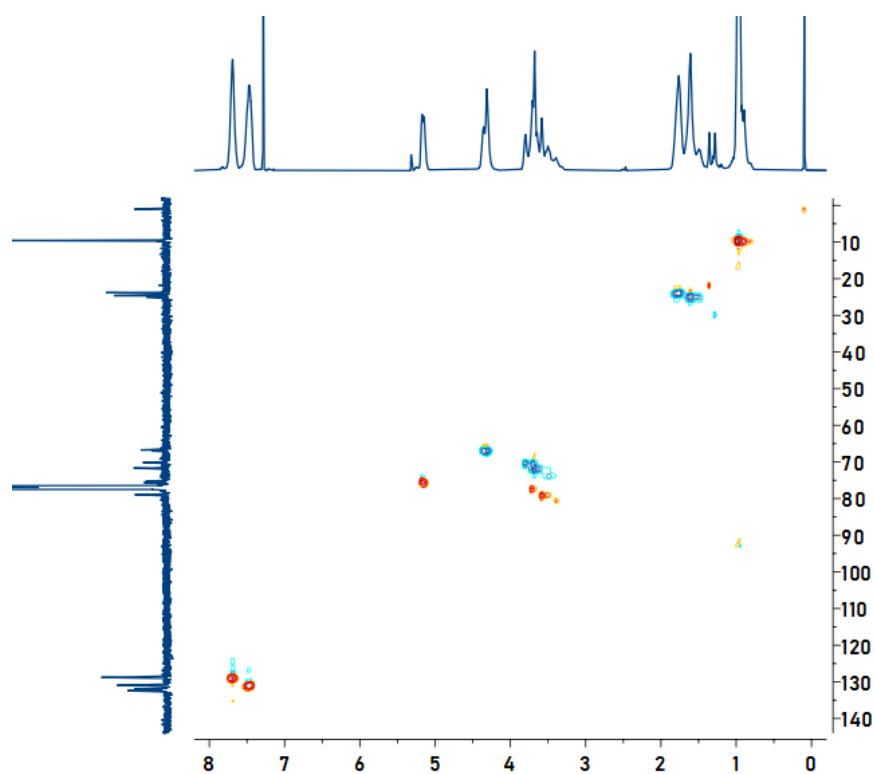


Figure S8.2.18: (^1H , ^{13}C)-HSQC NMR spectrum from the reaction of **P4**, from Table 2.1.

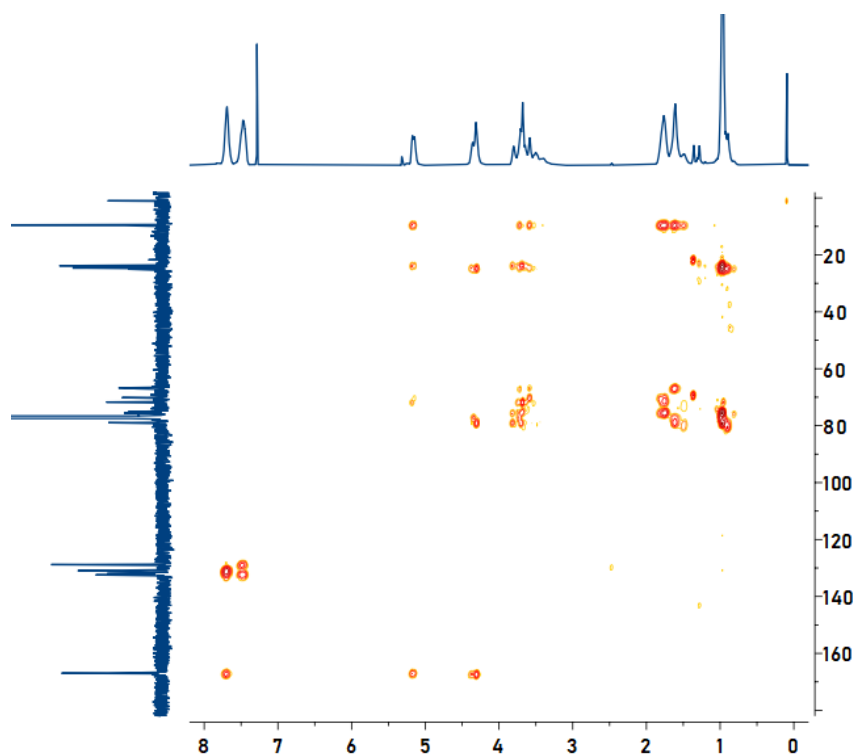


Figure S8.2.19: (^1H , ^{13}C)-HMBC NMR spectrum from the reaction of **P4**, from Table 2.1.

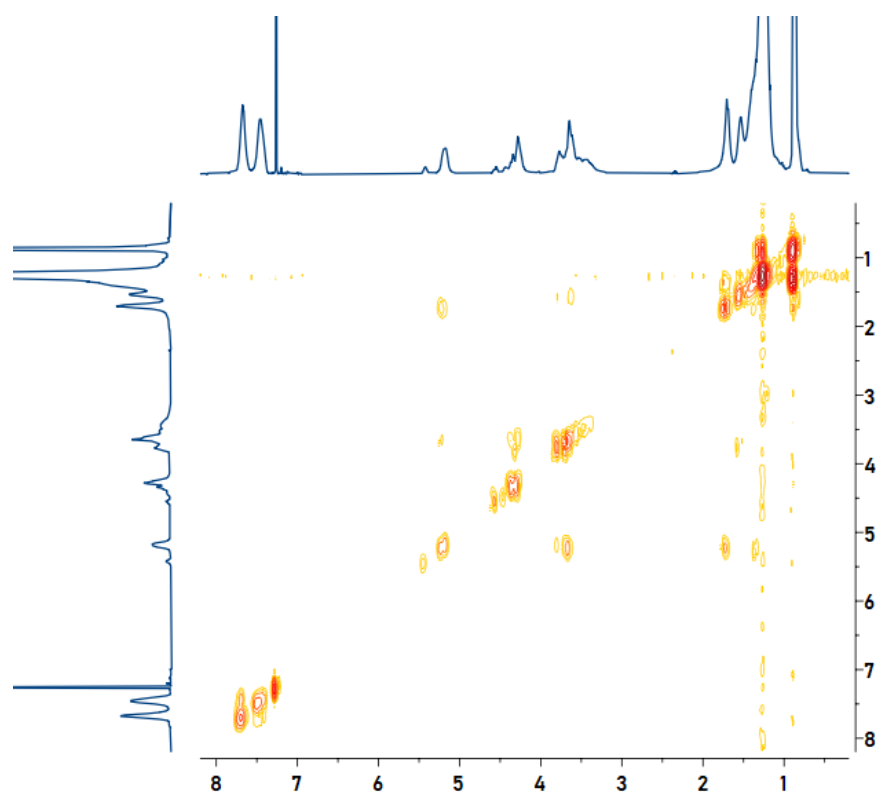


Figure S8.2.22: ^1H COSY NMR spectrum from the reaction of **[1]**:**[PA]**:**[EDD]** = 1: 50: 643, Table 2.1, **P5** (400 MHz, CDCl_3).

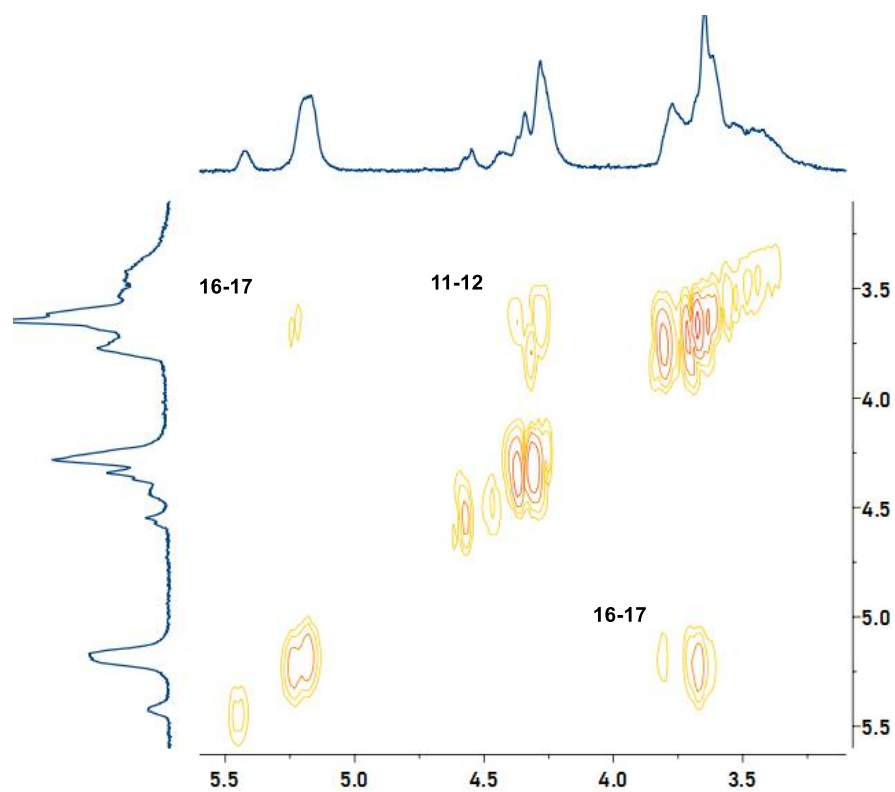


Figure S8.2.23: ^1H COSY NMR spectrum from the reaction of **[1]**:**[PA]**:**[EDD]** = 1: 50: 643, Table 2.1, **P5** (400 MHz, CDCl_3).

8.2.1.1.10 NMR Spectra for P6

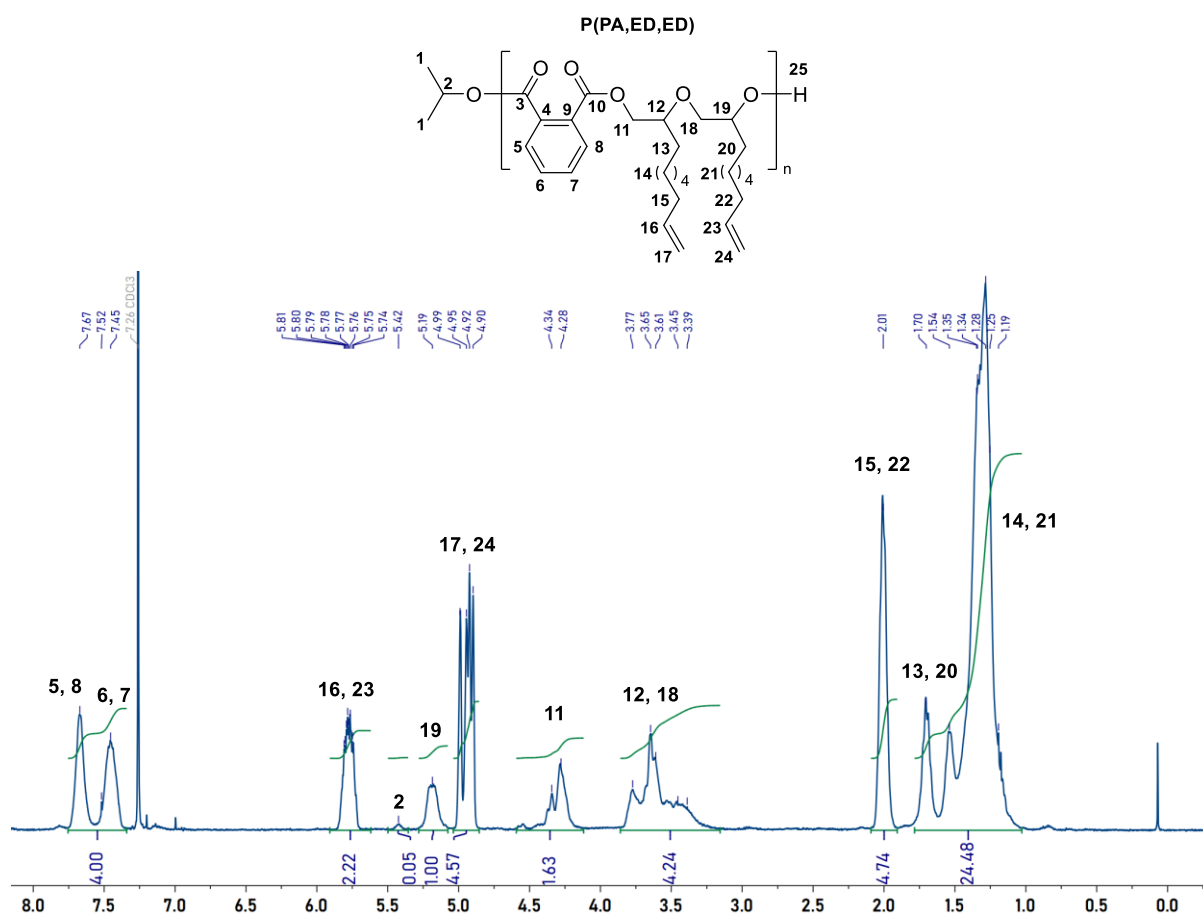


Figure S8.2.24: ^1H NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{ED}] = 1: 50: 770$, (work-up in $\text{MeOH}/\text{CH}_2\text{Cl}_2$). Spectrum corresponds to Table 2.1, **P6** (400 MHz, CDCl_3).

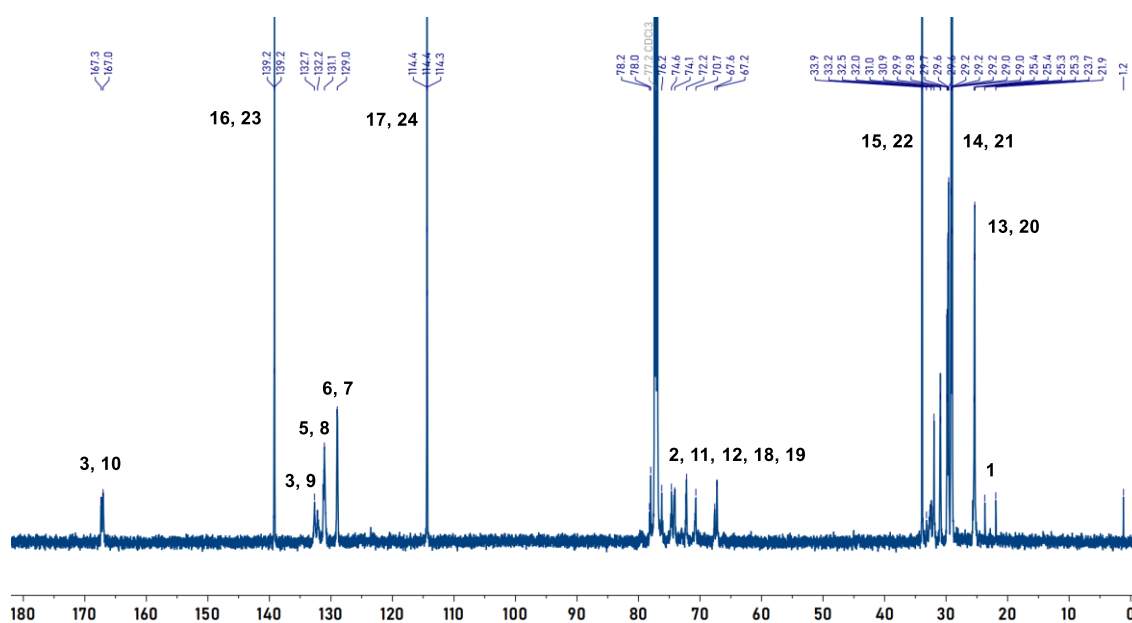


Figure S8.2.25: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{ED}] = 1: 50: 770$, Table 2.1, **P6** (151 MHz, CDCl_3).

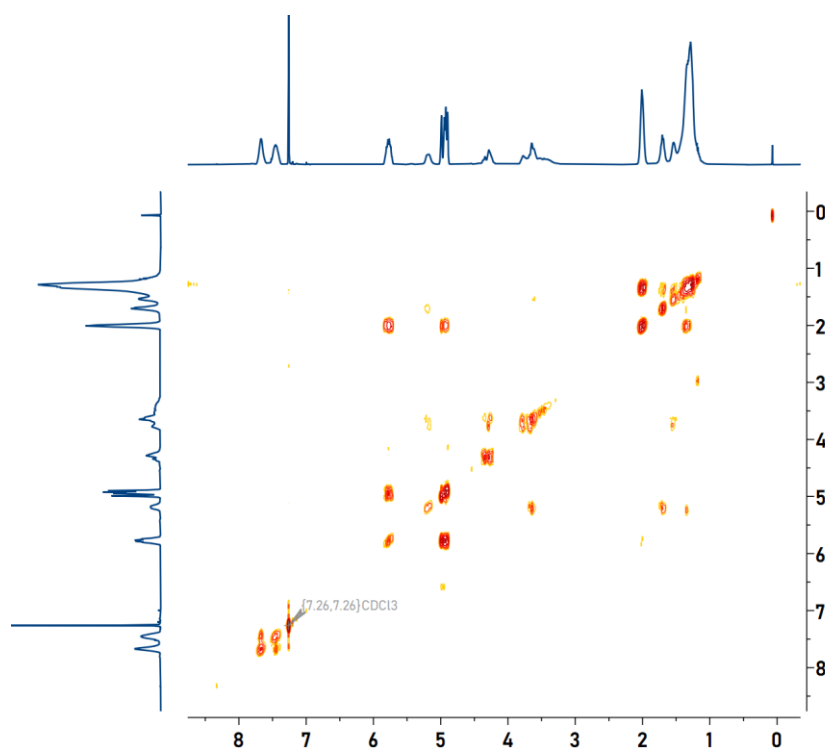


Figure S8.2.26: ^1H COSY NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{ED}] = 1: 50: 770$, Table 2.1, **P6** (400 MHz, CDCl_3).

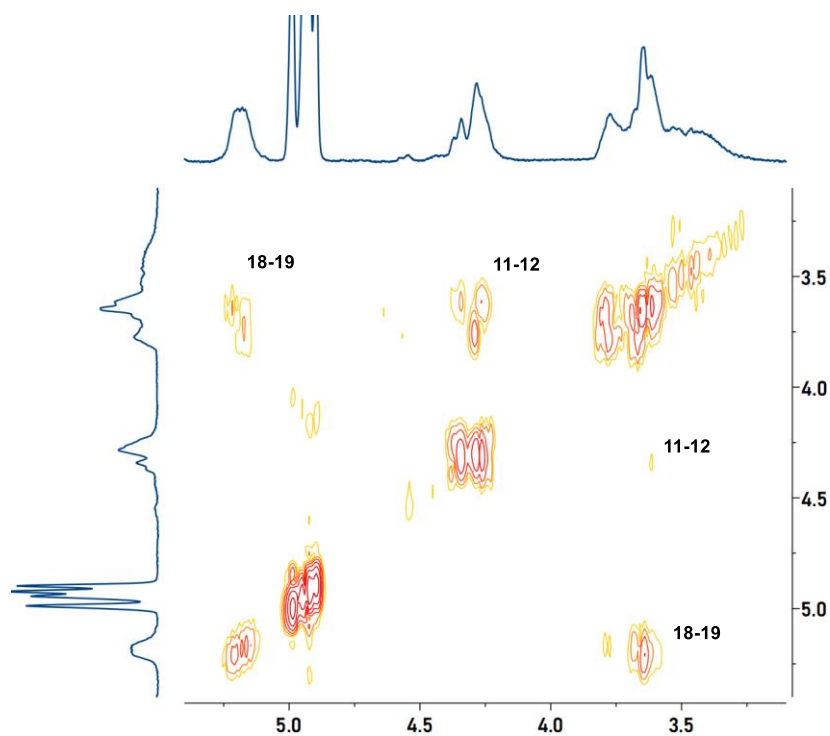


Figure S8.2.27: Magnified ^1H COSY NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{ED}] = 1: 50: 770$, Table 2.1, **P6** (400 MHz, CDCl_3).

8.2.1.1.11 NMR Spectra for P7

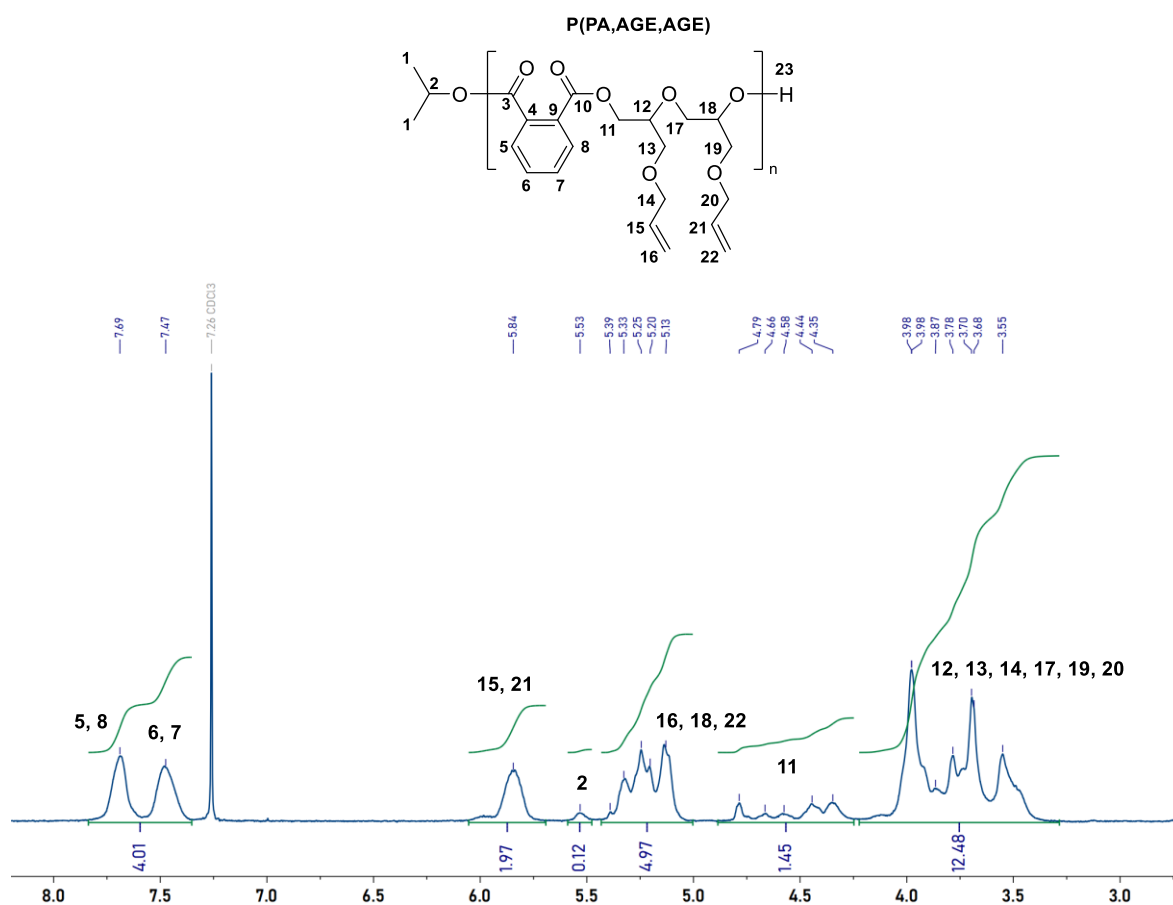


Figure S8.2.28: ^1H NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{AGE}] = 1: 50: 911$, (work-up in MeOH/ CH_2Cl_2). Spectrum corresponds to Table 2.1, **P7** (400 MHz, CDCl_3).

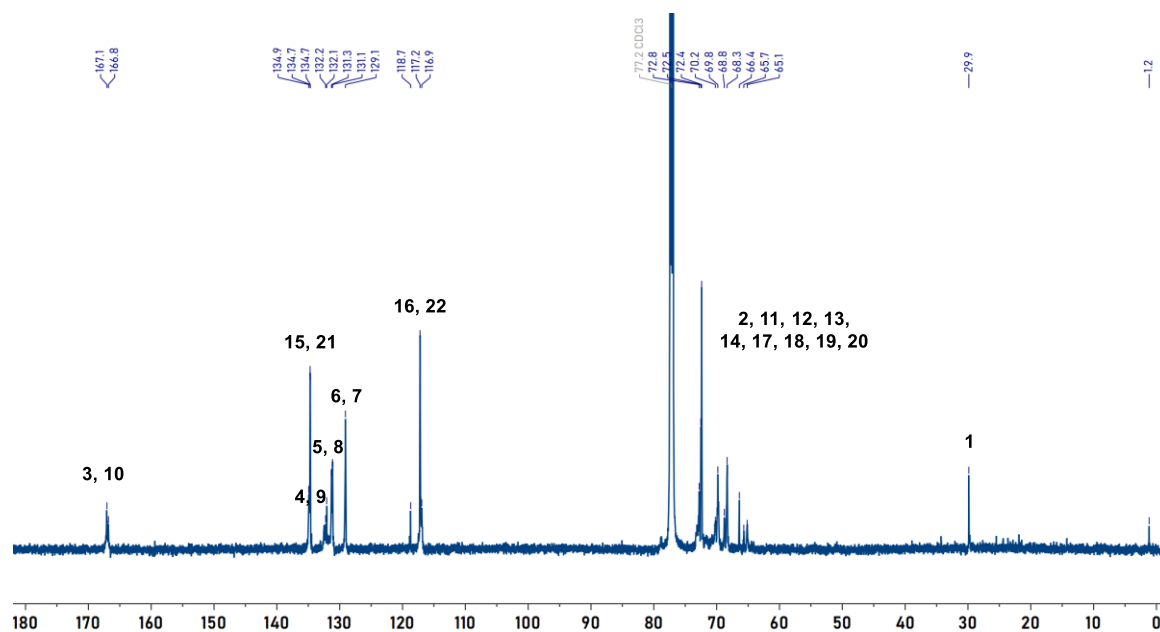


Figure S8.2.29: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{AGE}] = 1: 50: 911$, Table 2.1, **P7** (151 MHz, CDCl_3).

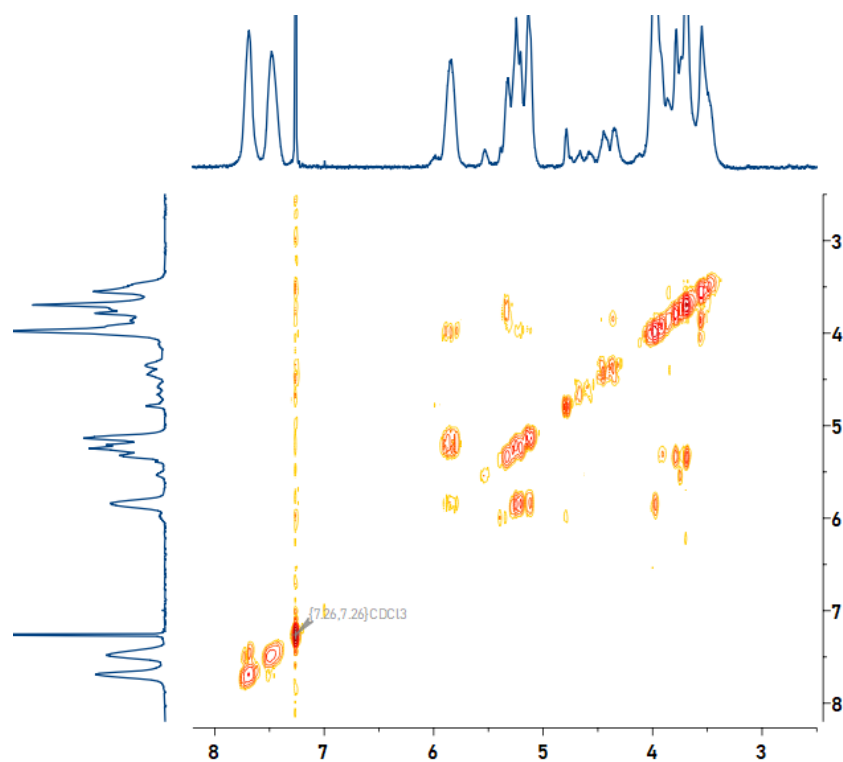


Figure S8.2.30: ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{PA}]:[\text{AGE}] = 1: 50: 911$, Table 2.1, **P7** (400 MHz, CDCl_3).

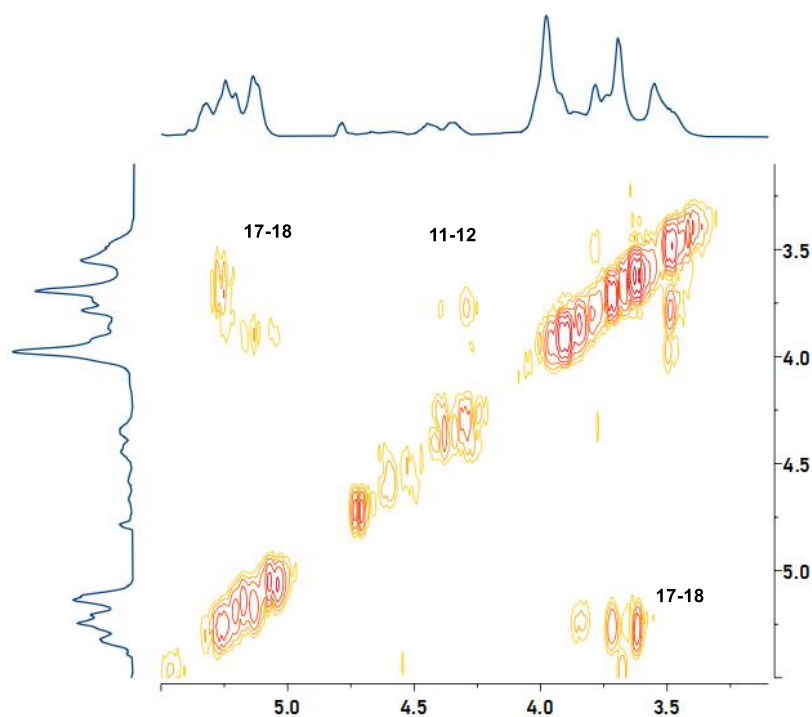


Figure S8.2.31: Magnified ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{PA}]:[\text{AGE}] = 1: 50: 911$, Table 2.1, **P7** (400 MHz, CDCl_3).

8.2.1.1.12 NMR Spectra for P8

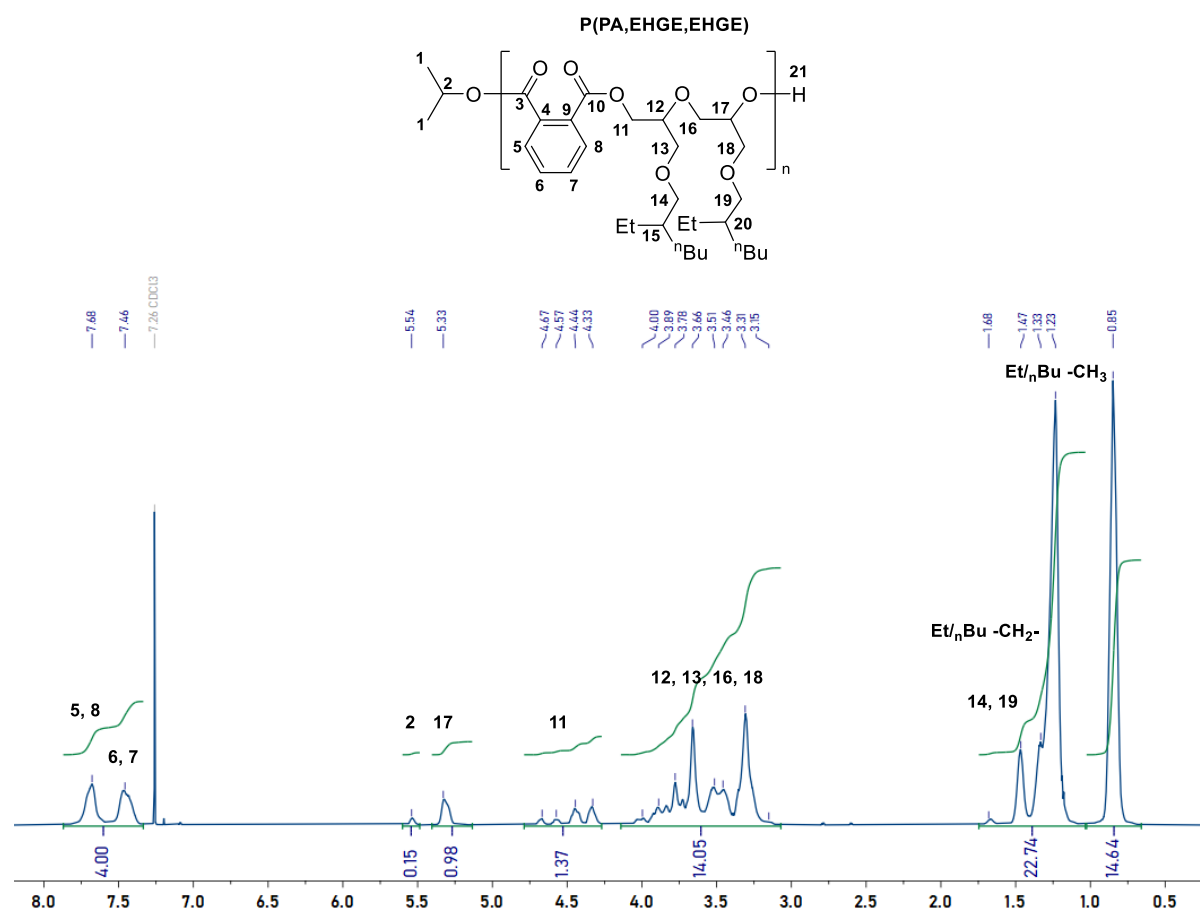


Figure S8.2.32: ¹H NMR spectrum from the reaction of [1]:[PA]:[EHGE] = 1: 50: 602, (work-up in MeOH/CH₂Cl₂). Spectrum corresponds to Table 2.1, **P8** (400 MHz, CDCl₃).

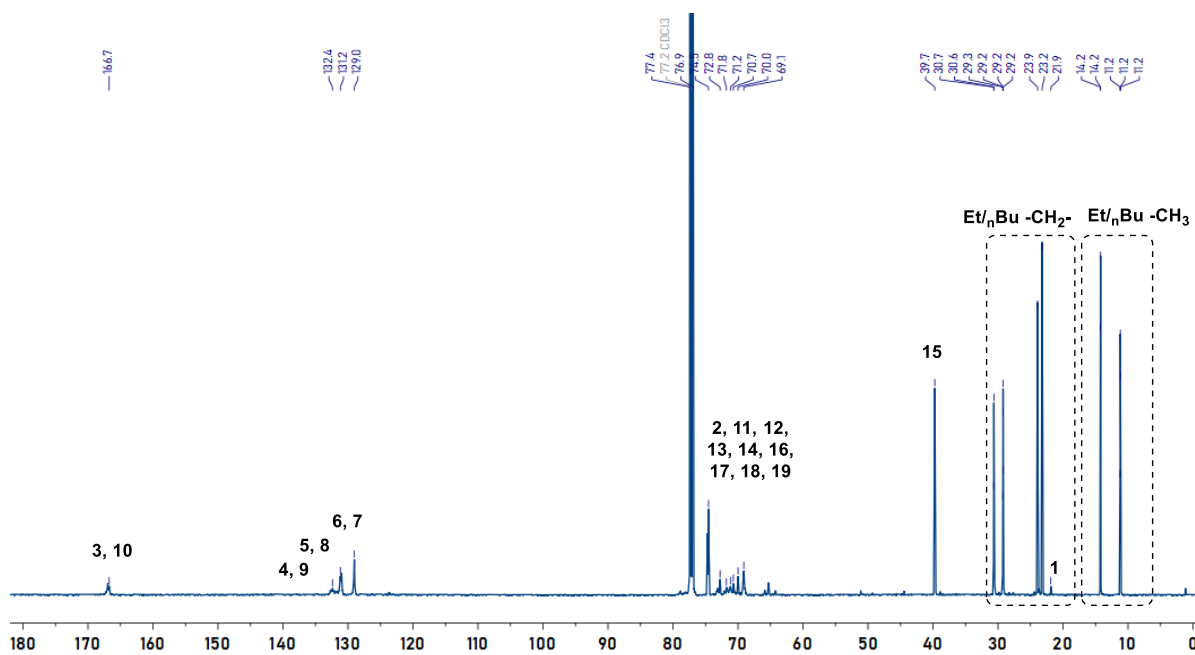


Figure S8.2.33: ¹³C{¹H} NMR spectrum from the reaction of [1]:[PA]:[EHGE] = 1: 50: 602, Table 2.1, **P8** (151 MHz, CDCl₃).

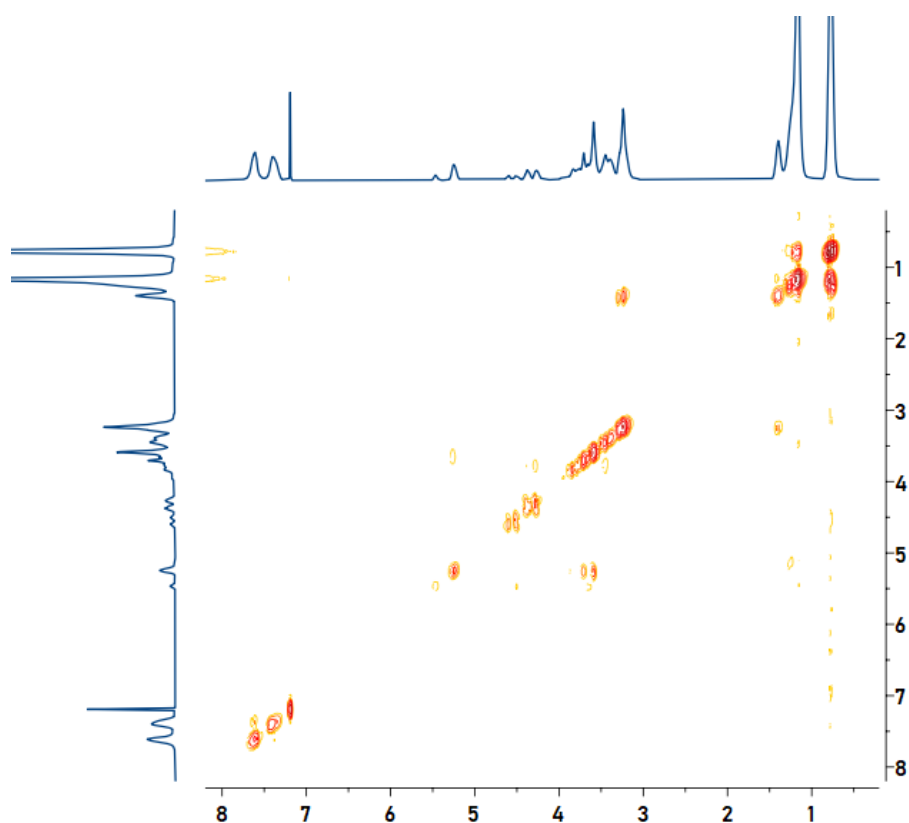


Figure S8.2.34: ^1H COSY NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{EHGE}] = 1: 50: 602$, Table 2.1, **P8** (400 MHz, CDCl_3).

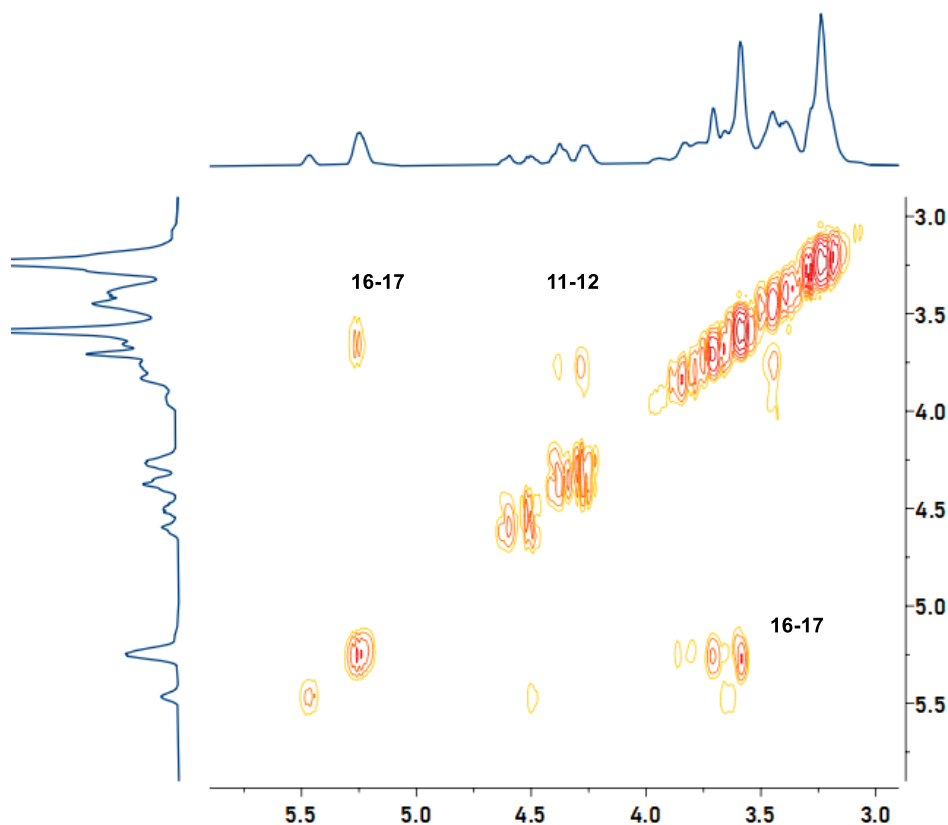


Figure S8.2.35: Magnified ^1H COSY NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{EHGE}] = 1: 50: 602$, Table 2.1, **P8** (400 MHz, CDCl_3).

8.2.1.1.13 NMR Spectra for P9

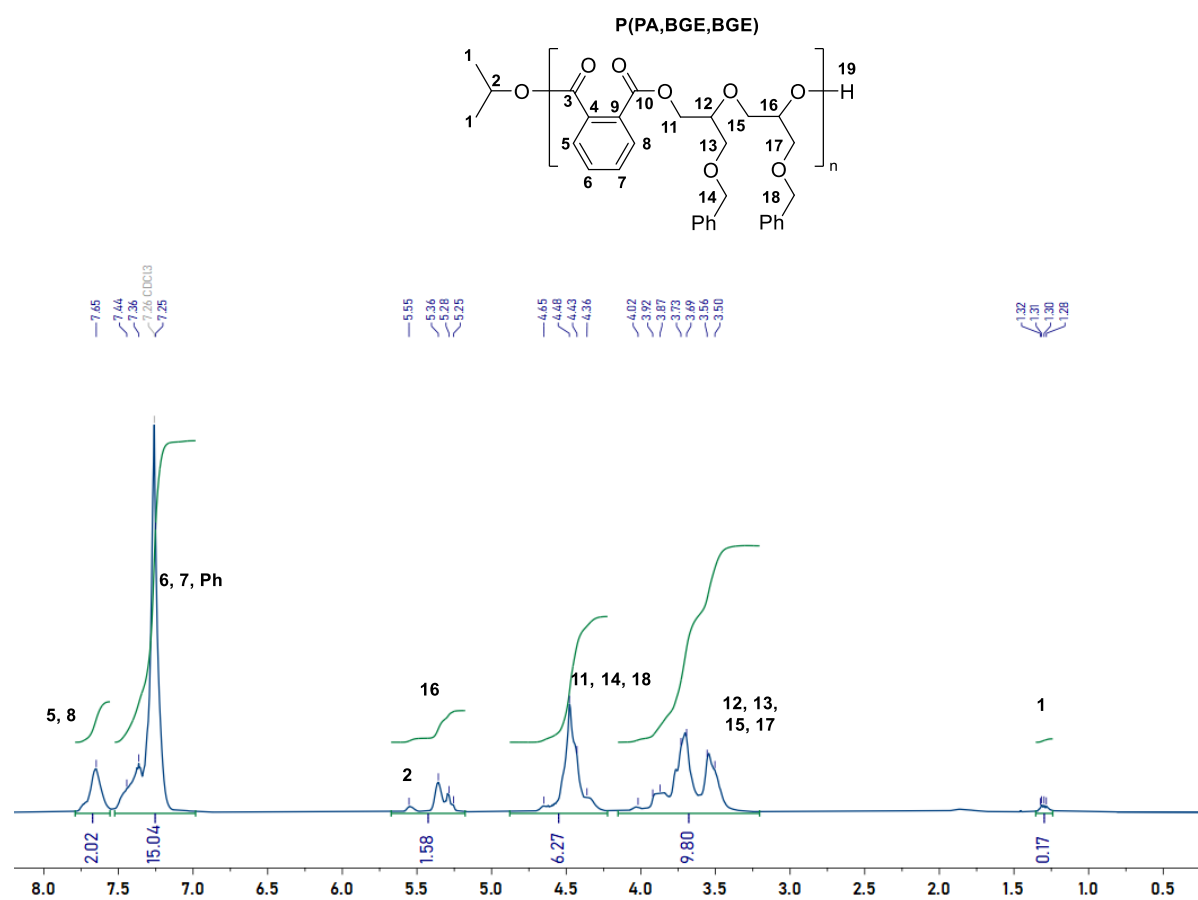


Figure S8.2.36: ¹H NMR spectrum from the reaction of [1]:[PA]:[BGE] = 1: 50: 565, (work-up in MeOH/CH₂Cl₂). Spectrum corresponds to Table 2.1, **P9** (400 MHz, CDCl₃).

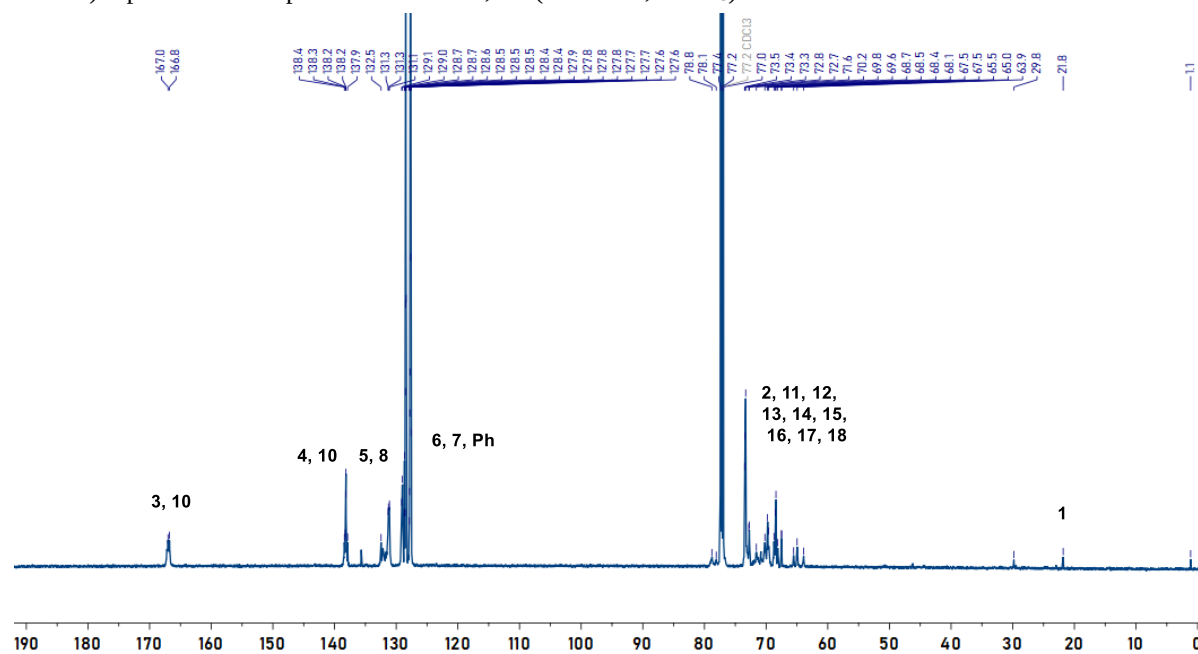


Figure S8.2.37: ¹³C{¹H} NMR spectrum from the reaction of [1]:[PA]:[BGE] = 1: 50: 565, Table 2.1, **P9** (151 MHz, CDCl₃).

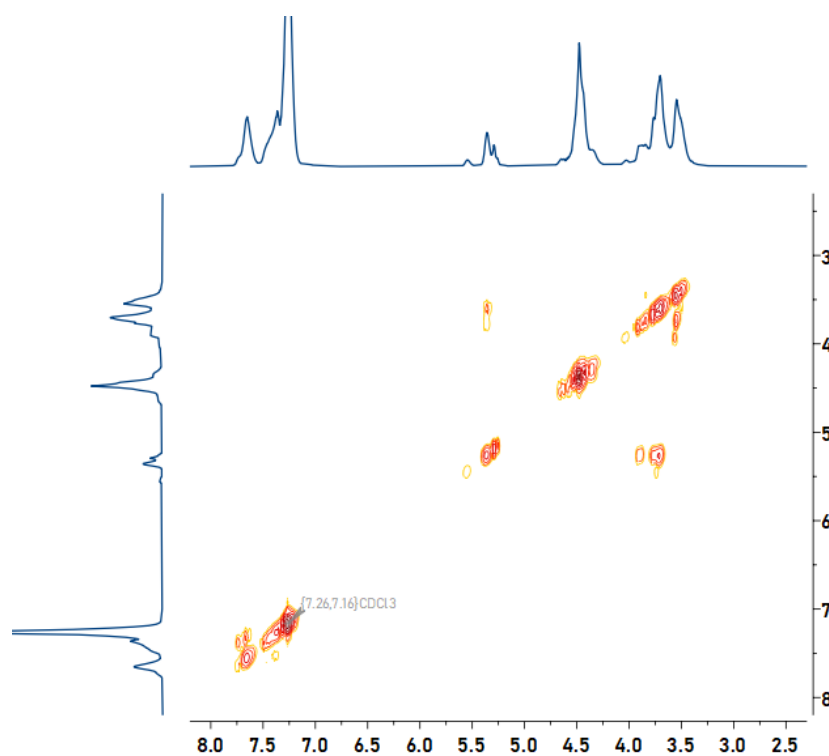


Figure S8.2.38: ^1H COSY NMR spectrum from the reaction of **[1]**:**[PA]**:**[BGE]** = 1: 50: 565, Table 2.1, **P9** (400 MHz, CDCl_3).

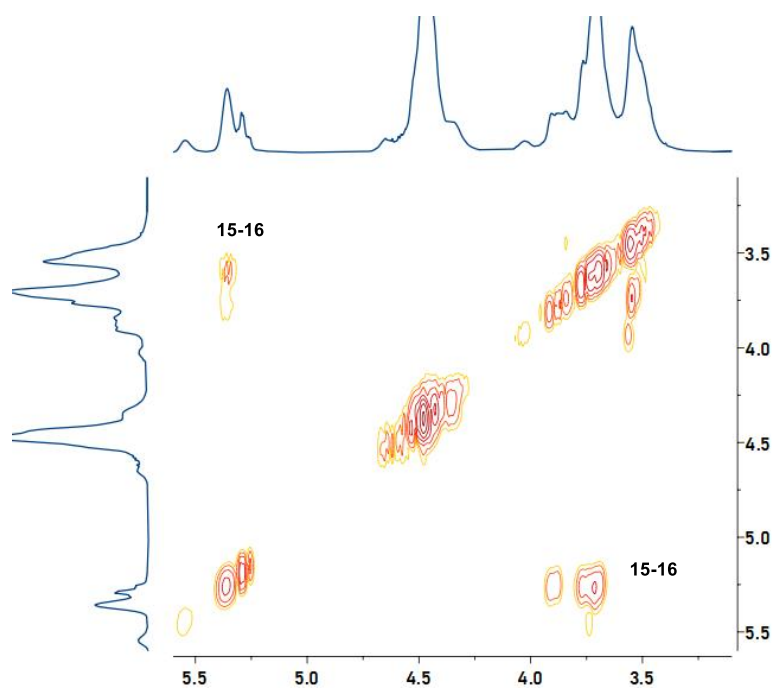


Figure S8.2.39: Magnified ^1H COSY NMR spectrum from the reaction **[1]**:**[PA]**:**[BGE]** = 1: 50: 565, Table 2.1, **P9** (400 MHz, CDCl_3).

8.2.1.1.14 NMR Spectra for P10

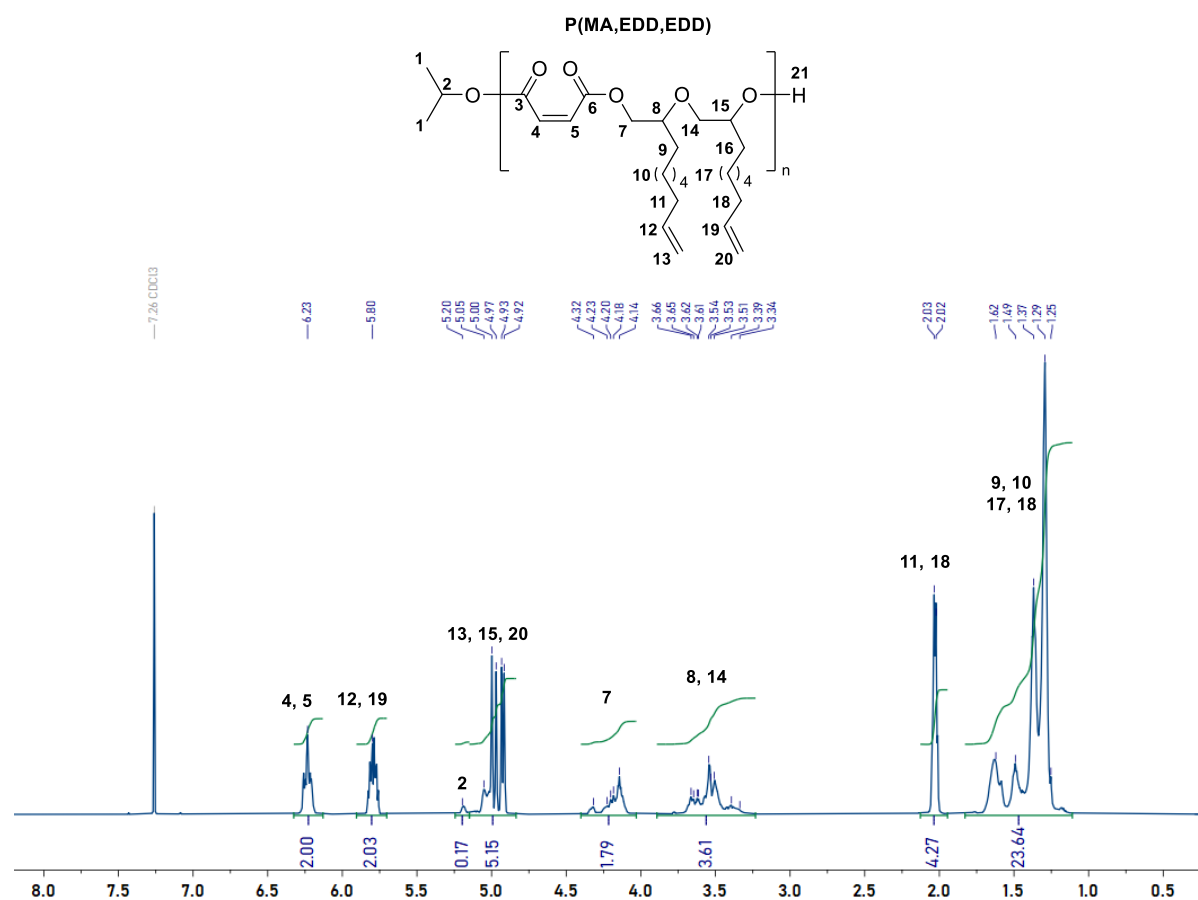


Figure S8.2.40: ^1H NMR spectrum from the reaction of $[1]:[\text{MA}]:[\text{ED}] = 1: 50: 770$, (work-up in $\text{MeOH}/\text{CH}_2\text{Cl}_2$). Spectrum corresponds to Table 2.1, **P10** (400 MHz, CDCl_3).

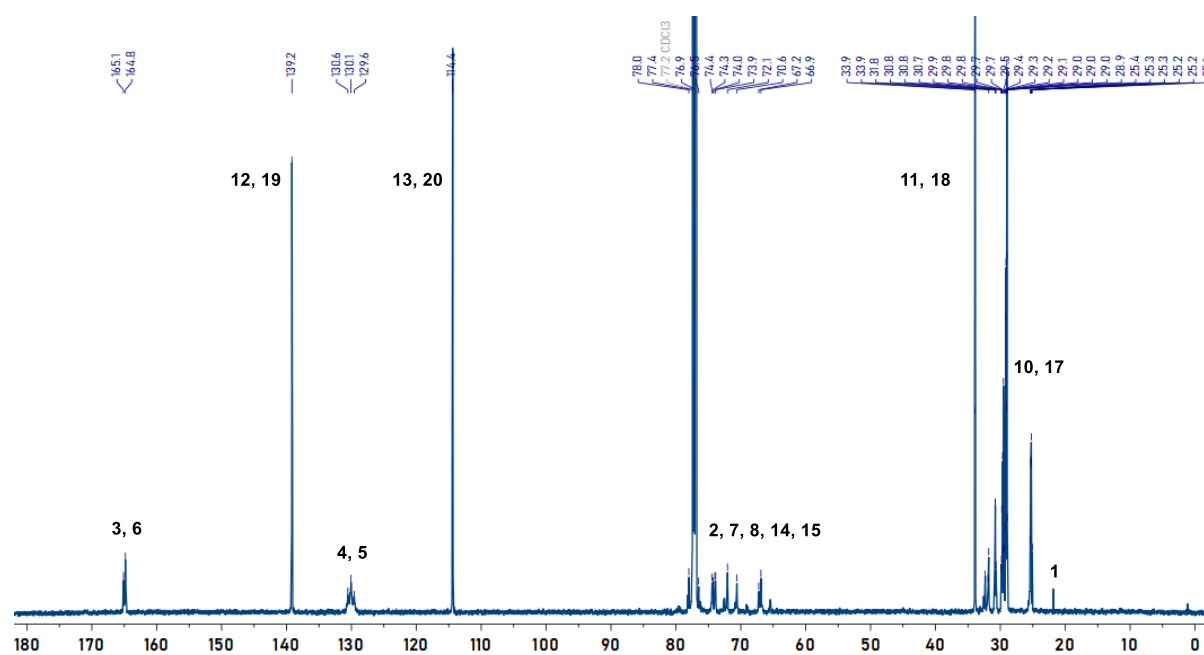


Figure S8.2.41: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of $[1]:[\text{MA}]:[\text{ED}] = 1: 50: 770$, Table 2.1, **P10** (151 MHz, CDCl_3).

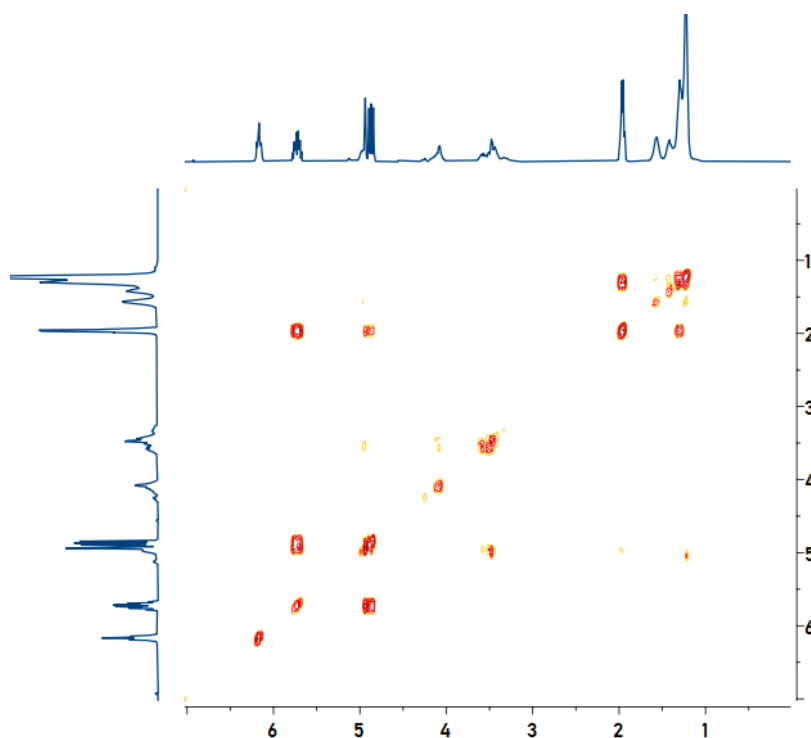


Figure S8.2.42: ^1H COSY NMR spectrum from the reaction of $[1]:[\text{MA}]:[\text{ED}] = 1: 50: 770$, Table 2.1, **P10** (400 MHz, CDCl_3).

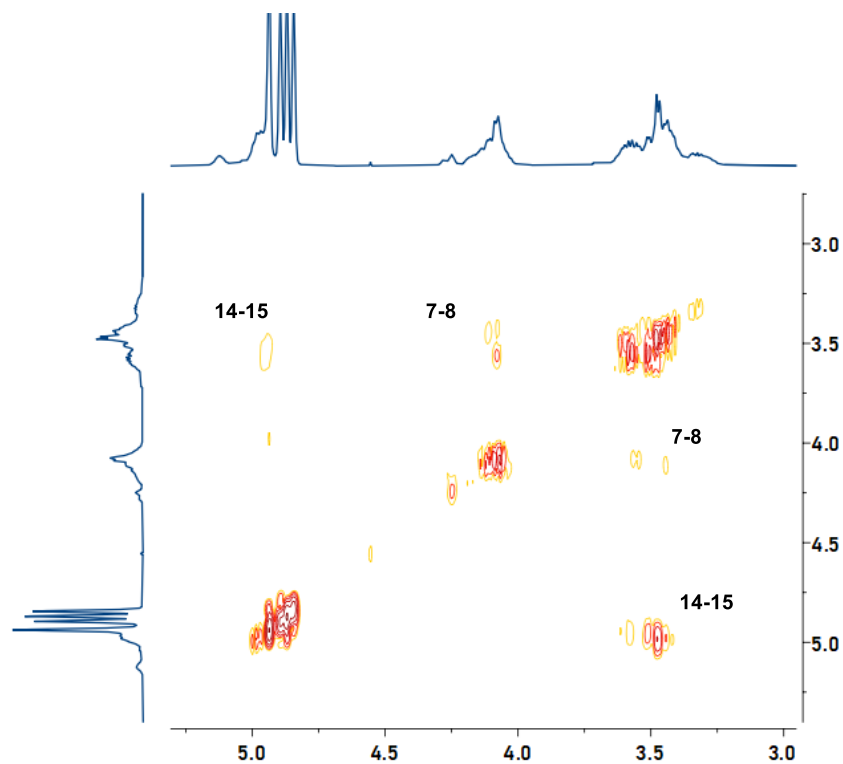


Figure S8.2.43: Magnified ^1H COSY NMR spectrum from the reaction of $[1]:[\text{MA}]:[\text{ED}] = 1: 50: 770$, Table 2.1, **P10** (400 MHz, CDCl_3).

8.2.1.2 GPC Data for Polymers Described in Table 2.1

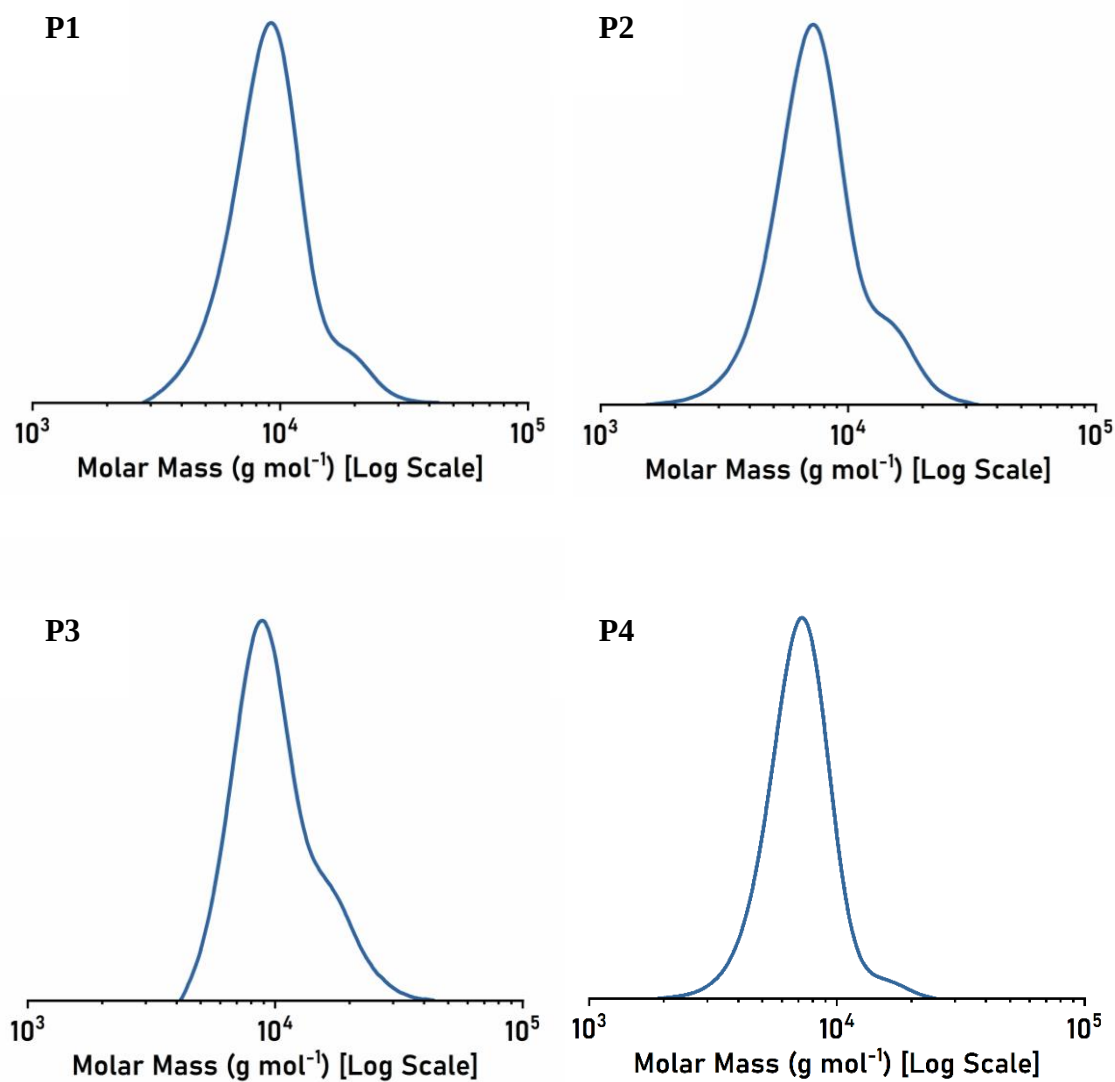


Figure S8.2.44: GPC chromatograms for polymers described in Table 2.1, **P1-4**.

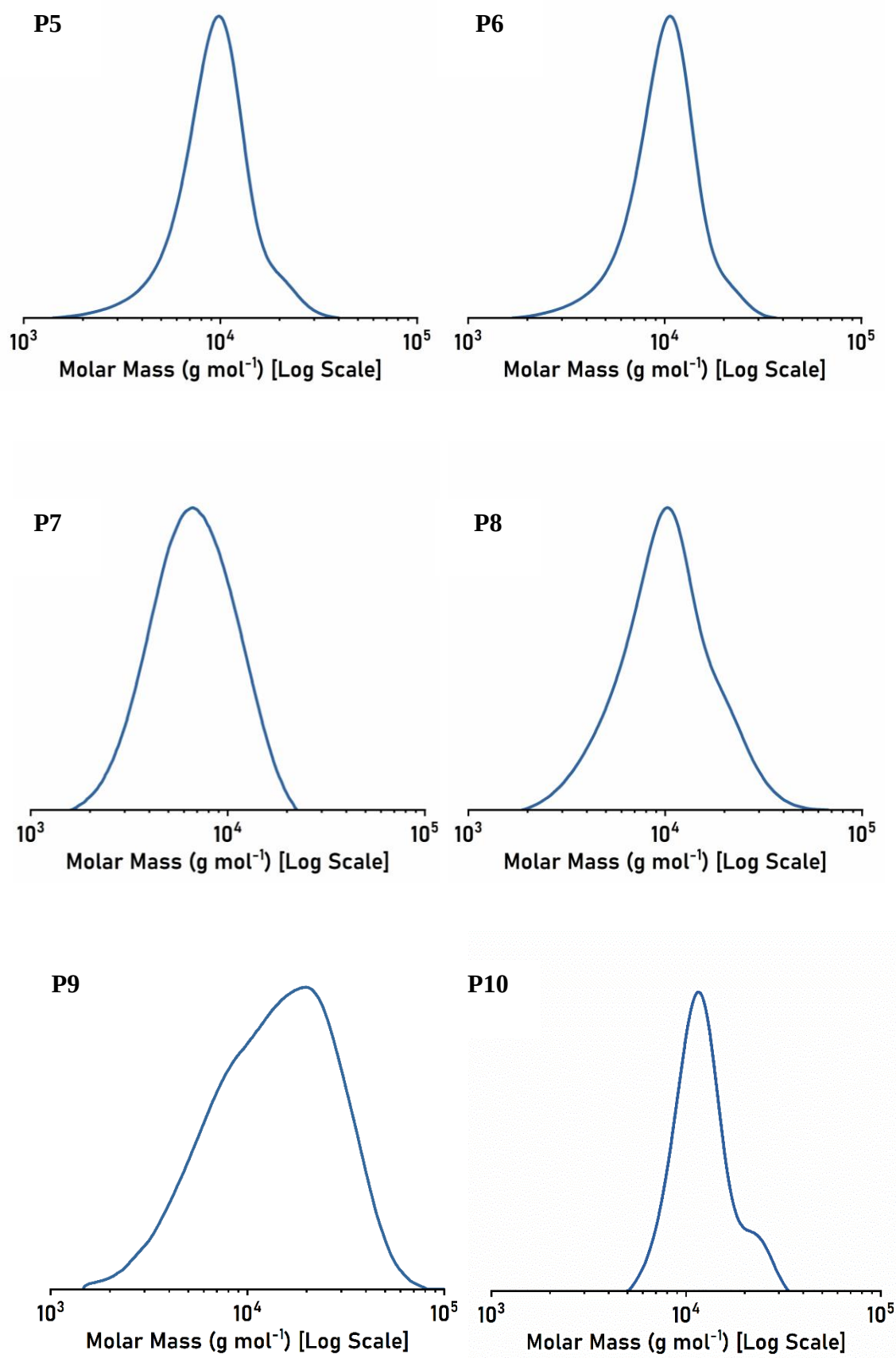


Figure S8.2.45: GPC chromatograms for polymers described in Table 2.1, **P5-10**.

8.2.1.3 Kinetic Data for Polymers Described in Table 2.1

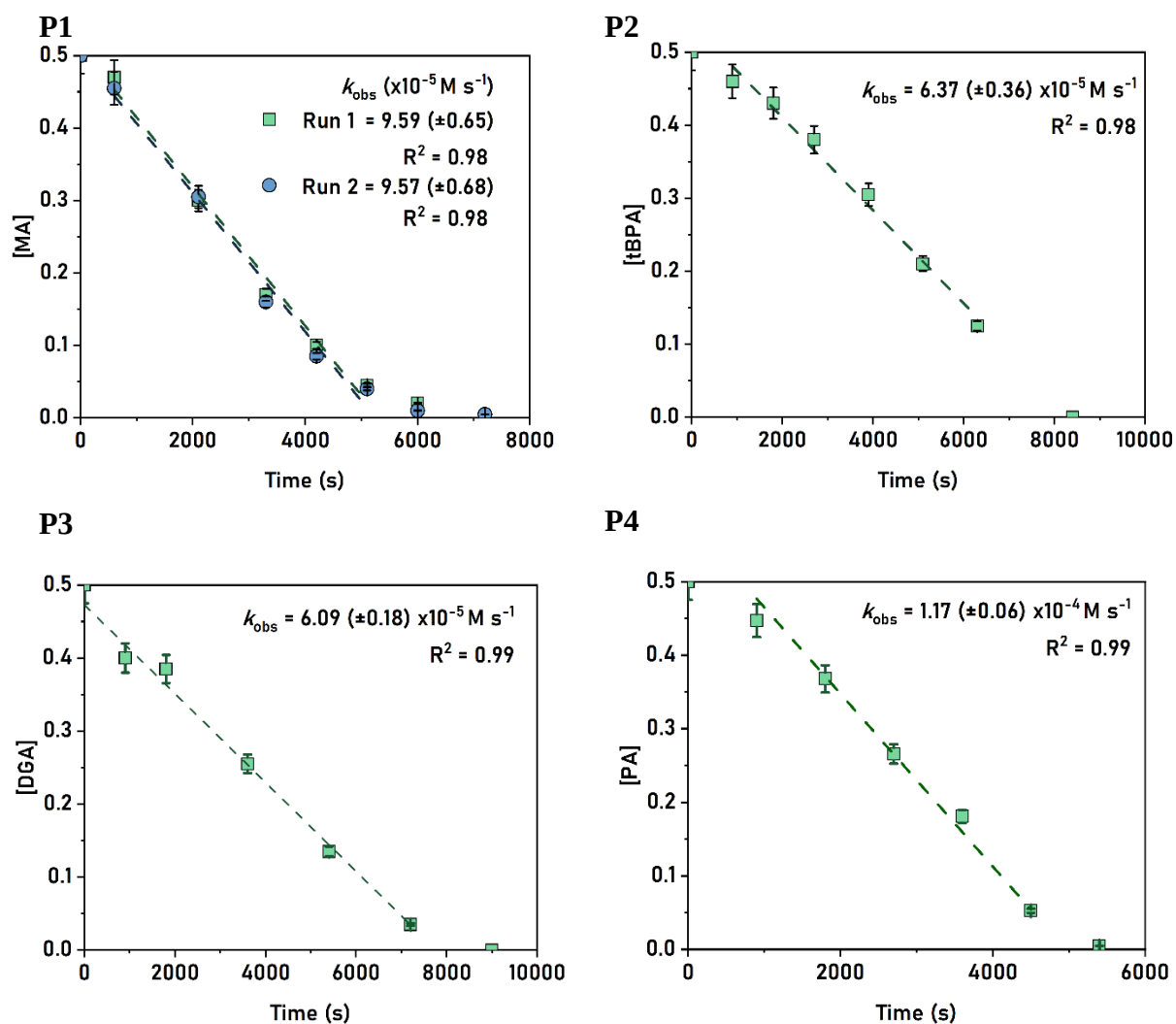


Figure S8.2.46: Plots of anhydride concentration vs. time, with linear fits to the data. The order in anhydride concentration was determined from the gradients of the linear fit. In these experiments [Anhydride] = 0.5 M. This diagram applies to the polymers described in Table 2.1, **P1-4**.

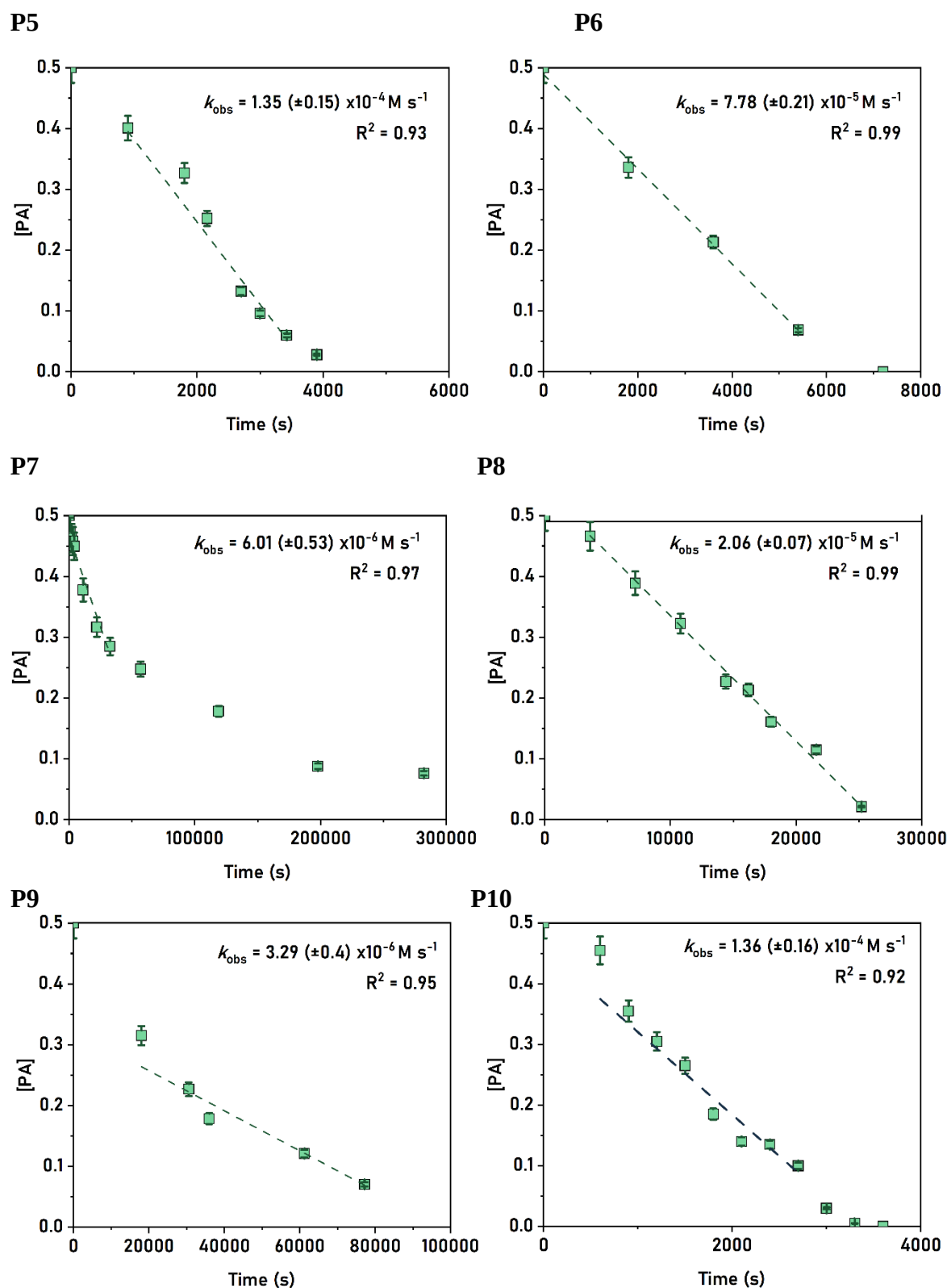


Figure S8.2.47: Plots of anhydride concentration vs. time, with linear fits to the data. The order in anhydride concentration was determined from the gradients of the linear fit. In these experiments [Anhydride] = 0.5 M. This diagram applies to the polymers described in Table 2.1, **P5-10**.

8.2.1.4 DSC Data for Polymers Described in Table 2.1

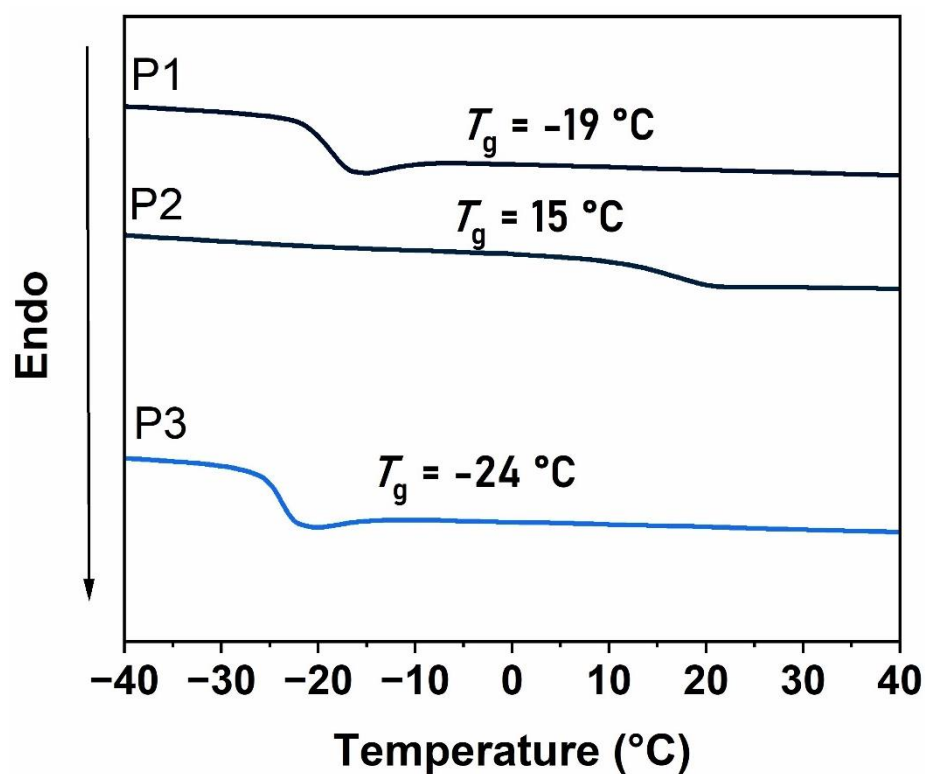


Figure S8.2.48: DSC Thermograms for Polymers P1-3.

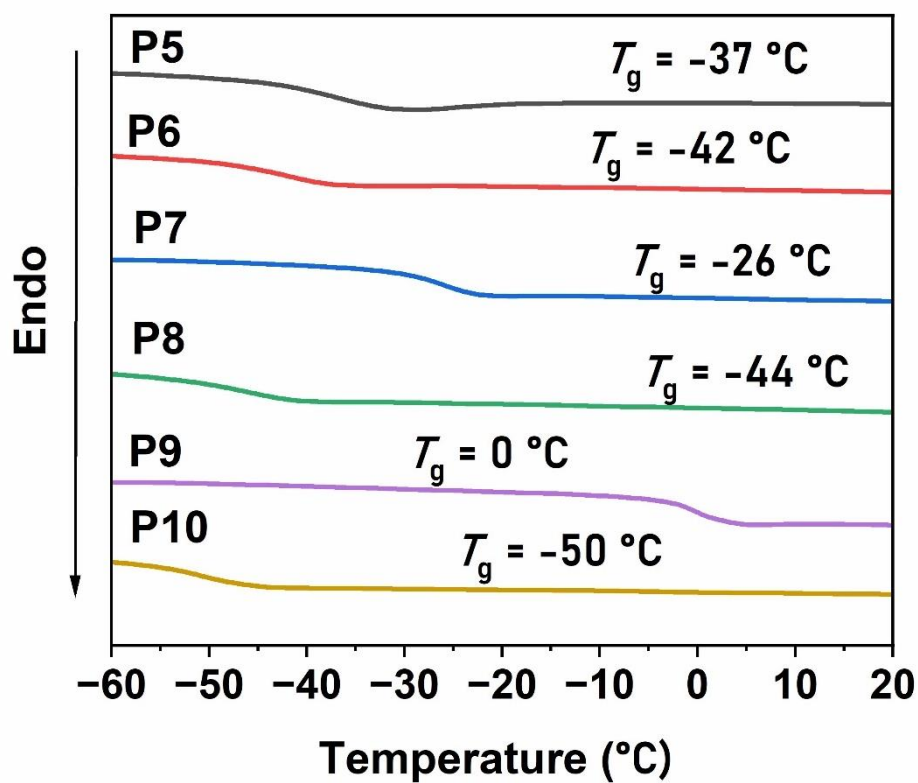


Figure S8.2.49: DSC Thermograms for Polymers P5-10.

8.2.1.5 TGA Data for Polymers Described in Table 2.1

Table S8.2.1: TGA Data for P1-10

Polymer (#)	Anhyd	Epoxide	$T_{d,5}$ (°C) ^g	$T_{d,95}$ (°C) ^g	Notes
P1	MA	BO	306	486	
P2	tBPA	BO	311	387	
P3	DGA	BO	270	362	
P4 ³	PA	BO	318	379	Ref. 3
P5	PA	EDD	317	390	
P6	PA	ED	308	485	
P7	PA	AGE	294	>600	6% Mass remaining at 600 °C
P8	PA	EHGE	310	396	
P9	PA	BGE	283	450	
P10	MA	ED	344	576	

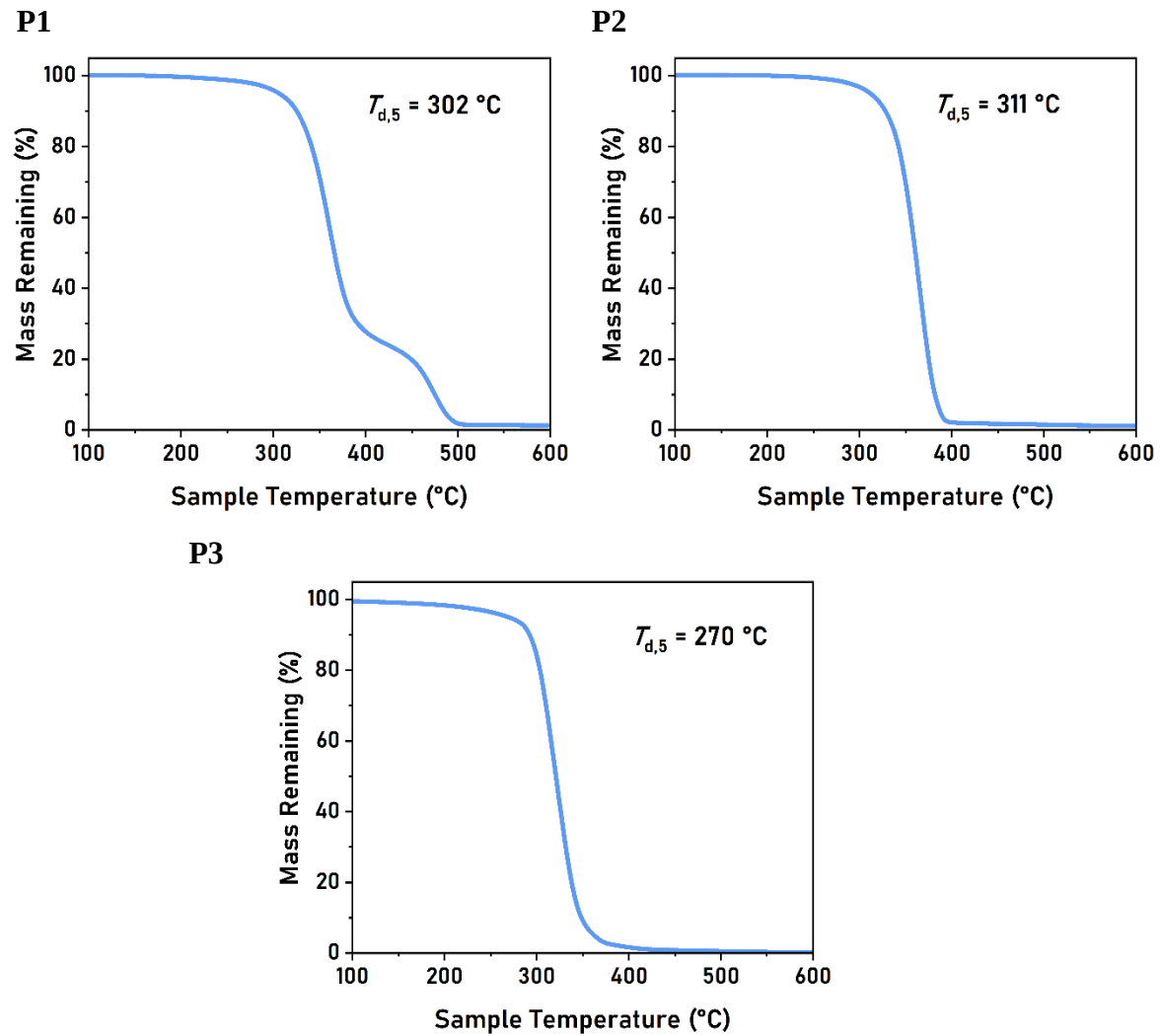
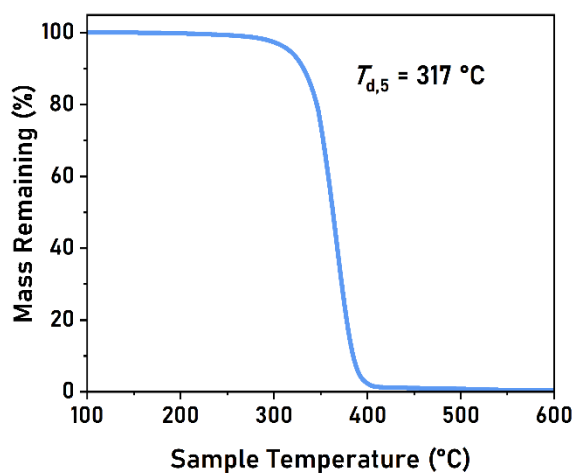
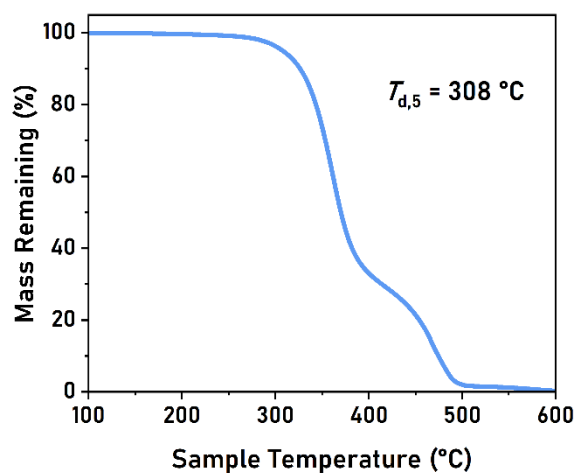
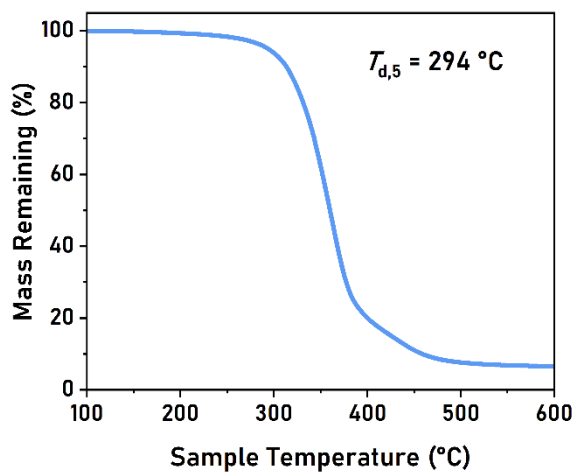
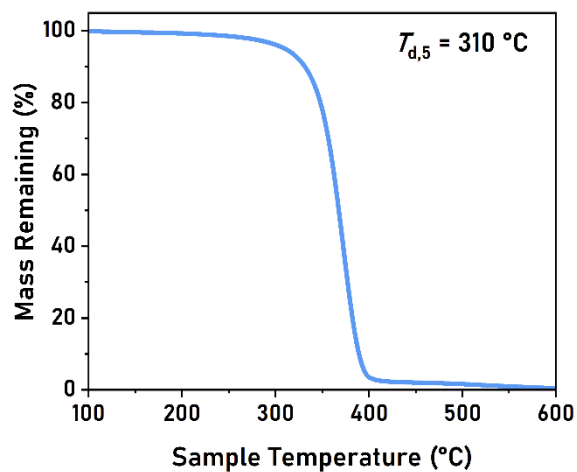
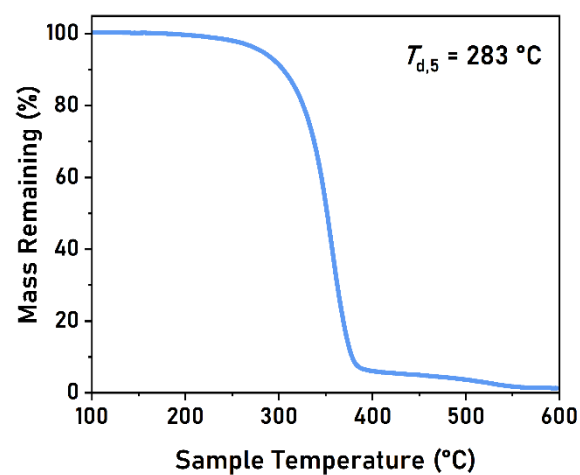
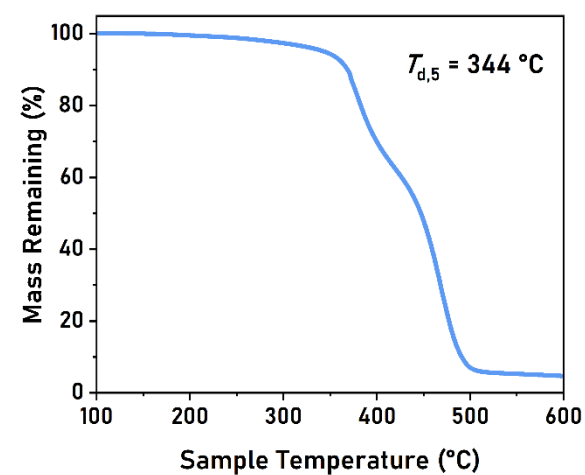


Figure S8.2.50: TGA data for P1-3.

P5**P6****P7****P8****P9****P10****Figure S8.2.51:** TGA data for **P5-10**.

8.2.2 Data for P1'

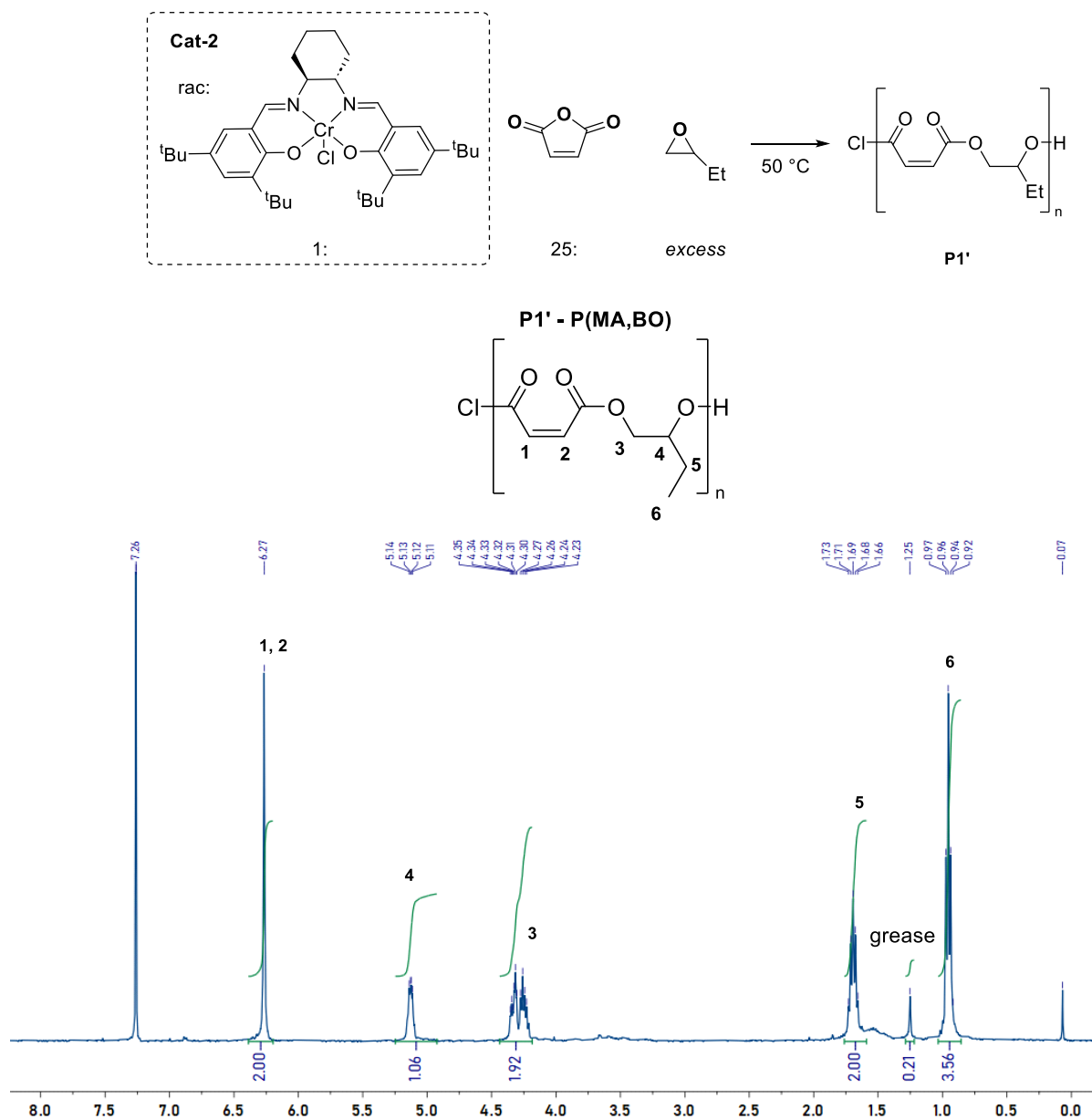


Figure S8.2.52: ^1H NMR spectrum from the reaction of $[2]:[\text{MA}]:[\text{BO}] = 1: 25: 1150$, (work up $\text{MeOH}/\text{CH}_2\text{Cl}_2$). Spectrum corresponds to Table 2.1, **P1'** (400 MHz, CDCl_3).

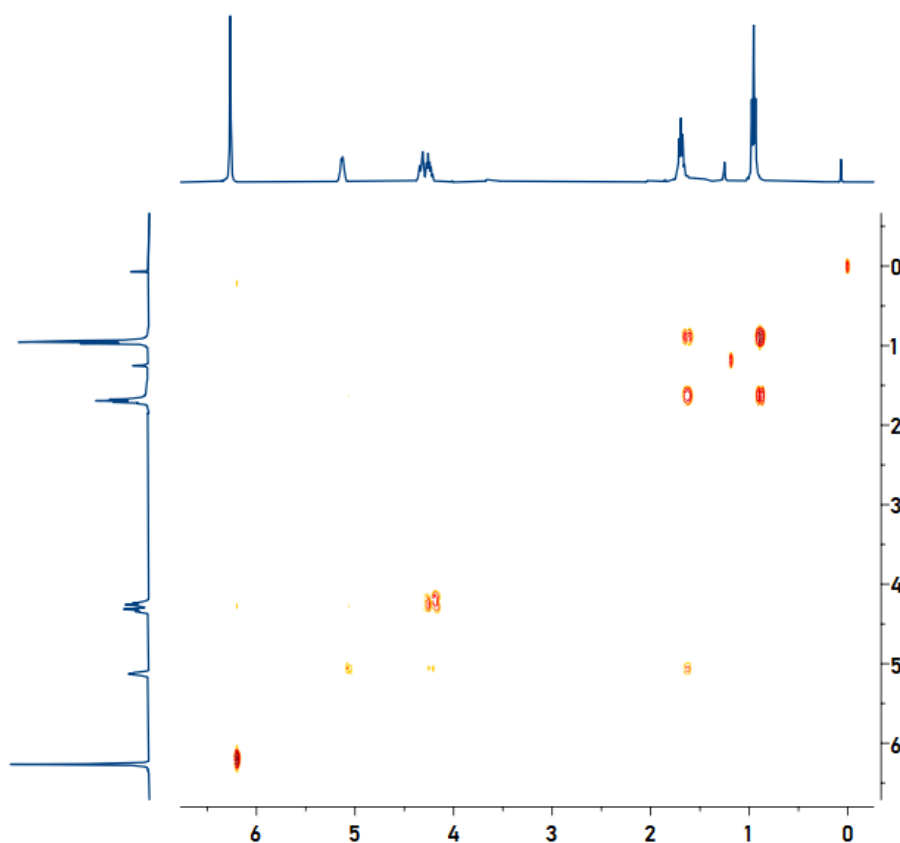


Figure S8.2.53: ¹H COSY NMR spectrum from the reaction of [2]:[MA]:[BO] = 1: 25: 1150, Table 2.1, **P1'** (400 MHz, CDCl₃).

