



# Sequence Selective Ring-opening Terpolymerisation Facilitates Higher Order Switchable Catalysis

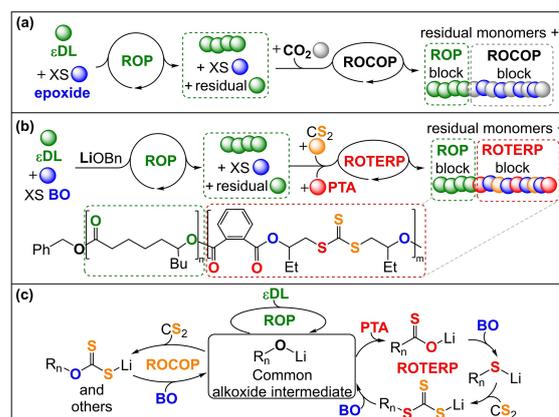
Alex J. Plajer\*<sup>[a]</sup>

Sequence selective ring-opening terpolymerisation (ROTERP) allows the design of block polymerisation cascades with three distinct mechanistic cycles. Ring-opening polymerisation (ROP), ring-opening copolymerisation (ROCOP) and ROTERP can be

combined in cascades where the onset of the most complex process suppresses the occurrence of the simpler ones. The cascades furthermore enable the incorporation of different heteroallenes between blocks.

## Introduction

The selective construction of complex yet well-defined products with useful properties is an increasingly important aspect of sustainable catalysis.<sup>[1]</sup> Achieving the controlled assembly of multiple components unnecessary and hence saves time and effort spent on these steps.<sup>[2,3]</sup> In polymerisation catalysis this can result in control over the monomer sequences and polymer microstructures which has the added benefit of rationally modulating the obtained materials' properties.<sup>[4–6]</sup> This can for example accomplish the synthesis of block polymers that find many applications ranging from elastomers to therapeutics.<sup>[7]</sup> In this respect many recent efforts are concerned with the development of catalytic polymerisation methodologies to access degradable heteroatom containing polymers.<sup>[8–13]</sup> In this context the concept of switchable catalysis evolved as a mechanistically elegant tool for the synthesis of heteroatom containing block polymers.<sup>[14,15]</sup> A suitable catalyst first mediates the ring-opening polymerisation (ROP) of for example lactones yielding polyesters with epoxides present in the mixture that do not undergo polymerisation until another monomer (e.g. a heteroallene) is added (Figure 1(a)). This causes the termination of ROP and the onset of heteroallene/epoxide ring-opening copolymerisation (ROCOP) to form a heteropolycarbonate ROCOP block connected to the polyester ROP polymer.<sup>[16]</sup> Switchable catalysis is enabled by the circumstance that the alkoxide resting states encountered in ROP are short living



**Figure 1.** (a)  $\epsilon$ DL ROP to CO<sub>2</sub>/epoxide switchable catalysis; (b)  $\epsilon$ DL ROP to PTA/CS<sub>2</sub>/epoxide switchable catalysis; (c) intermediate speciation of ROP and proposed intermediate speciation of ROCOP and ROTERP all involving a common alkoxide intermediate. Abbreviations:  $\epsilon$ DL =  $\epsilon$ -decalactone, BO = butylene oxide, PTA = phthalic thioanhydride, R<sub>n</sub> = polymer chain.

intermediates in ROCOP while the heterocarbonate/carboxylate resting states of ROCOP exclusively insert epoxide and not lactones due to chain-end chemoselectivities and linkage stabilities.<sup>[17–21]</sup> Recently, we realised alternating ring-opening terpolymerisation (ROTERP) of ternary monomer mixtures comprising phthalic thioanhydride (PTA), CS<sub>2</sub> or PhNCS and butylene oxide (BO) or propylene oxide (PO).<sup>[22,23]</sup> Here, simple lithium benzyloxide (LiOBn) selectively forms poly(ester-*alt*-ester-*alt*-heterocarbonates) in up to 98% selectivity with respect to the erroneous links from ROCOP (i.e. thioesters from PTA/BO ROCOP or heterocarbonates from CS<sub>2</sub>/BO or PhNCS/BO ROCOP).<sup>[24–31]</sup> The polymers show an unusual “head-to-head-*alt*-tail-to-tail” selectivity, meaning that ester groups sit next to tertiary carbon centres while heterocarbonates sit next to secondary carbon centres. We furthermore reported mechanistic switching of LiOBn catalysed  $\epsilon$ -decalactone ( $\epsilon$ DL) ROP in BO to PTA/(CS<sub>2</sub> or PhNCS)/BO ROTERP through addition of PTA and the corresponding heteroallene to polymerising  $\epsilon$ DL in BO (Figure 1(b)).<sup>[22,23]</sup> This procedure eventually forms polydecalactone (PDL)-*b*-poly(ester-*alt*-ester-*alt*-heterocarbonate) block polymers and the onset of ROTERP hence suppresses the occurrence of  $\epsilon$ DL ROP.

