

Switch Catalysis: From Monomer Mixtures to Sequence-Controlled Block Copolymers

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Summary

A ‘Switch’ catalysis method is reviewed whereby a single catalyst is switched between ring-opening polymerisation and ring-opening copolymerisation cycles. It allows the efficient synthesis of block copolymers from mixtures of lactones, epoxides, anhydrides and carbon dioxide. In order to use and further develop such ‘Switch’ catalysis, it is important to understand how to monitor the catalysis and characterise the product block copolymers. Here, a step-by-step guide to both the catalysis and the identification of block copolymers is presented.

Introduction

Block copolymers are a particularly interesting class of macromolecules as they feature covalently linked, chemically distinct, polymer blocks.^[1] Many block copolymers phase-separate to form nanostructures either in the solid state or in solution – these domain structures are responsible for moderating the overall physical and chemical properties.^[2, 3] Current applications include thermoplastic elastomers and as compatibilisers for polymer blends, however, there is also significant interest in their use in fields as diverse as medicine, nanotechnology, lithography, photonics and electronics.^[4-9] There are already a range of successful methods to synthesise block copolymers and generally these apply either *in situ* approaches or post-polymerisation modifications.

The *in situ* approach generally applies living polymerisation methods where sequential monomer additions are used to build up the individual blocks.^[10-14] The *in situ* method is generally preferable to post-polymerisation coupling because it reduces intermediate purification steps and obviates problems of low reactivity of polymer chain ends in coupling reactions. The ring-opening polymerisation (ROP) of lactones is such a living polymerisation route to aliphatic polyesters and a wide range of different catalysts have been reported for this process.^[15-18] An alternative approach to polyesters and polycarbonates under living conditions is the ring-opening alternating copolymerisation (ROCOP) from epoxides/CO₂ and epoxides/anhydrides; so far, there are fewer catalysts reported for ROCOP than for ROP.^[19-22]

In terms of block copolymers, there are reports of post-polymerisation modifications and tandem catalyses which apply both ROP and ROCOP to prepare block copolymers. In 2012, our group reported the preparation of α,ω -hydroxyl terminated poly(cyclohexene carbonate) using a di-zinc catalyst.^[23, 24] This macro-initiator was subsequently used, with an yttrium catalyst, in lactide ring-opening polymerisation.

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This method enabled the production of ABA triblock copolymers.^[25] Darensbourg and co-workers reported a one-pot tandem catalysis method whereby a metal salen catalyst was used for epoxide/CO₂ ROCOP and an organo-catalyst was applied for lactide ROP; the two processes were linked by the addition of water as a chain transfer agent.^[26] This concept was extended to prepare block copoly(carbonate-*b*-lactide)s^[25, 26], poly(carbonate-*b*-ether)s and poly(carbonate-*b*-phosphoester)s.^[27, 28] It was also reported that heterogeneous double metal cyanide catalysts for epoxide/CO₂ ROCOP could be used with tin octanoate catalysts for lactide ROP to produce copolymers with a proposed tapering multi-block structure.^[29] It should be noted that studies using heterogeneous catalysts are necessarily more complex due to the limited understanding of the active sites and thereby of chain growth and exchange reactions.

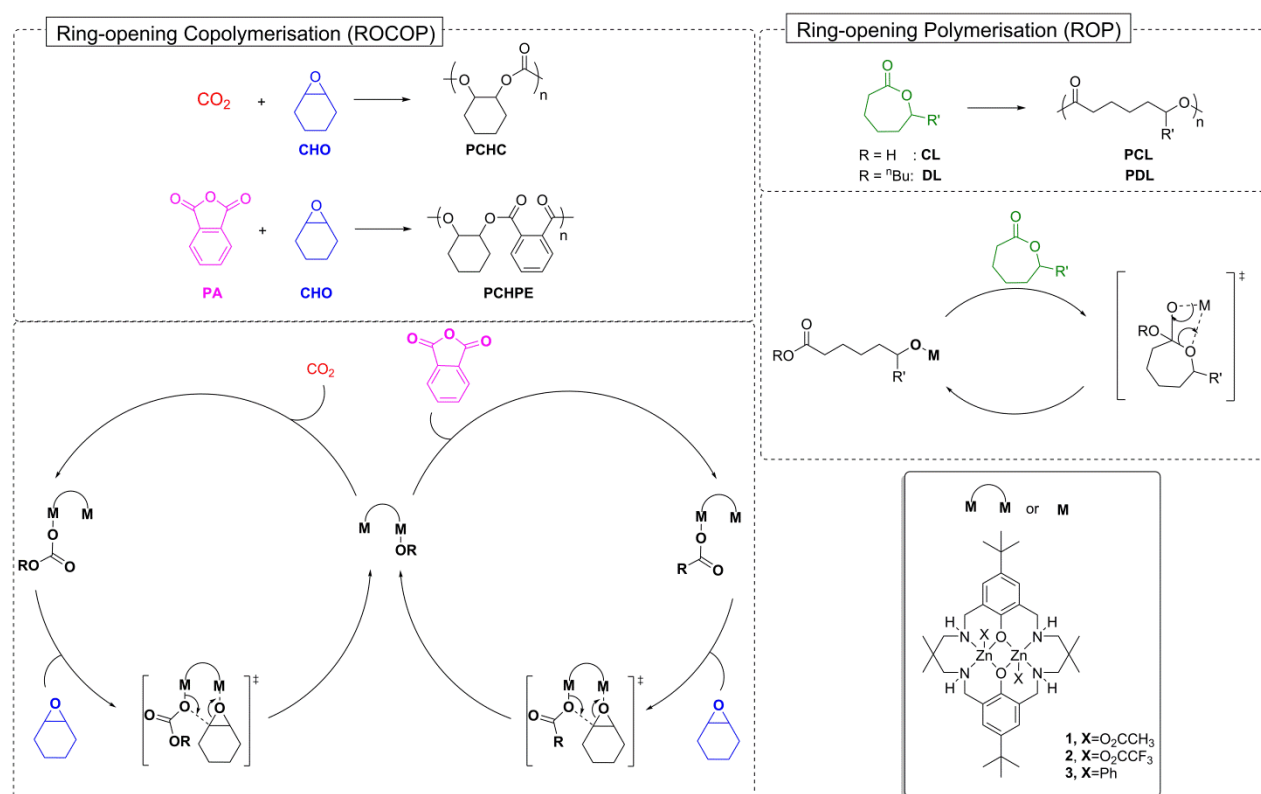
In terms of mixing together monomers for ROCOP and ROP processes, Döring and co-workers reported in 2006 that zinc β -diiminate catalysts could be used to prepare copolymers from lactide, cyclohexene oxide and carbon dioxide, but the precise structures were not investigated in detail.^[30] Furthermore, a number of zinc heterogeneous surfaces, including zinc glutarate and zinc adipate, were reported to copolymerise lactide, epoxide and carbon dioxide – nonetheless understanding of copolymer structure was severely hampered by very broad molecular weight distributions and a lack of insight into the active site structures.^[31]