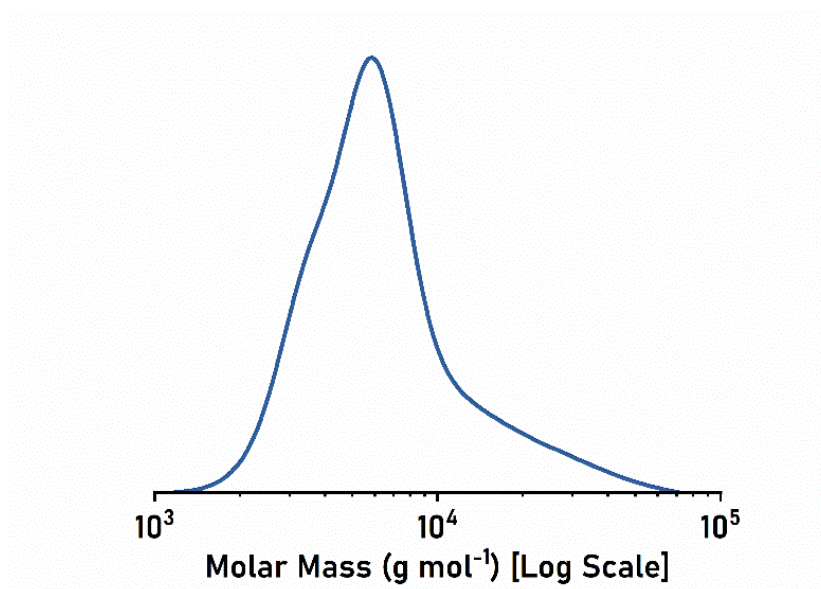


Figure S8.2.54: GPC chromatogram for **P1'**.

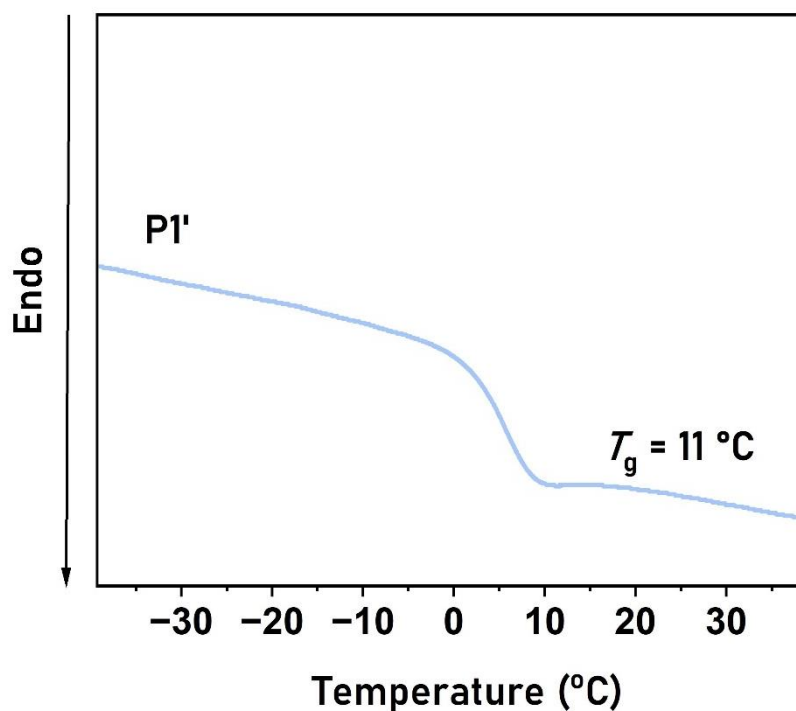
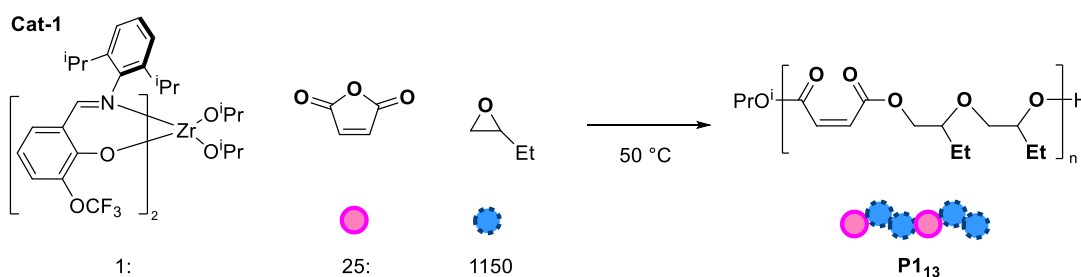


Figure S8.2.55: DSC Thermograms for Polymers **P1'**.

8.2.3 MALDI-ToF Data for **P1₁₃**

Synthesis of **P1₁₃**



Scheme S8.2.2: Synthesis of **P1₁₃** from **1**, MA and BO.

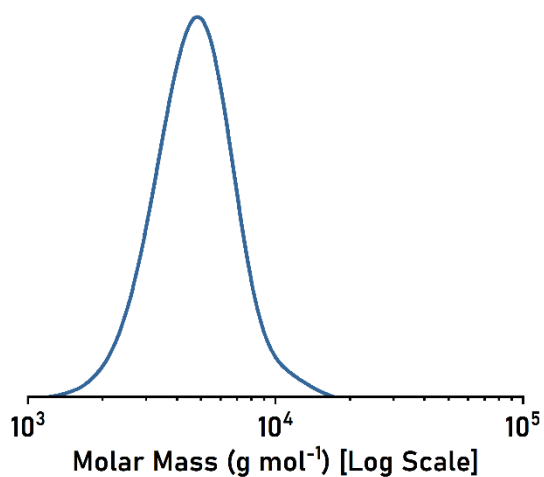


Figure S8.2.56: GPC chromatogram for polymers described in Scheme S8.2.2, **P1₁₃**.

Table S8.2.2: Selected assignments of analytes observed from the MALDI-ToF spectrum of **P1₁₃**.

DP of anhydride (n)	m = 0	m = 1	m = 2	m = 3	m = 4
8	2035.74	2107.768	2179.797	2251.834	2323.862
9	2277.768	2349.807	2423.9383	2493.899	2565.955
10	2519.839	2591.898	2663.944	2736.004	2808.067
11	2761.925	2834.012	2906.072	2978.128	3050.191
12	3004.071	3076.133	3148.195	3220.247	3292.293
13	3246.187	3318.243	3390.291	3462.336	3534.376
14	3488.274	3560.31	3632.342	3704.362	3776.382

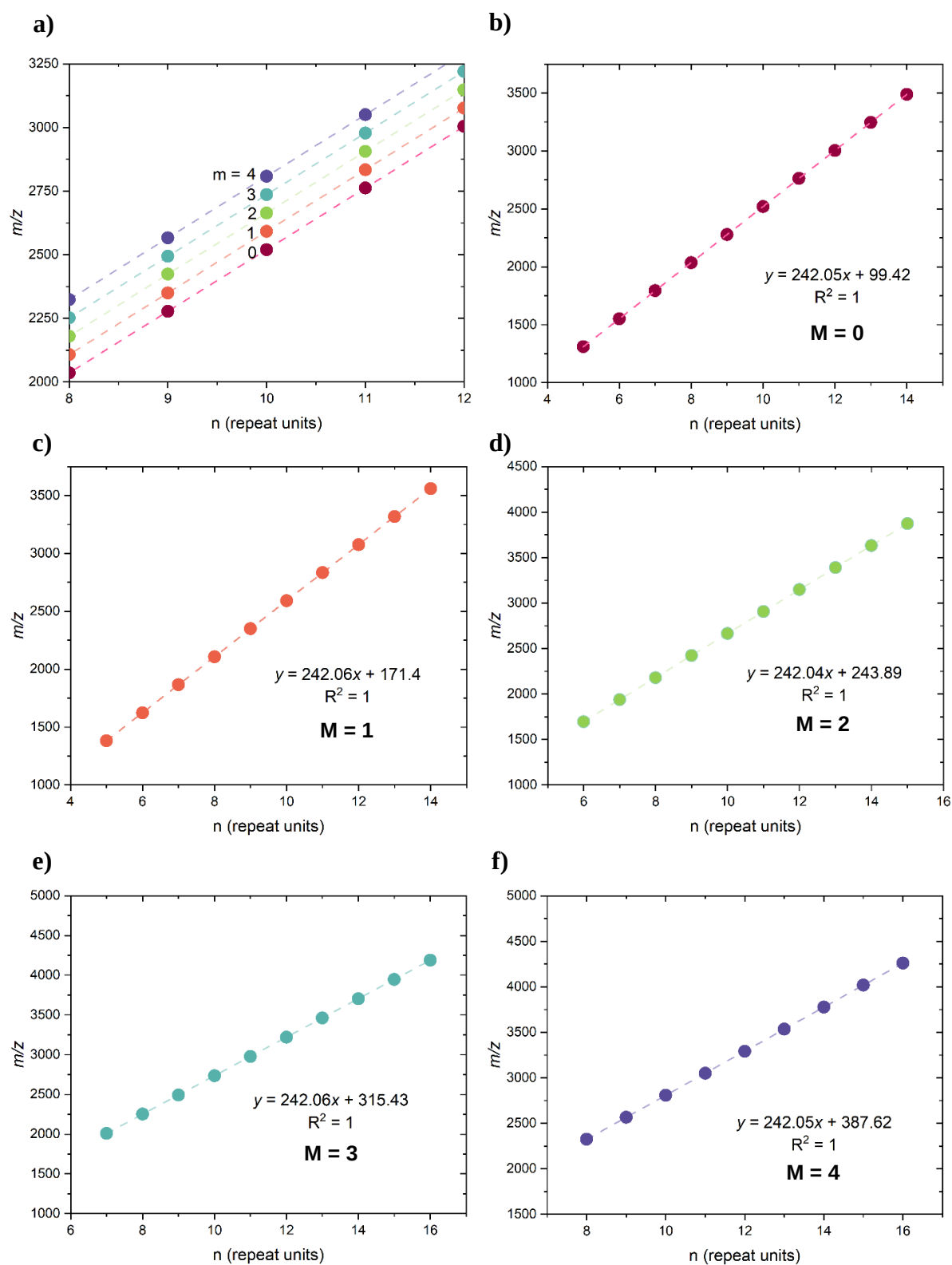


Figure S8.2.57: Plots of m/z values vs the number of MA-BO-BO repeat units (n) from the MALDI-TOF spectrum, in Figure 2.4, separated by the number of additional BO units (m), where end groups = ${}^i\text{PrOH} + \text{K}^+ = 99.19 \text{ g mol}^{-1}$, $n = 242.12 \text{ g mol}^{-1}$ and $m = 72.11 \text{ g mol}^{-1}$. a) Zoomed overlay of each m/z distribution of m ; Plot of m/z values of MA-BO-BO repeats where b) $m = 0$, c) $m = 1$, d) $m = 2$, e) $m = 3$ and f) $m = 4$.

8.2.4 Characterization Data for Polymers Described in Scheme 2.2 – Cyclic Ethers

8.2.4.1 NMR Spectra for Polymers Described in Scheme 2.2

8.2.4.1.1 NMR Spectra for P11

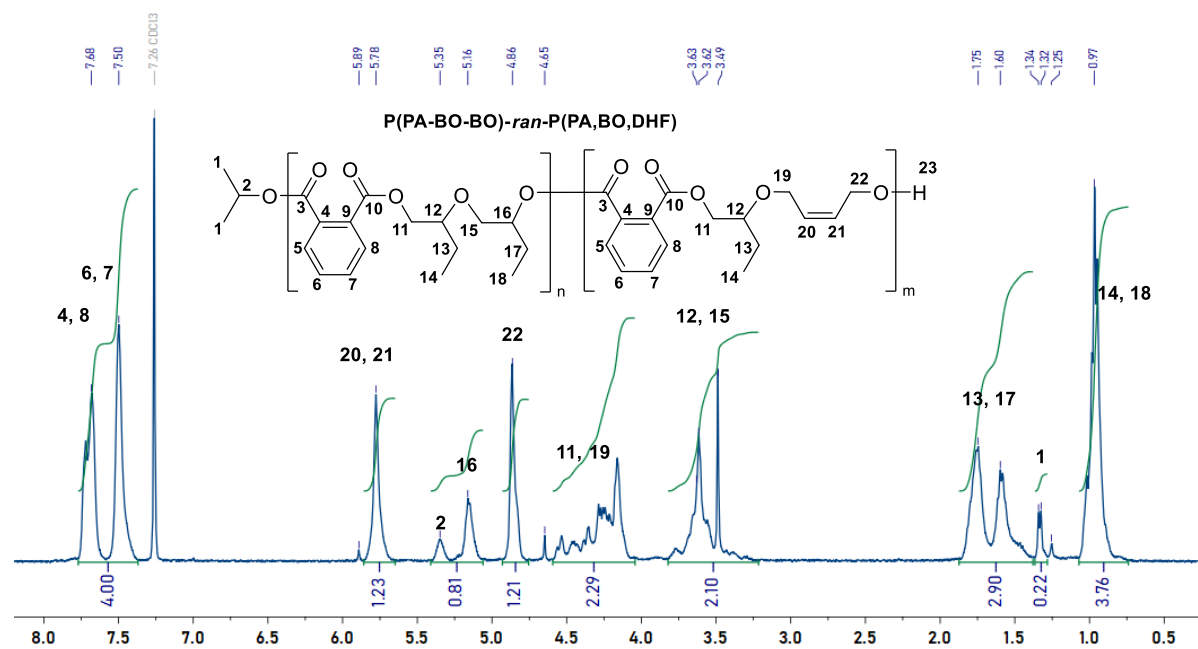


Figure S8.2.58: ^1H NMR spectrum from the reaction of [1]:[PA]:[BO]:[DHF] = 1: 50: 228: 1154, (work-up in MeOH/ CH_2Cl_2). Spectrum corresponds to Scheme 2.2, **P11** (400 MHz, CDCl_3).

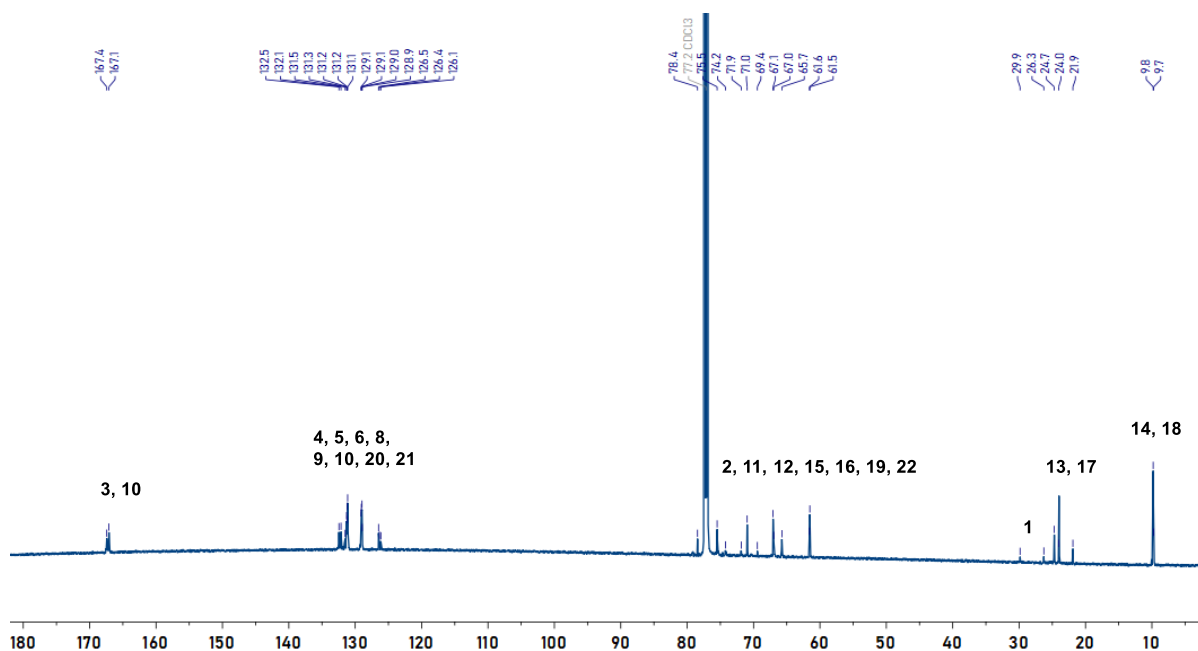


Figure S8.2.59: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of [1]:[PA]:[BO]:[DHF] = 1: 50: 228: 1154, after work-up in MeOH/DCM. Spectrum corresponds to Scheme 2.2, **P11** (151 MHz, CDCl_3).

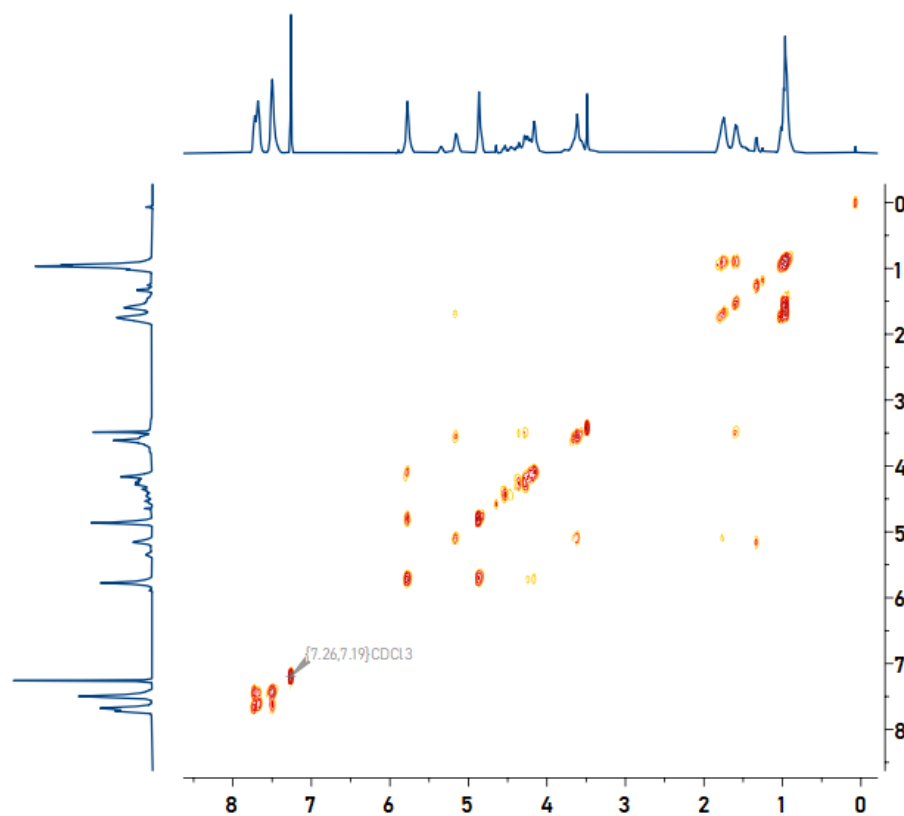


Figure S8.2.60: ^1H COSY NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{BO}]:[\text{DHF}] = 1:50:228:1154$, Scheme 2.2, **P11** (400 MHz, CDCl_3).

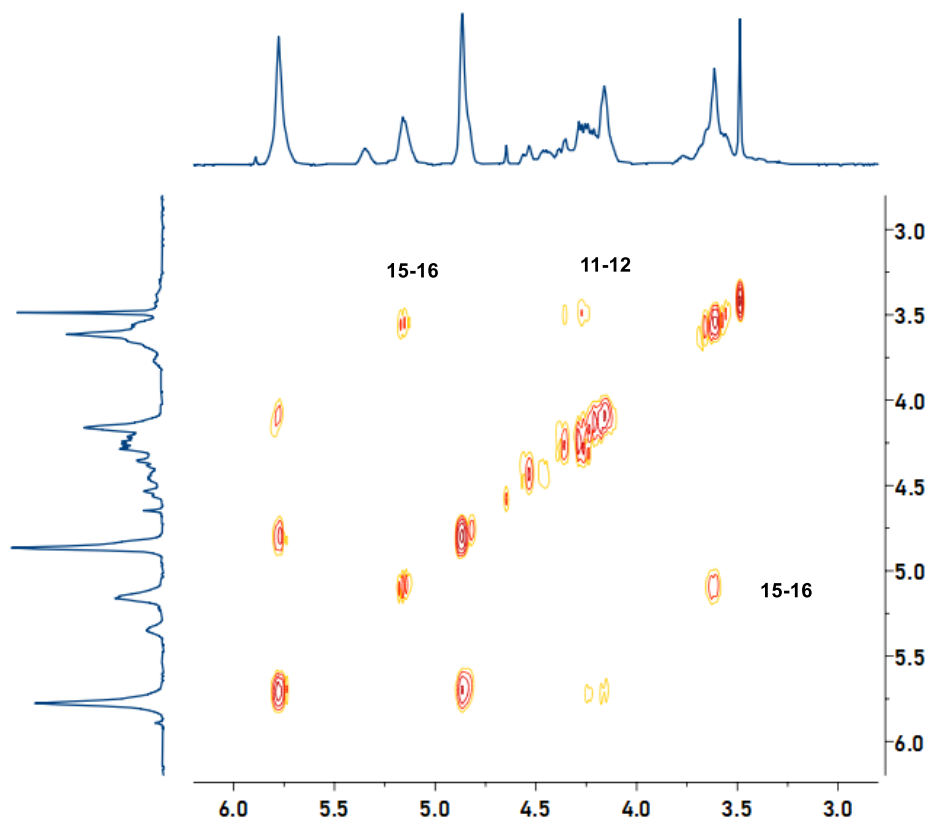


Figure S8.2.61: Magnified ^1H COSY NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{BO}]:[\text{DHF}] = 1:50:228:1154$, Scheme 2.2, **P11** (400 MHz, CDCl_3).

8.2.4.1.2 NMR Spectra for P12

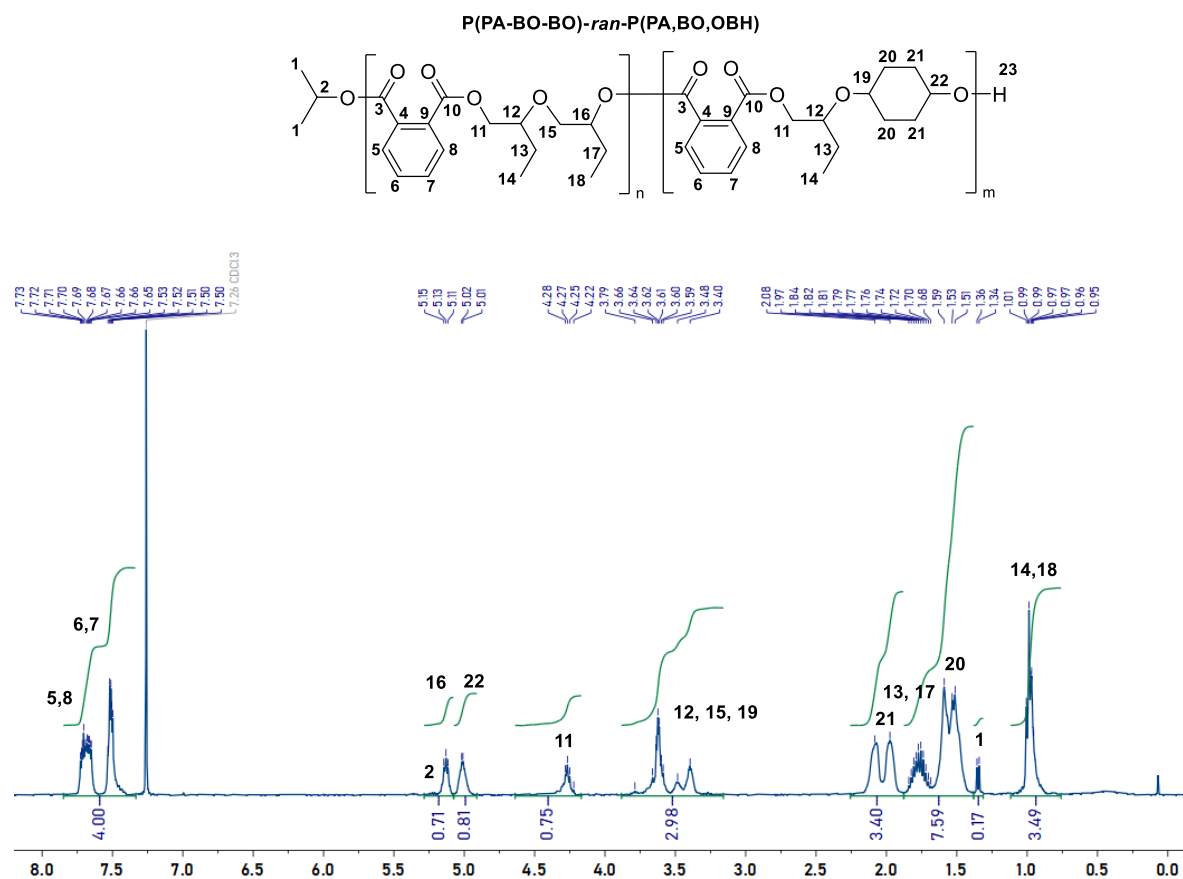


Figure S8.2.62: ^1H NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{BO}]:[\text{OBH}] = 1: 50: 228: 986$, (work-up in MeOH/ CH_2Cl_2). Spectrum corresponds to Scheme 2.2, **P12** (400 MHz, CDCl_3).

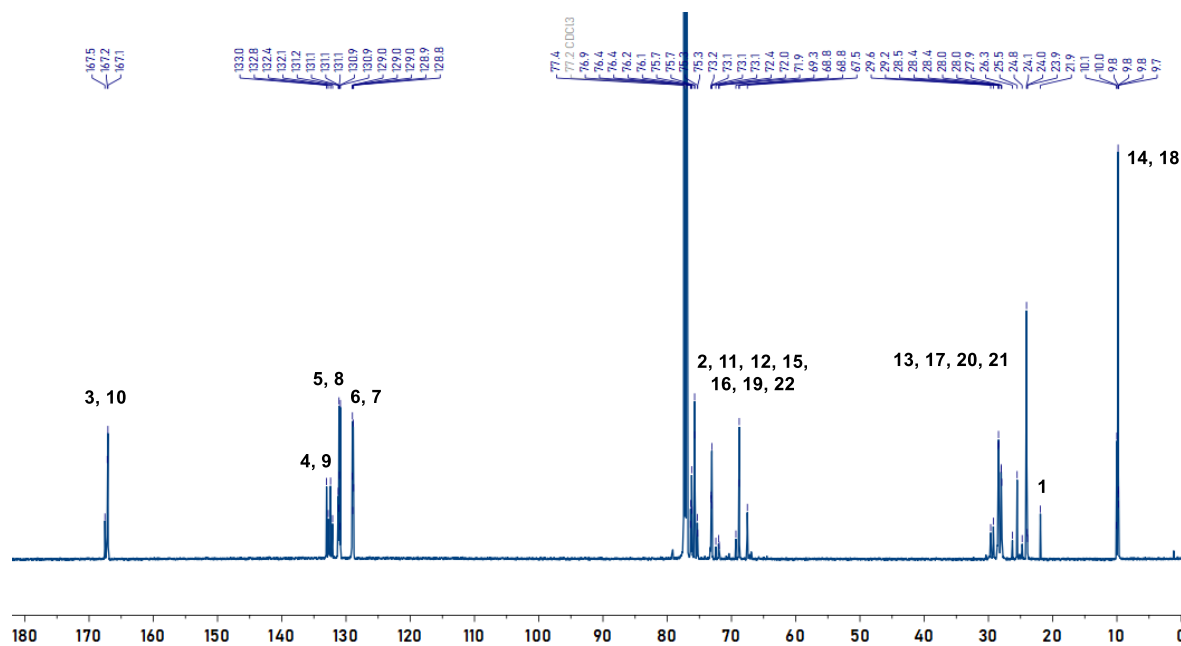


Figure S8.2.63: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of $[1]:[\text{PA}]:[\text{BO}]:[\text{OBH}] = 1: 50: 228: 986$, Scheme 2.2, **P12** (151 MHz, CDCl_3).

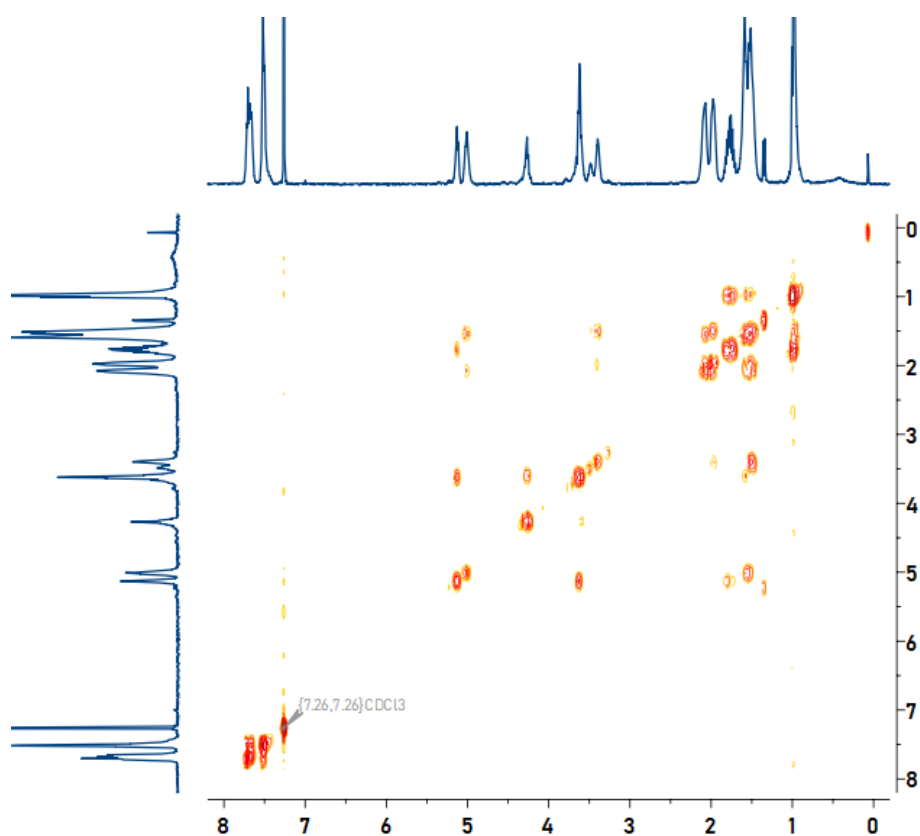


Figure S8.2.64: ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{PA}]:[\text{BO}]:[\text{OBH}] = 1: 50: 228: 986$, Scheme 2.2, **P12** (400 MHz, CDCl_3).

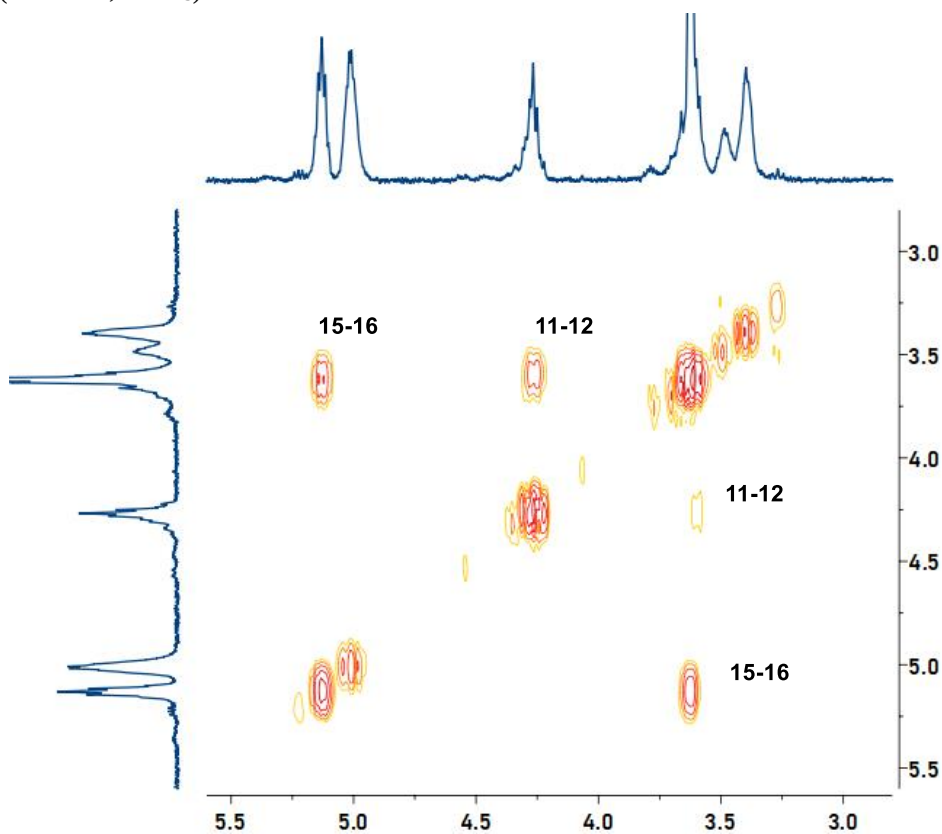


Figure S8.2.65: Magnified ^1H COSY NMR spectrum from the reaction of $[\mathbf{1}]:[\text{PA}]:[\text{BO}]:[\text{OBH}] = 1: 50: 228: 986$, Scheme 2.2, **P12** (400 MHz, CDCl_3).

8.2.4.2 GPC Data for Polymers Described in Scheme 2.2

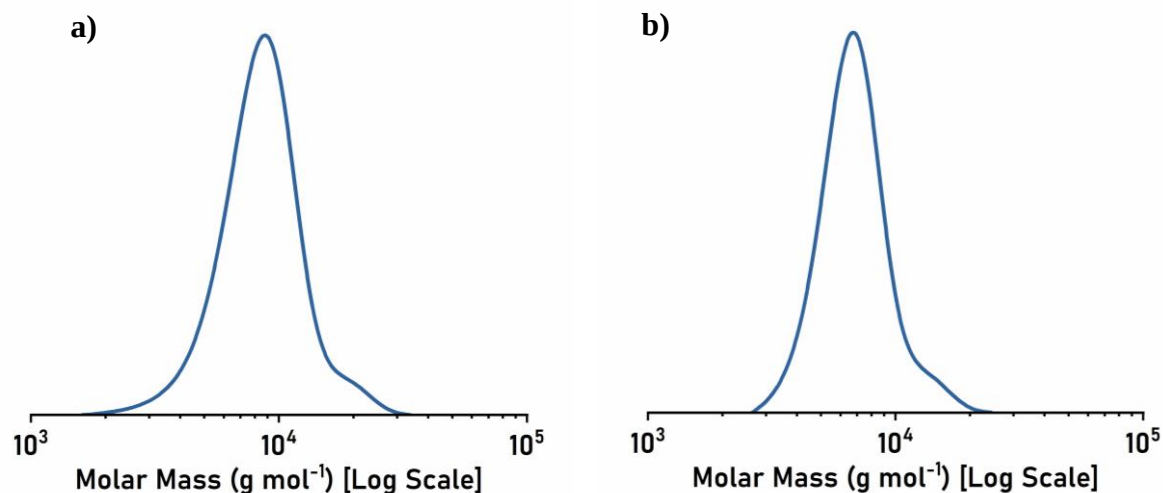


Figure S8.2.66: GPC chromatograms for polymers described in Scheme 2.2, a) **P11** and b) **P12**.

8.2.4.3 Kinetic Data for Polymers Described in Scheme 2.2

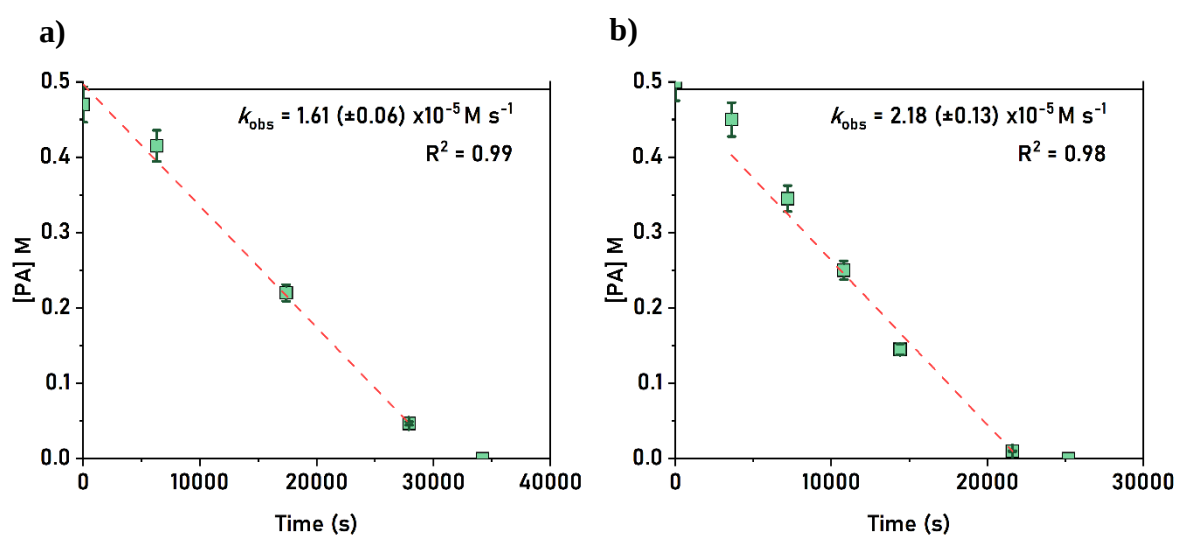
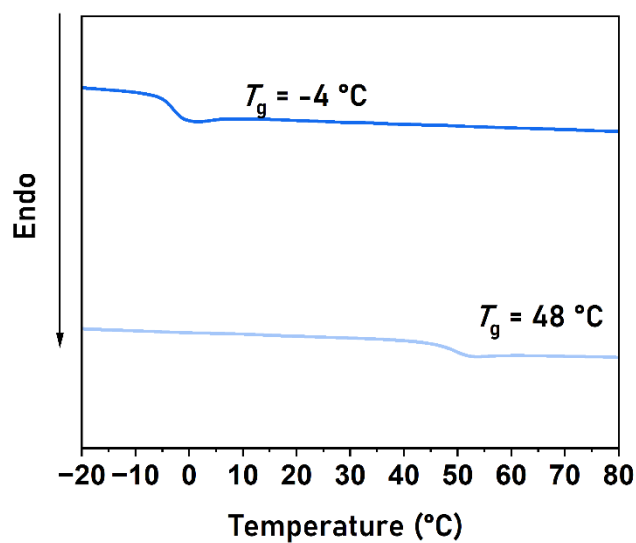


Figure S8.2.67: Plots of anhydride concentration vs. time, with linear fits to the data. The order in PA concentration was determined from the gradients of the linear fit. In these experiments [PA] = 0.5 M. This diagram applies to the polymers described in Scheme 2.2, a) **P11** and b) **P12**.

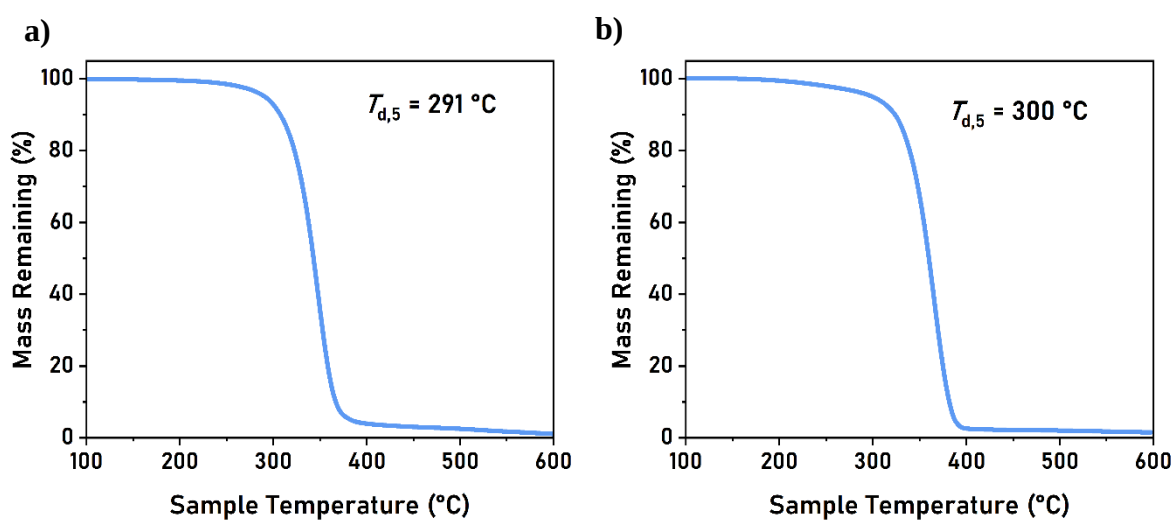
8.2.4.4 DSC Data for Polymers Described in Scheme 2.2

Figure S8.2.68: DSC Thermograms for Polymers in Scheme 2.2, **P11** (top) and **P12** (bottom).

8.2.4.5 TGA Data for Polymers Described in Scheme 2.2

Table S8.2.3: TGA Data for polymers described in Scheme 2.2, **P11** and **P12**.

Polymer	Anhyd.	Epoxide	Cyclic Ether	$T_{d,5}$ (°C)	$T_{d,95}$ (°C)
P11	PA	BO	DHF	291	383
P12	PA	BO	OBH	300	388

Figure S8.2.69: TGA data for polymers described in Scheme 2.2, a) **P11** and b) **P12**.

8.2.5 Data for Polymers Described in Scheme 2.3 – Post-Polymerization Functionalization

8.2.5.1 NMR data for Polymers Described in Scheme 2.3

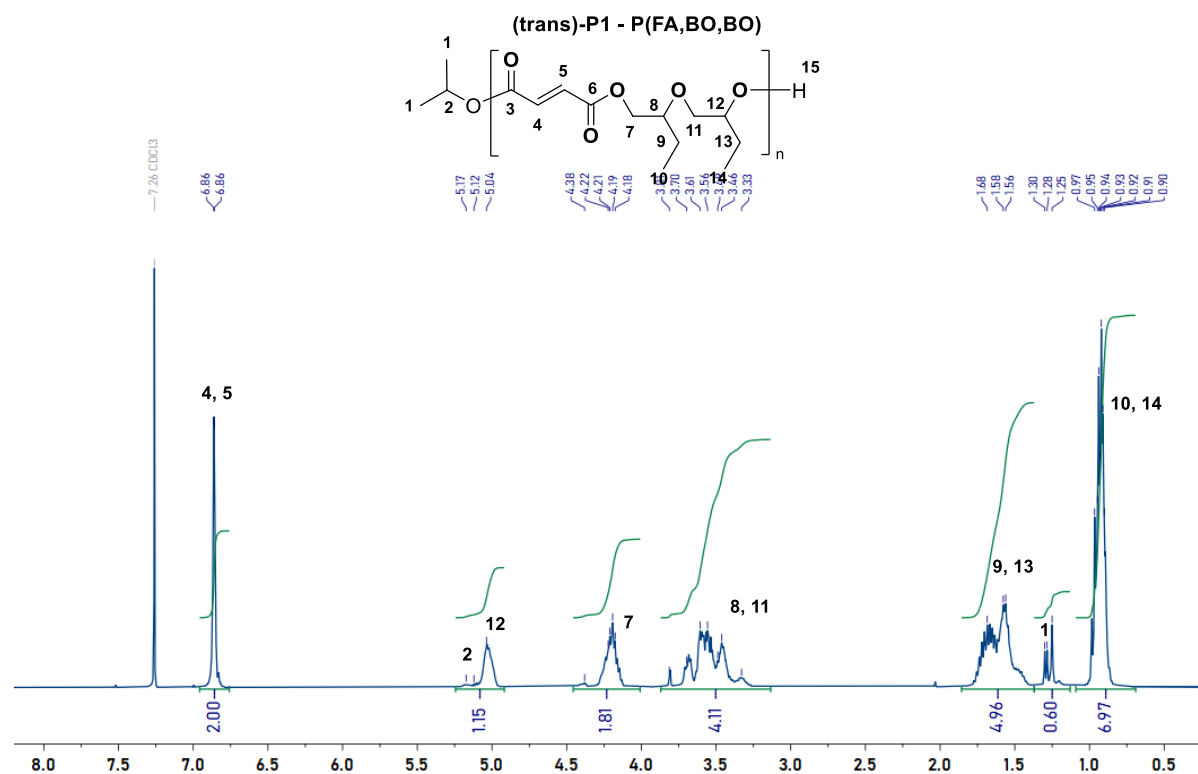
8.2.5.1.1 NMR Spectra for (*trans*)-P1

Figure S8.2.70: ^1H NMR spectrum from the reaction of **P1** with HNEt_2 , (work-up in $\text{MeOH}/\text{CH}_2\text{Cl}_2$). Spectrum corresponds to Scheme 2.3 and Table S3, (*trans*)-**P1** (400 MHz, CDCl_3).

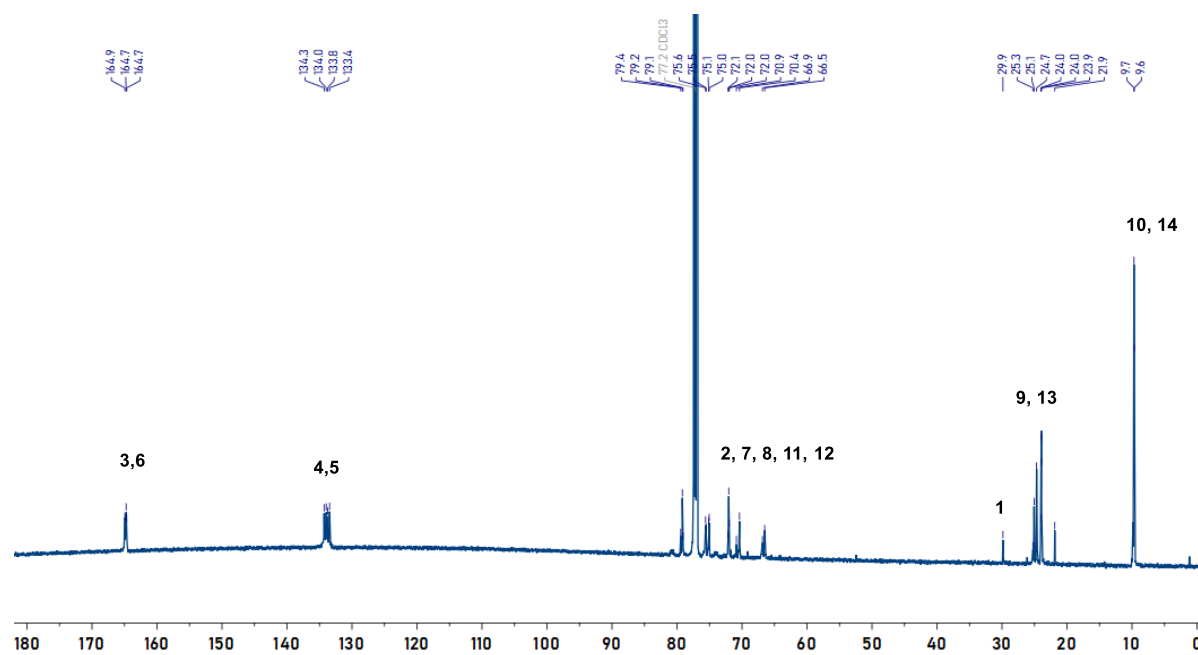


Figure S8.2.71: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of **P1** with HNEt_2 , Scheme 2.3 and Table 2.3, (*trans*)-**P1** (151 MHz, CDCl_3).

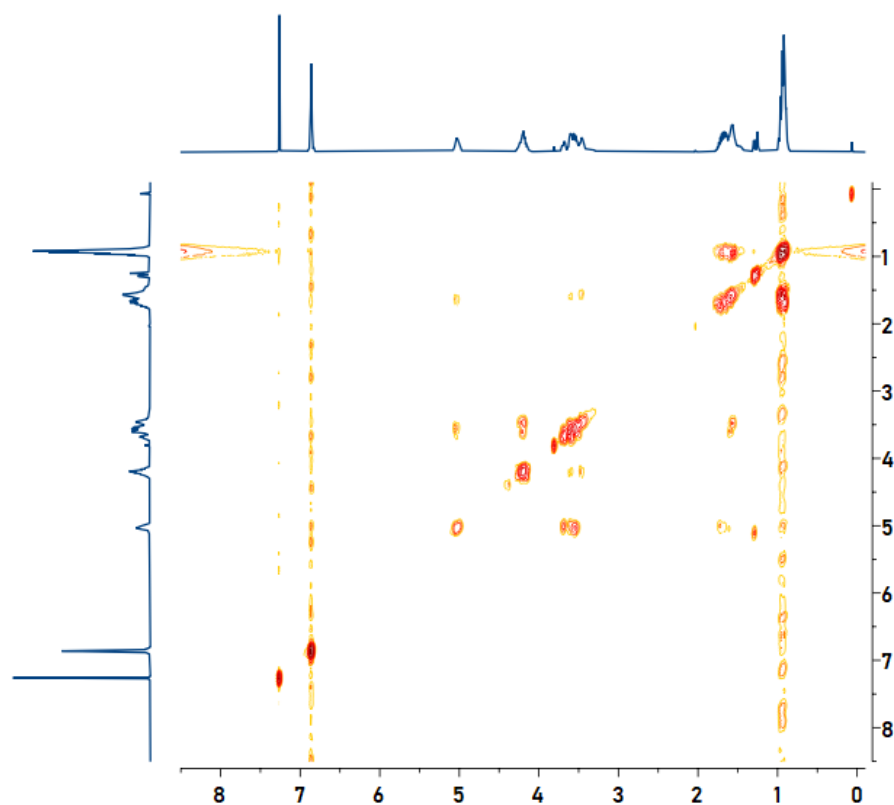


Figure S8.2.72: ^1H COSY NMR spectrum from the reaction of **P1** with HNEt_2 , Scheme 2.3 and Table 2.3, (*trans*)-**P1** (400 MHz, CDCl_3).

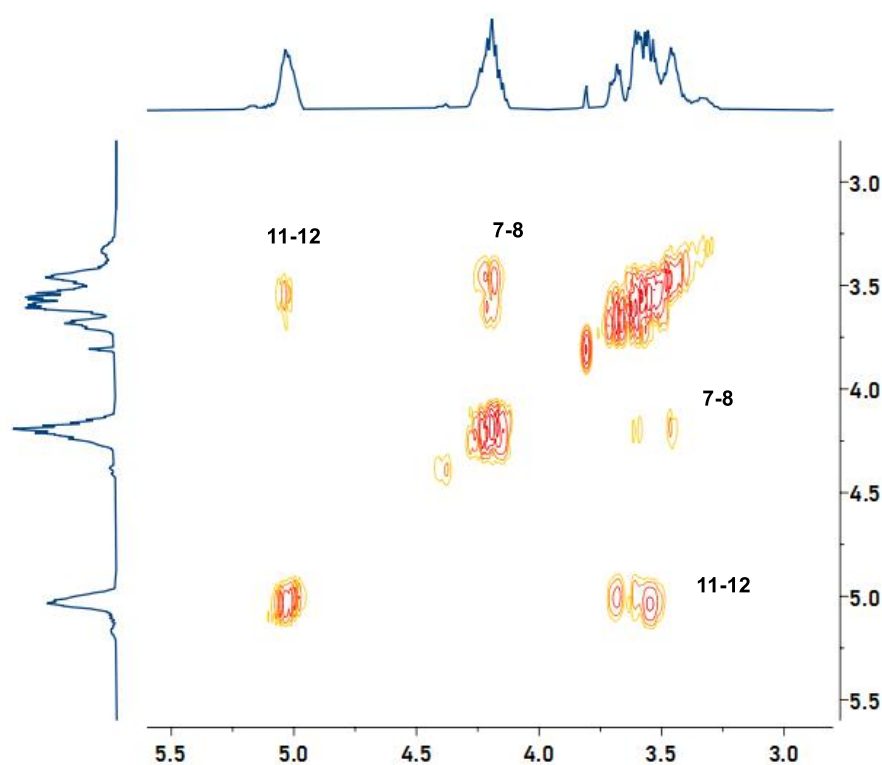


Figure S8.2.73: Magnified ^1H COSY NMR spectrum from the reaction of **P1** with HNEt_2 , Scheme 2.3 and Table 2.3, (*trans*)-**P1** (400 MHz, CDCl_3).

8.2.5.1.4 NMR Spectra for P10s

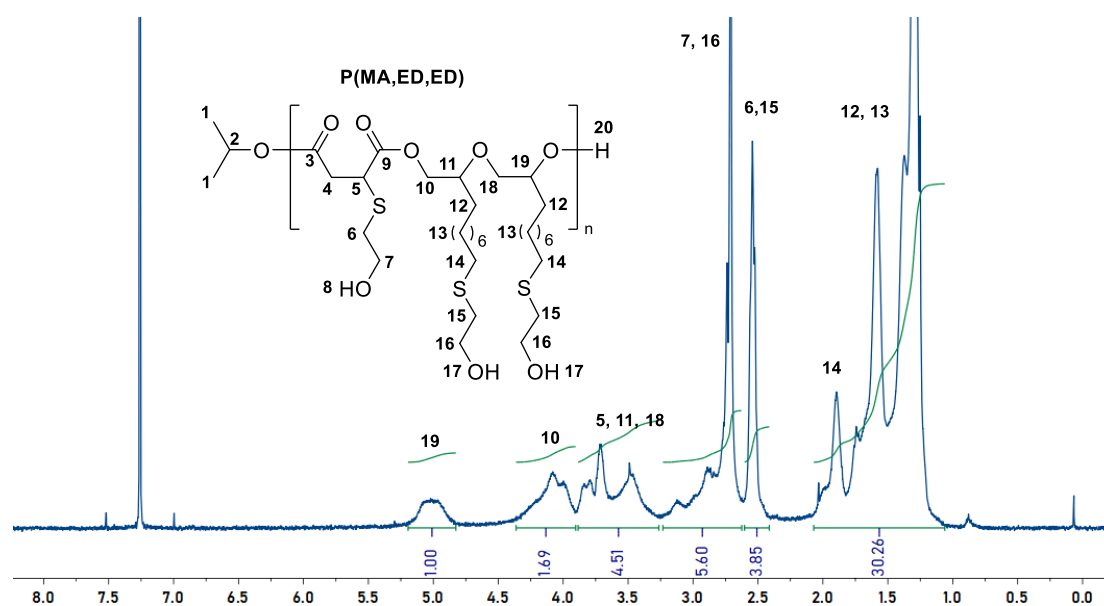


Figure S8.2.76: ^1H NMR spectrum from the reaction of **P10s** after work-up in pentane. Spectrum corresponds to Scheme 2.3 and Table 2.3, **P10s** (400 MHz, CDCl_3).

8.2.5.2 GPC Data for Polymers Described in Table S2.3 and Scheme 2.3 – Post-Polymerization Functionalization

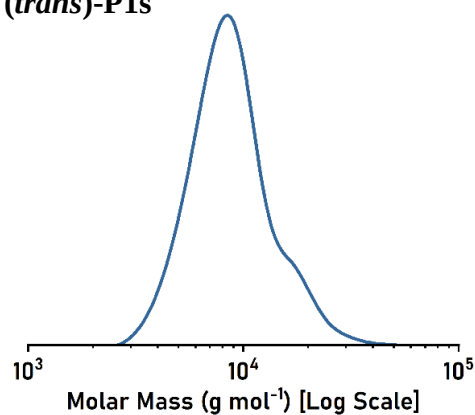
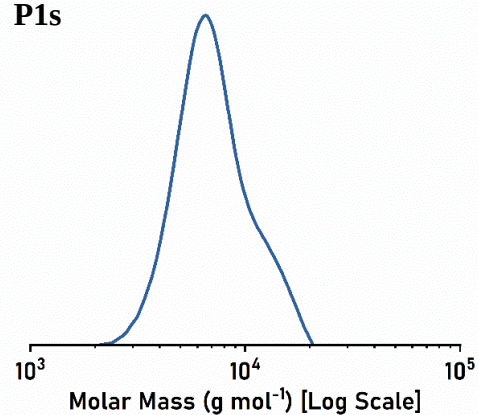
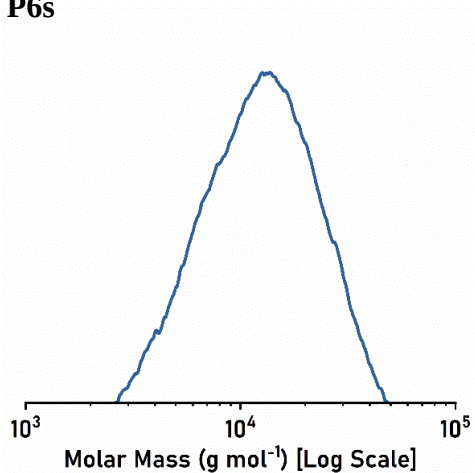
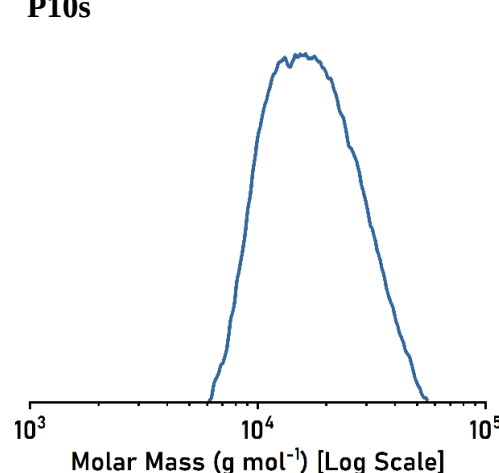
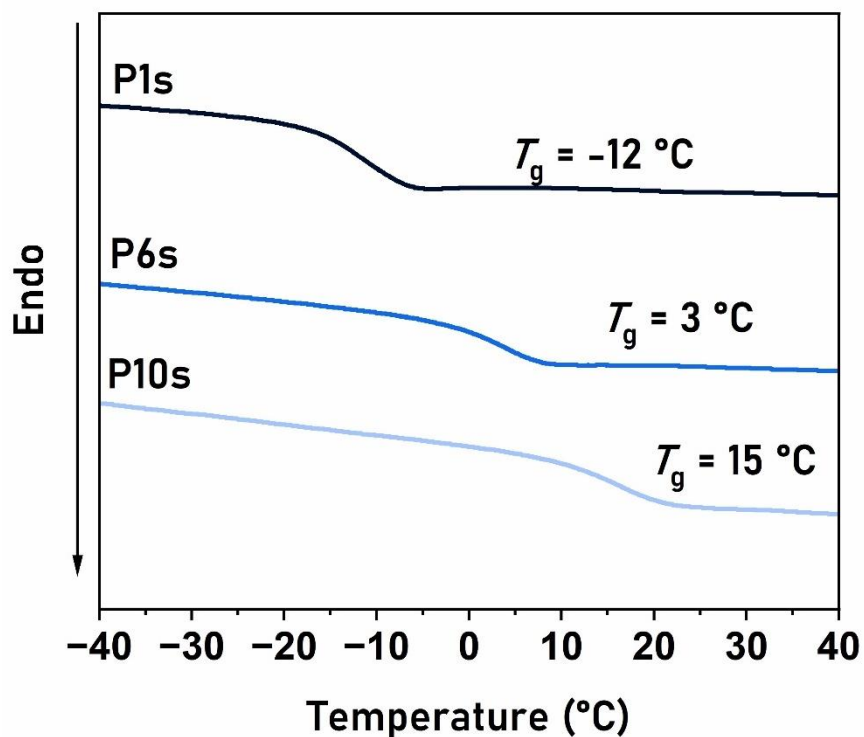
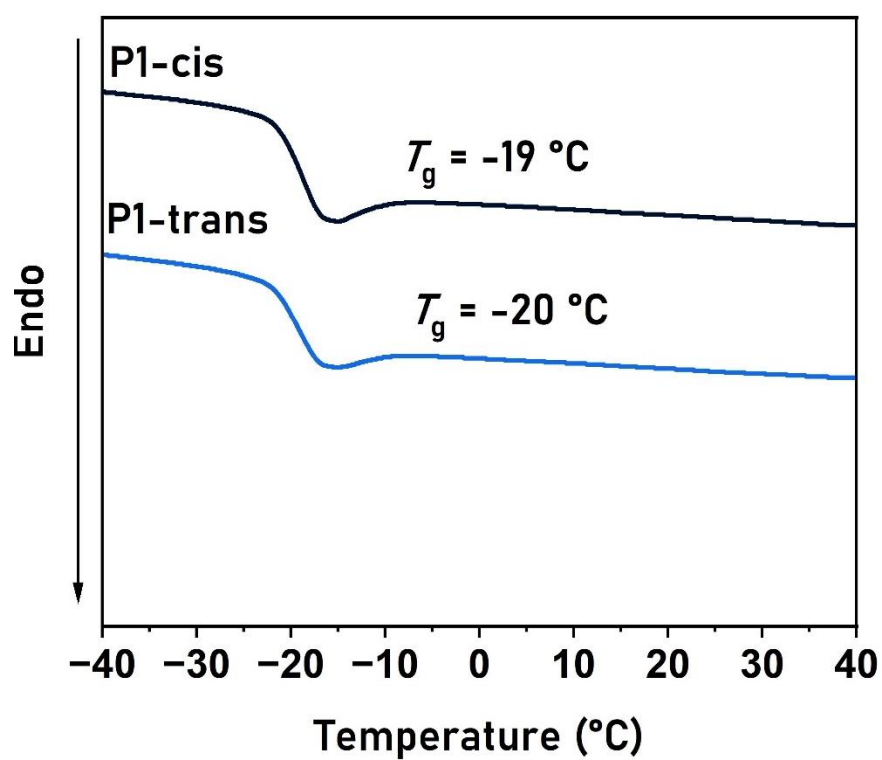
(trans)-P1s**P1s****P6s****P10s**

Figure S8.2.77: GPC chromatograms for polymers described in Scheme 2.3, **(trans)-P1**, **P1s**, **P6s** and **P10s**.

8.2.5.3 DSC Data for Polymers Described in Scheme 2.3 and Table 2.3

Figure S8.2.78: DSC Thermograms for polymers described in Scheme 2.3, **P1s**, **P6s**, and **P10s**.Figure S8.2.79: DSC Thermograms for polymers described in Scheme 2.3, **P1-cis** and **P1-trans**.

8.2.5.4 TGA Data of P1s, P6s and P10s

Table S8.2.4: TGA Data for polymers described in Scheme 2.3, P1s, P6s and P10s.

Polymer	Anhyd.	Epoxide	$T_{d,5}$ (°C)	$T_{d,95}$ (°C)	$T_{d,5}$, pre- functionalisation (°C) [#]	$\Delta T_{d,5}$, pre- and post- functionalisation (°C)
P1s	MA	BO	222	482	306 [P1]	84
P6s	PA	ED	307	450	308 [P6]	1
P10s	MA	ED	319	251	344 [P10]	25

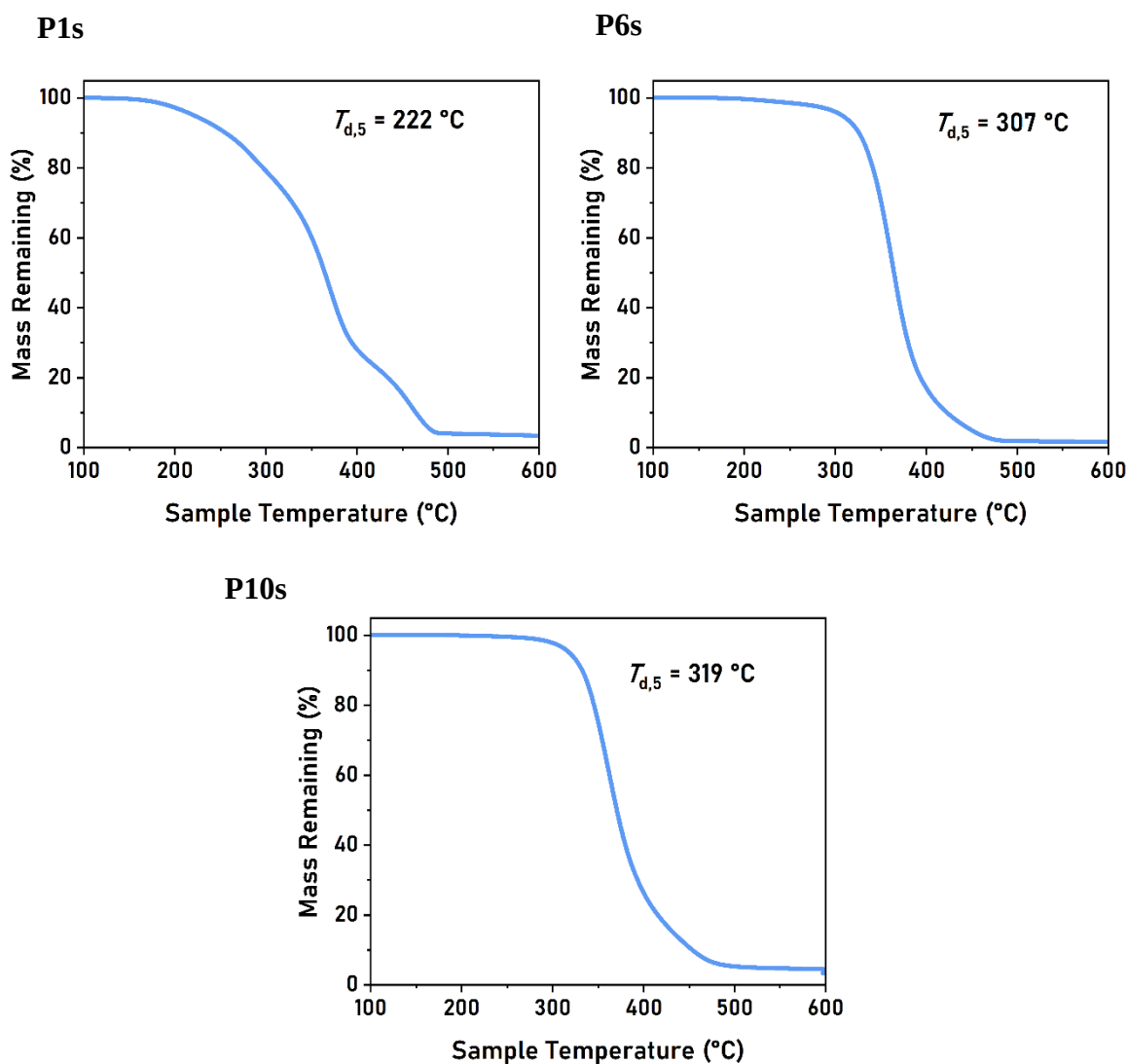


Figure S8.2.80: TGA data for polymers described in Scheme 3, P1s, P6s, and P10s.

8.3: Chapter 3 - Toughened Commercial Poly(L-Lactide) (PLLA) Using Degradable and Recyclable Poly(Ester-*alt*-Ether)-*b*-PLLA

8.3.1 Characterization Data for Polymers Described in Table 3.1

8.3.1.1 NMR Spectra for Polymers Described in Table 3.1

8.3.1.1.1 NMR Spectra for P10

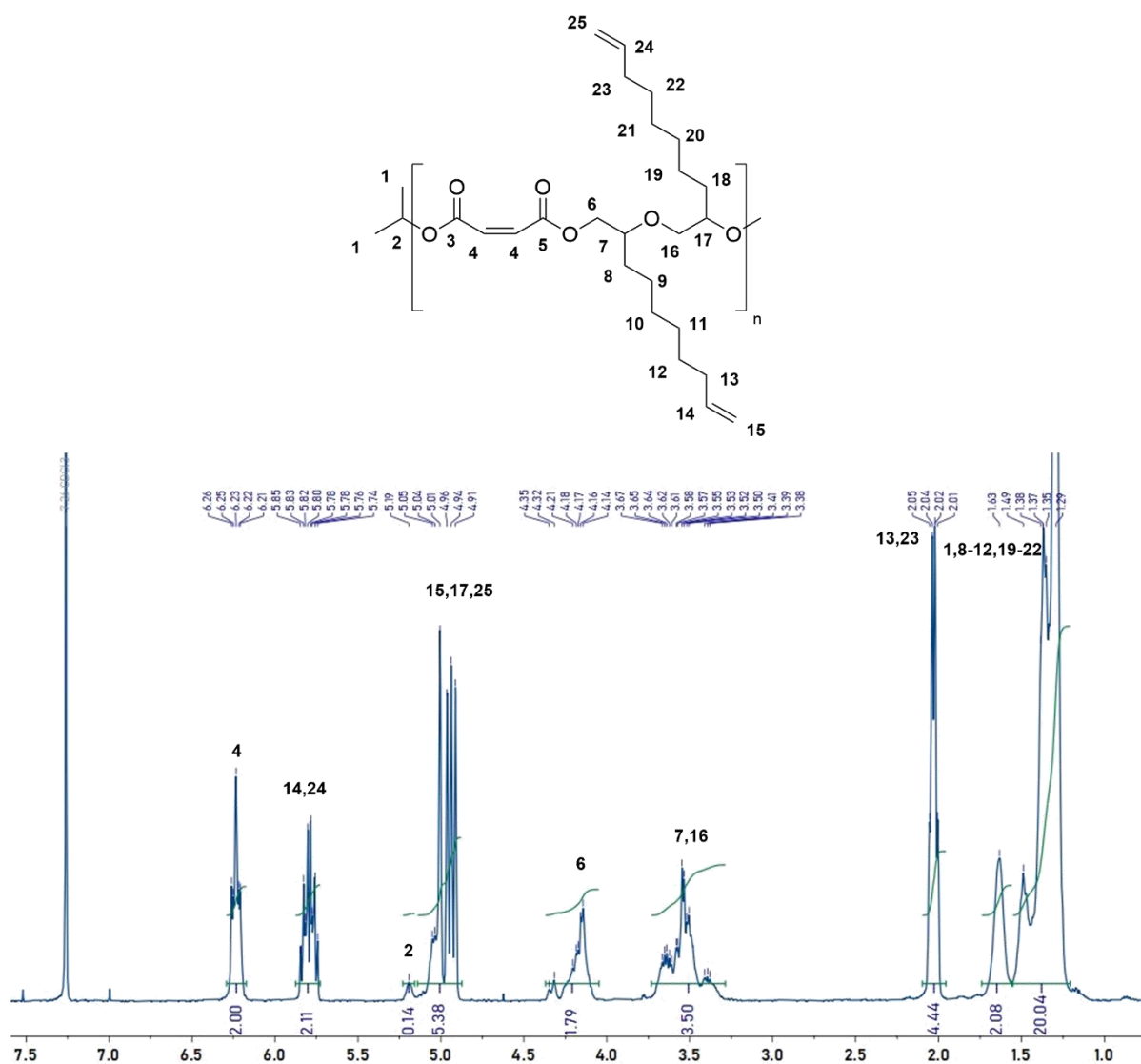


Figure S8.3.1: ¹H NMR spectrum of **P14** (with assignment, Table 3.1, **P10**) (400 MHz, CDCl₃). Reaction conditions: [1] = 10 mM in 1 mL epoxide, [1] : [MA] : [ED] = 1 : 50 : 546, 50 °C.

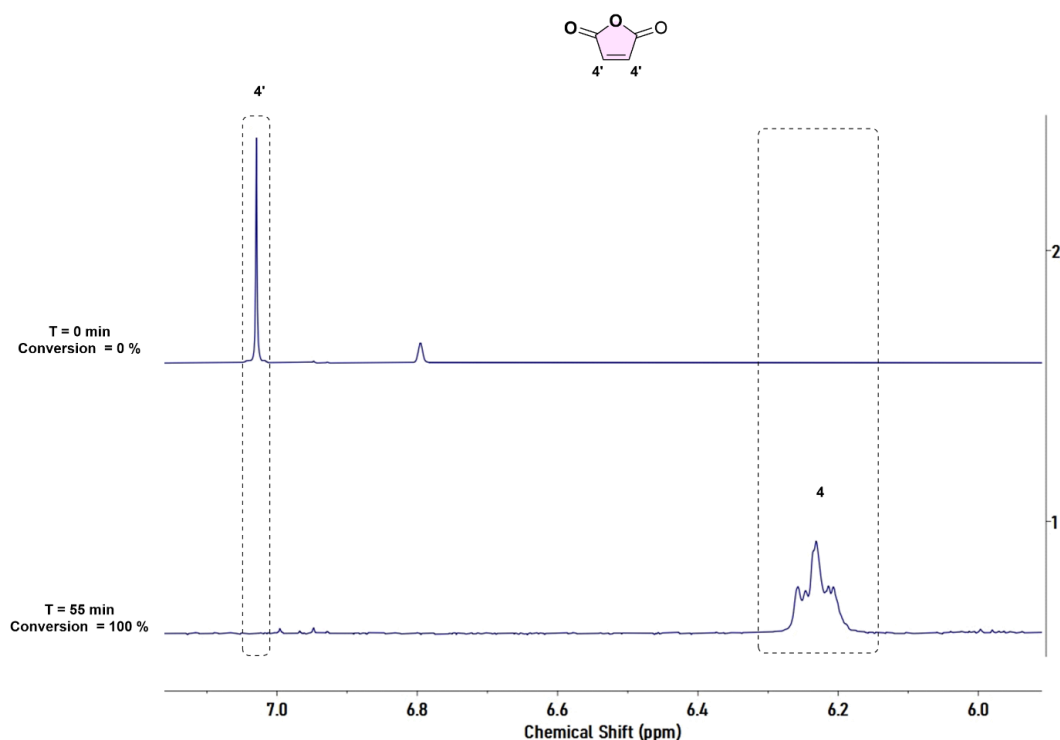


Figure S8.3.2: ^1H NMR spectrum the initial reaction contents before (top) and after complete (bottom) polymerisation of **P10**, showing MA monomer signal ($4'$) at 7.03 ppm in the initial (0 min), top spectrum, and the absence of MA in the bottom spectrum after full conversion (55 min), and the presence of polymerised signal (4) below.

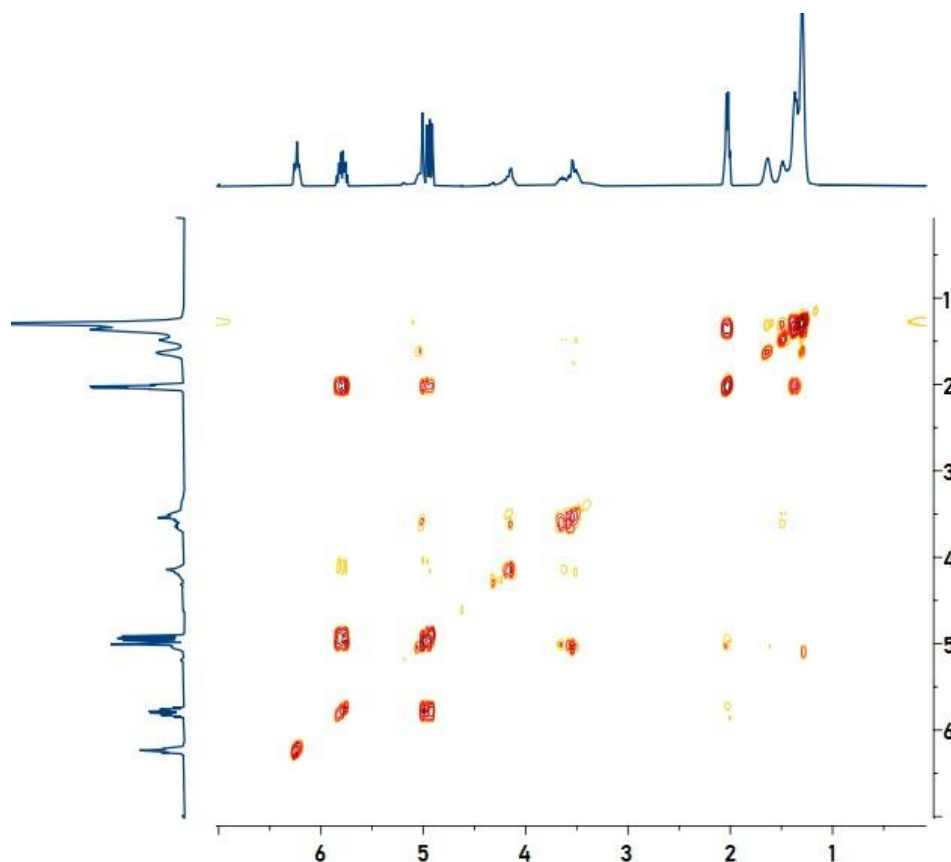


Figure S8.3.3: ^1H COSY NMR spectrum of **P10** (Table 3.1, **P10**) (400 MHz, CDCl_3). Reaction conditions: $[1] = 10$ mM in 1 mL epoxide, $[1] : [\text{MA}] : [\text{ED}] = 1 : 50 : 546$, 50°C .

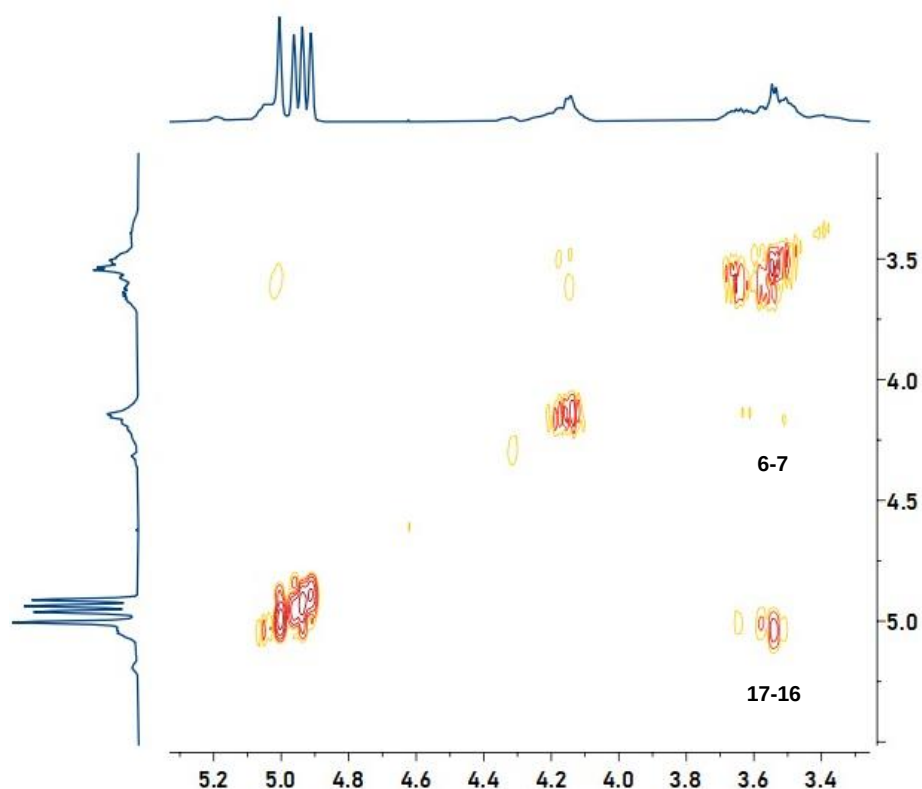


Figure S8.3.4: Magnified ^1H COSY NMR spectrum of **P10** (Table 3.1, **P10**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[1]** : **[MA]** : **[ED]** = 1 : 50 : 546, 50 °C. This region shows correlation of the methine and methylene ester regions (17 and 6) to the ether signal (7 and 16), but not to one another.

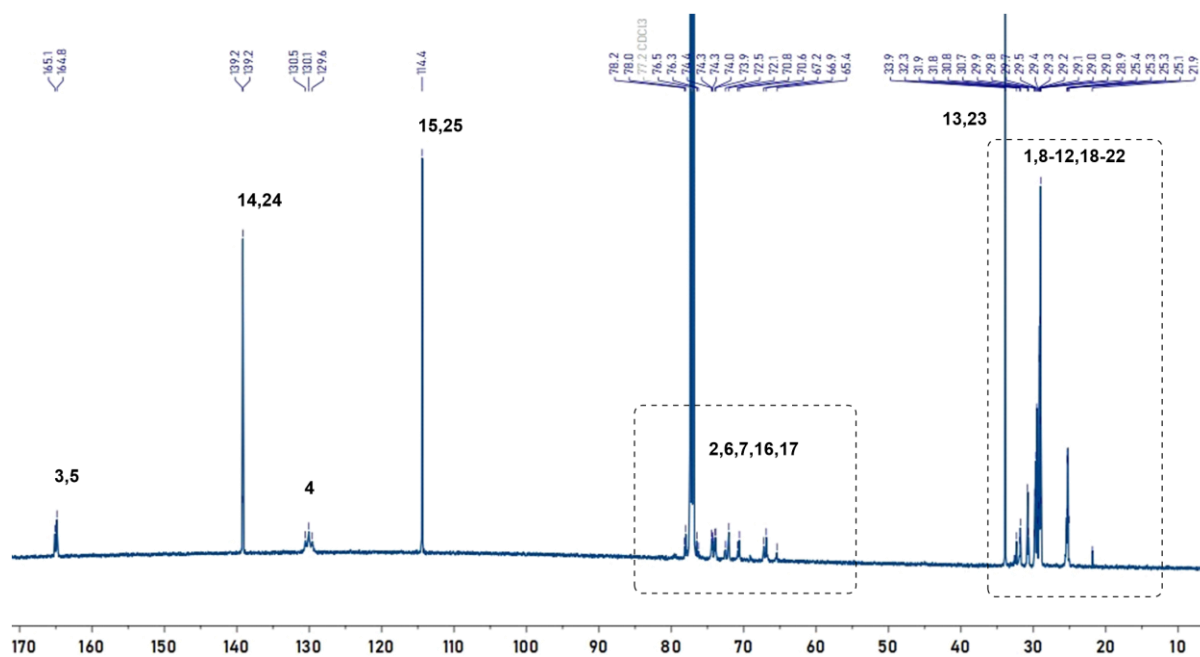


Figure S8.3.5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P10** (Table 3.1) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[1]** : **[MA]** : **[ED]** = 1 : 50 : 546, 50 °C.

8.3.1.1.2 NMR Spectra for P10'

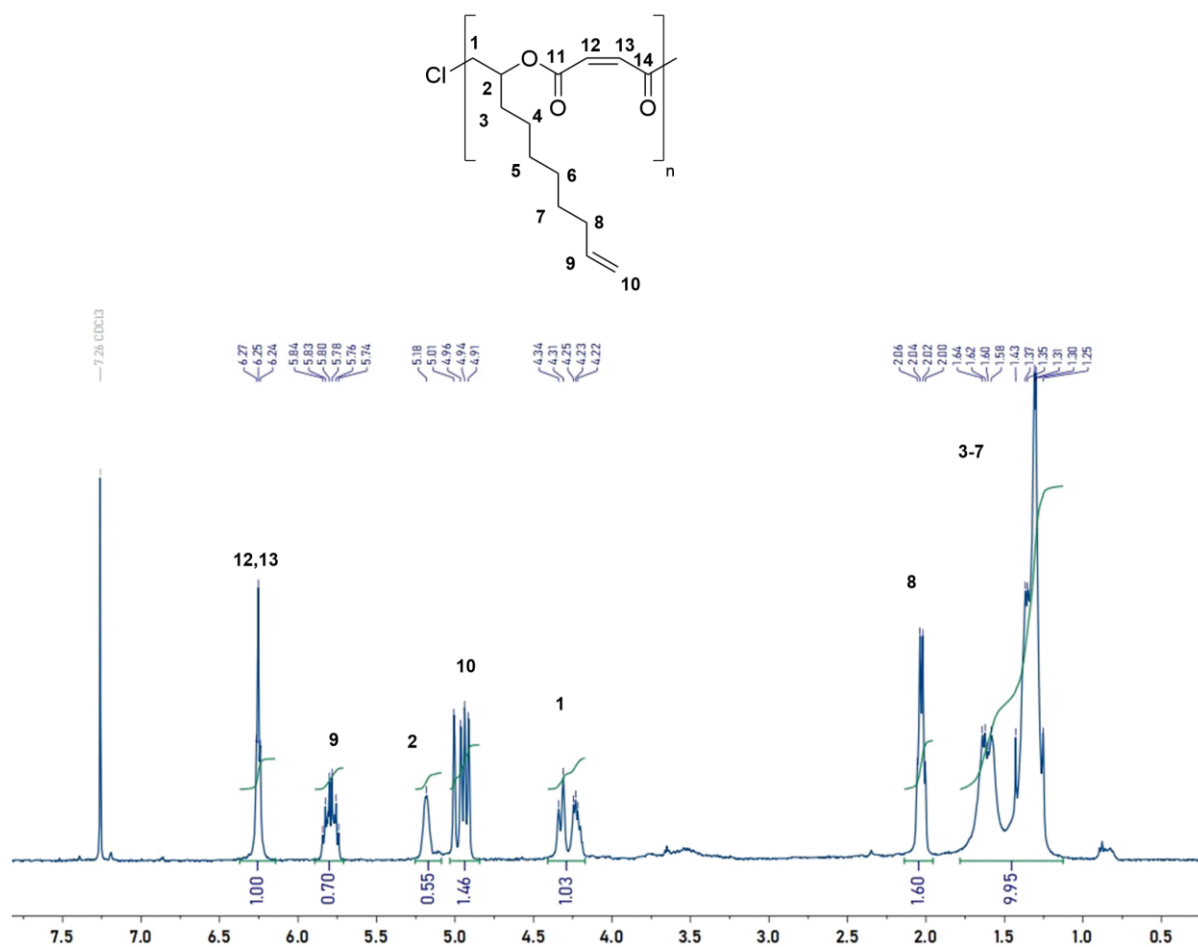


Figure S8.3.6: ¹H NMR spectrum of **P10'** (with assignment, Table 3.1, **P10'**) (400 MHz, CDCl₃). Reaction conditions: [2] = 0.01 mmol in 1 mL epoxide, [2] : [MA] : [ED] = 1: 25: 546, 50 °C.

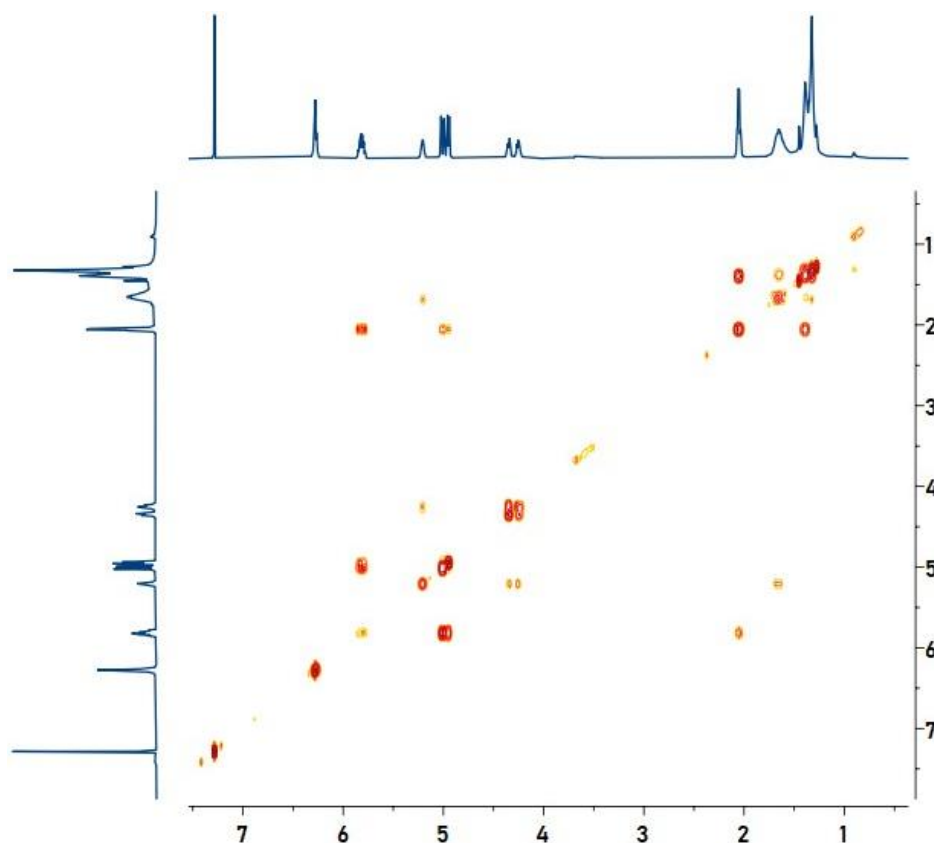


Figure S8.3.7: ¹H COSY NMR spectrum of **P10'** (Table 3.1, **P10'**) (400 MHz, CDCl₃). Reaction conditions: [2] = 0.01 mmol in 1 mL epoxide, [2] : [MA] : [ED] = 1: 25: 546, 50 °C.

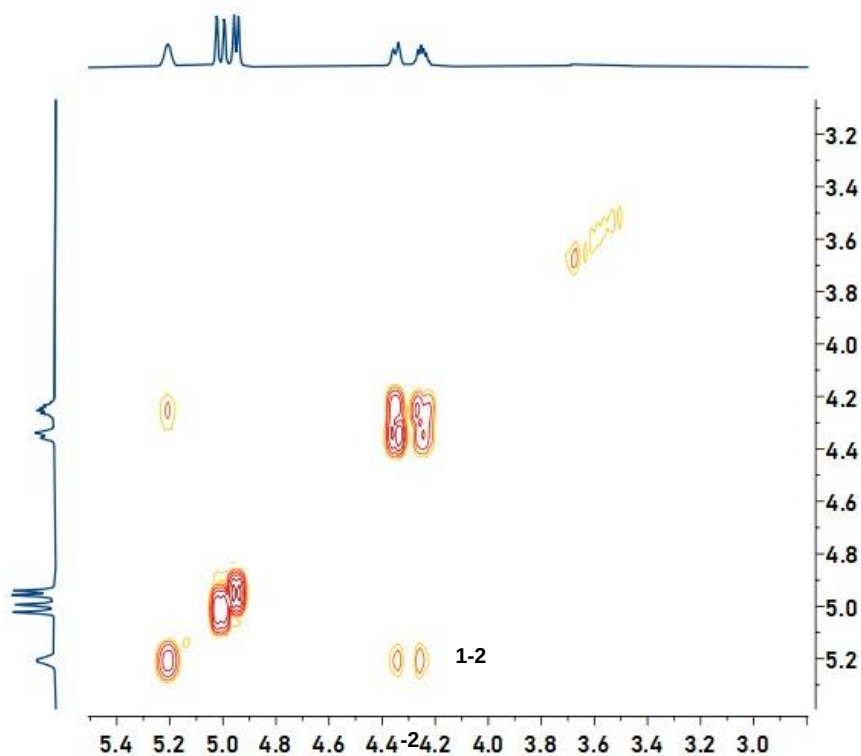


Figure S8.3.8: Magnified ¹H COSY NMR spectrum of **P10'** (Table 3.1, **P10'**) (400 MHz, CDCl₃). Reaction conditions: [2] = 0.01 mmol in 1 mL epoxide, [2] : [MA] : [ED] = 1: 25: 546, 50 °C. Showing correlation of signals 1 and 2 (methylene/methine ester) to one another, and not to the ether region.

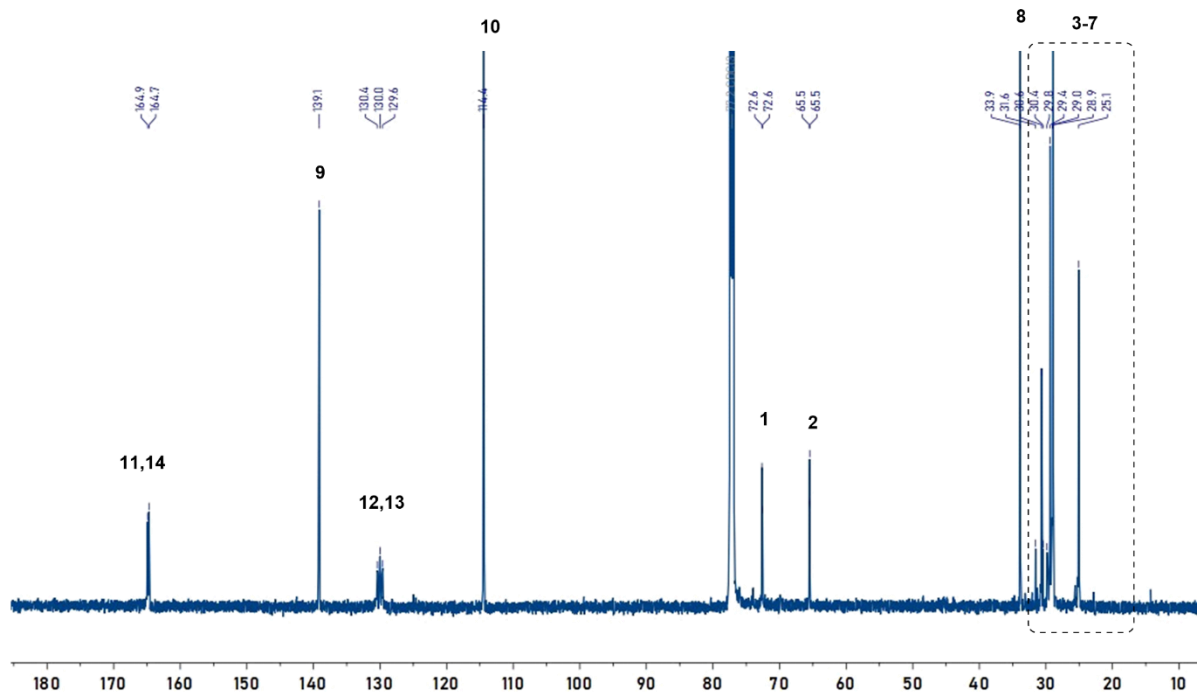


Figure S8.3.9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P10'** (Table 3.1) (151 MHz, CDCl_3). Reaction conditions: $[\mathbf{2}] = 0.01$ mmol in 1 mL epoxide, $[\mathbf{2}] : [\text{MA}] : [\text{ED}] = 1 : 25 : 546$, 50°C .

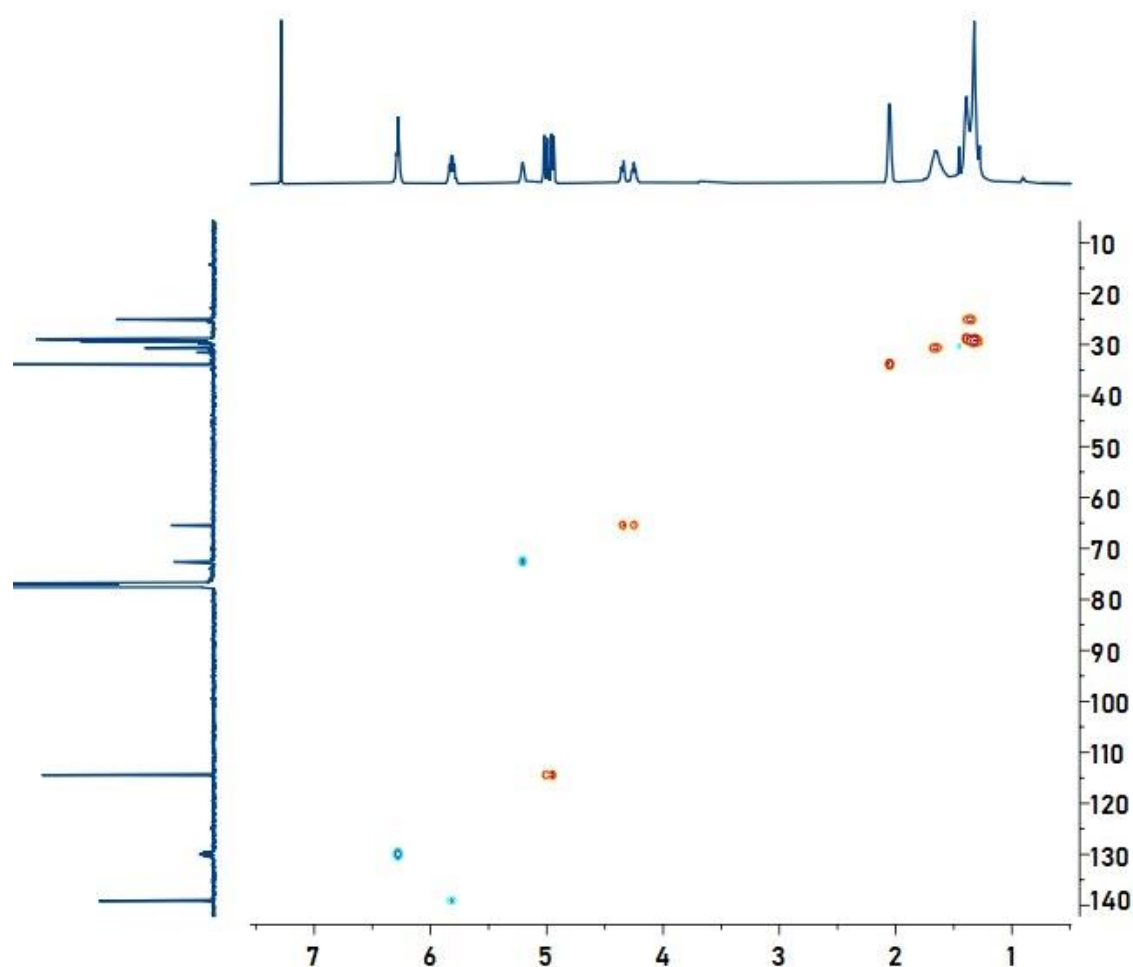


Figure S8.3.10: HSQC $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P10'** (Table 3.1, **P10'**) (400 MHz, CDCl_3). Reaction conditions: $[\mathbf{2}] = 0.01$ mmol in 1 mL epoxide, $[\mathbf{2}] : [\text{MA}] : [\text{ED}] = 1 : 25 : 546$, 50°C .