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/cctc.202200867>

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A preliminary investigation into the intermediate speciation of ROTERP identified that as for ROP and ROCOP alkoxide intermediates are also involved here (Figure 1(c)) implying that all three catalytic cycles could be linked together into one cascade. As noted above, we observed that the occurrence of ROTERP suppresses ROP as well as either of the parent ROCOP processes while ROCOP itself suppresses ROP which lets us hypothesise that this could enable clean mechanistic switching between all three catalytic cycles within one sequence, which we report in this contribution.

## Results and Discussion

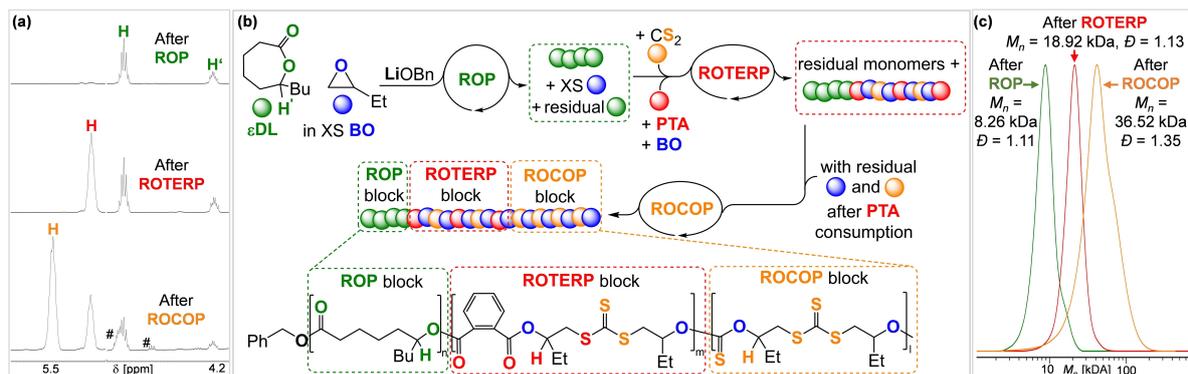
Our investigation starts from the realisation that in our previously reported  $\epsilon$ DL ROP to PTA/CS<sub>2</sub>/BO ROTERP switch an excess of BO and CS<sub>2</sub> remains in the reaction mixture after all PTA is consumed.<sup>[22]</sup> Therefore, we hypothesised that ROTERP could be followed by CS<sub>2</sub>/BO ROCOP if the catalysis is continued after full PTA consumption. Accordingly, we performed LiOBn (1 eq.) catalysed ROP of  $\epsilon$ DL (50 eq.) in BO (250 eq.) at ambient temperature for 12 min which resulted in the clean formation of PDL ( $M_n$  = 8.26 kDa,  $\bar{D}$  = 1.11). Addition of PTA (50 eq.), BO (750 eq.) and CS<sub>2</sub> (2000 eq.) results in the cessation of ROP (on the NMR detection limit as established by <sup>1</sup>H NMR aliquot analysis) and heating to 80 °C initiates ROTERP (Figure 2, SI Section S2). After 20 min full PTA consumption was established by <sup>1</sup>H NMR aliquot analysis (ESI Figure S2) which marks the completion of the ROTERP phase. A poly(ester-*alt*-ester-*alt*-trithiocarbonate) block grows increasing the molecular weight to  $M_n$  = 18.92 kg/mol ( $\bar{D}$  = 1.13). ROTERP occurs in 97% selectivity under these conditions, meaning that only 3% thioester links from erroneous co-occurring PTA/BO ROCOP and no thiocarbonate links from CS<sub>2</sub>/BO ROCOP form similar to our previous report on the stand-alone ROTERP process.<sup>[22]</sup> However after ROTERP, there remains an excess of CS<sub>2</sub> and BO left in the reaction mixture which in principle should facilitate a continuation of the polymerisation. We observed previously that after full PTA consumption in PTA/CS<sub>2</sub>/BO ROTERP the reaction