In 2014, our group presented a new ‘Switch’ catalysis approach in which the ROP and ROCOP are combined in one-pot using a well-defined homogeneous catalyst. It allows the rational incorporation of different monomers via two distinct catalytic cycles so as to produce selectively block copolyesters and copoly(ester-*b*-carbonate)s.^[32-35]

‘Switch’ Catalysis

The term ‘Switch’ catalysis is widely used to describe a change in the chemical reactivity by an external stimulus such as thermal, redox, photochemical, and mechanical stimuli.^[36, 37] In the context of this review, ‘Switch’ catalysis refers to a change in polymerisation mechanism from ROP to ROCOP and *vice versa* (Scheme 1). It is important to emphasise the difference between the ‘Switch’ method and terpolymerisations, the latter of which may apply monomer mixtures but only a single polymerisation process, e.g. ROP or ROCOP, to form block copolymers.^[38-46] Terpolymerisations do not contain any type of mechanistic switch and are therefore conceptually different to ‘Switch’ catalysis.

The two different polymerisation processes comprising ‘Switch’ catalysis are illustrated in Scheme 1.^[20, 47, 48] The ROCOP process is an alternating copolymerisation whereby a metal-alkoxide reacts with CO₂ or an anhydride to generate a metal carbonate or carboxylate intermediate. These intermediates react with an epoxide to regenerate the metal alkoxide. The two-step process thus involves cycling between alkoxide-carbonate or alkoxide-carboxylate intermediates to build up the polycarbonate or polyester chains. In contrast, ROP involves only the ring-opening process and the sole intermediate is a metal alkoxide species. The metal alkoxide undergoes sequential reactions with lactones to generate the growing polymer chain. Thus, although the reactions are related they are not mechanistically the same – there are differences in the number and the nature of the intermediates.



Scheme 1. The key pathways for ring-opening copolymerisations (ROCOP) and ring opening polymerisations (ROP)

Our group reported ‘Switch’ catalysis using dizinc catalyst **1** (Scheme 1),^[24] the catalyst had already been extensively studied in CO₂/epoxide ROCOP enabling polymerisations at 1 atm of CO₂.^[49, 50] Moreover, **1** was also studied in polymerisations using carbon dioxide captured from a coal-fired power station. It was tolerant to common impurities found in carbon dioxide and from any capture process.^[51] Detailed mechanistic studies of **1** by NMR spectroscopy, *in situ* ATR-IR spectroscopy and computational analysis using DFT enabled a ‘chain-shuttling mechanism’ to be proposed whereby the rate-determining step is the ring-opening of the epoxide.^[49, 50, 52-54] The nucleophilic ring-opening of the epoxide is facilitated by a dinuclear mechanism in which one metal binds the epoxide and the other provides a labile carbonate. Following this, the activity could successfully be increased with heterodinuclear catalysts.^[22, 55] We have also reported that catalyst **1** is active for the epoxide/anhydride ROCOP and have very recently demonstrated that selective terpolymerisations using a range of different anhydrides/epoxide/carbon dioxide lead to block copoly(ester-carbonate)s.^[56, 57]

Nonetheless, **1** was inactive for the ROP of lactones, as exemplified by reactions between **1** and ϵ -caprolactone which failed to yield any polyester. However, ROP was ‘switched on’ upon the addition of either sub-stoichiometric or excess epoxide (CHO). Furthermore, the epoxide was only present as a chain-end group and there was no evidence on any ether linkages in the polyester (which would form from competitive epoxide ROP). The switch-on and the selectivity was rationalised by the reaction between **1** and an equivalent of epoxide to form an alkoxide, which could act as an initiator for ROP. The reaction of **1** with a mixture of CO₂, CL and CHO resulted in only the formation of polycarbonate. The production of block copolymers was possible if the polycarbonate block was produced and then the CO₂ was removed (by rapid cycles of vacuum-nitrogen), the ROP was then ‘switched’ on and a polyester block was formed (Figure 1, right). Considering the proposed mechanisms for the ROP and ROCOP, it is clear that there is a common zinc-alkoxide intermediate in both processes. The selectivity could be interpreted to arise due to a higher rate of carbon dioxide insertion compared to lactone ring-opening at the zinc-alkoxide intermediate. Further analysis revealed that the zinc carbonate, which was formed from the insertion of CO₂, was unreactive in lactone ROP, even under forcing conditions, and indeed ROP could be ‘switched-off’ by

addition of carbon dioxide into polymerisations.^[33] Thus, the chemistry of the zinc-oxygen bond of the growing polymer chain is responsible for the selectivity for ROCOP or ROP processes during the polymerisation.^[35]