8.3.1.1.3 NMR Spectra for P10-PLLA

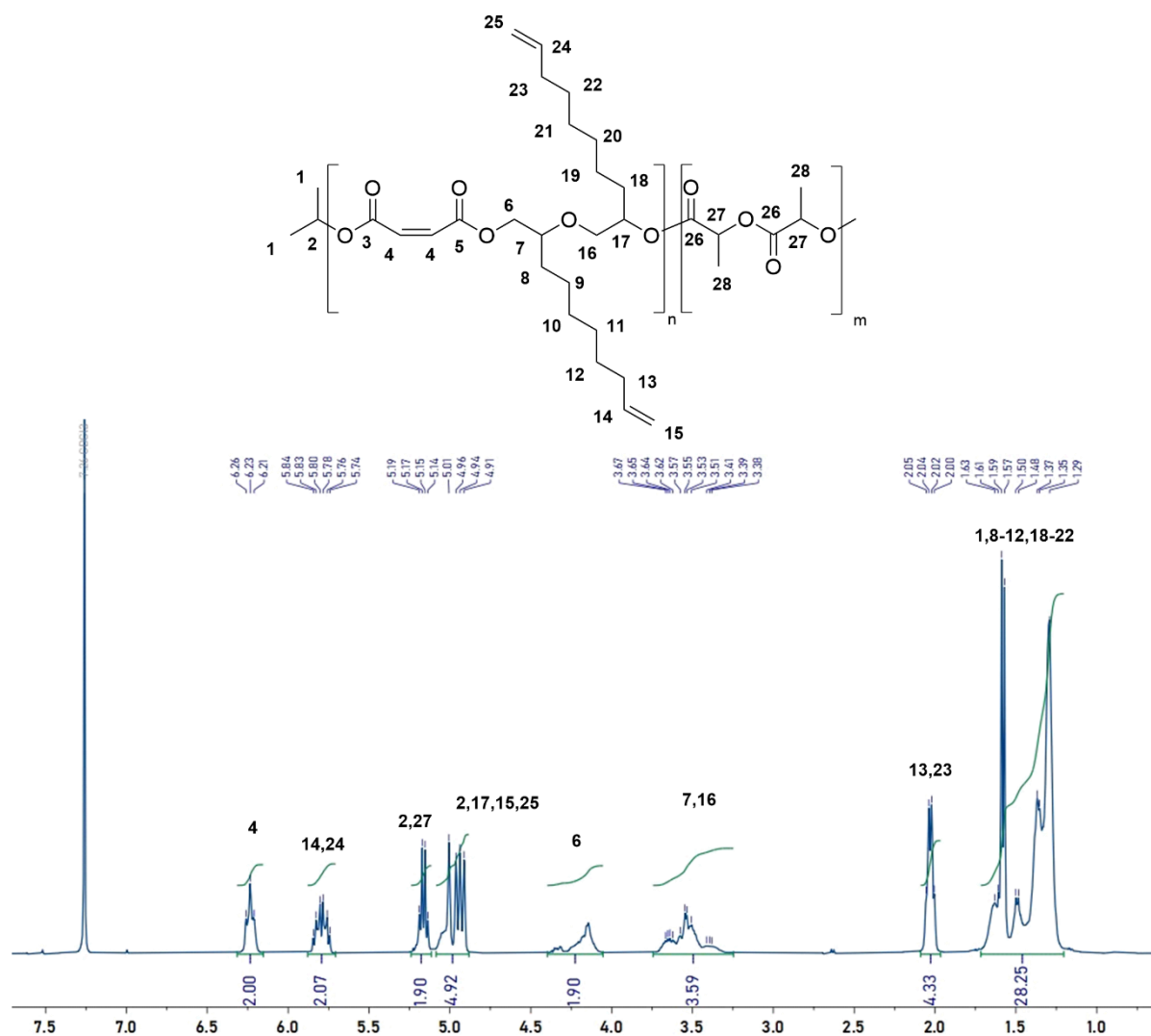


Figure S8.3.11: ^1H NMR spectrum of **P10-PLLA** (with assignment, Table 3.1, **P10-PLLA**) (400 MHz, CDCl_3). Reaction conditions: $[\mathbf{1}] = 10 \text{ mM}$ in 1 mL epoxide, $[\mathbf{1}] : [\text{MA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

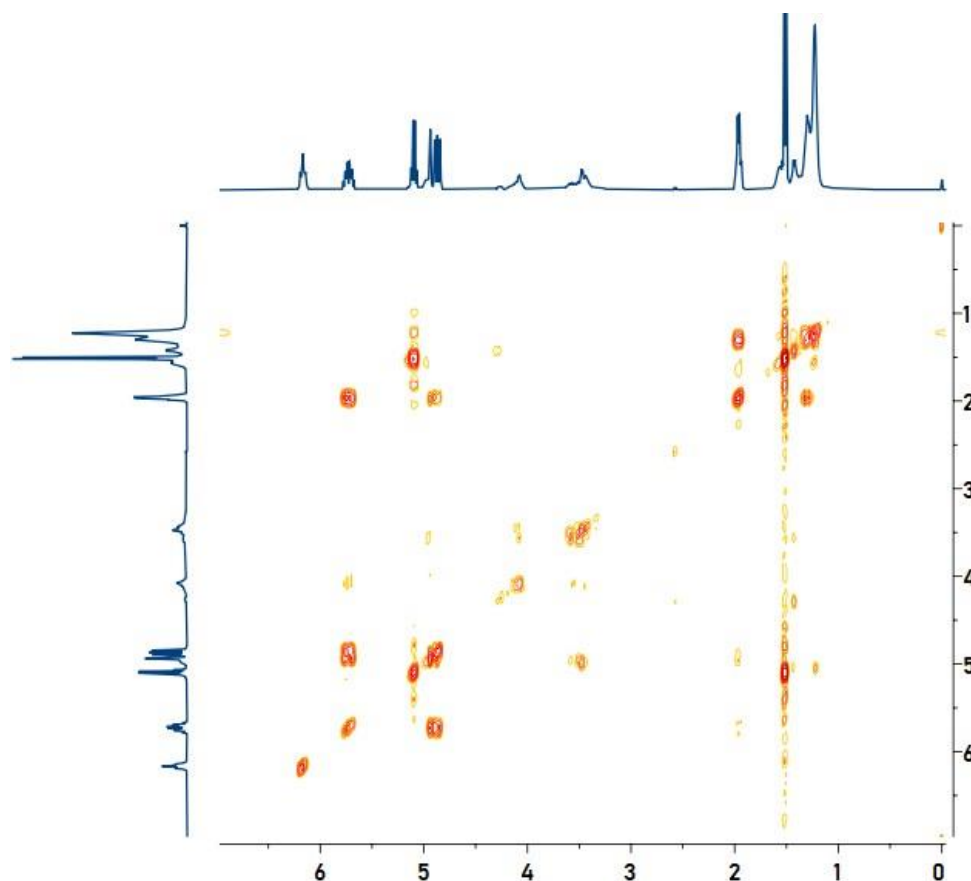


Figure S8.3.12: ^1H COSY NMR of **P10-PLLA** (with assignment, Table 3.1, **P10-PLLA**) (400 MHz, CDCl_3). Reaction conditions: $[\mathbf{1}] = 10$ mM in 1 mL epoxide, $[\text{Cat}] : [\text{MA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

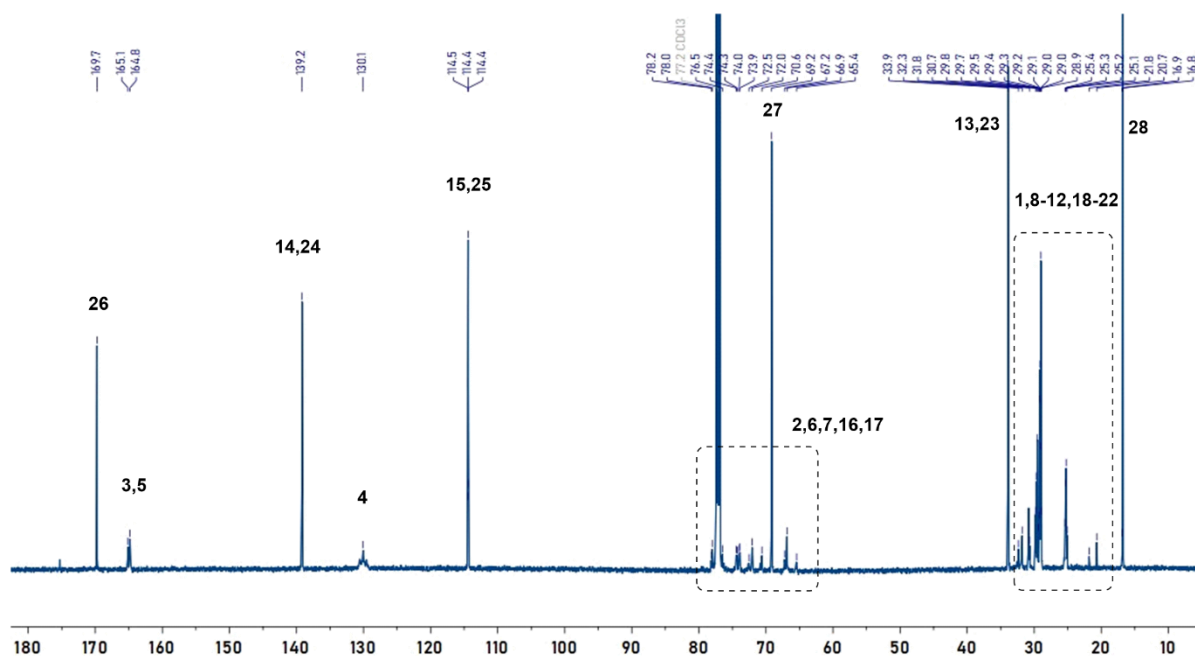


Figure S8.3.13: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P10-PLLA** (Table 3.1) (151 MHz, CDCl_3). Reaction conditions: $[\mathbf{1}] = 10$ mM in 1 mL epoxide, $[\text{Cat}] : [\text{MA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

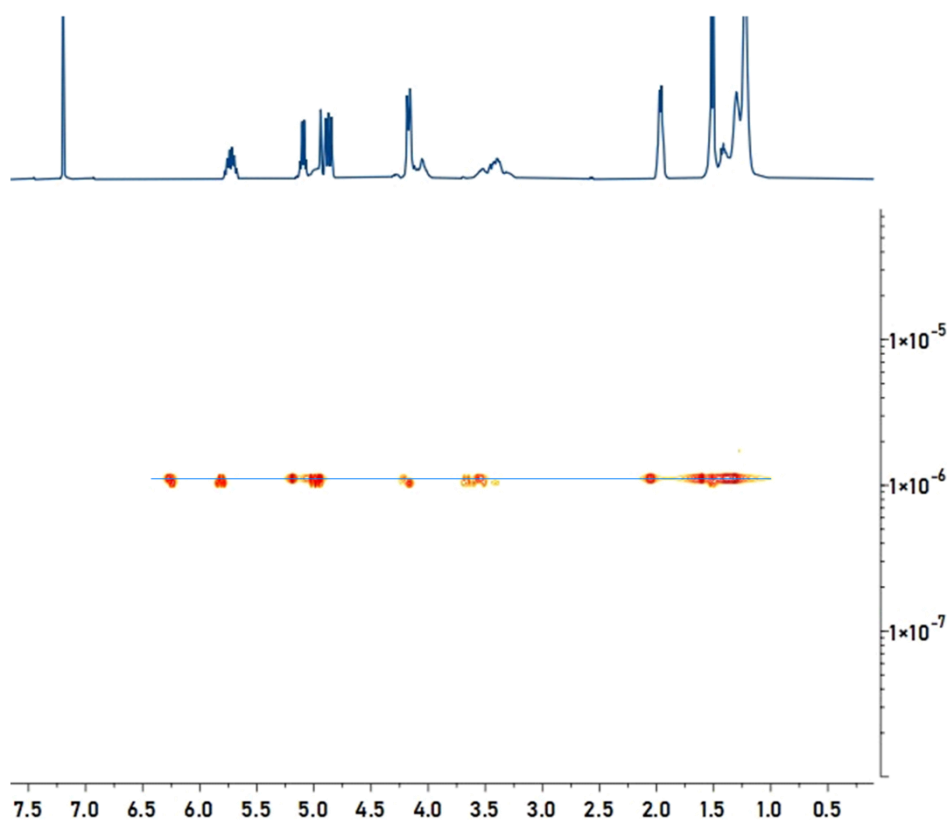


Figure S8.3.14: DOSY NMR spectrum of **P10-PLLA** (Table 3.1, **P10-PLLA**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [MA] : [LA] : [ED] = 1 : 50 : 50 : 546, 50 °C.

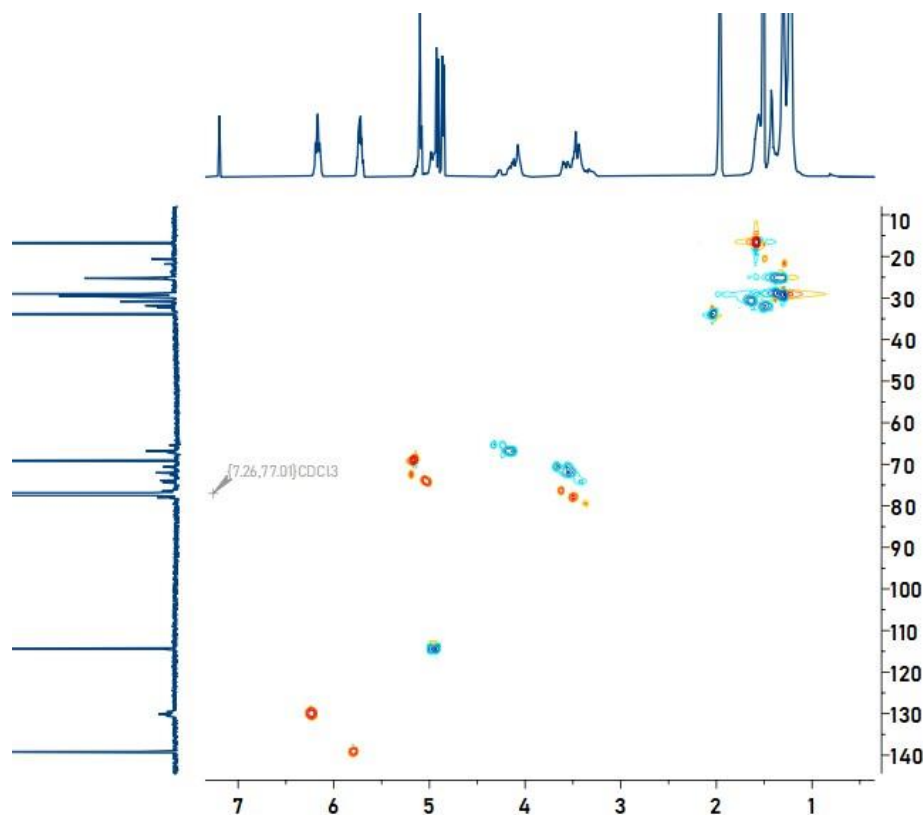


Figure S8.3.15: HSQC ^{13}C - $\{^1\text{H}\}$ NMR spectrum of **P10-PLLA** (Table 3.1, **P10-PLLA**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [MA] : [LA] : [ED] = 1 : 50 : 50 : 546, 50 °C.

8.3.1.1.4 NMR Spectra for P10-PLLA*

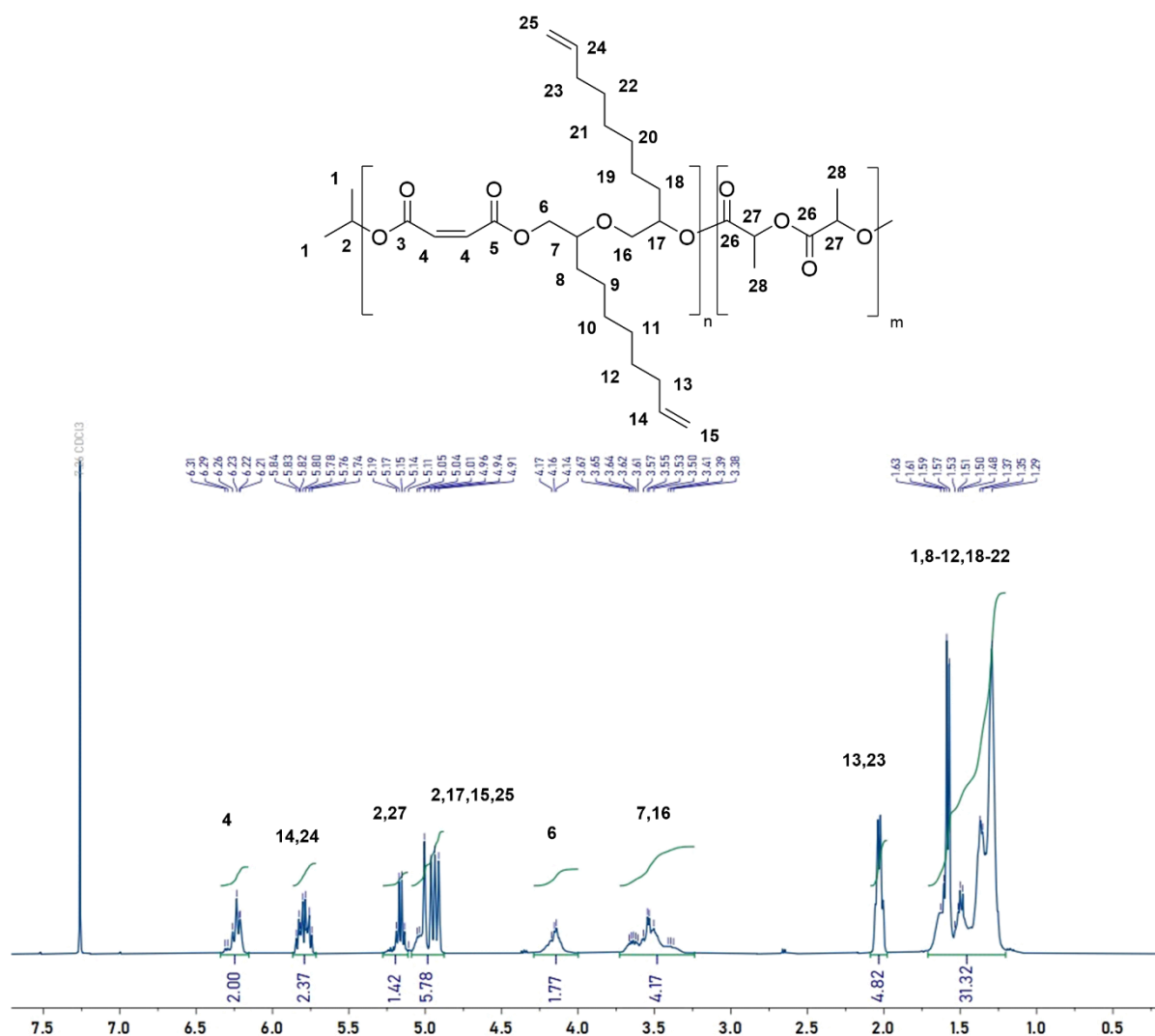


Figure S8.3.16: ¹H NMR spectrum of **P10-PLLA*** (with assignment, Table 3.1, **P10-PLLA***) (400 MHz, CDCl₃)
 Reaction conditions: [1] = 10 mM in 1 mL epoxide, [Cat] : [MA] : [LA] : [ED] = 1 : 50 : 50 : 546, 50 °C.

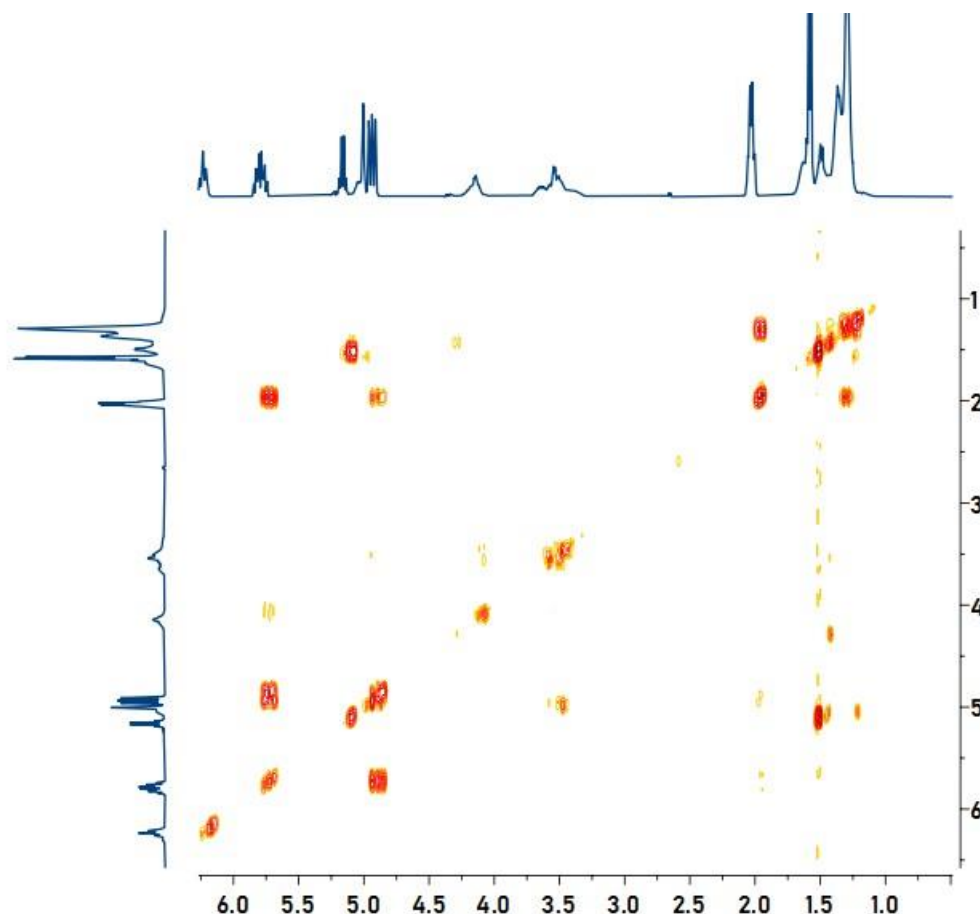


Figure S8.3.17: ^1H COSY NMR spectrum of **P10-PLLA*** (Table 3.1, **P10-PLLA***) (400 MHz, CDCl_3). Reaction conditions: $[\mathbf{1}] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{MA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

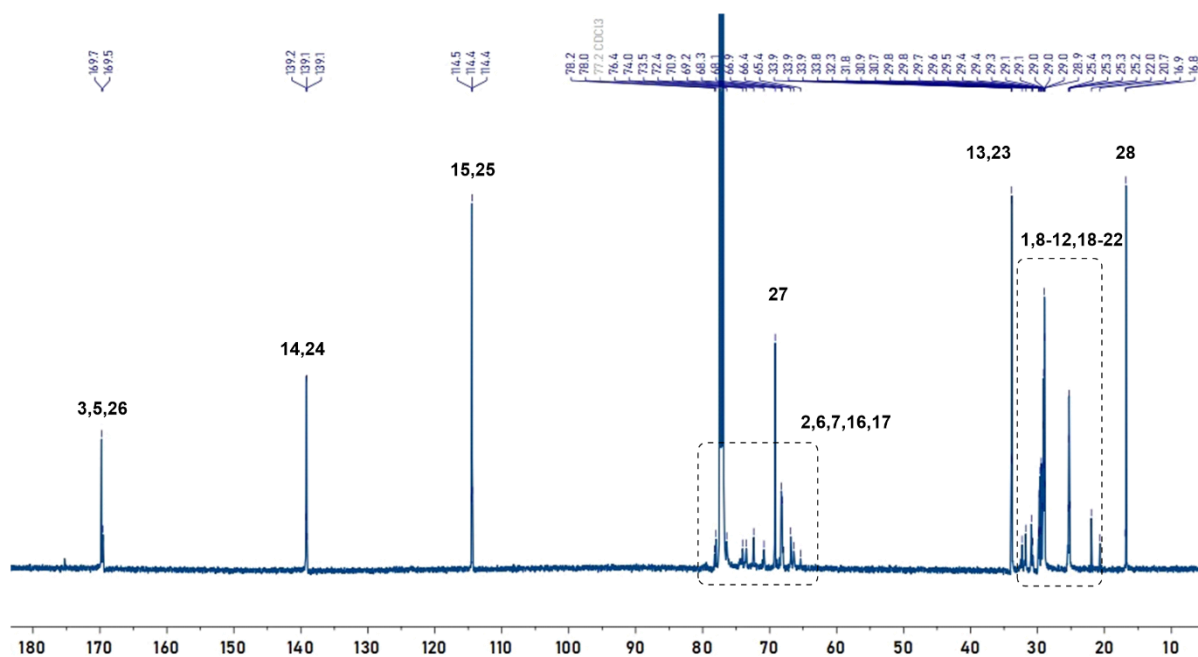


Figure S8.3.18: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P10-PLLA*** (Table 3.1) (151 MHz, CDCl_3). Reaction conditions: $[\mathbf{1}] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{MA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

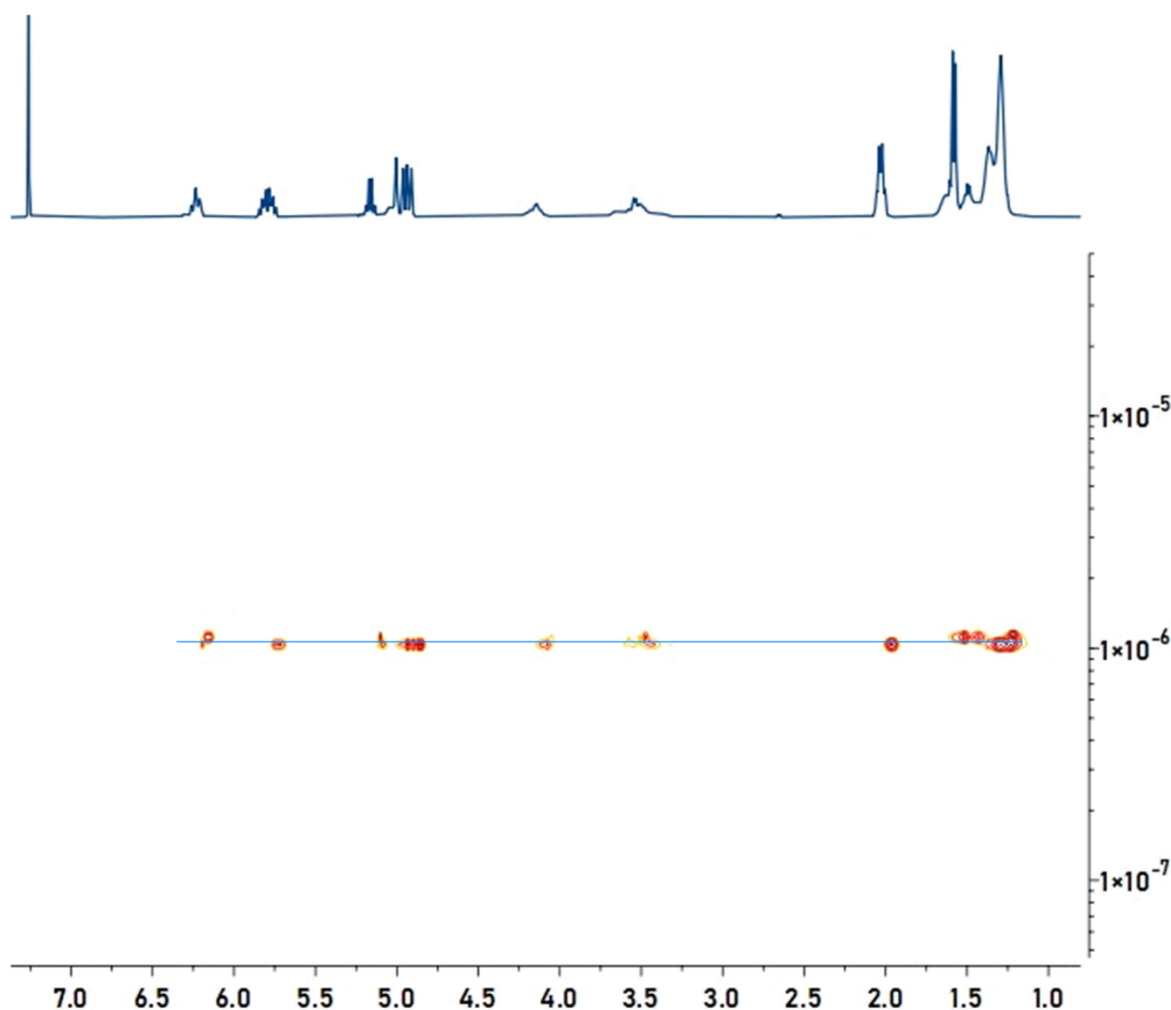


Figure S8.3.19: DOSY NMR spectrum of **P10-PLLA*** (Table 3.1, **P10-PLLA***) (500 MHz, CDCl_3). Reaction conditions: $[1] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{MA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

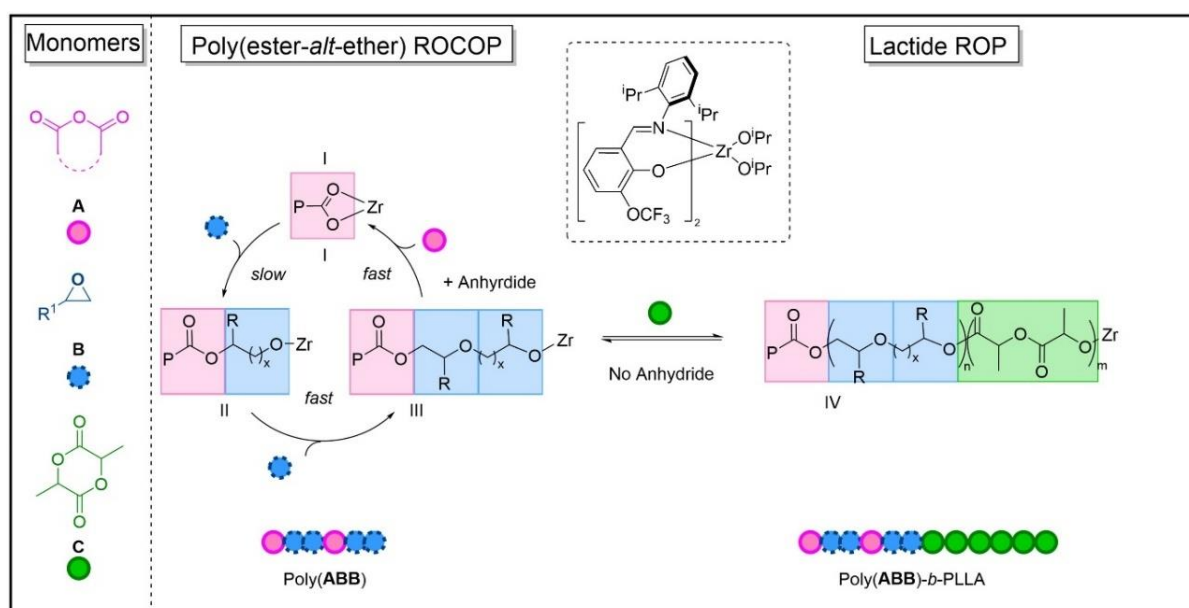


Figure S8.3.20: Illustration of 'switch' catalysis between poly(ester-alt-ether) ROCOP and Lactide ROP.

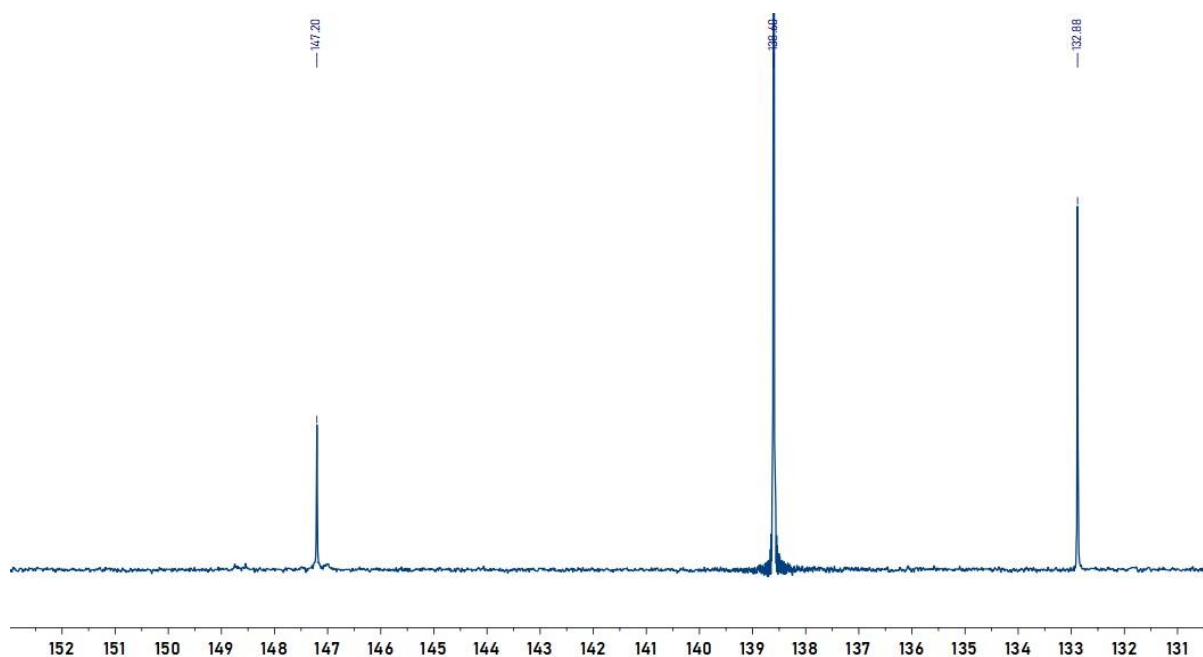


Figure S8.3.23: $^{31}\text{P}\{^1\text{H}\}$ NMR end-group analysis of **P10-PLLA*** diblock copolymer synthesised through switch catalysis using catalyst **1**. The spectrum was obtained from the reaction **P10-PLLA*** with tetramethylethylene chlorophosphite (162 MHz, CDCl_3). The major polymer resonance at 147.2 ppm is characteristic of a secondary alcohol polymer end-group, respectively, and is the only polymer peak observed.¹

8.3.1.1.5 NMR Spectra for P13

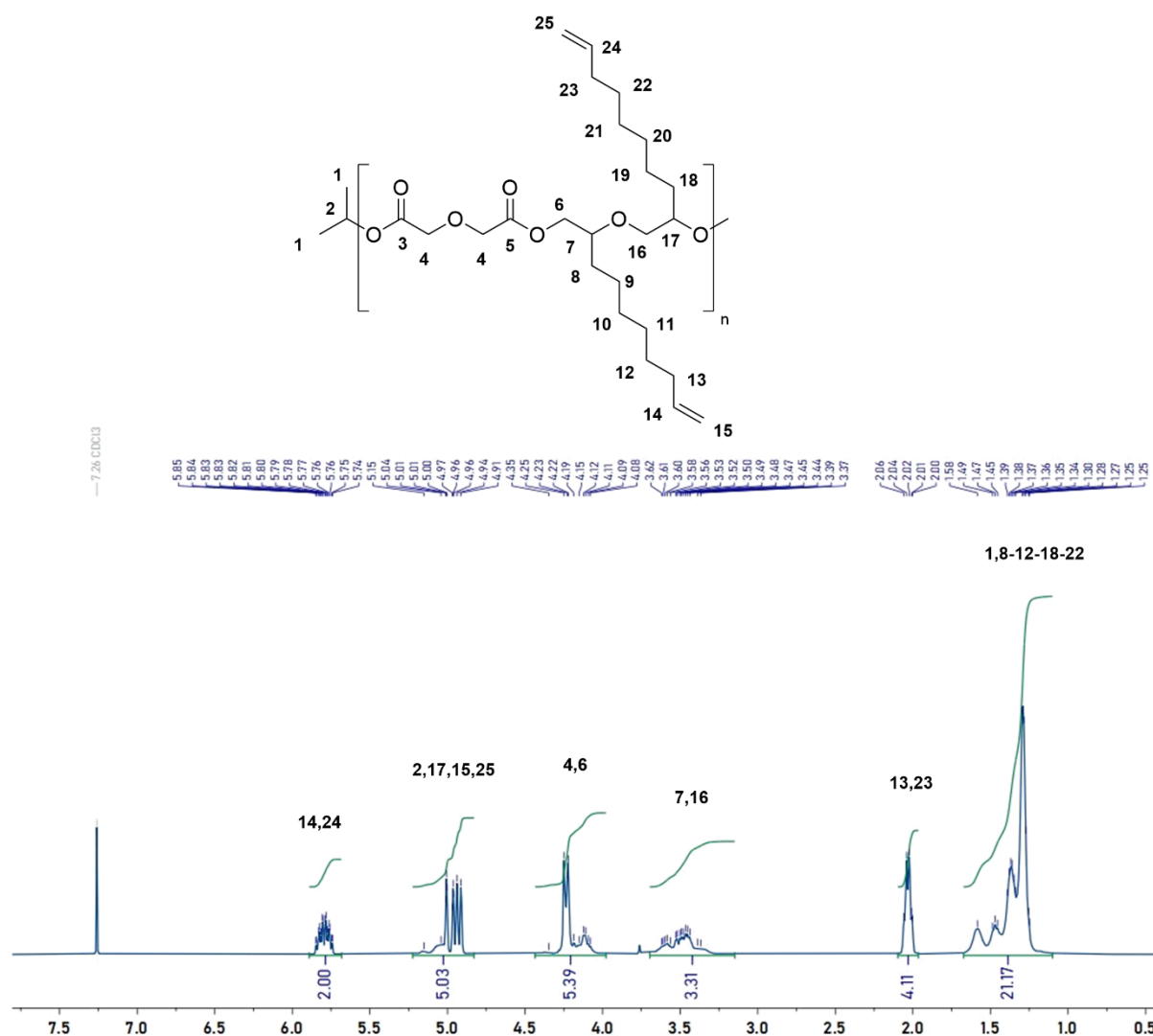


Figure S8.3.24: ^1H NMR spectrum of **P13** (with assignment, Table 3.1, **P13**) (400 MHz, CDCl_3). Reaction conditions: $[1] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{DGA}] : [\text{ED}] = 1 : 50 : 546$, 50°C .

From crude ^1H NMR aliquots, it was evident that all of the DGA monomer was consumed, as evidenced by the loss of the singlet at 4.43 ppm. In order to calculate the DP of DGA, it was assumed that both OⁱPr ligands initiate polymerisation, i.e. DP= 25. The DP of epoxide was calculated by normalising the signal from the internal vinylic proton (14 and 24) to 2. The combined signals from protons 17,15,25 at 5 ppm, the combined signals of 4 and 6 between 4 and 4.4 ppm, and the combined signals of 7 and 16 between 3.18 and 3.7 ppm, were added, to give the total signal in this region. From this the total number of epoxide protons were taken away (10), to give a signal of for the 4 PDGA protons. This was then divided by 4

to get the signal arising from the DGA proton. The ratio of epoxide : anhydride, from signal 14,24 : 4, was then used to establish the epoxide DP.

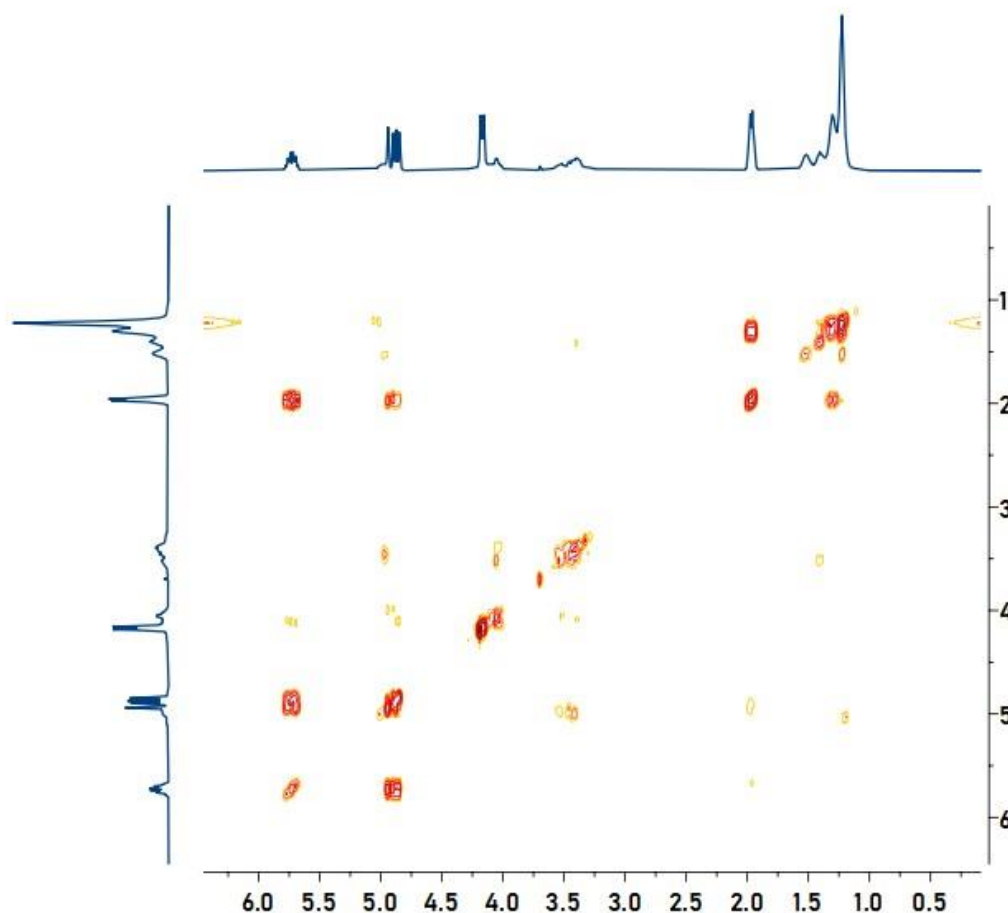


Figure S8.3.25: ^1H COSY NMR spectrum of **P13** (Table 3.1, **P13**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [ED] = 1 : 50 : 546, 50 °C.

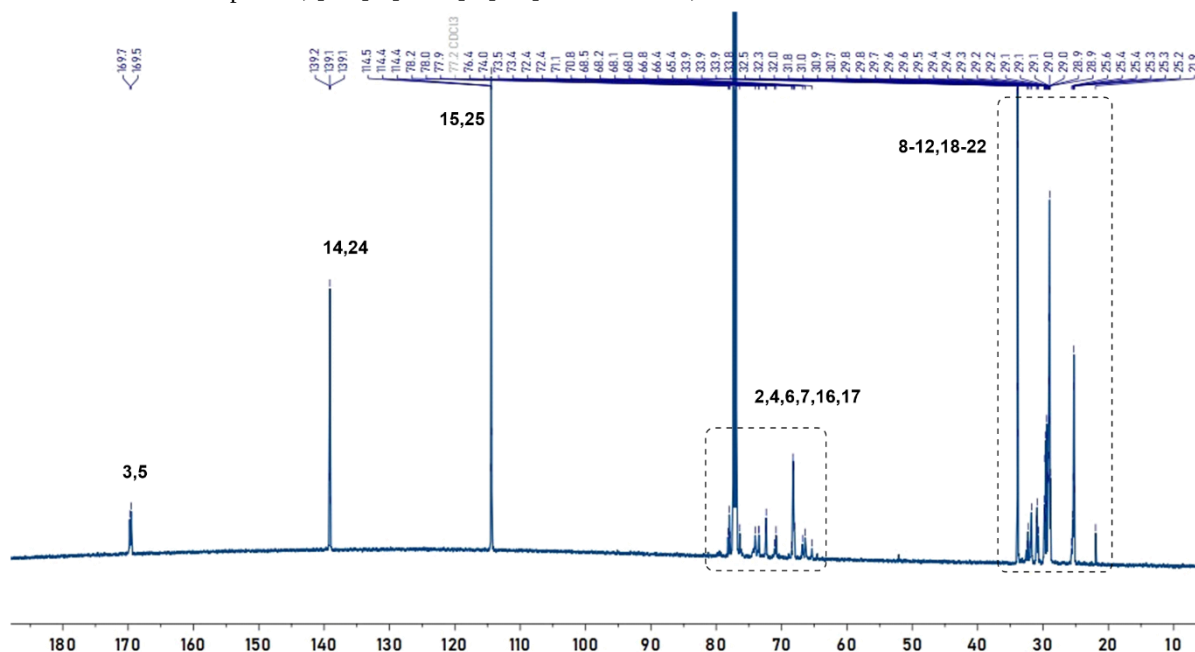


Figure S8.3.26: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P13** (Table 1, **P13**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [ED] = 1 : 50 : 546, 50 °C.

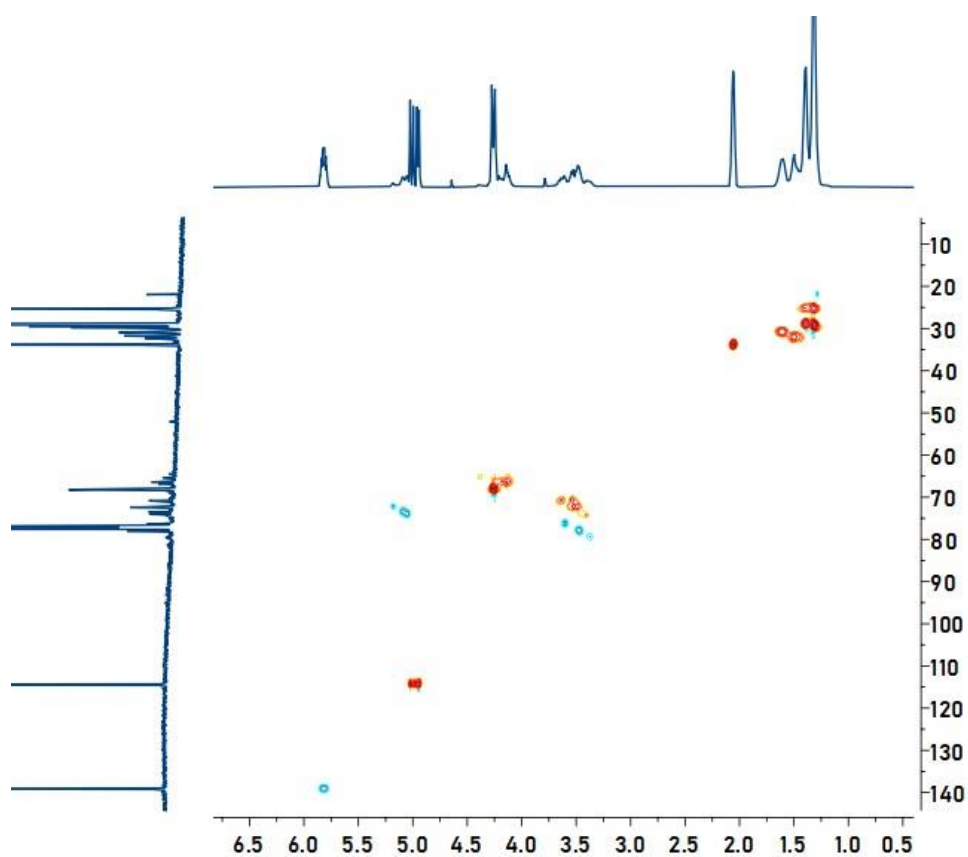


Figure S8.3.27: (^1H , ^{13}C) HSQC NMR spectrum of **P13** (Table 3.1, **P13**) (CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[ED]** = 1 : 50 : 546, 50 °C.

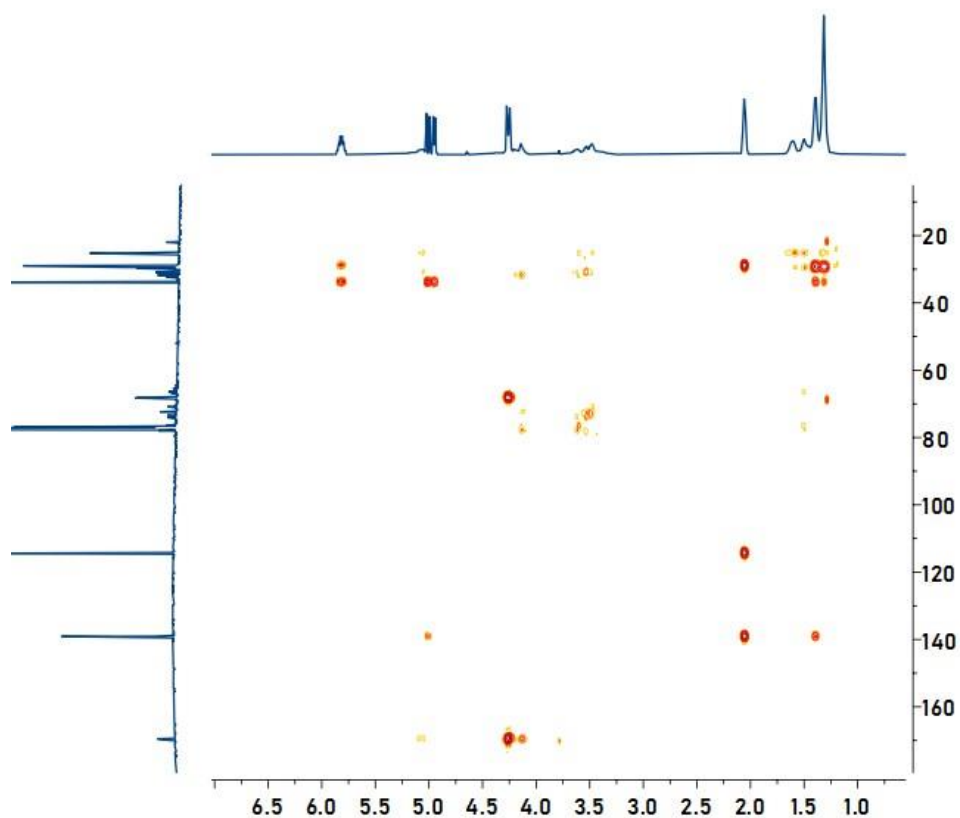


Figure S8.3.28: (^1H , ^{13}C)-HMBC NMR spectrum of **P13** (Table 3.1, **P13**) (CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[ED]** = 1 : 50 : 546, 50 °C.

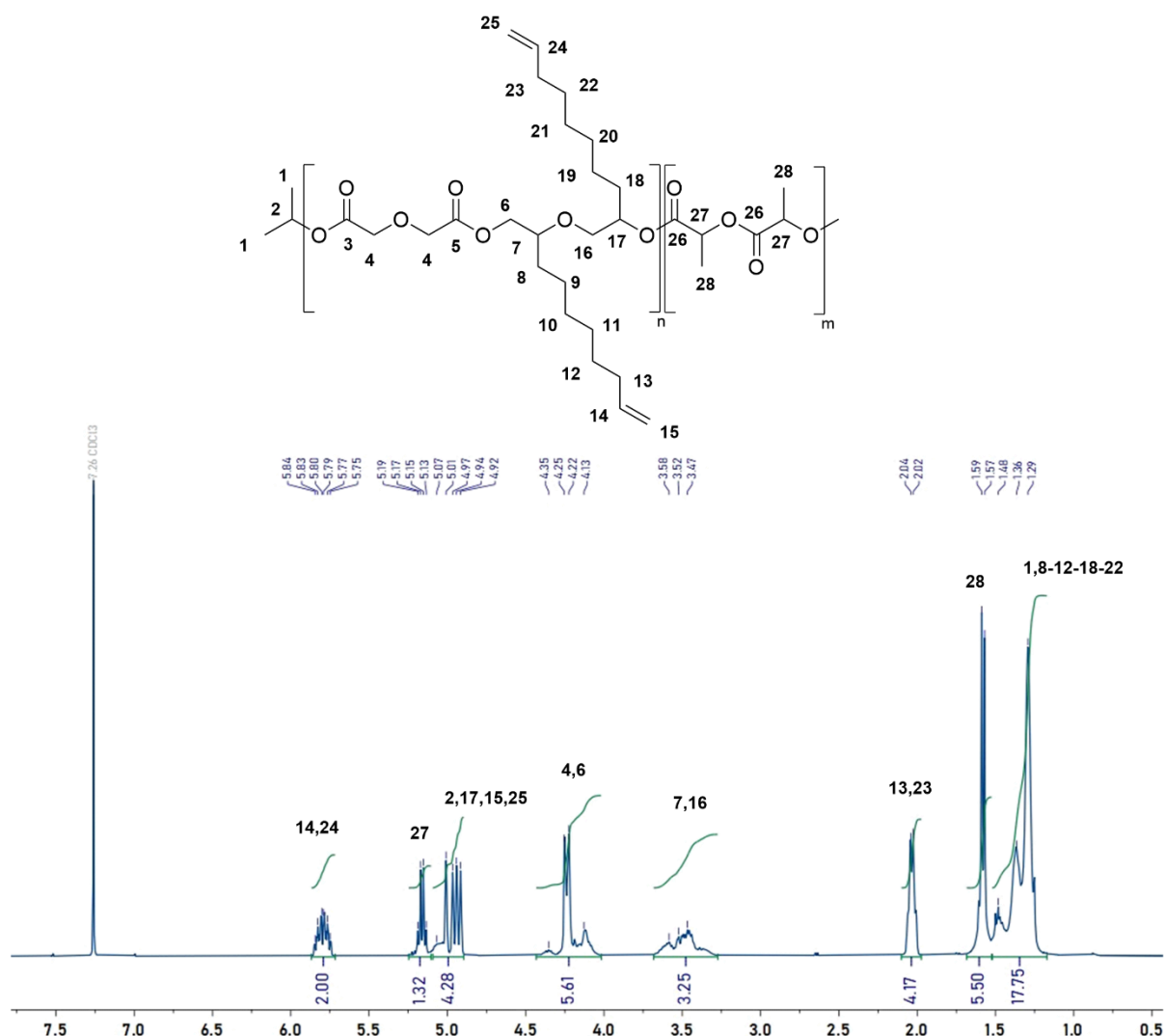
8.3.1.1.6 NMR Spectra for P13₂₅-PLLA₂₃

Figure S8.3.29: ^1H NMR spectrum of **P13₂₅-PLLA₂₃** (with assignment, Table 3.1, **P13₂₅-PLLA₂₃**) (400 MHz, CDCl_3). Reaction conditions: $[1] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{DGA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

From crude ^1H NMR aliquots, it was evident that all of the DGA monomer was consumed, as evidenced by the loss of the singlet at 4.43 ppm. In order to calculate the DP of DGA, it was assumed that both OⁱPr ligands initiate polymerisation, i.e. DP= 25. The DP of epoxide was calculated by normalising the signal from the internal vinylic proton (14 and 24) to 2. The combined signals from protons 17,15,25 at 5 ppm, the combined signals of 4 and 6 between 4 and 4.4 ppm, and the combined signals of 7 and 16 between 3.18 and 3.7 ppm, were added, to give the total signal in this region. From this the total number of epoxide protons were taken away (10), to give a signal of for the 4 PDGA protons from signal 4. This was then divided by 4 to get the signal for a DGA proton. The DP of epoxide was then determined from

the ratio of the signals 14,24 : 4. The DP of PLLA was obtained by ratio of the integral of resonance 27 from PLLA, against the integral for the DGA resonance 4.

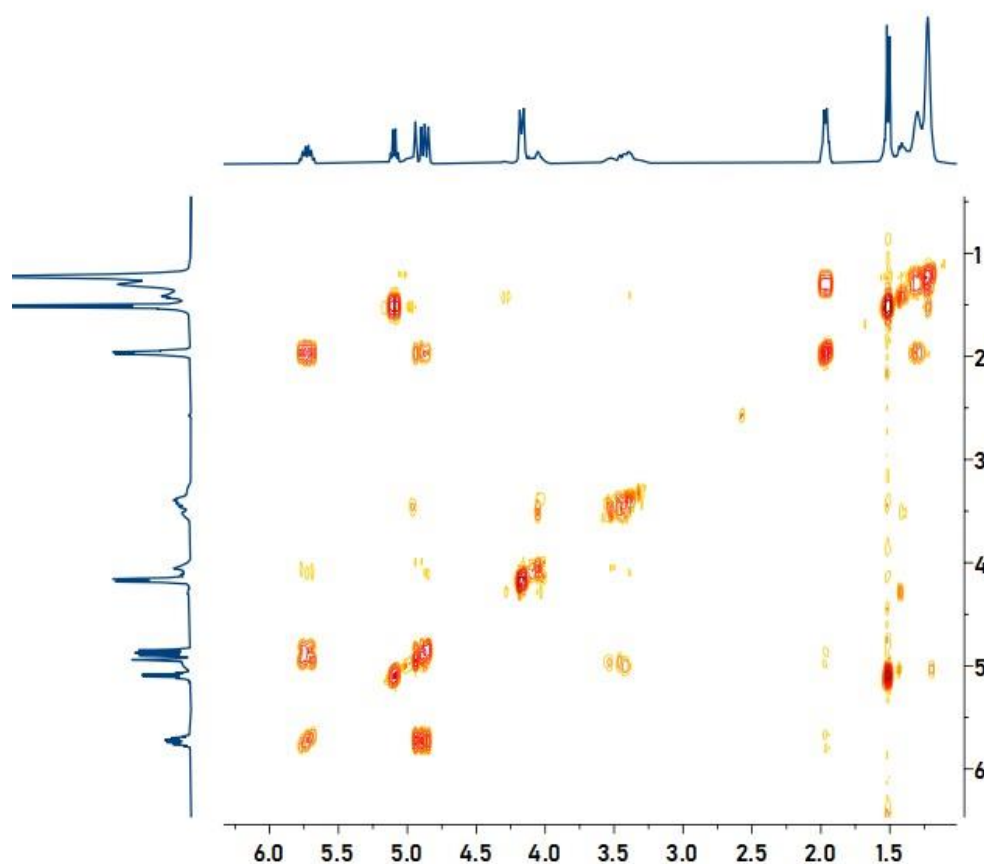


Figure S8.3.30: ^1H COSY NMR spectrum of **P13₂₅-PLLA₂₃** (Table 3.1, **P13₂₅-PLLA₂₃**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 50 : 546, 50 °C.

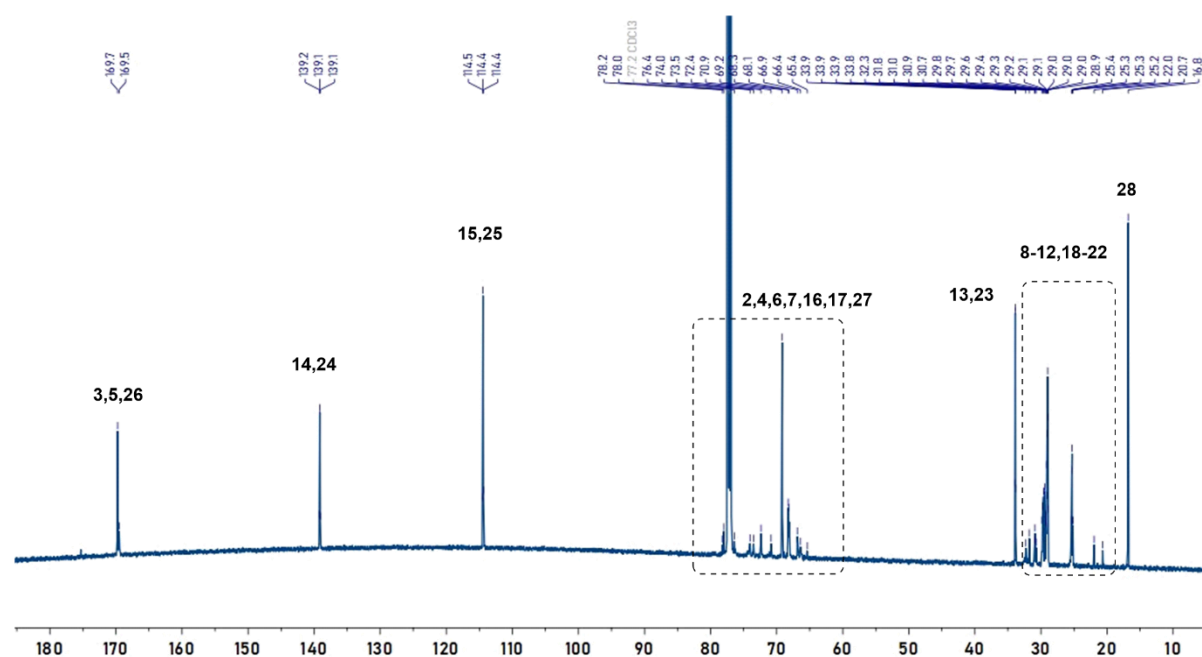


Figure S8.3.31: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P13₂₅-PLLA₂₃** (Table 3.1, **P13₂₅-PLLA₂₃**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 50 : 546, 50 °C.

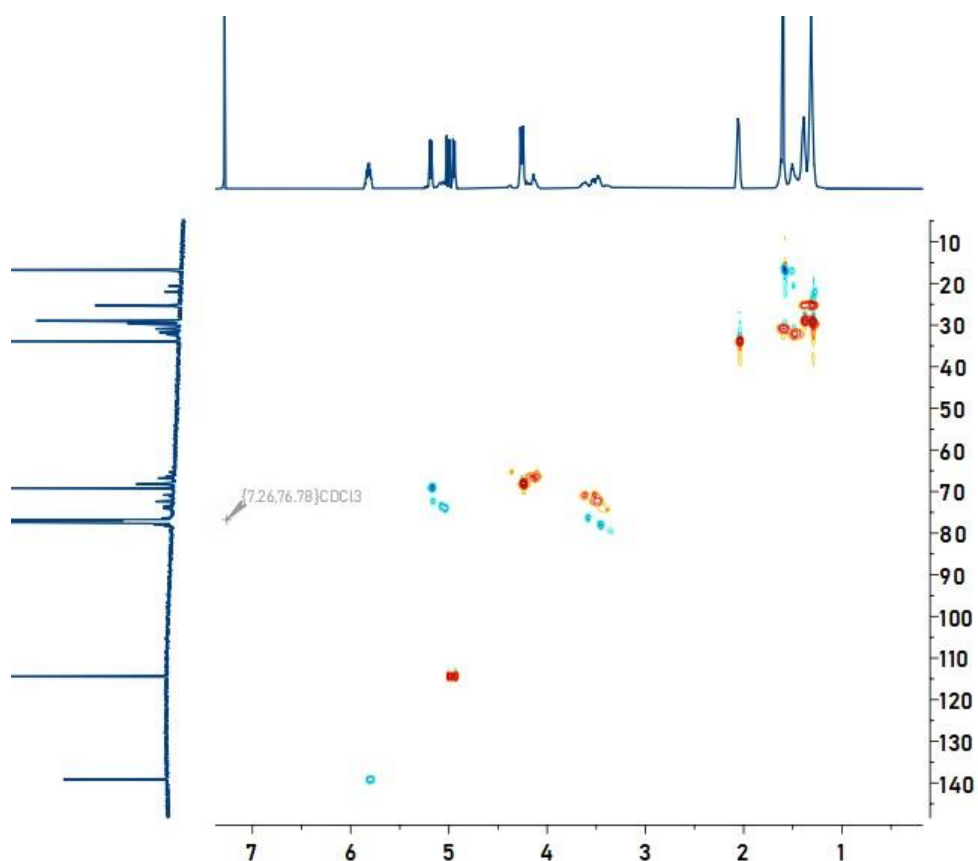


Figure S8.3.32: HSQC (^1H , ^{13}C) NMR spectrum of **P13₂₅-PLLA₂₃** (Table 3.1, **P13₂₅-PLLA₂₃**) (CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 50 : 546, 50 °C.

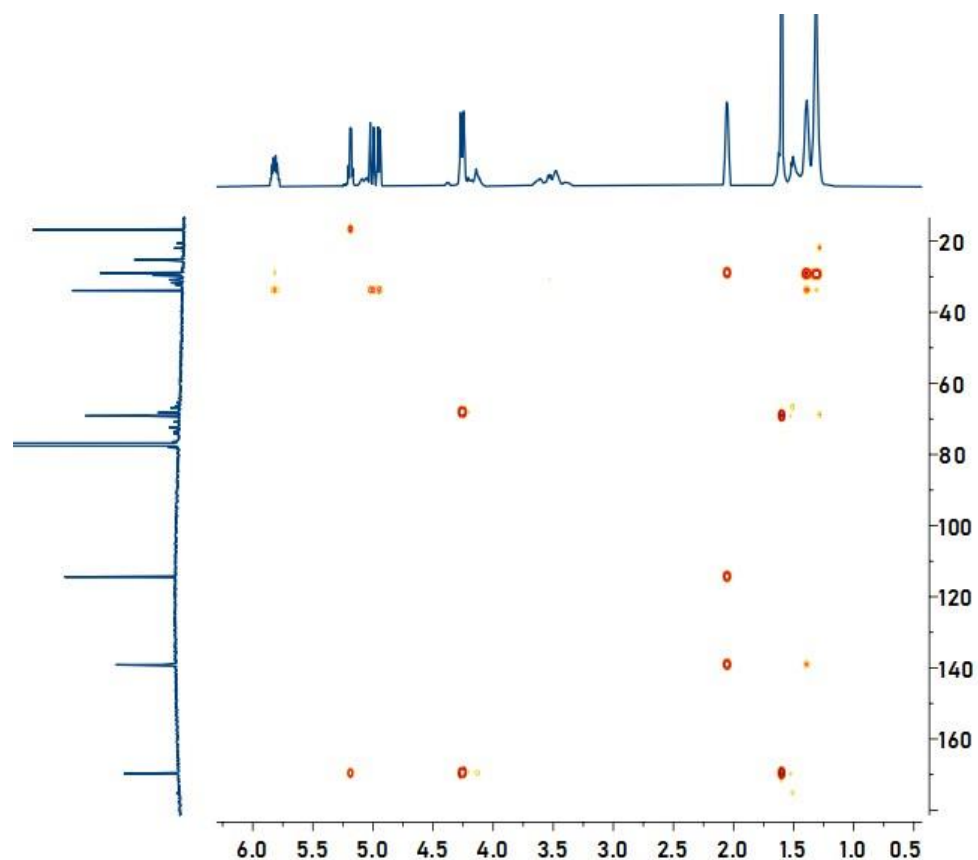


Figure S8.3.33: HMBC (^1H , ^{13}C) NMR spectrum of **P13₂₅-PLLA₂₃** (Table 3.1, **P13₂₅-PLLA₂₃**) (CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 50 : 546, 50 °C.

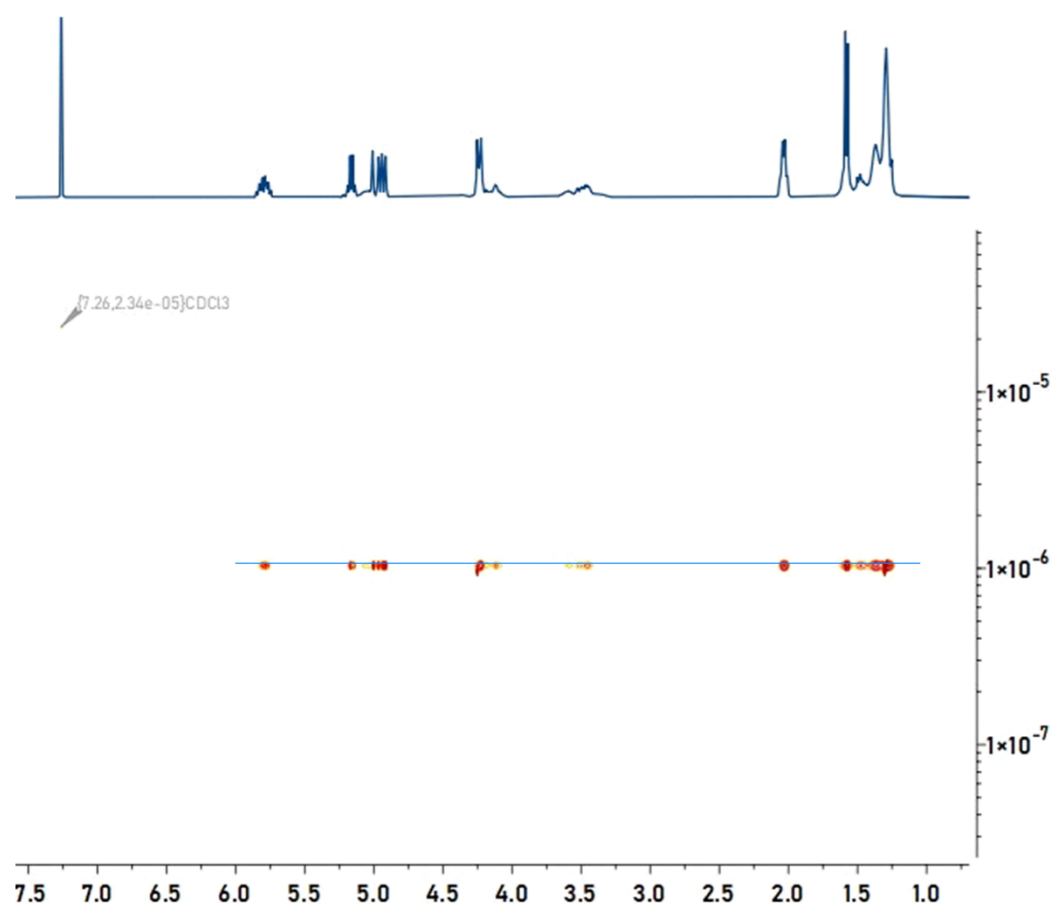


Figure S8.3.34: DOSY NMR spectrum of **P13₂₅-PLLA₂₃** (Table 3.1, **P13₂₅-PLLA₂₃**) (500 CDCl_3). Reaction conditions: $[\mathbf{1}] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{DGA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 50 : 546$, 50°C .

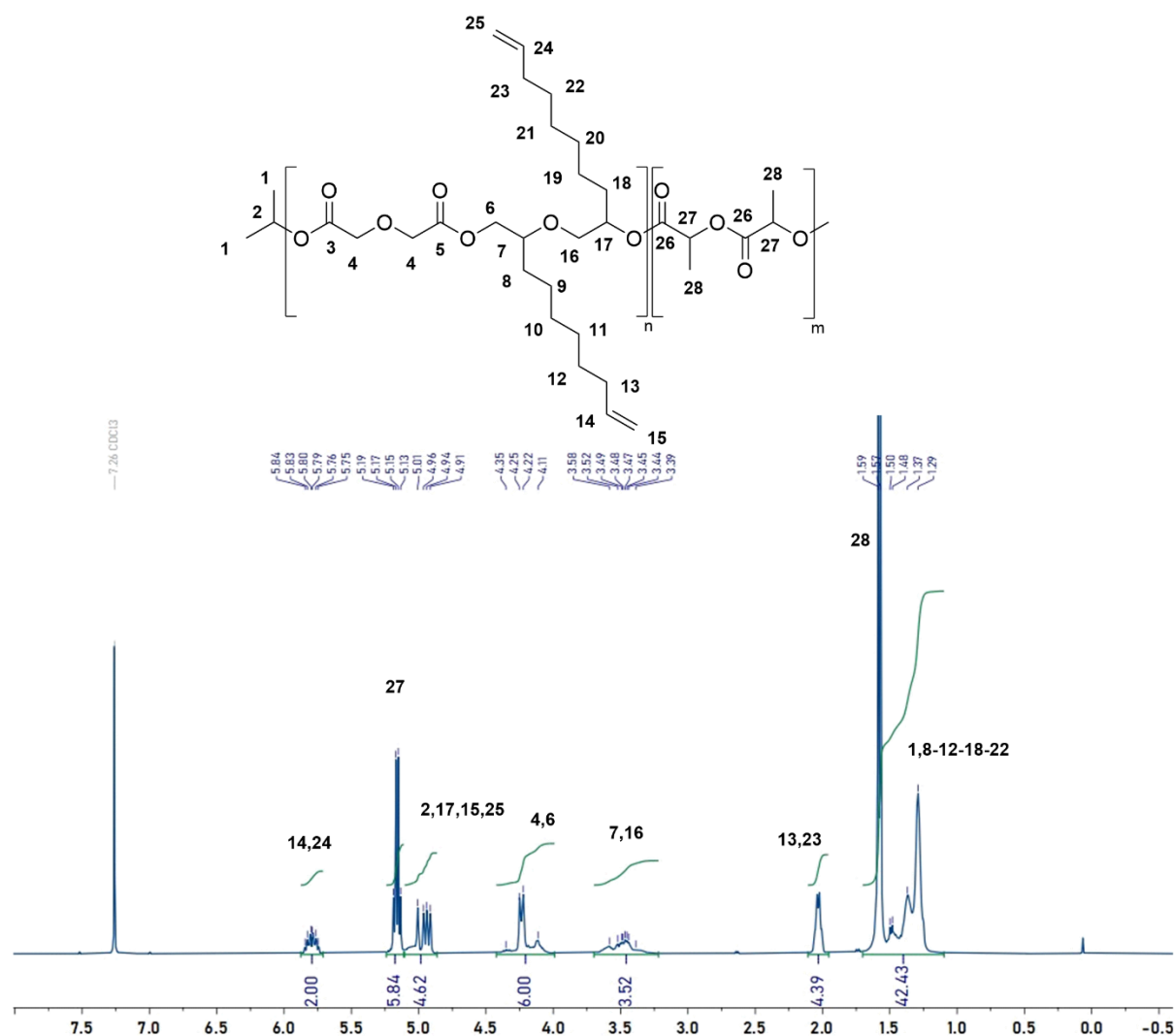
8.3.1.1.7 NMR Spectra for **P13₂₅-PLLA₆₈**

Figure S8.3.35: ¹H NMR spectrum of **P13₂₅-PLLA₆₈** (with assignment, Table 3.1, **P13₂₅-PLLA₆₈**) (400 MHz, CDCl₃). Reaction conditions: [**1**] = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 150 : 546, 50 °C.

The DP was calculated as per Section 8.3.1.1.6 ‘NMR Spectra for **P13₂₅-PLLA₂₃**’.

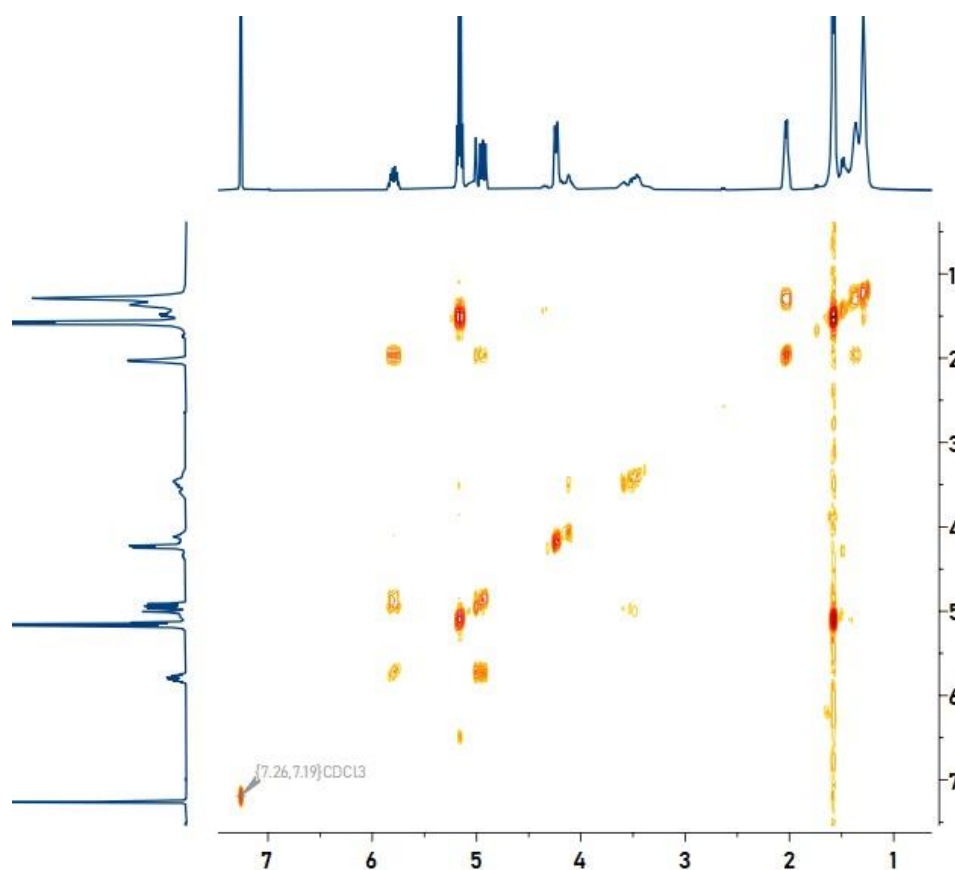


Figure S8.336: ^1H COSY NMR spectrum of **P13₂₅-PLLA₆₈** (Table 3.1, **P13₂₅-PLLA₆₈**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 150 : 546, 50 °C.

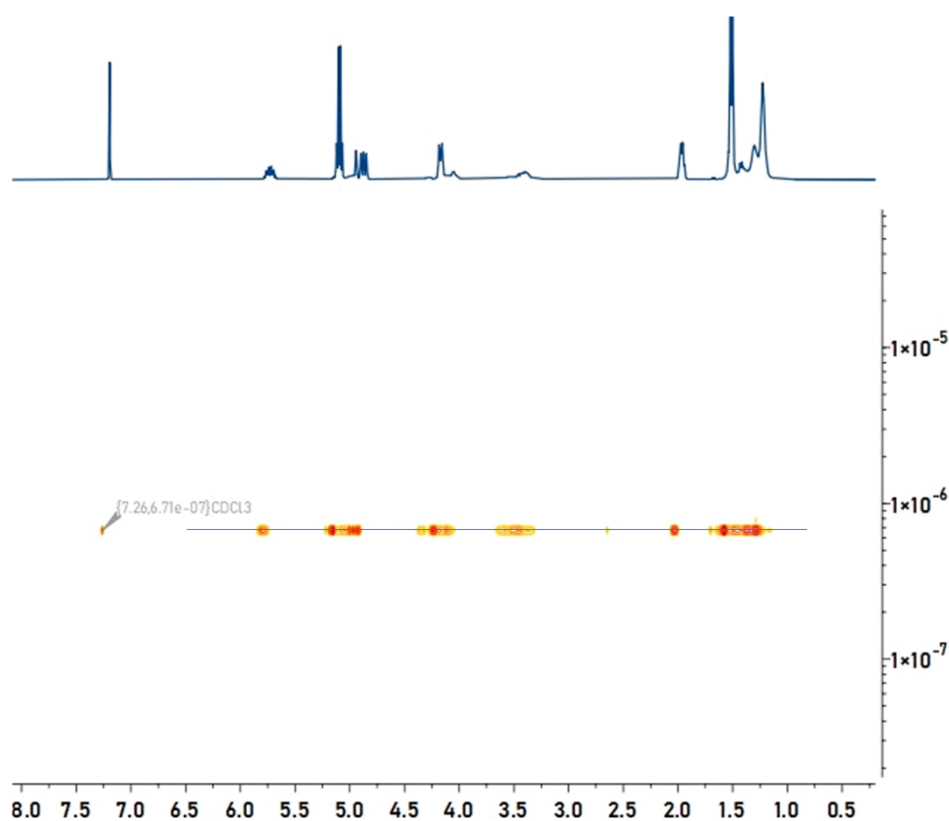


Figure S8.337: DOSY NMR spectrum of **P13₂₅-PLLA₆₈** (Table 3.1, **P13₂₅-PLLA₆₈**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 150 : 546, 50 °C.

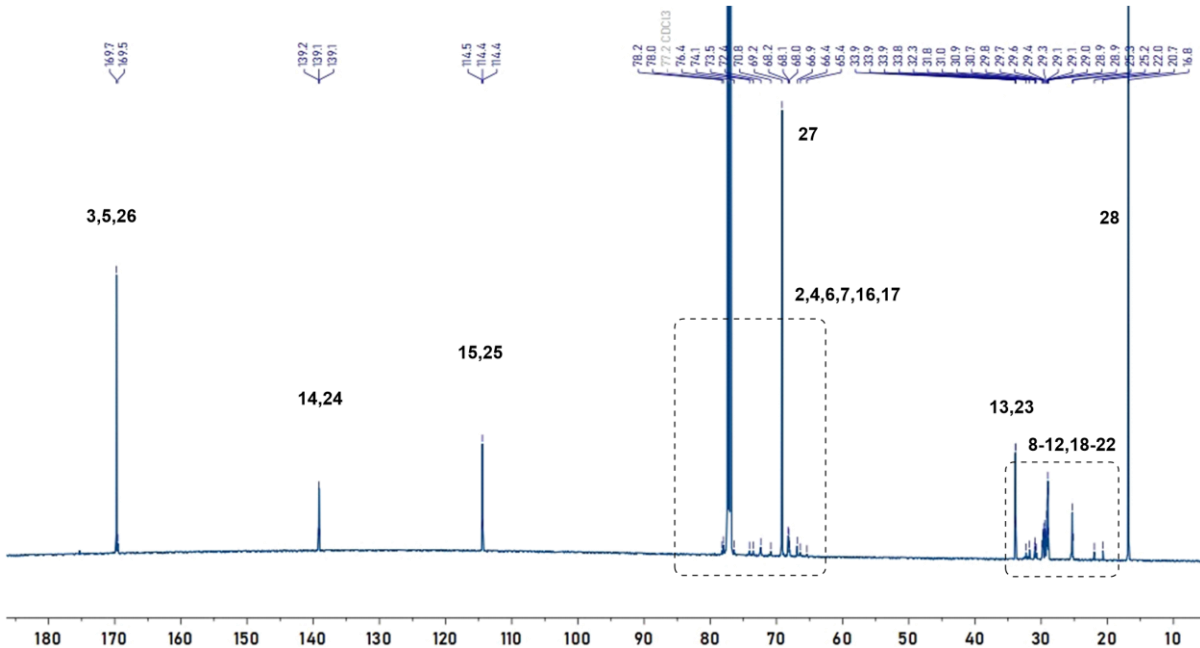


Figure S8.3.38: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P13₂₅-PLLA₆₈** (Table 3.1, **P13₂₅-PLLA₆₈**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 50 : 150 : 546, 50 °C.

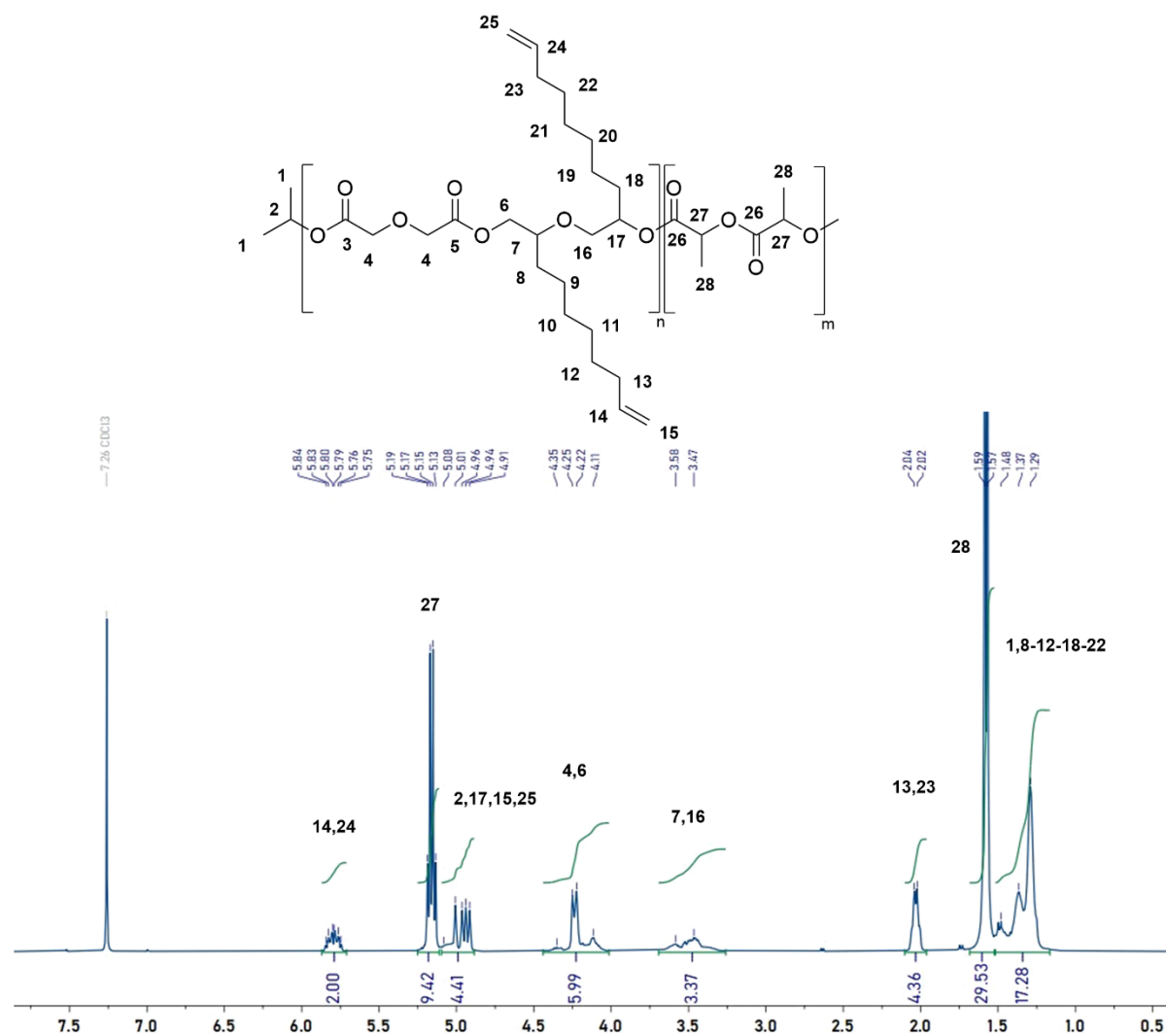
8.3.1.1.8 NMR Spectra for **P13₂₅-PLLA₁₂₅**

Figure S8.3.39: ^1H NMR spectrum of **P13₂₅-PLLA₁₂₅** (with assignment, Table 3.1, **P13₂₅-PLLA₁₂₅**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 50 : 250 : 546, 50 $^\circ\text{C}$.

The DP was calculated as per Section 8.3.1.1.6 ‘NMR Spectra for **P13₂₅-PLLA₂₃**’.

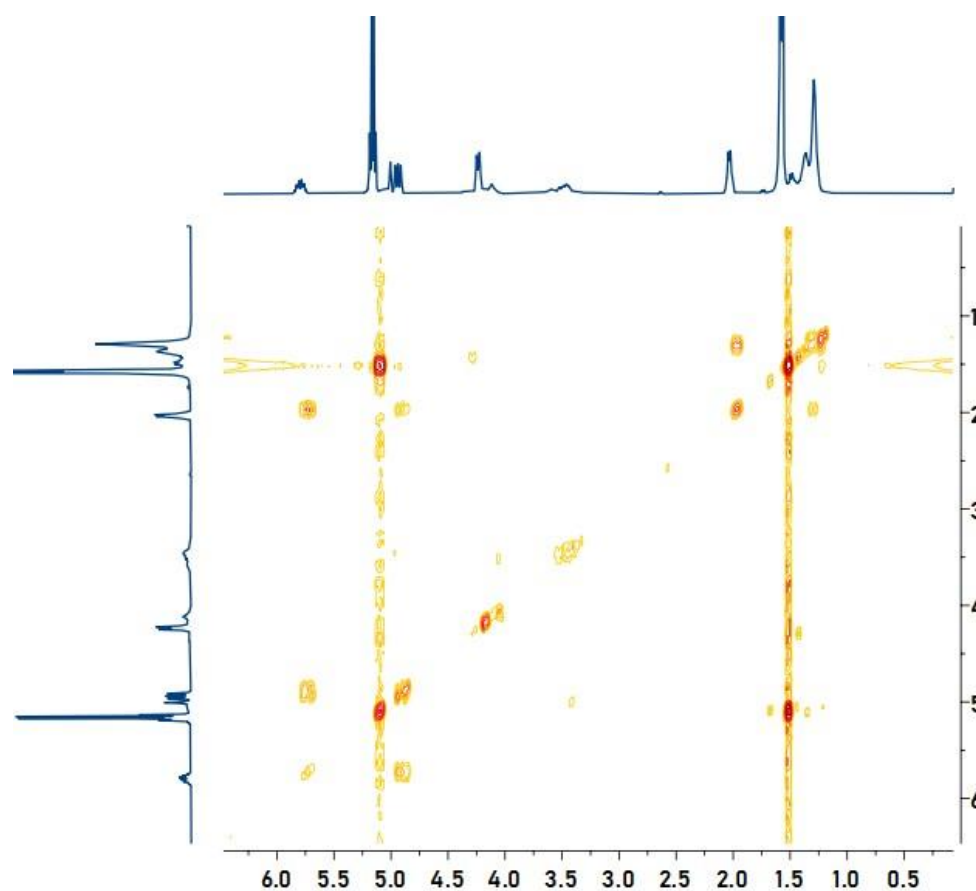


Figure S8.3.40: ^1H COSY NMR spectrum of **P13₂₅-PLLA₁₂₅** (Table 3.1, **P13₂₅-PLLA₁₂₅**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 250 : 546, 50 °C.

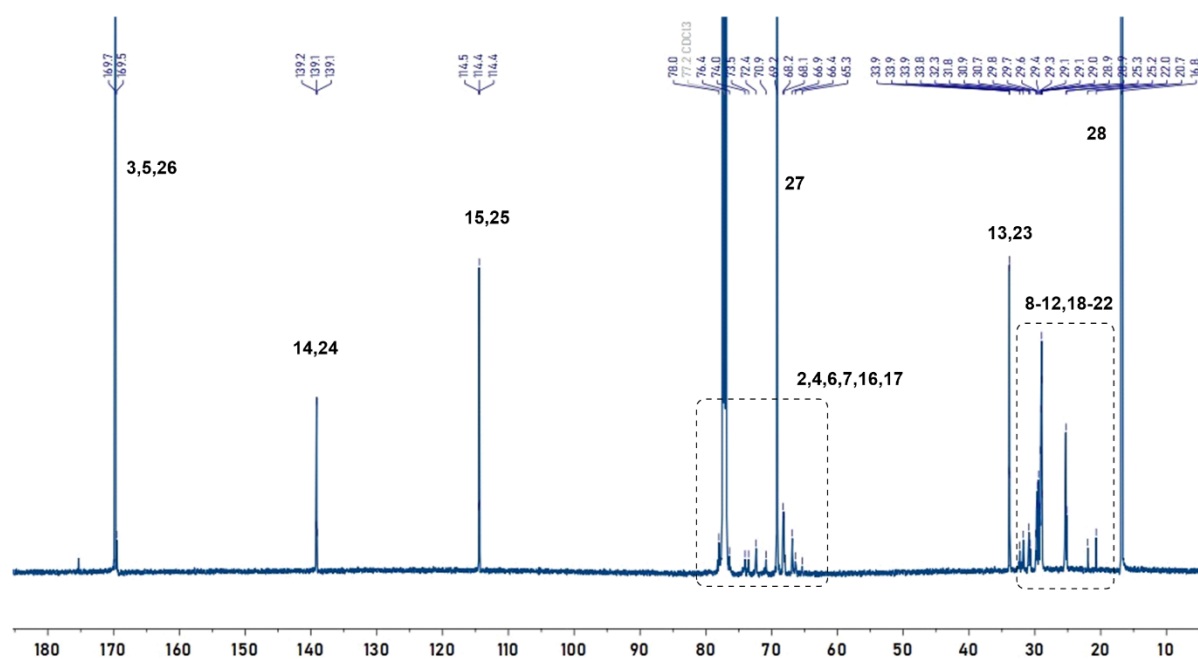


Figure S8.3.41: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P13₂₅-PLLA₁₂₅** (Table 3.1, **P13₂₅-PLLA₁₂₅**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 50 : 250 : 546, 50 °C.

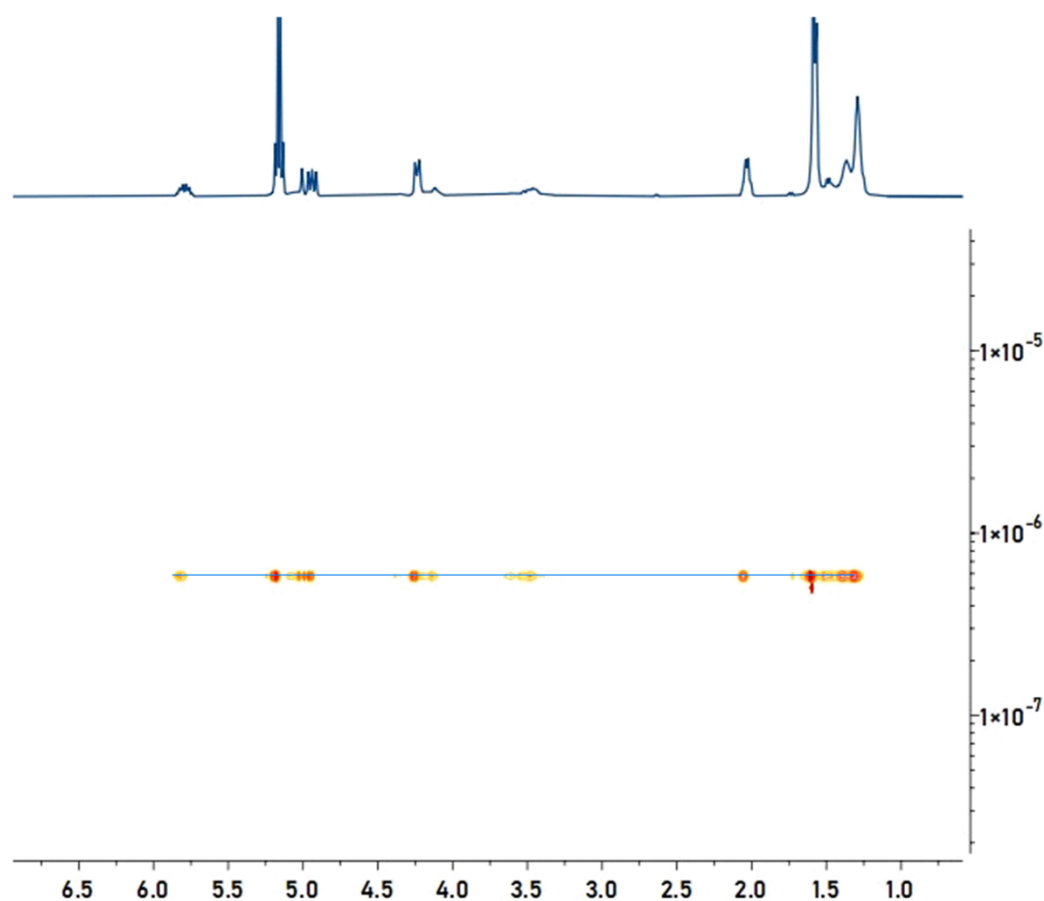


Figure S8.3.42: DOSY NMR spectrum of **P13₂₅-PLLA₁₂₅** (Table 3.1, **P13₂₅-PLLA₁₂₅**) (CDCl_3). Reaction conditions: $[\mathbf{1}] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{DGA}] : [\text{LA}] : [\text{ED}] = 1 : 50 : 250 : 546$, 50°C .

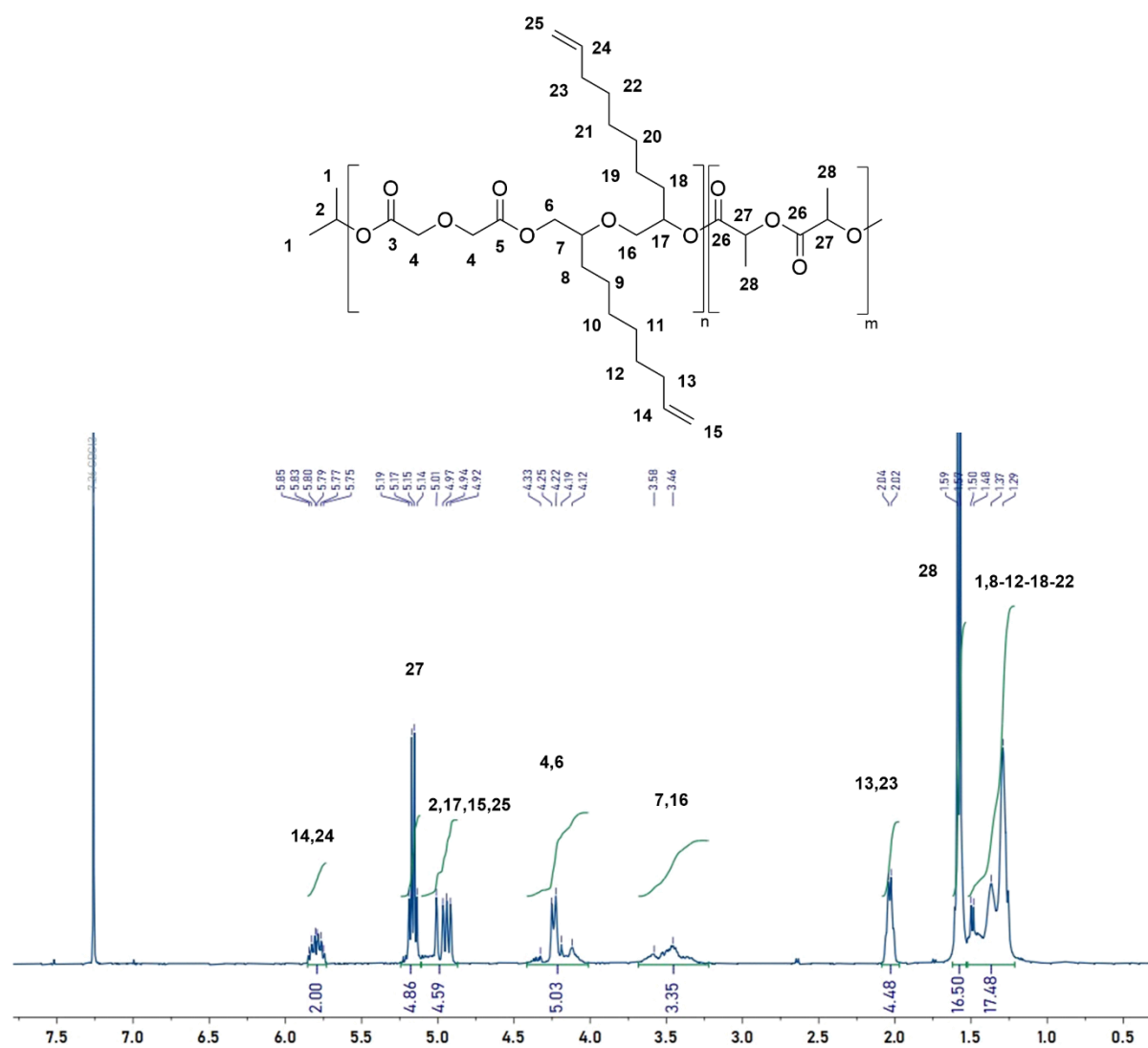
8.3.1.1.9 NMR Spectra for P138-PLLA₂₆

Figure S8.3.43: ^1H NMR spectrum of **P138-PLLA₂₆** (with assignment, Table 3.1, **P138-PLLA₂₆**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 15 : 50 : 546, 50 $^\circ\text{C}$.

The DP was calculated as per Section 8.3.1.1.6 ‘NMR Spectra for **P1325-PLLA₂₃**’.