switches to CS<sub>2</sub>/BO coupling producing exclusively cyclic dithiocarbonate at 80 °C.<sup>[22]</sup> Reports by Werner and coworkers indicated however that the coupling process yields polymers at lower reaction temperature as high reaction temperatures evoke the entropically favoured production of the small molecule product.<sup>[25]</sup> Accordingly, the mixture was brought to room temperature and left to react for another 4 h during which CS<sub>2</sub>/BO ROCOP occurred confirming our initial hypothesis that switching from ROTERP to ROCOP is feasible. A polythiocarbonate block grows increasing the  $M_n$  to 36.52 kDa ( $\bar{D}$  = 1.35). It approximately comprises 43% monothio –O–(C=S)–O– and trithio –S–(C=S)–S– links respectively and 12% other (thio)carbonate links which is similar to results reported by Werner and coworkers on Li catalysed CS<sub>2</sub>/BO ROCOP.<sup>[25,32]</sup> Due to overlapping <sup>1</sup>H NMR resonances for the respective linkages, the linkage ratios were approximated by integration of the relative integrals of the quaternary carbon resonances (ESI Section S1 and Figure S5).<sup>[22,23]</sup> Hence, our  $\epsilon$ DL ROP to PTA/CS<sub>2</sub>/BO ROTERP to CS<sub>2</sub>/BO ROCOP cascade ultimately forms a PDL-*b*-poly(ester-*alt*-ester-*alt*-trithiocarbonate)-*b*-poly(thiocarbonate) with 3% ROCOP links in the ROTERP block and compositionally pure ROP and ROCOP blocks. Switchable catalysis and block polymer formation were established by a combination of methods: (i) no  $\epsilon$ DL is consumed during ROTERP and ROCOP and the <sup>13</sup>C{<sup>1</sup>H} PDL C=O NMR resonance at 173.4 ppm remains a single sharp singlet showing the cessation of ROP and the absence of transesterification processes between the ROP and ROTERP/ROCOOP blocks (ESI Figure S5); (ii) the  $M_n$  increase is consistent with the growth of existing chains rather than the initiation of new ones and also fulfils statistical consideration for block polymer formation (ESI Figure S9);<sup>[33]</sup> (iii) <sup>31</sup>P{<sup>1</sup>H} NMR end group analysis shows the consumption of all PDL end groups (ESI Figure S46);<sup>[34]</sup> (iv) the composition of the resulting block polymer remains unchanged through multiple precipitations from DCM/MeOH and THF/Pentane and (v) DOSY NMR spectroscopy shows a single diffusion coefficient for the produced polymer supporting that the blocks are joint (ESI Figure S25); (vi) DSC analysis exhibits an averaged  $T_g$  at 6.3 °C suggesting block miscibility in the solid state (ESI Figure S7) as the glass transition for the stand-alone constituents occur at  $T_g^{PDL} \approx -50.2$  °C,  $T_g^{ROTERP} \approx 22.6$  °C and  $T_g^{ROCOOP} \approx 9.0$  °C;<sup>[22,25,35]</sup> (vii) TGA analysis shows a stepwise thermal decomposition profile with two  $T_{d,onset}$  at ca. 125 °C for the ROCOP block and at ca. 300 °C for the ROP block (ESI Figure S8) which correspond well to the  $T_{d,onset}$  of the stand-alone polymers.<sup>[25,36]</sup> Employing Na or K in place of Li resulted in unappreciable PTA turnover during the ROTERP stage of the catalysis supporting that Li acts as a catalyst rather than a spectator counteraction for the OBn initiator (that we could identify to end up incorporated in the final product, ESI Figure S3). Taken together our results confirm switchable catalysis and block polymer formation and all points of this paragraph are also fulfilled for the other block polymers described in this report.