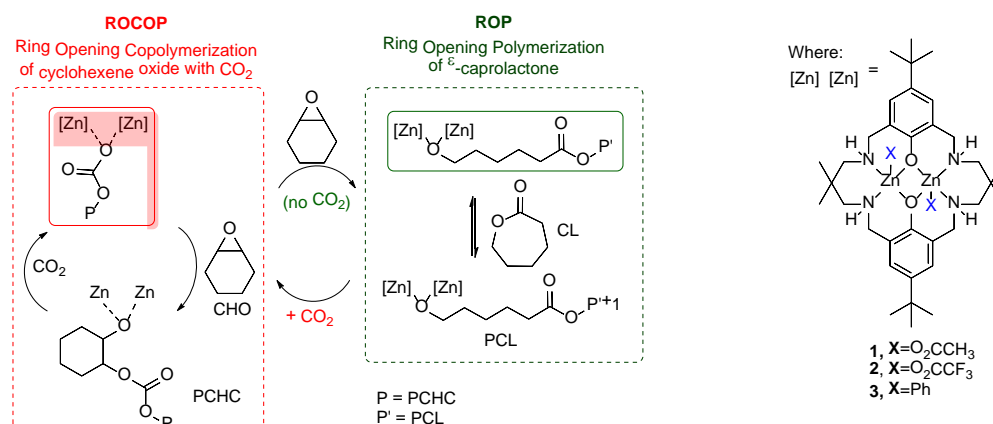


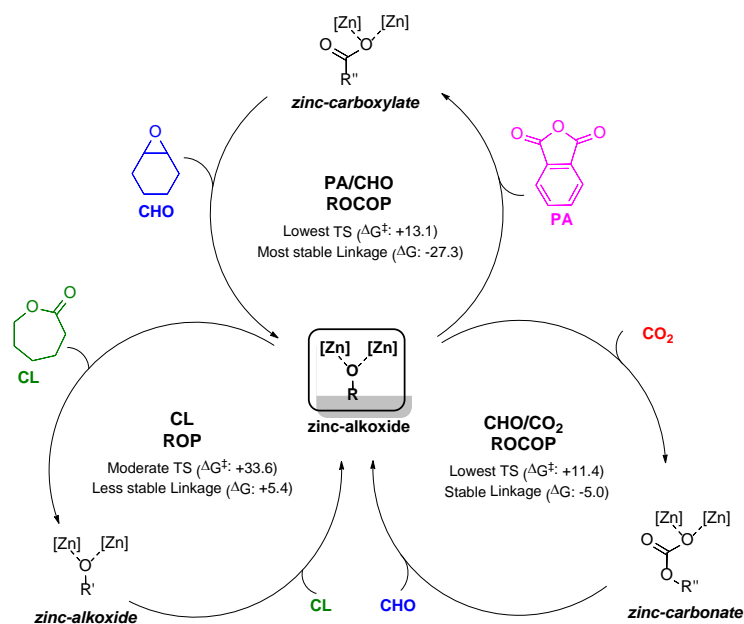
Figure 1. Illustration of 'Switch' catalysis (polymer structures are given in Scheme 1).

The 'Switch' catalysis was applied to prepare ABA triblock copoly(ester-*b*-carbonate-*b*-ester)s from mixtures of epoxide/carbon dioxide/lactone using catalyst **2** (X = trifluoroacetate).^[33] Earlier studies of ROCOP using catalyst **2** demonstrated that it produced α,ω-dihydroxyl terminated polycarbonates and, in separate work, investigated the influence of 1,2-cyclohexane diol groups as initiators for ROP.^[25, 57] The related catalytic phenomenon was also substantiated by research by Darensbourg and co-workers, using metal-salen catalysts with trifluoroacetate initiating groups, who also observed the selective formation of a α,ω-dihydroxyl terminated polycarbonates.^[27] It was proposed that the expected trifluoroacetate end-group is easily hydrolysed, either during or after polymerisation to produce the dihydroxyl terminated chains. The investigation of 'Switch' catalysis using catalyst **2** led to the selective production of ABA block copolymers and demonstrated a range of different compositions and block lengths.

'Switch' catalysis using mixtures of epoxide/anhydride/lactone was also explored using catalyst **3** (X=Ph) with a diol, once again exploiting the potential to produce telechelic polymers.^[34, 58] Well-defined ABA block copolyesters were formed from mixtures of CHO, PA and ε-decalactone (DL). Multiblock copolyesters with up to heptablocks could be synthesised by a second monomer mixture addition - such a method may offer advantages over alternative living polymerisation methods which would require seven additions to access related heptablocks.