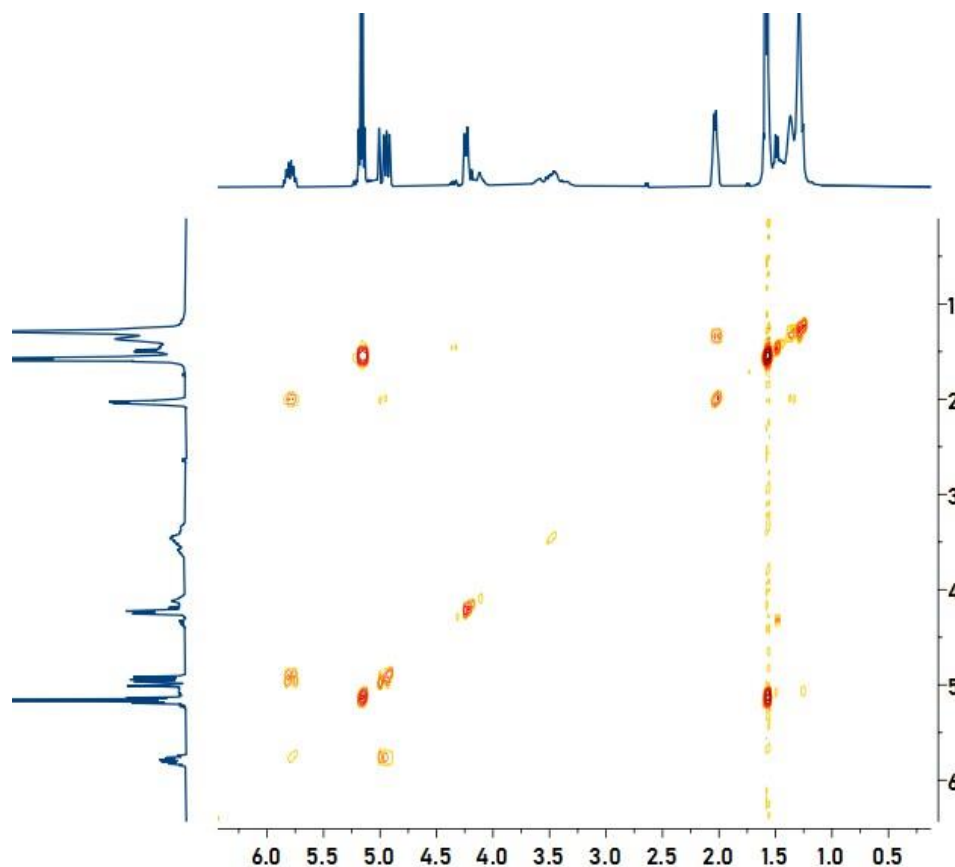


Figure S8.3.44: ^1H COSY NMR spectrum of **P138-PLLA₂₆** (Table 3.1, **P138-PLLA₂₆**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 15 : 50 : 546, 50 °C.

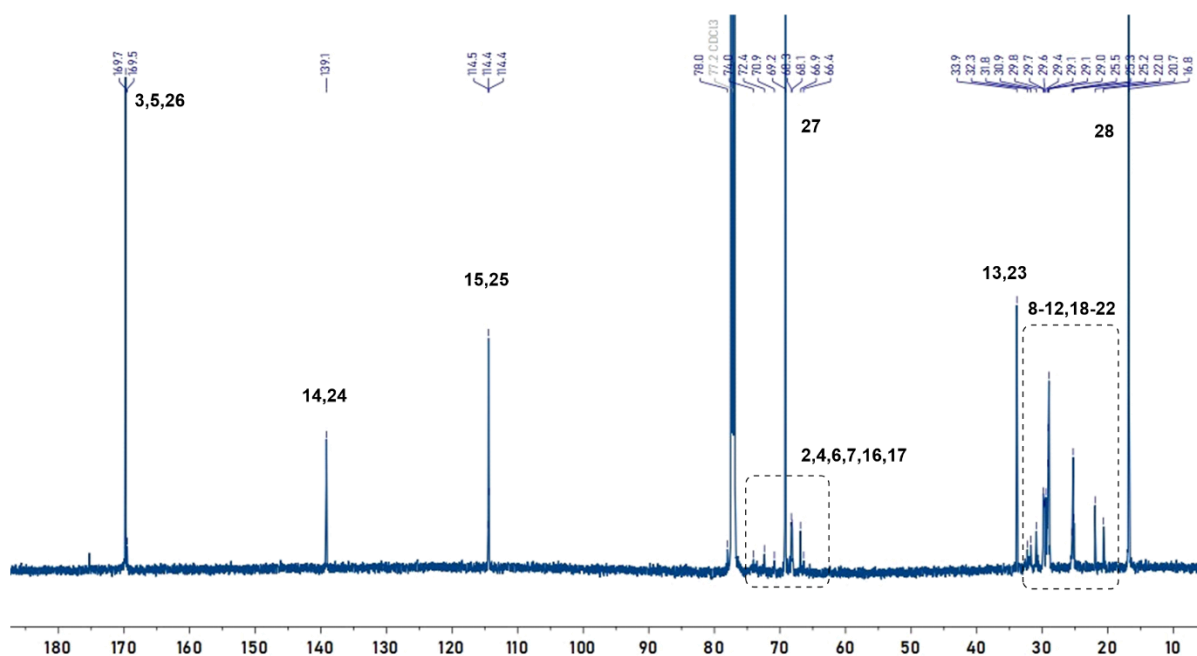


Figure S8.3.45: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P138-PLLA₂₆** (Table 3.1, **P138-PLLA₂₆**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 15 : 50 : 546, 50 °C.

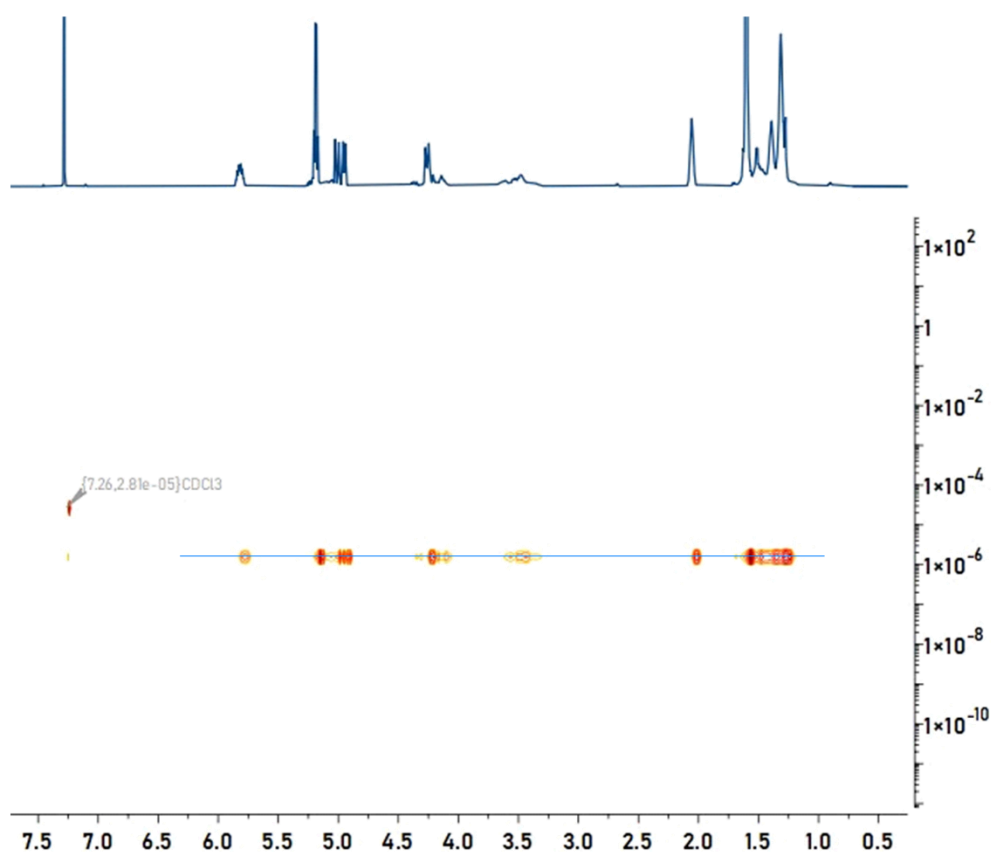


Figure S8.3.46: DOSY NMR spectrum of **P138-PLLA₂₆** (Table 3.1, **P138-PLLA₂₆**) (CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 15 : 50 : 546, 50 °C.

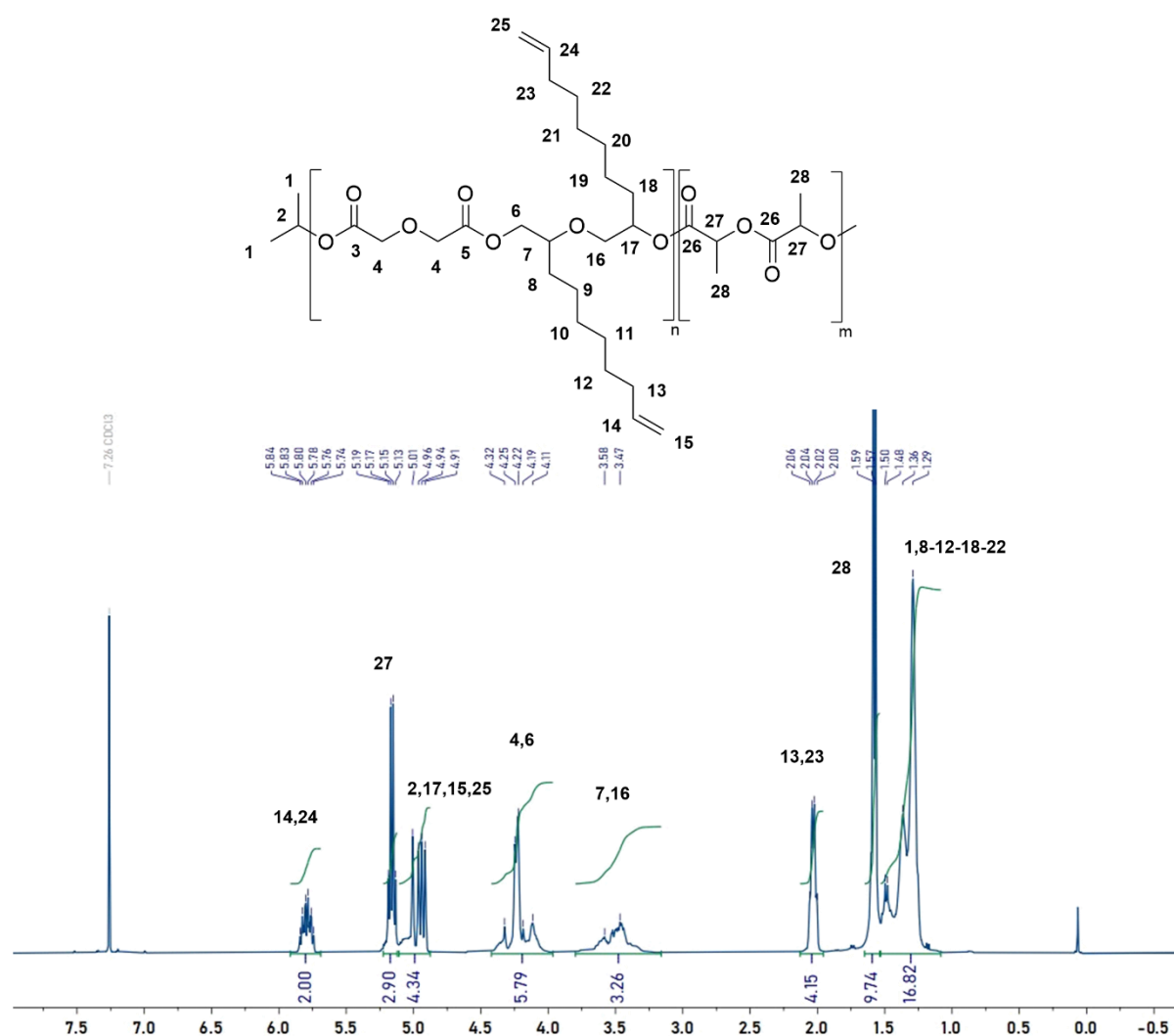
8.3.1.1.10 NMR Spectra for **P13₁₅-PLLA₂₇**

Figure S8.3.47: ^1H NMR spectrum of **P13₁₅-PLLA₂₇** (with assignment, Table 3.1, **P13₁₅-PLLA₂₇**) (400 MHz, CDCl_3). Reaction conditions: $[\mathbf{1}] = 10 \text{ mM}$ in 1 mL epoxide, $[\text{Cat}] : [\text{DGA}] : [\text{LA}] : [\text{ED}] = 1 : 30 : 50 : 546$, 50°C .

The DP was calculated as per Section 8.3.1.1.6 ‘NMR Spectra for **P13₂₅-PLLA₂₃**’.

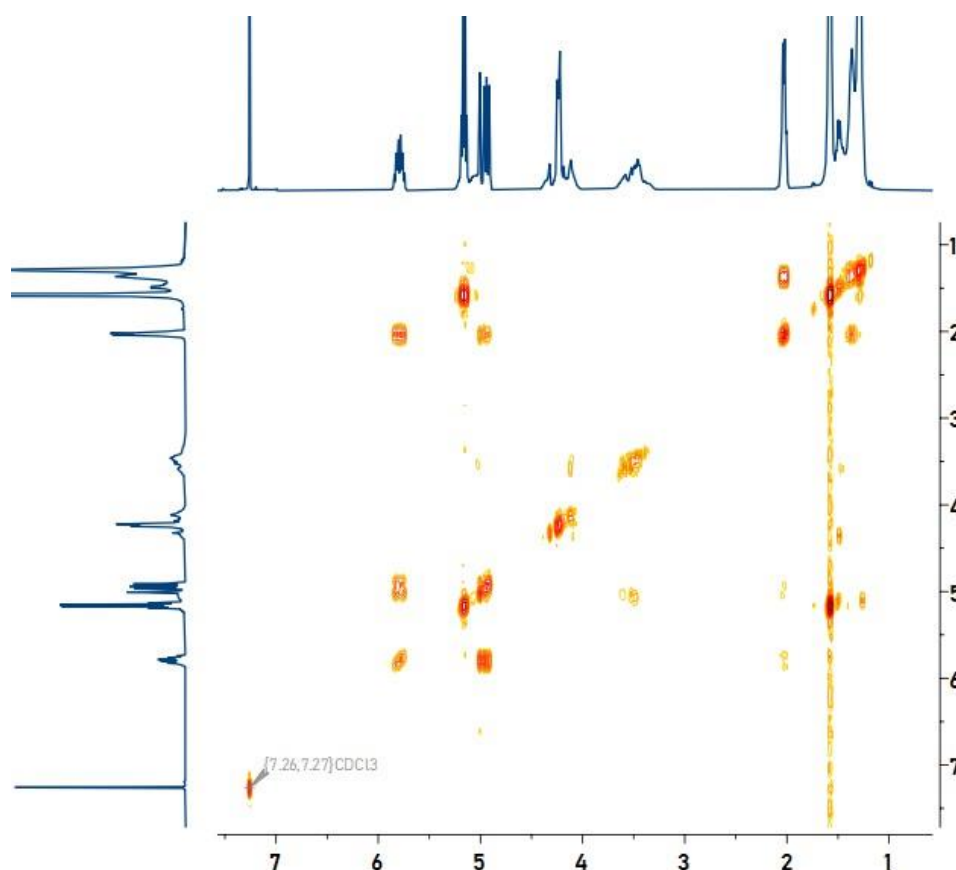


Figure S8.3.48: ^1H COSY NMR spectrum of **P13₁₅-PLLA₂₇** (Table 3.1, **P13₁₅-PLLA₂₇**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 30 : 50 : 546, 50 °C.

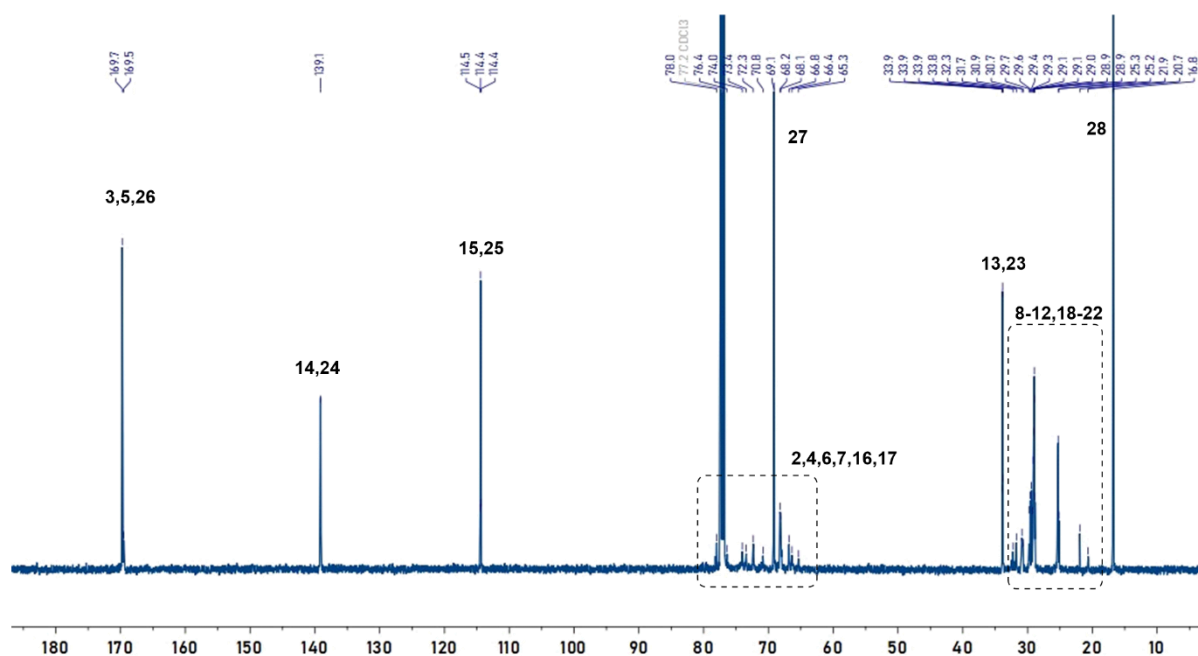


Figure S8.3.49: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P13₁₅-PLLA₂₇** (with assignment, Table 3.1, **P13₁₅-PLLA₂₇**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 30 : 50 : 546, 50 °C.

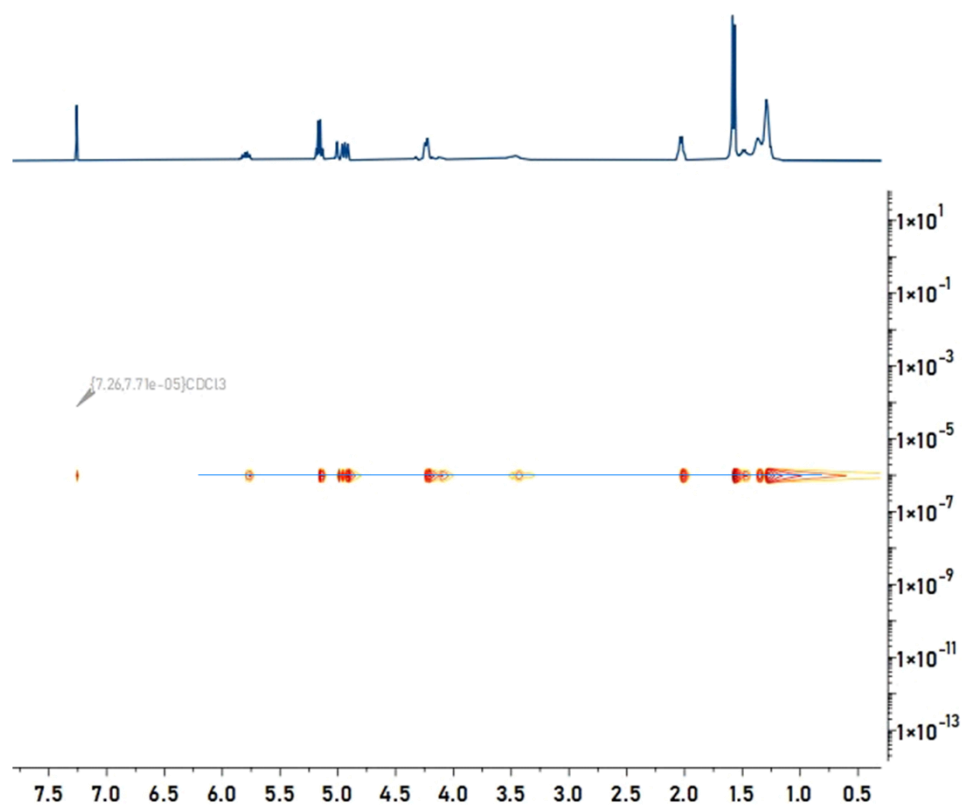


Figure S8.3.50: DOSY NMR spectrum from the reaction of [Cat]:[DGA]:[LA]:[ED] = 1: 30 : 50: 546, **P13₁₅-PLLA₂₇** (500 MHz, CDCl₃).

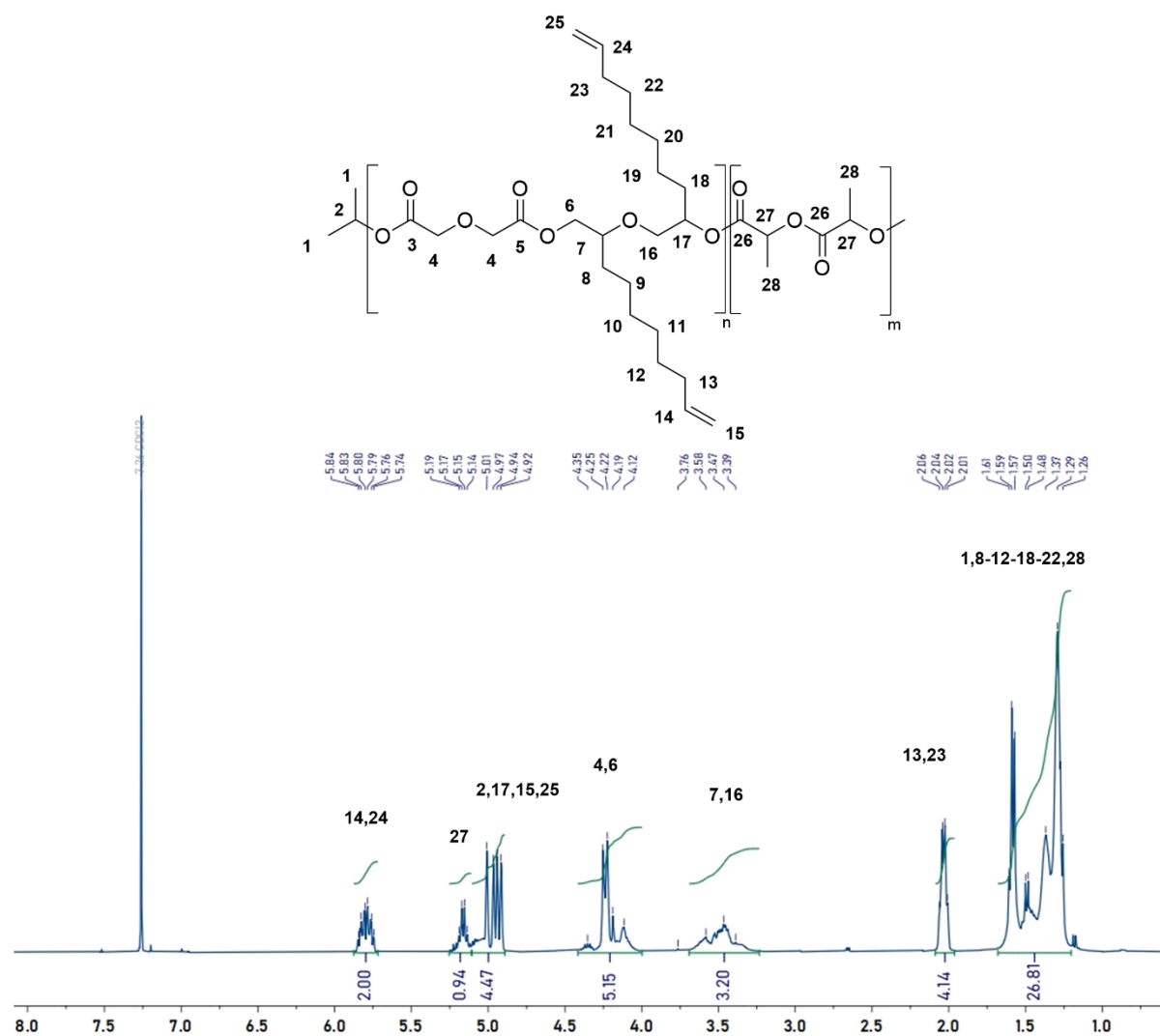
8.3.1.1.11 NMR Spectra for P13₈-PLLA₉

Figure S8.3.51: ¹H NMR spectrum of P13₈-PLLA₉ (with assignment, Table 3.1, P13₈-PLLA₉) (400 MHz, CDCl₃). Reaction conditions: [1] = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 15 : 15 : 546, 50 °C.

The DP was calculated as per Section 8.3.1.1.6 ‘NMR Spectra for P13₂₅-PLLA₂₃’.

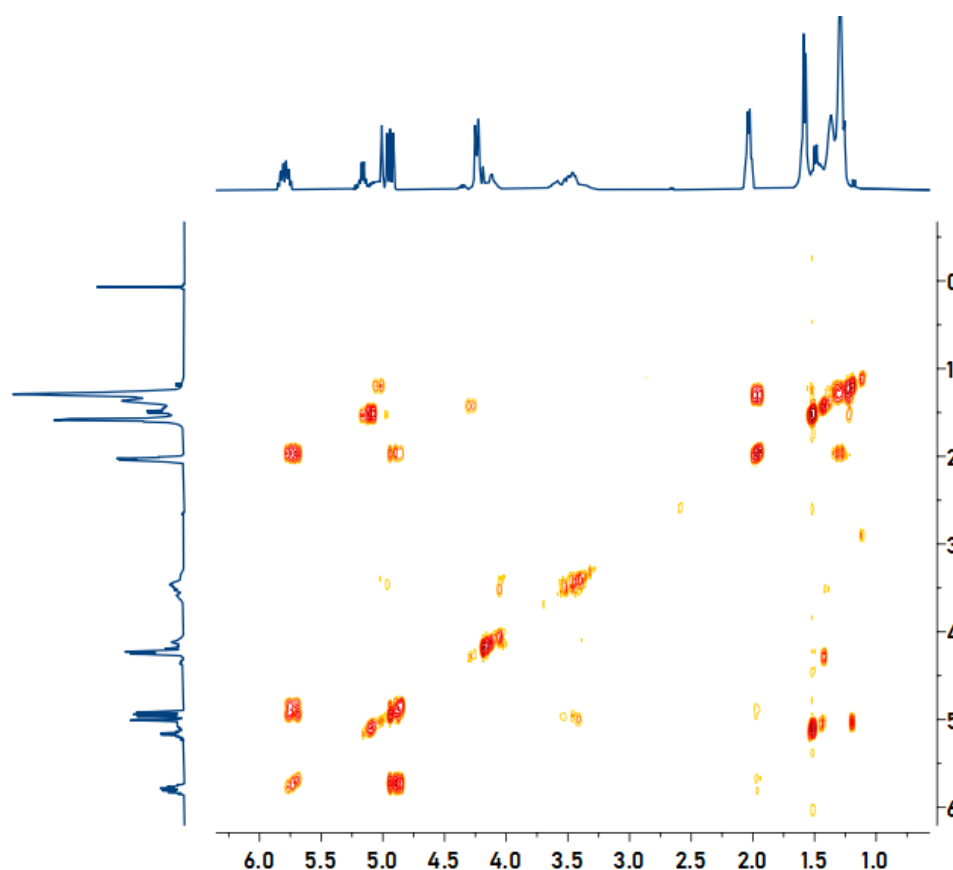


Figure S8.3.52: ^1H COSY NMR spectrum of **P138-PLLA₉** (Table 3.1, **P138-PLLA₉**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 15 : 15 : 546, 50 °C.

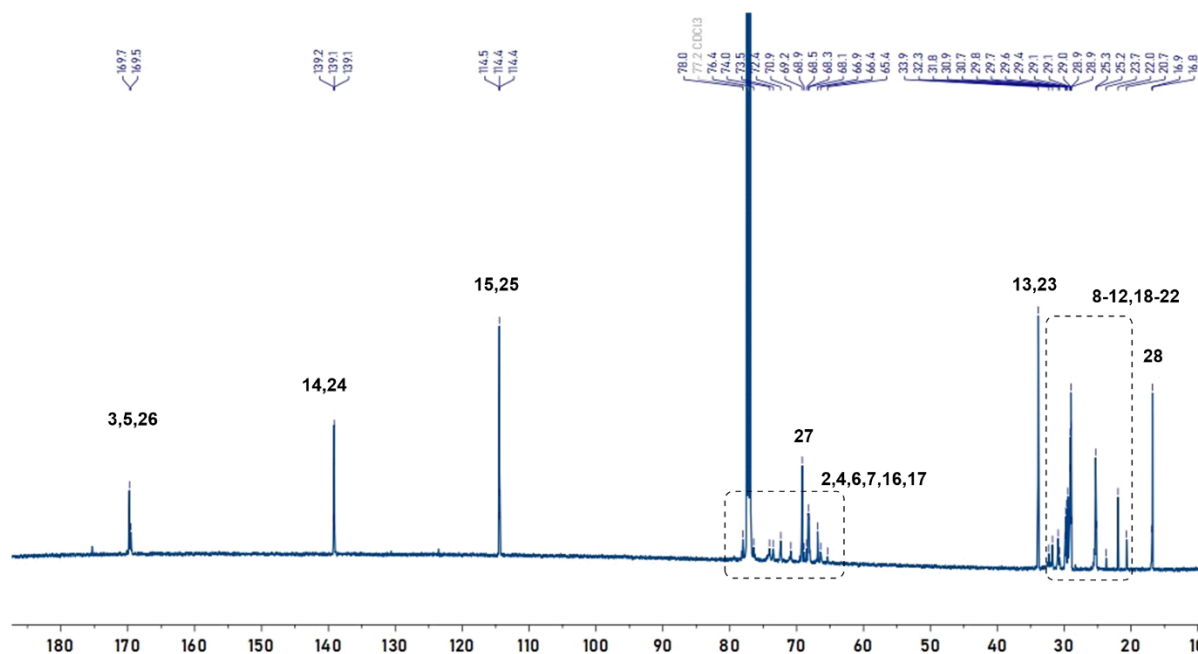


Figure S8.3.53: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P138-PLLA₉** (with assignment, Table 3.1, **P138-PLLA₉**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 15 : 15 : 546, 50 °C.

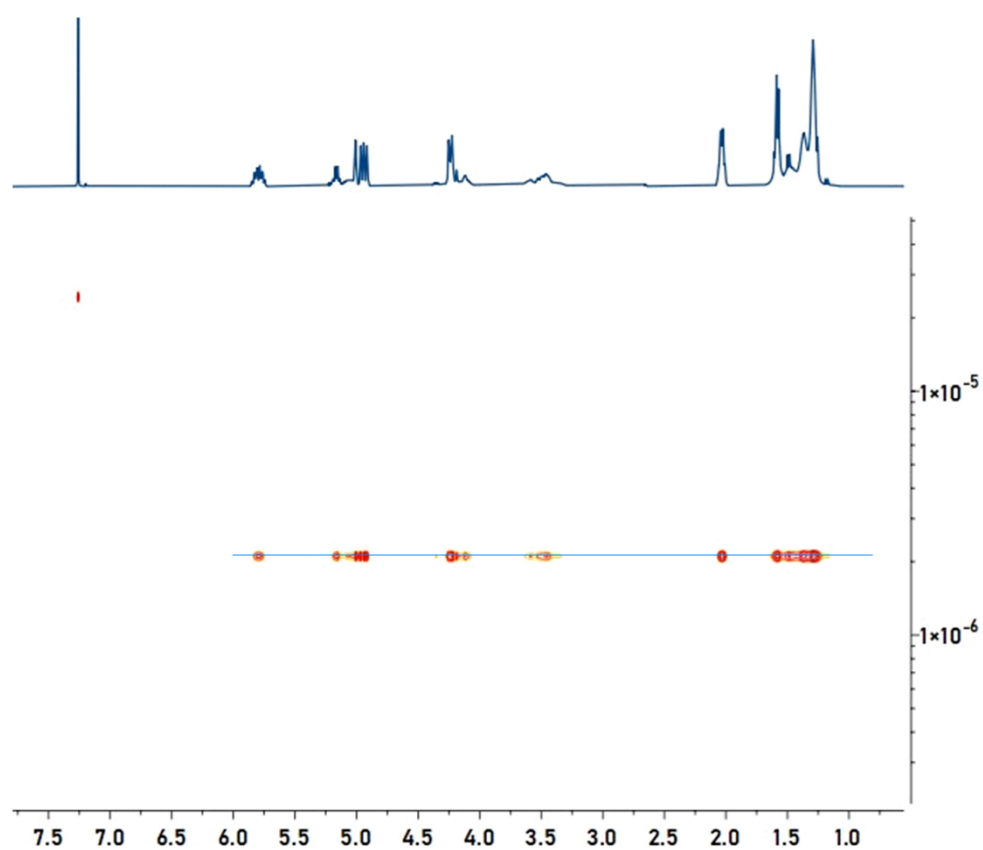


Figure S8.3.54: DOSY NMR spectrum of **P138-PLLA₉** (Table 3.1, **P138-PLLA₉**) (400 MHz, CDCl₃). Reaction conditions: [1] = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 15 : 15 : 546, 50 °C.

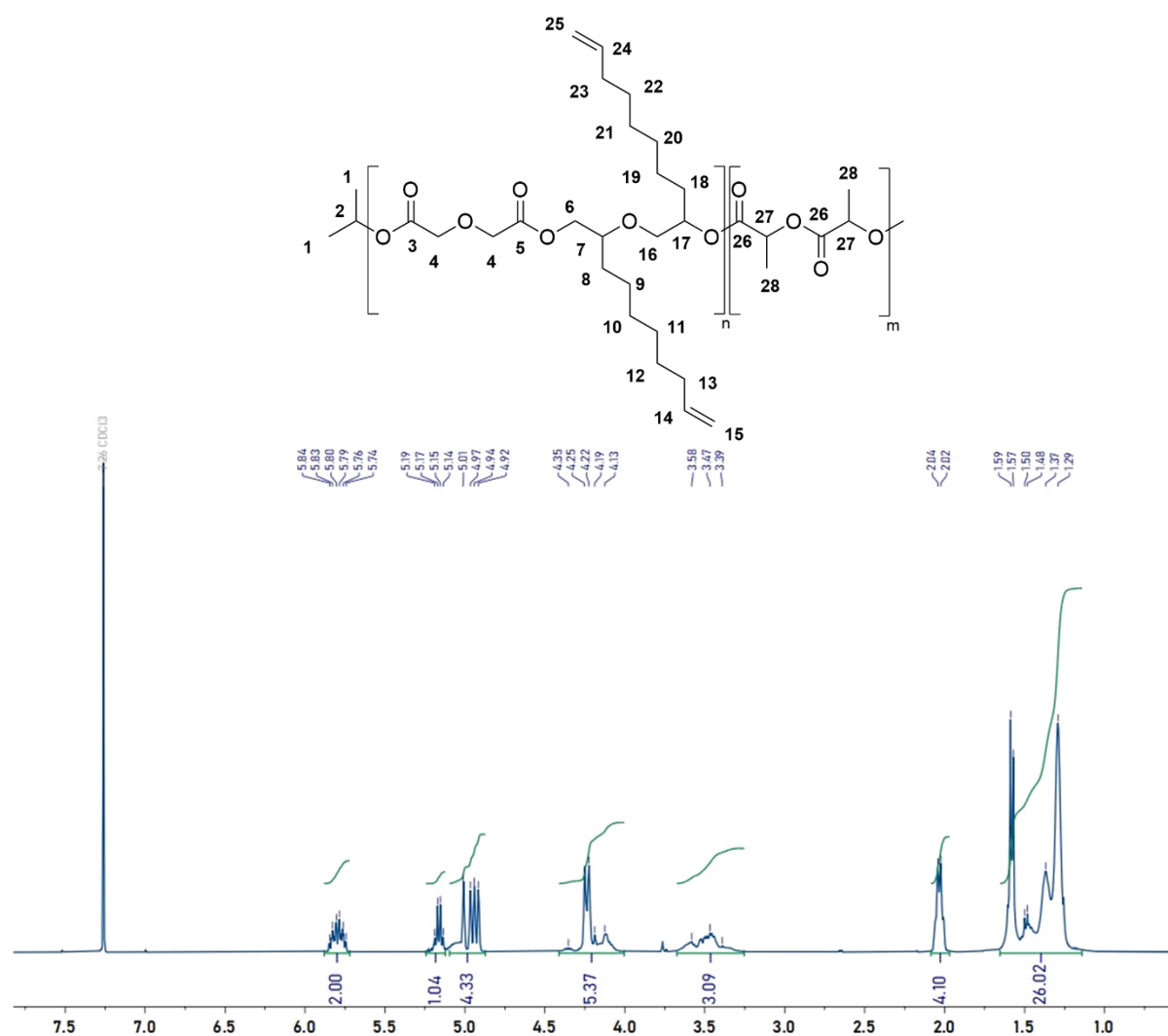
8.3.1.1.12 NMR Spectra for **P13₁₂-PLLA₁₅**

Figure S8.3.55: ^1H NMR spectrum of **P13₁₂-PLLA₁₅** (with assignment, Table 3.1, **P13₁₂-PLLA₁₅**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 25 : 25 : 546, 50 $^\circ\text{C}$.

The DP was calculated as per Section 8.3.1.1.6 ‘NMR Spectra for **P13₂₅-PLLA₂₃**’.

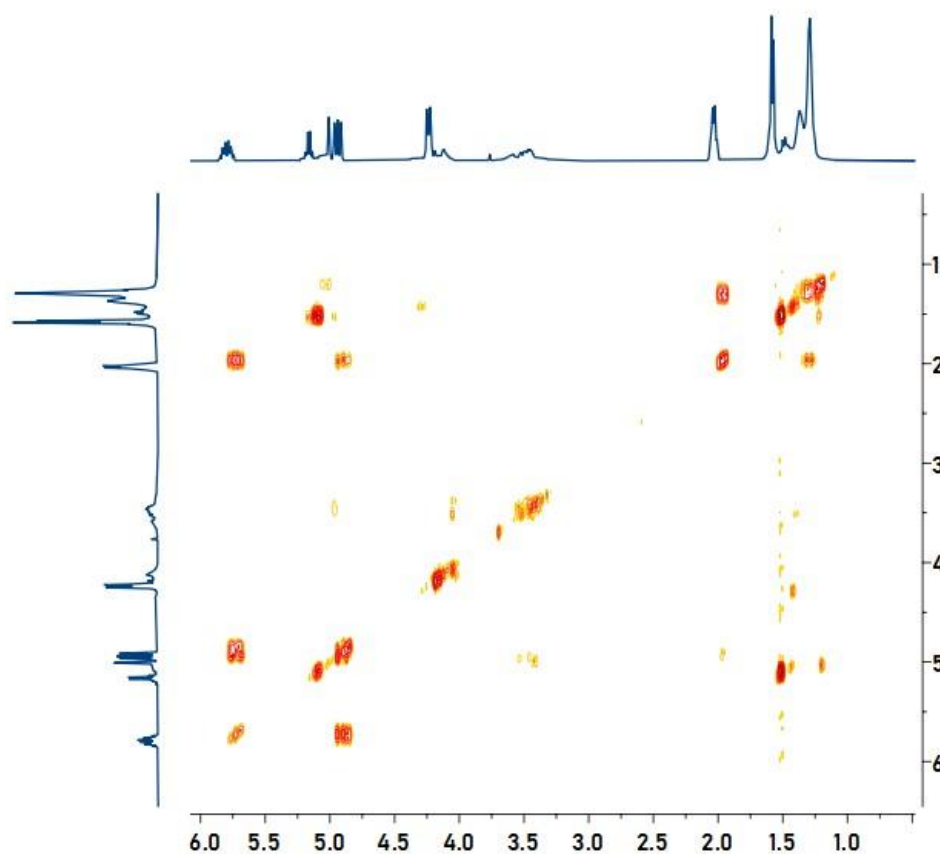


Figure S8.356: ^1H COSY NMR spectrum of **P13₁₂-PLLA₁₅** (Table 3.1, **P13₁₂-PLLA₁₅**) (400 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 25 : 25 : 546, 50 °C.

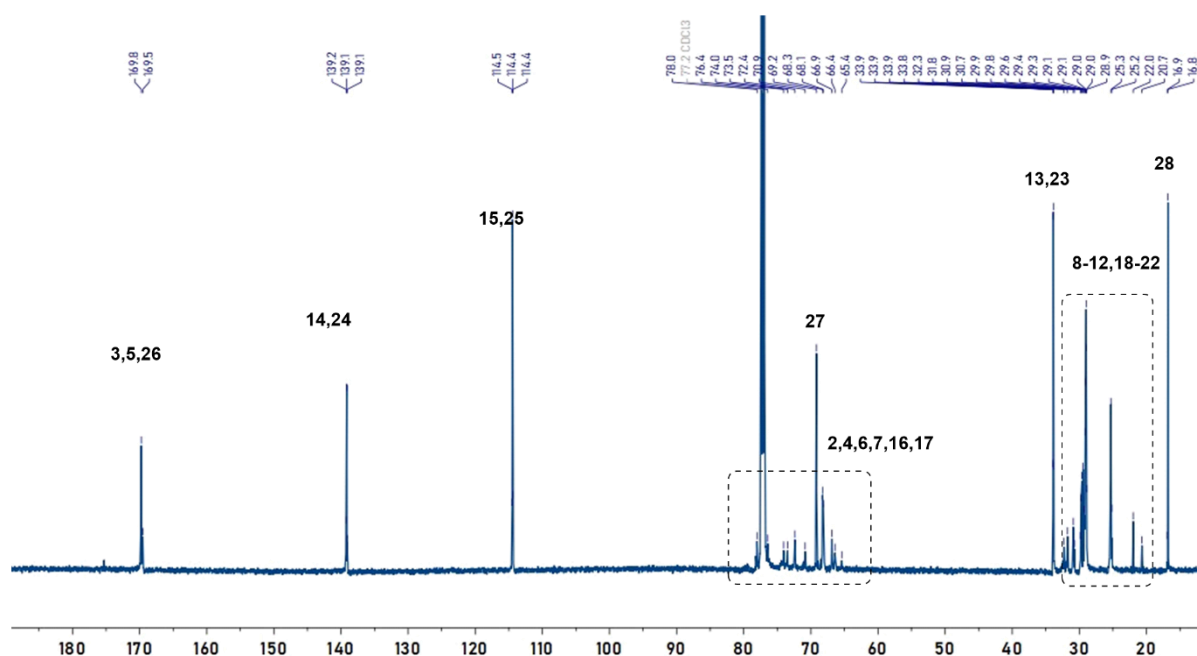


Figure S8.357: ^{13}C NMR spectrum of **P13₁₂-PLLA₁₅** (with assignment, Table 3.1, **P13₁₂-PLLA₁₅**) (151 MHz, CDCl_3). Reaction conditions: **[1]** = 10 mM in 1 mL epoxide, **[Cat]** : **[DGA]** : **[LA]** : **[ED]** = 1 : 25 : 25 : 546, 50 °C.

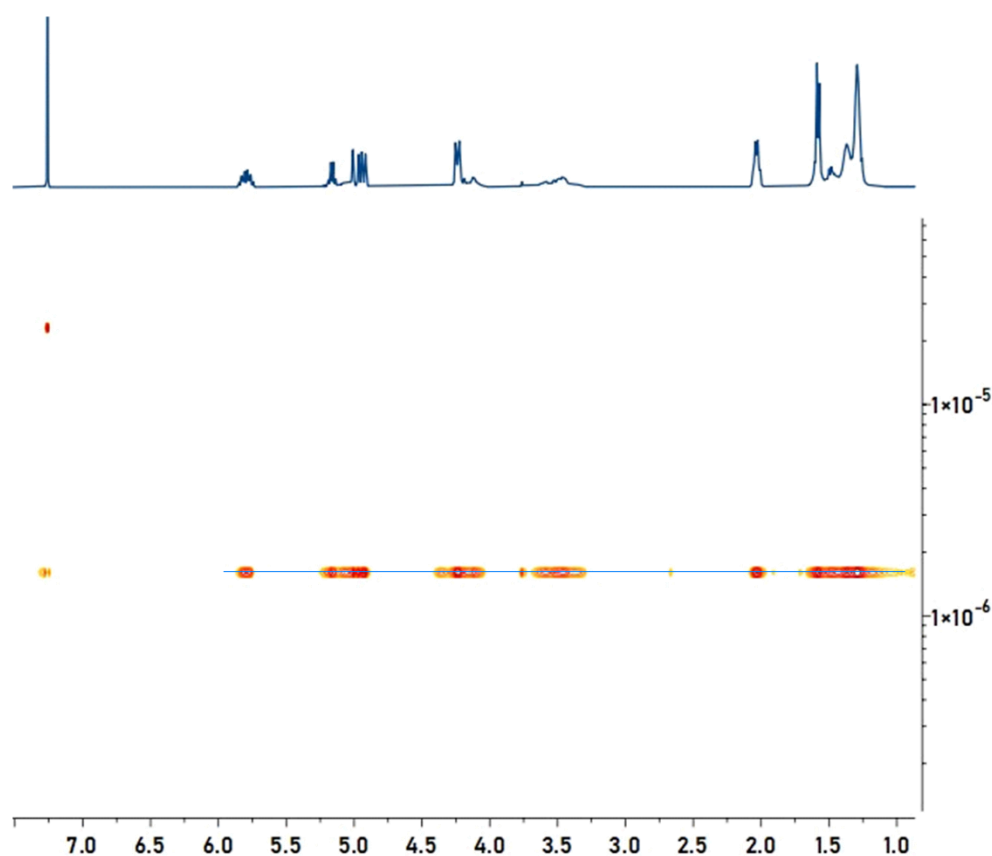


Figure S8.3.58: DOSY NMR spectrum of **P13₁₂-PLLA₁₅** (Table 3.1, **P13₁₂-PLLA₁₅**) (500 MHz, CDCl₃). Reaction conditions: [**1**] = 10 mM in 1 mL epoxide, [Cat] : [DGA] : [LA] : [ED] = 1 : 25 : 25 : 546, 50 °C.

8.3.1.2 GPC data for Polymers Described in Table 3.1

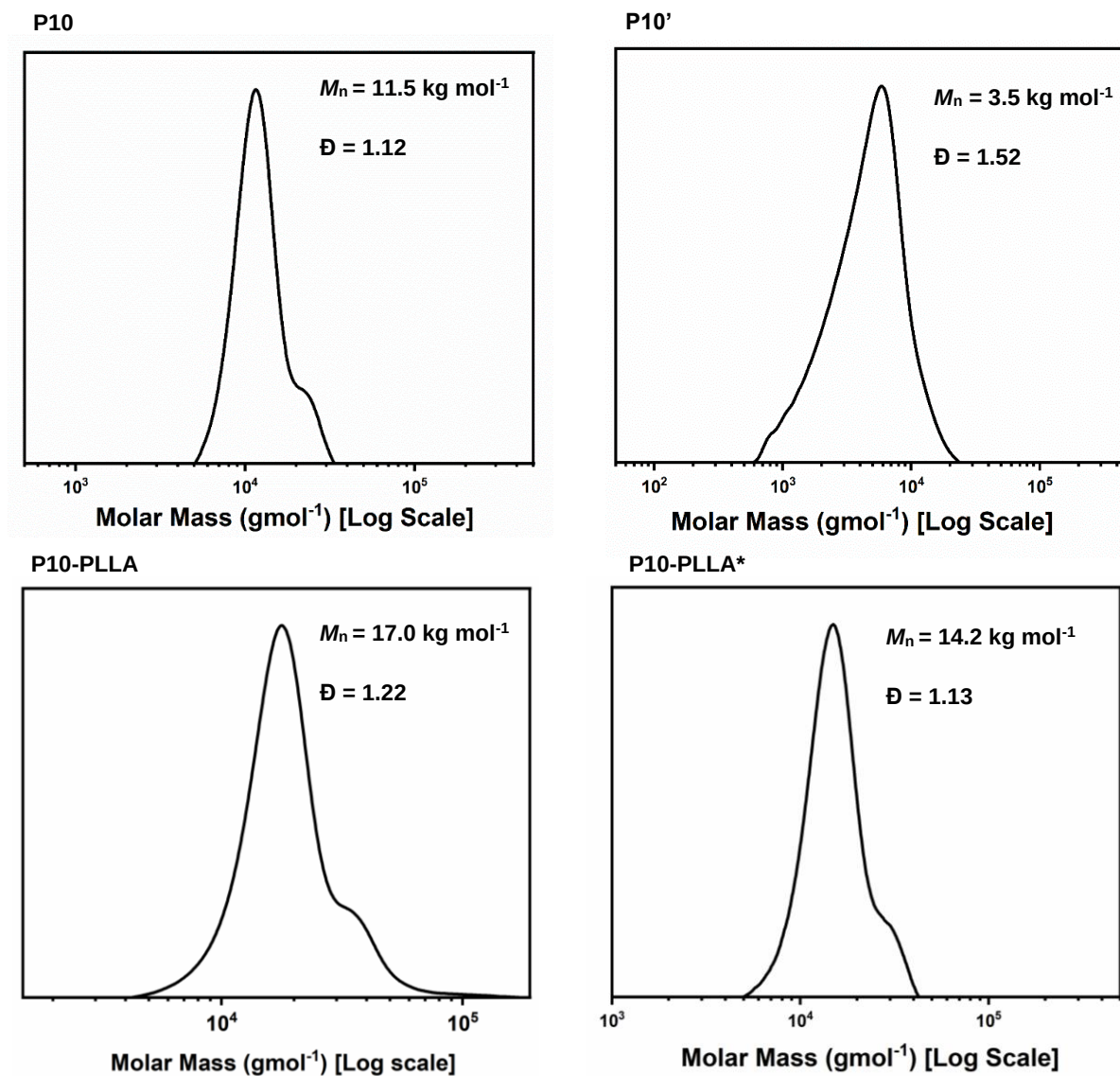


Figure S8.3.59: GPC chromatograms for polymers described in Table 3.1, **P10**, **P10'**, **P10-PLLA** and **P10-PLLA***, all polymers utilising MA and ED monomers.

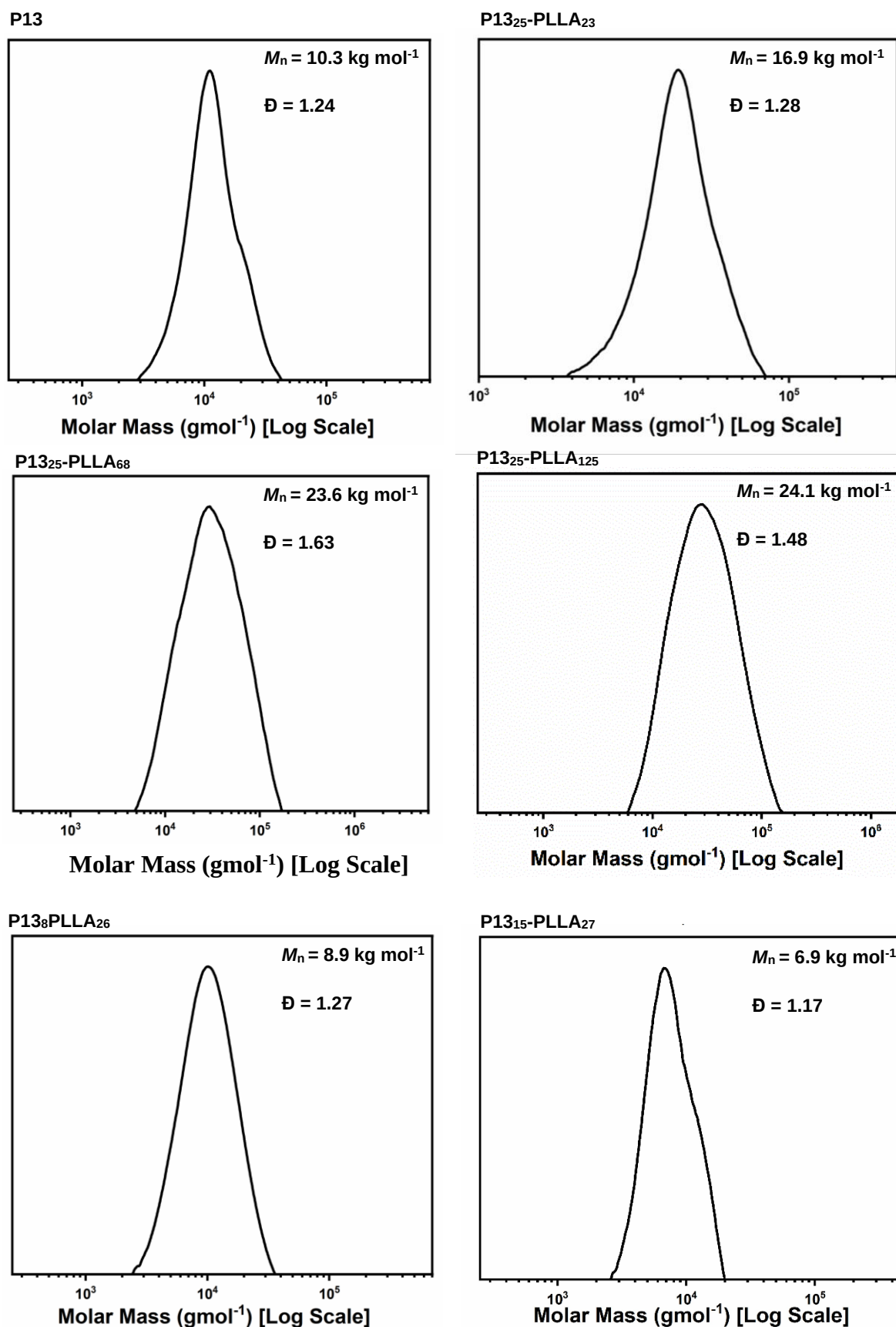


Figure S8.3.60: GPC chromatograms for polymers described in Table 3.1 utilising DGA and ED monomers.

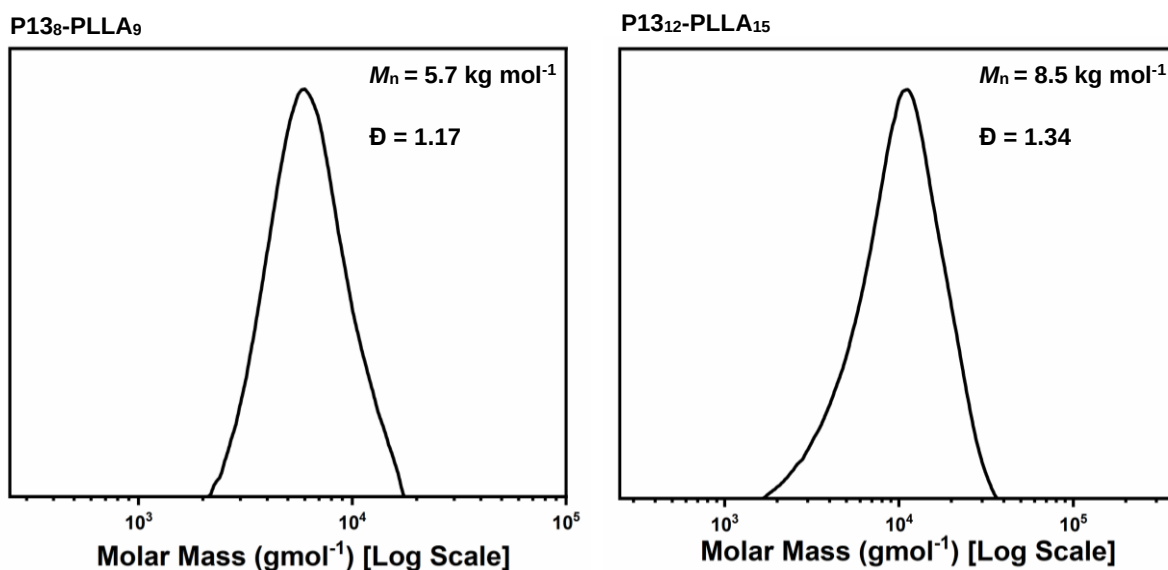


Figure S8.3.61: GPC chromatograms for polymers described in Table 3.1 also utilising DGA and ED monomers.

8.3.1.3 DSC data for Polymers Described in Table 3.1

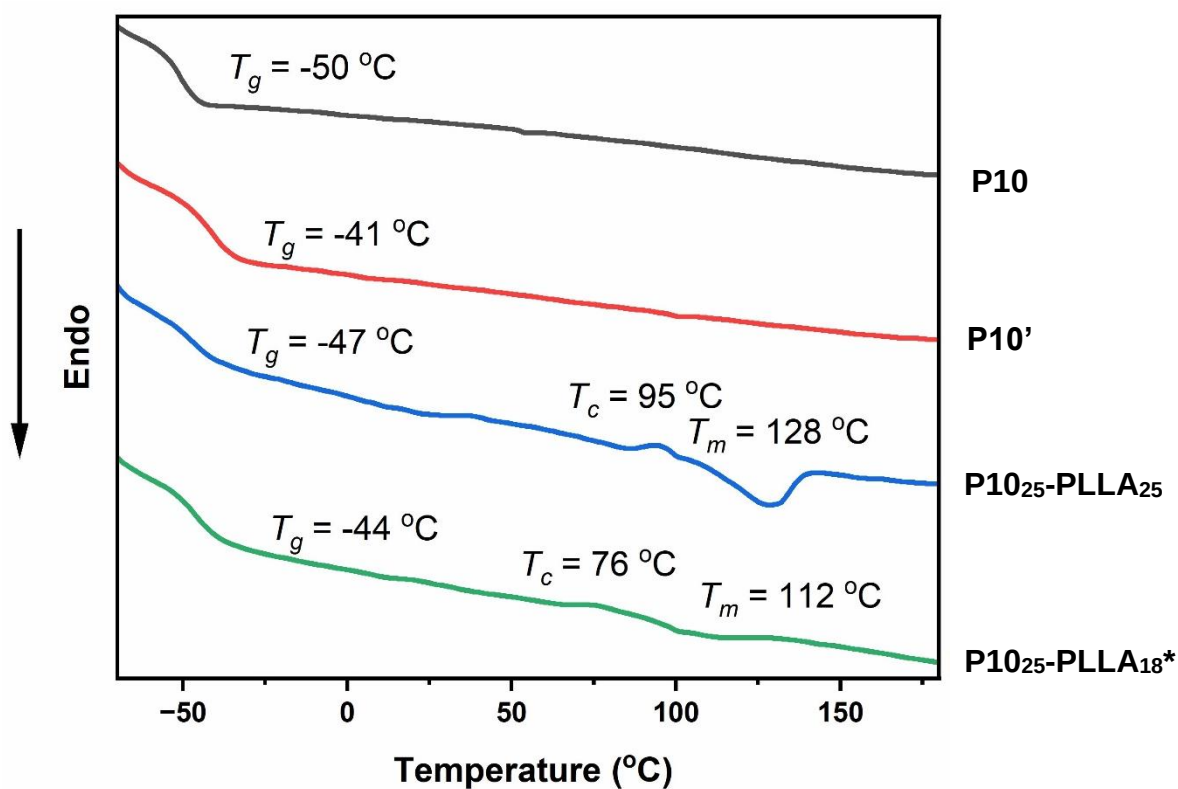


Figure S8.3.62: DSC thermogram of the polymers **P10**, **P10'**, **P10-PLLA** and **P10-PLLA***.

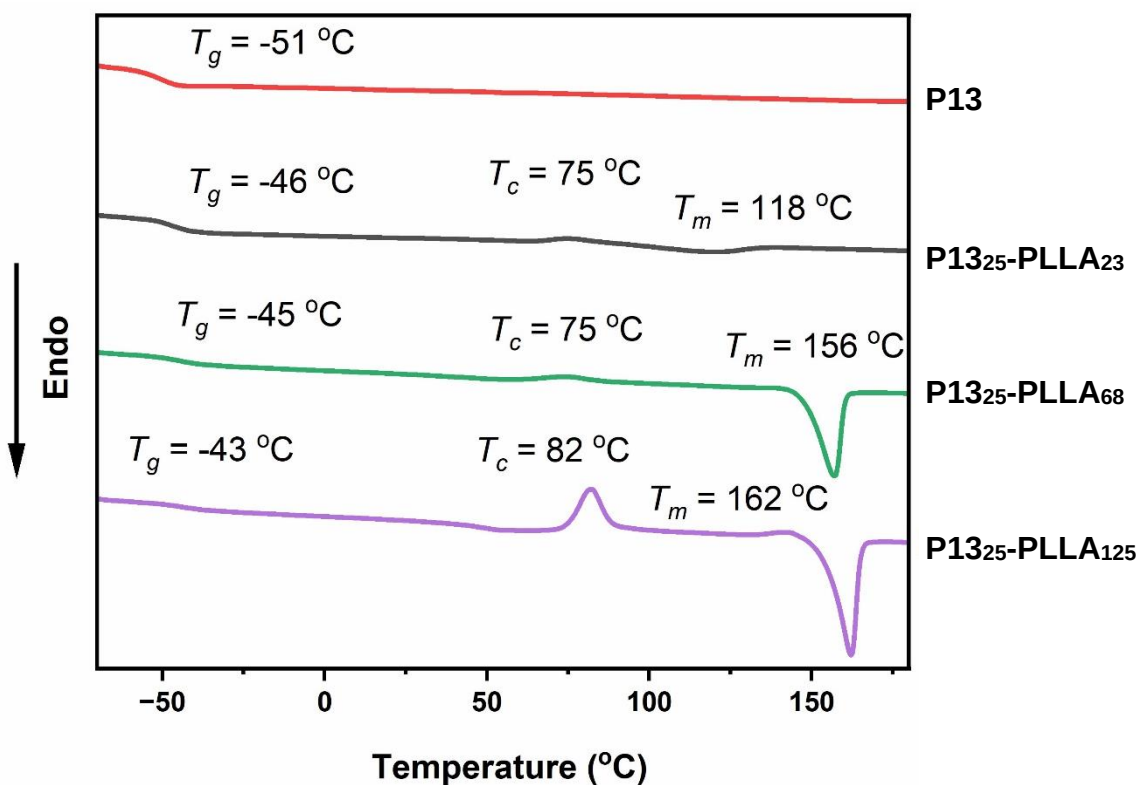


Figure S8.3.63: DSC Thermograms for Polymers **P13**, **P13₂₅-PLLA₂₃**, **P13₂₅-PLLA₆₈** and **P13₂₅-PLLA₁₂₅**.

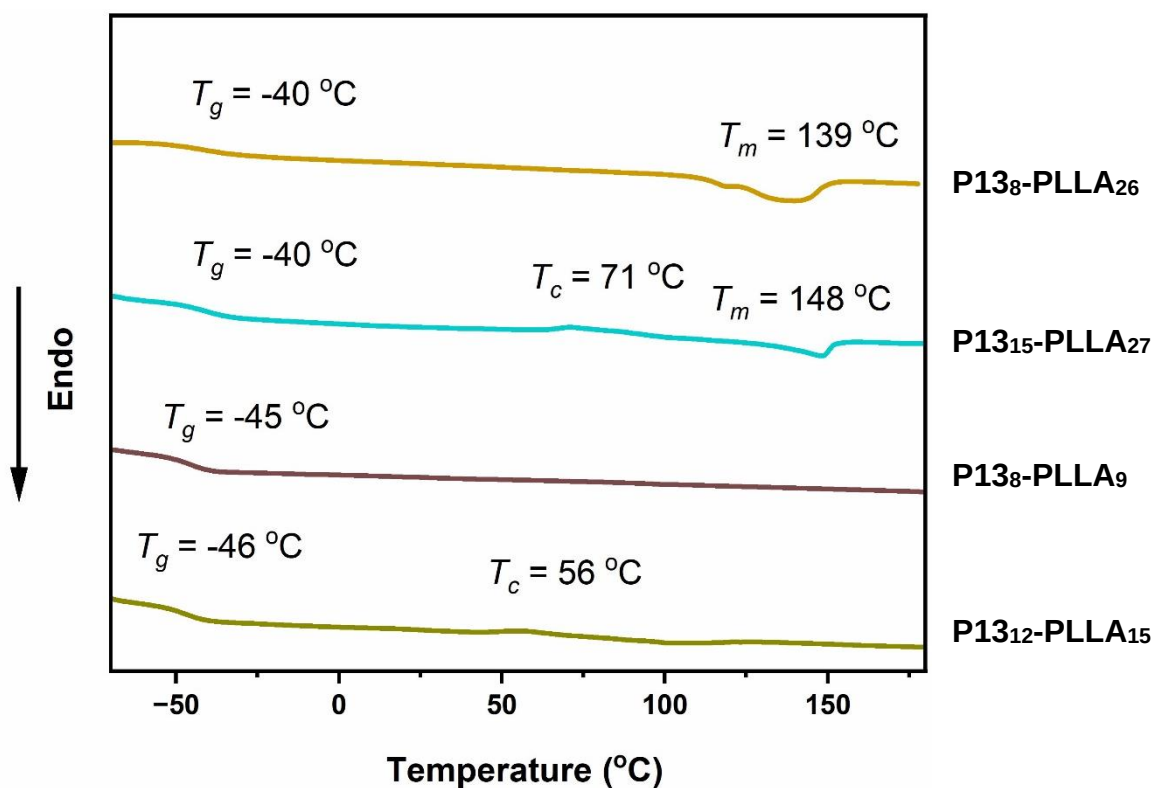


Figure S8.3.64: DSC Thermograms for Polymers **P13₈-PLLA₂₆**, **P13₁₅-PLLA₂₇**, **P13₈-PLLA₉** and **P13₁₂-PLLA₁₅**.

8.3.1.4 TGA data for Polymers Described in Table 3.1

Table S8.3.1: Summary of TGA data for polymers described in Table 3.1.

Polymer	$T_{d,5}$ (°C)	$T_{d,95}$ (°C)
P10 (MA-ED-ED)	340	569
P10' (MA-ED)	323	566
P10-PLLA	237	499
P10-PLLA*	255	500
P13 (DGA-ED-ED)	296	489
P13₂₅-PLLA₂₃	253	492
P13₂₅-PLLA₆₈	224	479
P13₂₅-PLLA₁₂₅	275	479
P13₈-PLLA₂₆	251	485
P13₁₅-PLLA₂₇	243	491
P13₈-PLLA₉	237	491
P13₁₂-PLLA₁₅	249	488

In TGA experiments, polymer samples were heated from 30 to 700 °C at a rate of 10 °C min⁻¹, under N₂ flow 12 mL min⁻¹.

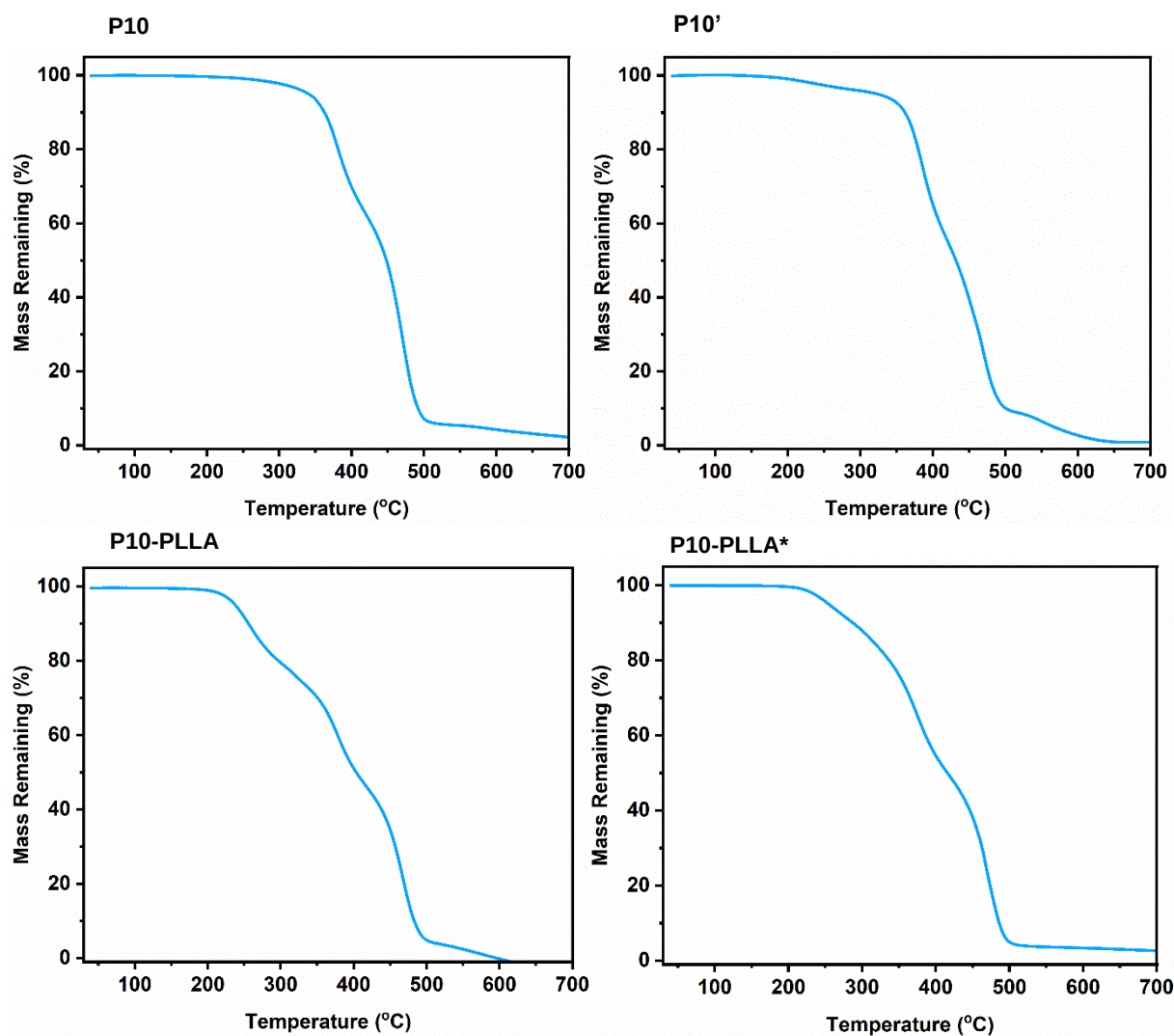


Figure S8.3.65: TGA traces of the polymers **P10**, **P10'**, **P10-PLLA** and **P10-PLLA***.

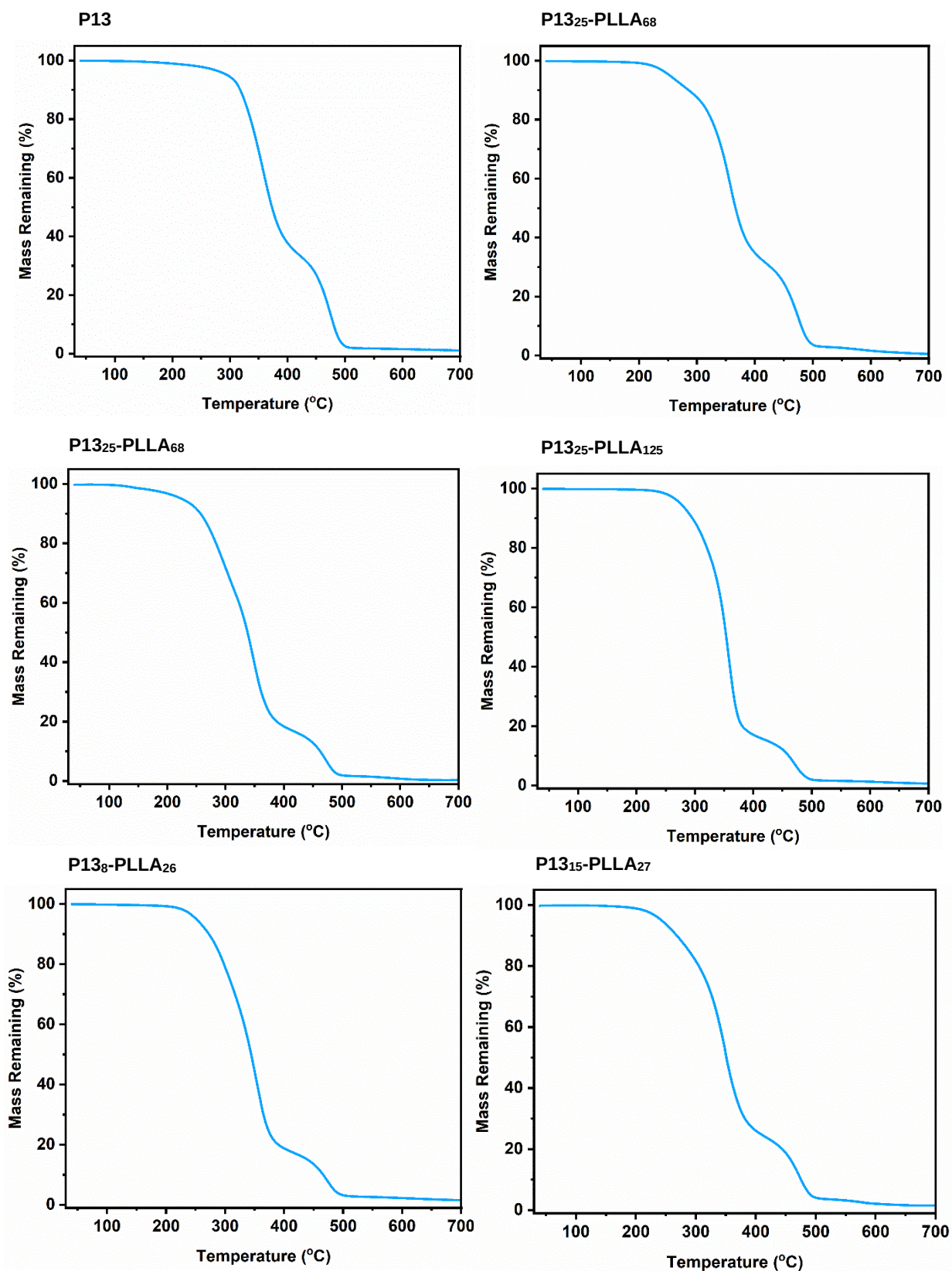


Figure S8.3.66: TGA traces of the polymers **P13**, **P13₂₅-PLLA₂₃**, **P13₂₅-PLLA₆₈** and **P13₂₅-PLLA₁₂₅**, **P13₈-PLLA₂₆** and **P13₁₅-PLLA₂₇**.

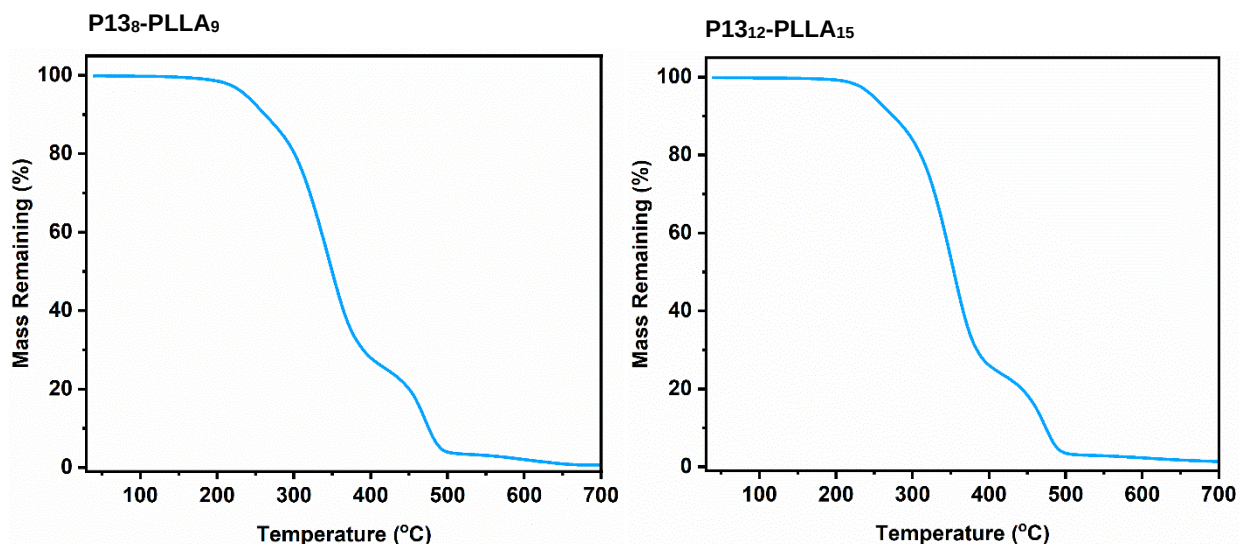


Figure S8.3.67: TGA traces of the polymers **P13₈-PLLA₉** and **P13₁₂-PLLA₁₅**.

8.3.2 Blend Synthesis and Characterisation

8.3.2.1 DSC Data for Blends Described in Table 3.2

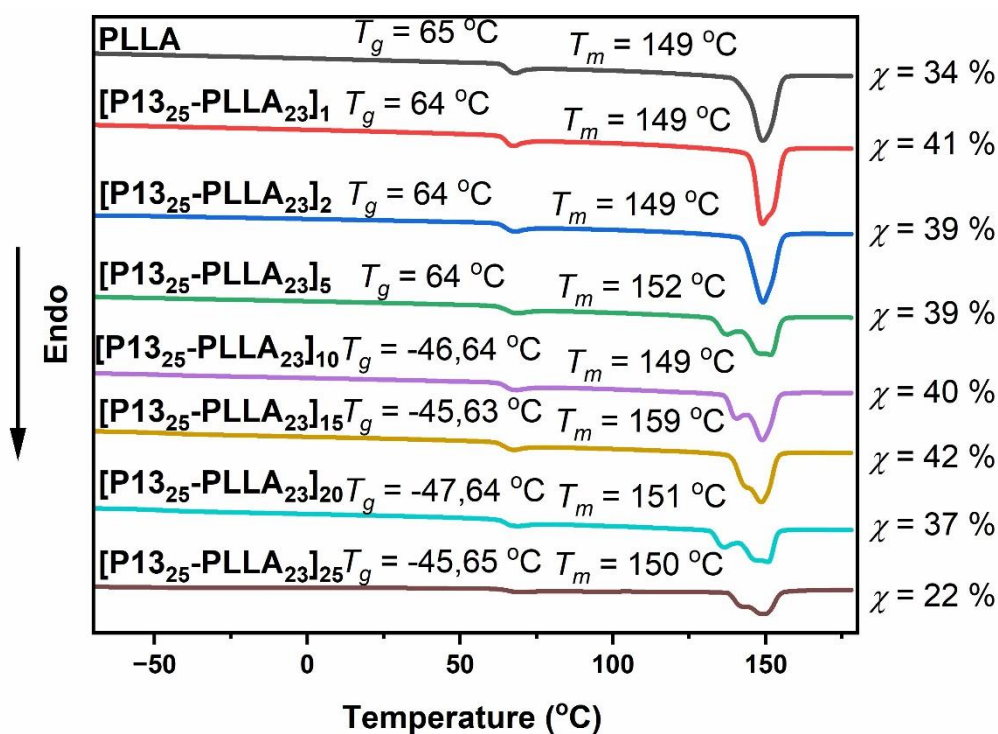


Figure S8.3.68: DSC thermogram of PLLA blends with various wt% of **P13₂₅-PLLA₂₃**. Data was obtained from the first heating cycle, and experiments were conducted at 10 °C min⁻¹ heating rate from -80 to 180 °C. χ is the crystallinity, reported in Table 3.2 of chapter 3, and, for which the calculation is demonstrated in section 8.3.2.3.

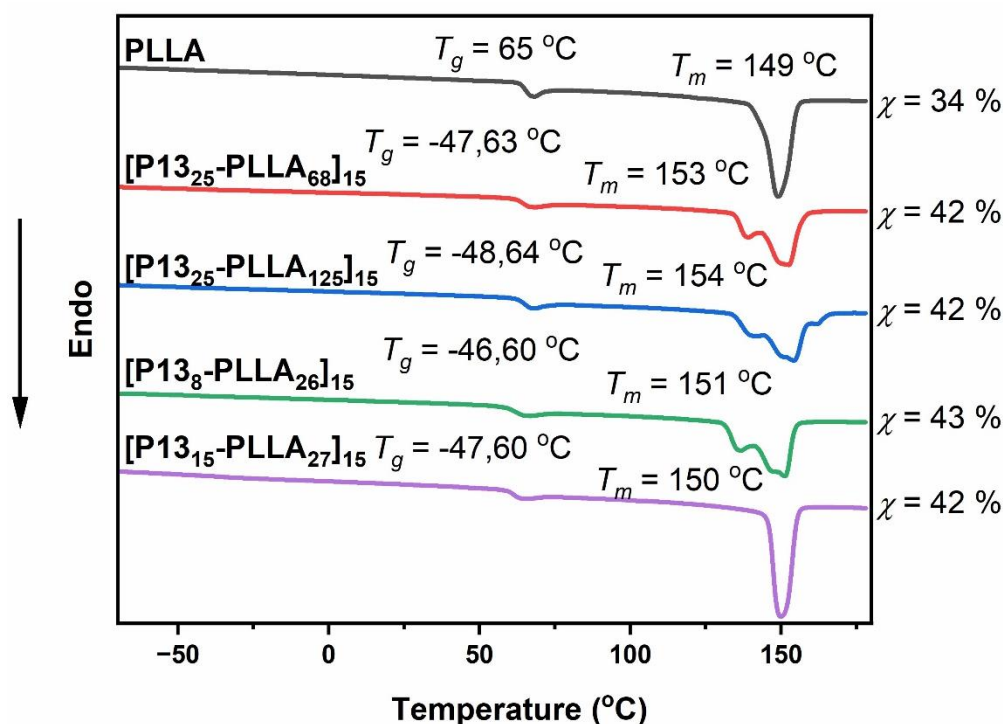


Figure S8.3.69: DSC thermogram of the PLLA blends of 15 wt% of polymers **P13₂₅-PLLA₆₈** and **P13₂₅-PLLA₁₂₅**, **P13₈-PLLA₂₆** and **P13₁₅-PLLA₂₇** with varying PLLA and **P13** block DPs. Data was obtained from the first heating cycle, and experiments were conducted at 10 °C min⁻¹ heating rate from -80 to 180 °C. χ is the crystallinity, reported in Table 3.2 of chapter 3, and, for which the calculation is demonstrated in section 8.3.2.3.

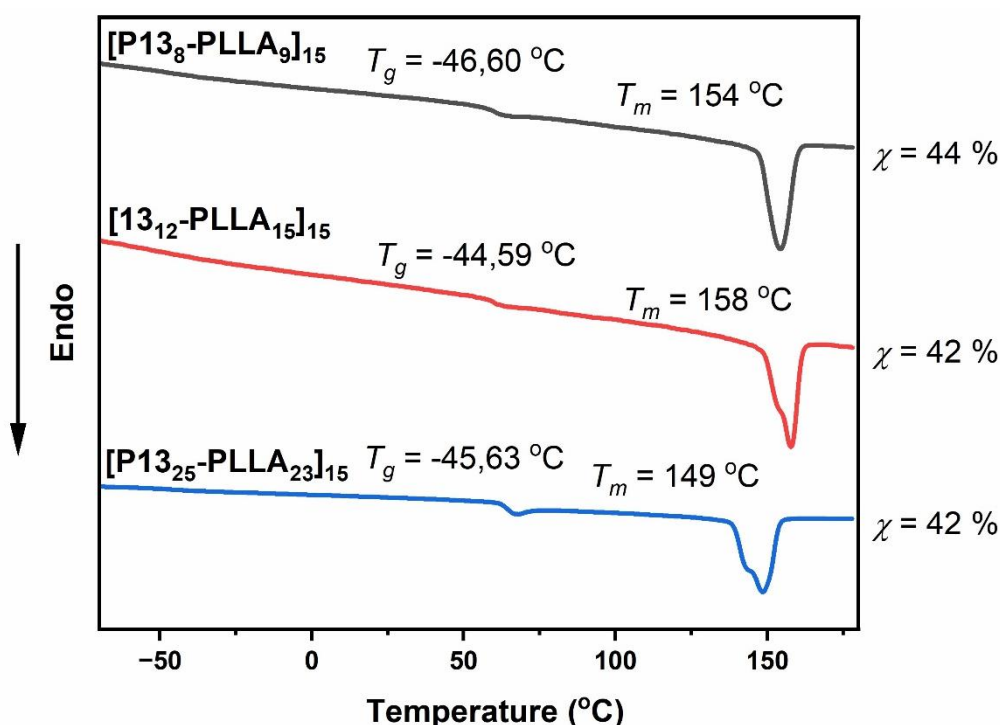


Figure S8.3.70: DSC thermogram of the PLLA blends with 15 wt% of polymers **P13₂₅-PLLA₂₃**, **P13₁₂-PLLA₁₅** and **P13₈-PLLA₉**. In this series of block polymers, the ratio of DP for the PLLA and **P13** block have been kept constant, while the overall DP was been changed, to assess the effect of overall molecular weight of the block polymer. Data was obtained from the first heating cycle, and experiments were conducted at 10 °C min⁻¹ heating rate from -80 to 180 °C. χ is the crystallinity, reported in Table 3.2 of chapter 3, and, for which the calculation is demonstrated in section 8.3.2.3.

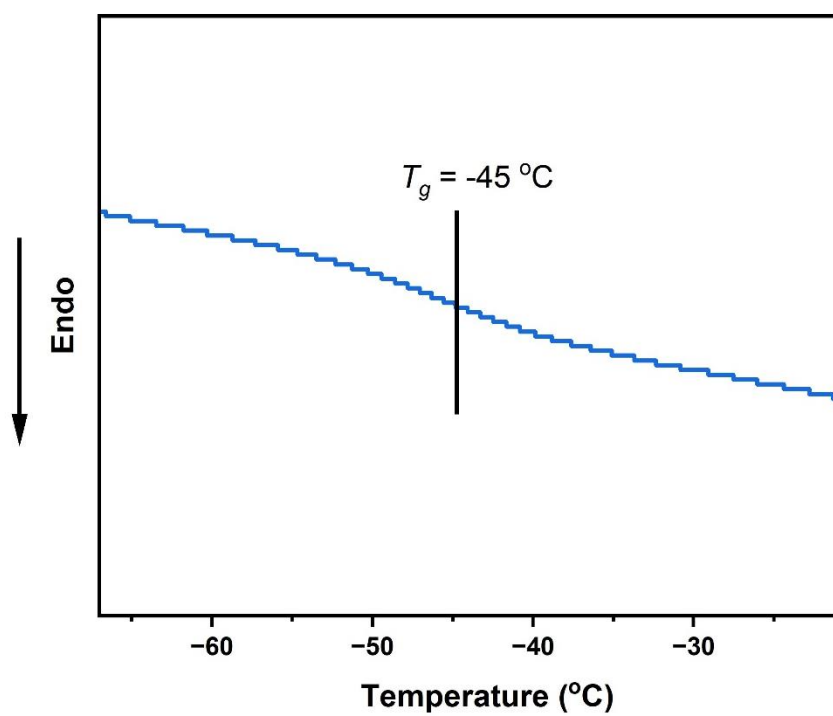
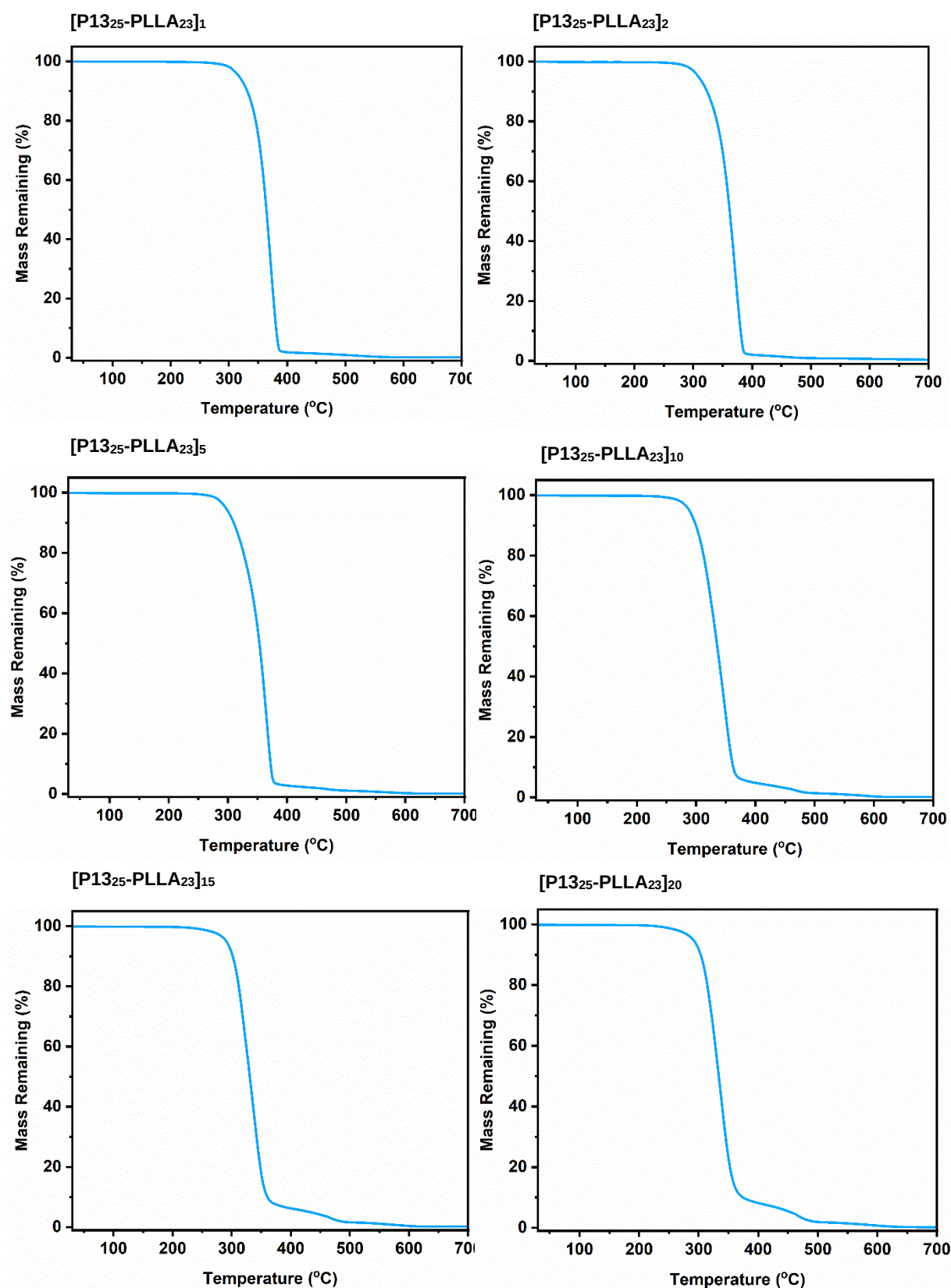


Figure S8.3.71: DSC thermogram of blend **[P13₂₅-PLLA₂₃]₁₅** zoomed into the region between -20 and -65 °C to demonstrate the lower T_g observed, which is unchanged from the block copolymer (T_g **P13₂₅-PLLA₂₃** = -46 °C).

8.3.2.2 TGA Data for Blends Described in Table 3.2

Figure S8.3.72: TGA traces of PLLA blends with various 1-20 wt% of **P13₂₅-PLLA₂₃** diblock toughening agent.

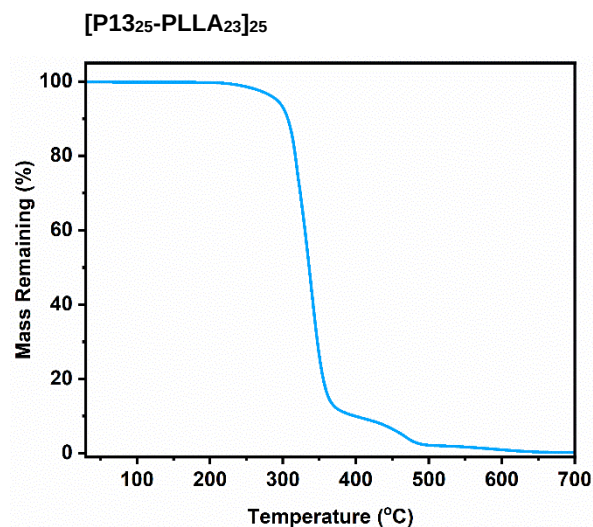


Figure S8.3.73: TGA trace of PLLA blend with 25 wt% of **P13₂₅-PLLA₂₃** diblock toughening agent.

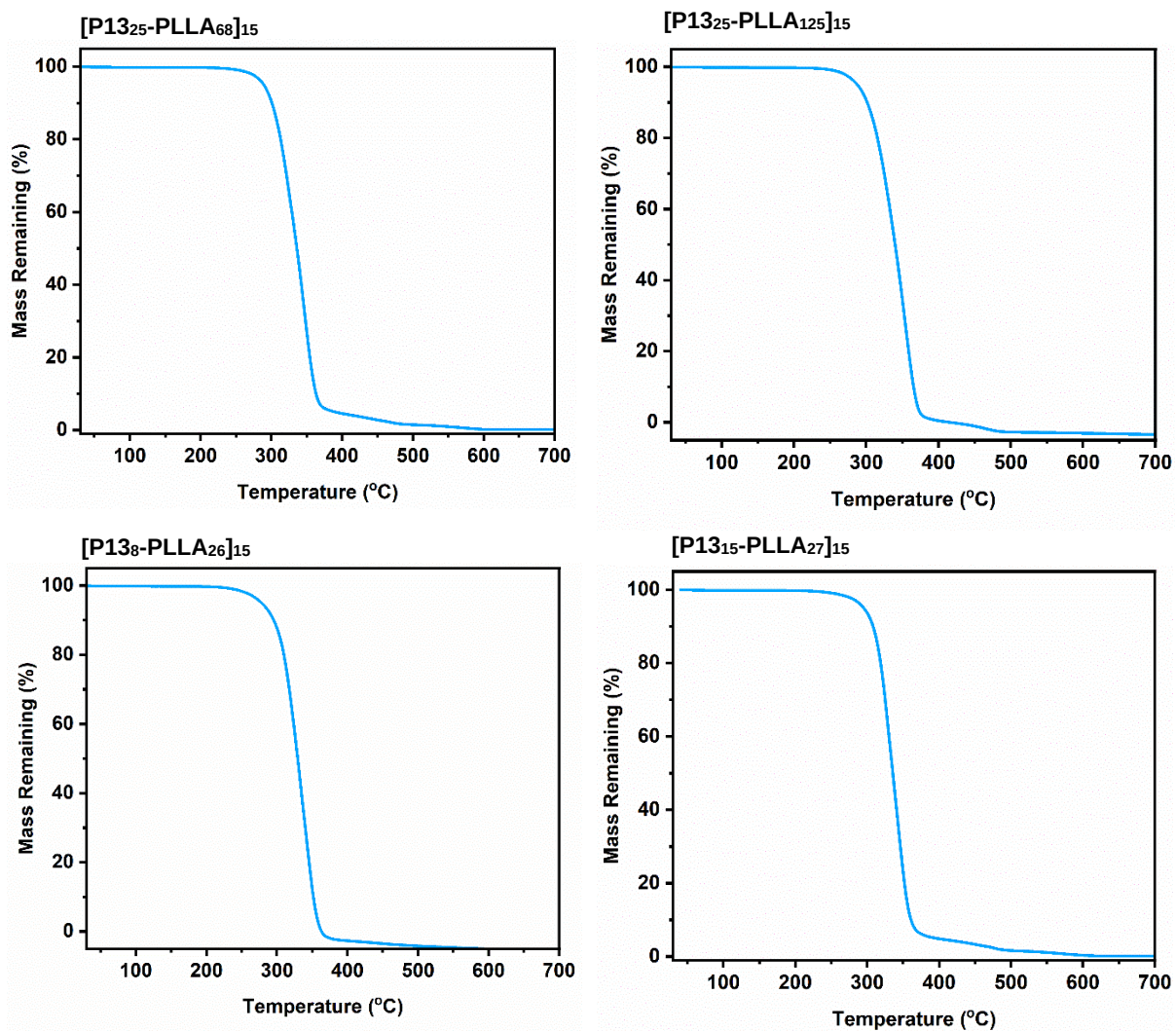


Figure S8.3.74: TGA traces of the PLLA blends of **P13₂₅-PLLA₆₈** and **P13₂₅-PLLA₁₂₅**, **P13₈-PLLA₂₆** and **P13₁₅-PLLA₂₇**.

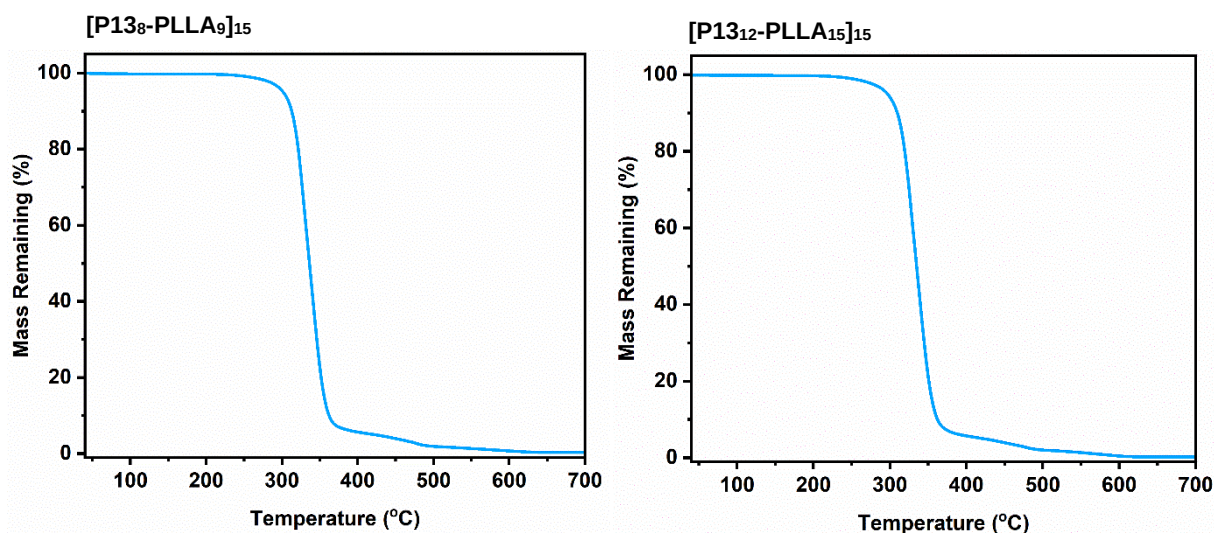


Figure S8.3.75: TGA traces of the PLLA blends with 15 wt% of **P138-PLLA₉** and **P1312-PLLA₁₅**.

Table S8.3.2: TGA data for blend samples in Table 3.2.

Blend	$T_{d,5}$ (°C)	$T_{d,95}$ (°C)
PLLA	321	381
[P1325-PLLA ₂₃] ₁ *	317	384
[P1325-PLLA ₂₃] ₂ *	308	383
[P1325-PLLA ₂₃] ₅ *	296	376
[P1325-PLLA ₂₃] _{7.5} *	288	432
[P1325-PLLA ₂₃] ₁₀ *	291	456
[P1325-PLLA ₂₃] ₁₅ *	290	456
[P1325-PLLA ₂₃] ₂₀ *	292	464
[P1325-PLLA ₆₈] ₁₅ *	289	456
[P1325-PLLA ₁₂₅] ₁₅ *	288	370
[P138-PLLA ₂₆] ₁₅ **	278	356
[P1315-PLLA ₂₇] ₁₅ **	295	395
[P138-PLLA ₉] ₁₅ ^Δ	301	421
[P1312-PLLA ₁₅] ₁₅ ^Δ	296	422

Polymer samples were heated from 30 to 700 °C, at a rate of 10 °C min⁻¹, under N₂ flow 12 mL min⁻¹.

8.3.2.3 Calculation of crystallinity

Crystallinity %, χ , was calculated by;

$$\chi = \frac{\Delta H_m}{93.6} \times 100\%$$

Where ΔH_m is the melting enthalpy (J/g) obtained by the DSC experiment and 93.6 J/g is the ΔH_m for 100% crystalline PLLA in J/g.⁴

To make these measurements, the sample was cooled at 10 °C/min to -80 °C, followed by heating to 180 °C at the same rate. It was during this first heating cycle that the crystallinity data was used to calculate crystallinity χ . It was used to understand the thermal properties of the annealed films used for mechanical testing.

8.3.2.4 Rheology for Blends Samples in Table 3.2

Table S8.3.3: Melt rheology of high molecular weight commercial PLLA blends with various wt% **P13₂₅-PLLA₂₃**.

Blend	G'^a Max (MPa)	G''^a Plateau (MPa)	$\eta^*{}^b$ (Pa·s)
PLLA	0.42	0.19	10335
[P13 ₂₅ -PLLA ₂₃] _{7.5}	0.28	0.11	8467
[P13 ₂₅ -PLLA ₂₃] ₁₅	0.1	0.05	3789
[P13 ₂₅ -PLLA ₂₃] ₂₅	0.07	0.04	3536

All measurements were conducted in the linear viscoelastic region: 1% amplitude strain, 100-0.01 Hz, at 170°C. ^aAs measured at 100 Hz. ^bAs measured at 0.01 Hz.

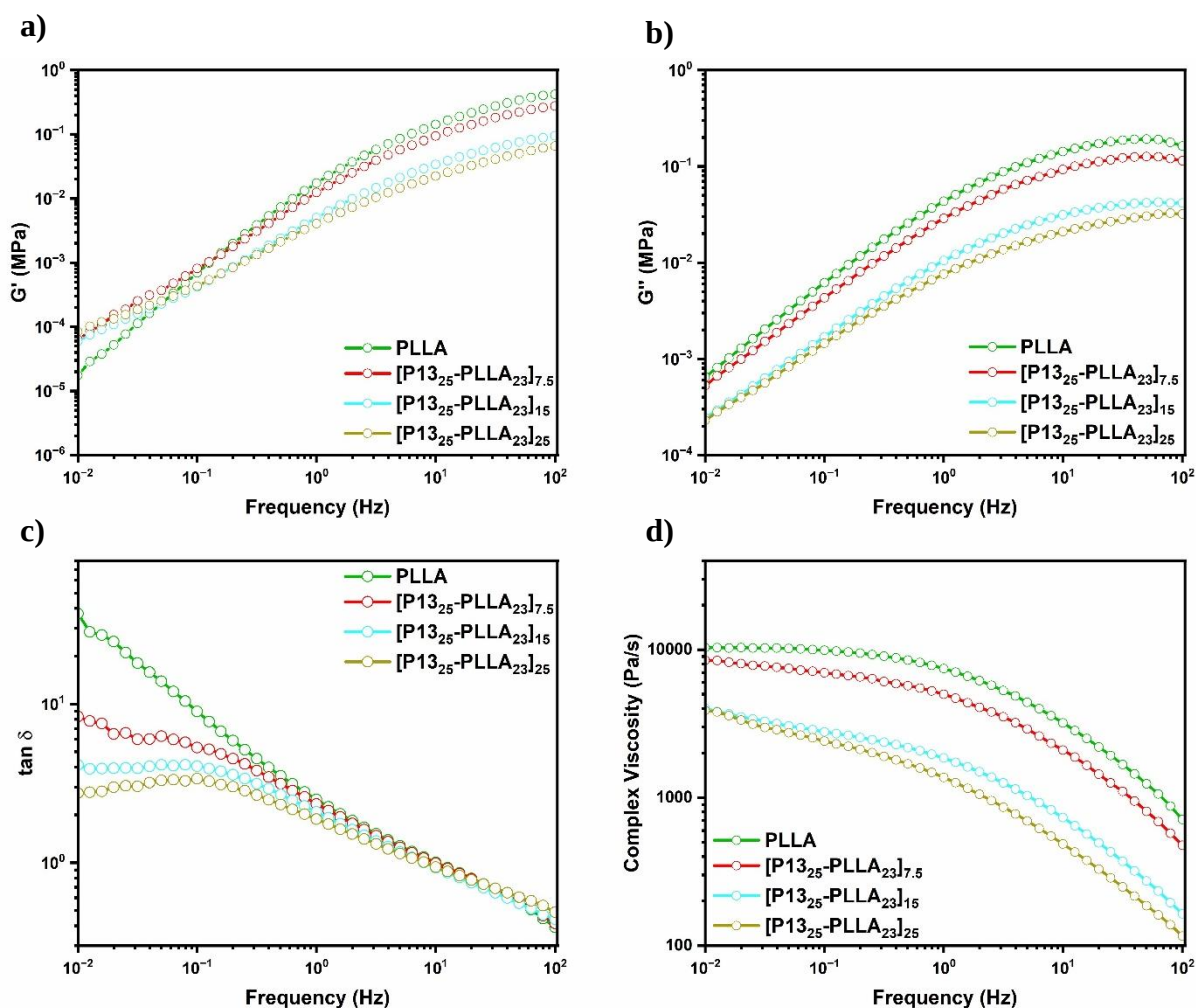


Figure S8.3.76: Frequency dependence of the rheological properties a) Elastic modulus (G'), b) viscous modulus (G'') c) $\tan \delta$ as well as d) the complex viscosity (η^*) measured by melt rheology of PLLA blends with 0, 7.5, 15 and 25 wt% **P13₂₅-PLLA₂₃**. The PLLA control sample is shown for comparison (green). All measurements were conducted in the linear viscoelastic region: 1% amplitude strain, 100-0.01 Hz, at 170°C.

8.3.2.5 DMTA Data for blends Described in Table 3.2

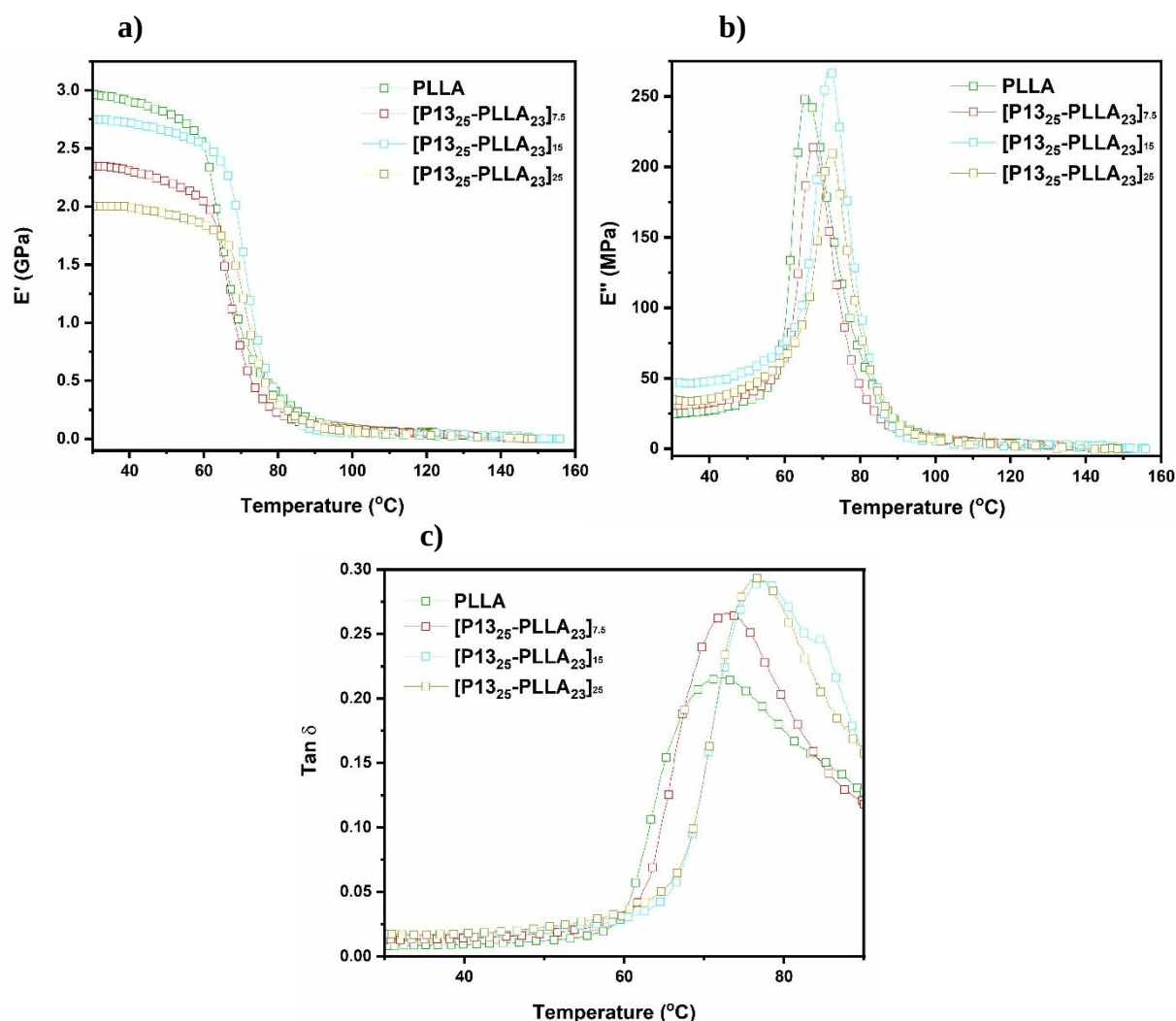


Figure S8.3.77: DMTA of PLLA blends with 0, 7.5, 15 and 25 wt% **P13₂₅-PLLA₂₃**. The a) storage modulus (E'), b) Loss modulus (E'') and c) $\tan \delta$ are shown for each. The **PLLA** standard (green) data are shown for comparison. Samples were heated from 30 °C to 170 °C, at a rate of 2 °C min⁻¹, with a frequency of 1 Hz, 0.001 N pre-load force and 0.015 % strain amplitude.

Table S8.3.4: DMTA analysis of PLLA blends with 0, 7.5, 15 and 25 wt% **P13₂₅-PLLA₂₃**.

Blend	Peak E'' - T_g (°C) ^a	Peak $\tan \delta$ - T_g (°C) ^a
PLLA	66	72
[P13 ₂₅ -PLLA ₂₃] _{7.5}	68	73
[P13 ₂₅ -PLLA ₂₃] ₁₅	72	77
[P13 ₂₅ -PLLA ₂₃] ₂₅	72	77

^aDMTA was carried out using a TA Instruments Q850 RSA-G2 Solids Analyser. Samples were heated from 30 °C to 170 °C, at a rate of 2 °C min⁻¹, with a frequency of 1 Hz, 0.001 N pre-load force, and 0.015% strain amplitude.

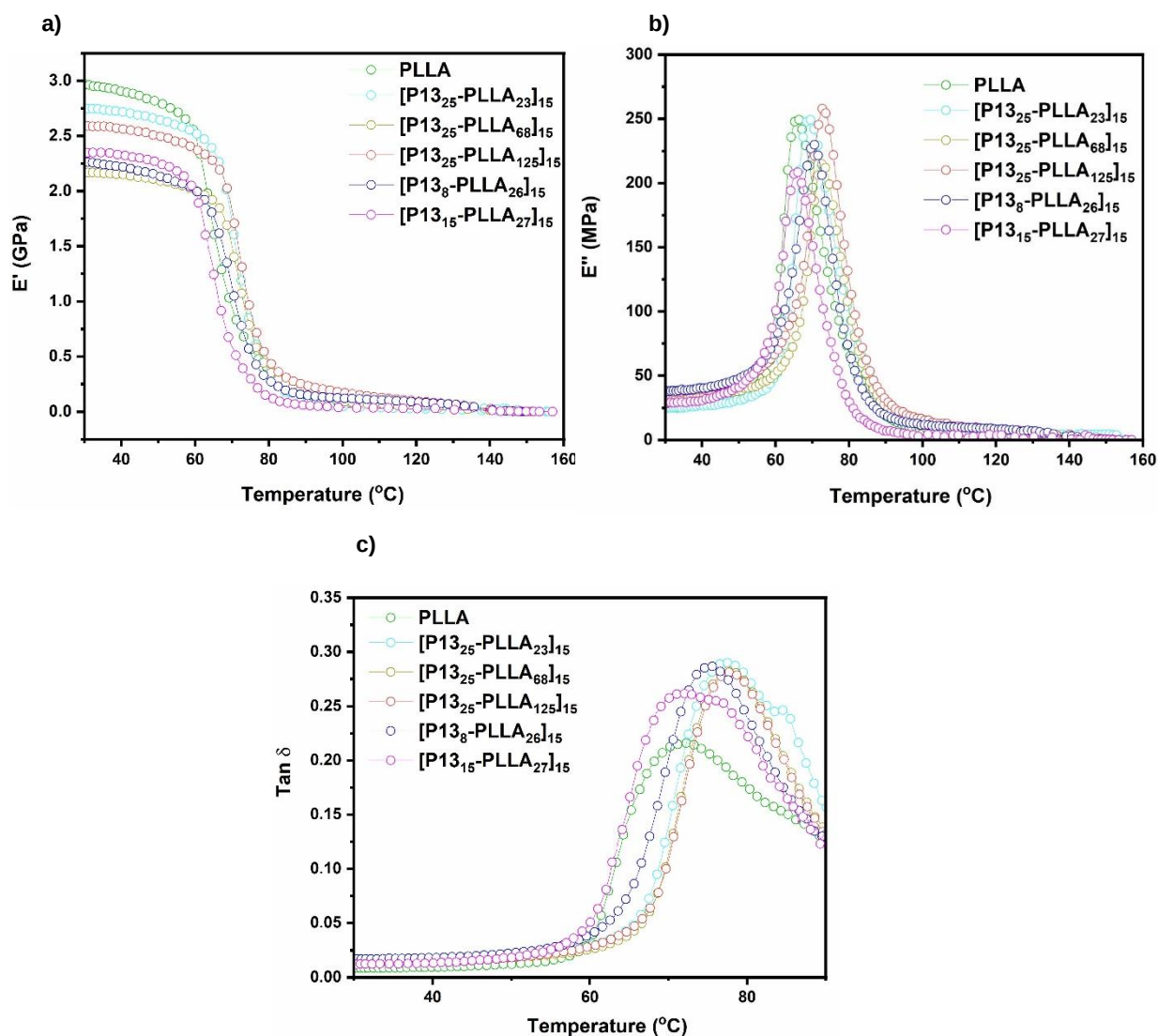


Figure S8.3.78: DMTA of [P13₂₅-PLLA₂₃]₁₅, [P13₂₅-PLLA₆₈]₁₅, [P13₂₅-PLLA₁₂₅]₁₅, [P13₈-PLLA₂₆]₁₅ and [P13₁₅-PLLA₂₇]₁₅ with varying PLLA and P13 compositions. The a) storage modulus (E'), b) Loss modulus (E'') and c) tan δ are shown. The PLLA standard (green) data are shown for comparison. Samples were heated from 30 °C to 170 °C, at a rate of 2 °C min⁻¹, with a frequency of 1 Hz, 0.001 N pre-load force and 0.015 % strain amplitude.

8.3.2.6 The Effect of Block Polymer Composition and MW

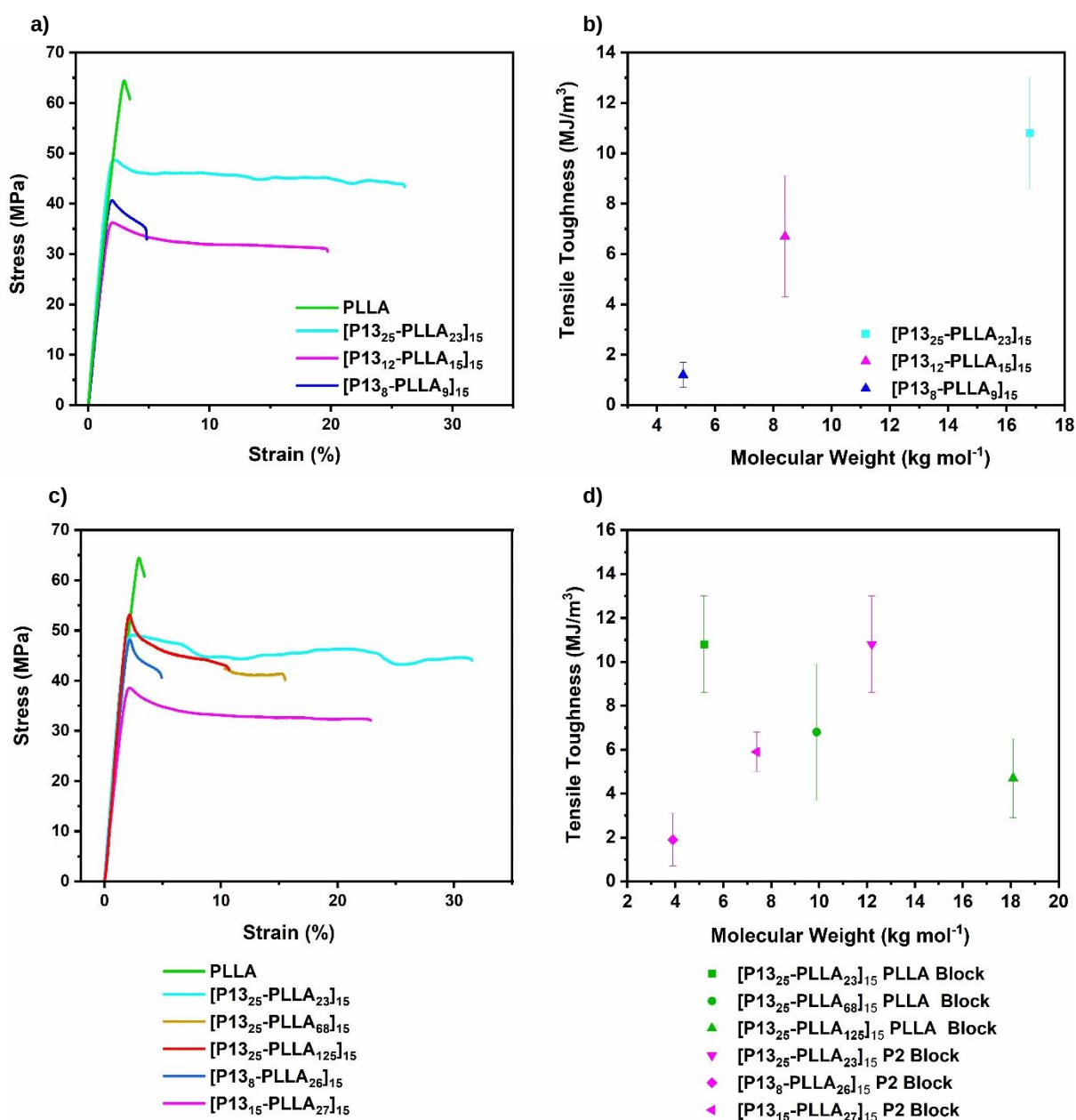


Figure S8.3.79: Mechanical data for a series of blends exploring the effect of a) and b), overall DP of the block polymer, as well as c) and d), the effect of the PLLA and poly(ester-*alt*-ether) (P13) block DP. a) and c) Representative stress versus strain data from tensile tests (each data point is the average of 5 tensile measurements). b) Plot showing tensile toughness vs block polymer M_n . d) plot showing tensile toughness of blend vs PLLA block (green) and poly(ester-*alt*-ether) block (pink) M_n . Each data point is the average of 5 tensile measurements.

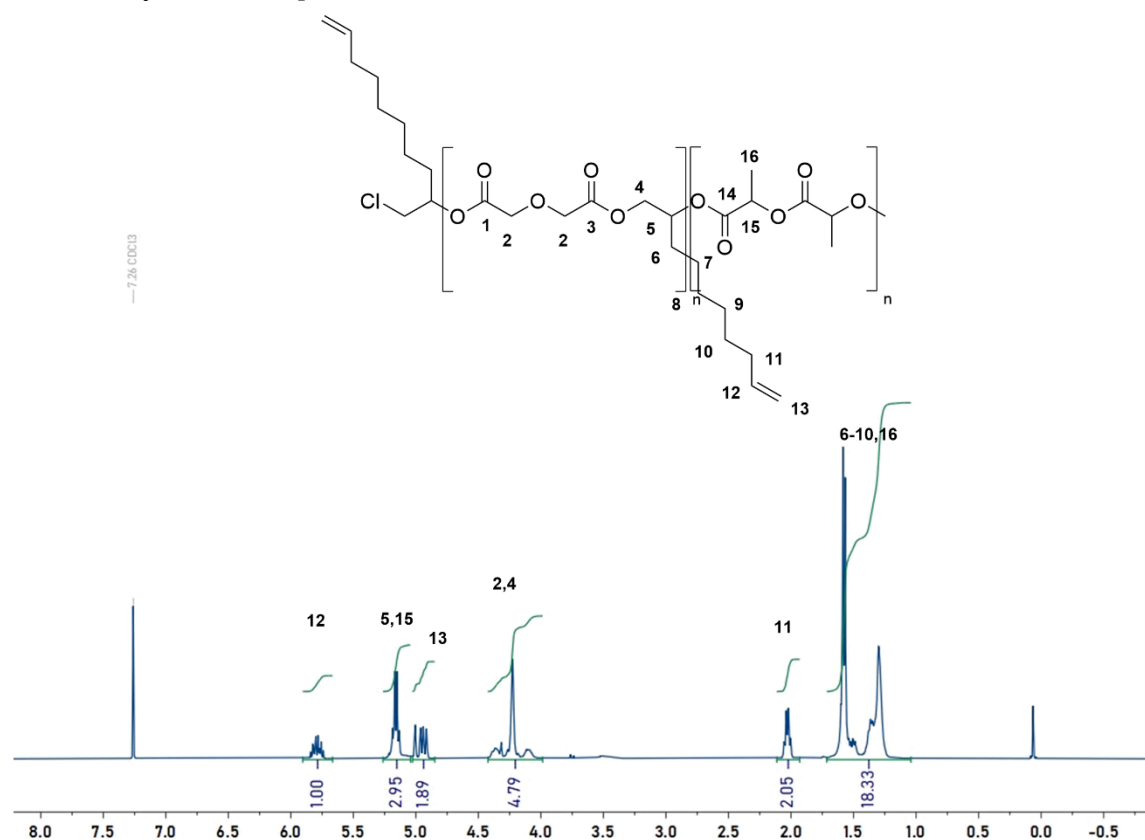
8.3.2.7 AB Polyester vs ABB Poly(Ester-*alt*-Ether); Blending Control8.3.2.7.1 Synthesis of [P13'₂₅-PLLA₂₆]₁₅

Figure S8.3.80: ^1H NMR spectrum of **P13'₂₅-PLLA₂₆** (with assignment) (400 MHz, CDCl_3). Reaction conditions: $[2] = 0.01$ mmol in 1 mL epoxide, $[\text{Cat}] : [\text{DGA}] : [\text{ED}] = 1 : 25 : 546$, 50°C .

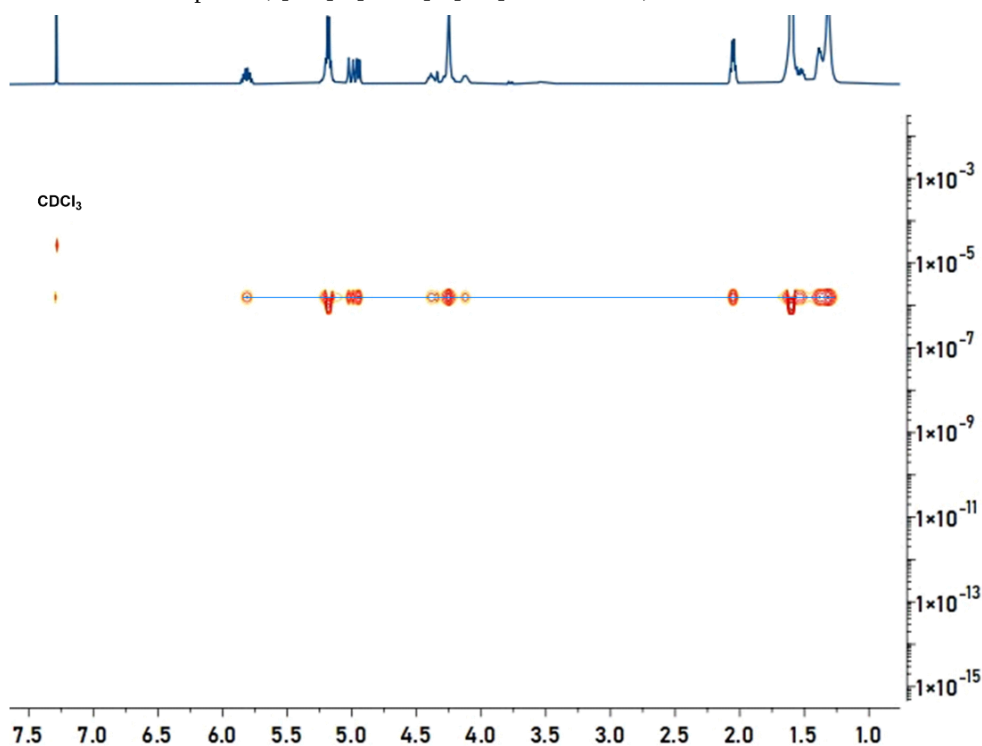


Figure S8.3.81: DOSY NMR spectrum of **P13'₂₅-PLLA₂₆** (with assignment) (400 MHz, CDCl_3). Reaction conditions: $[2] = 0.01$ mmol in 1 mL epoxide, $[\text{Cat}] : [\text{DGA}] : [\text{ED}] = 1 : 25 : 546$, 50°C .

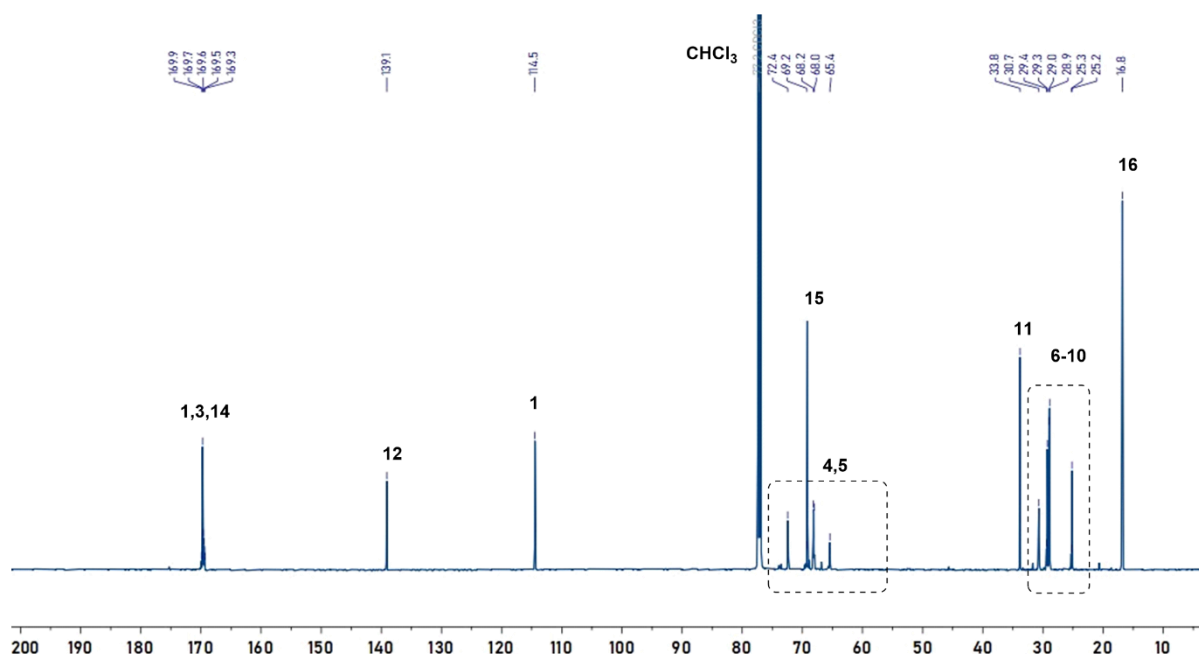


Figure S8.3.82: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum **P13'25-PLLA₂₆** (with assignment) (151 MHz, CDCl_3). Reaction conditions: **[2]** = 0.01 mmol in 1 mL epoxide, **[Cat]** : **[DGA]** : **[ED]** = 1: 25: 546, 50 °C.

Table S8.3.5: Synthesis and characterisation data comparison for **P13₂₅-PLLA₂₃** and **P13'25-PLLA₂₆**.^a

Polymer	Monomer Stoichiometry [Cat]:[Anhy]: [ED]:[L-LA]	Polymer DP [Anhy]:[ED]:[LA]^b	w_{PLLA} (%) ^c	$M_n(\text{Đ})$ [kg mol ⁻¹] ^d	M_n (Theo.) ^e	T_g (°C) ^f
P13₂₅-PLLA₂₃	1:50:546:50	25:56:23	0.26	16.9(1.28)	14.9	-46
P13'25-PLLA₂₆^g	1:25:546:25	25:26:26	0.35	11.3(1.45)	10.7	-21

^aReaction conditions: **[1]** = 10 mM in 1 mL epoxide, 50 °C. ^bDP of Anhydride was measured by monomer conversion data by integration of the monomer and polymer resonances in the ^1H NMR spectra of crude polymers. It is assumed both isopropoxide ligands initiate polymerisation. DP of ED and L-LA were determined by integration of the ^1H NMR spectra of purified polymer against the anhydride polymer resonance. ^cWeight fraction of PLLA blocks (w_{PLLA}) calculated based on monomer DP values form ^1H NMR spectra. ^dDetermined by gel permeation chromatography (GPC), using THF as the eluent, and calibrated using narrow MW polystyrene standards. ^eTheoretical M_n were calculated from the monomer conversion data and assume both isopropoxides initiate. ^fObtained from Differential Scanning Calorimetry (DSC, third heating cycle, 10 °C min⁻¹ heating rate). ^gReaction conditions: **[2]** = 10 mM in neat 1 mL epoxide.

8.3.2.7.2 PLLA Blending with **[P13'25-PLLA₂₆]₁₅**

Table S8.3.6: Tensile mechanical comparison of the poly(ester-*alt*-ether) **[P13₂₅-PLLA₂₃]₁₅** (light blue curve, Table 3.2 and Figure 3.3) and the polyester poly(ester-*alt*-ether) **P13'25-PLLA₂₆]₁₅**. Neat PLLA is shown for reference.

Blend	χ (%)	T_g (°C)	T_m (°C)	$T_{d,5}$ (°C)	E (GPa)	σ_y (MPa)	ϵ_B (%)	U_T (MJm ⁻³)
PLLA	34	65	149	321	2.9 ± 0.3	66.7 ± 4.3	3.4 ± 0.5	1.4 ± 0.3
[P13₂₅-PLLA₂₃]₁₅	42	63	149	291	3.1 ± 0.1	48.7 ± 1.2	24.5 ± 4.6	10.8 ± 2.2
[P13'25-PLLA₂₆]₁₅	41	62	153	316	2.6 ± 0.2	41.0 ± 3.3	25.1 ± 2.5	9.1 ± 2.5

^aCommercial PLLA was used in blending, provided by Goodfellow ME34-GL-000110 (M_n = 103.4(1.81) kg mol⁻¹ vs polystyrene standards in CHCl_3). ^bObtained from Differential Scanning Calorimetry (DSC, first heating cycle, 10 °C min⁻¹ heating rate from -80 to 180 °C). The enthalpies of crystallization and melting were determined by the integrated area of the exothermic peak and endothermic peaks respectively, while the crystallization and melting temperatures were obtained from the maximum and minimum of the exo- and endothermic peaks respectively. Crystallinity was calculated by $(\Delta H_m - \Delta H_{cc}) / \Delta H_{m,100} \times 100$, where $\Delta H_{m,100}$ is the enthalpy of melting for 100 % crystalline PLLA and is equal to 93.7 J/g. ^cObtained from TGA (Polymer samples were heated from 30 to 700 °C at a rate of 10 °C min⁻¹, under N_2 flow 12 mL min⁻¹). ^dUniaxial tensile measurements were conducted at 10 mm min⁻¹ extension rate. The mean values and standard deviations are calculated from measurements conducted independently on five separate specimens conforming to dimensions for ISO 527-2 type 5B. Tensile toughness was calculated from the area under the stress-strain plots.

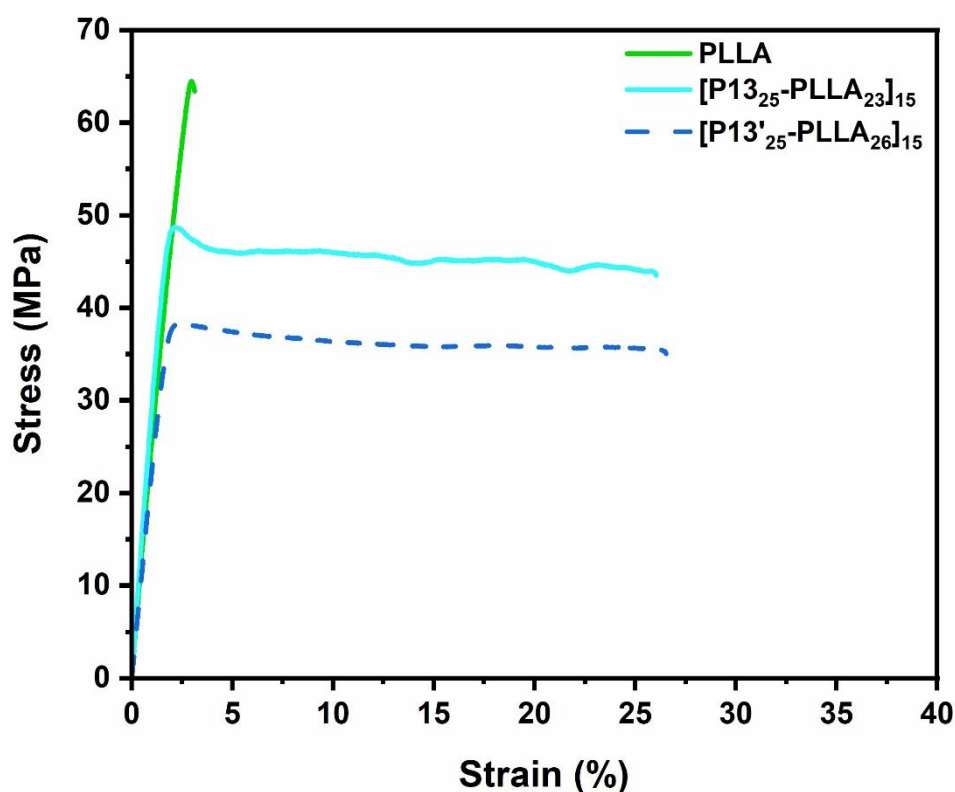


Figure S8.3.83: Tensile mechanical comparison of the poly(ester-*alt*-ether) **[P13₂₅-PLLA₂₃]₁₅** (light blue curve, Table 3.2 and Figure 3.3) and the polyester poly(ester-*alt*-ether) **P13'₂₅-PLLA₂₆]₁₅**. Neat PLLA is shown for reference.

8.3.3 Investigation of Alkene Stability

A series of control experiments were performed in order to determine whether the alkene in the *ED* repeat unit of the poly(ester-*alt*-ether) was undergoing any crosslinking during thermal annealing of the polymer blends. Firstly, a sample of the processed **[P13₂₅-PLLA₂₃]₁₅** polymer blend was dissolved in THF and subsequently analysed via GPC. The **P13₂₅-PLLA₂₃** sample (used in the experiment), had a M_n by GPC of 16.9 kg mol⁻¹ with a monomodal distribution ($\mathcal{D} = 1.28$) before blending. After blending the GPC trace remained monomodal with an M_n of 16.5 kg mol⁻¹ ($\mathcal{D} = 1.08$) (Figure S87 below). The molecular weight and dispersity both stayed consistent, demonstrating no change to the polymer throughout the annealing process. The **[P13₂₅-PLLA₂₃]₁₅** blend was then dissolved in CDCl₃ and a ¹H NMR spectrum was obtained (Figure S88). The signals correlating to the double bond protons of *ED* at 5.72 and 4.92 ppm were retained.

Furthermore, the block polymer **P13₂₅-PLLA₂₃** was subjected to the same conditions as employed in the PLLA blending, and was placed in the vacuum oven for 2 days at 60 °C, followed by ramping to 180 °C and holding for 10 minutes before slow cooling to room temperature overnight. The GPC traces before and after were both monomodal, with M_n ($\mathcal{D}$) by

GPC of 16.9(1.28) and 17.5(1.16) kgmol⁻¹ respectively (Figure S89 and Table S6). In a similar manner, the ¹H NMR spectrum of the thermally treated sample showed retention of the double bond (Figure S90), and the DP calculated from the NMR spectra before and after annealing for DGA:ED:L-LA were 25:56:23 and 25:44:21, respectively.

Lastly, **P13₂₅-PLLA₂₃** was held at 180 °C (the temperature of the blend annealing) for 60 minutes and monitored by DSC. No change was observed, resulting in a flat DSC trace over the 60 minutes (Figure S91). The M_n by GPC before and after the isotherm were 16.9(1.28) and 15.8(1.20) kg mol⁻¹ respectively. The ¹H NMR spectrum showed the alkene signal again, in the sample after DSC analysis (Figure S91 and S92 and Table S8).

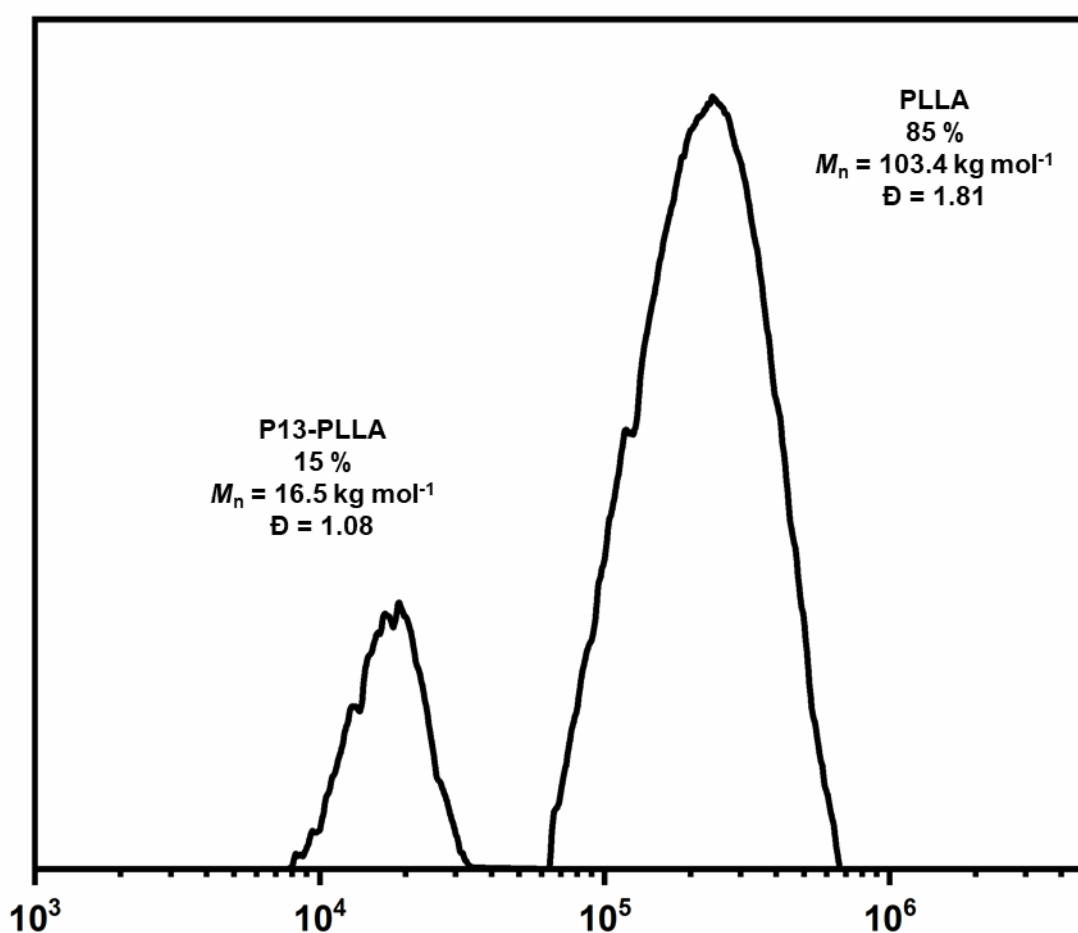


Figure S8.3.84: GPC trace of the PLLA blend with **[P13₂₅-PLLA₂₃]₁₅** dissolved in THF. The peak ratios are 15 and 85 % (as expected). The **P13₂₅-PLLA₂₃**. GPC results are presented in the table below of **[P13₂₅-PLLA₂₃]₁₅** show the same M_n and dispersity after processing.

Table S8.3.7: Molecular weight and dispersity data for **[P13₂₅-PLLA₂₃]₁₅** before and after.

Polymer	Mn(Đ) [kg mol ⁻¹]c
Before – [P13₂₅-PLLA₂₃]₁₅	16.9(1.28)
After – [P13₂₅-PLLA₂₃]₁₅	16.5(1.08)

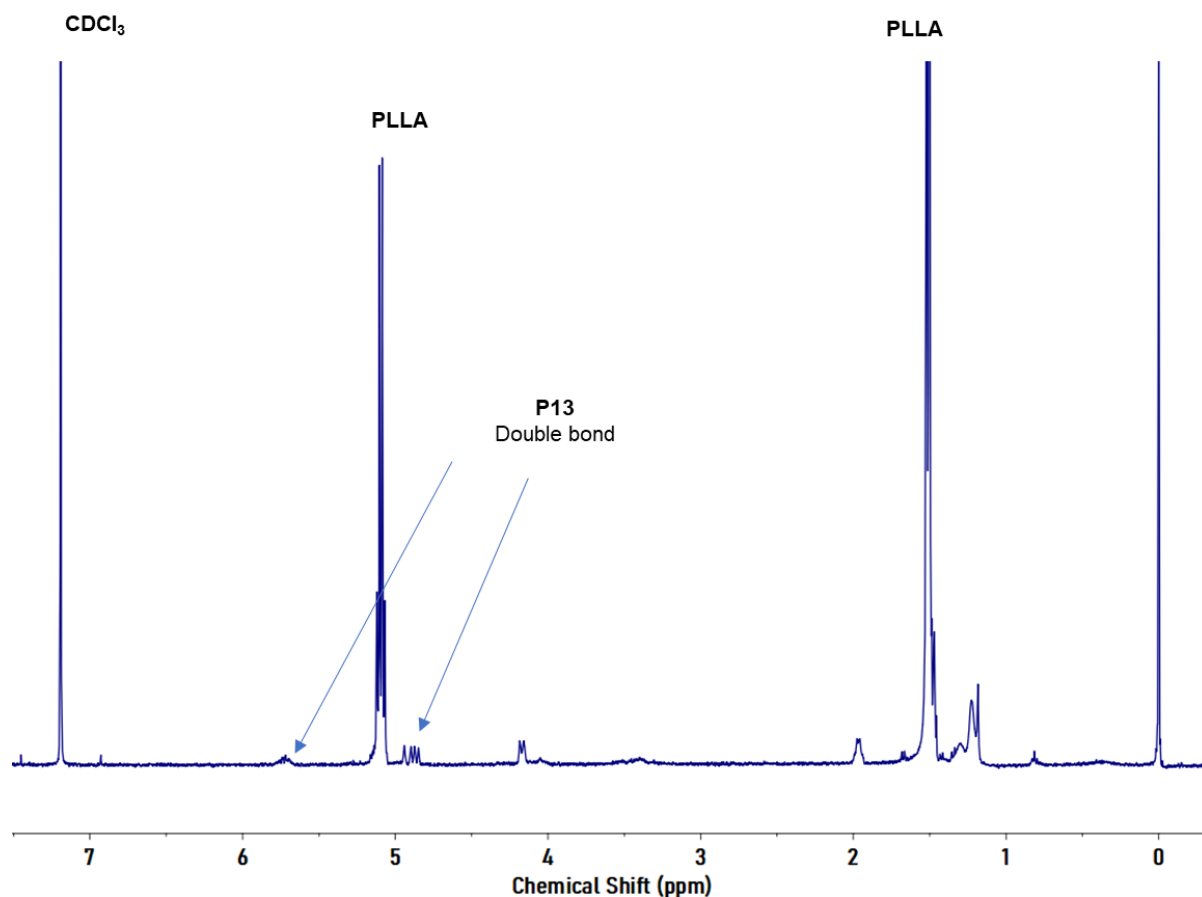


Figure S8.3.85: ^1H NMR spectrum of the PLLA blend $[\text{P13}_{25}\text{-PLLA}_{23}]_{15}$. The alkene resonances in $\text{P13}_{25}\text{-PLLA}_{23}$ are at 4.8 and 5.8 ppm.

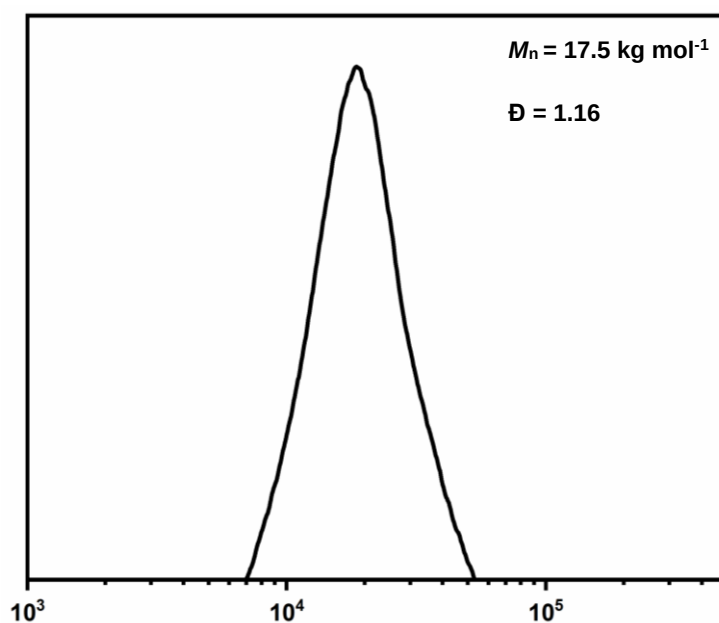


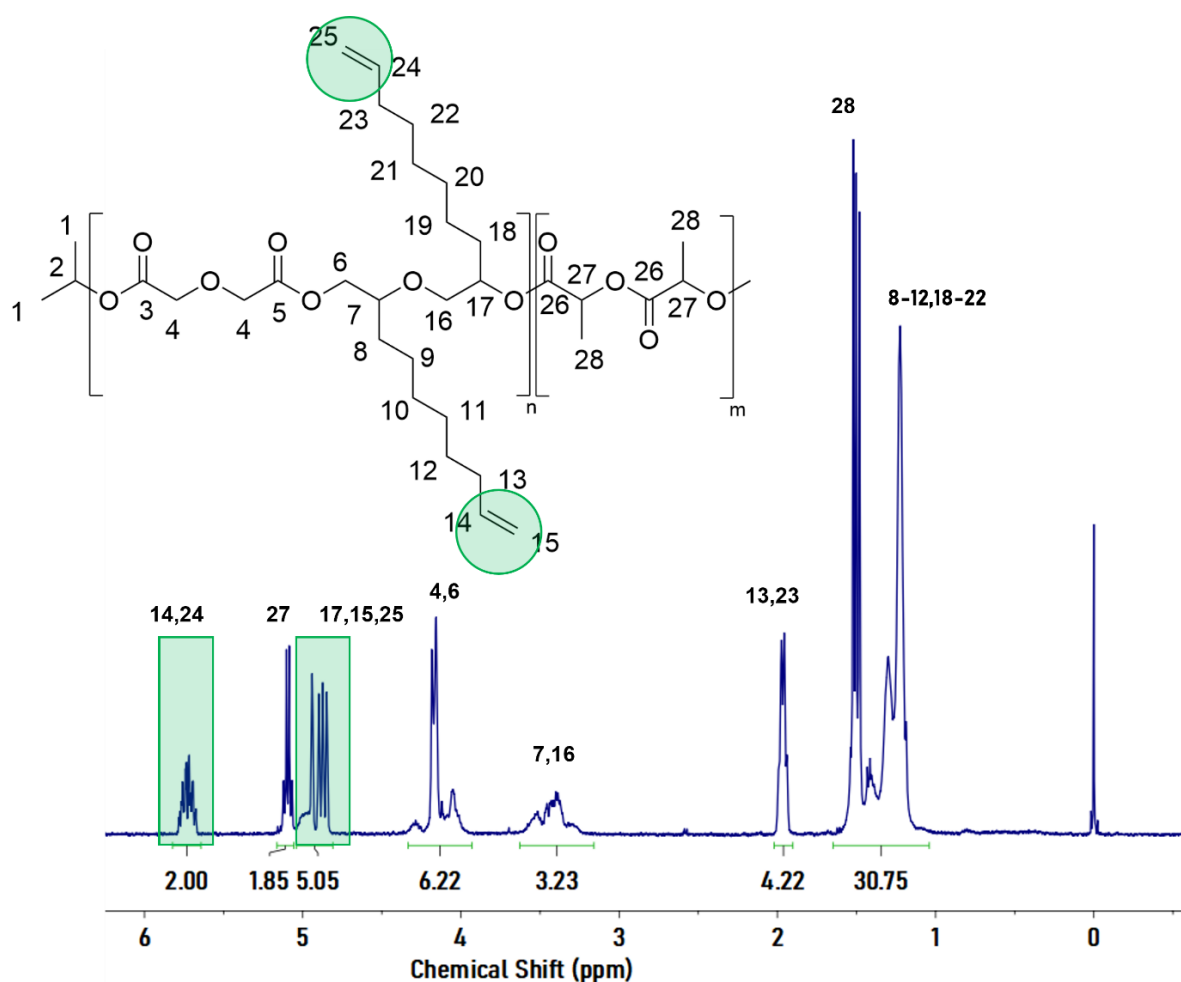
Figure S8.3.86: GPC trace of $\text{P13}_{25}\text{-PLLA}_{23}$ sample, after annealing under identical conditions to the PLLA blend synthesis (vacuum oven at 60 °C for 2 days, then 180 °C for 10 minutes, followed by slow cooling to room temperature overnight). The M_n and D remain consistent before and after, 16.9(1.28) kg mol^{-1} and 17.5(1.16) kg mol^{-1} , respectively.

Table S8.3.8: Molecular weight and polydispersity data for **P13₂₅-PLLA₂₃** before and after annealing under blending conditions to ascertain the stability of the alkene.

Polymer	$M_n(\bar{D})$ [kg mol ⁻¹]
Before Annealing – P13₂₅-PLLA₂₃	16.9(1.28)
After Annealing – P13₂₅-PLLA₂₃	17.5(1.16)

Table S8.3.9: Degree of polymerisation for **P13₂₅-PLLA₂₃** before and after annealing under blending conditions to ascertain the stability of the alkene.

Polymer	Deg. Of Pol. (DP) [DGA]:[ED]:[LA]
Before Annealing – P13₂₅-PLLA₂₃	25:56:36
After Annealing – P13₂₅-PLLA₂₃	25:44:21

**Figure S8.3.87:** ¹H NMR spectrum of **P13₂₅-PLLA₂₃**, after annealing under identical conditions to the blends used in this study (vacuum oven at 60 °C for 2 days, 180 °C for 10 minutes, followed by slow cooling to room temperature). The alkene resonances are at 4.8 and 5.8 ppm.

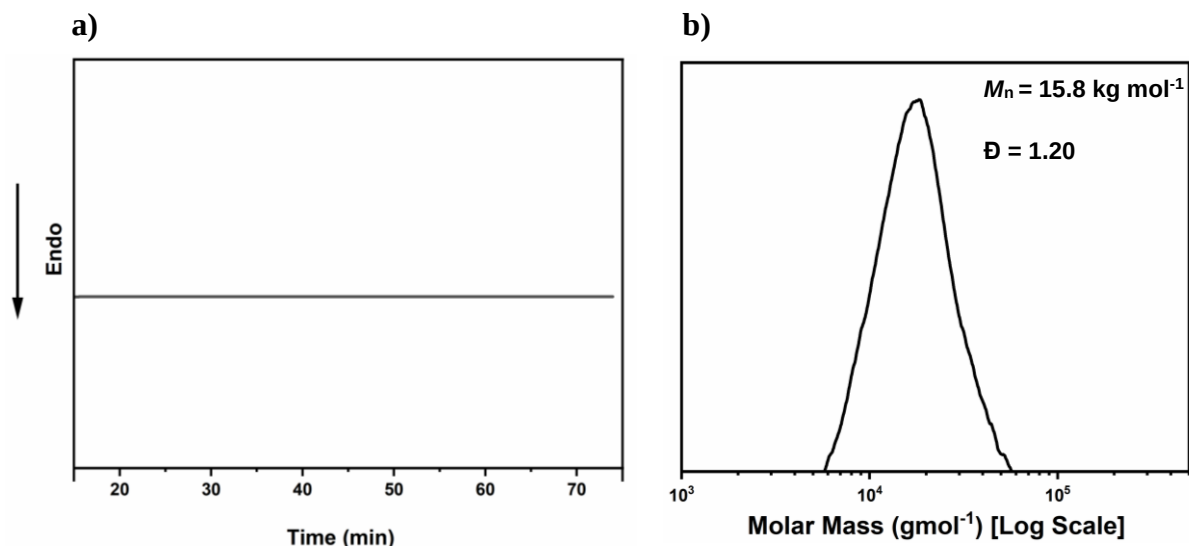


Figure S8.3.88: (a) A DSC isotherm for **P13₂₅-PLLA₂₃** at 180 °C for 60 min, and (b) the subsequent GPC trace of **P13₂₅-PLLA₂₃**. The DSC isotherm showed no change, and the M_n and Đ by GPC in THF stayed the same before (16.9(1.28) kg mol⁻¹) and after (15.8(1.20) kg mol⁻¹), suggesting stability of the alkene at these temperatures (the temperature of blend annealing used in this study).

Table S8.3.10: Molecular weight and polydispersity data for **P13₂₅-PLLA₂₃** before and after DSC isotherm at 180 °C for 60 minutes, to ascertain the stability of the alkene.

Polymer	$M_n(\text{Đ})$ [kg mol ⁻¹] ^c
Before DSC isotherm – P13₂₅-PLLA₂₃	16.9(1.28)
After DSC isotherm – P13₂₅-PLLA₂₃	15.8(1.20)

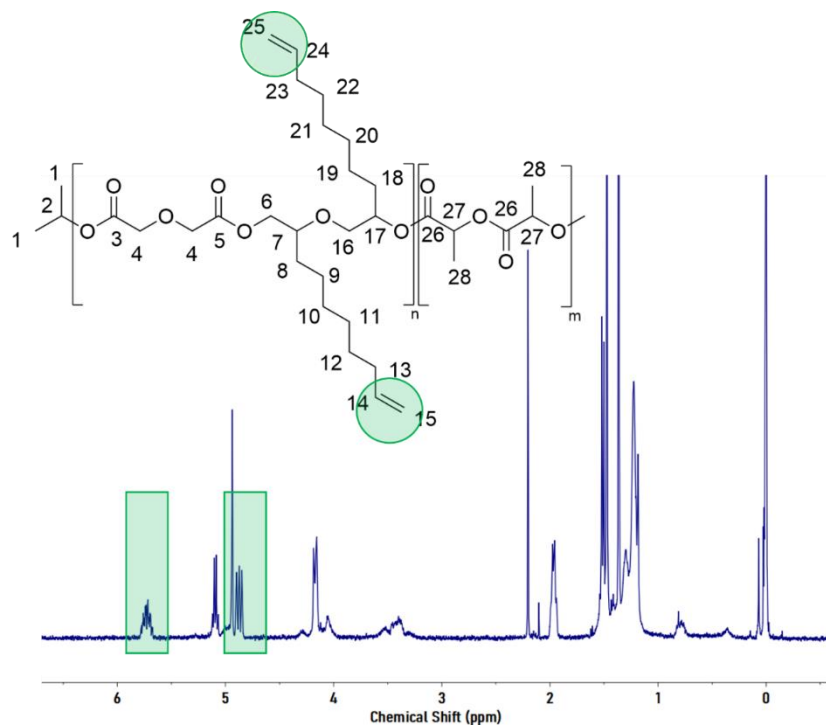


Figure S8.3.89: ¹H NMR spectrum of **P13₂₅-PLLA₂₃** after a DSC isotherm at 180 °C for 60 min.

8.3.4 Chemical Depolymerisation

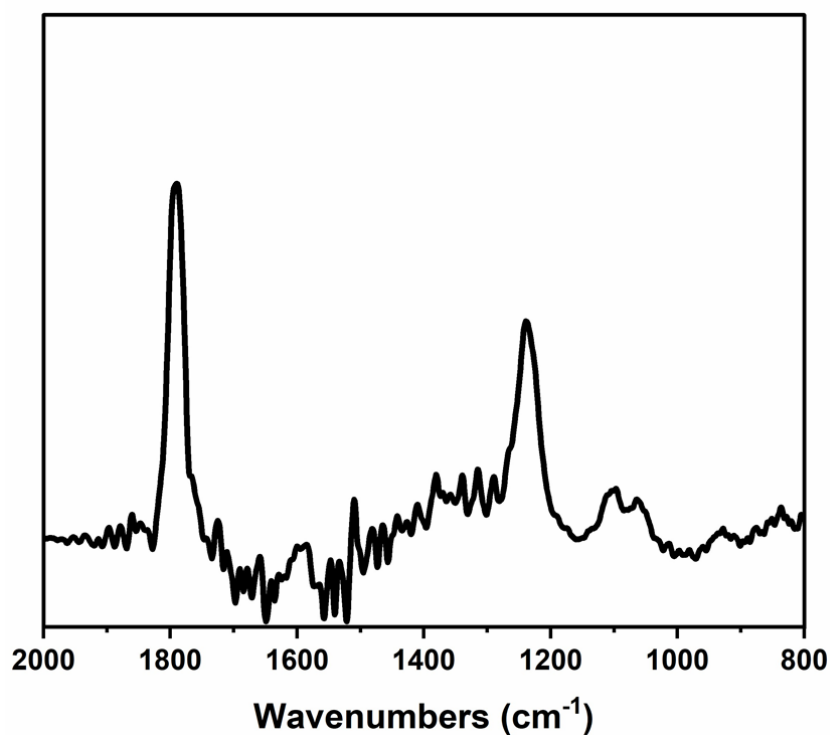


Figure S8.3.90: The TGA-IR spectrum of the 180 °C isotherm, matching 100 % with the library search for lactide.

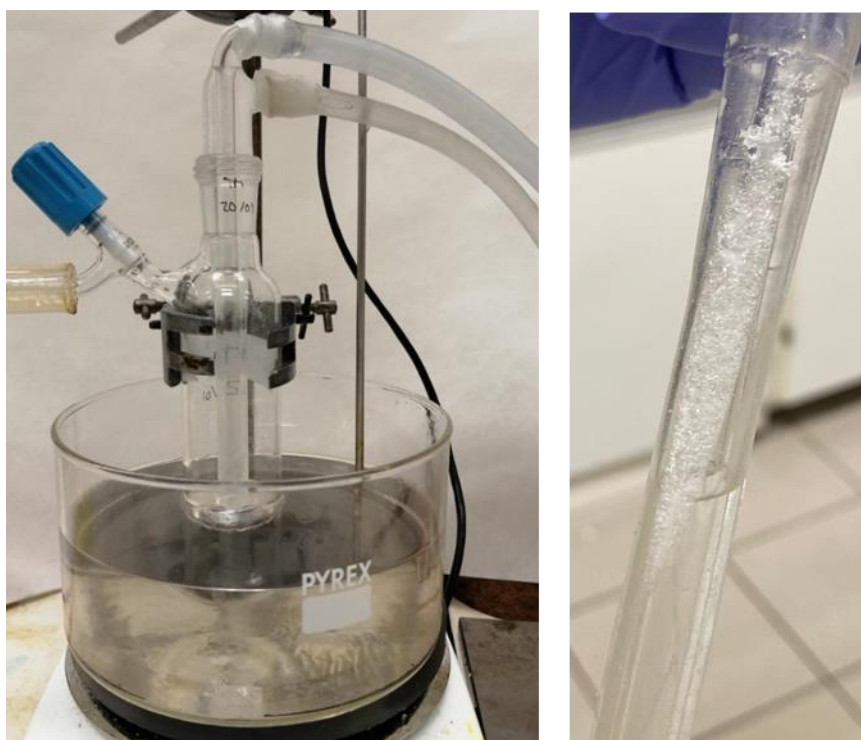


Figure S8.3.91: The Experimental set-up of the lab-scale chemical recycling of the polymer blend **[P13₂₅-PLLA₂₃]₁₀** to determine Lactide Selectivity.

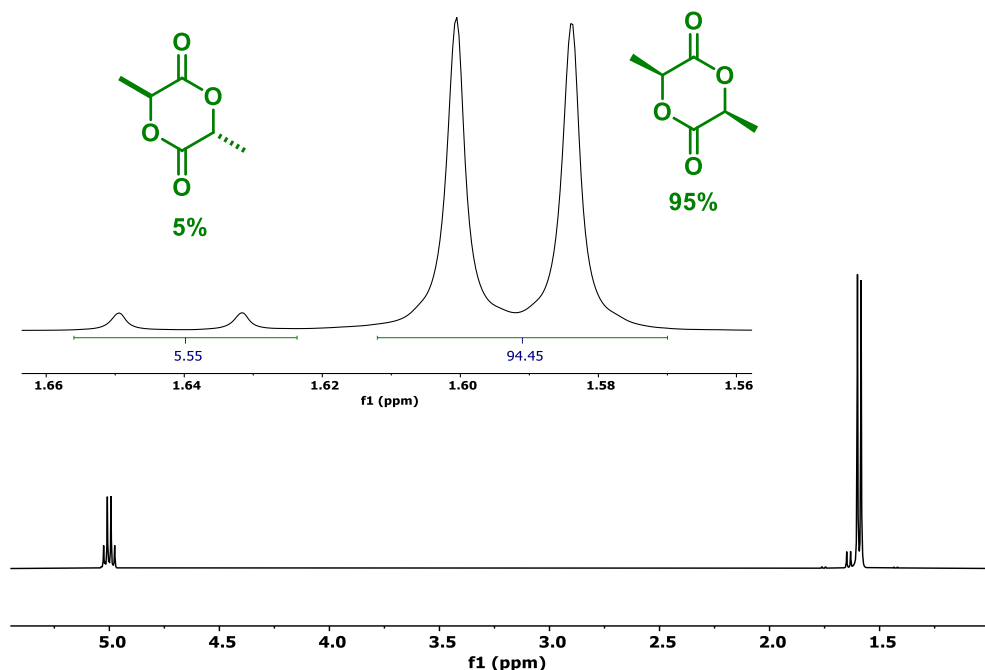


Figure S8.3.92: ^1H NMR spectrum of the product collected by sublimation after chemical recycling of the polymer blend **[P13₂₅-PLLA₂₃]₁₀** at 180 °C. Inset shows a 5 : 95 meso : L-Lactide ratio which is exactly in line with the starting PLLA composition (95 % PLLA : 5 % Meso PLA).

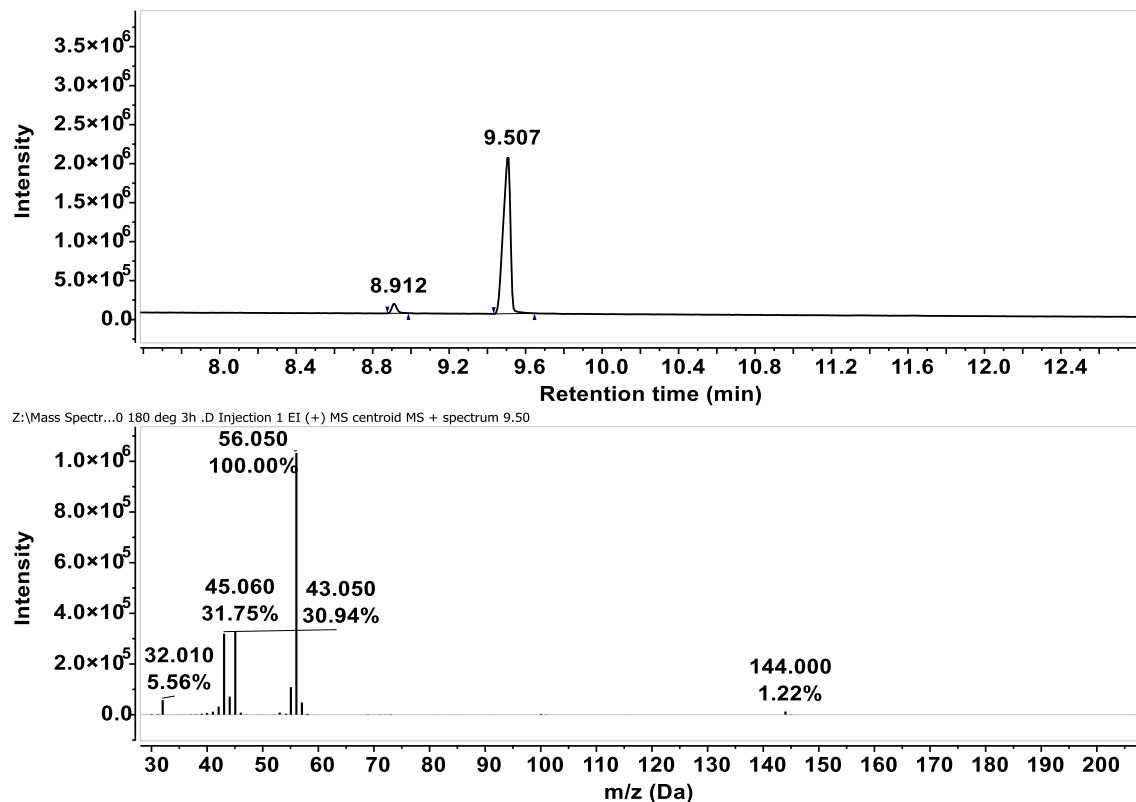


Figure S8.3.93: GC-MS chromatograms of chemical recycling of the polymer blend **[P13₂₅-PLLA₂₃]₁₀**. The data show L-lactide at 9.507 and meso-LA at 8.912 minutes. Below is the ESI mass spectrum of the L-lactide fraction (9.507 min) showing the molecular ion at 144 m/z .

8.3.5 Enzymatic Degradation

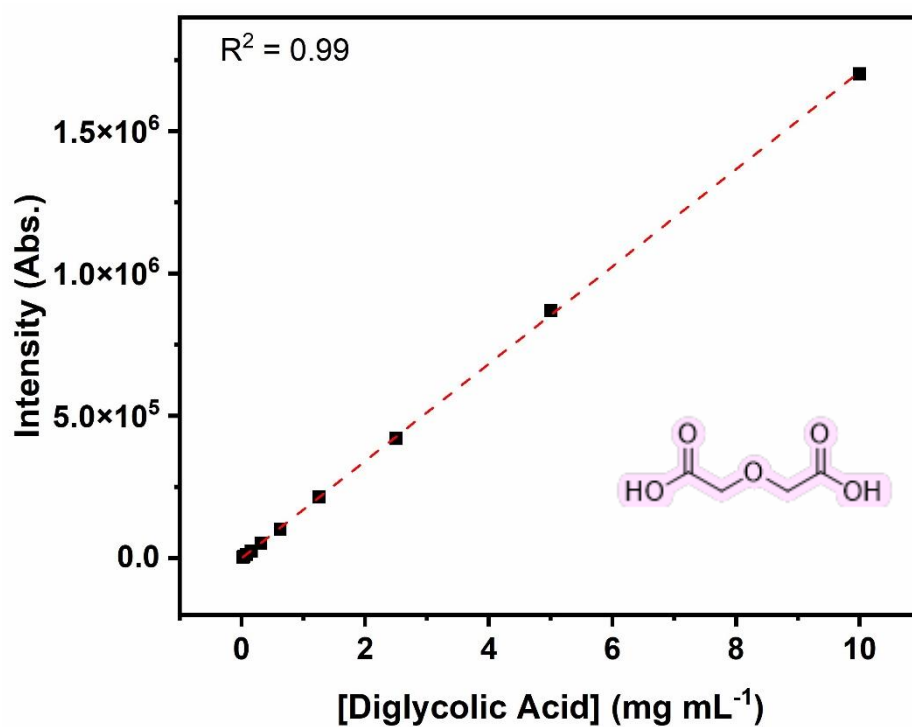
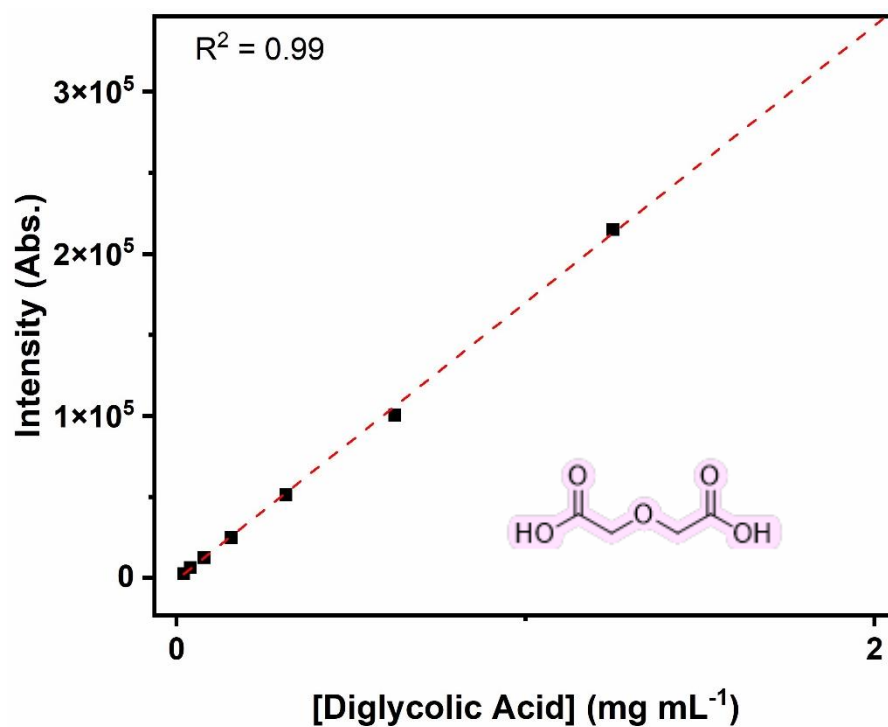


Figure S8.3.94: HPLC calibration data for diglycolic acid, with linear fit.

Figure S8.3.95: HPLC calibration data for diglycolic acid, between 0-3 mg mL⁻¹ with linear fit.

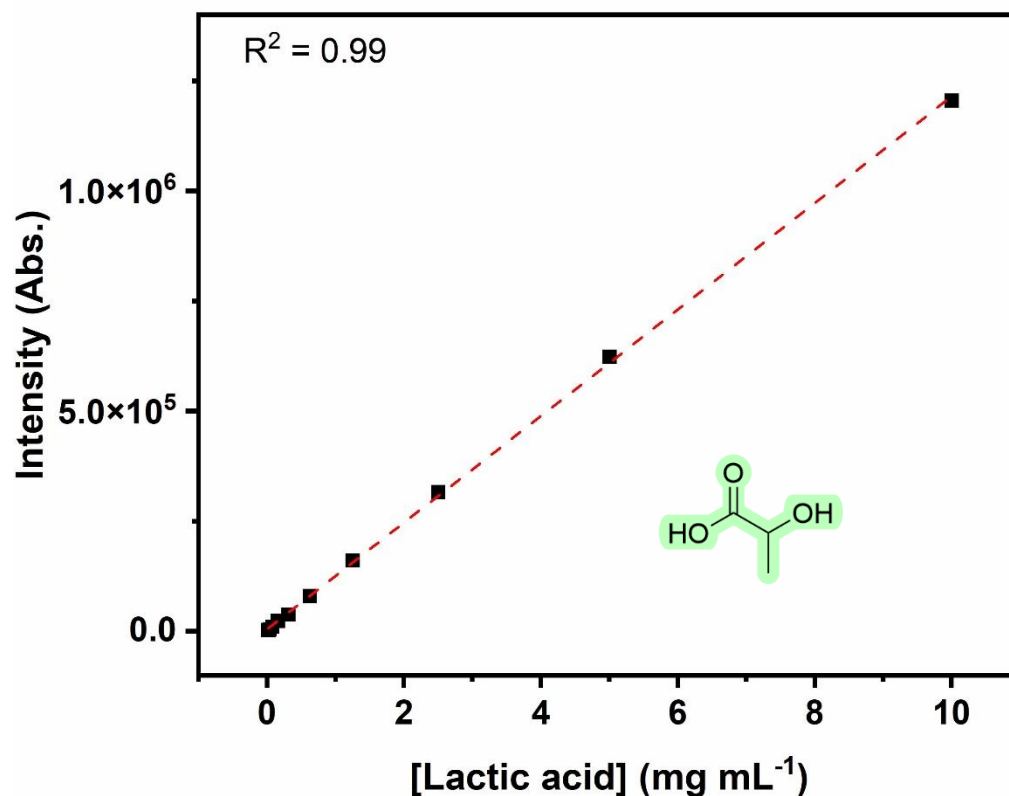


Figure S8.3.96: HPLC calibration data for L-lactic acid, with linear fit shown.

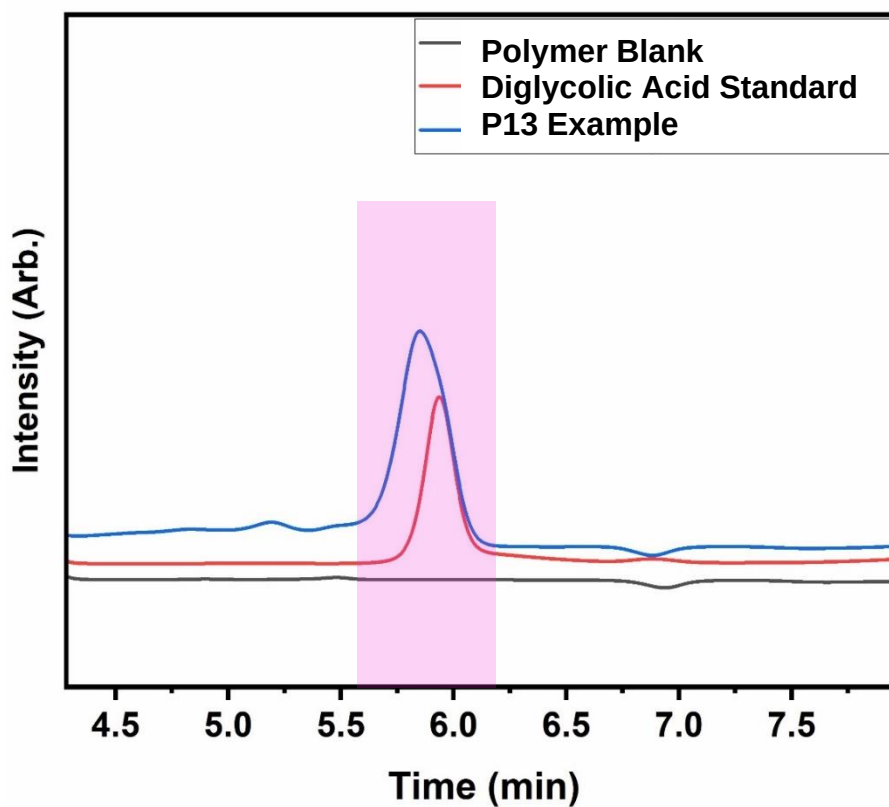


Figure S8.3.97: Comparison of a negative control (P13, buffer, no enzyme – black curve), diglycolic acid standard sample (red curve), and an example of a sample of P13 during enzymatic degradation experiments (blue curve). The pink zone indicates the diglycolic acid elution time. P13 $M_n = 10.3$, $\bar{D} = 1.24$ (Table 1).

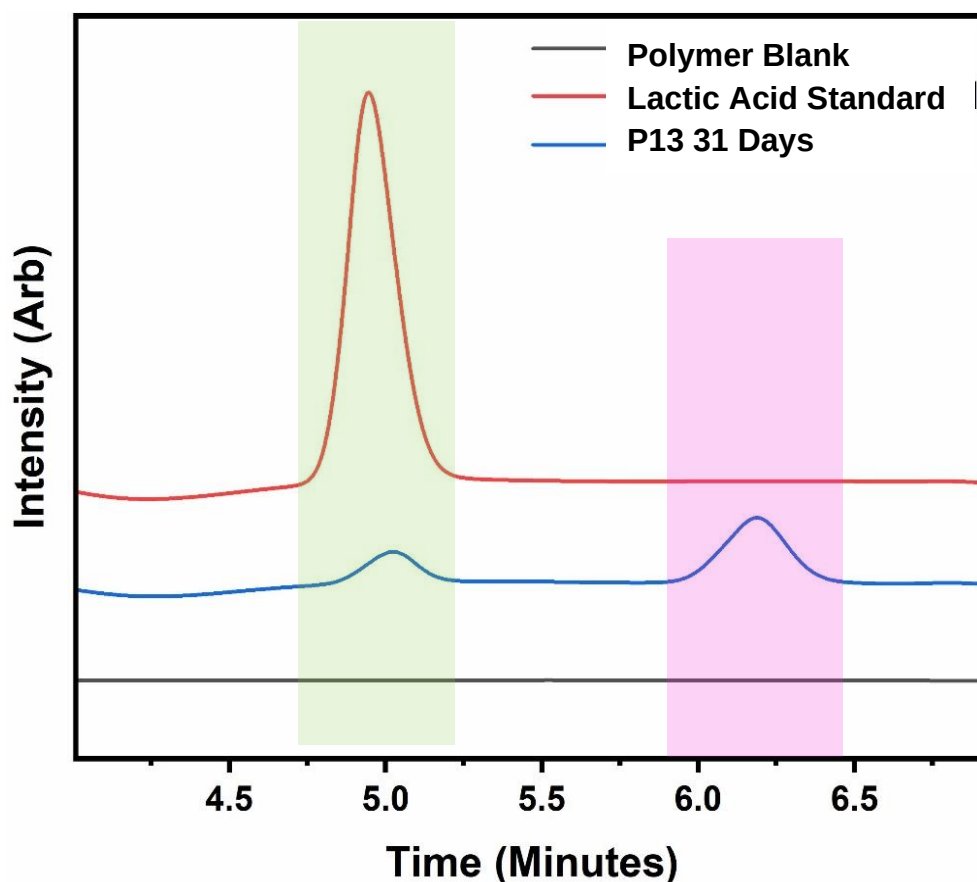


Figure S8.3.98: Comparison of a negative control (P13₂₅-PLLA₂₃, buffer, no enzyme – black curve), lactic acid standard sample (red curve), and an example of a sample of P13-PLLA during enzymatic degradation experiments after 31 days (blue curve). The pink zone indicates the diglycolic acid elution time and the green zone indicates the lactic acid elution time.

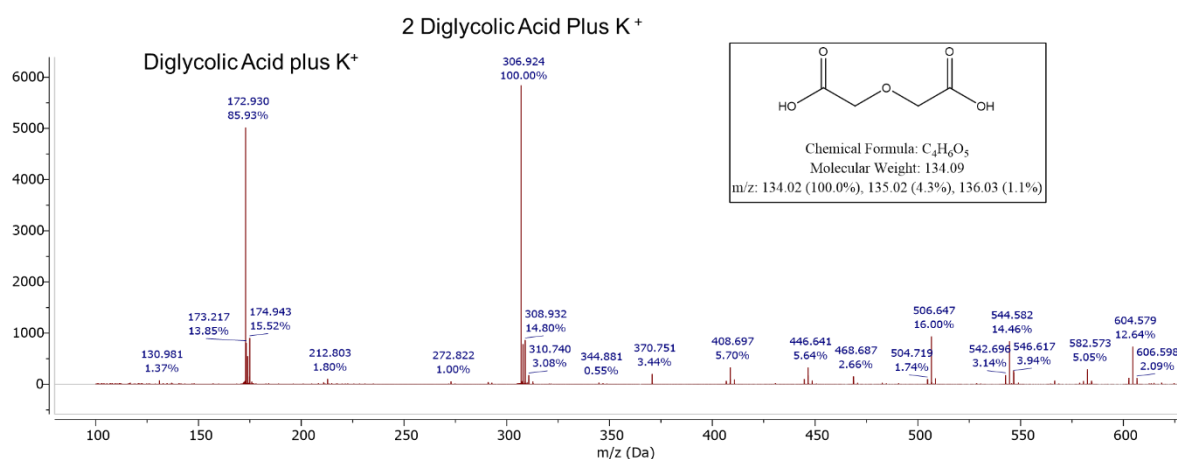


Figure S8.3.99: Positive mode ESI-MS of the HPLC fraction eluting at 5.7-6.1 minutes (diglycolic acid). The plot shows the formation of both the molecular ion (+ K⁺) and the diglycolic acid/K⁺ species (N.B the HPLC is conducted with KH₂PO₄ solution as the mobile phase).

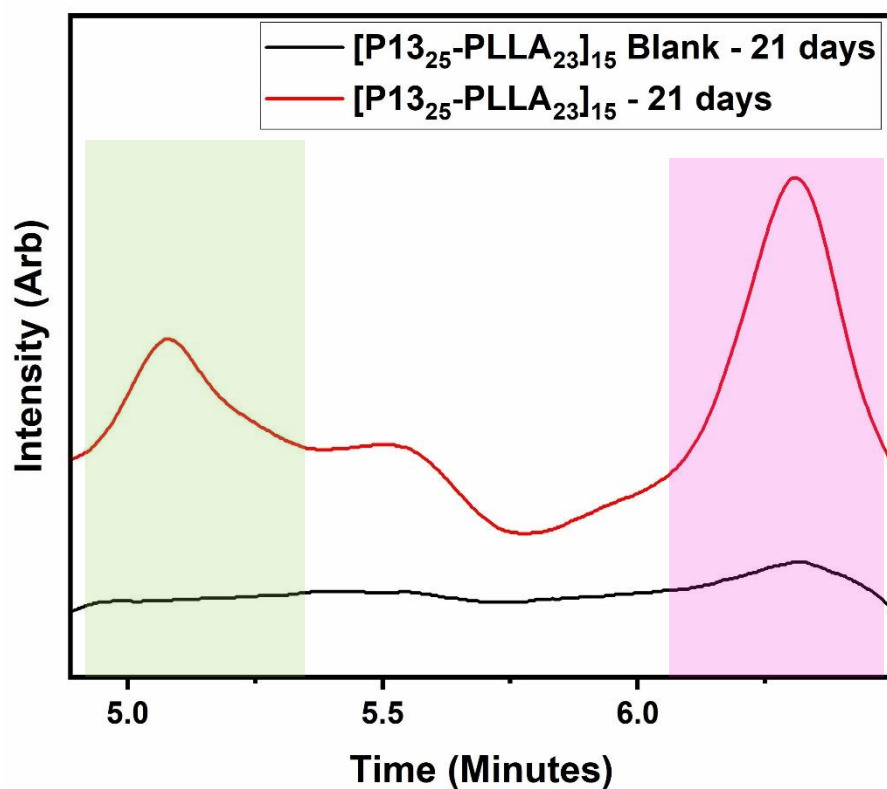


Figure S8.3.100: HPLC chromatogram of the polymer blend $[P13_{25}\text{-}PLLA_{23}]_{15}$ after 21 days. The data shows the formation of products eluting at 6.1 min (diglycolic acid, pink) and 4.9 min (lactic acid, green).

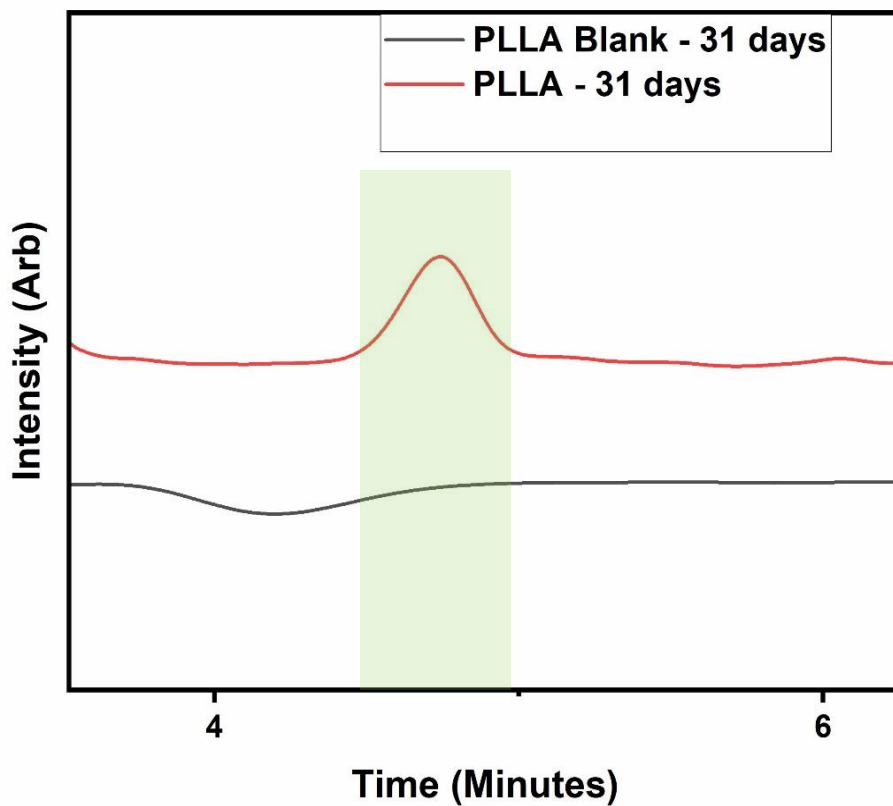


Figure S8.3.101: HPLC chromatogram of the **PLLA** (used in the blends) after 34 days, showing a peak at 4.9 min corresponding lactic acid (green).

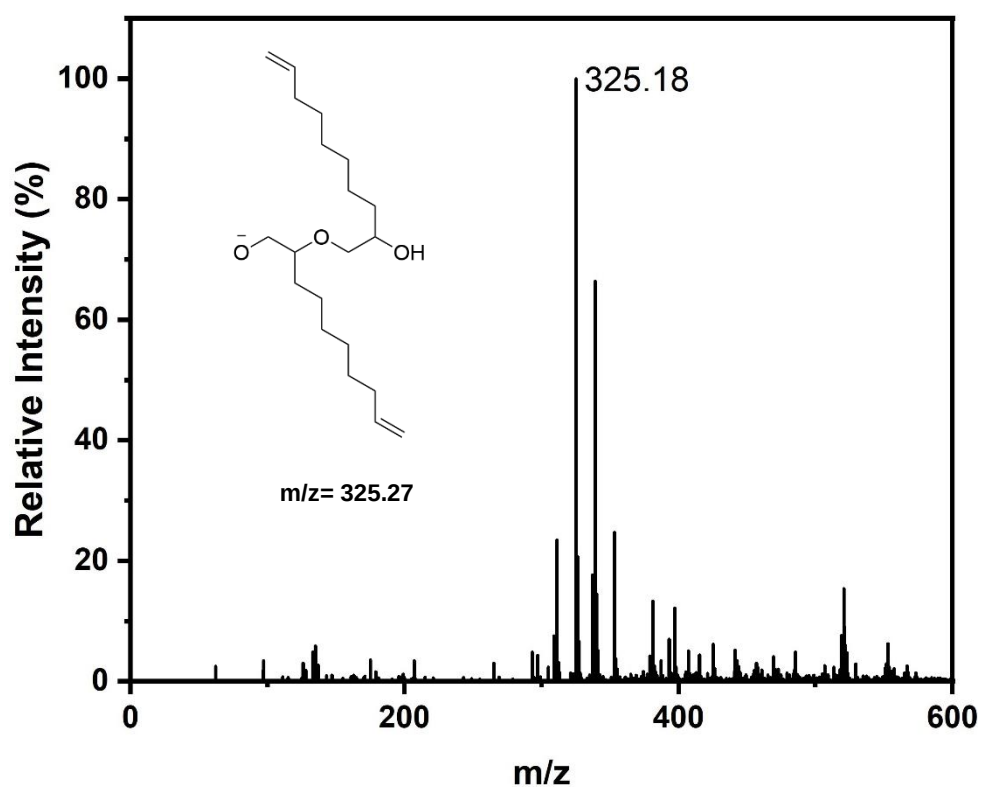


Figure S102: Mass spectrum of the enzymatic degradation of **P13** (Figure 6c), after drying to remove solvent, showing the presence of the ether-diol.

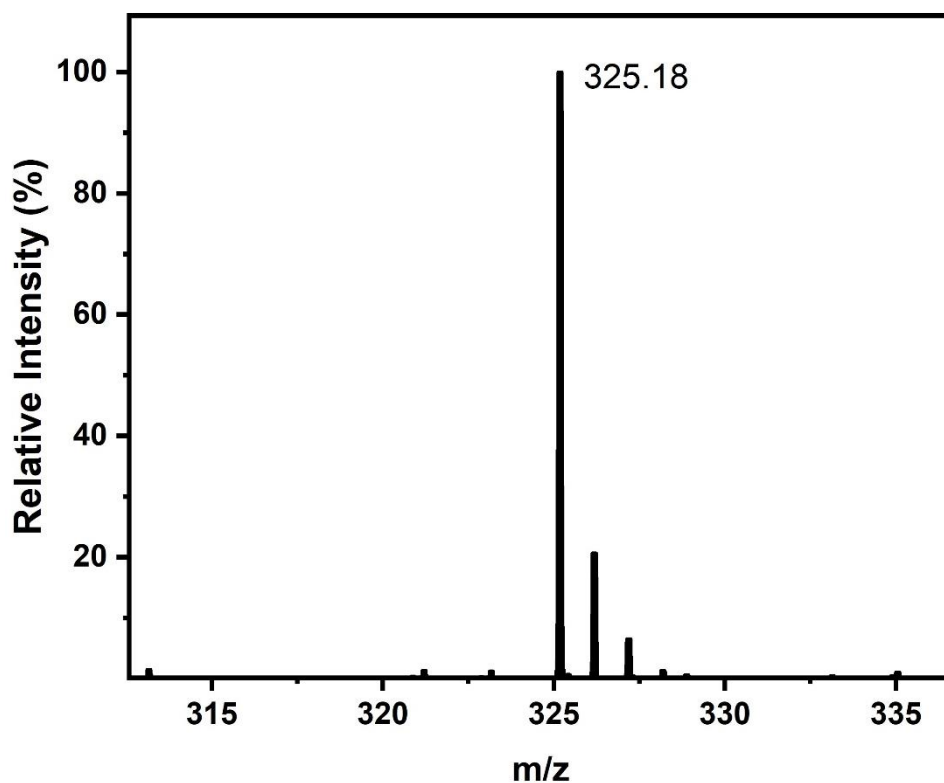


Figure S103: Mass spectrum of the enzymatic degradation of **P13** (Figure 6c), after drying to remove solvent, zoomed into the region 315-335 m/z , showing the presence of the ether-diol.

8.3.6 Comparison of PLLA Blends vs Commercial Plastics

8.3.6.1 Description of Commercial Materials Data Acquisitions

Data was obtained for commercial PS, ABS and HIPS data from MatWeb (www.matweb.com), a material database of commercial material property data provided directly by companies. The database reports the range, average value, and the number of data points used to calculate the average, as well as data sheets for individual materials. Data was also obtained from ULTRUS material database for individual materials (ulprospector.com).

8.3.6.2 PS

Table S8.3.11: Thermal-mechanical properties for a range of commercial PS samples.

Polymer Grade	Tensile Yield Strength – (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)	T _g (°C)
PS Molded, Unreinforced ^m	4.22 - 59.0 Average value: 32.3 No. of samples: 73	5.50 - 59.0 Average value: 41.0 No. of samples: 106	0.400 - 70.0 Average value: 13.7 No. of samples: 121	0.894 - 3.55 Average value: 2.78 No. of samples: 80	83.0 - 100 Average value: 90.5 No. of samples: 6
PS Extrusion Grade ^m	5.20 - 52.4 Average value: 34.9 No. of samples: 27	0.100 - 53.0 Average value: 22.9 No. of samples: 41	1.00 - 70.0 Average value: 21.0 No. of samples: 40	0.976 - 3.45 Average value: 2.53 No. of samples: 46	-
PS Heat Resistant Grade ^m	20.0 - 59.0 Average value: 45.9 No. of samples: 51	22.0 - 62.0 Average value: 47.1 No. of samples: 84	1.80 - 60.0 Average value: 9.16 % No. of samples: 102	1.79 - 3.38 Average value: 2.97 No. of samples: 89	89.0 – 104 Average value: 98.0 No. of samples: 7
PS Transparent Grade ^m	34.0 - 55.0 Average value: 43.6 No. of samples: 53	35.0 - 59.0 Average value: 46.1 No. of samples: 34	1.00 - 35.0 Average value: 3.14 No. of samples: 68	2.59 - 4.71 Average value: 3.14 No. of samples: 58	-
PS Flame Retardant ^m	14.0 - 55.0 Average value: 26.6 No. of samples: 79	12.4 - 48.3 Average value: 26.1 No. of samples: 63	1.00 - 80.0 Average value: 40.7 No. of samples: 109	1.38 - 3.45 Average value: 2.12 No. of samples: 31	-

^mMatWeb material data-base. - = not reported.

8.3.6.3 ABS

Table S8.3.12: Thermal-mechanical properties for a range of commercial ABS samples.

Polymer Grade	Tensile Yield Strength – (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)	T _g (°C)
ABS sheet ^m	28.8 - 42.7 Average: 36.6 No. of samples: 35	15.9 - 42.0 Average value: 34.3 No. of samples: 41	7.80 – 190 Average value: 77. No. of samples: 5	1.83 - 5.33 Average value: 2.17 No. of samples: 25	-
ABS molded ^m	2.00 - 77.0 Average value: 44.8 No. of samples: 624	2.60 - 73.1 Average value: 41.0 No. of samples: 346	1.40 – 110 Average value: 28.5 No. of samples: 493	0.778 - 21.2 Average value: 2.35 No. of samples: 356	105 – 109 Average value: 107 No. of samples: 9
ABS impact grade (molded) ^m	22.1 - 93.1 Average value: 42.3 No. of samples: 197	24.0 – 138 Average value: 40.6 No. of samples: 107	3.00 - 87.0 Average value: 24.3 No. of samples: 142	1.40 - 5.33 Average value: 2.12 No. of samples: 93	105 – 108 Average value: 107 No. of samples: 4
ABS heat resistant (molded) ^m	33.0 – 170 Average value: 47.5 No. of samples: 166	19.6 - 63.0 Average value: 44.1 No. of samples: 83	2.50 - 70.0 Average value: 21.8 No. of samples: 127	1.70 - 2.70 Average value: 2.29 No. of samples: 64	108 – 127 Average value: 116 No. of samples: 9
ABS – extruded ^m	13.0 - 65.0 Average value: 44.7 No. of samples: 173	22.1 - 74.0 Average value: 38.6 No. of samples: 60	3.00 - 150 Average value: 48.4 No. of samples: 136	1.00 - 2.65 Average value: 2.04 No. of samples: 64	108 – 109 Average value: 108 No. of samples: 3
ABS (transparent molded) ^m	30.4 - 55.9 Average value: 44.3 No. of samples: 41	30.0 - 57.0 Average value: 43.8 No. of samples: 25	10.0 - 70.0 Average value: 28.7 No. of samples: 43	1.35 - 2.35 Average value: 1.91 No. of samples: 12	-

^mMatWeb material data-base. - = not reported.

8.3.6.4 HIPS

Table S8.3.13: Thermal-mechanical properties for a range of commercial HIPS samples.

Polymer Grade	Tensile Yield Strength – (MPa)	Ultimate Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (GPa)	T _g (°C)
PS (impact modified) ^m	2.35 - 200 Average value: 25.8 No. of samples: 388	12.4 – 240 Average value: 26.9 No. of samples: 278	1.30 – 350 Average value: 45.2 No. of samples: 451	0.155 - 3.47 Average value: 1.97 No. of samples: 300	
INEOS Styrolution PS 454N HIPS ^m	27	-	25	-	-
INEOS Styrolution PS 576H HIPS ^m	30	-	30	2.05	-
Chevron Phillips EB6025 HIPS - High Impact Polystyrene ^m	24	-	-	2	-
Dow AIM® 4900 High Impact Styrenic Resin ^m	22.1	15.9	40	1.79	-
Americas Styrenics Styron® 6010 High Impact Polystyrene ^m	27	23	48	1.97	-
Versalis Impressio® HIPS E05 3D Printing Filament Grade High Impact Polystyrene ^m	22	28	70	1.9	-
LG Chemical ALPHALAC SF510 HIPS ^m	26.5	-	51	2.11	-
3DXMAX® HIPS 3D Filament ^u	-	43	18	1.1	100
Adell PS IF-10 ^u	-	26.2	40	-	-
API II 545 ^u	-	27.6	50	1.93	-
BioBlend® XD 26150 ^u	-	25	5	0.81	-
ECOGRAN® PSCI BLK ^u	-	20	50	2.150	-
Edistir® R 540E ^u	24	29	60	2	-
ESTASTIR HG 0808 ^u	29	25	40	-	-

^mMatWeb material data-base. - = not reported. ^uULProspector.