The fundamental basis for 'Switch' catalysis was further investigated using DFT.^[32] The entire cycle of monomer additions was explored using catalyst **1** and the differences between the relative barriers and stabilities of intermediates compared. In particular, the different insertions into the metal alkoxide intermediate enabled comparisons between the different pathways. It was found that a combination of the thermodynamic stability of the formed linkages and the kinetic barriers for the different reaction pathways could rationalise the experimentally observed selectivity in 'Switch' catalysis (Scheme 2). Starting from the zinc alkoxide intermediate and investigating the insertions of epoxide (CHO), CO₂, anhydride (PA) and lactone (CL), three pathways were possible: (i) The reaction with anhydride leads to the most stable linkage and has a low energy transition state, (ii) the reaction with CO₂, which also forms a stable linkage and has the lowest energy transition state, and (iii) the reaction with CL, which forms the least stable linkage and has a moderate energy transition state. Accordingly, the ROP of CL has the least favourable thermodynamics and kinetics and indeed is not observed experimentally until the consumption/removal of the other monomers. When comparing the insertion of anhydride *vs.* CO₂, the insertion of PA leads to more stable linkages while both have similar energy barriers. Thus, experimentally the ROCOP of PA/CHO occurs selectively over the ROCOP of CHO/CO₂. It was also interesting to observe that the

barrier for epoxide ROP is very high and cannot be accessed under the experimental conditions, thereby explaining the lack of ether linkages in any of the polymer blocks.



Scheme 2. Possible mechanisms and their theoretical evaluation of a zinc alkoxide in a mixed monomer feedstock of CHO, CO₂, PA and CL (kcal mol⁻¹).^[32]

Very recently, Rieger *et al.* applied the ‘Switch’ catalysis concept with a different di-zinc catalyst supported by a β -diiminate ligand, and using a mixture of CHO, CO₂ and β -butyrolactone (BBL).⁴⁹ At 40 atm pressure of CO₂ selective ROCOP of epoxide/CO₂ occurred first and was followed by the ROP of BBL to build up block copolymers. However, at 3 atm CO₂ there was no selectivity and random copolymers were formed. In this case, the carbon dioxide pressure was important to achieve good selectivity and switchability.

‘Switch’ catalysis : A guide to block copolymer identification

‘Switch’ catalysis enables the production of multi-block copolymers and has the potential to allow production of a particular block sequence. When implementing and testing catalysts for this process, it is important to fully characterise the products and processes. The main challenges in working with monomer mixtures are: (i) monomer discrimination and (ii) formation of block copolymers over alternative structures, such as random copolymers or even homopolymers. To address these challenges, a series of experiments is proposed to distinguish between block copolymers and statistical copolymers (from the random insertion of monomers) or mixtures of homopolymers (Figure 2). The following guide is meant to illustrate this ‘decision tree’. However, it should be noted that suitable proof for block copolymers and ‘Switch’ catalysis is not limited to the suggested experiments and should be extended based on the specific research questions and findings. In the flow diagram, a ‘No’ outcome suggests the system cannot be considered for ‘Switch’ catalysis and a change to the catalytic system in terms of conditions, choice of monomers or catalyst (and/or co-catalyst, if applicable) would be necessary as a next step.

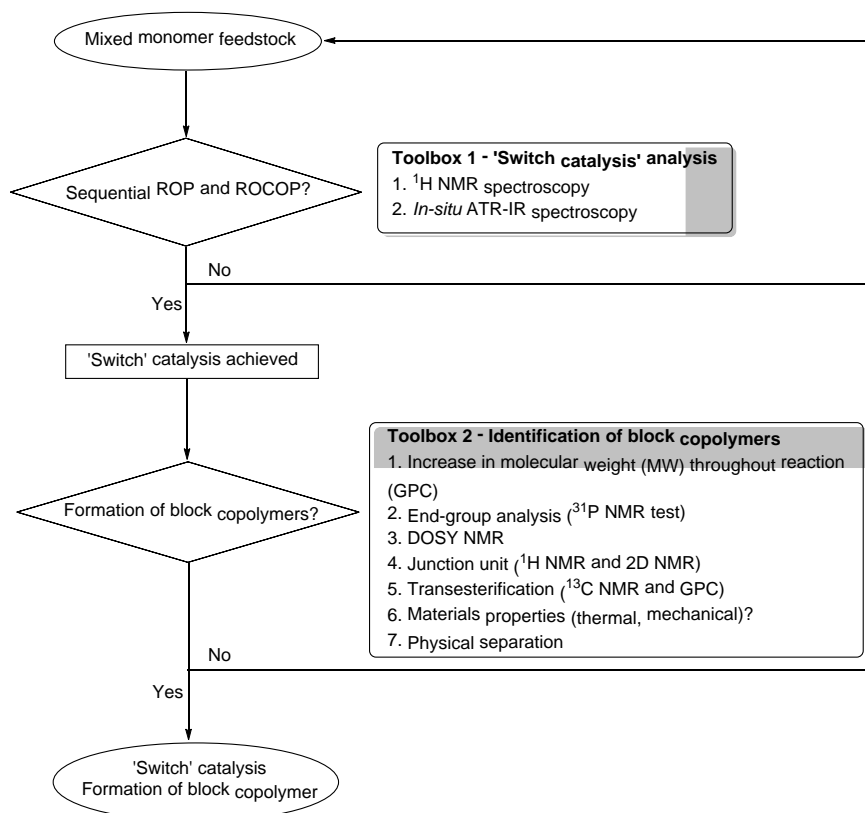
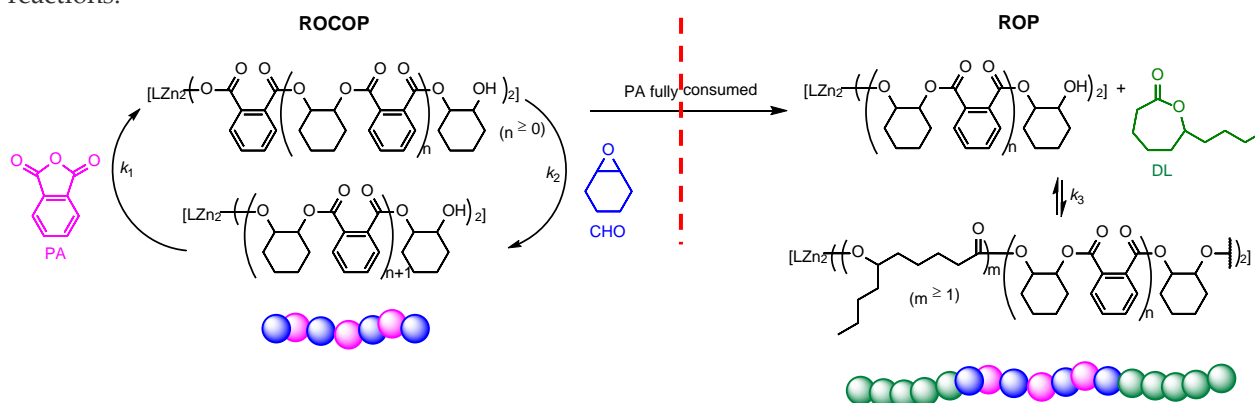