8.4: Chapter 4 - Poly(Ester-*alt*-Ether) Catalysis: Improving Understanding and Scope

8.4.1 Catalyst Synthesis and Characterisation

8.4.1.1 $\text{Zr}(\text{L}2)_2(\text{O}^i\text{Pr})_2$

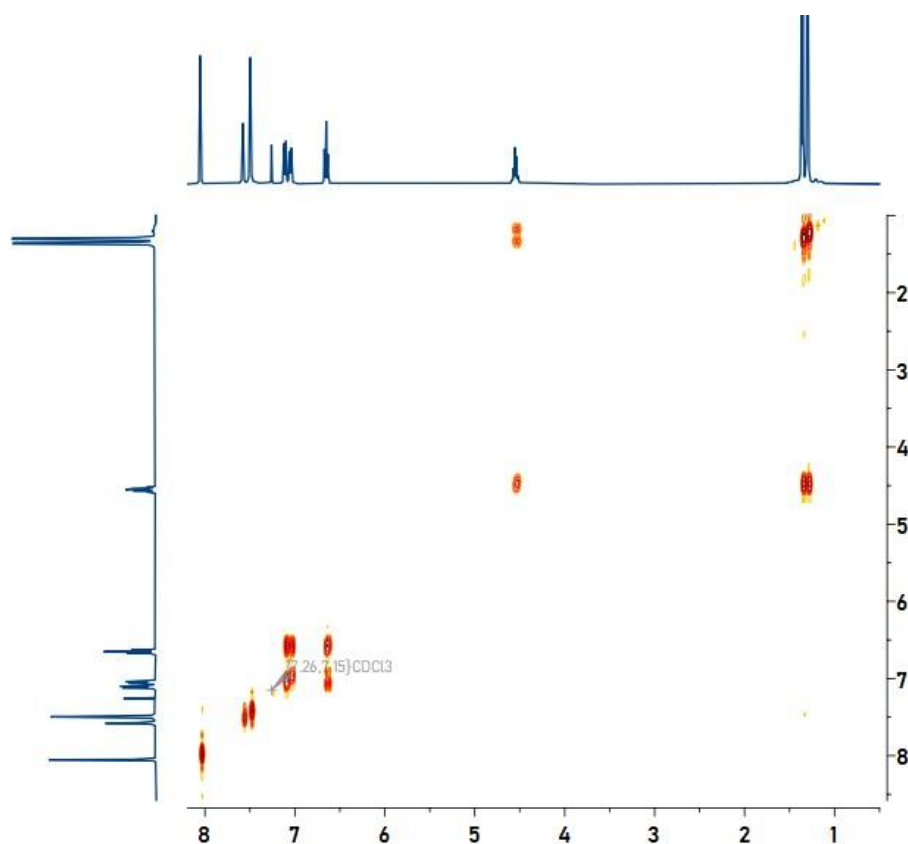


Figure S8.4.1: ^1H COSY NMR spectrum of $\text{Zr}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3).

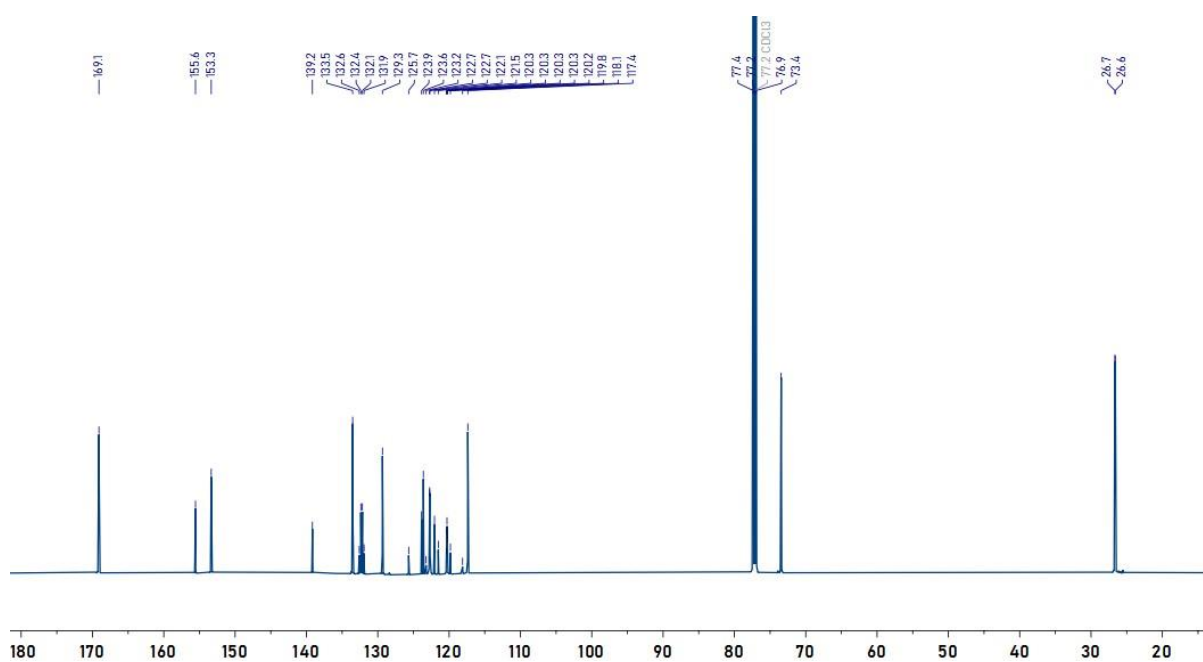


Figure S8.4.2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Zr}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ (151 MHz, CDCl_3).

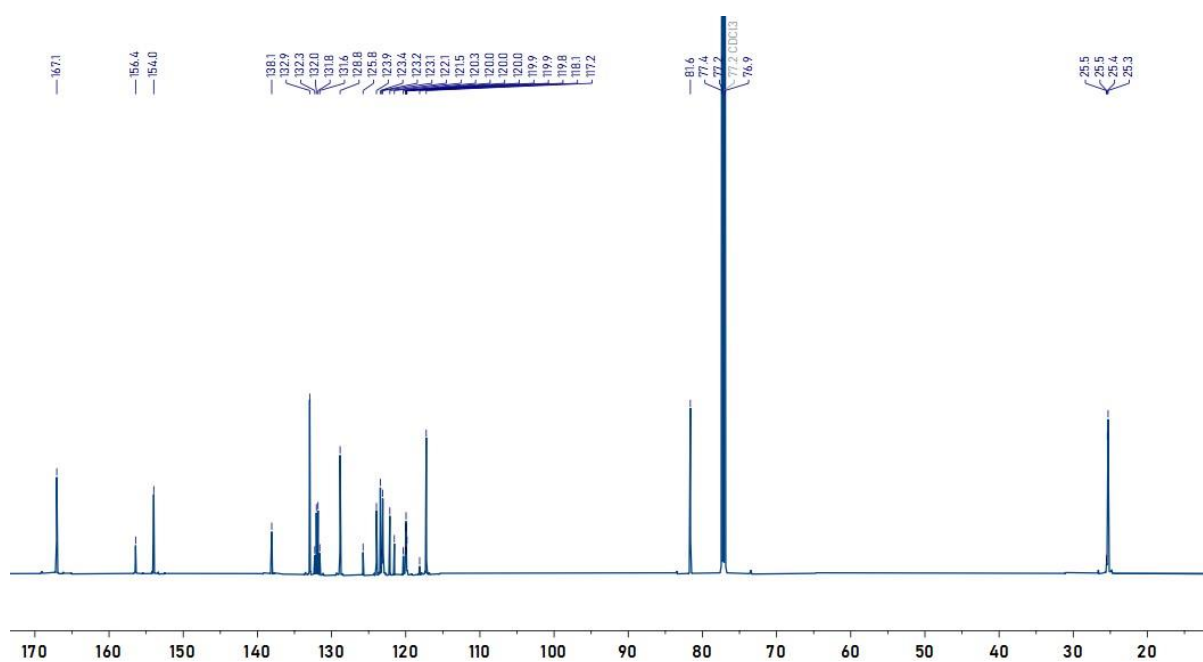


Figure S8.4.5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Ti}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ (151 MHz, CDCl_3).

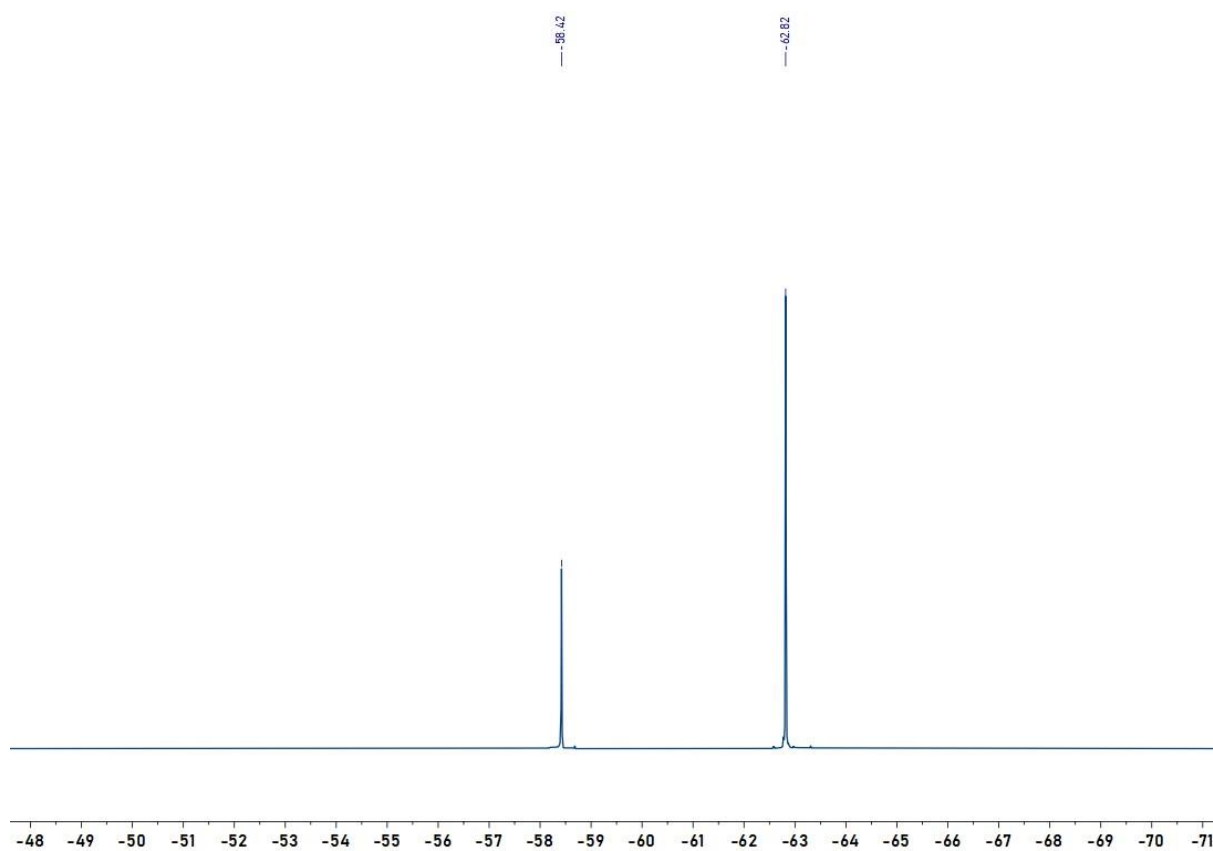


Figure S8.4.6: ^{19}F NMR spectra of $\text{Ti}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3).

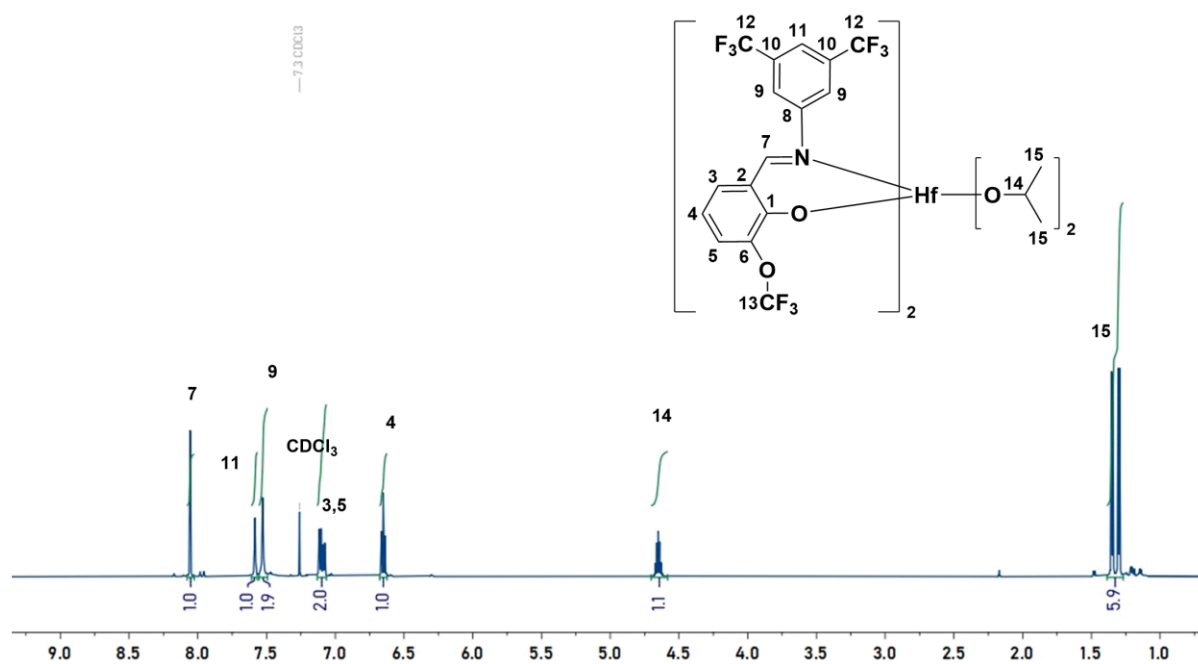
8.4.1.3 Hf(L2)₂(OⁱPr)₂

Figure S8.4.7: ¹H NMR spectra of Hf(L2)₂(OⁱPr)₂ (400 MHz, CDCl₃, with assignments).

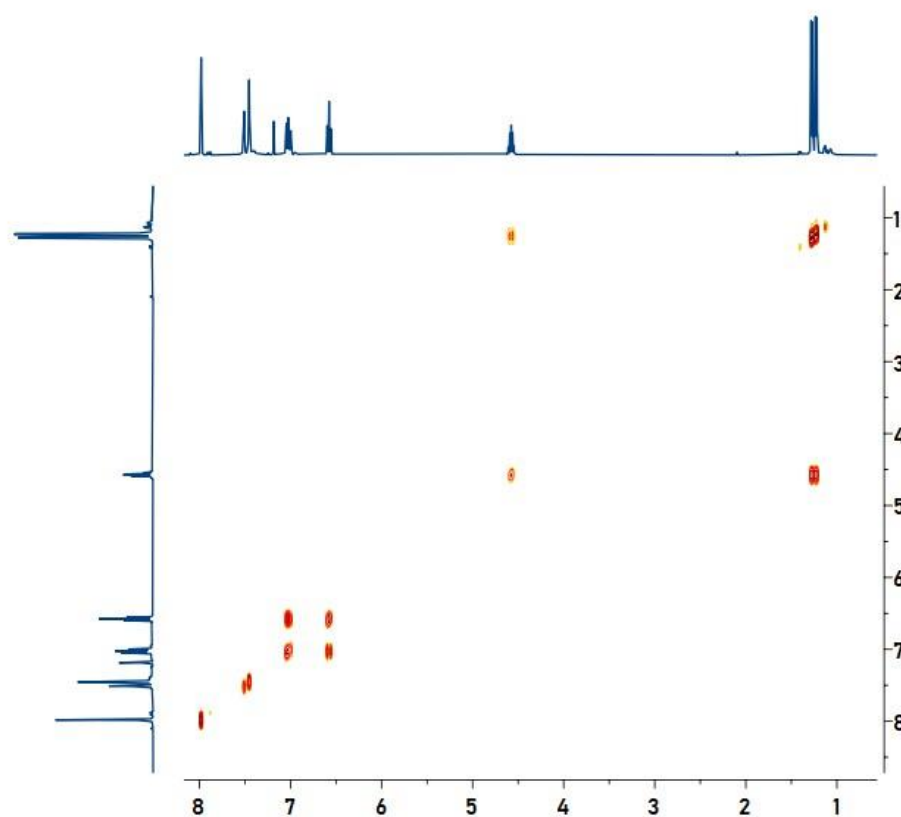


Figure S8.4.8: ¹H COSY NMR spectrum of Hf(L2)₂(OⁱPr)₂ (400 MHz, CDCl₃).

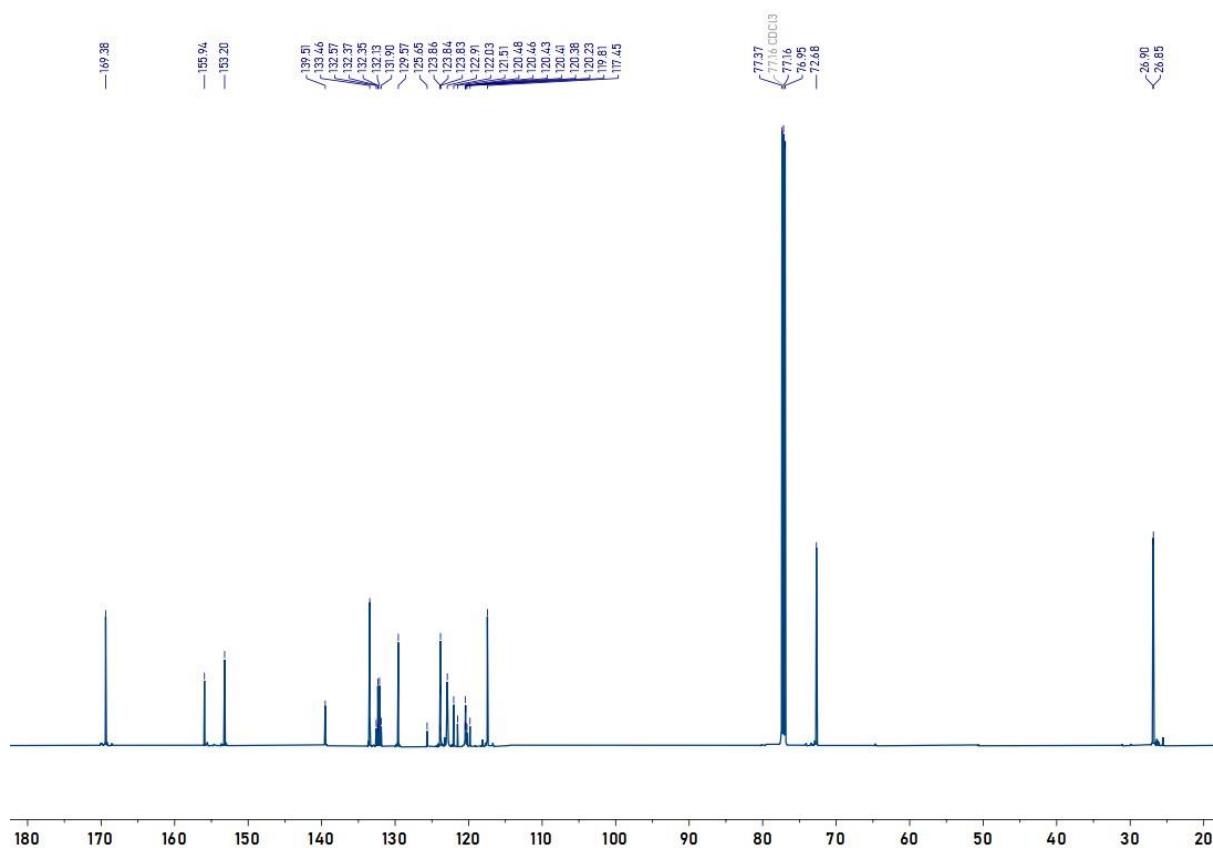


Figure S8.4.9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Hf}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ (151 MHz, CDCl_3).

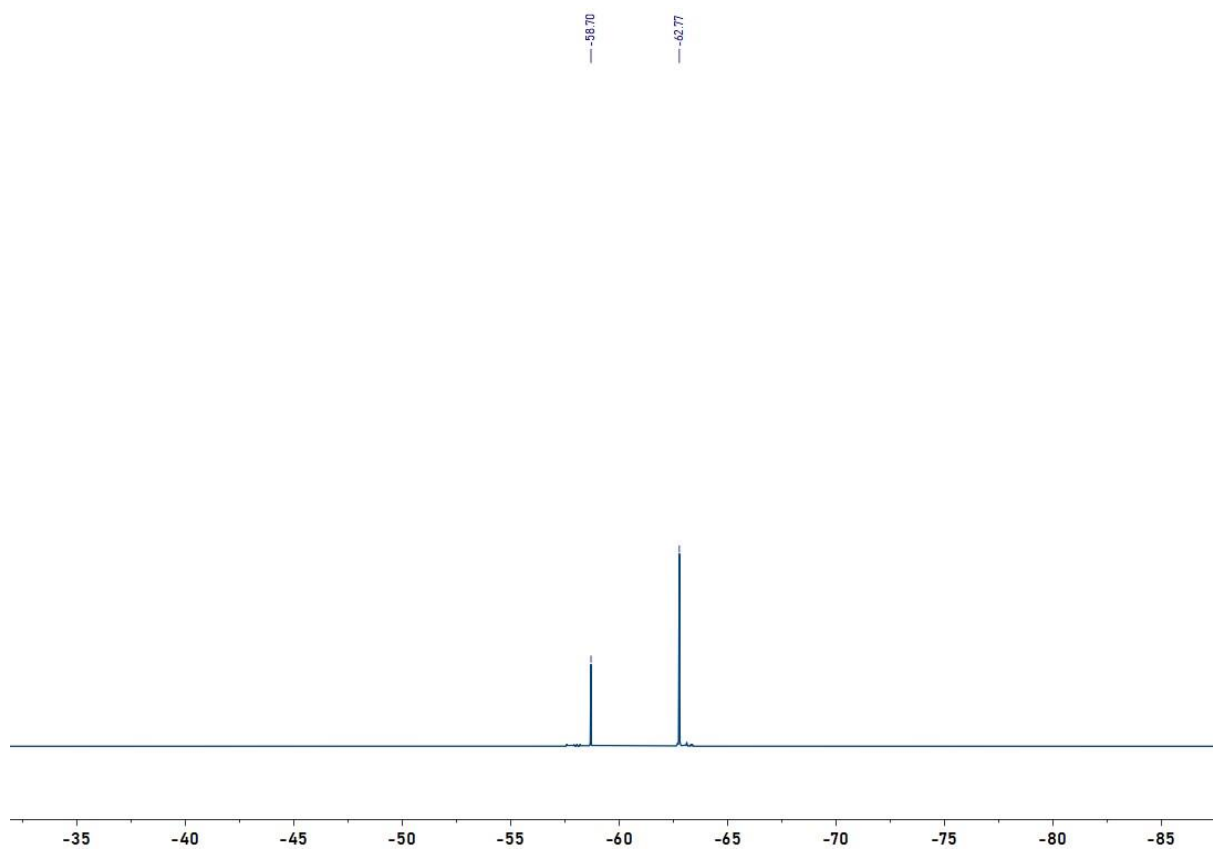


Figure S8.4.10: ^{19}F NMR spectra of $\text{Hf}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3).

8.4.1.4 L3

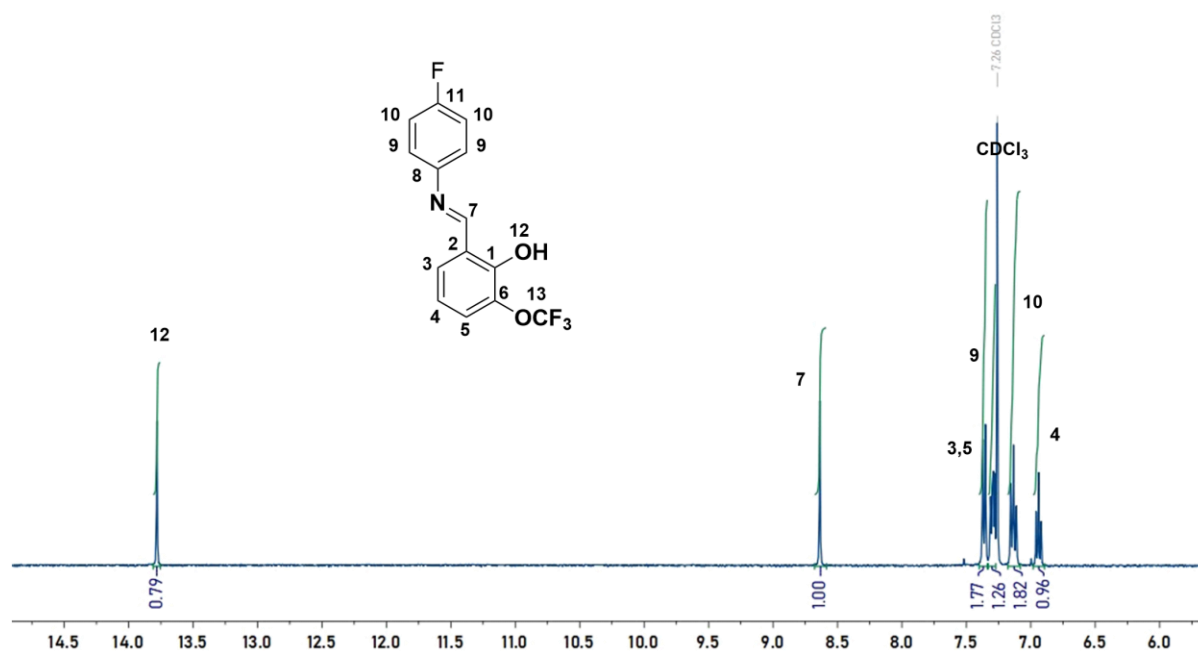


Figure S8.4.11: ^1H NMR spectra of L3 (400 MHz, CDCl_3 , with assignments).

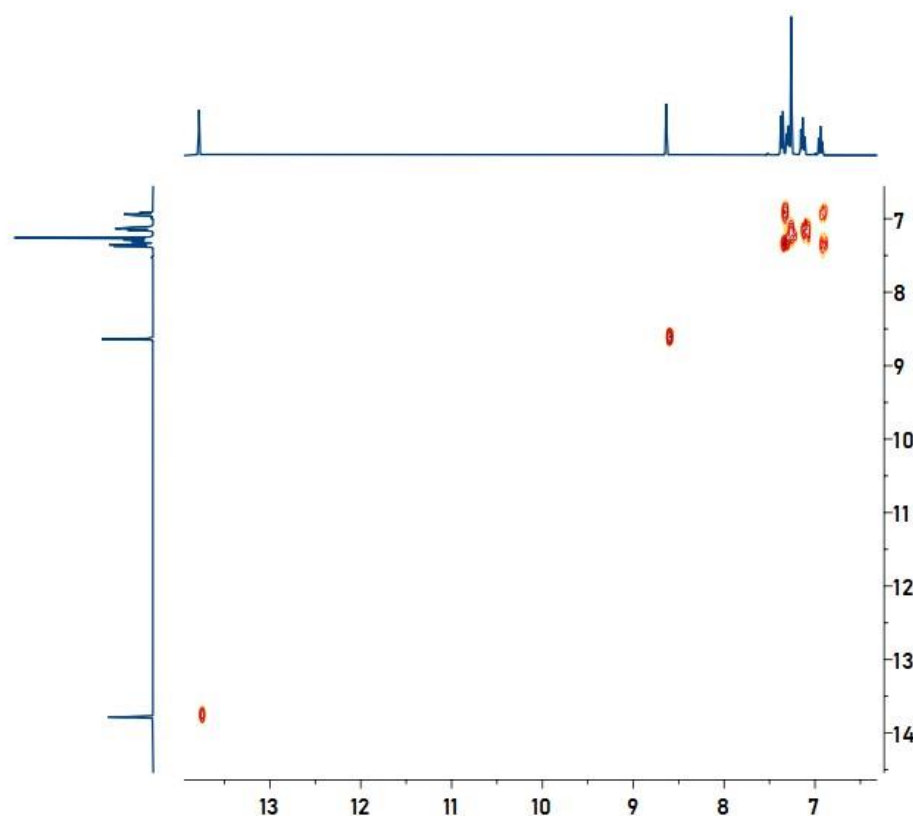


Figure S8.4.12: ^1H COSY NMR spectrum of L3 (400 MHz, CDCl_3).

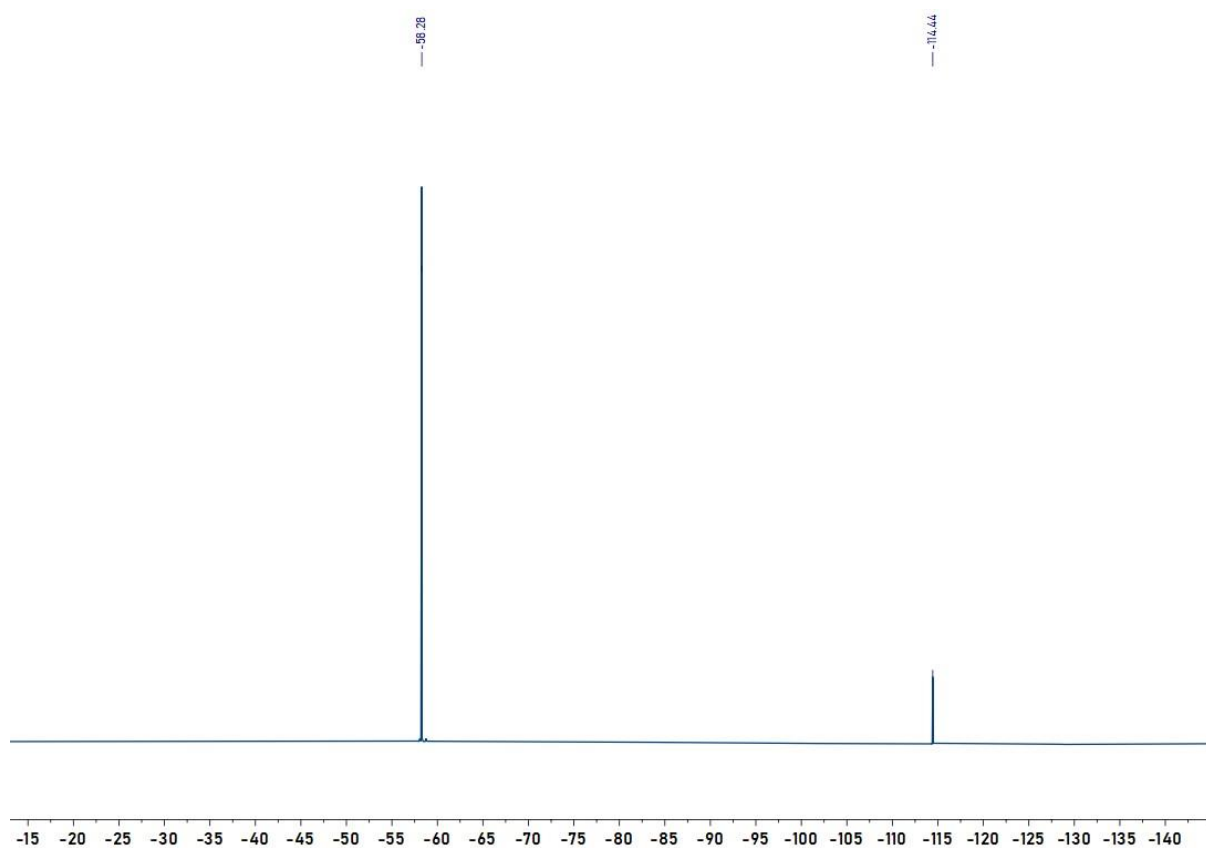


Figure 4.8.13: ^{19}F NMR spectra of **L3** (400 MHz, CDCl_3).

8.4.1.5 $\text{Zr}(\text{L3})_2(\text{O}^i\text{Pr})_2$

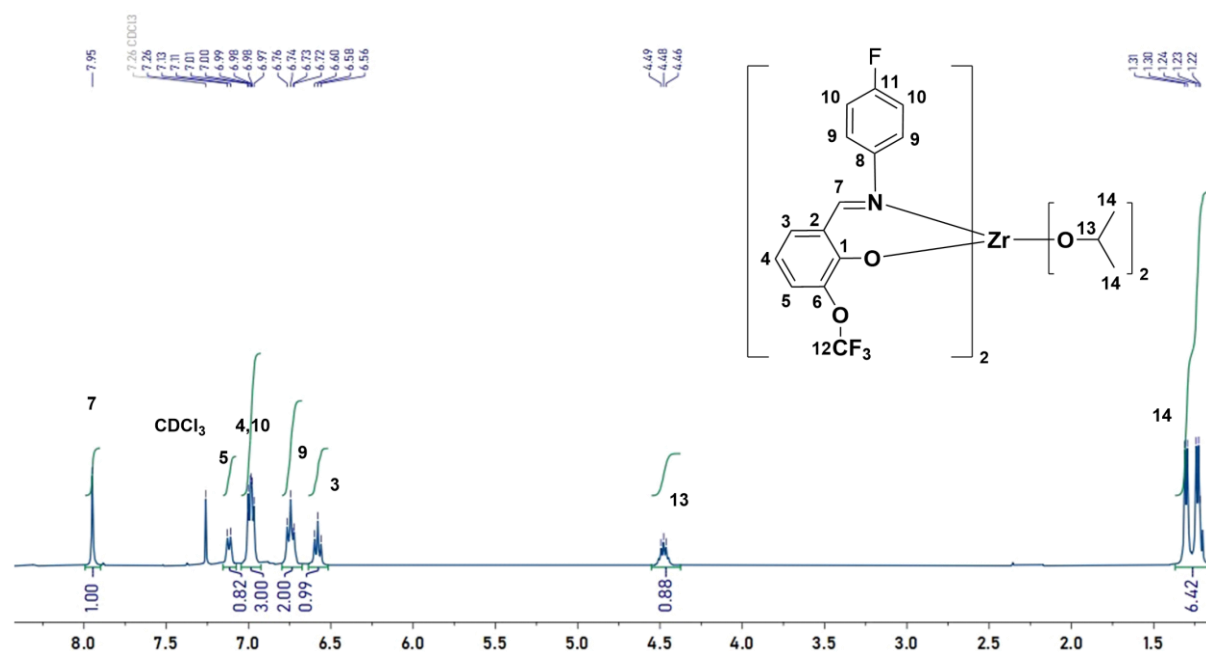


Figure S8.4.14: ^1H NMR spectra of $\text{Zr}(\text{L3})_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3 , with assignments).

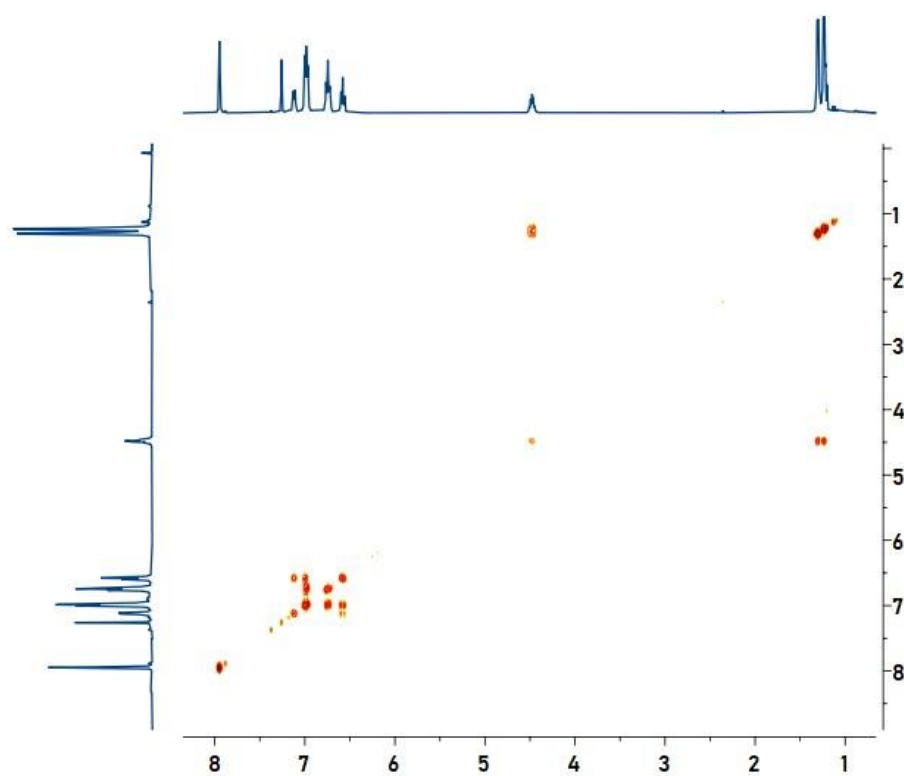


Figure S8.4.15: ^1H COSY NMR spectrum of $\text{Zr}(\text{L3})_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3).

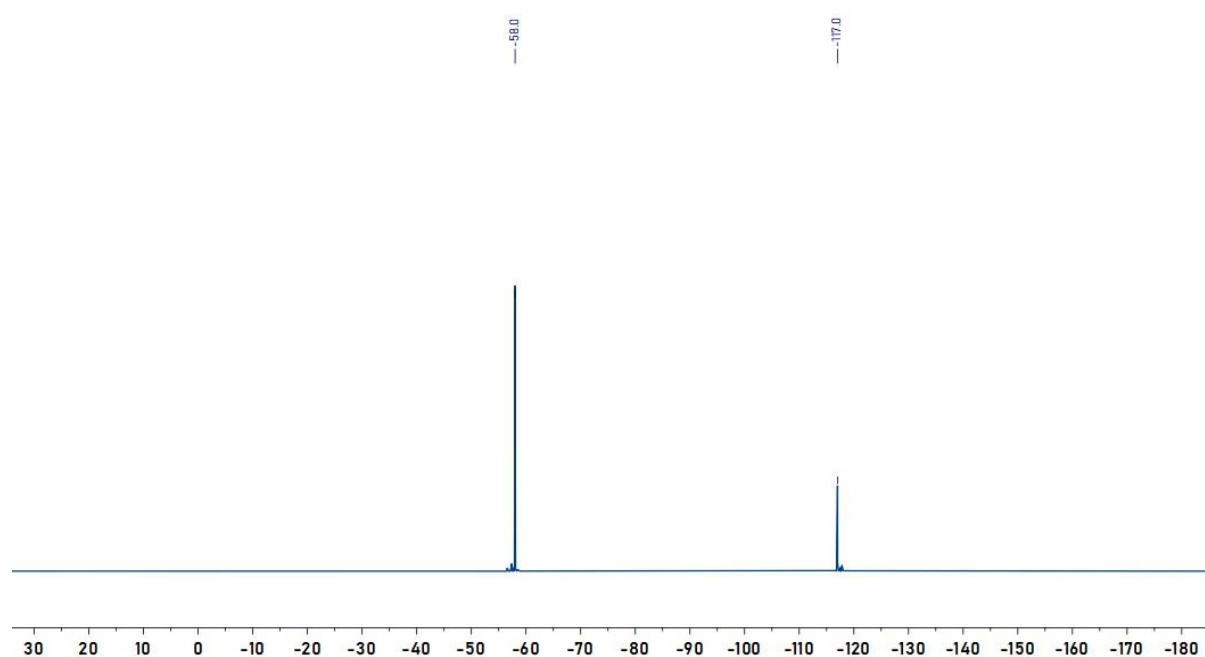


Figure S8.4.16: ^{19}F NMR spectra of $\text{Zr}(\text{L3})_2(\text{O}^i\text{Pr})_2$ (400 MHz, CDCl_3).

8.4.1.6 L4

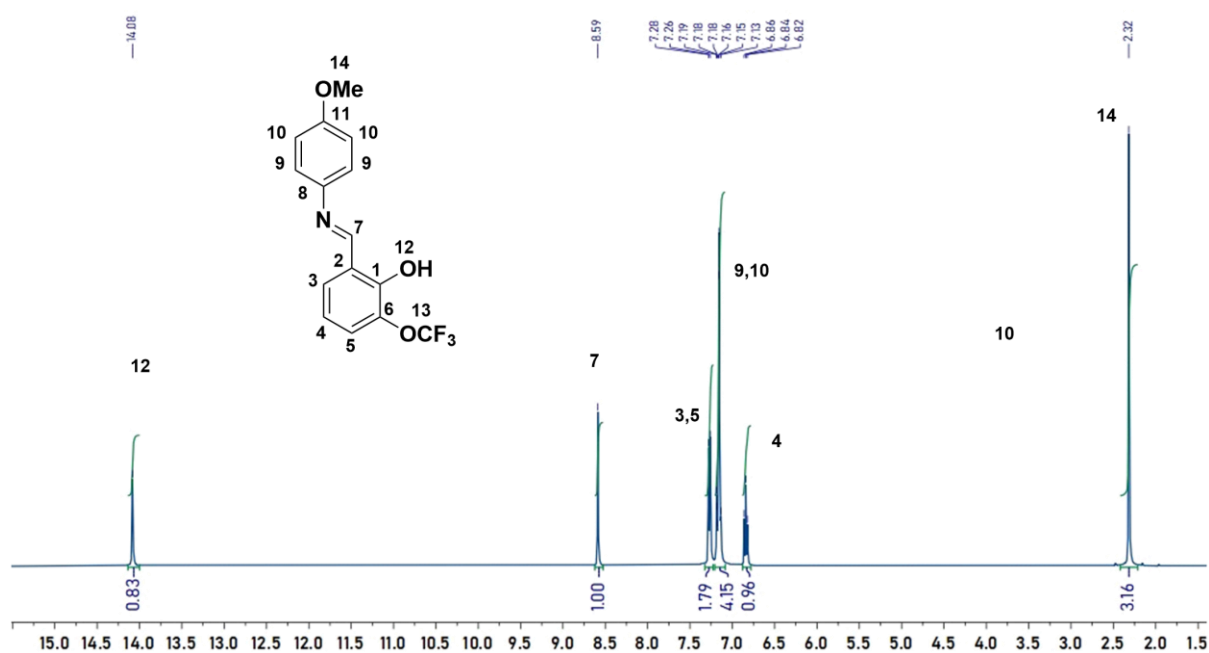


Figure S8.4.17: ^1H NMR spectra of L4 (400 MHz, CDCl_3 , with assignments).

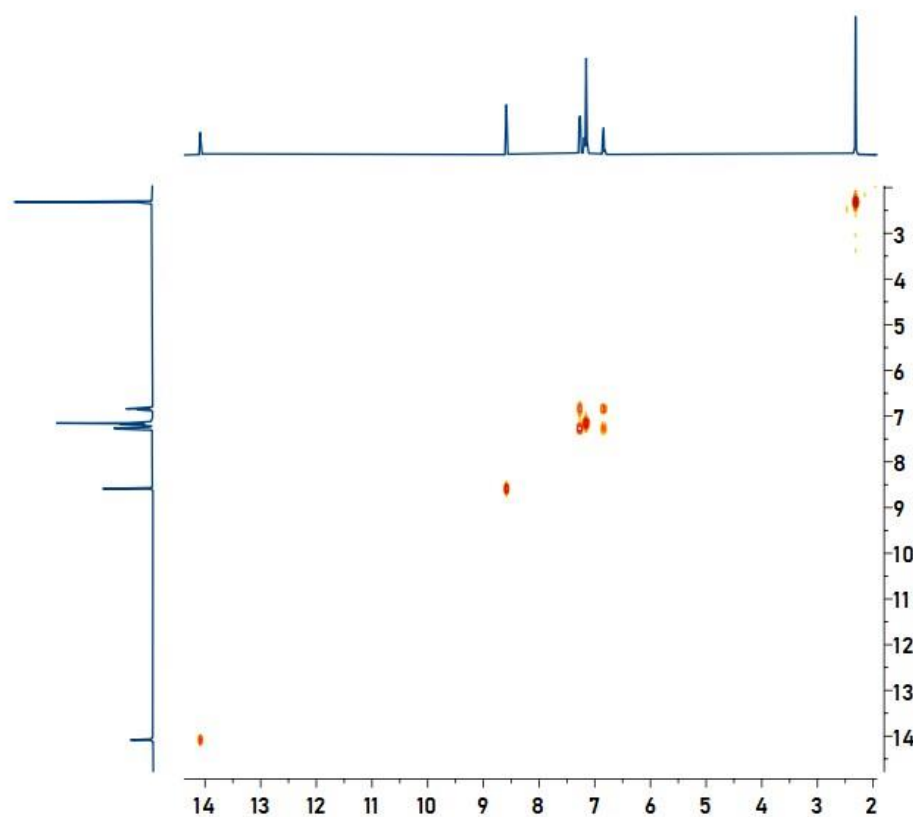


Figure S8.4.18: ^1H COSY NMR spectrum of L4 (400 MHz, CDCl_3).

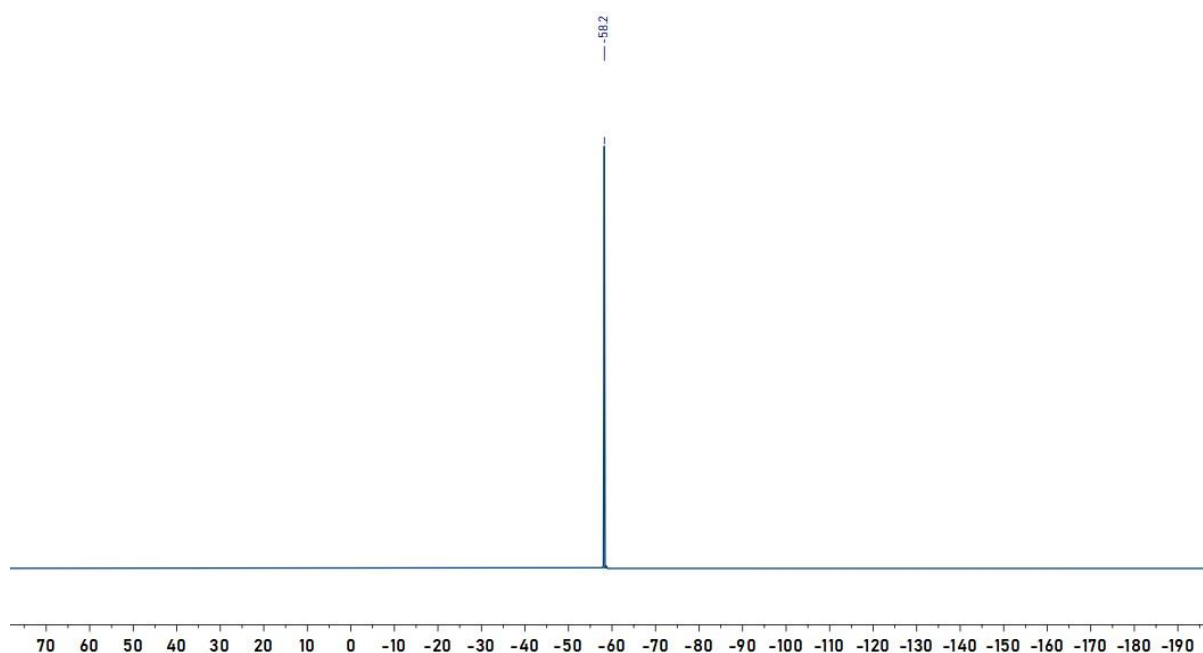


Figure 4.8.19: ^{19}F NMR spectra of **L4** (400 MHz, CDCl_3).

8.4.1.7 $\text{Zr}(\text{L4})_2(\text{O}^i\text{Pr})_2$

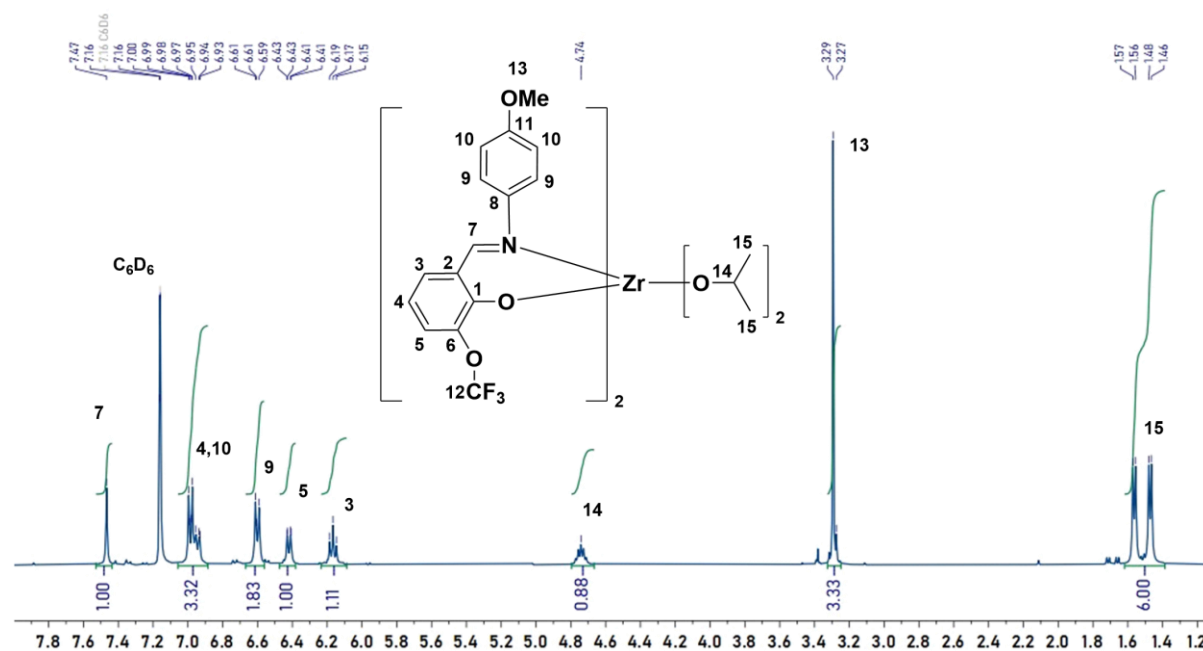


Figure S8.4.20: ^1H NMR spectra of $\text{Zr}(\text{L4})_2(\text{O}^i\text{Pr})_2$ (400 MHz, C_6D_6 , with assignments).

8.4.1.8 L5

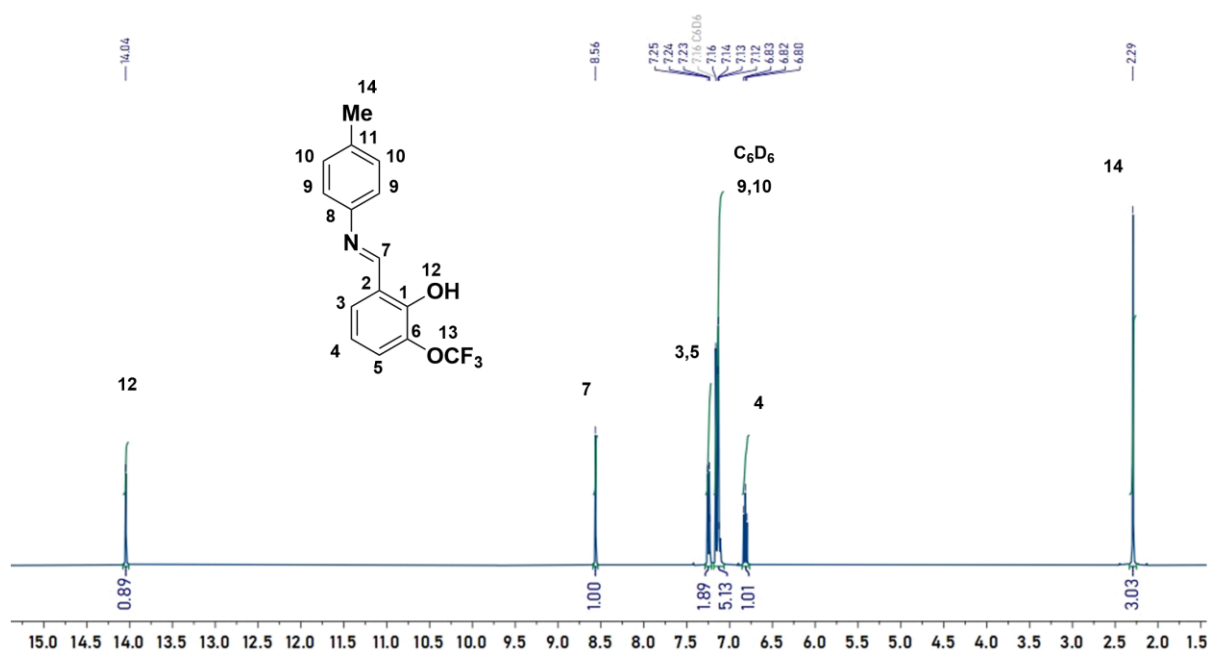


Figure S8.4.21: ¹H NMR spectra of L5 (400 MHz, C₆D₆, with assignments).

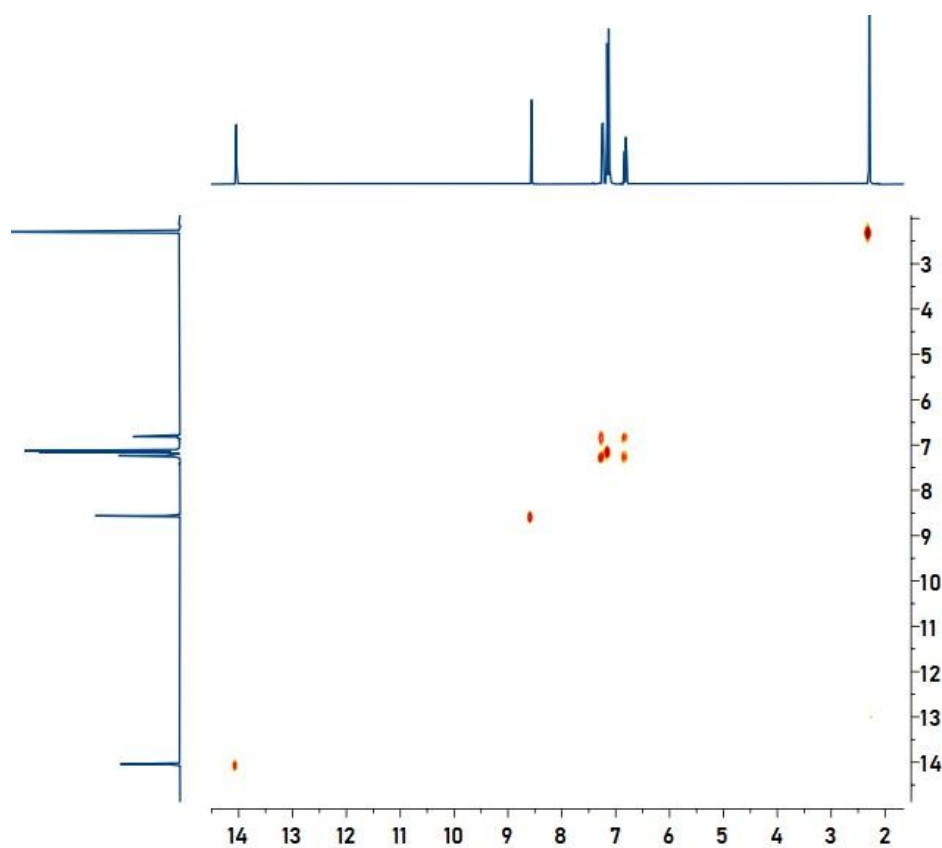


Figure S8.4.22: ¹H COSY NMR spectrum of L5 (400 MHz, C₆D₆).

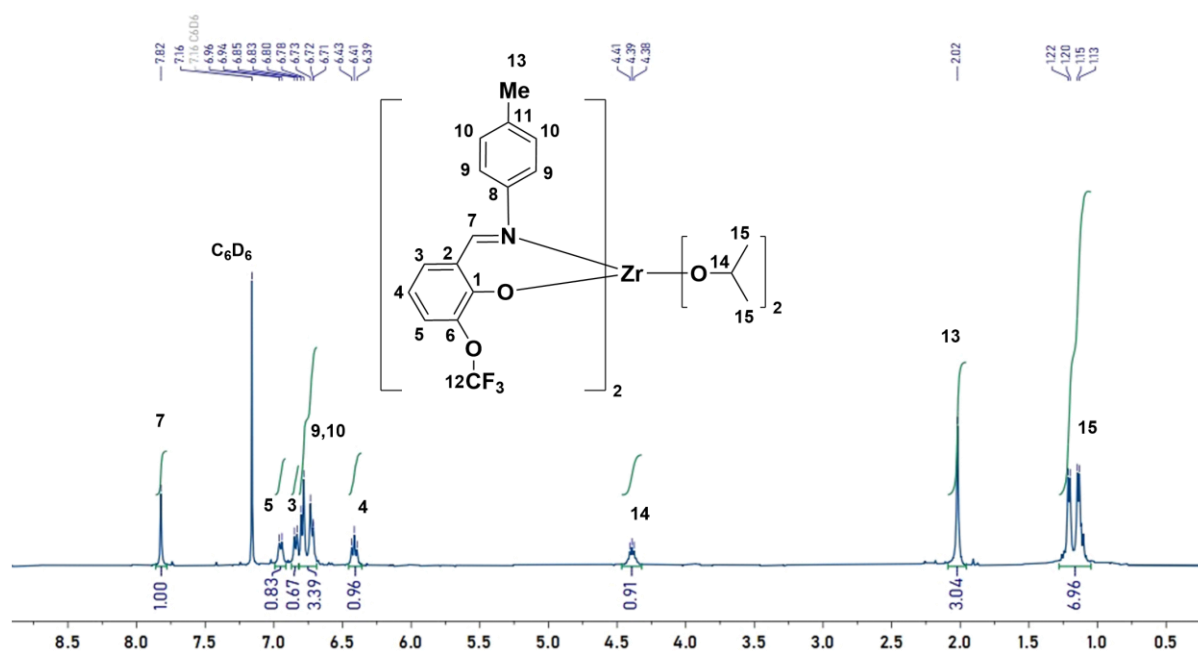
8.4.1.7 $\text{Zr}(\text{L5})_2(\text{O}^i\text{Pr})_2$ 

Figure S8.4.23: ^1H NMR spectra of $\text{Zr}(\text{L5})_2(\text{O}^i\text{Pr})_2$ (400 MHz, C_6D_6 , with assignments).

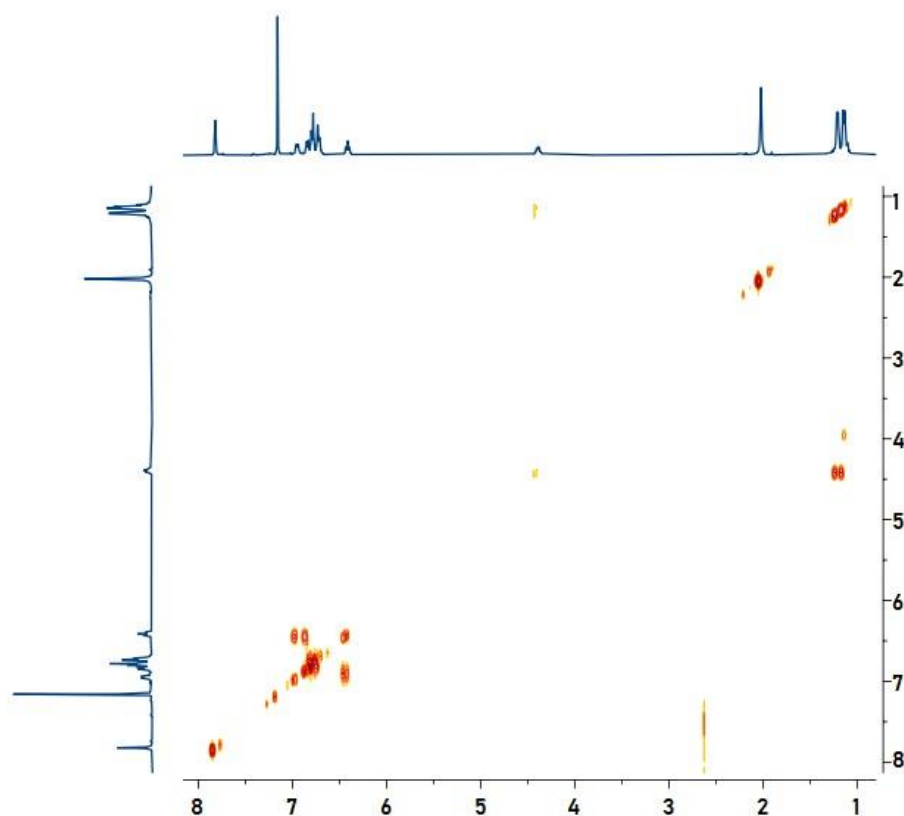


Figure S8.4.24: ^1H COSY NMR spectrum of $\text{Zr}(\text{L5})_2(\text{O}^i\text{Pr})_2$ (400 MHz, C_6D_6).

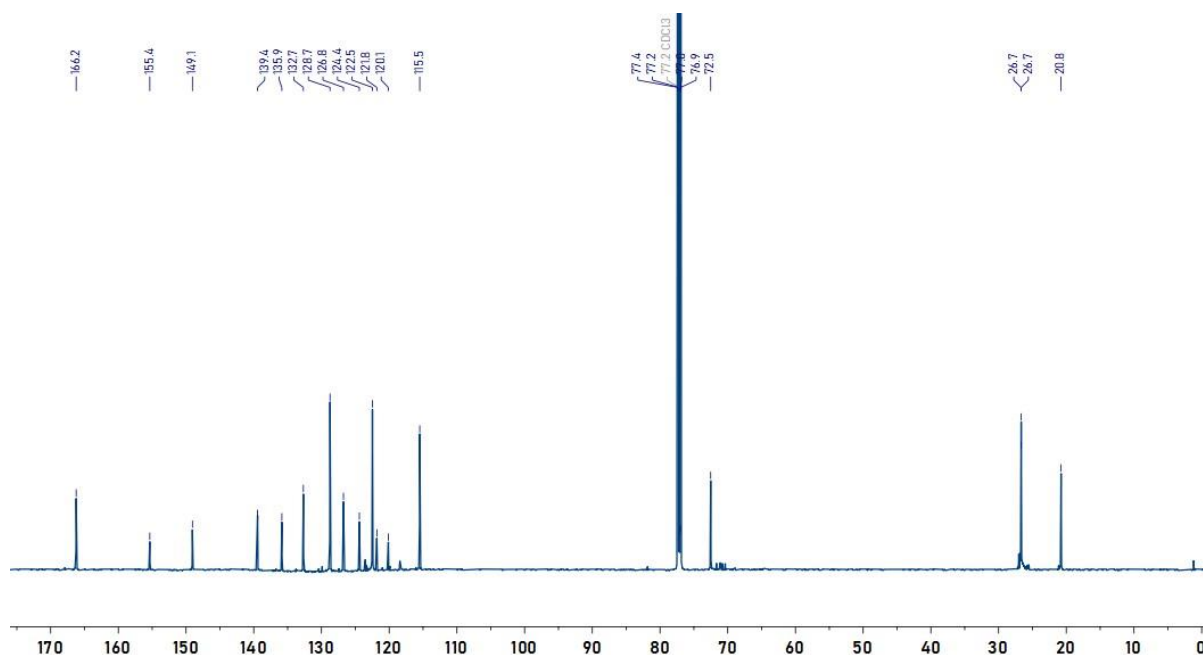


Figure S8.4.25: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Zr}(\text{L}5)_2(\text{O}^i\text{Pr})_2$ (151 MHz, CDCl_3).

8.4.2 Characterization Data for Polymers Described in Table 4.1 - $\text{M}(\text{L})_2(\text{O}^i\text{Pr})_2$ catalysts

8.4.2.1 $\text{Ti}(\text{L}2)_2(\text{O}^i\text{Pr})_2$ – Entry 3

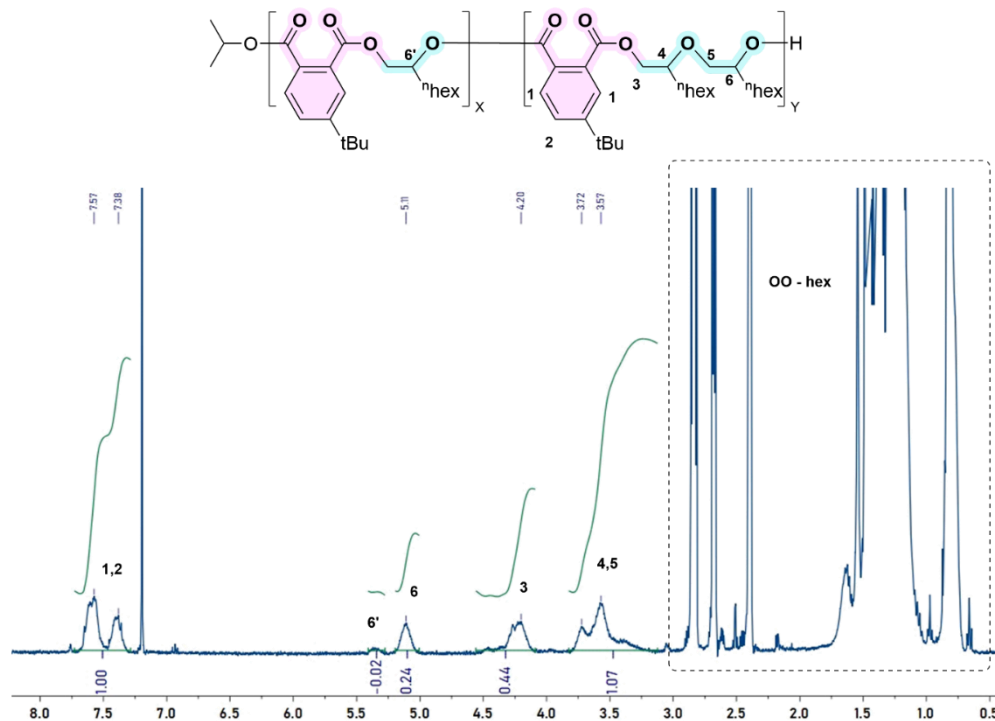


Figure S8.4.26: Crude ^1H NMR spectrum from the reaction of $[\text{Ti}(\text{L}2)_2(\text{O}^i\text{Pr})_2]:[\text{tBuPA}]:[\text{OO}] = 1: 50: 654$, 1 mL OO. Spectrum corresponds to Table 4.1, entry 3 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 7.2 \text{ kg mol}^{-1}$.

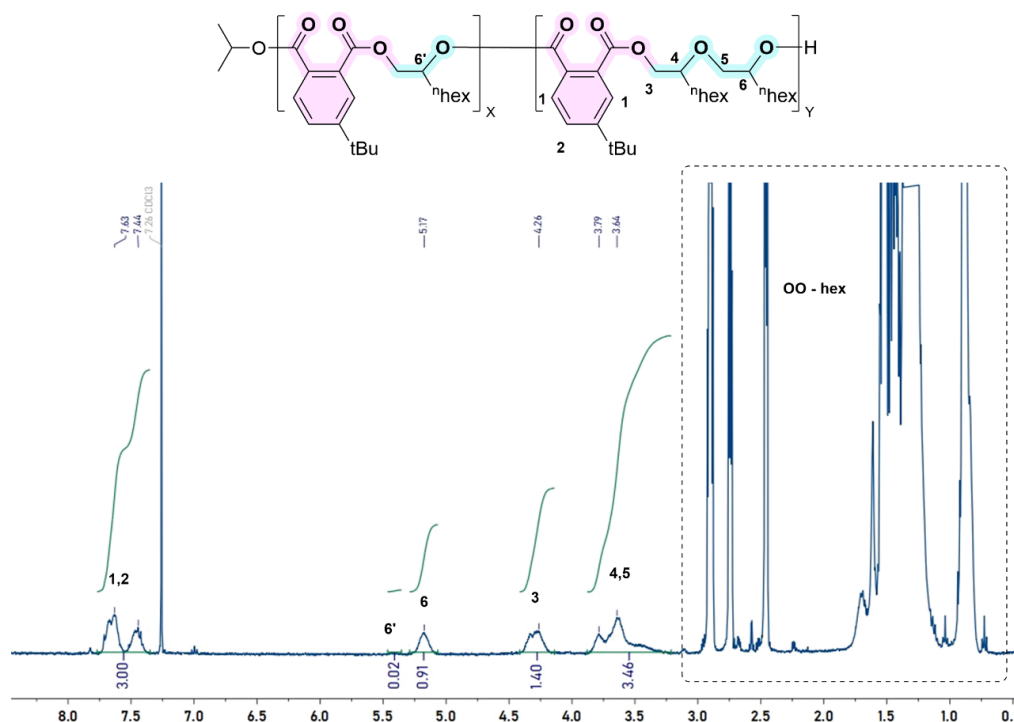
8.4.2.2 Hf(L2)₂(OiPr)₂ – Entry 4

Figure S8.4.27: Crude ¹H NMR spectrum from the reaction of [Hf(L2)₂(OiPr)₂]:[tBuPA]:[OO] = 1: 50: 654, 1 mL OO. Spectrum corresponds to Table 4.1, entry 4 (400 MHz, CDCl₃). *M*_{n,NMR} = 7.1 kg mol⁻¹.

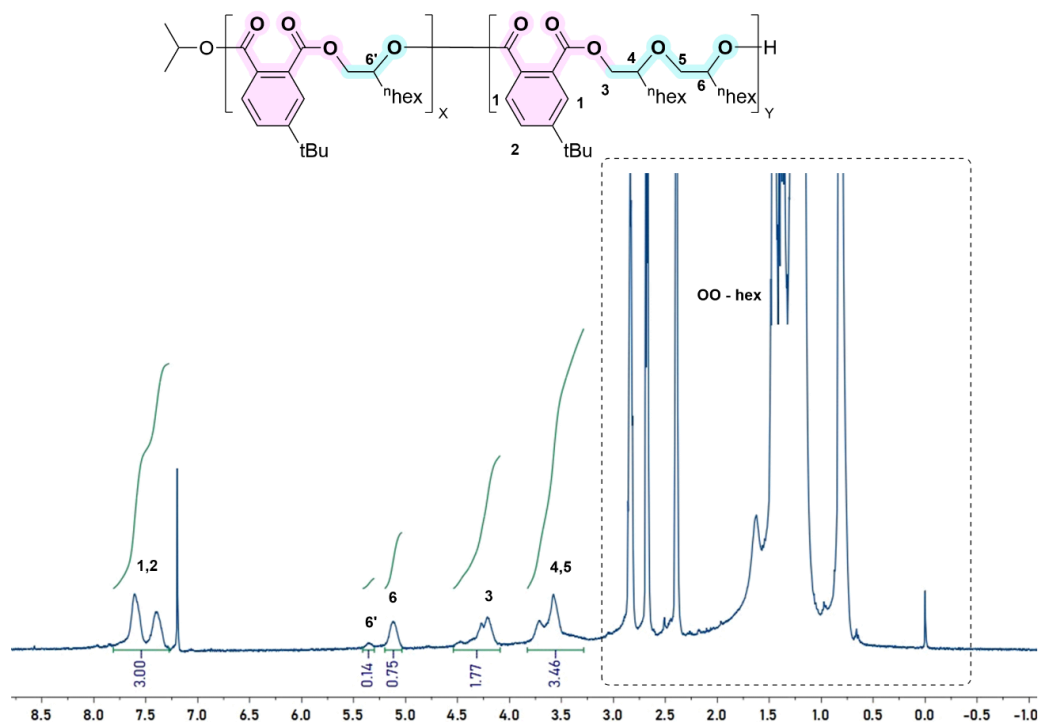
8.4.2.3 Zr(L3)₂(OiPr)₂ – Entry 5

Figure S8.4.28: Crude ¹H NMR spectrum from the reaction of [Zr(L3)₂(OiPr)₂]:[tBuPA]:[OO] = 1: 50: 654, 1 mL OO. Spectrum corresponds to Table 4.1, entry 5 (400 MHz, CDCl₃). *M*_{n,NMR} = 8.4 kg mol⁻¹.

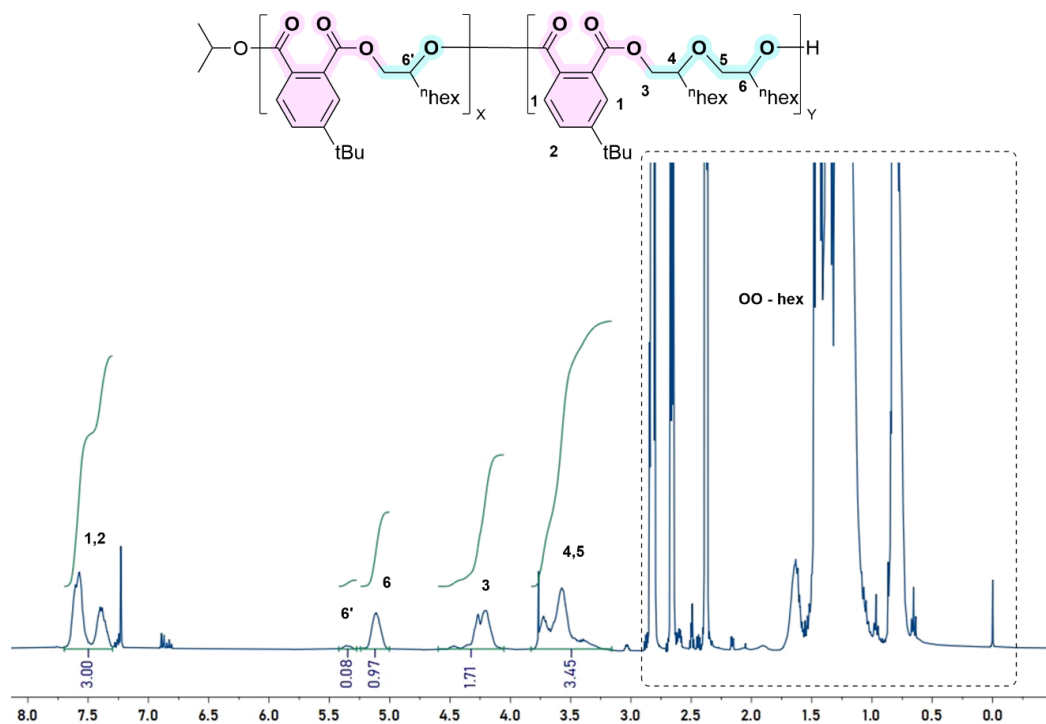
8.4.2.4 $\text{Zr}(\text{L4})_2(\text{O}^i\text{Pr})_2$ – Entry 6

Figure S8.4.29: Crude ^1H NMR spectrum from the reaction of $[\text{Zr}(\text{L4})_2(\text{O}^i\text{Pr})_2]:[\text{tBuPA}]:[\text{OO}] = 1: 50: 654$, 1 mL OO. Spectrum corresponds to Table 4.1, entry 6 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 7.9 \text{ kg mol}^{-1}$.

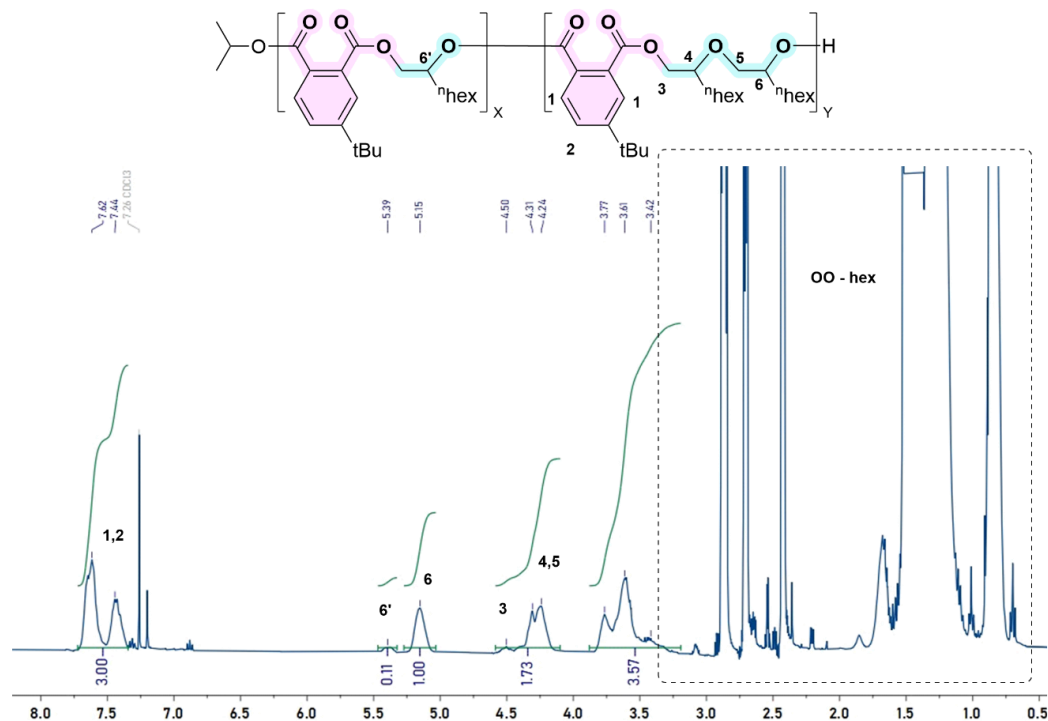
8.4.2.5 $\text{Zr}(\text{L5})_2(\text{O}^i\text{Pr})_2$ – Entry 7

Figure S8.4.30: Crude ^1H NMR spectrum from the reaction of $[\text{Zr}(\text{L5})_2(\text{O}^i\text{Pr})_2]:[\text{tBuPA}]:[\text{OO}] = 1: 50: 654$, 1 mL OO. Spectrum corresponds to Table 4.1, entry 7 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 7.0 \text{ kg mol}^{-1}$.

8.4.2.6 DSC Kinetics

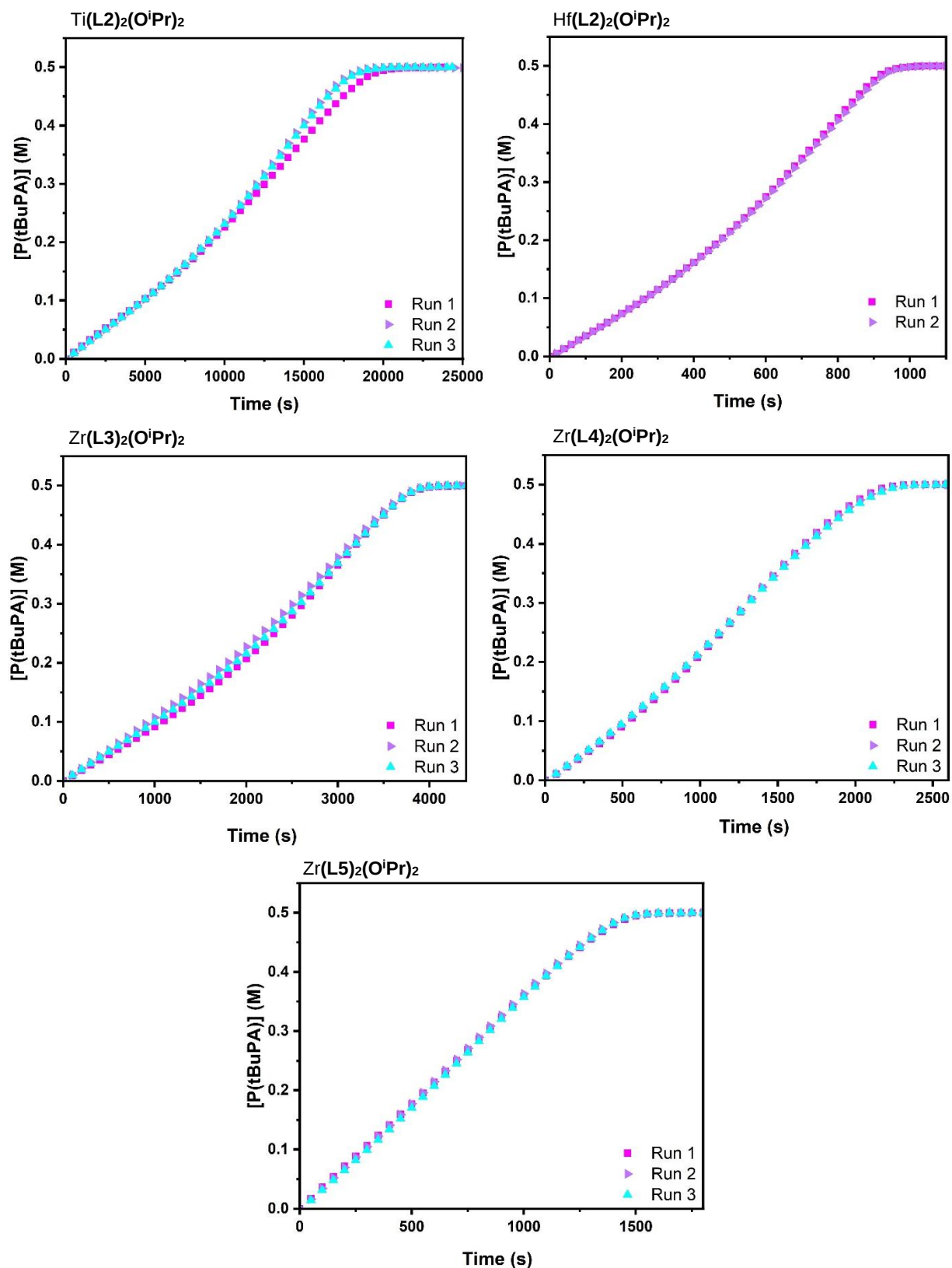


Figure S8.4.31: DSC thermograms for the reaction of $[M(L)_2(O^iPr)_2] : [tBuPA] : [OO] = 1 : 50 : 654$, 1 mL OO, 120 °C, Table 4.1 entries 2-7. The reaction was performed in triplicate.

8.4.3 Characterization Data for Polymers Described in Table 4.2 - Zr(X)₄ Catalysts – Co-ligand Effect

8.4.3.1 Zr(OEt)₄– Entry 2

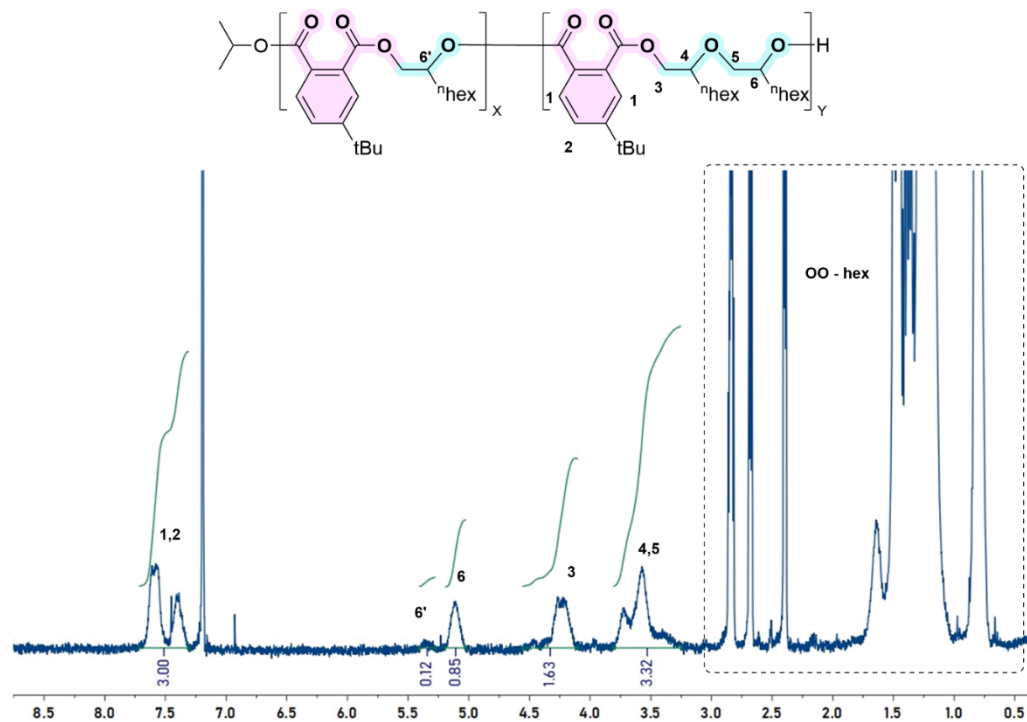


Figure S8.4.32: Crude ¹H NMR spectrum from the reaction of [Zr(OEt)₄]:[tBuPA]:[OO] = 1: 50: 654, 1 mL OO. Spectrum corresponds to Table 4.2, entry 2 (400 MHz, CDCl₃). *M*_{n,NMR} = 6.3 kg mol⁻¹.

8.4.3.2 Zr(Oct)₄– Entry 3

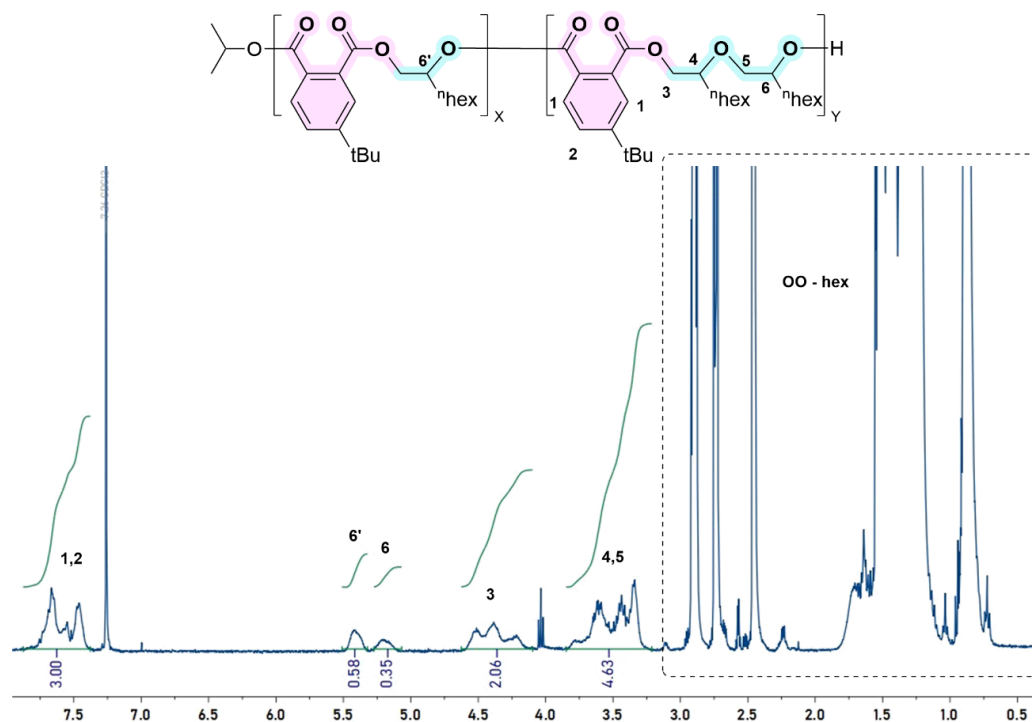


Figure S8.4.33: Crude ¹H NMR spectrum from the reaction of [Zr(Oct)₄]:[tBuPA]:[OO] = 1: 50: 654, 1 mL OO. Spectrum corresponds to Table 4.2, entry 2 (400 MHz, CDCl₃). *M*_{n,NMR} = 2.4 kg mol⁻¹.

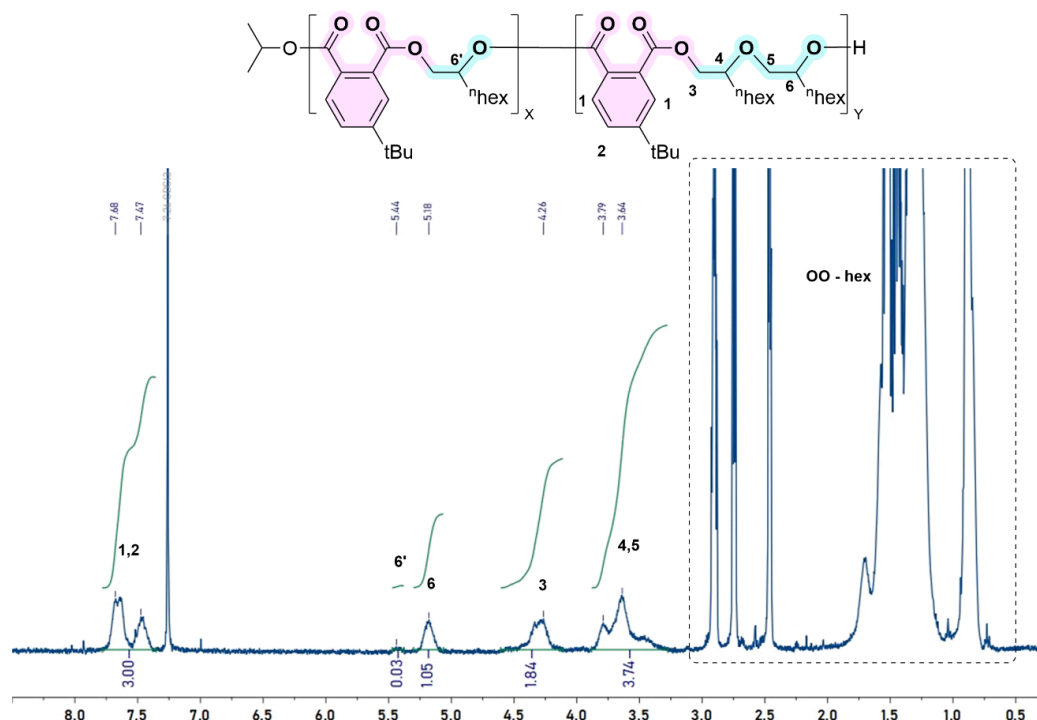
8.4.3.3 Zr(Cl)₄– Entry 4

Figure S8.4.34: Crude ^1H NMR spectrum from the reaction of $[\text{Zr}(\text{Cl})_4]:[\text{tBuPA}]:[\text{OO}] = 1: 50: 654$, 1 mL OO. Spectrum corresponds to Table 4.2, entry 2 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 5.3 \text{ kg mol}^{-1}$.

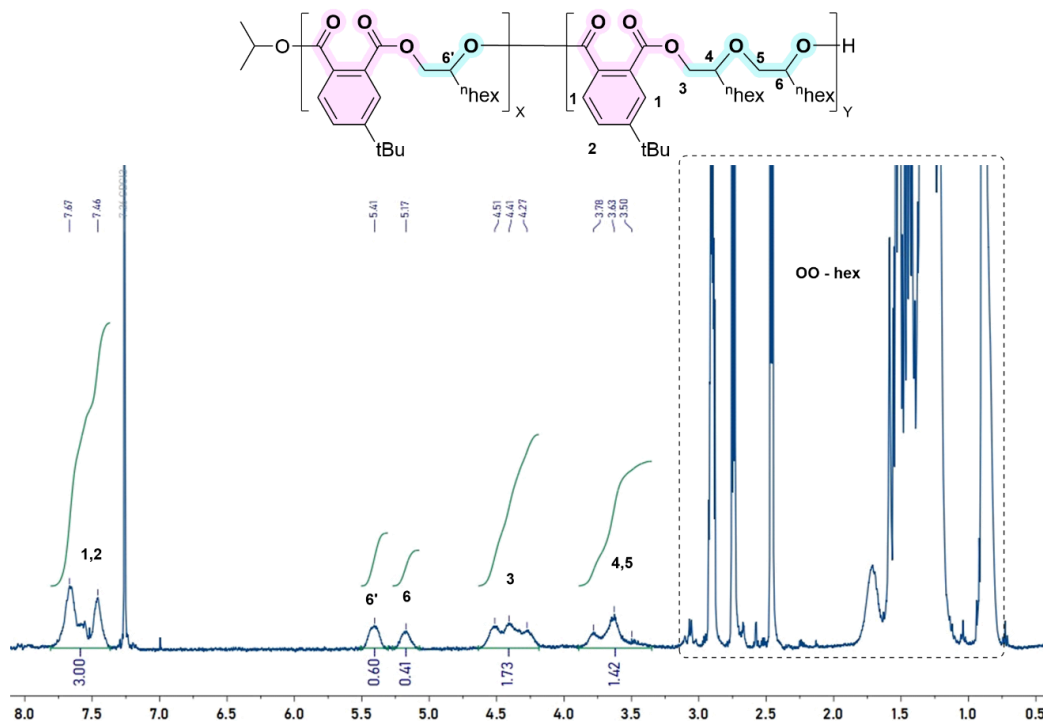
8.4.3.4 Zr(NMe₂)₄– Entry 5

Figure S8.4.35: Crude ^1H NMR spectrum from the reaction of $[\text{Zr}(\text{NMe}_2)_4]:[\text{tBuPA}]:[\text{OO}] = 1: 50: 654$, 1 mL OO. Spectrum corresponds to Table 4.2, entry 2 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 5.0 \text{ kg mol}^{-1}$.

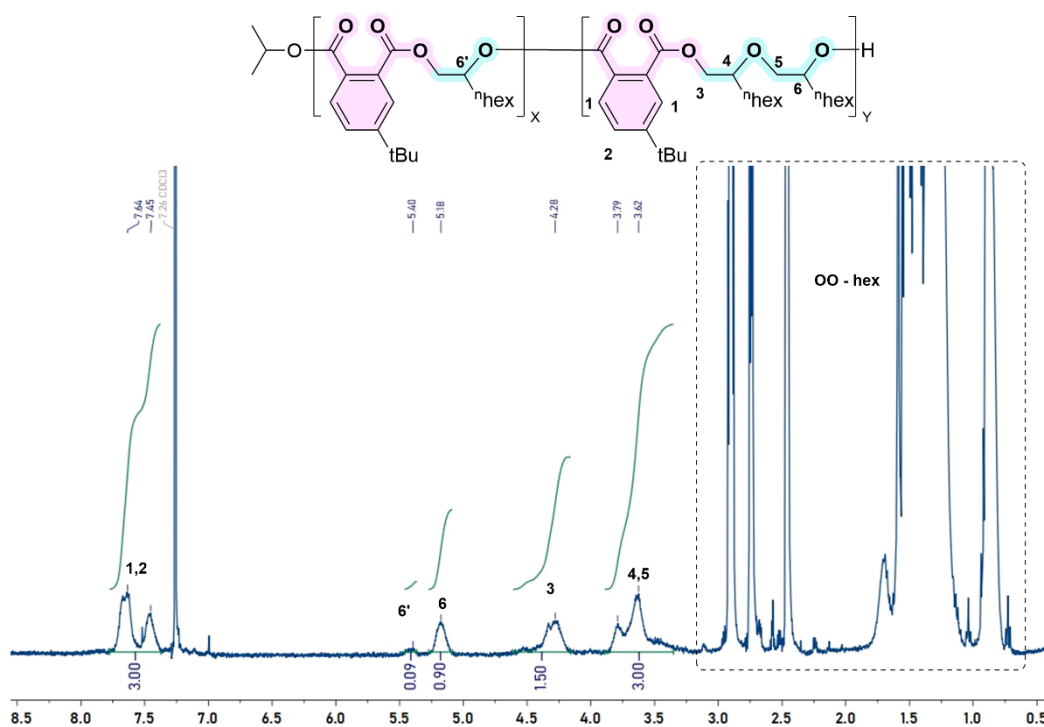
8.4.3.5 Zr(Bn)₄– Entry 6

Figure S8.4.36: Crude ¹H NMR spectrum from the reaction of [Zr(Bn)₄]:[tBuPA]:[OO] = 1: 50: 654, 1 mL OO. Spectrum corresponds to Table 4.2, entry 2 (400 MHz, CDCl₃). *M*_{n,NMR} = 7.4 kg mol⁻¹.

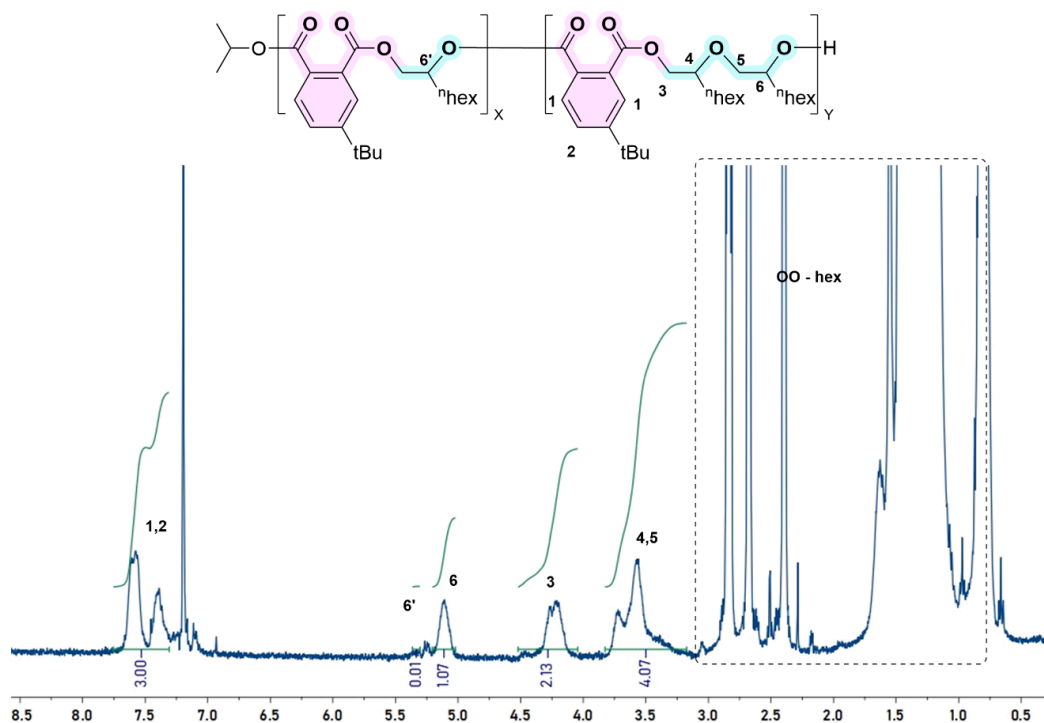
8.4.3.6 Zr(Bn)₄ + (HOBn)₂– Entry 7

Figure S8.4.37: Crude ¹H NMR spectrum from the reaction of [Zr(Bn)₄]:[tBuPA]:[OO] = 1: 50: 654, 1 mL OO. Spectrum corresponds to Table 4.2, entry 2 (400 MHz, CDCl₃). *M*_{n,NMR} = 5.2 kg mol⁻¹.

8.4.2.7 DSC Kinetics

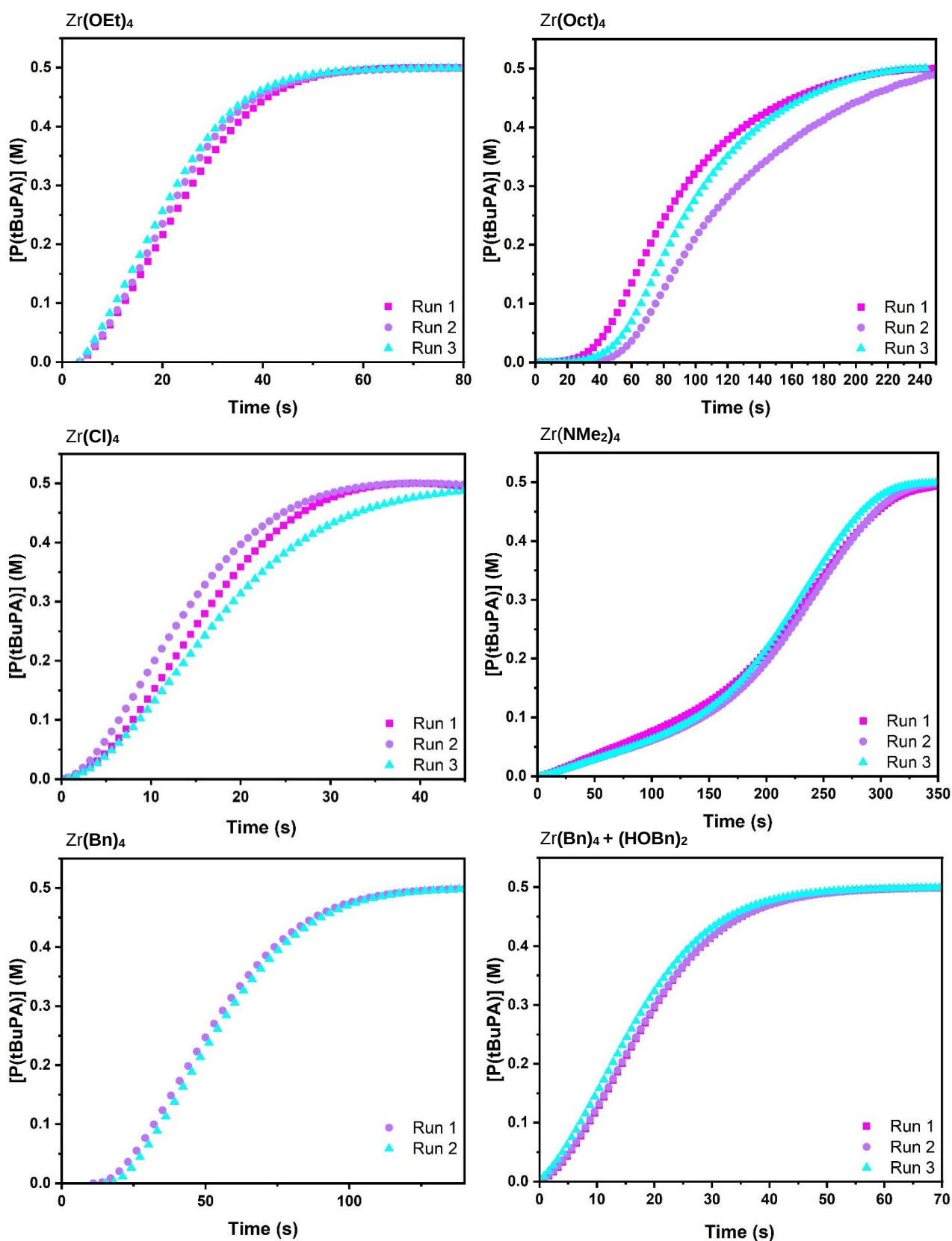


Figure S8.4.38: DSC thermograms for the reaction of $[Zr(X)_4] : [tBuPA] : [OO] = 1 : 50 : 654$, 1 mL OO, 120 °C, Table 4.2 entries 2-7. The reaction was performed in triplicate (for $Zr(Bn)_4$, only two runs were used).

8.4.4 Characterization Data for Polymers Described in Table 4.3 – Zr/Hf(Bn)₄ + (HOBn)_x Catalysts – PA/EDD

8.4.4.1 Zr Example; Zr(Bn)₄ + (HOBn)₅ – Entry 3

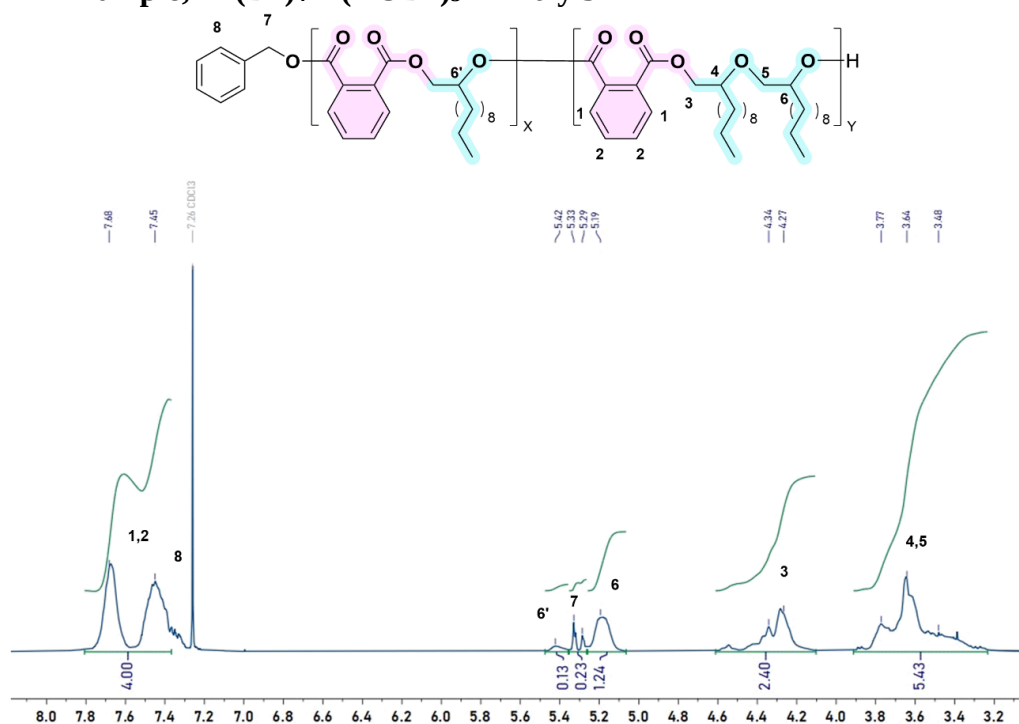


Figure S8.4.39: Purified ¹H NMR spectrum from the reaction of [Zr(Bn)₄]:[PA]: [HOBn]:[EDD] = 1: 50: 5: 1 mL EDD. Spectrum corresponds to Table 4.3, entry 3 (400 MHz, CDCl₃). *M_{n,NMR}* = 4.7 kg mol⁻¹.

8.4.4.2 Hf Example; Zr(Bn)₄ + (HOBn)₅ – Entry 7

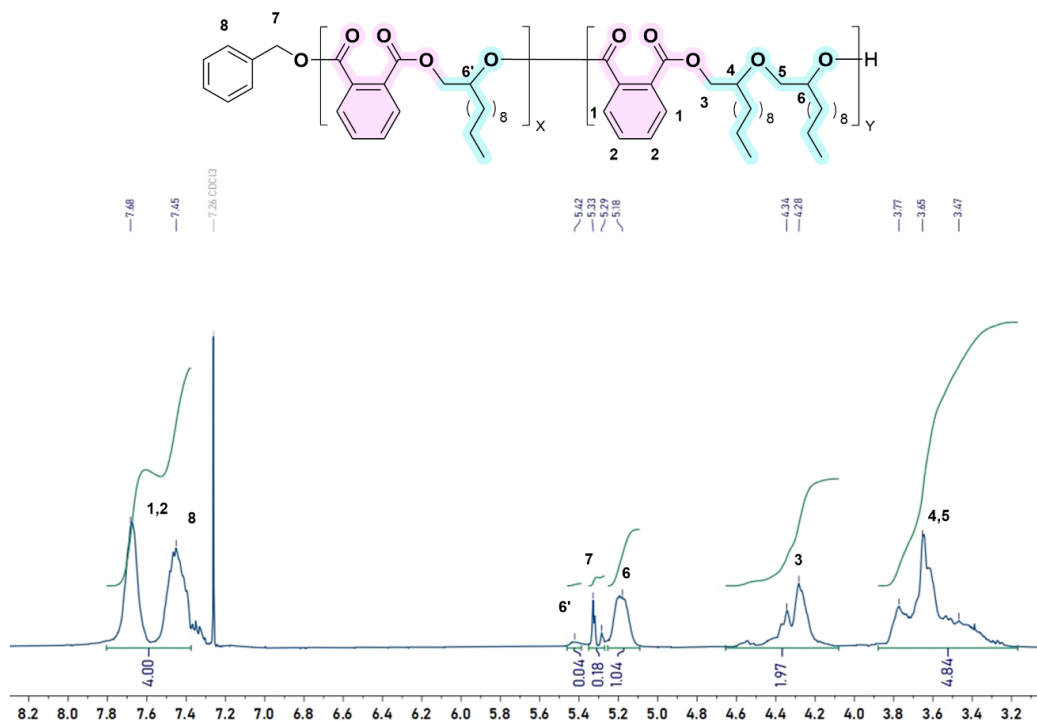


Figure S8.4.40: Purified ¹H NMR spectrum from the reaction of [Hf(Bn)₄]:[PA]:[HOBn]:[EDD]:[CHD] = 1: 50: 5: 1 mL EDD. Spectrum corresponds to Table 4.3, entry 7 (400 MHz, CDCl₃). *M_{n,NMR}* = 4.6 kg mol⁻¹.

8.4.5 Characterization Data for Polymers Described in Table 4.4 – $\text{Hf}(\text{Bn})_4 + (\text{HOBn})_x$ Catalyst – PA/BO

8.4.5.1 Example; $\text{Hf}(\text{Bn})_4 + (\text{HOBn})_5$ – Entry 5

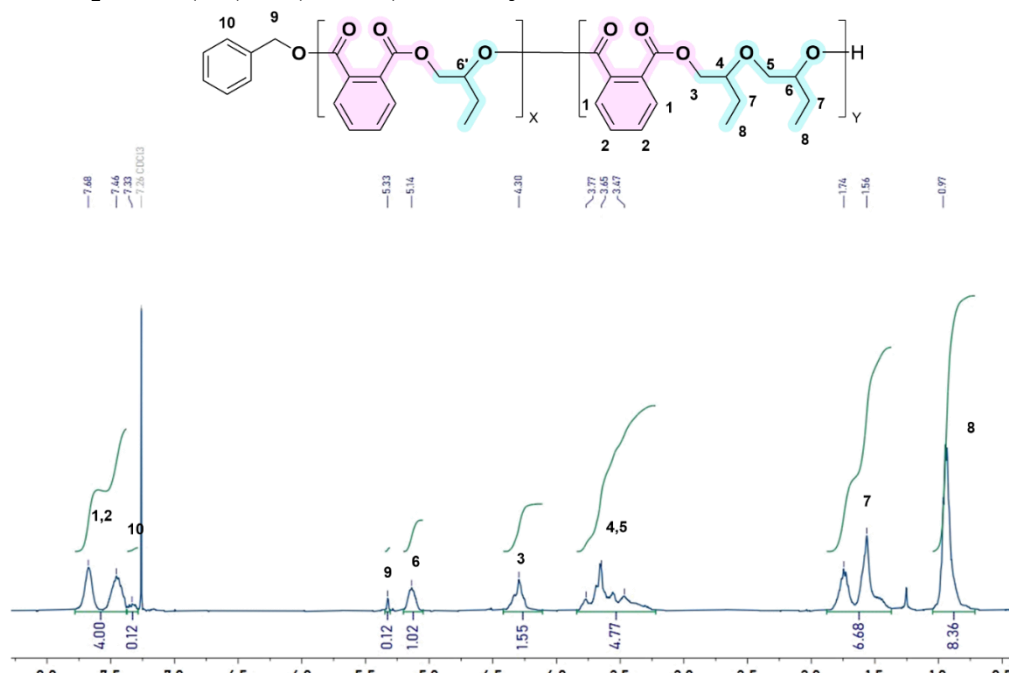


Figure S8.4.41: Purified ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[\text{BnOH}]:[\text{BO}] = 1: 50: 5: 1$ mL BO. Spectrum corresponds to Table 4.4, entry 5 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 3.1 \text{ kg mol}^{-1}$.

8.4.6 Characterization Data for Polymers Described in Table 4.5 – Functional End-groups

8.4.6.1 Example; $\text{Hf}(\text{Bn})_4 + (2\text{-Bromoethanol})_2$ – Entry 1

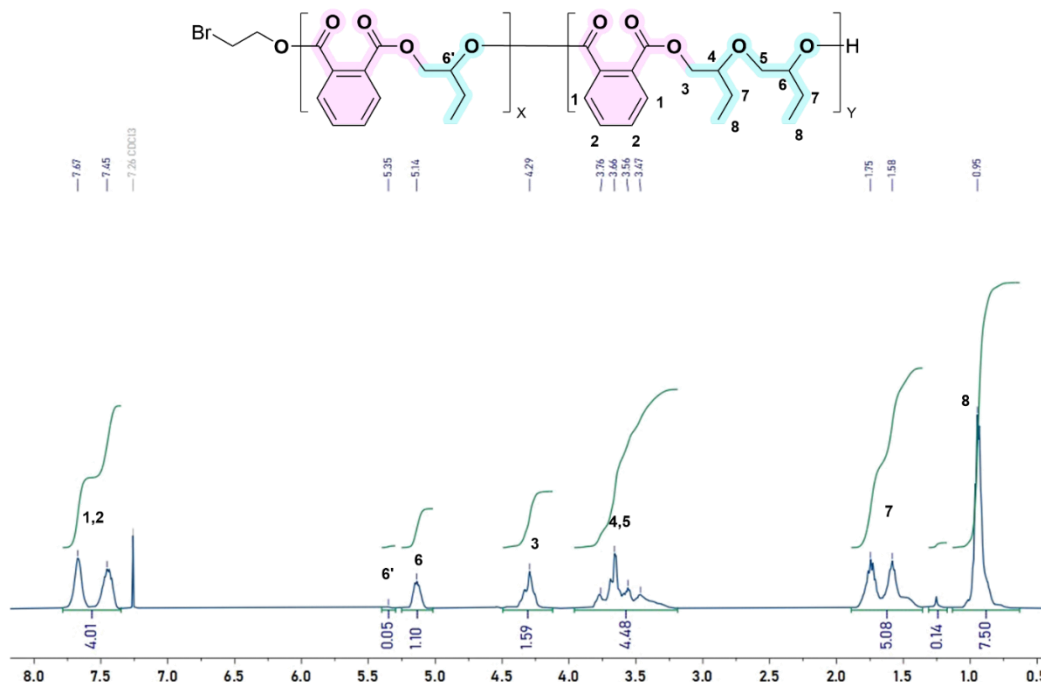


Figure S8.4.42: Purified ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[2\text{-Bromoethanol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 1 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.6 \text{ kg mol}^{-1}$.

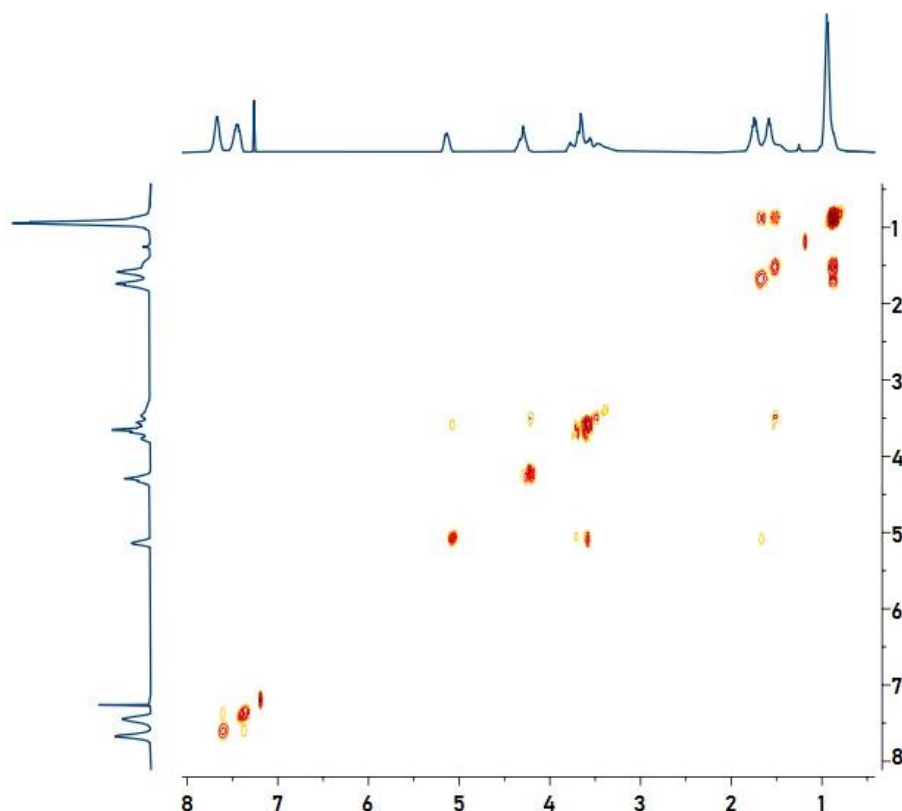


Figure S8.4.43: Purified COSY NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[2\text{-Bromoethanol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 1 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.6 \text{ kg mol}^{-1}$.

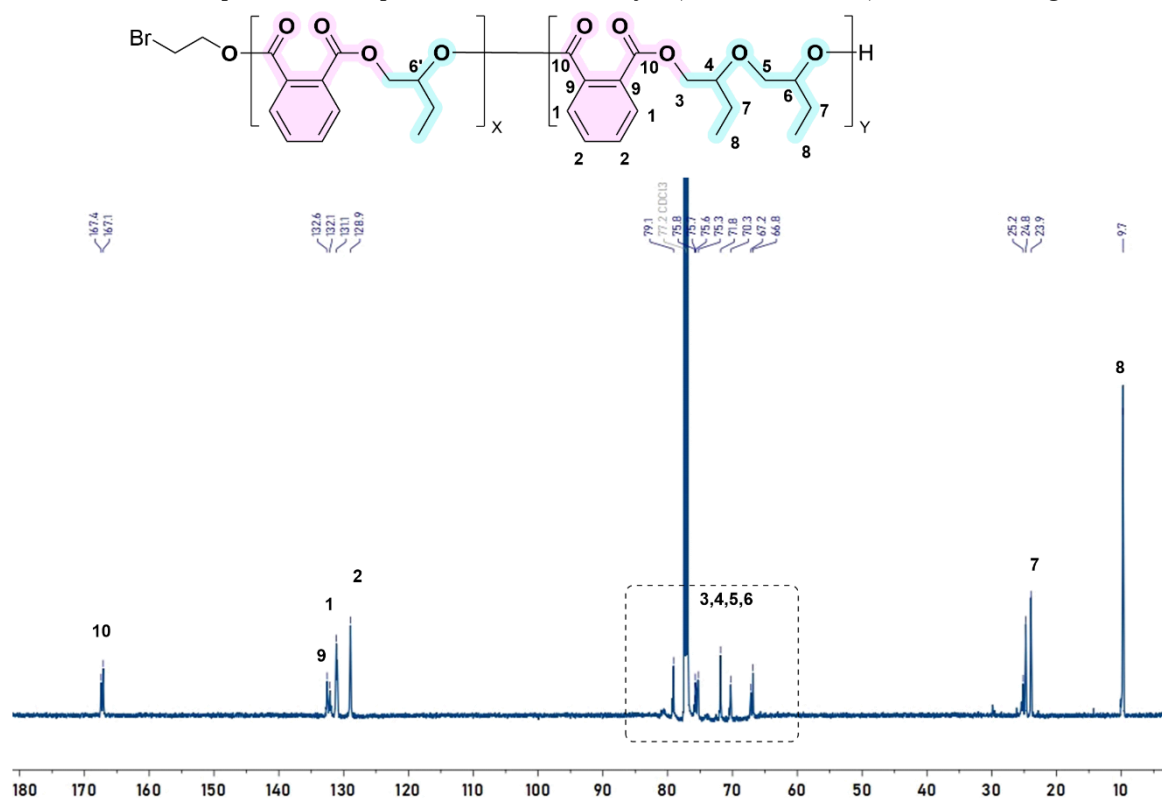


Figure S8.4.44: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[2\text{-Bromoethanol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 1 (151 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.6 \text{ kg mol}^{-1}$.

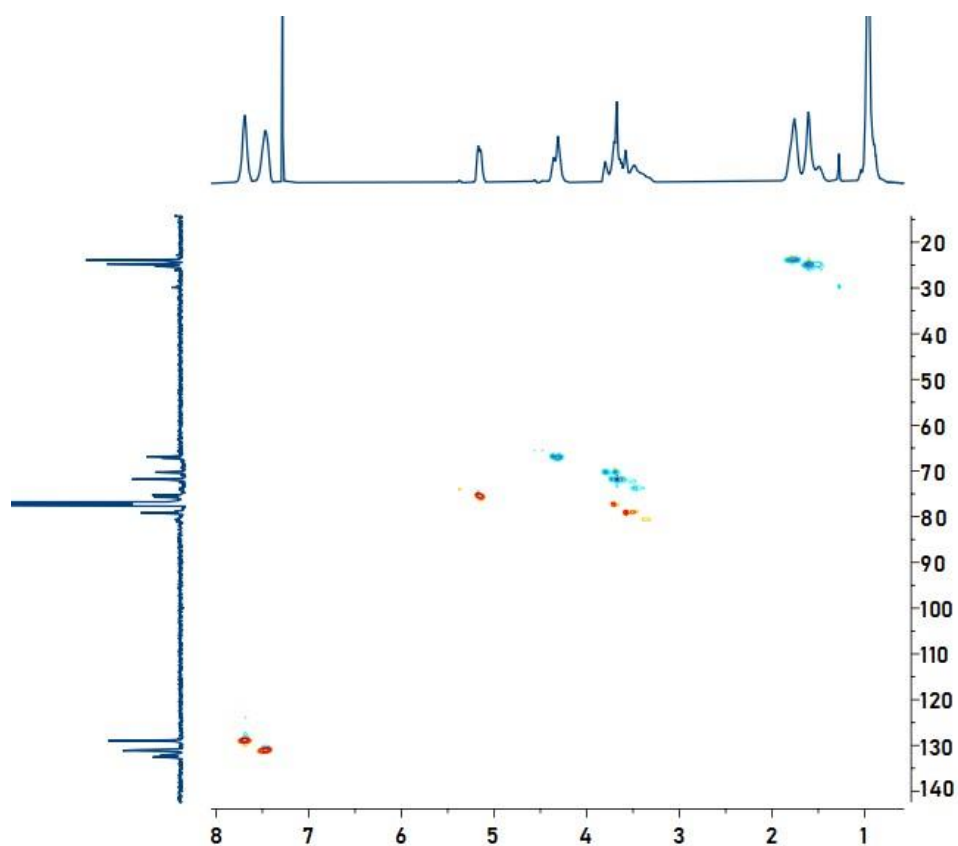


Figure S8.4.45: (^1H , ^{13}C)-HSQC NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[2\text{-Bromoethanol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 1 (CDCl_3). $M_{\text{n,NMR}} = 4.6 \text{ kg mol}^{-1}$.

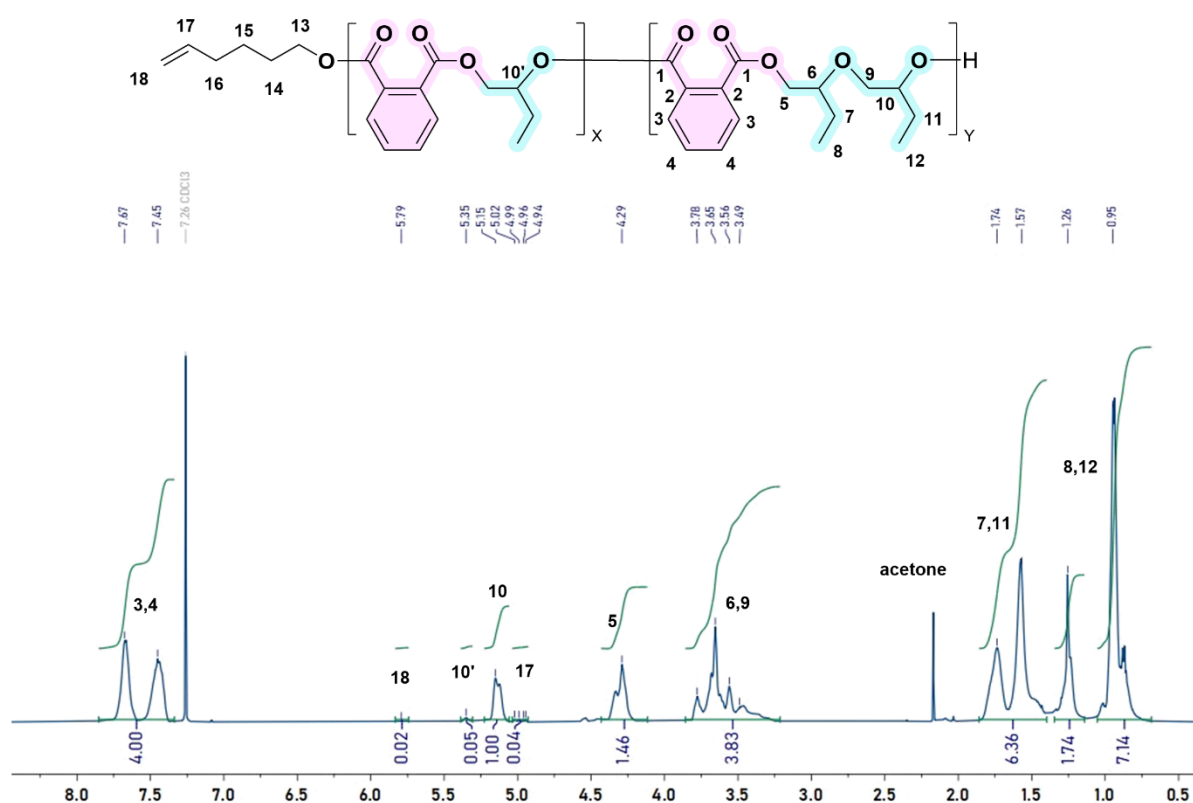
8.4.6.2 Example; $\text{Hf}(\text{Bn})_4 + (5\text{-Hexen-1-ol})_2$ – Entry 2

Figure S8.4.46: Purified ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexen-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 2 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.9 \text{ kg mol}^{-1}$.

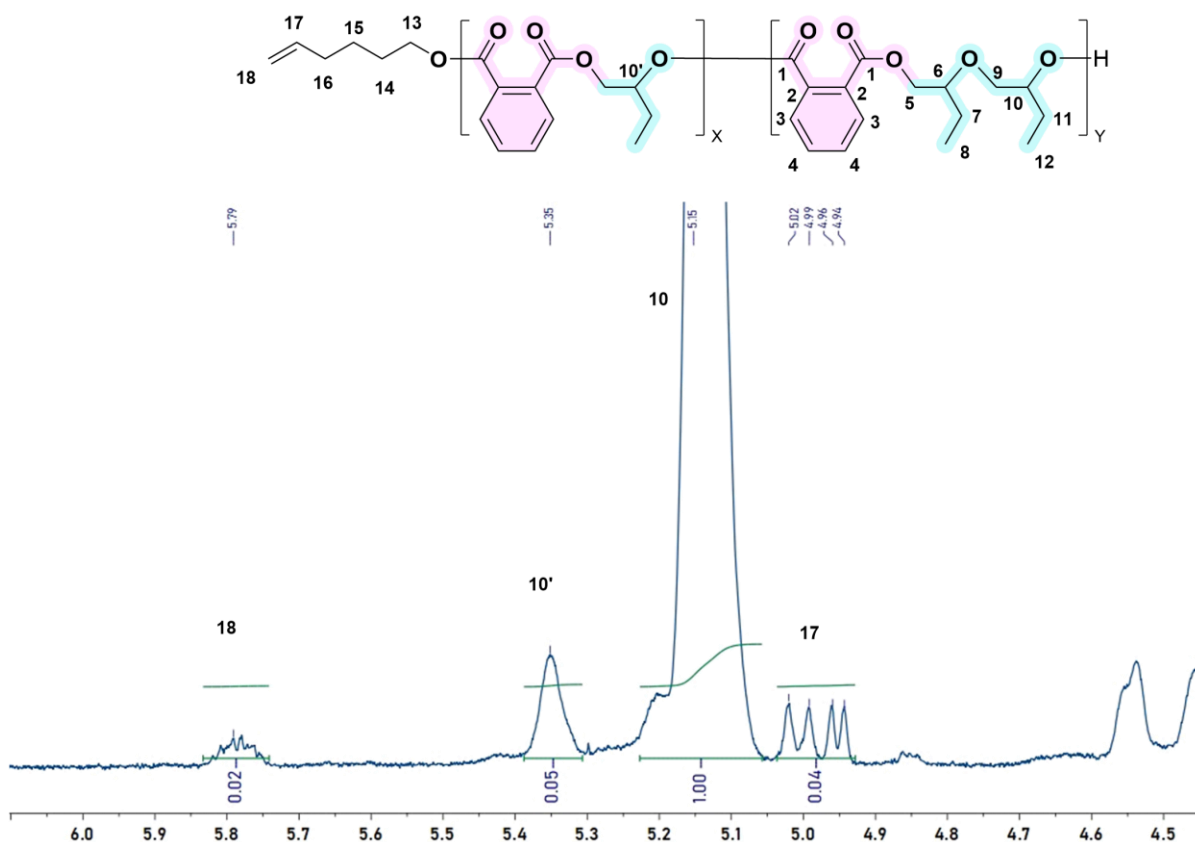


Figure S8.4.47: $(^1\text{H}, ^{13}\text{C})$ -HSQC NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexen-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Zoomed into the region displaying possible alkene peaks at 5.79 (18) and 5.02 (17).

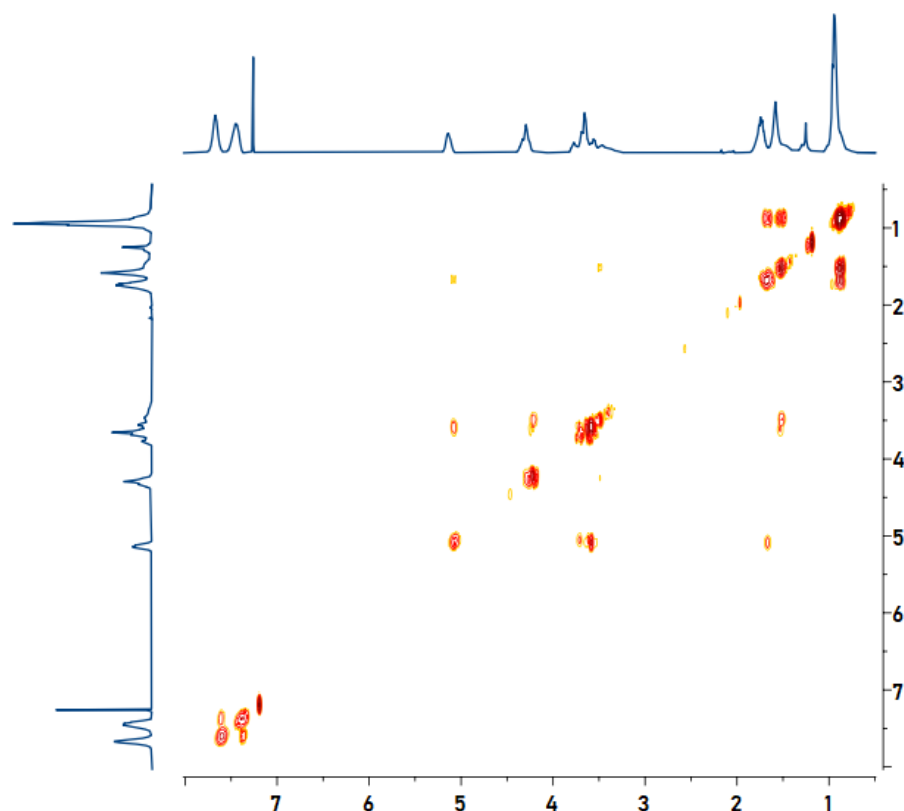


Figure S8.4.48: Purified COSY NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexen-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 2 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.9 \text{ kg mol}^{-1}$.

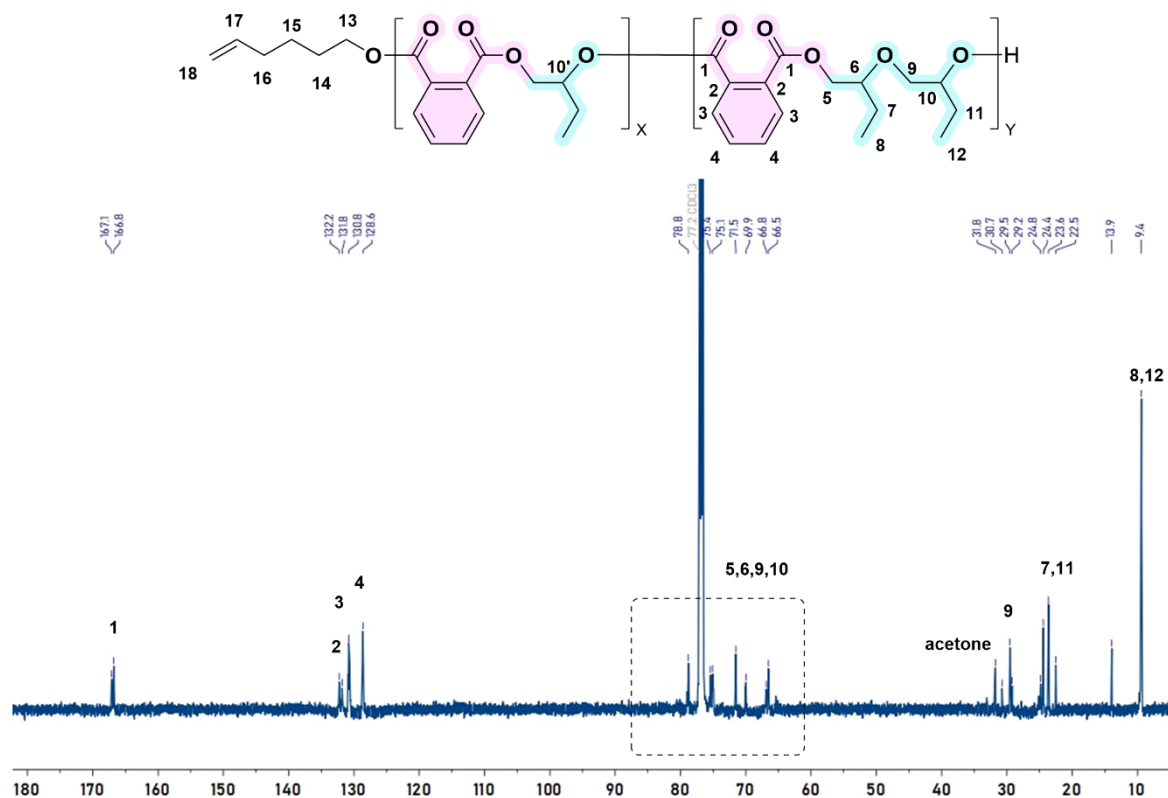


Figure S8.4.49: $^{13}\text{C}\{^1\text{H}\} \text{ } ^1\text{H}$ NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexen-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 2 (151 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.9 \text{ kg mol}^{-1}$.

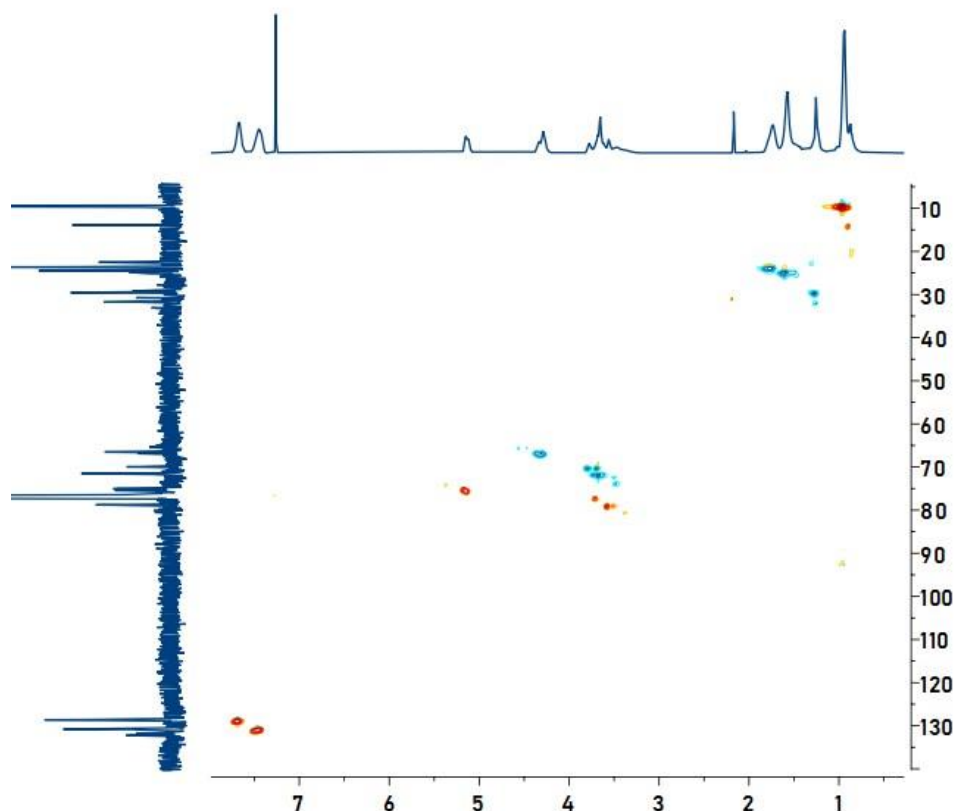


Figure S8.4.50: (^1H , ^{13}C)-HSQC NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexen-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 2 (CDCl_3). $M_{n,\text{NMR}} = 4.9 \text{ kg mol}^{-1}$.

8.4.6.3 Example; $\text{Hf}(\text{Bn})_4 + (5\text{-Hexyn-1-ol})_2$ – Entry 3

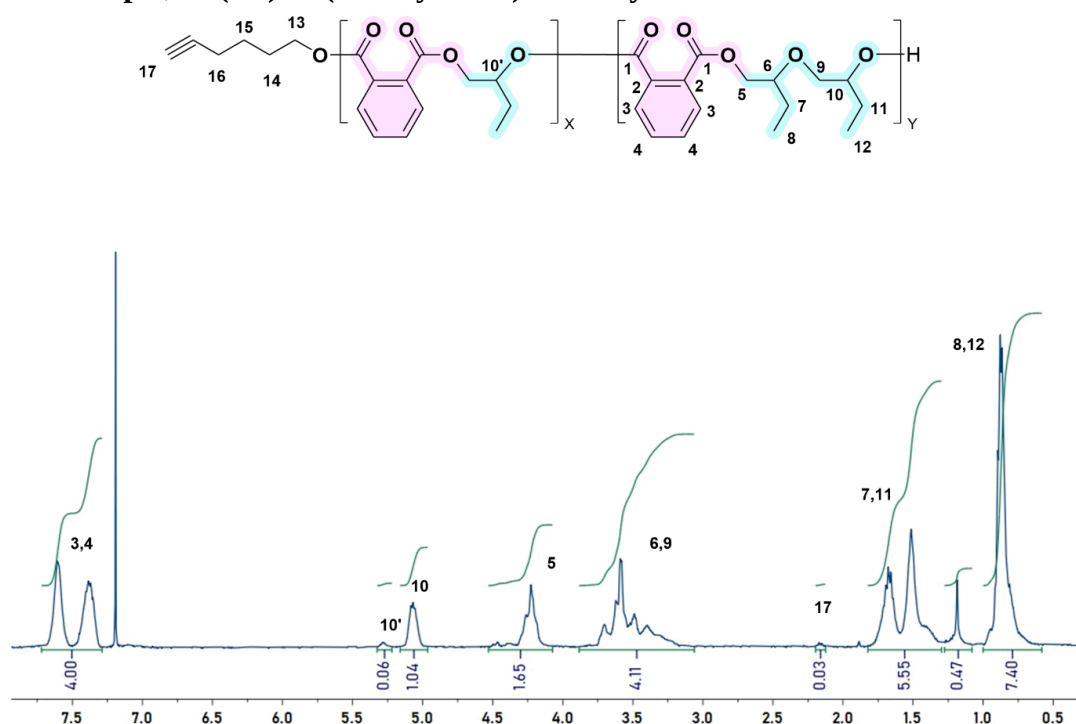


Figure S8.4.51: Purified ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexyn-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 3 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.6 \text{ kg mol}^{-1}$.

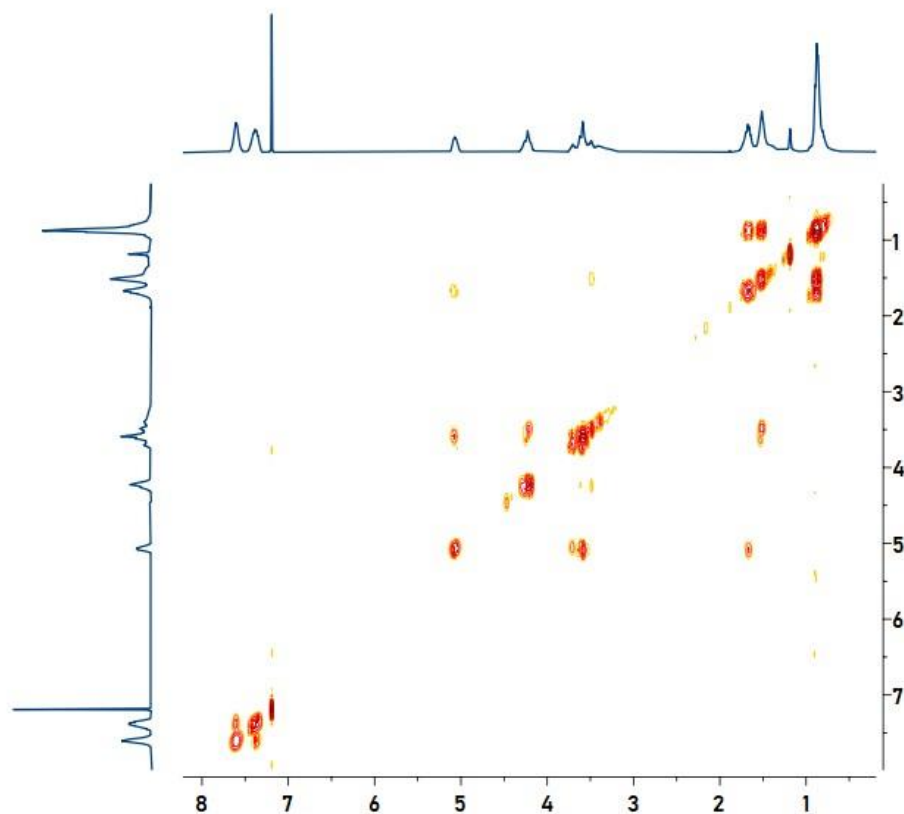


Figure S8.4.52: COSY ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexyn-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 3 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.6 \text{ kg mol}^{-1}$.

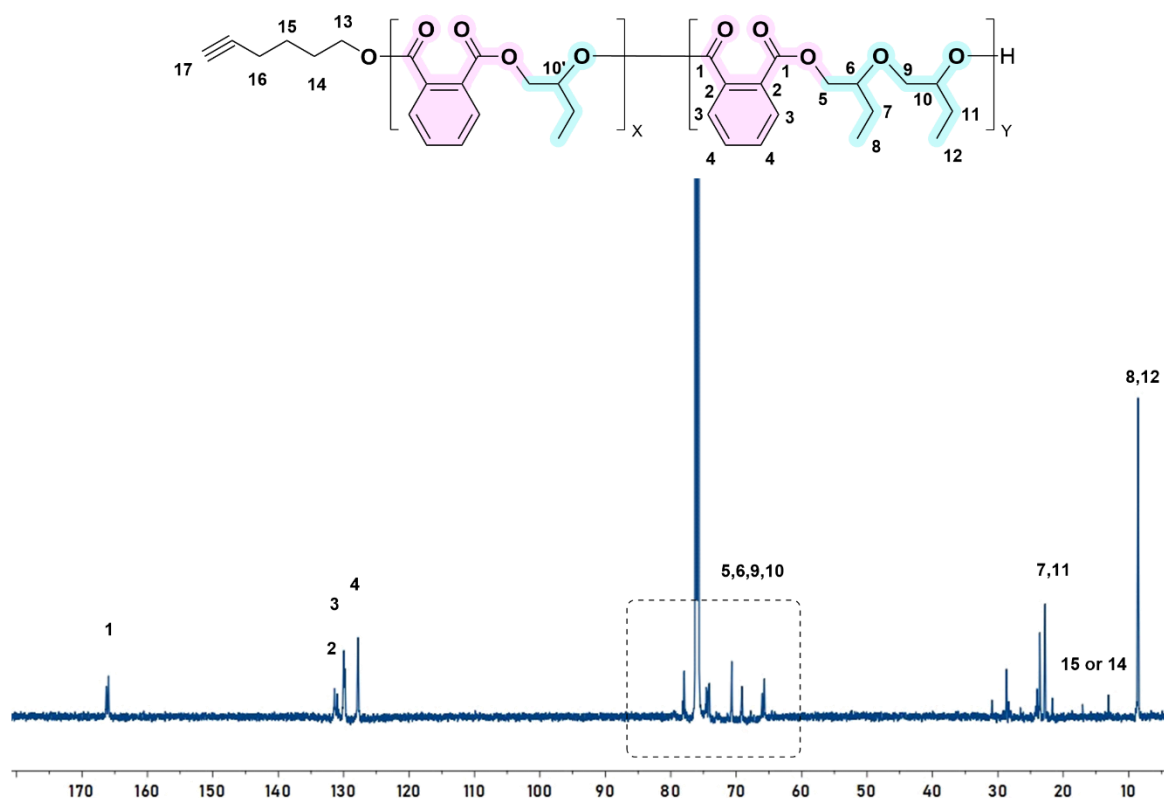


Figure S8.4.53: $^{13}\text{C}\{^1\text{H}\}$ ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexyn-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 3 (151 MHz, CDCl_3). $M_{n,\text{NMR}} = 4.6 \text{ kg mol}^{-1}$.

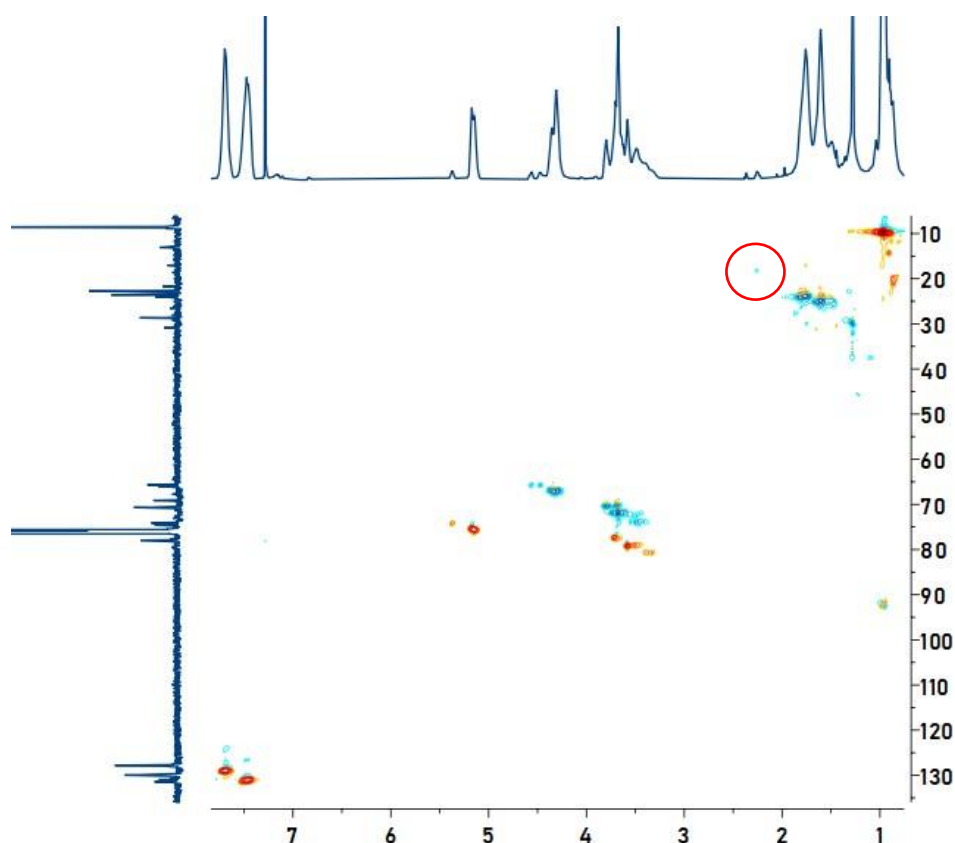


Figure S8.4.54: (^1H , ^{13}C)-HSQC ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[5\text{-Hexyn-1-ol}]:[\text{BO}] = 1: 50: 2: 1$ mL BO. Spectrum corresponds to Table 4.5, entry 3 (CDCl_3). $M_{n,\text{NMR}} = 4.6 \text{ kg mol}^{-1}$.

8.4.7 Characterization Data for Polymers Described in Table 4.6 – Polymer Architecture

8.4.7.1 Example; $\text{Hf}(\text{Bn})_4 + \text{CHD}$ – Entry 2

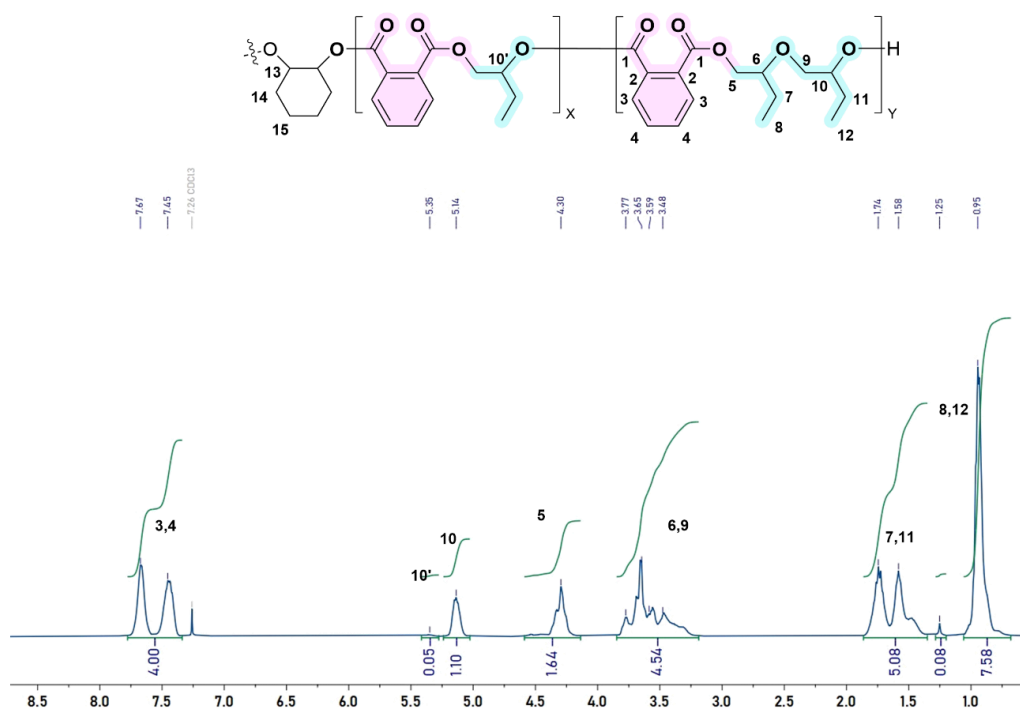


Figure S8.4.55: Purified ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[\text{CHD}]:[\text{BO}] = 1: 50: 1: 1$ mL BO. Spectrum corresponds to Table 4.6, entry 2 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 9.6 \text{ kg mol}^{-1}$.

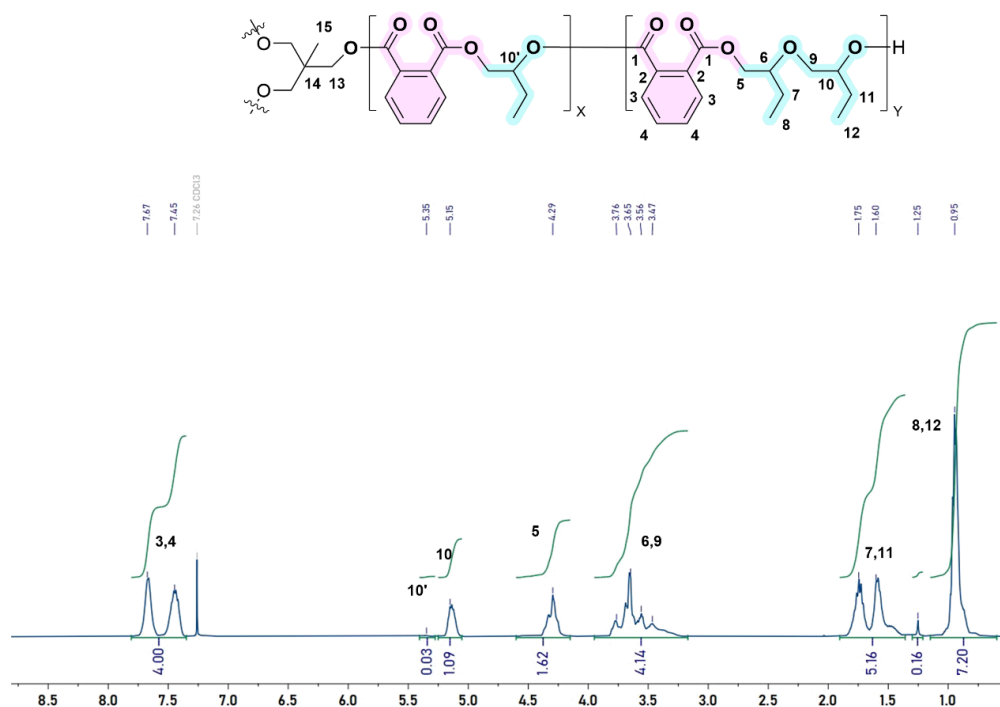
8.4.7.2 Example; $\text{Hf}(\text{Bn})_4$ + TMP – Entry 3

Figure S8.4.56: Purified ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[\text{TMP}]:[\text{BO}] = 1: 50: 2/3: 1$ mL BO. Spectrum corresponds to Table 4.6, entry 3 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 10.7 \text{ kg mol}^{-1}$.

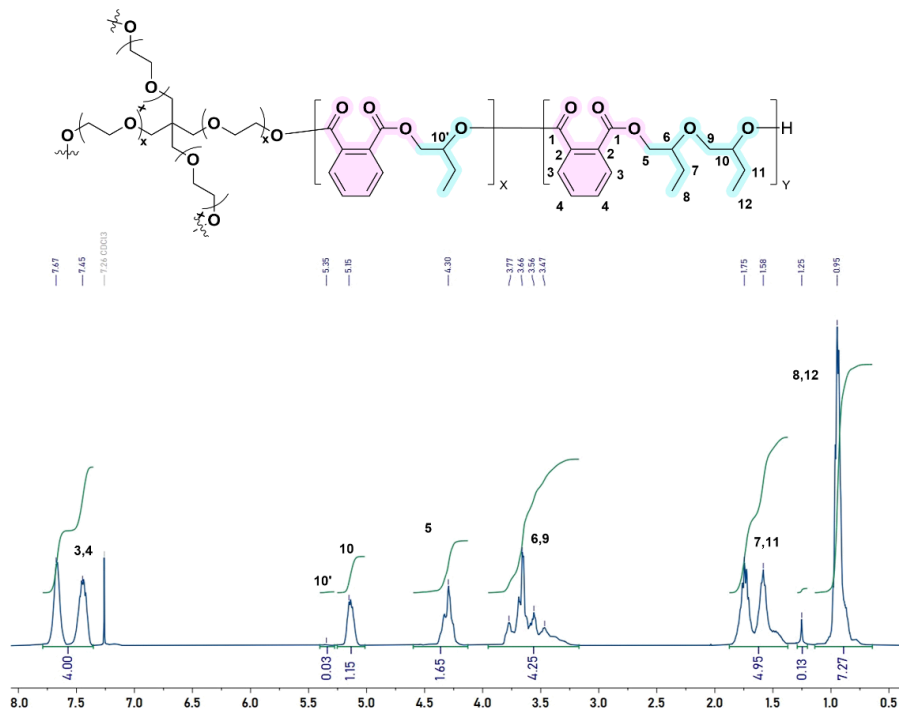
8.4.7.3 Example; $\text{Hf}(\text{Bn})_4$ + PE – Entry 4

Figure S8.4.57: Purified ^1H NMR spectrum from the reaction of $[\text{Hf}(\text{Bn})_4]:[\text{PA}]:[\text{PE}]:[\text{BO}] = 1: 50: 2/4: 1$ mL BO. Spectrum corresponds to Table 4.6, entry 4 (400 MHz, CDCl_3). $M_{n,\text{NMR}} = 8.5 \text{ kg mol}^{-1}$.

S8.4.8 Single Crystal X-ray Diffraction

Table S8.4.1: Summary of crystallographic refinement data for **Ti(L2)₂(OⁱPr)₂**, **Zr(L2)₂(OⁱPr)₂**, **Hf(L2)₂(OⁱPr)₂** and **Zr(L4)₂(OⁱPr)₂**.

Complex	Ti(L2)₂(OⁱPr)₂	Hf(L2)₂(OⁱPr)₂	Zr(L2)₂(OⁱPr)₂	Zr(L4)₂(OⁱPr)₂
Identification code	031RWFK21	025RWFK21	001RWFK21	003src22
Empirical formula	C ₄₂ H ₃₄ F ₁₈ N ₂ O ₇ Ti	C ₄₂ H ₇₂ F ₁₈ HfN ₂ O ₇	C _{36.97} H ₂₈ F ₁₈ N ₂ O ₆ Zr	C ₃₆ F ₆ N ₂ O ₈ Zr
Formula weight	1068.61	1237.50	1029.43	793.60
Temperature/K	150.00(19)	150.04(19)	150.0(2)	150.01(10)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	P-1	I2/a	C2/c	P2 ₁ /n
a/Å	12.7072(4)	16.4077(3)	20.3116(2)	13.98850(10)
b/Å	13.6282(3)	20.6226(2)	17.4998(2)	15.2939(2)
c/Å	15.6767(4)	16.7538(3)	23.5926(3)	19.1409(2)
α/°	106.575(2)	90	90	90
β/°	97.230(2)	117(6)	96.1980(10)	102.7200(10)
γ/°	114.490(3)	90	90	90
Volume/Å ³	2273.30(12)	5069(238)	8336.95(17)	3994.48(7)
Z	2	4	8	4
ρ _{calc} /cm ³	1.561	1.621	1.640	1.320
μ/mm ⁻¹	2.739	4.834	3.337	2.934
F(000)	1080.0	2512.0	4110.0	1552.0
Crystal size/mm ³	0.1 × 0.07 × 0.06	0.168 × 0.092 × 0.065	0.180 × 0.098 × 0.075	0.16 × 0.101 × 0.080
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.128 to 152.218	7.294 to 152.376	6.684 to 152.492	7.132 to 152.656
Index ranges	-15 ≤ h ≤ 15, -15 ≤ k ≤ 17, -19 ≤ l ≤ 19	-20 ≤ h ≤ 20, -24 ≤ k ≤ 25, -21 ≤ l ≤ 21	-25 ≤ h ≤ 25, -15 ≤ k ≤ 21, -29 ≤ l ≤ 29	-15 ≤ h ≤ 17, -15 ≤ k ≤ 19, -22 ≤ l ≤ 23
Reflections collected	23758	69940	51017	25501
Independent reflections	9355 [R _{int} = 0.0324, R _{sigma} = 0.0353]	5285 [R _{int} = 0.0594, R _{sigma} = 0.0203]	8680 [R _{int} = 0.0357, R _{sigma} = 0.0242]	8282 [R _{int} = 0.0242, R _{sigma} = 0.0258]
Data/restraints/parameters	9355/0/689	5285/18/325	8680/0/589	8282/0/478
Goodness-of-fit on F ²	1.049	1.106	1.053	1.037
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0556, wR ₂ = 0.1541	R ₁ = 0.0318, wR ₂ = 0.0910	R ₁ = 0.0500, wR ₂ = 0.1412	R ₁ = 0.0681, wR ₂ = 0.2318
Final R indexes [all data]	R ₁ = 0.0634, wR ₂ = 0.1651	R ₁ = 0.0344, wR ₂ = 0.0936	R ₁ = 0.0572, wR ₂ = 0.1491	R ₁ = 0.0702, wR ₂ = 0.2354
Largest diff. peak/hole / e Å ⁻³	0.80/-0.51	0.71/-0.60	1.94/-1.31	4.91/-0.49

8.5: Degradable, Recyclable and Toughened High Molar Mass Poly(cyclopentene carbonate) (PCPC) Blends for Sustainable Alternative Thermoplastic Materials

8.5.1 Polymer Synthesis and Characterisation

8.5.1.1 NMR Data for Polymers Described in Table 5.1

8.5.1.1.1 Synthesis and Characterisation of P5

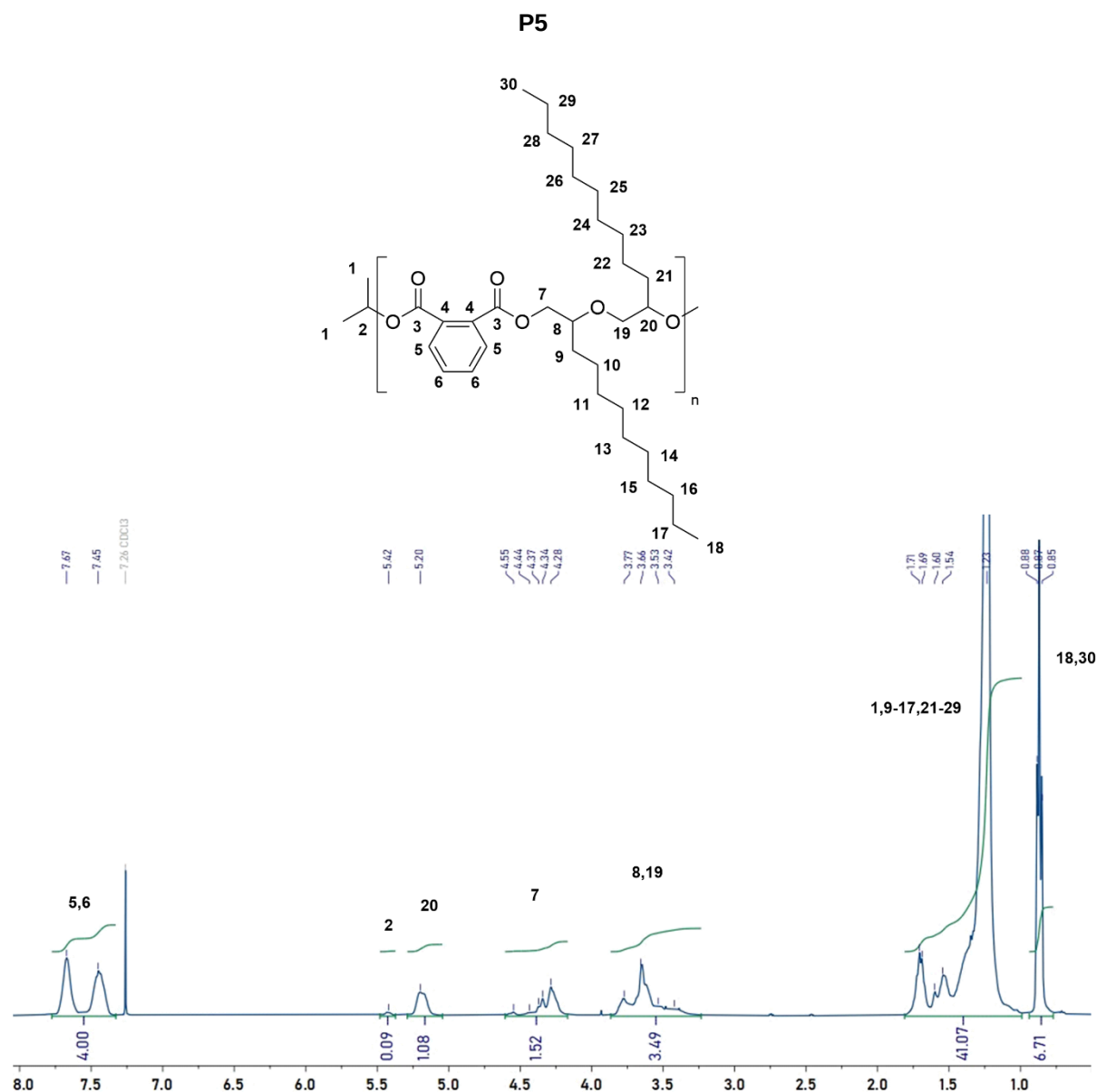


Figure S8.5.1: ¹H NMR spectrum of **P5** (with assignment, Table 5.1, **P5**) (400 MHz, CDCl₃). Reaction conditions: [3] = 12.8 mM in 1 mL epoxide, [Cat] : [PA] : [EDD] = 1 : 125 : 350, 50 °C.

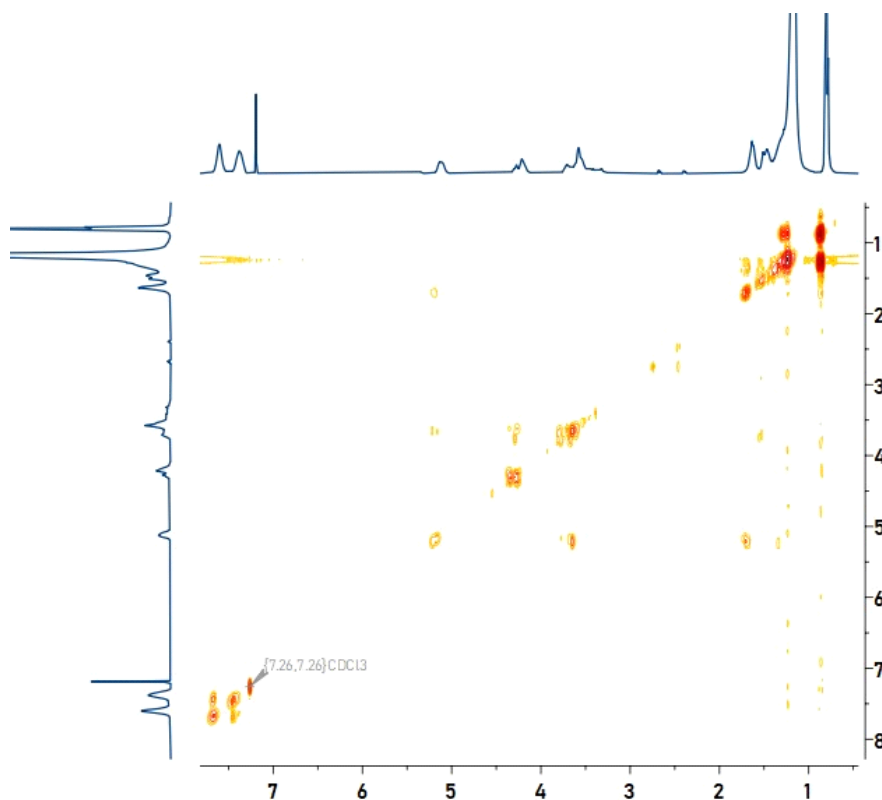


Figure S8.5.2: ^1H COSY NMR spectrum of **P5** (Table 5.1, **P5**) (400 MHz, CDCl_3). Reaction conditions: **[3]** = 12.8 mM in 1 mL epoxide, [Cat] : [PA] : [EDD] = 1 : 125 : 350, 50 °C.

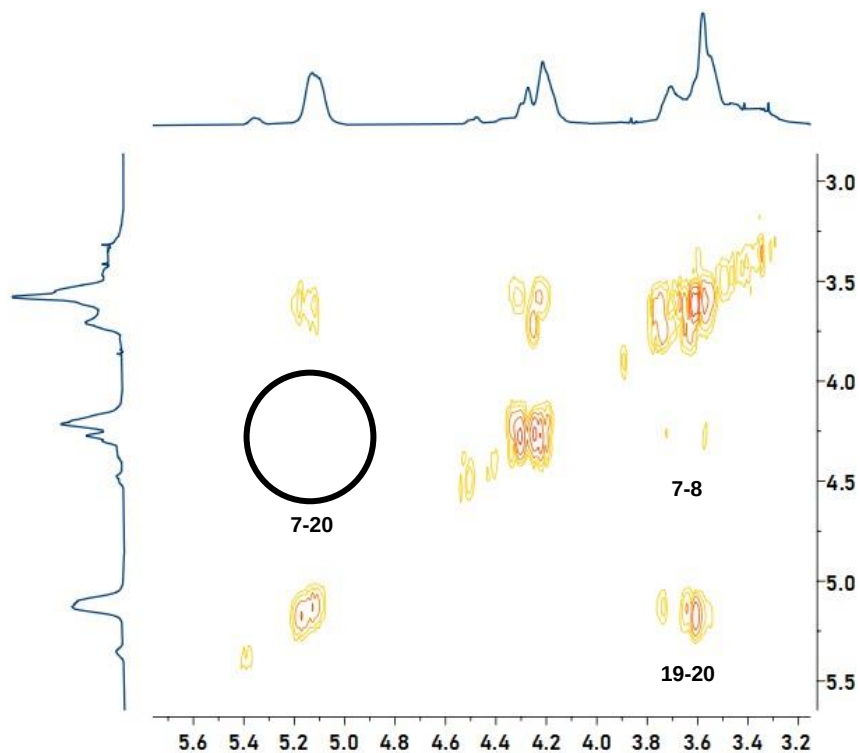


Figure S8.5.3: Magnified ^1H COSY NMR spectrum of **P5** (Table 5.1, **P5**) (400 MHz, CDCl_3). Reaction conditions: **[3]** = 12.8 mM in 1 mL epoxide, [Cat] : [PA] : [EDD] = 1 : 125 : 350, 50 °C. This region shows correlation of the methine and methylene ester regions (7 and 20) to the ether signal (8 and 19), but not to one another (shown as black circle).

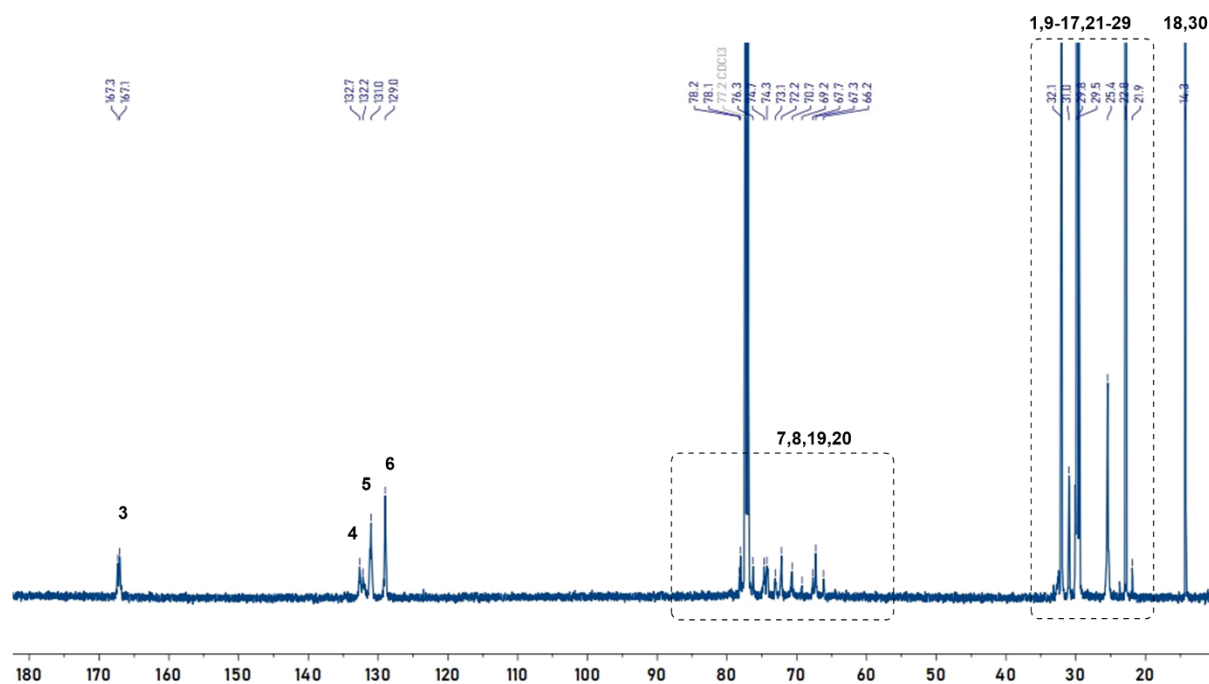


Figure S8.5.4: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P5** (Table 5.1, **P5**) (151 MHz, CDCl_3). Reaction conditions: **[3]** = 12.8 mM in 1 mL epoxide, [Cat] : [PA] : [EDD] = 1 : 125 : 350, 50 °C.

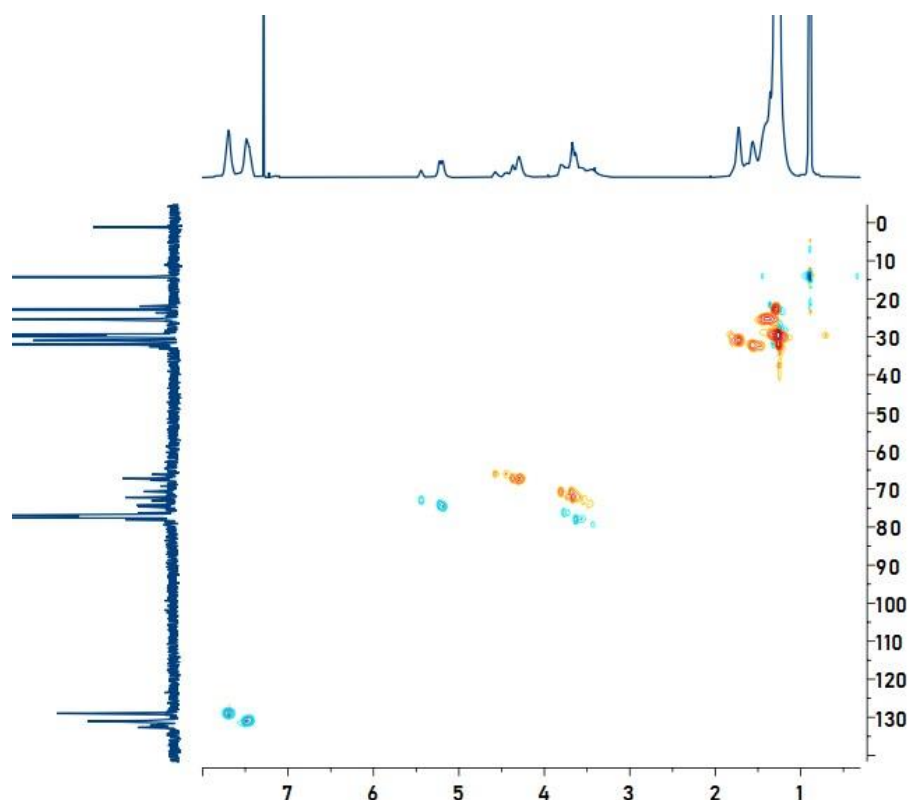


Figure S8.5.5: HSQC $^{13}\text{C}\{-^1\text{H}\}$ NMR spectrum of **P5** (Table 5.1, **P5**) (400 MHz, CDCl_3). Reaction conditions: **[3]** = 12.8 mM in 1 mL epoxide, [Cat] : [PA] : [EDD] = 1 : 125 : 350, 50 °C.

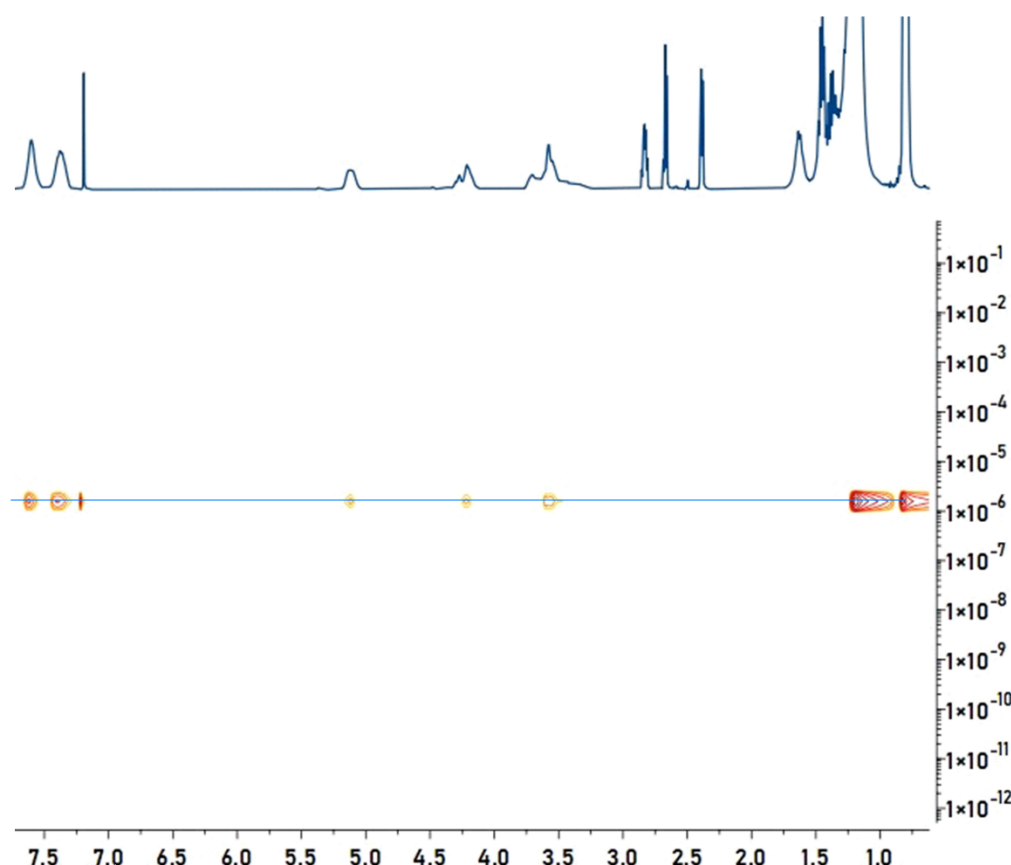


Figure S8.5.6: DOSY NMR spectrum of **P5** (Table 5.1, **P5**) (400 MHz, CDCl_3). Reaction conditions: **[3]** = 12.8 mM in 25 mL epoxide, [Cat] : [PA] : [EDD] = 1 : 125 : 350, 50 °C.

Calculation of DP **P5**:

The conversion of PA was measured against its polymeryl species (PA = 7.98 ppm vs P(PA) 7.67 ppm).

$$PA \text{ conversion (\%)} = \frac{\text{Total integral of } P(PA)}{\text{Total integral of PA and } P(PA)} \times 100$$

From this, the DP for PA could be calculated from the starting ratios of reagents ([Cat]:[PA]:[EDD]) where [cat] = 1, and it was assumed that all isoproxides (4) and isopropanol species (1) of the catalyst **3** initiated.

$$DP \text{ for PA} = \frac{PA \text{ conversion (\%)} \times [PA]_0}{\text{No. of initiators}}$$

Next, to calculate the sum of polymerised Epoxydodecane, the P(PA) integral was set to 4, (the number of protons for 1 equivalent of P(PA)) and integrated against the P(EDD) signals (the methine ester (20), methylene ester (7) and methine/methylene ether (8 and 19)

protons), then dividing by the proposed number of protons in this region (6), to give the relative equivalents of P(EDD) in the polymer.

$$DP \text{ for } P(EDD) = DP \text{ for } PA \times \text{Equivalents of } P(EDD)$$

8.5.1.1.2 Synthesis and Characterisation of P5-PCPC

P5-PCPC

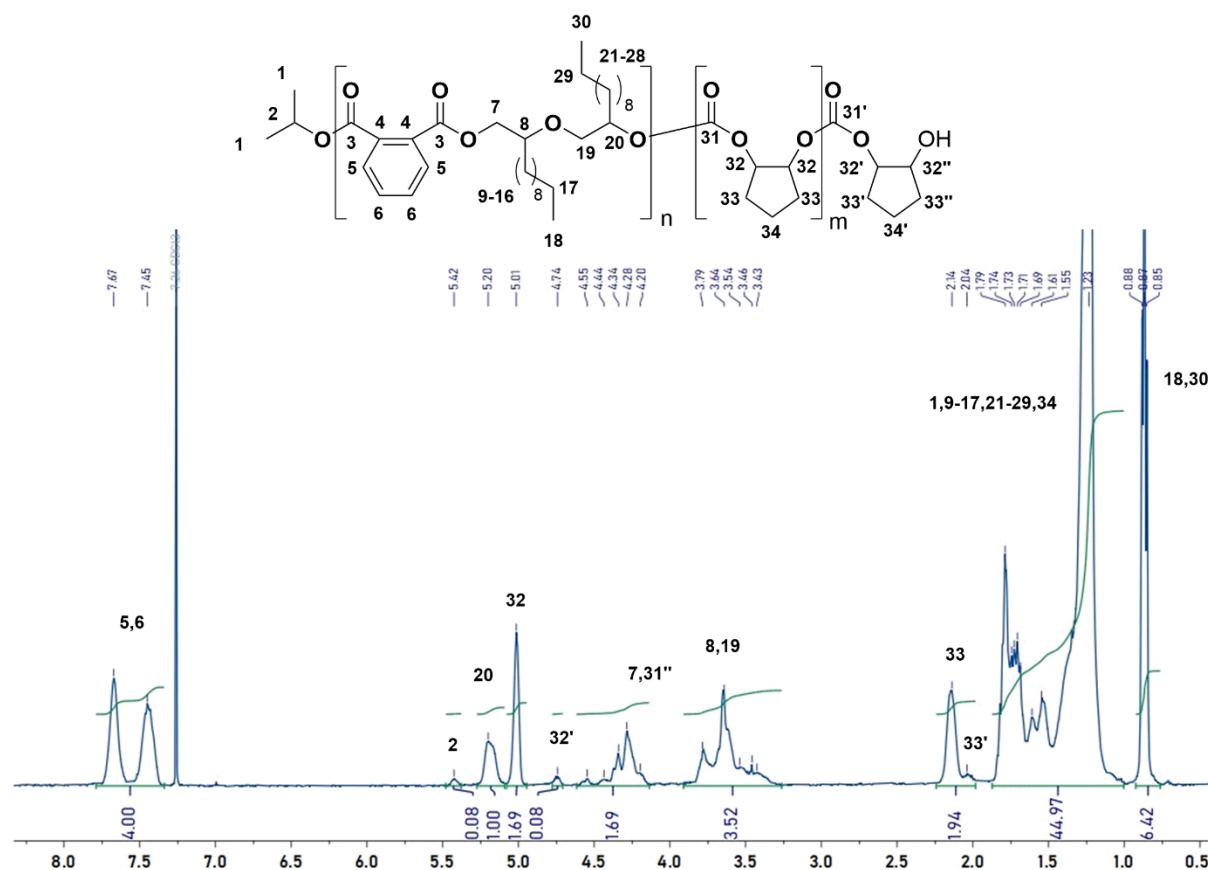


Figure S8.5.7: ¹H NMR spectrum of **P5-PCPC** (with assignment, Table 5.1, **P5-PCPC**) (400 MHz, CDCl₃). Reaction conditions: **[4]** = 10 mM in 1 mL epoxide, [Cat] : **[P5]** : **[CPO]** = 1 : 19 : 960, 1 bar CO₂ pressure, 80 °C.

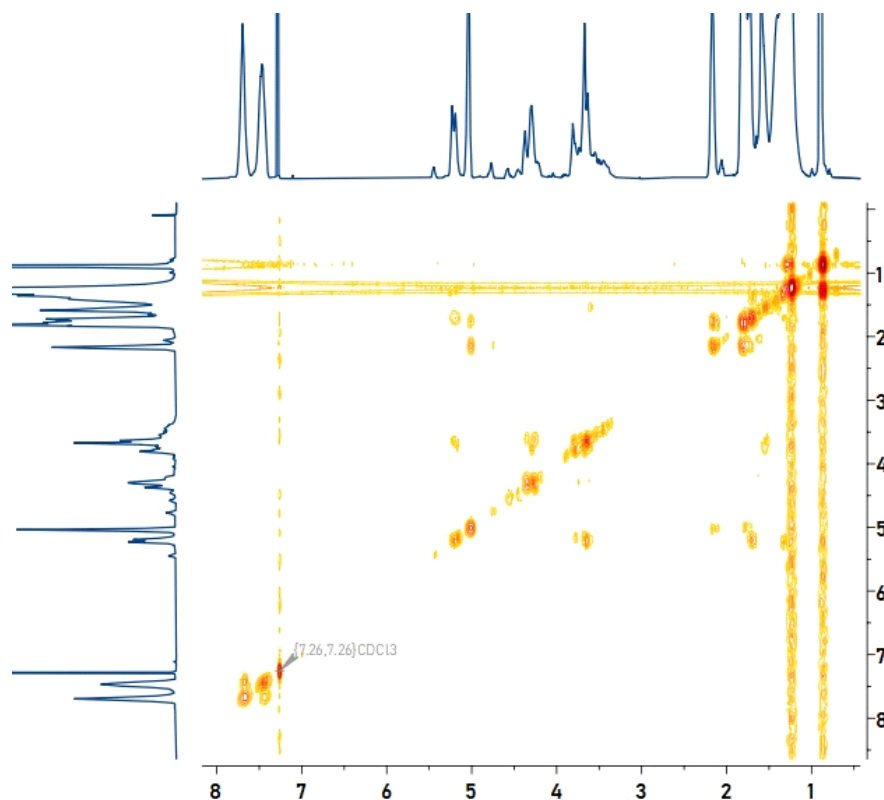


Figure S8.5.8: ^1H COSY NMR spectrum of **P5-PCPC** (Table 5.1, **P5-PCPC**) (400 MHz, CDCl_3). Reaction conditions: **[4]** = 10 mM in 1 mL epoxide, [Cat] : **[P5]** : [CPO] = 1 : 19 : 960, 1 bar CO_2 pressure, 80 $^\circ\text{C}$.

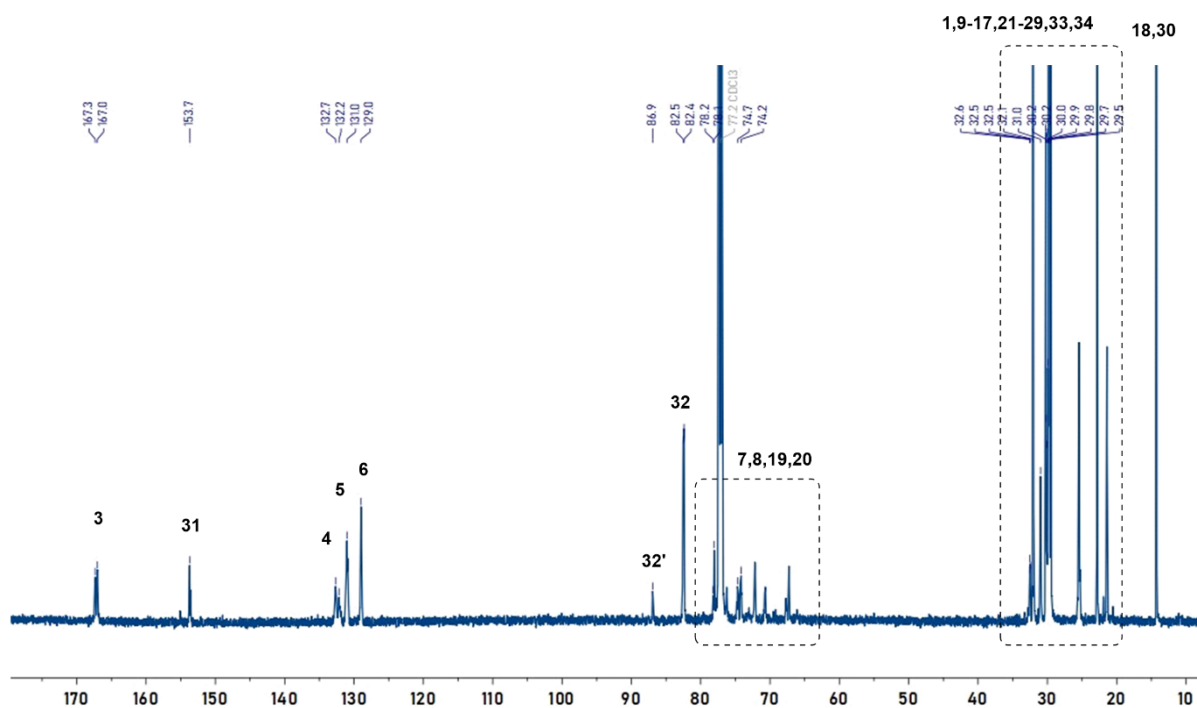


Figure S8.5.9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P5-PCPC** (Table 5.1, **P5-PCPC**) (151 MHz, CDCl_3). Reaction conditions: **[4]** = 10 mM in 1 mL epoxide, [Cat] : **[P5]** : [CPO] = 1 : 19 : 960, 1 bar CO_2 pressure, 80 $^\circ\text{C}$.

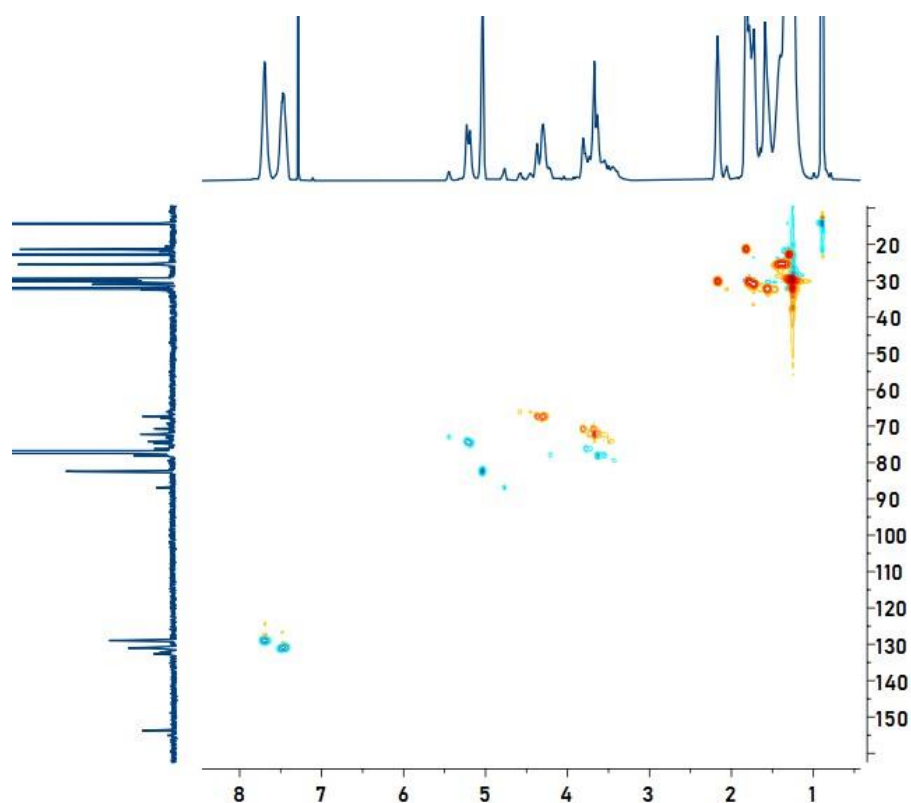


Figure S8.5.10: HSQC ^{13}C - $\{^1\text{H}\}$ NMR spectrum of **P5-PCPC** (Table 5.1, **P5-PCPC**) (400 MHz, CDCl_3). Reaction conditions: **[4]** = 10 mM in 1 mL epoxide, [Cat] : **[P5]** : [CPO] = 1 : 19 : 960, 1 bar CO_2 pressure, 80 $^\circ\text{C}$.

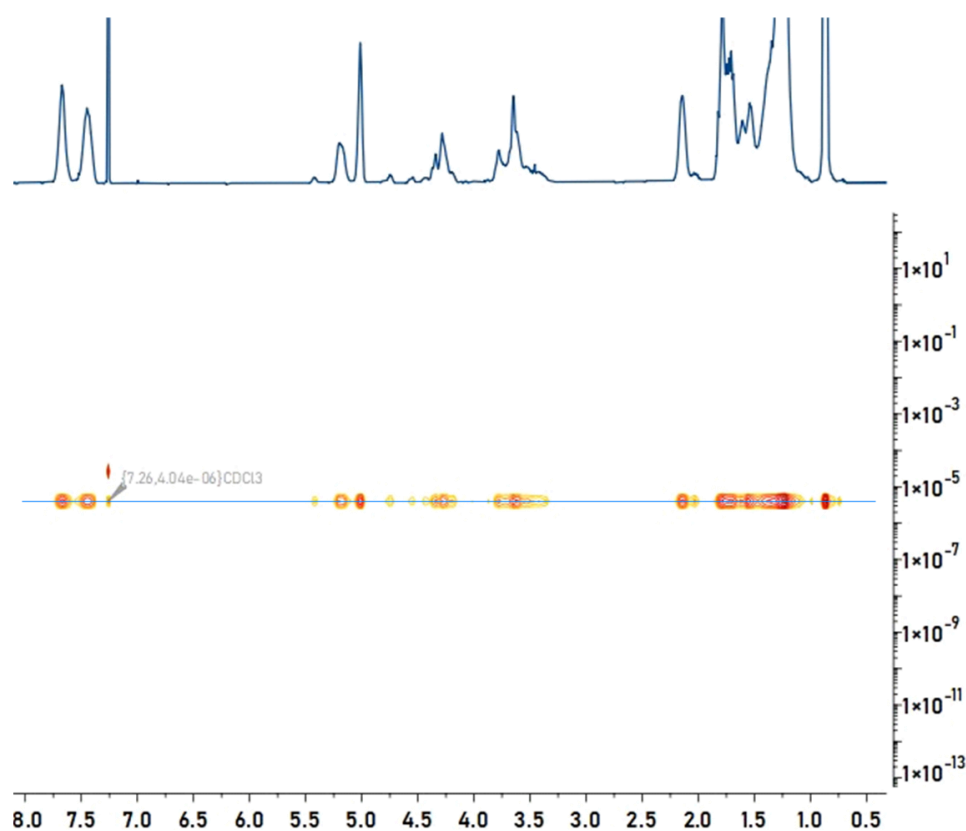


Figure S8.5.11: DOSY NMR spectrum of **P5-PCPC** (Table 5.1, **P5-PCPC**) (400 MHz, CDCl_3). Reaction conditions: **[4]** = 10 mM in 1 mL epoxide, [Cat] : **[P5]** : [CPO] = 1 : 19 : 960, 1 bar CO_2 pressure, 80 $^\circ\text{C}$.

Calculation of DP P5-PCPC:

The DP of PA, EDD and CPO were calculated using the relative integral of the end group signal 32' from CPOH end group, to the P(PA) signal (5 and 6), P(EDD) methine ester signal (20) and the P(CPO) methine signal (32).

$$DP \text{ for PA} = \frac{\text{Integral of 5 and 6}}{4}$$

$$DP \text{ for EDD} = \frac{\text{Integral of 20}}{1}$$

$$DP \text{ for CPO} = \frac{\text{Integral of 32}}{2}$$

8.5.1.1.3 Synthesis and Characterisation of P5-PCHC

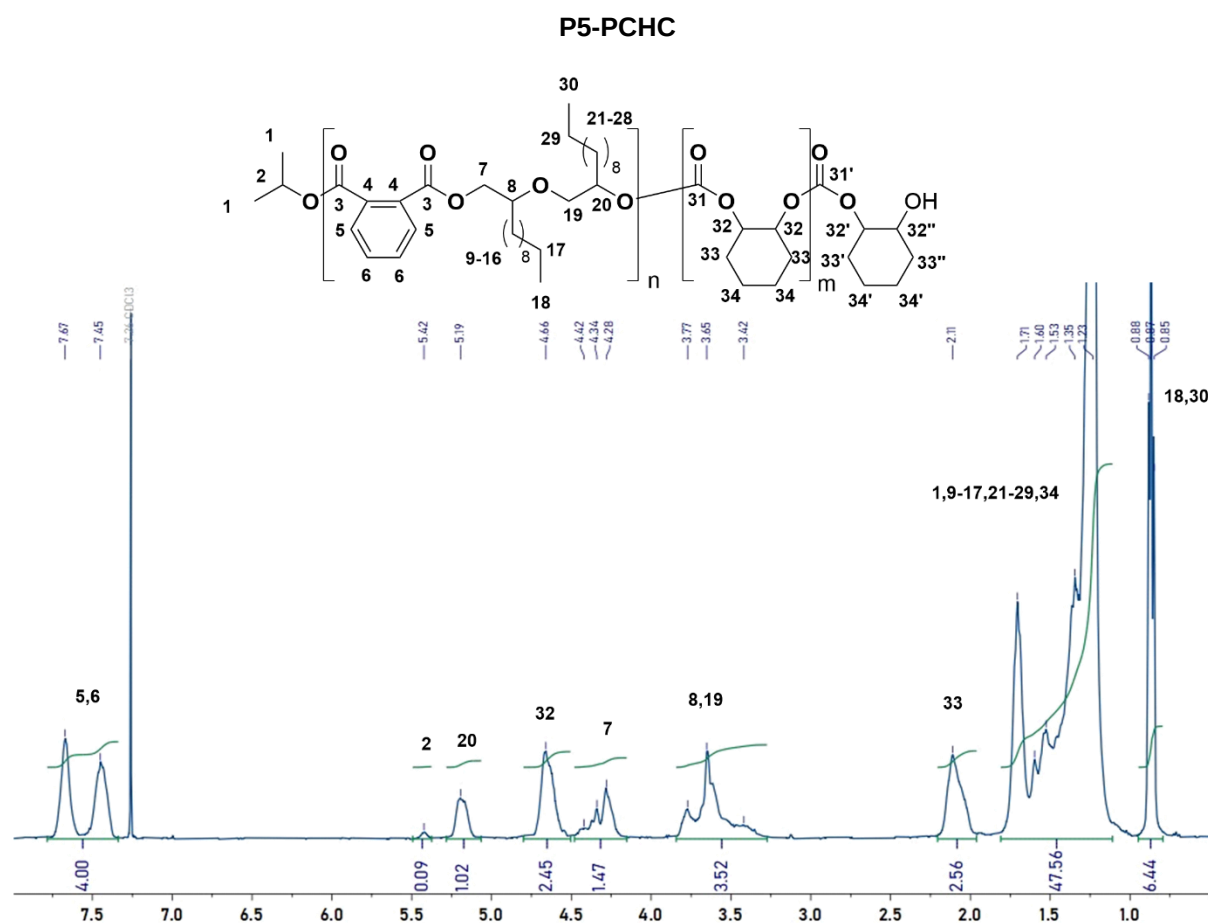


Figure S8.5.12: ¹H NMR spectrum of **P5-PCHC** (with assignment, Table 5.1, **P5-PCHC**) (400 MHz, CDCl₃). Reaction conditions: **[4]** = 5 mM in 2 mL epoxide, **[Cat]** : **[P5]** : **[CHO]** = 1 : 31 : 1976, 1 bar CO₂ pressure, 80 °C.