Figure 2. Guide to the formation of block copolymers using ‘Switch’ catalysis.

Starting from a mixed monomer feedstock, the first area to investigate is whether there is selectivity between ROCOP and ROP (or *vice versa*) over a random incorporation of monomers. The investigation of monomer selectivity can be achieved by *in situ* monitoring or aliquot analysis using spectroscopy, with ^1H NMR or *in-situ* ATR-IR spectroscopy being particularly useful (Figure 3). Figure 3 illustrates the *in situ* monitoring using ATR-IR spectroscopy of ‘Switch’ catalysis using catalyst **3**, cyclohexane diol and mixtures of CHO, PA and DL. During the first 150 mins, the only absorptions that change correspond to the formation of polyester by ROCOP – i.e. the anhydride is consumed and the polyester band increases in intensity. At approximately 150 mins, the anhydride is fully consumed (as confirmed by ^1H NMR spectroscopy analysis of an aliquot) and after this point, the ROP process occurs as observed by the decrease in resonance assigned to the lactone and the increase in the aliphatic polyester resonance. Figure 3 also includes the characteristic wavenumbers which are used to monitor some of the ‘Switch’ catalysis reactions.



Species	Wavenumber (cm ⁻¹)	Ref.
PCHC	935; 1010; 1237; 1275	[33, 35]

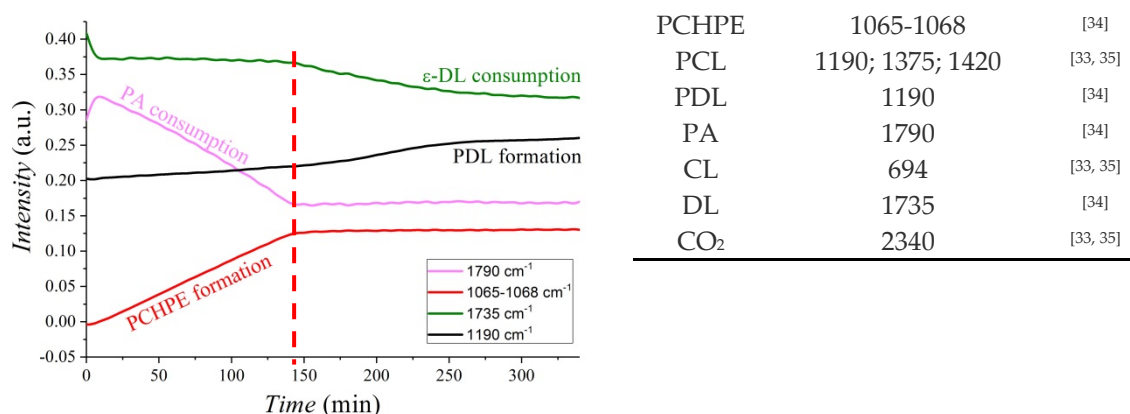


Figure 3. *In-situ* ATR-IR spectrum for the formation of copoly(PDL-*b*-PCHPE-*b*-PDL) (left) and indicative wavenumbers for different species for monitoring by *in-situ* ATR-IR spectroscopy (wavenumbers obtained from neat compounds, right). Monomer and polymer structures are given in Scheme 1.^[34]

Using *in situ* spectroscopy, the sequential occurrence of ROCOP and ROP can be identified but the composition of the product is not yet known – the same results would be observed if a mixture of homopolymers or a block copolymer were formed. To understand the polymer composition, a range of further experiments are presented to characterise the block copolymers (‘Toolbox 2’ in Figure 2):

1. Monitoring by Gel permeation chromatography (GPC): A continuous increase in molecular weight is expected if copolymers are formed. One common method to assess the polymer molecular weight as the reaction progresses is by aliquot analysis using gel permeation chromatography (GPC). Typically, this involves calibration by narrow-molecular weight standards, such as polystyrene, to convert elution time to molecular weight. It should be noted that other methods to determine molecular weight (intrinsic viscosity) should also show the same phenomenon in the case of copolymer formation (Figure 4). Where the polymer backbone contains a chromophore, detection based on ultra-violet visible absorption is recommended in addition to the usual detection based on refractive index (RI) – clearly additional detection methods are expected to correspond to related number and positions of the observed peaks (Figure 4). It is important to note that increases in molecular weight alone do not unambiguously confirm block copolymer formation, for example this technique is not suitable to detect low levels of transesterification in the backbone.

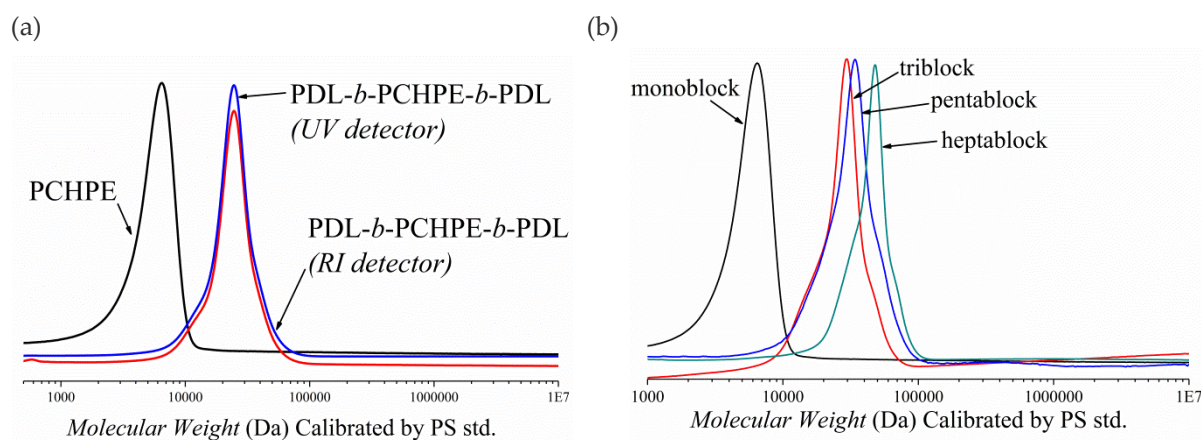
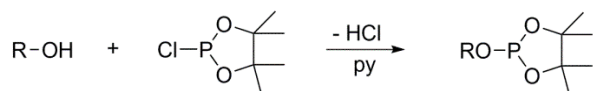


Figure 4. Representative GPC monitoring of ‘Switch’ catalysis, an increase in molecular weight can be observed after the incorporation of DL.^[34]

2. End-group Analysis: The formation of block copolymers corresponds to a chain extension reaction and as such the end-groups of inner block(s) should not be present after the addition of outer block(s). Thus, titrations to determine the nature and quantity of end-groups can be used to confirm block formation. One useful method of end-group analysis in the context of hydroxyl-terminated polymers is *via* a quantitative reaction with a phosphorus containing reagent and the use of $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy as an analytical method. In particular, the reaction of hydroxyl end-groups with 2-chloro-4,4,5,5-tetramethyl dioxaphospholane is used to form phosphites which show differing chemical shifts depending on the end-group environment.^[59] It is important to use an internal standard and in our work Bisphenol A (BPA) is applied. One limitation of this technique is the stability of the polymer (particular polyesters) towards pyridine, which is used as a base to capture hydrochloric acid, which is released during the reaction.



Species	^{31}P shift (ppm) ^a	Ref.
PCHPE	147.1	[34]
PCL	147.8	[59]
PDL	149.2	[34]
BPA	138.6	[59]

^a Measured in CDCl_3 at room temperature.

Figure 5. End-group analysis by $^{31}\text{P}\{^1\text{H}\}$ NMR (polymer structures given in Scheme 1).

3. DOSY NMR: Diffusion-ordered NMR spectroscopy (DOSY) enables an estimation of polymer diffusion rates. In the case of a block copolymer, a single diffusion coefficient is expected with all blocks expected to diffuse at the same rate, whereas two coefficients are expected for a mixture of polymers. The figure below illustrates the single diffusion coefficient observed for the block copolyester formed by ‘Switch’ catalysis and compares against the two diffusion coefficients observed in the spectrum of a blend of the constituent polyesters (Figure 6).