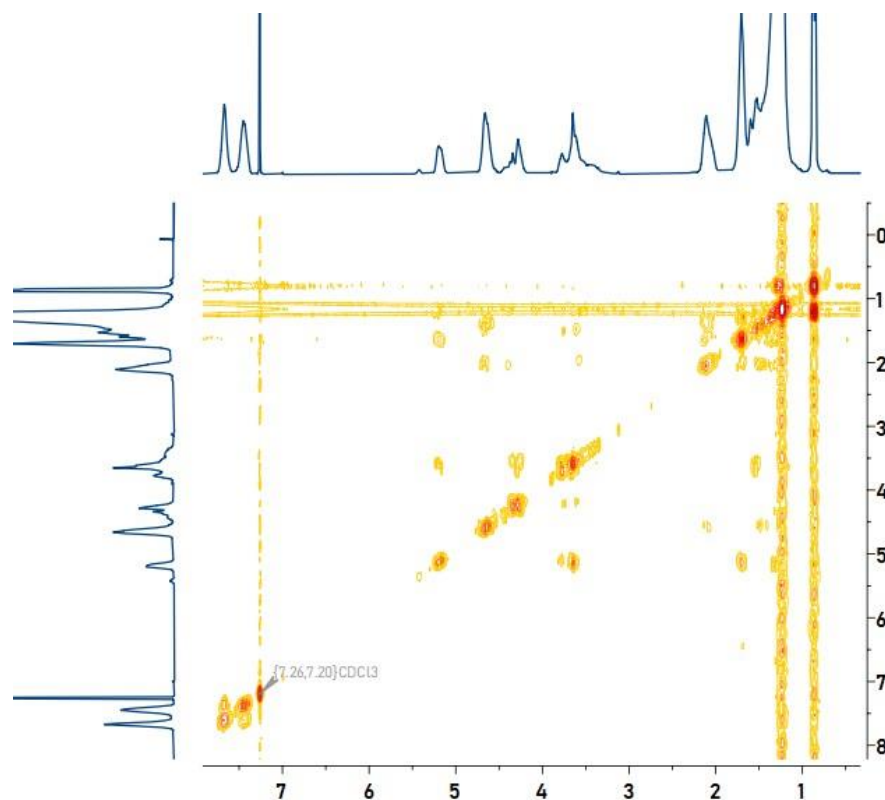


Figure S8.5.13: ^1H COSY NMR spectrum of **P5-PCHC** (Table 5.1, **P5-PCHC**) (400 MHz, CDCl_3). Reaction conditions: **[4]** = 5 mM in 2 mL epoxide, [Cat] : **[P5]** : **[CHO]** = 1 : 31 : 1976, 1 bar CO_2 pressure, 80 °C.

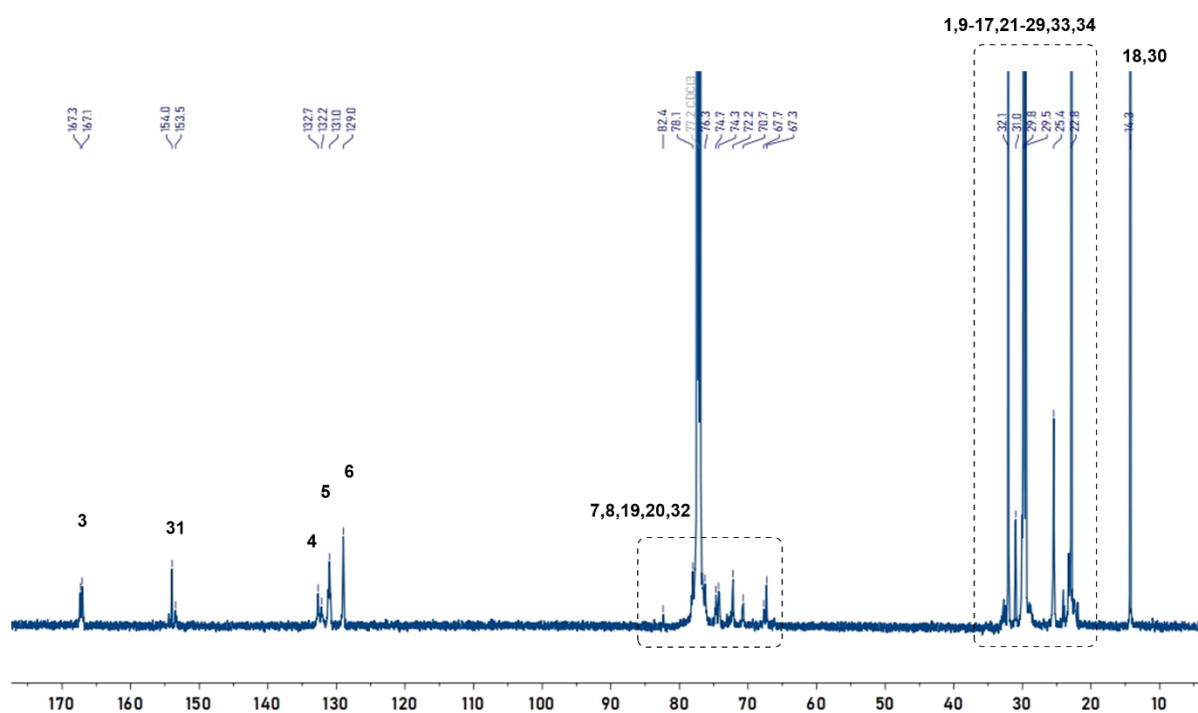


Figure S8.5.14: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P5-PCHC** (Table 5.1, **P5-PCHC**) (151 MHz, CDCl_3). Reaction conditions: **[4]** = 5 mM in 2 mL epoxide, [Cat] : **[P5]** : **[CHO]** = 1 : 31 : 1976, 1 bar CO_2 pressure, 80 °C.

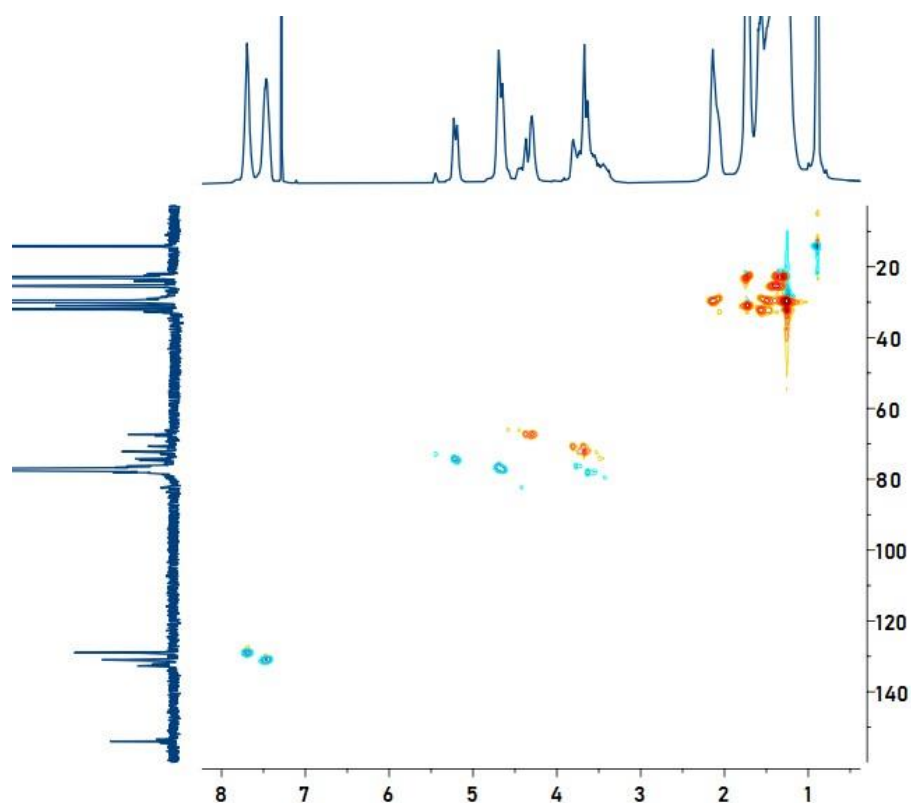


Figure S8.5.15: HSQC ^{13}C - $\{^1\text{H}\}$ NMR spectrum of **P5-PCHC** (Table 5.1, **P5-PCHC**) (400 MHz, CDCl_3). Reaction conditions: **[4]** = 5 mM in 2 mL epoxide, **[Cat]** : **[P5]** : **[CHO]** = 1 : 31 : 1976, 1 bar CO_2 pressure, 80 $^\circ\text{C}$.

Calculation of DP P5-PCHC:

The DP of P(PA) and P(EDD) were calculated as per section SX above. To calculate the sum of polymerised cyclohexene oxide, the P(PA) integral (peaks 5 and 6) were set to 4, (the number of protons for 1 equivalent of P(PA)) and integrated against the P(CHO) methine proton (32), and divided by 2 (the number of CHO methine protons from peak 32), to give the relative equivalents of P(CHO) in the polymer. Then;

$$DP \text{ for } P(\text{CHO}) = DP \text{ for } PA \times \text{Equivalents of } P(\text{CHO})$$

8.5.1.1.4 P NMR End-group Analysis

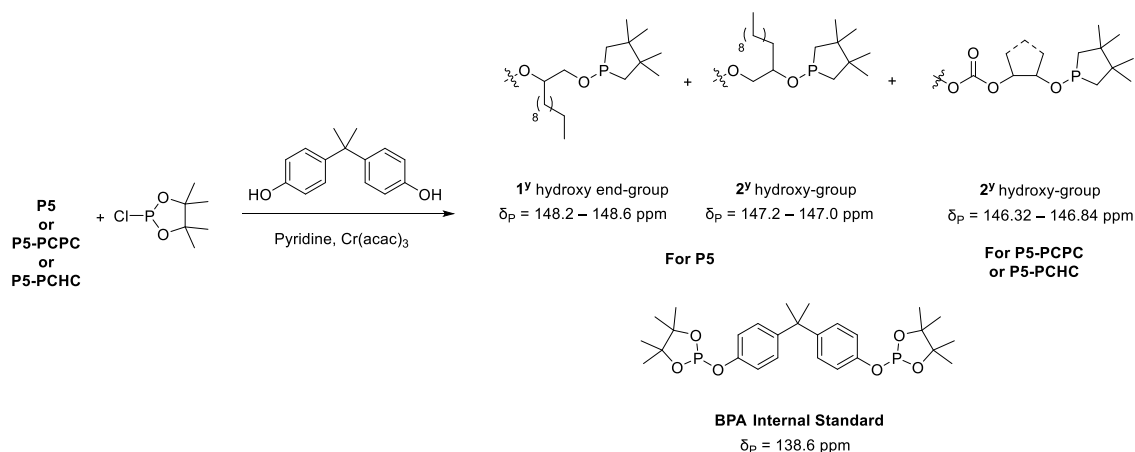


Figure S8.5.16: End group analysis was performed according to literature.¹ **P5**, **P5-PCPC**, or **P5-PCHC** (20 mg) was dissolved in CDCl_3 (0.5 mL) and a solution (20 μL) containing Cr(acac)_3 (5.5 mg) and internal standard, bisphenol A (400 mg) in pyridine (10 mL) was added followed by 20 μL of tetramethylethylene chlorophosphite. The polymer was then analysed by $^{31}\text{P}\{^1\text{H}\}$ NMR.

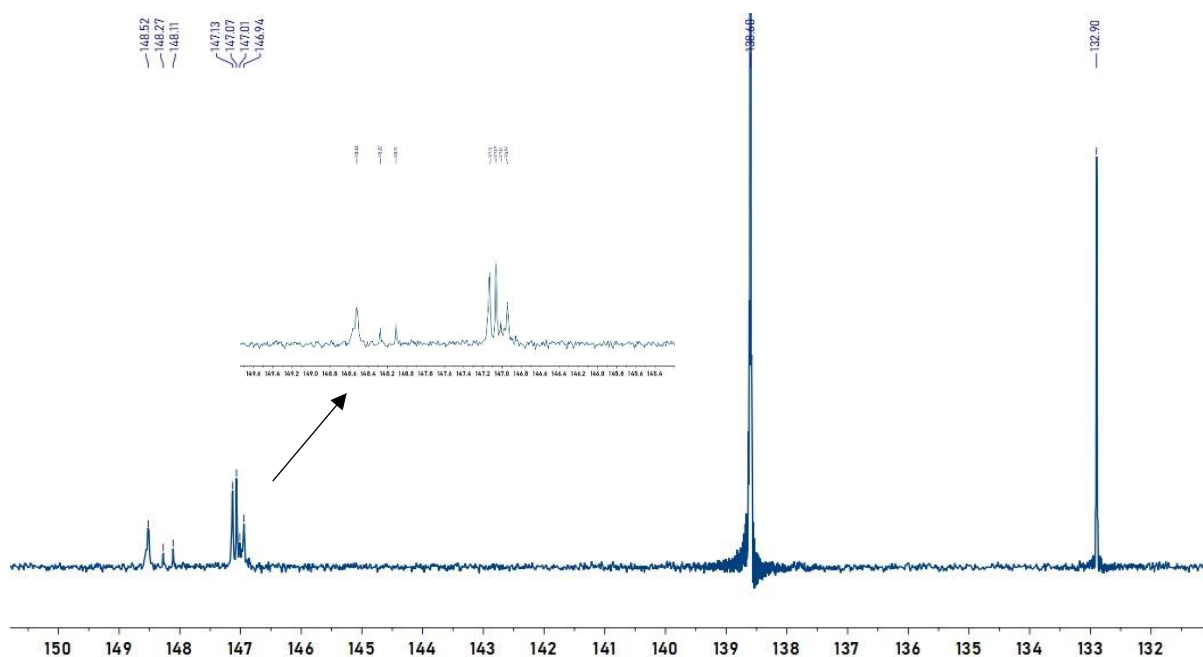


Figure S8.5.17: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum from the reaction **P5** with tetramethylethylene chlorophosphite (162 MHz, CDCl_3). The polymer resonances at 148.1–148.5 and 146.9–147.1 ppm are characteristic of a mixture of primary and secondary alcohol polymer end-groups, respectively.¹

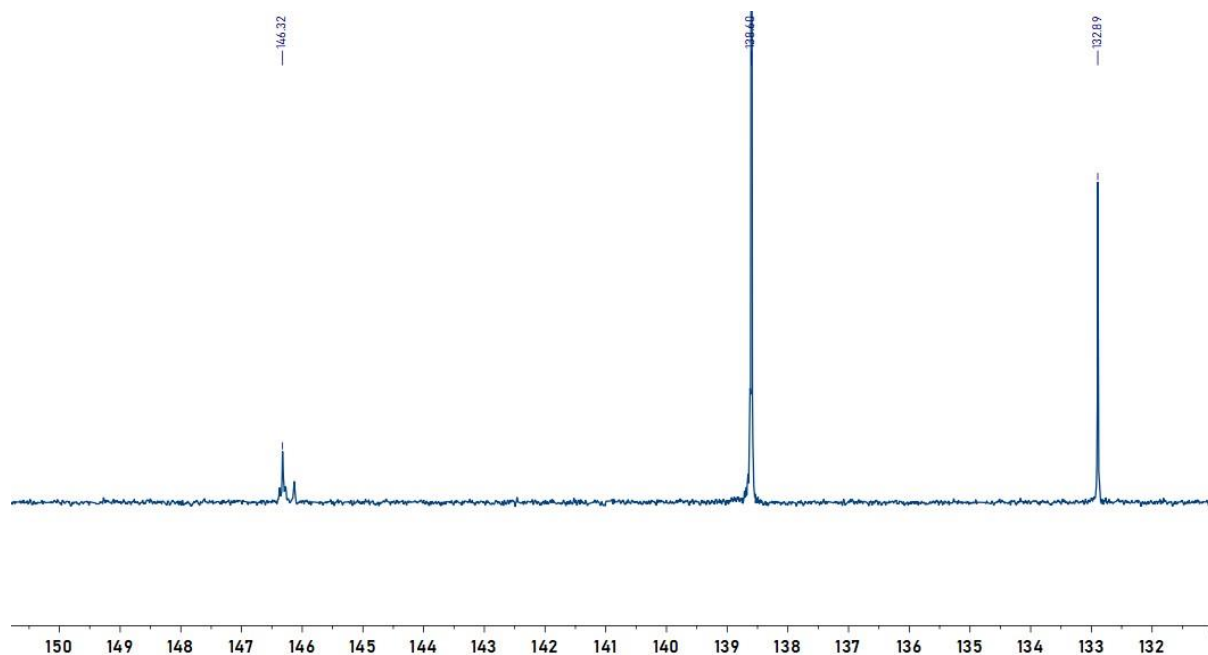


Figure S8.5.18: $^{31}\text{P}\{^1\text{H}\}$ NMR end-group analysis of **P5-PCHC**. The spectrum was obtained from the reaction **P5-PCHC** with tetramethylethylene chlorophosphite (162 MHz, CDCl_3). The major polymer resonance at 146.3 ppm is characteristic of a secondary alcohol polymer end-group, respectively, and is the only polymer peak observed.¹

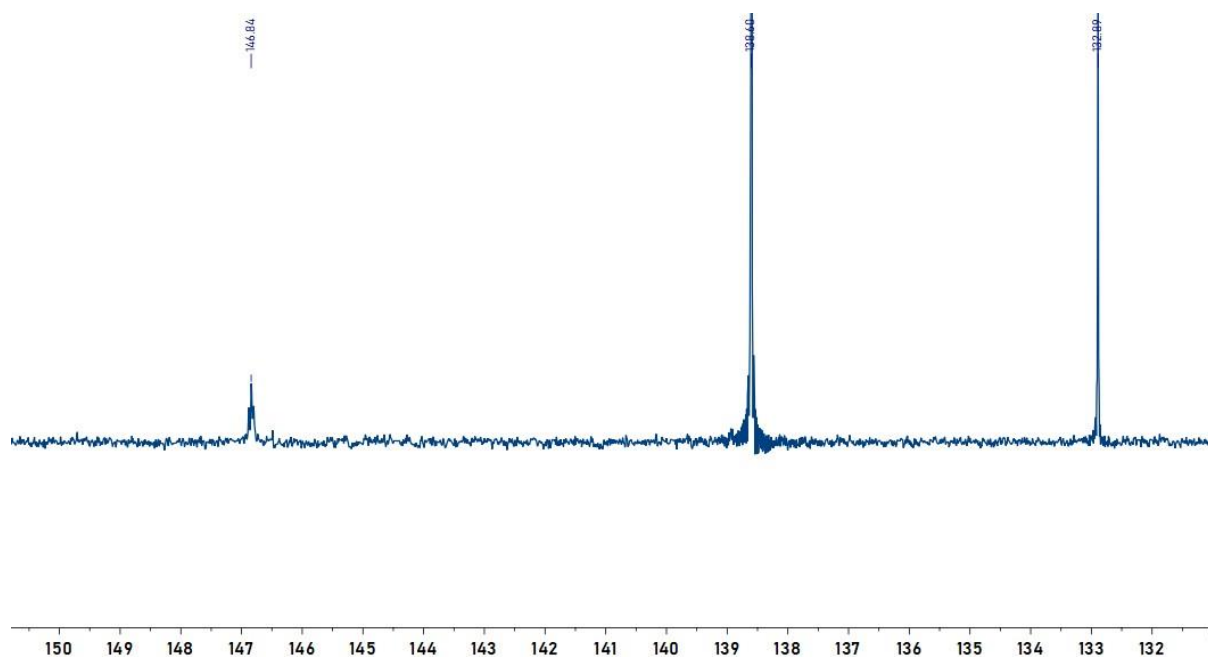


Figure S8.5.19: $^{31}\text{P}\{^1\text{H}\}$ NMR end-group analysis of **P5-PCPC**. The spectrum was obtained from the reaction **P5-PCPC** with tetramethylethylene chlorophosphite (162 MHz, CDCl_3). The major polymer resonance at 146.8 ppm is characteristic of a secondary alcohol polymer end-group, respectively, and is the only polymer peak observed.¹

8.5.1.1.5 Synthesis of PCPC

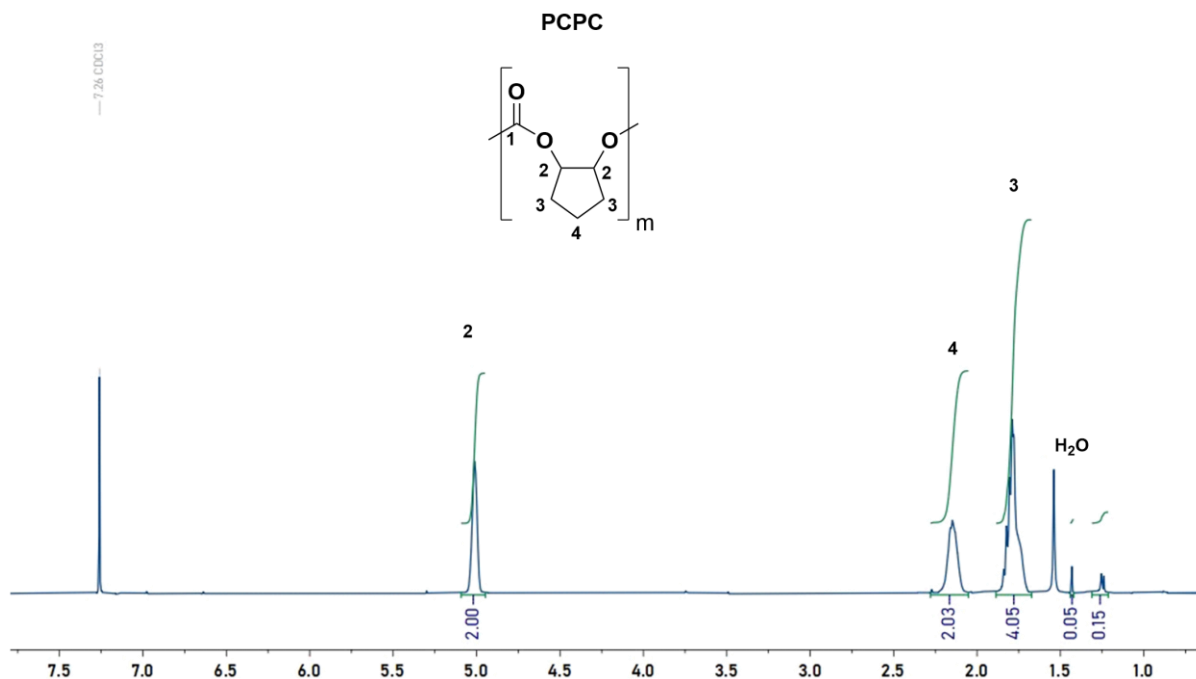


Figure S8.5.20: ¹H NMR spectrum of High molar mass **PCPC** (with assignment, Table 5.1, **PCPC**) (400 MHz, CDCl₃). Reaction conditions: **[5]** = 0.3 mM in 15 mL epoxide (with 12 mL added toluene), [Cat] : [CHD] : [CPO] = 1 : 4 : 20,000, 20 bar CO₂ pressure, 100 °C.

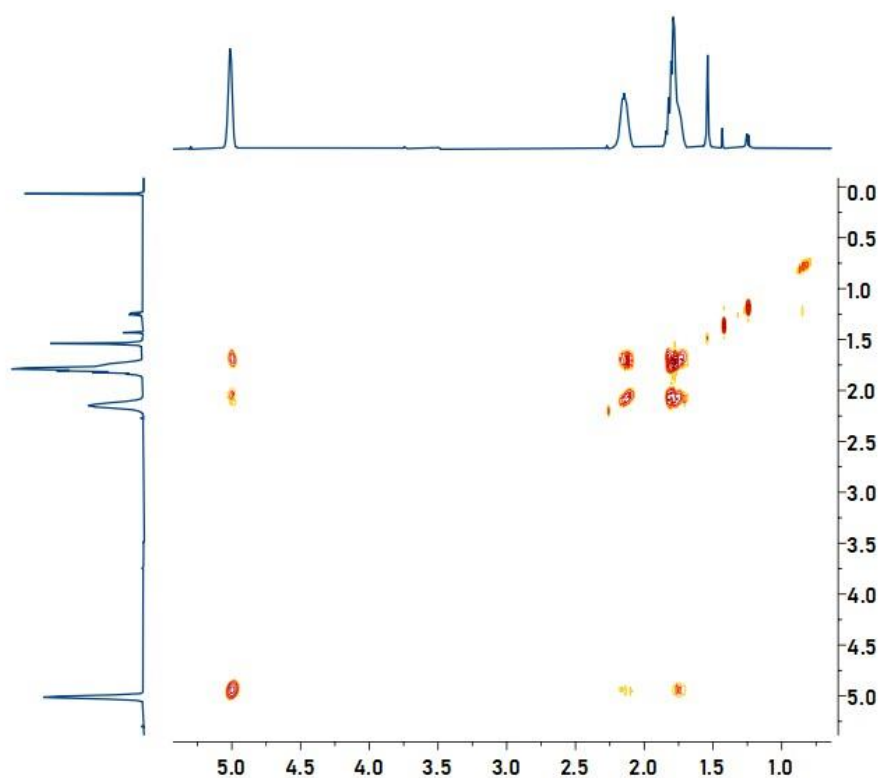


Figure S8.5.21: COSY ¹H NMR spectrum of High molar mass **PCPC** (Table 5.1, **PCPC**) (400 MHz, CDCl₃). Reaction conditions: **[5]** = 5 mM in 2 mL epoxide, [Cat] : **[P5]** : [CHD] : [CPO] = 1 : 31 : X : 1976, 1 bar CO₂ pressure, 80 °C.

Calculation of DP PCPC:

Reaction conditions: $[5] = 0.3 \text{ mM}$ (1 eq), CHD = 1.26 mM (4 eq) CPO = 15 mL (172 mol, 20 000 eq), toluene 12 mL, 20 bar CO_2 , 100 °C, 164 hr.

The Equivalents of epoxide were multiplied by the conversion (0.93, determined by ^1H NMR spectroscopy), divided by the equivalents of CTA (4 CHD and 2 acetate), and multiplied by the formula molar mass of one PCPC repeat unit ($128.13 \text{ g mol}^{-1}$).

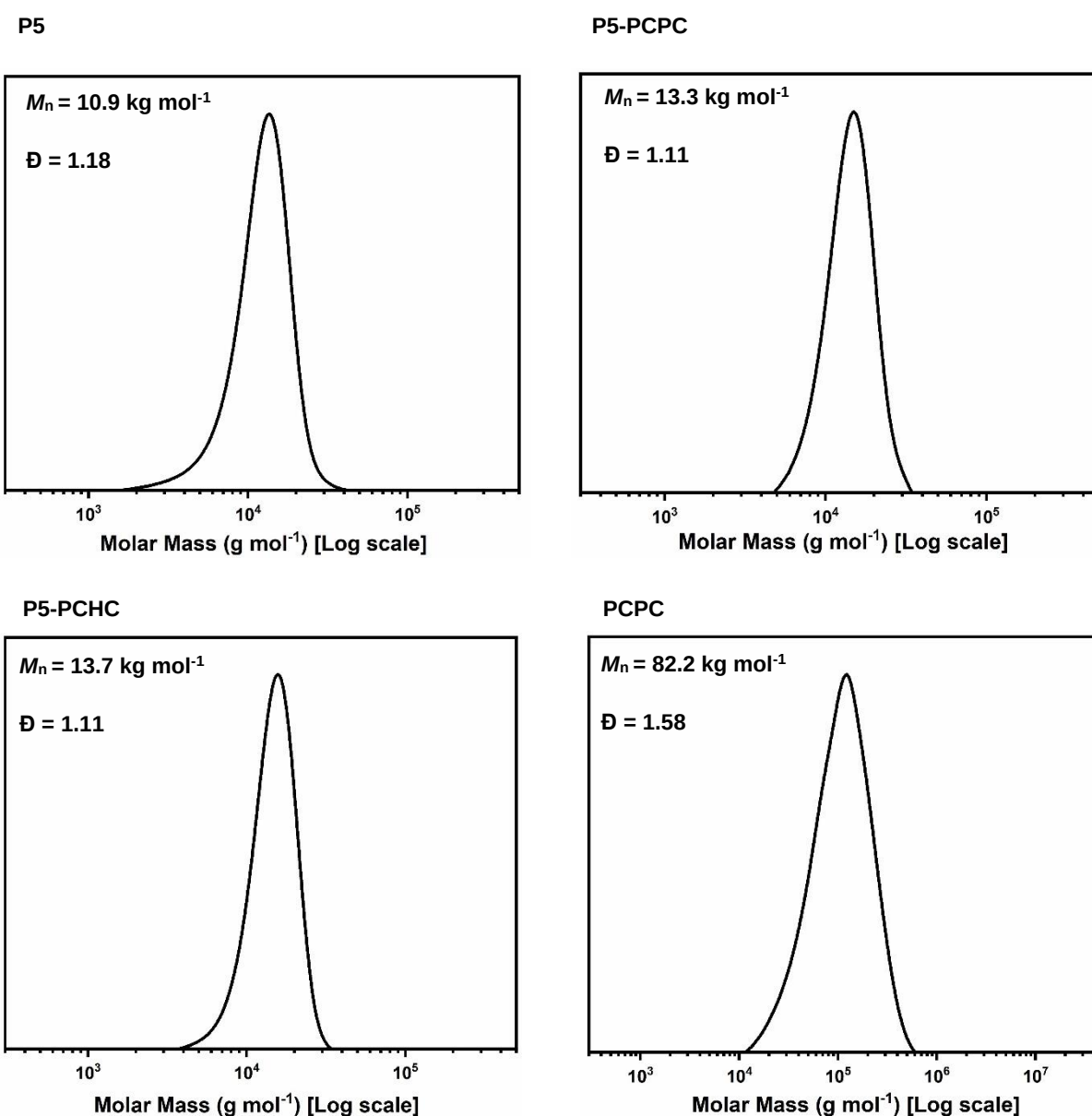
8.5.1.2 GPC data for Polymers Described in Table 5.1

Figure S8.5.22: GPC chromatograms for polymers described in Table 5.1.

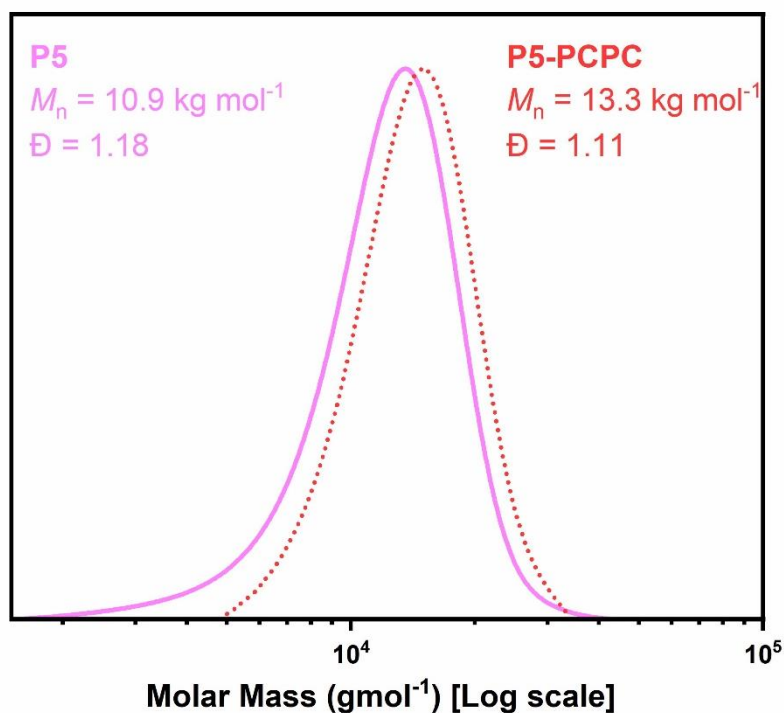


Figure S8.5.23: Overlay of GPC chromatograms for **P5** (pink solid trace), poly(ester-*alt*-ether) used as a macroinitiator for the ROCOP of CO₂ and CPO, and **P5-PCPC** block copolymer (red dashed line) after ROCOP with catalyst **4**, Demonstrating the addition of 2.4 kg mol⁻¹ PCPC block to **P5**.

8.5.1.3 DSC data for Polymers Described in Table 5.1

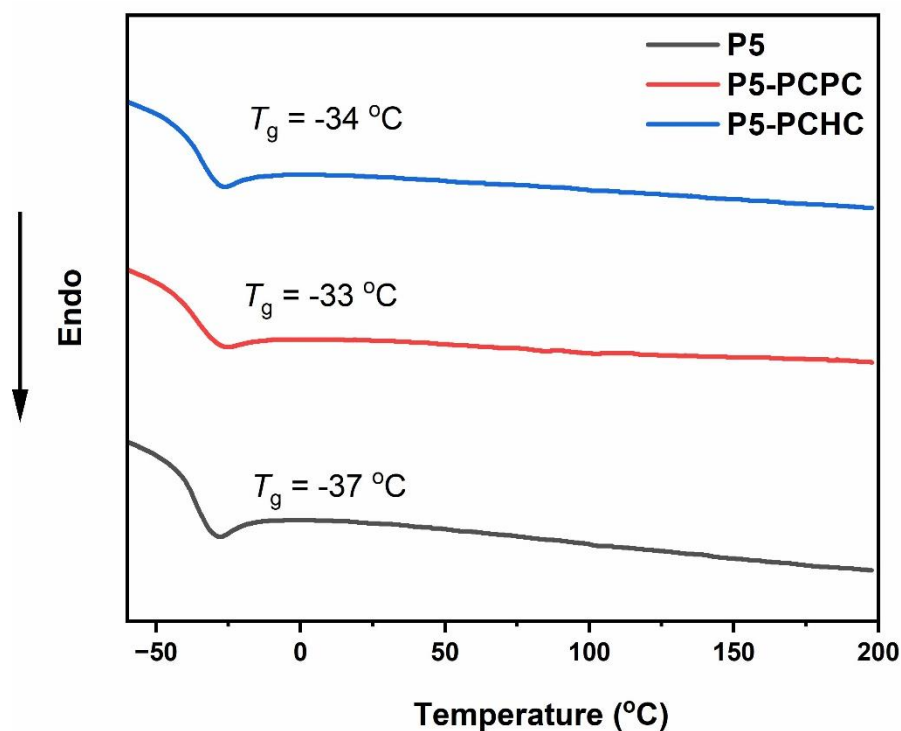


Figure S8.5.24: DSC thermogram of the polymers **P5**, **P5-PCPC** and **P5-PCHC**.

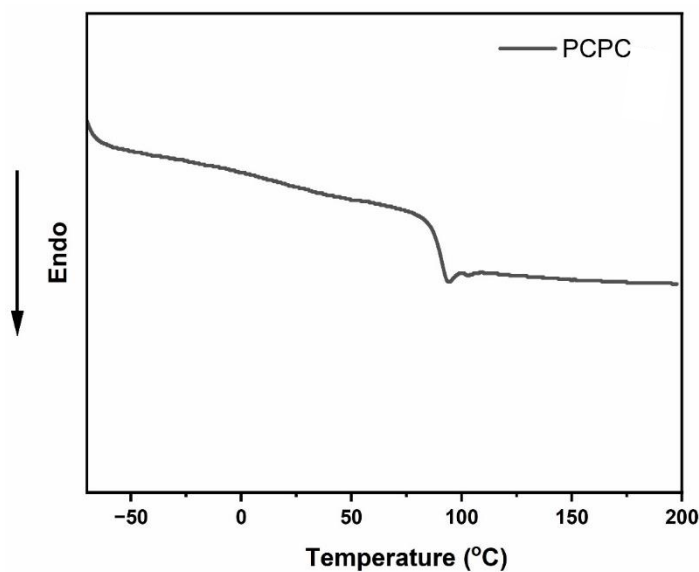


Figure S8.5.25: DSC thermogram of the polymer PCPC.

8.5.1.4 TGA data for Polymers Described in Table 5.1

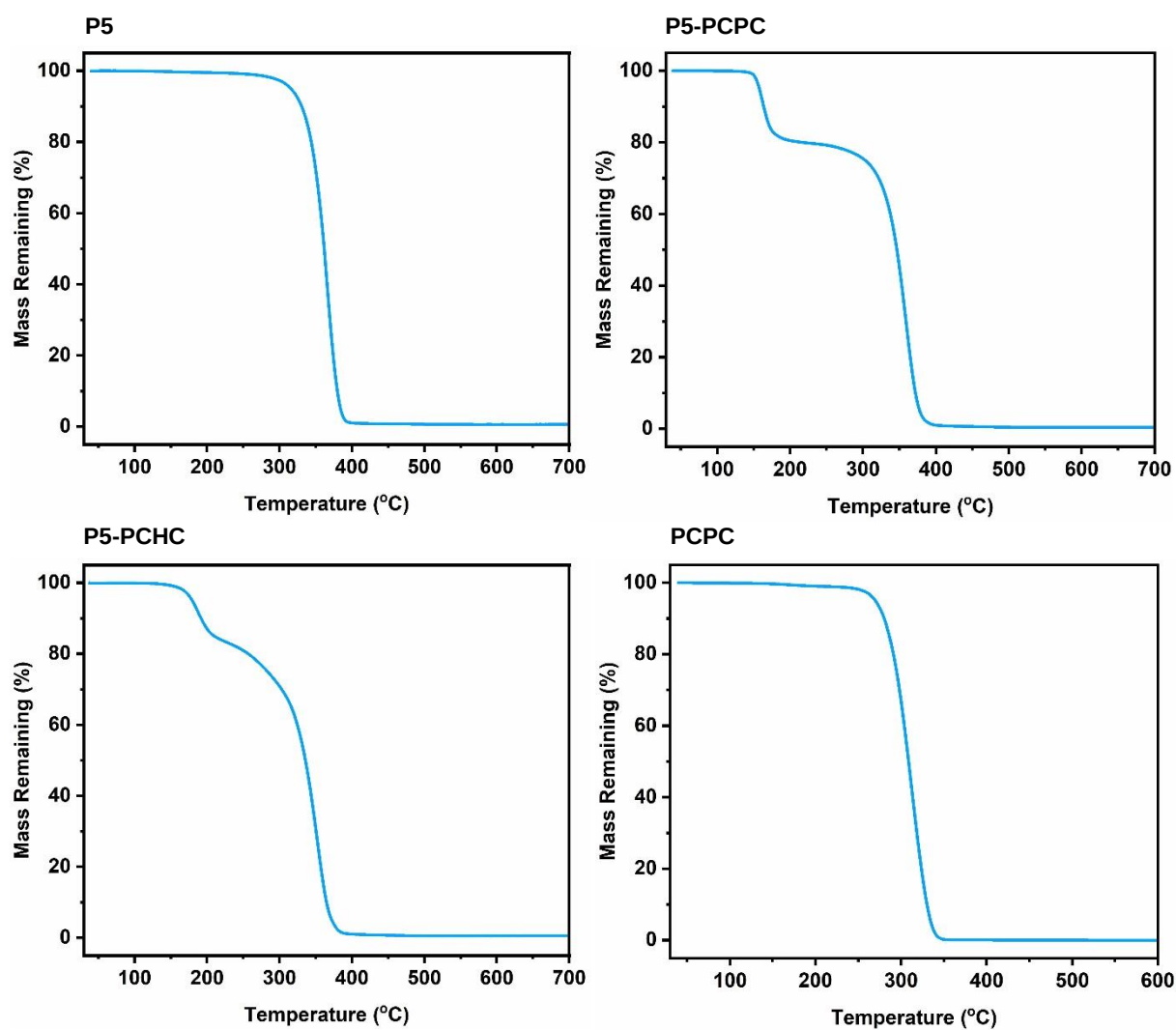


Figure S8.5.26: TGA traces for polymers described in Table 5.1.

8.5.2 Blend Synthesis and Characterisation

8.5.2.1 DSC Data for Blends Described in Table 5.2

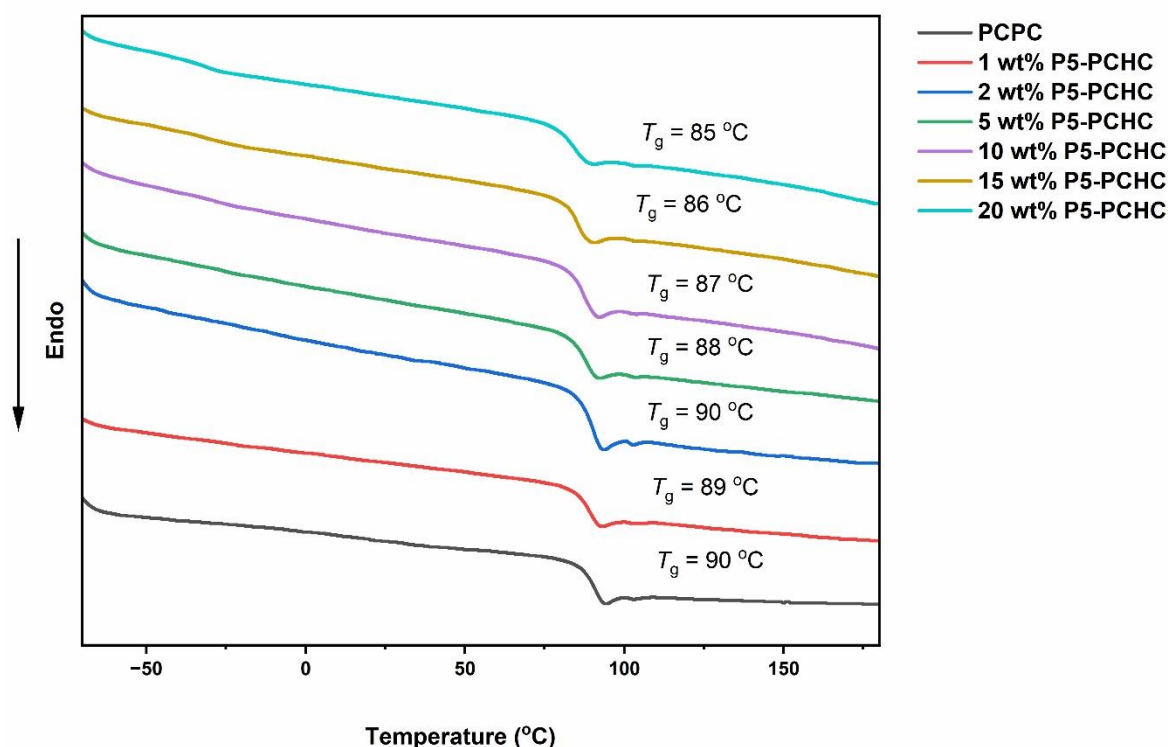


Figure S8.5.27: DSC thermogram of PCPC blends with various wt% of **P5-PCHC**. Data was obtained from the third heating cycle, and experiments were conducted at 10 °C min^{-1} heating rate from -80 to 180 °C .

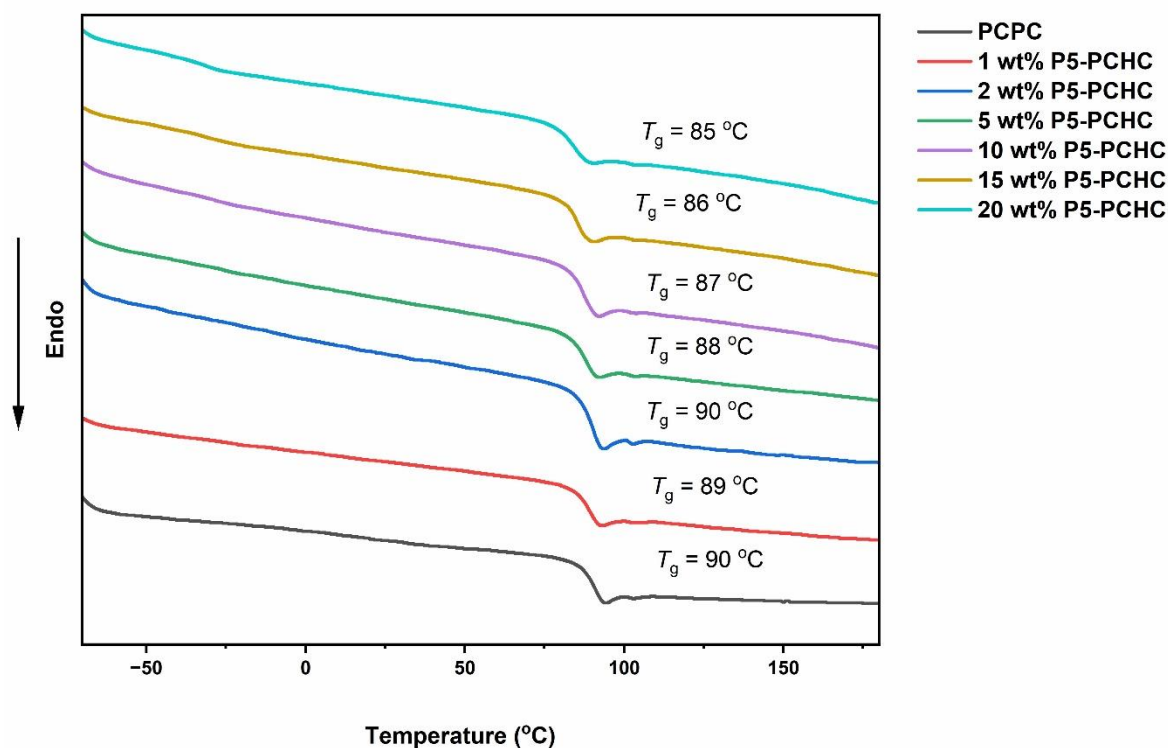


Figure S8.5.28: DSC thermogram of PCPC blends with various wt% of **P5-PCPC**. Data was obtained from the third heating cycle, and experiments were conducted at 10 °C min^{-1} heating rate from -80 to 180 °C .

8.5.2.2 TGA Data for Blends Described in Table 5.2

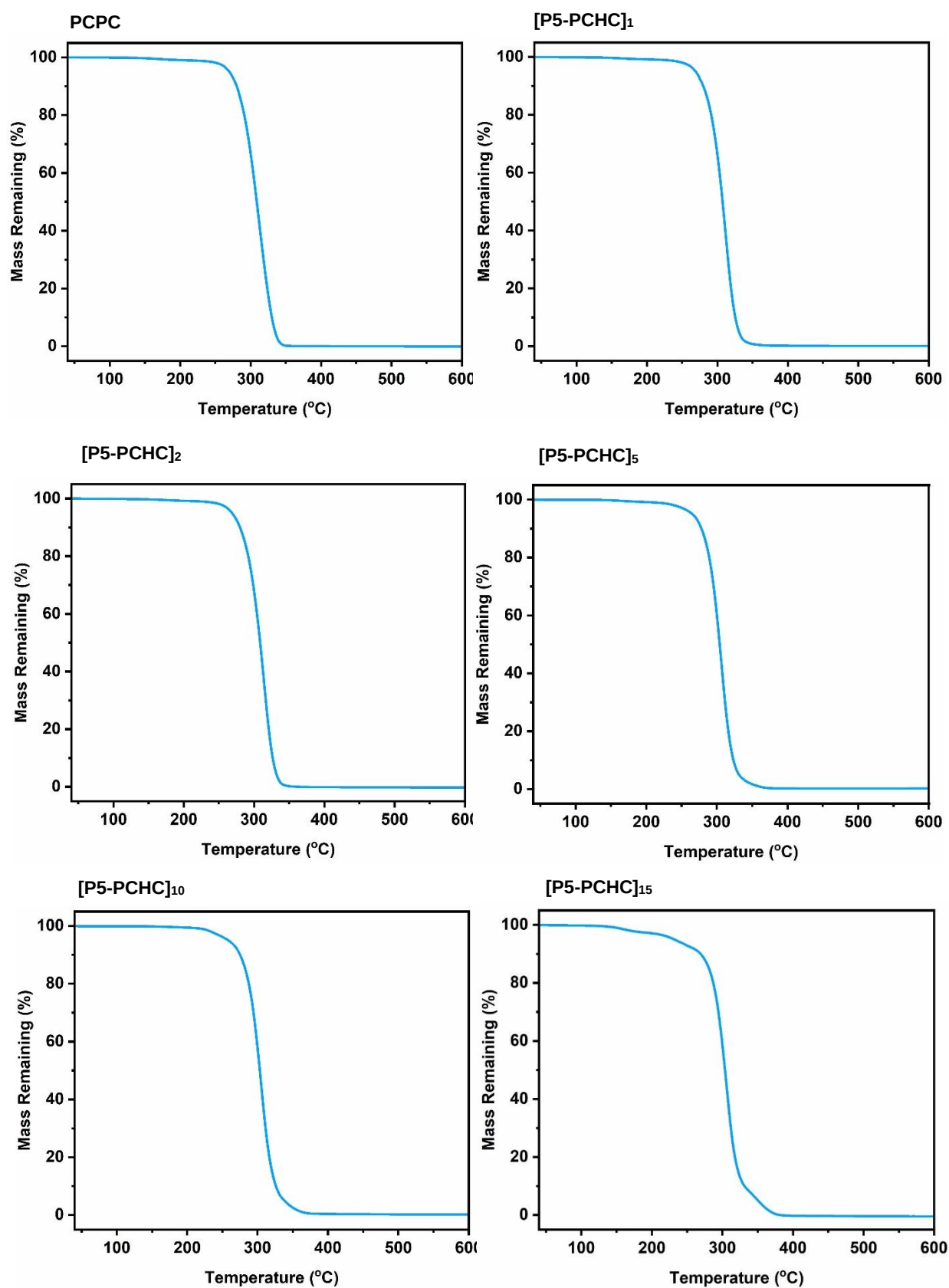


Figure S8.5.29: TGA traces of PCPC blends with various wt% (1-15 wt%) of **P5-PCHC** diblock toughening agent.

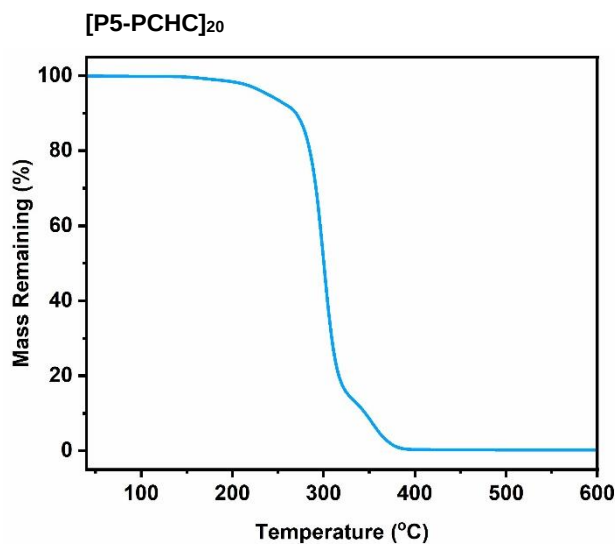


Figure S8.5.30: TGA trace of PCPC blends with 20 wt% of **P5-PCHC** diblock toughening agent.

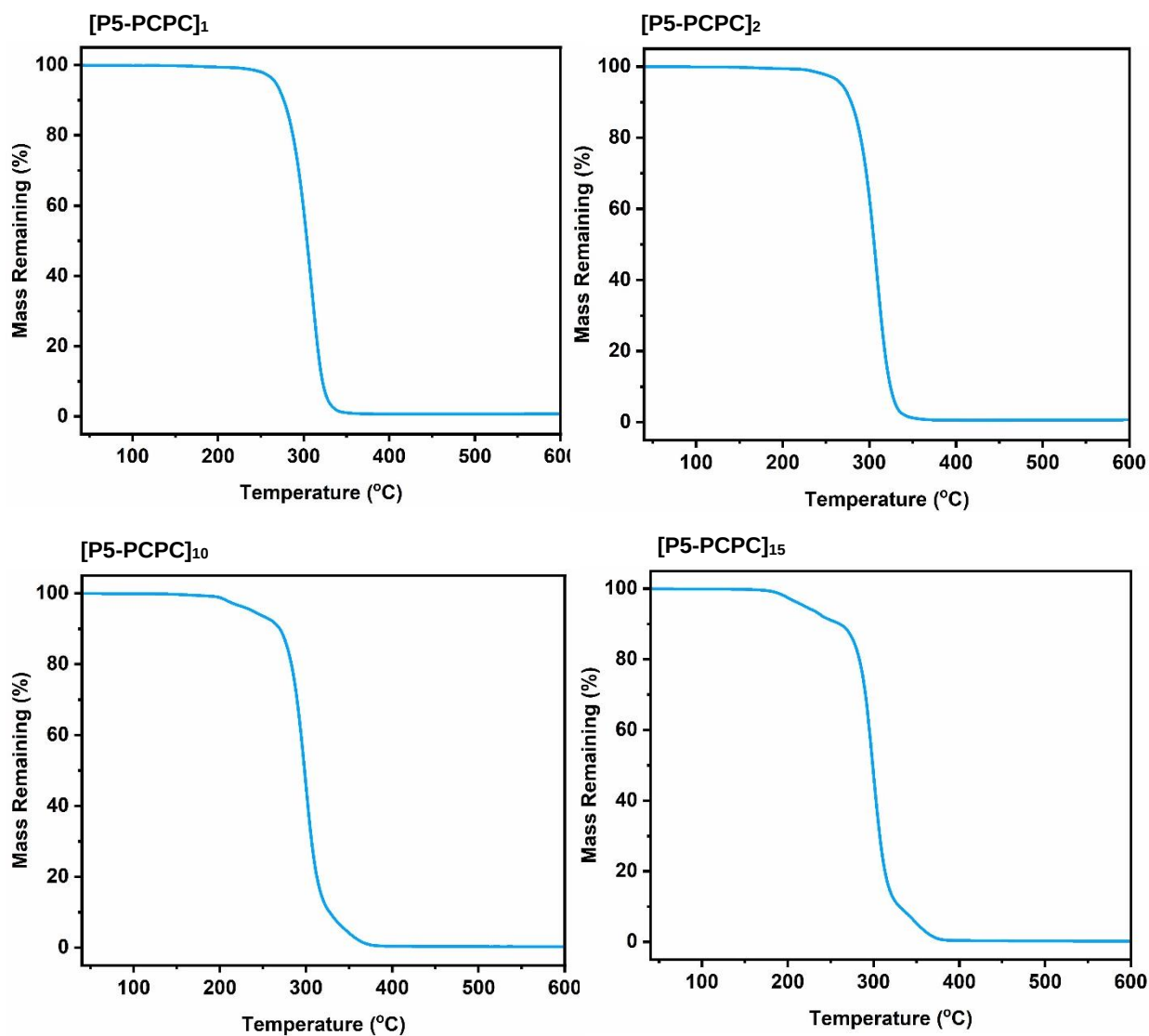


Figure S8.5.31: TGA traces of PCPC blends with various wt% (1-15 wt%) of **P5-PCHC** diblock toughening agent.

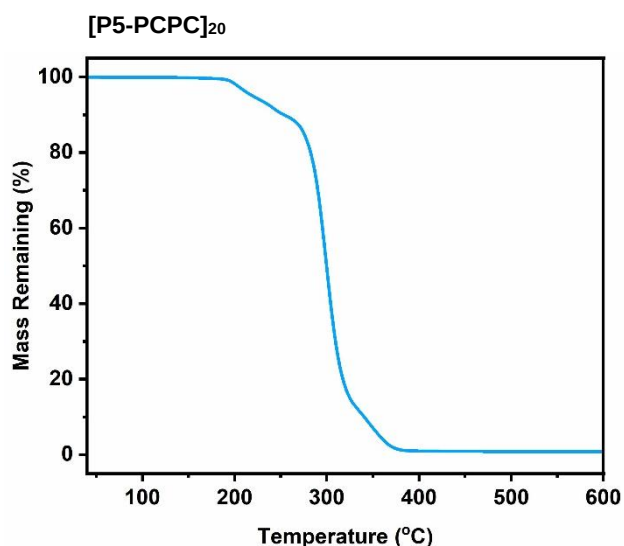


Figure S8.5.32: TGA traces of PCPC blends with 20 wt% of **P5-PCHC** diblock toughening agent.

8.5.2.3 Control Blends – PCPC/P5 ([P5]₅) and PCPC/PCHC ([PCHC]₅)

8.5.2.3.1 Synthesis of Low Molar Mass PCHC₂₀

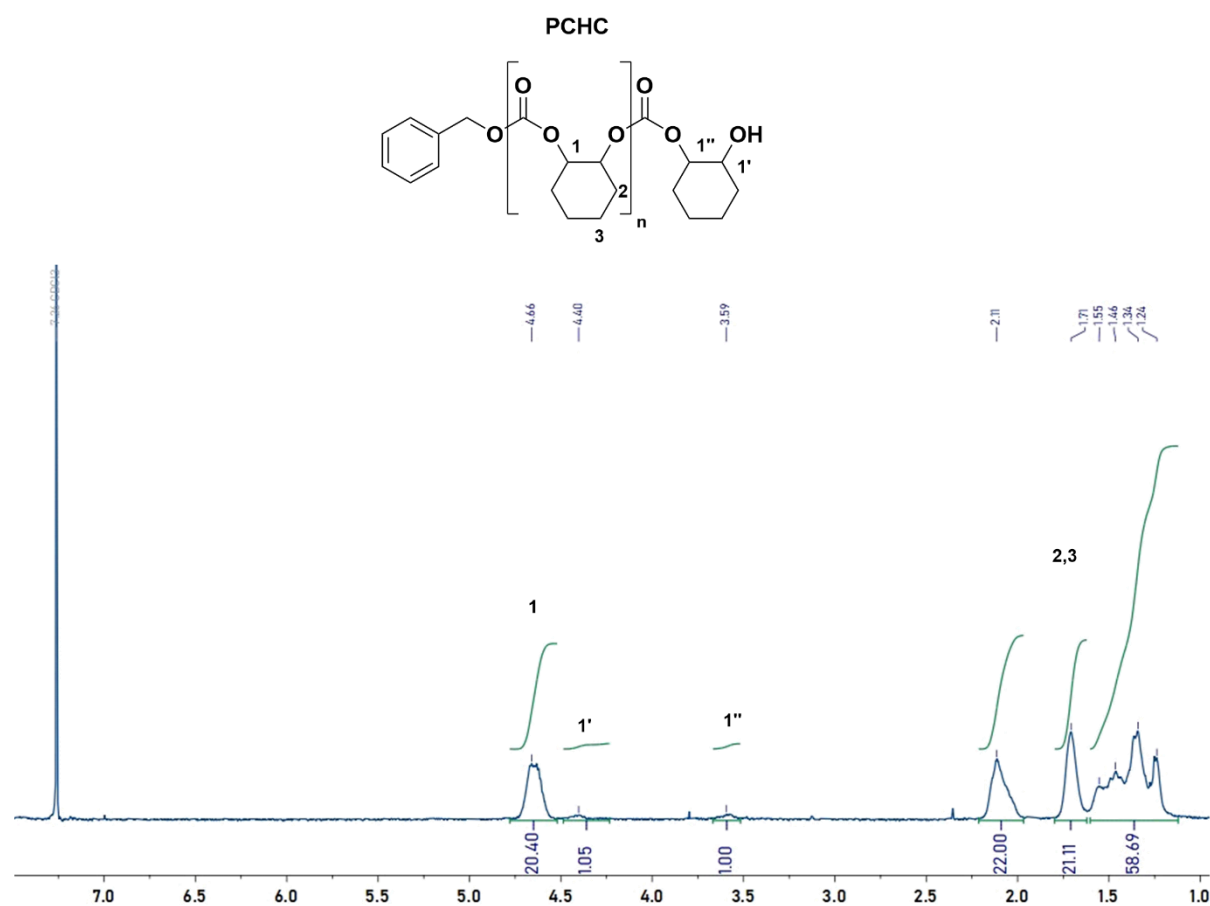
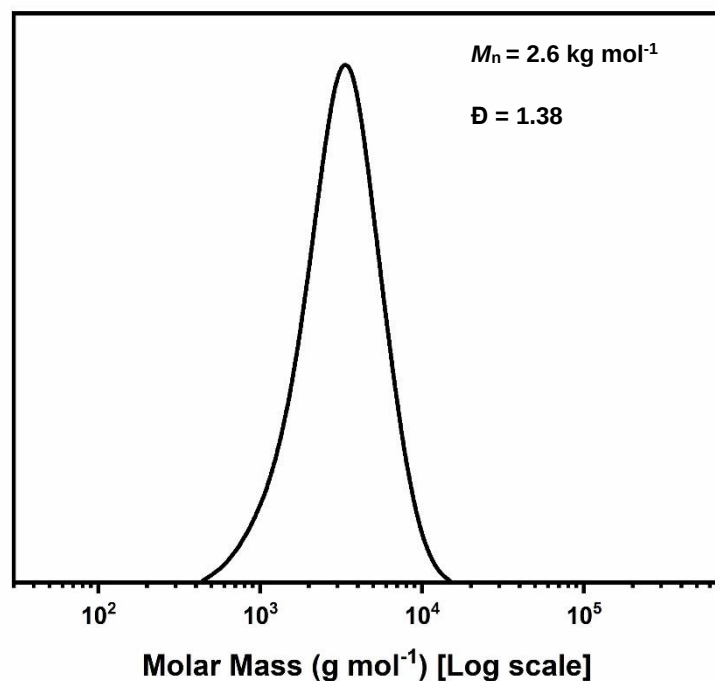


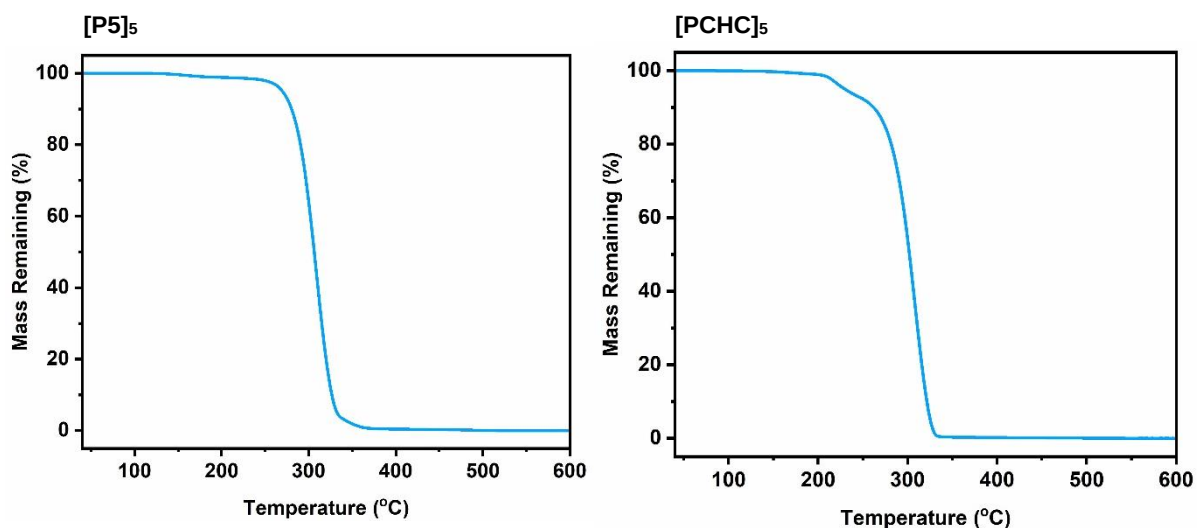
Figure S8.5.33: ¹H NMR spectrum of **PCHC**₂₀ (with assignment) (400 MHz, CDCl₃). Reaction conditions: **[4]** = 10 mM in 1.0 mL CHO, **[4]** : **[PA]** : **[CHO]** = 1 : 10 : 1180, 80 °C.

Table 8.5.1: Overview of polymer synthesis and characterisation data for **PCHC₂₀**.

Polymer	DP [PCHC]	$M_n(\bar{D})$ [kg mol ⁻¹] ^d	M_n (Th.) ^e	T_g (°C) ^f
PCHC ₂₀	20	2.6(1.38)	2.8	99

**Figure S8.5.34:** GPC chromatograms for **PCHC₂₀**.

8.5.2.3.2 Control Blend Thermal Data

**Figure S8.5.35:** TGA traces of PCPC blends with 5 wt% of **P5** poly(ester-*alt*-ether) homopolymer and 5wt% low molar mass PCHC (**PCHC₂₀**).

8.5.3 Miscibility Studies

8.5.3.1 Poly(ester-alt-ether) in PCPC

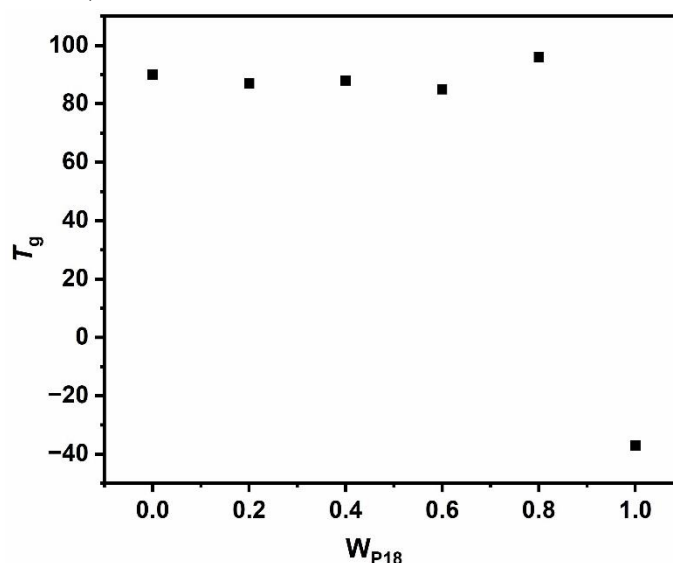


Figure S8.5.36: T_g vs the weight fraction of **P5** (W_{P5}) in PCPC blends. DSC thermograms were obtained for 0, 0.2, 0.4, 0.6, 0.8 and 1.0 W_{P5} blends. The plot shows no change in the T_g with changing composition, indicating the two polymers are immiscible. The same high molar mass PCPC as used in polymer blending studies was used here.

8.5.3.2 PCHC in PCPC

Blends from 20-80 wt% low molar mass PCHC in high molar mass PCPC were prepared by dissolving 100 mg total material in DCM, solvent casting, and then drying thoroughly in a vacuum oven at 60 °C for 2 days.

Table S8.5.2: Overview of polymer synthesis and characterisation data for **PCHC₂₀**.

Polymer	DP [PCHC]	$M_n(\bar{D})$ [kg mol ⁻¹]	M_n (NMR)
PCHC₂₀	20	2.6(1.38)	2.8
PCHC₄₇	47	5.5(1.09)	6.7
PCHC₉₂	92	10.8(1.11)	13.1

Table S8.5.3: Summary of DSC thermograms of the PCPC blends of **PCHC₂₀**, **PCHC₄₇** and **PCHC₉₂** polymers (where for PCHC_z, z = CHO DP), varying the wt% PCHC.

PCPC:PCHC wt%	T_{g1PCPC}	T_{g2PCHC}
PCHC₂₀		
100:0	90	-
80:20	89	-
60:40	93	-
0:100	-	99
PCHC₄₇		
100:0	90	-
60:40	93	113
40:60	93	113
20:80	93	115
0:100	-	115
PCHC₉₂		
100:0	90	-
80:20	88	117
60:40	89	119
40:60	84	114

Data was obtained from the first heating cycle, and experiments were conducted at 10 °C min⁻¹ heating rate from -80 to 130 °C.

8.5.4 Morphology

Table S8.5.4: Summary of the average particle sizes (diameter) and average interparticle distances (pre-tensile testing) for a select number of poly(ester-*alt*-ether)-*b*-PC/PCPC polymer blends. The mechanical properties are also shown for comparison.

Blend	σ_Y (MPa)	ξ_B (%)	U_T (MJ m ⁻³)	Particle Diameter (μm)	Interparticle Distance (μm)
[P5-PCHC] ₁	47.2 $\pm$ 2.6	20.4 $\pm$ 2.9	7.8 $\pm$ 1.2	0.71	1.73
[P5-PCHC] ₅	38.1 $\pm$ 2.1	82.1 $\pm$ 10.1	28.1 $\pm$ 4.1	1.46	1.28
[P5-PCHC] ₁₀	29.1 $\pm$ 2.6	95.1 $\pm$ 23.3	25.8 $\pm$ 5.8	1.80	1.59
P5-PCHC] ₂₀	24.8 $\pm$ 2.0	122.6 $\pm$ 17.4	26.4 $\pm$ 3.9	2.30	1.27
[P5-PCPC] ₁	50.6 $\pm$ 3.1	7.0 $\pm$ 1.7	2.4 $\pm$ 0.9	0.99	4.56
[P5-PCPC] ₂	53.9 $\pm$ 2.7	31.9 $\pm$ 8.9	13.9 $\pm$ 3.7	0.77	1.41
[P5-PCPC] ₅	43.6 $\pm$ 3.8	54.8 $\pm$ 24.4	21.6 $\pm$ 8.2	1.92	2.38
[P5-PCPC] ₁₀	31.6 $\pm$ 2.2	45.6 $\pm$ 6.2	13.6 $\pm$ 2.0	3.00	1.94
[P5-PCPC] ₂₀	37.3 $\pm$ 4.0	12.8 $\pm$ 2.1	4.2 $\pm$ 1.2	2.87	2.66

Samples were mounted in an ultramicrotome (Leica UC7) and the cut edge polished using a freshly cut-glass knife. Polished samples were mounted on SEM stubs (Agar AGG3160) and coated with gold using a Quorum Q150R-ES. Samples were then imaged at 2 kV with a Zeiss Sigma 300 FEG-SEM and SE2 detector. Particle diameters and interparticle distances were analysed using ImageJ software, analysing 3 images per sample (60-100 particles), and were measured by the diameter of the 'crater' left by the particle. For any particles where microtoming may have slightly damaged the shape of the particle 'crater', measurements of diameter were taken perpendicular to the direction of slicing.

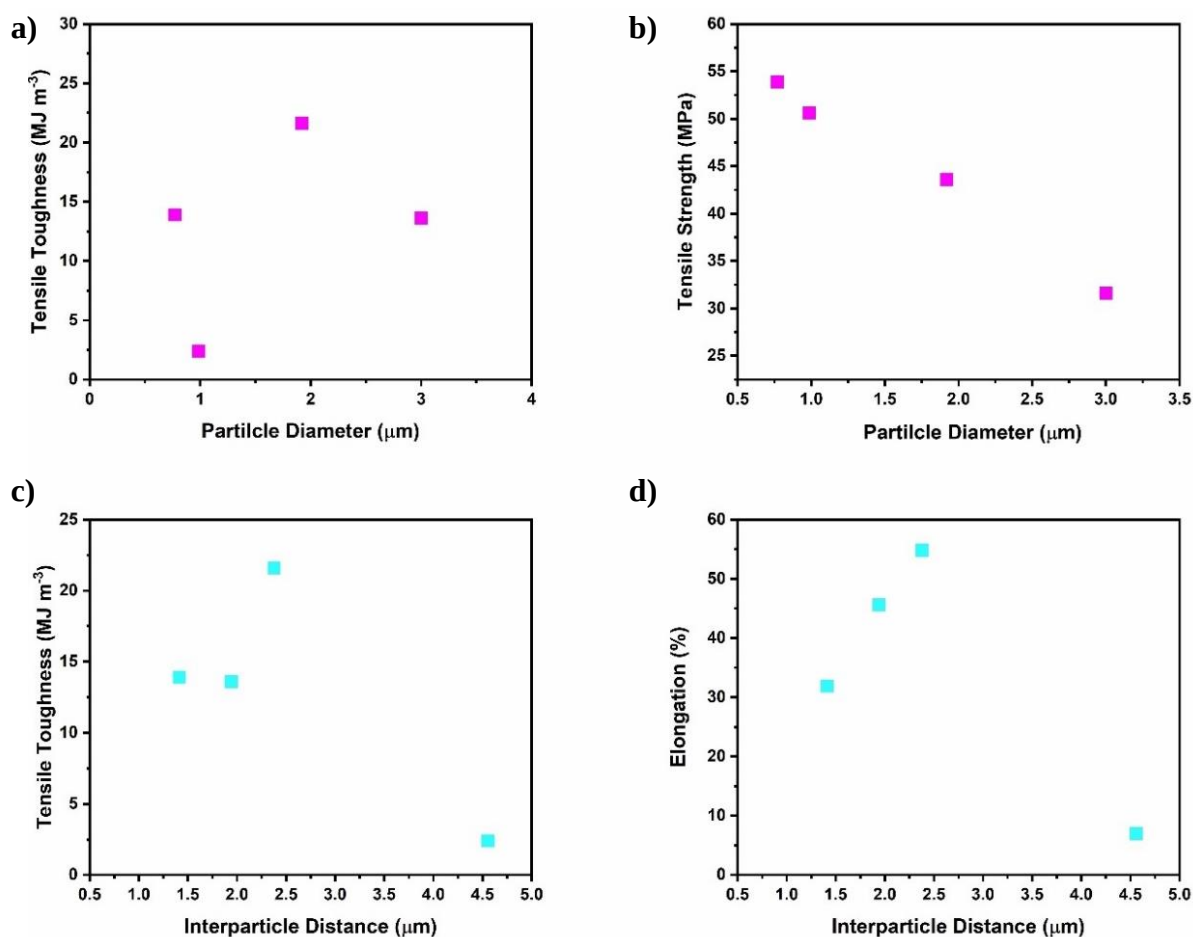


Figure S8.5.37: A summary of morphological-mechanical property correlations for [P5-PCPC]_x blends. a) tensile toughness (MJ m⁻³) vs particle diameter (μm), b) tensile strength (MPa) vs particle diameter (μm), c) tensile toughness (MJ m⁻³) vs interparticle distance (μm) and d) elongation at break vs interparticle distance (μm).

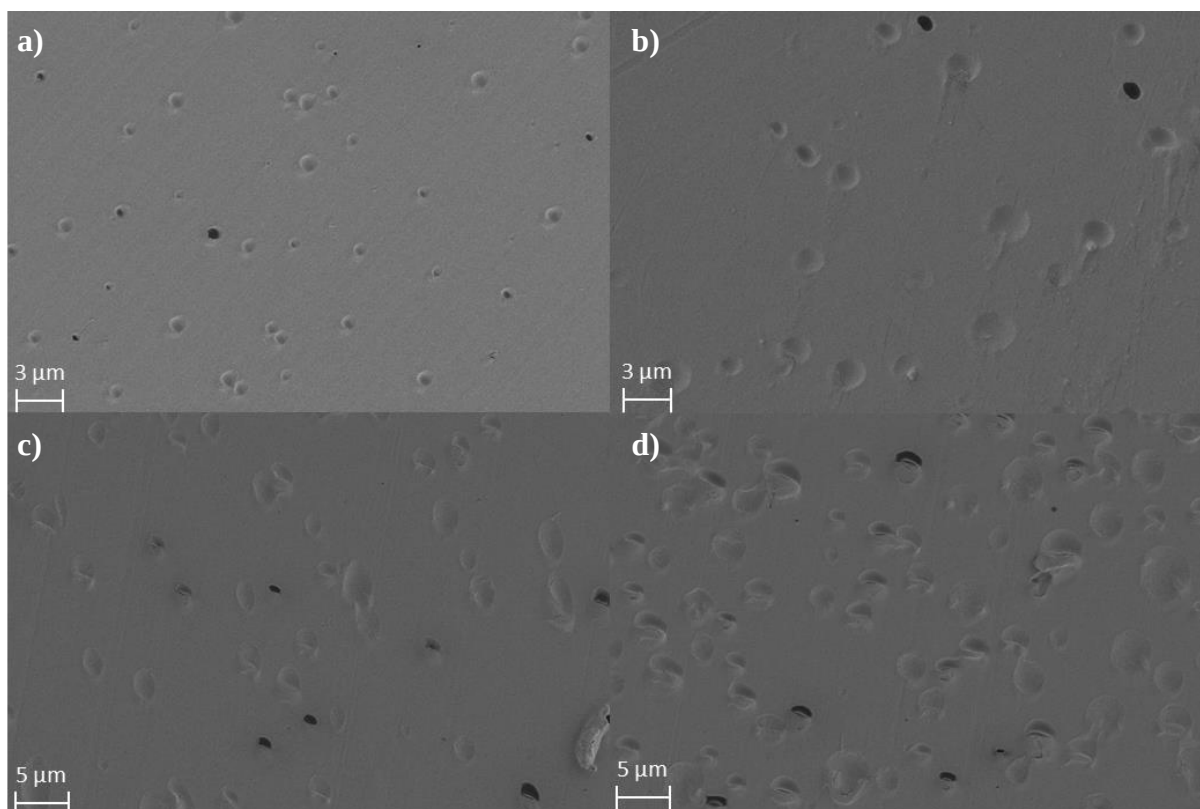


Figure S8.5.38: Representative SEM images of $[P5-PCHC]_z$ PCPC blends, before tensile testing (prepared by microtoming). a) $[P5-PCHC]_1$, b) $[P5-PCHC]_5$, c) $[P5-PCHC]_{10}$ and d) $[P5-PCHC]_{15}$ (sample magnification illustrated).

8.5.5 Mechanical Recycling

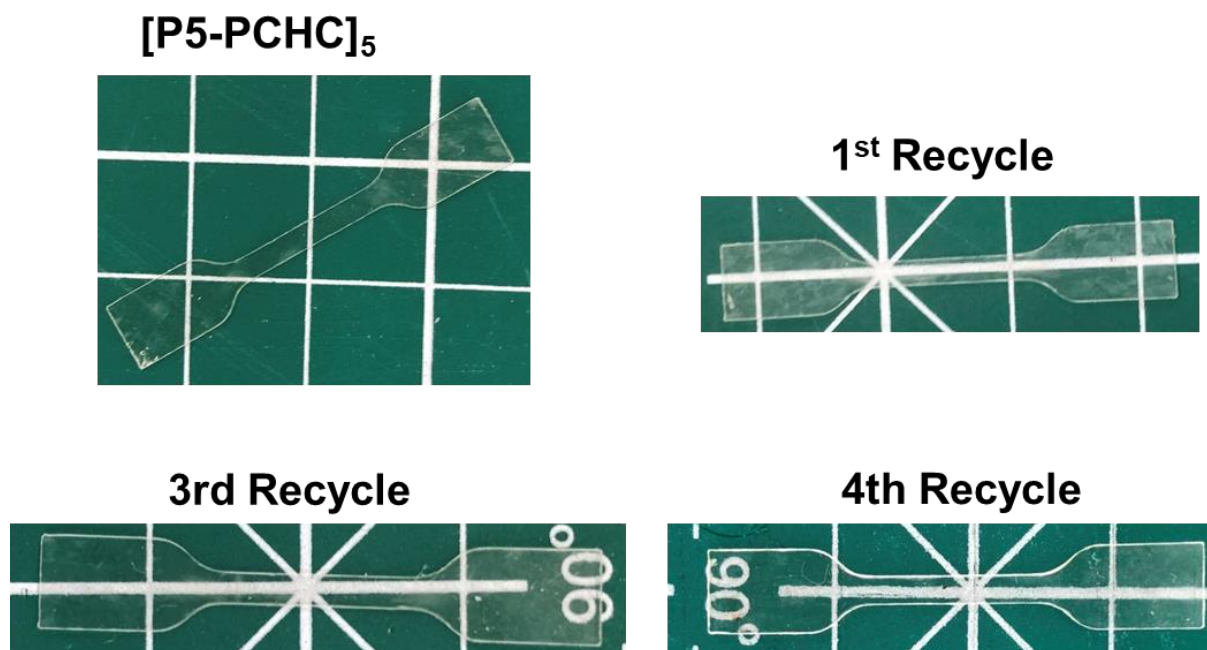


Figure S8.5.39: representative tensile specimens of $[P5-PCHC]_5$ during various cycles of mechanical recycling.

8.5.6 Chemical Depolymerisation

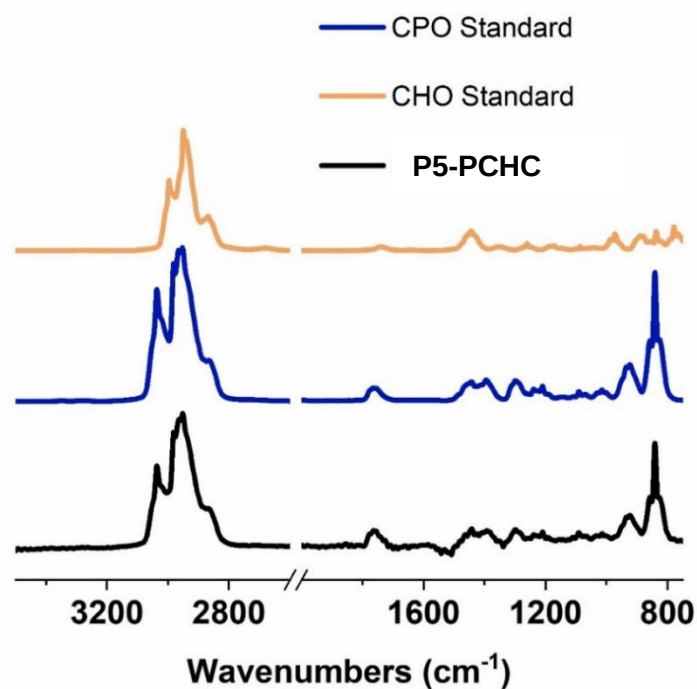


Figure S8.5.40: The TGA-IR spectrum of the 140 °C isotherm for **[P5-PCHC]₂₀**, with the recyclate (black) and CHO/CPO standards (yellow/blue).

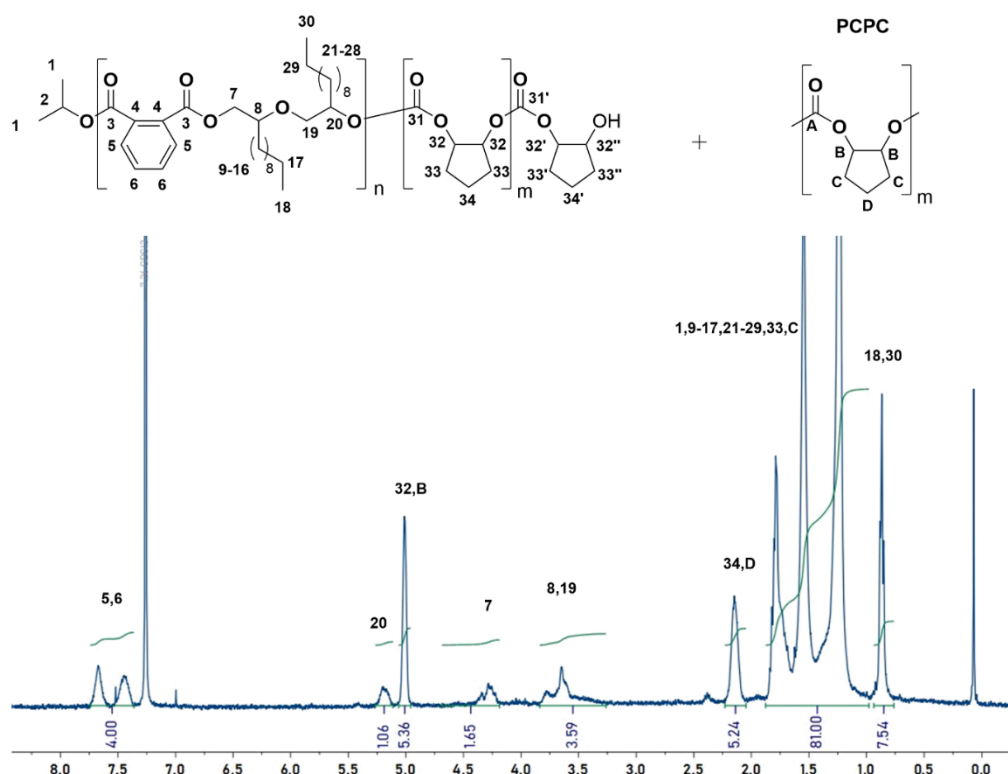


Figure S8.5.41: ^1H NMR spectrum of **[P5-PCPC]₂₀** (400 MHz, CDCl_3) after chemical depolymerisation (TGA – [5] : **[P5-PCPC]₂₀** = 1 : 1000, 140 °C isotherm, 50 minutes). The spectrum shows **P5-PCPC** diblock copolymer remaining after the TGA experiment, as well as a residual 1.8 equivalents of PCPC relative to PA (from the ratio of ring opened signals from PA : P(CPO), peaks 5,6 : 32,B). This corresponds to a CPO DP of 45, and M_n of residual PCPC = 5.7 kg mol $^{-1}$.

8.5.7 Enzymatic Degradation

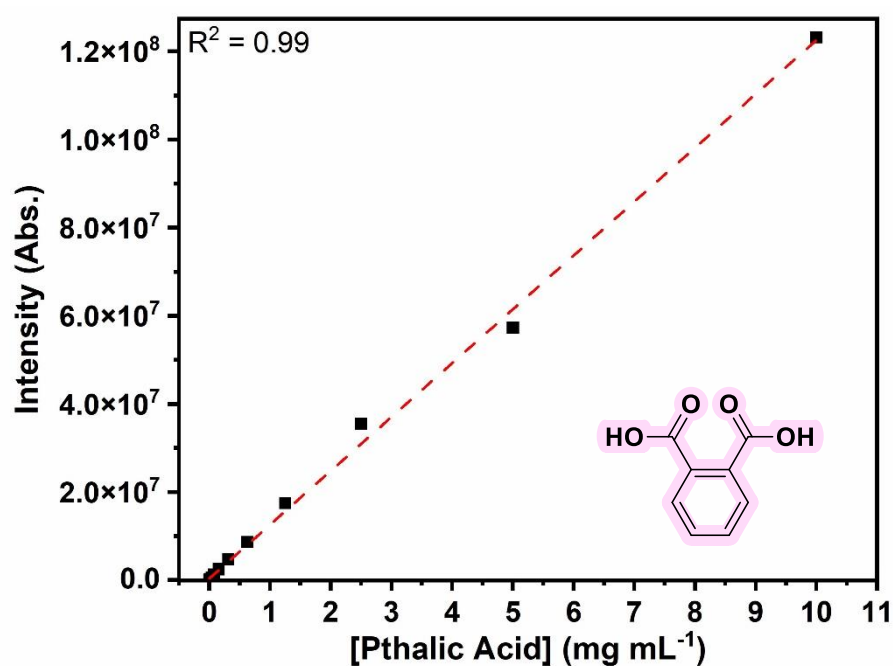


Figure S8.5.42: HPLC calibration data for Phthalic acid, with linear fit.

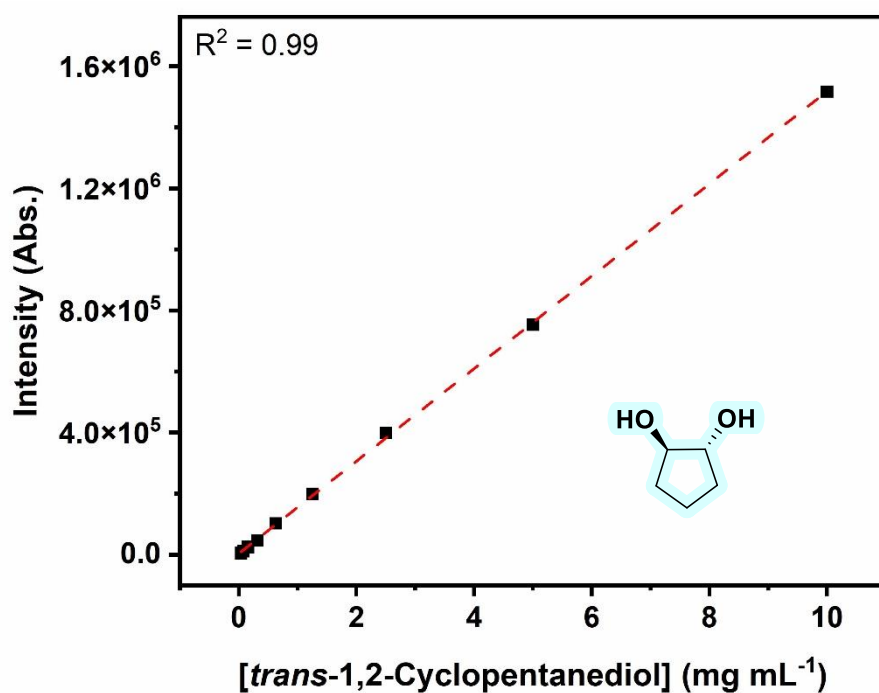


Figure S8.5.43: HPLC calibration data for trans-1,2-cyclopentanediol, with linear fit.

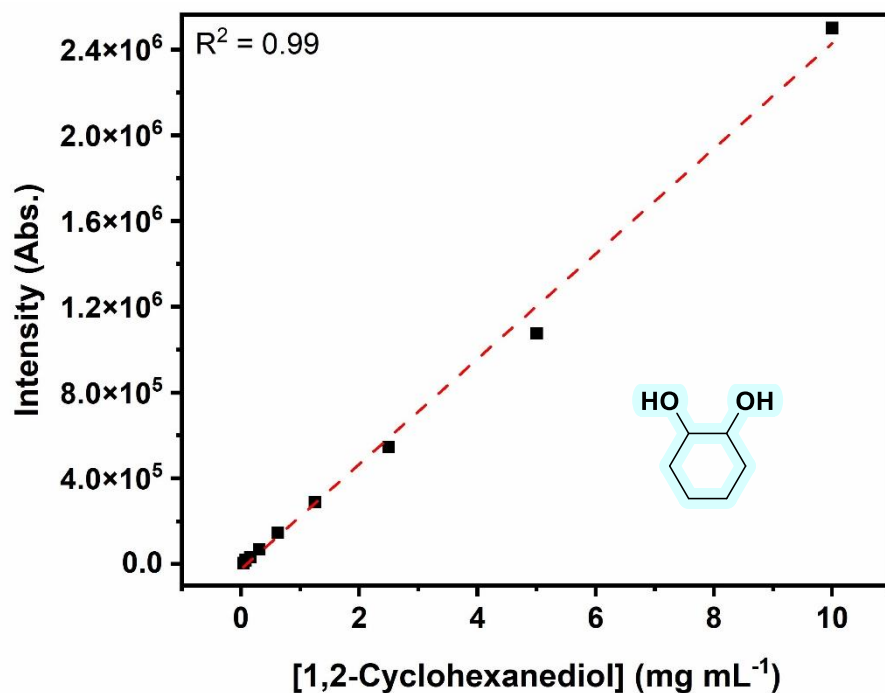


Figure S8.5.44: HPLC calibration data for 1,2-cyclohexanediol, with linear fit.

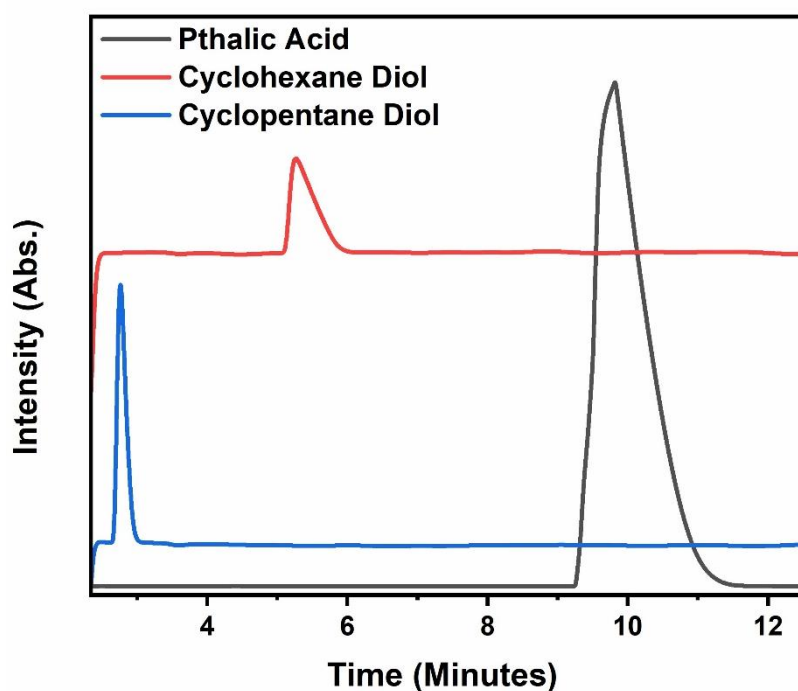


Figure S8.5.45: HPLC chromatogram of phthalic acid, 1,2-cyclohexanediol and trans-1,2-cyclopentanediol standards, showing that all three of these degradation products can be resolved with this method. The signals for CPD and CHD are from the RID, and the signal for phthalic acid is from the PDA detector (254 nm). HPLC Conditions; 1 mL min⁻¹ 95 % H₂O (0.2 % Formic acid) and 5 % acetonitrile (0.2 % Formic acid), Isocratic run, 30 °C oven temperature, RID and PDA Detection, 40 uL injection volume, on a velox SP-C18 (Shimadzu) column.

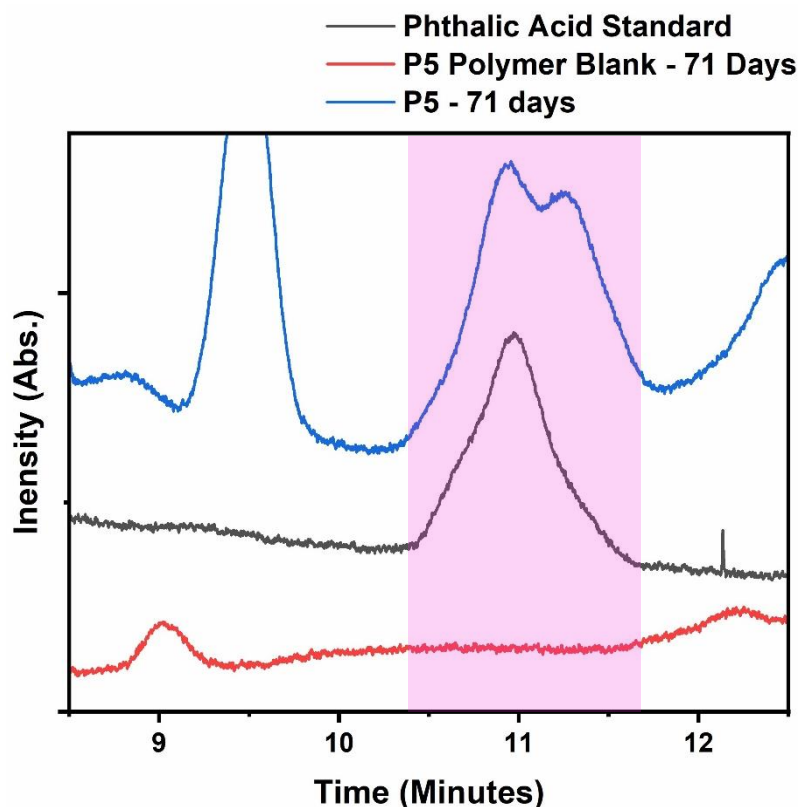


Figure S8.5.46: Comparison of a negative control (P5, buffer, no enzyme – red curve), phthalic acid standard sample (black curve), and an example of a sample of P5 during enzymatic degradation experiments after 71 days (blue curve). The pink zone indicates the Phthalic acid elution time. P5 $M_n = 10.9 \text{ kg mol}^{-1}$, $\bar{D} = 1.18$ (Table 5.1).

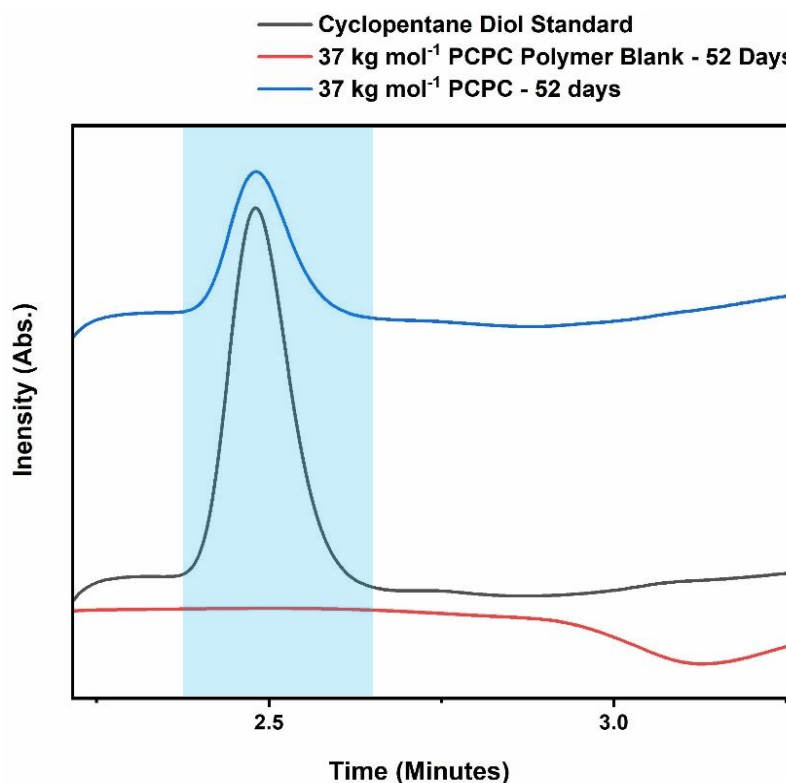


Figure S8.5.47: Comparison of a negative control PCPC, buffer, no enzyme – red curve), cyclopentane diol standard sample (black curve), and an example of a sample of PCPC during enzymatic degradation experiments after 52 days (blue curve). The blue zone indicates the cyclopentane diol elution time. PCPC $M_n = 37 \text{ kg mol}^{-1}$, $\bar{D} = 1.58$ (Table 5.1).

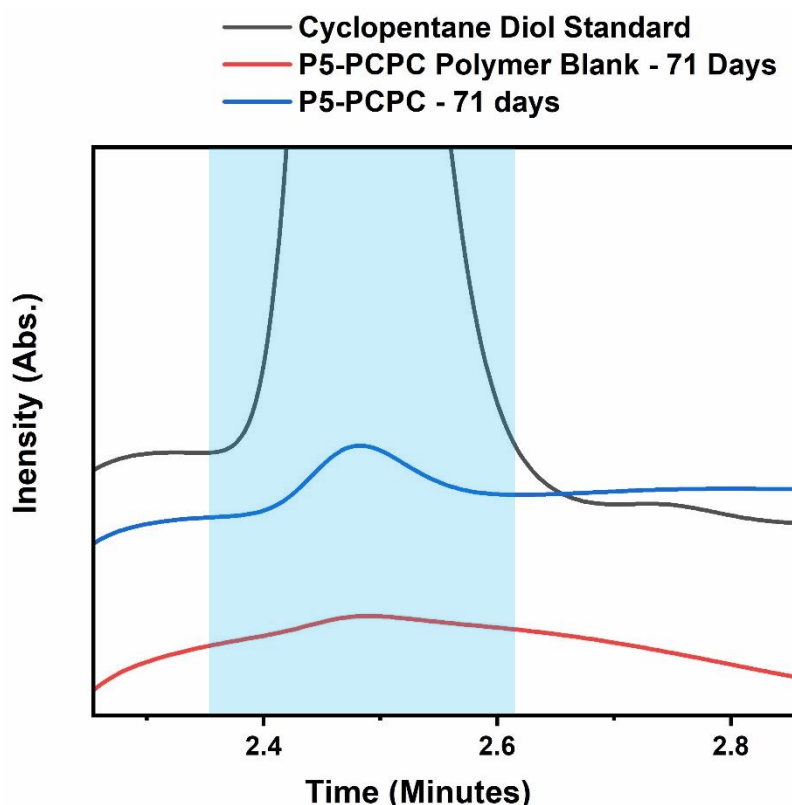


Figure S8.5.48: Comparison of a negative control **P5-PCPC**, buffer, no enzyme – red curve), cyclopentane diol standard sample (black curve), and an example of a sample of **P5-PCPC** during enzymatic degradation experiments after 52 days (blue curve). The blue zone indicates the cyclopentane diol elution time. **P5-PCPC** $M_n = 13.3 \text{ kg mol}^{-1}$, $\bar{D} = 1.11$ (Table 5.1).

8.6: References

1. A. Spyros, D. S. Argyropoulos and R. H. Marchessault, *Macromolecules*, 1997, **30**, 327–329.
2. Z.-H. Jiang, D. S. Argyropoulos and A. Granata, *Magn. Reson. Chem.*, 1995, **33**, 375–382.
3. R. W. F. Kerr and C. K. Williams, *J. Am. Chem. Soc.*, 2022, **144**, 6882–6893.
4. M. Nofar, in *Multiphase Polylactide Blends*, ed. M. Nofar, Elsevier, 2021, pp. 97–143.