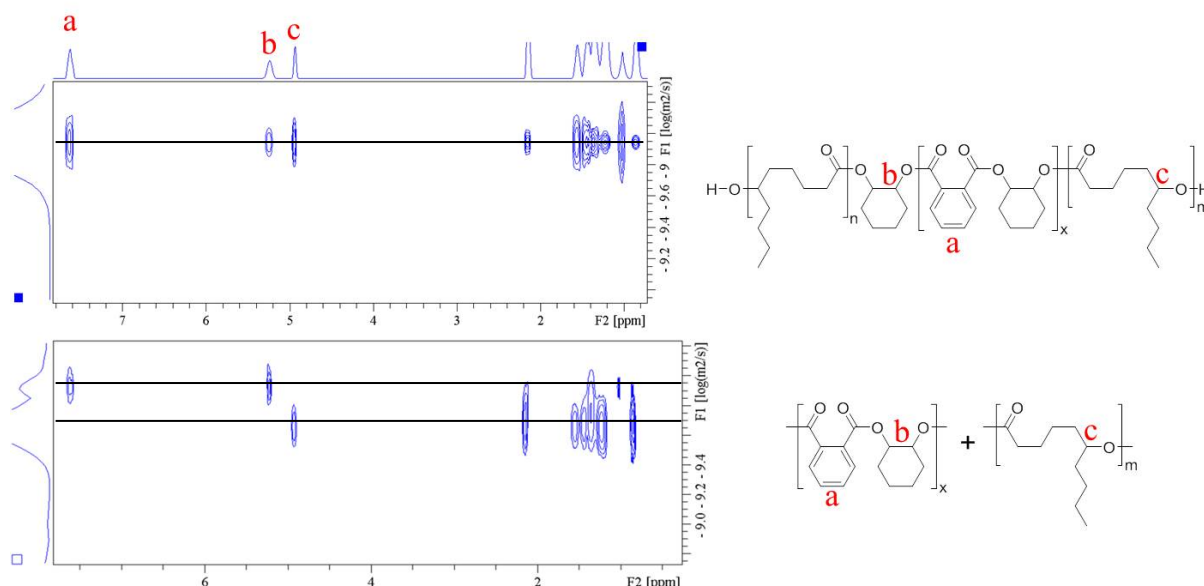


Figure 6. DOSY of block copolymer (top) *vs.* a mixture of homopolymers (bottom) in toluene- d_8 at room temperature.^[34]

4. Analysis of block junction signals: For block copolymers, the monomer unit that forms the covalent linkage between the two blocks often has a different chemical environment than the repeating units of the individual blocks and, as such, sometimes shows a distinct chemical shift in the ^1H NMR spectrum. The main chain and junction unit signals are often observed in ^1H NMR and can be assigned by 2D NMR

techniques. It should be noted that these signals are inherently of weak intensity, with intensity decreasing as the block length increases, as they are only present in a small fraction of the polymer. Nonetheless, analysis of integrals (under a range of relaxation times) can give an indication of the ratio of blocks:junctions and therefore be used to characterise the polymer product. In the present example, a block ratio of PCL:PCHC of 4:1 was obtained, which was within error with the ratio based on the integrals of the repeating unit (5:1, Figure 7).

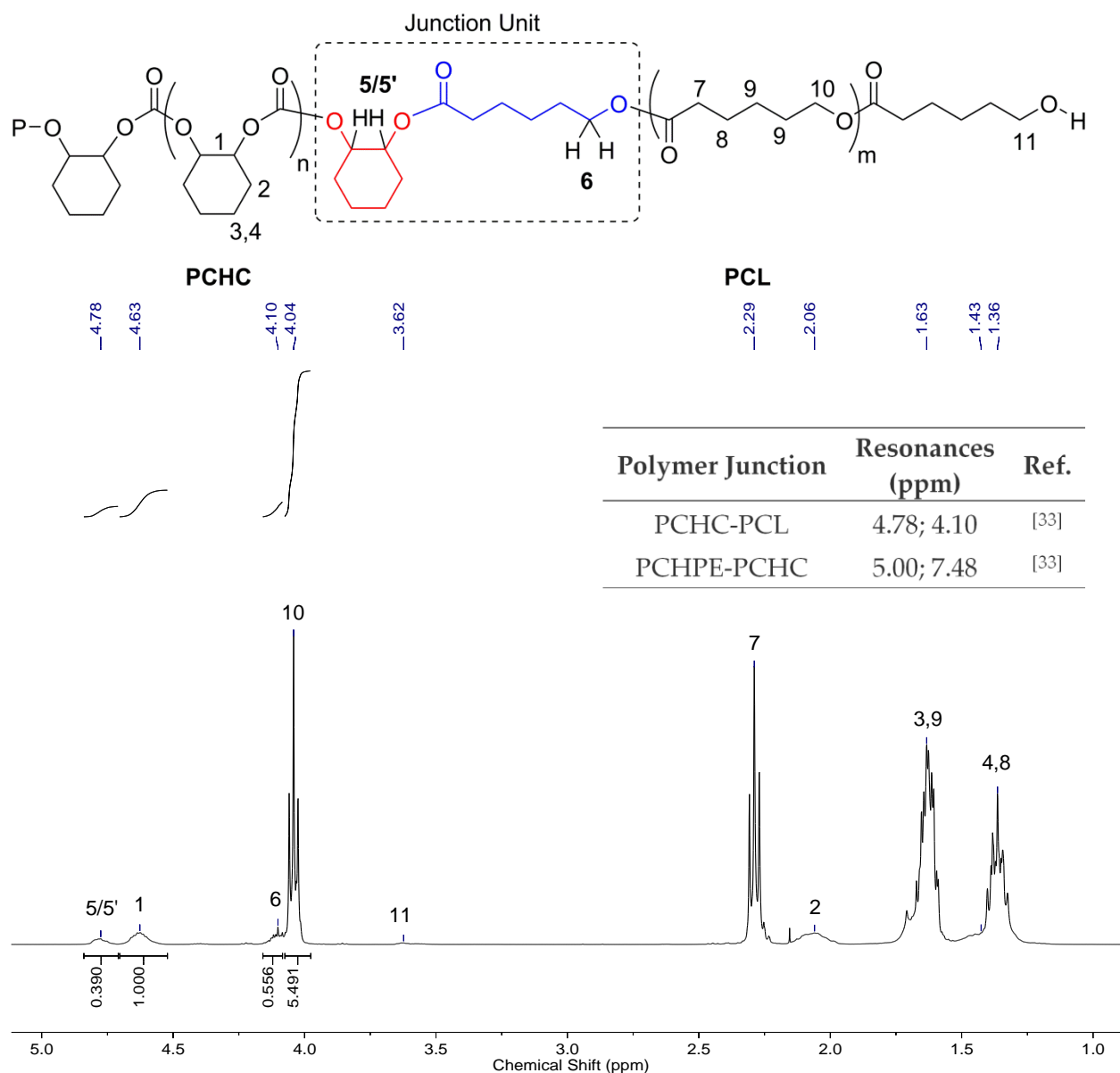


Figure 7. An example of an ^1H NMR spectrum, illustrating the junction signals.^[33] The chemical shifts assigned to common junctions for selected block copolymers (in CDCl_3 , top right). Polymer structures are given in Scheme 1.

5. Transesterification (^{13}C NMR and GPC): Transesterification is a side-reaction that could result in block scrambling. The extent of transesterification can be assessed using ^{13}C NMR spectroscopy most commonly in the case of block copoly(ester-carbonate)s or block copolyesters by analysis of the carbonyl region of the spectrum. In particular, control experiments where block copolymers are treated with a catalysts favouring transesterification, such as 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (TBD), can be used to reveal the signals expected for transesterified/randomised copolymer structures. The ^{13}C NMR of the block copolymer and

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the randomised copolymer can be compared and transesterification should be identified most clearly by changes to the carbonyl region (Figure 8). Moreover, extensive transesterification may also be observable by GPC, as broad molecular weight distributions are expected, sometimes with clear formation of higher/lower MW species.

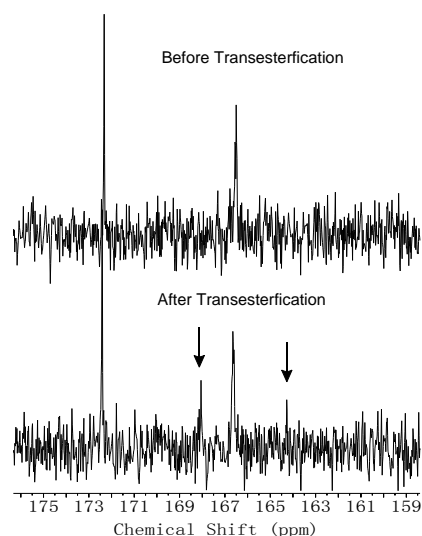


Figure 8. ^{13}C NMR showing transesterification of copoly(PDL-*b*-PCHPE-*b*-PDL) after the reaction with TBD.^[34]

6. Material Properties: The macroscopic properties of the resulting block copolymer should also be compared to the homopolymers. This includes, but is not restricted to, thermal and mechanical properties, such as glass-transition temperature, decomposition temperature and the modulus of elasticity, which can be characterised using differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and tensile tester, respectively. There are often distinct differences in thermal properties for block copolymers compared to mixtures of homopolymers or random structures, but generalisation are not possible as properties also correlate with block lengths and miscibility.

7. Physical Separation: Another test used to characterise block copolymers is to establish whether the block composition can be changed upon fractionation experiments. These typically involve washing the sample with solvents selective for a particular polymer and/or re-precipitation experiments (from solvent/non-solvent mixtures) and subsequent analysis of the samples using spectroscopy. It should not be possible to change the composition (i.e. ratio of block constituents) for a block copolymer, whereas mixtures of polymers can be separated using such techniques.

Future Directions

‘Switch’ catalysis is a method by which monomer mixtures can be selectively transformed into multi-block copolymers using a single catalyst which operates in two distinct catalytic cycles. So far, the method is still in its infancy and has been demonstrated for the production of block copoly(ester-carbonate)s and block copolyesters. This short and personal review has highlighted research from our group in developing the method and also laid out the methods of characterisation that should be used to determine whether other catalysts operate by ‘Switch’ catalysis. So far, our investigations have focussed exclusively on di-zinc catalysts, coordinated by a macrocyclic ancillary ligand, and mixtures of carbon dioxide, lactone, anhydride and epoxides. Very recently, the first demonstration of ‘Switch’ catalysis using another di-zinc catalyst, coordinated by a β -diiminate ligand, has been reported and used to prepare block copoly(ester-carbonates).^[60] The next phases of the development of the method should seek to explore other known catalysts for ROCOP and ROP reactions, for example metal salen or porphyrin complexes would be

interesting targets. In this context, the use of catalysts able to operate with lower temperatures so as to enable the incorporation of other epoxides, such as propylene oxide, is an important target. The development of 'Switch' catalysis should also address expanding the range of monomers able to operate by this mechanism, including functionalised epoxides/anhydrides, many of which are commercially available. As part of long-term studies it is of interest to expand yet wider the range of monomers including to other heterocumulenes, cyclic monomers (cyclic carbonates) and heterocycles, such as aziridines or thiiranes. In parallel with the catalytic development, it is important to fully characterise the new multi-block copolymers formed. One attraction of the 'Switch' catalysis method is the ability to form materials featuring 'hard' and 'soft' domains, which are expected to undergo phase separations and show potential as rigid plastics and/or thermoplastic elastomers. The detailed understanding and study of the polymer properties is important to realise the potential of the catalysis. Finally, the 'Switch' catalysis method could be expanded to include other polymerisation pathways and mechanisms and, as such, exploring the means to 'Switch' catalysts between different pathways remains a less-studied but fascinating future challenge in polymerisation catalysis.

Additional Information

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Competing Interests

CKW is a director of econic technologies.

Authors' Contributions

All authors have contributed to the review article.

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