Next, we were interested to see whether our new switchable catalysis can be further expanded by another ROCOP phase between ROP and ROTERP, which would result in a ROP to ROCOP to ROTERP to ROCOP polymerisation sequence



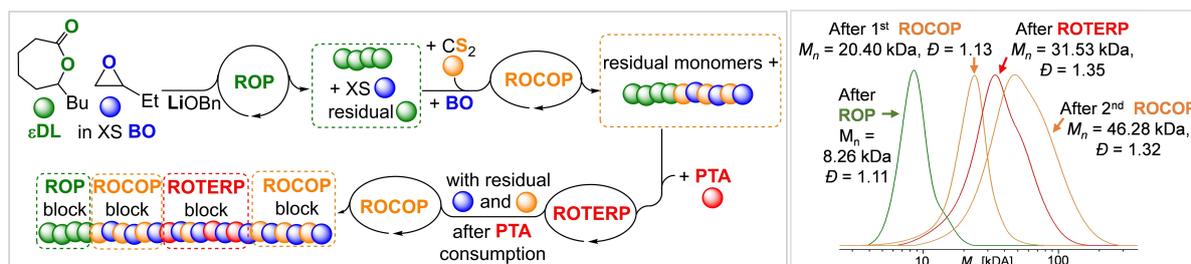
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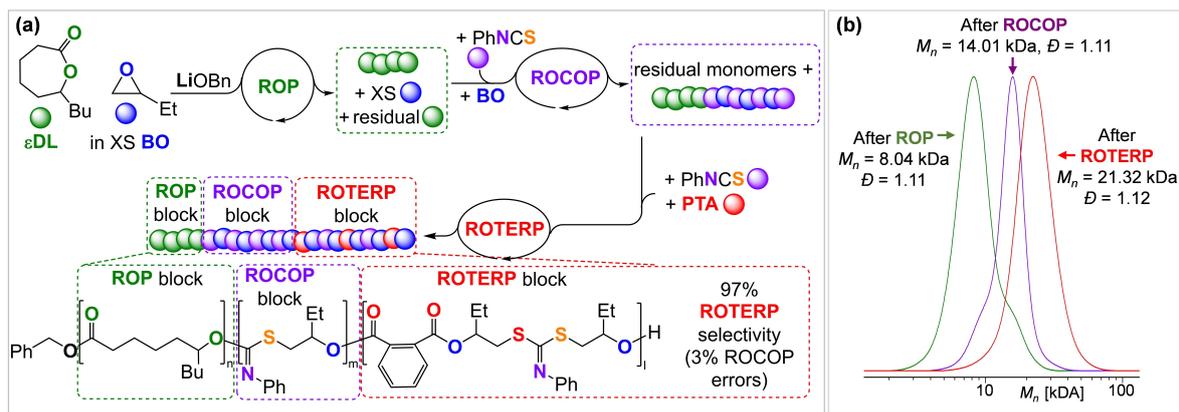
**Figure 2.** (a) Tertiary CH region of the <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, 400 MHz, 25 °C) of aliquots removed at different stages of switchable catalysis; # denotes side products of ROCOP phase. (b) Schematic of εDL ROP to PTA/CS<sub>2</sub>/BO ROTERP to CS<sub>2</sub>/BO ROCOP switchable catalysis sequence and polymer structure. (c) GPC traces of aliquots removed at different stages of switchable catalysis.

(Figure 3, ESI Section S4). Accordingly, we performed LiOBn catalysed ROP of εDL in BO under analogous conditions as outlined in the previous paragraph. Addition of CS<sub>2</sub> (2000 eq.) and BO (750 eq.) results in the cessation of ROP and the onset of CS<sub>2</sub>/BO ROCOP. Polymerisation for 35 min at ambient temperature increases the M<sub>n</sub> from 8.26 (Đ=1.11) to 20.4 kDa (Đ=1.13) and forms a poly(thiocarbonate) block as outlined above adjacent to the PDL block. Addition of PTA (50 eq.) during CS<sub>2</sub>/BO ROCOP terminates the ROCOP process and heating to 80 °C initiates ROTERP. No more scrambled thiocarbonate links (except for the ROTERP trithiocarbonate links) are generated once PTA is added and the left over εDL monomer from the terminated ROP phase also remains unconsumed during ROTERP. In reference to Figure 3 occurrence of ROTERP then forms a poly(ester-alt-ester-alt-trithiocarbonate) block from the chain end increasing the M<sub>n</sub> to 31.53 kDa (Đ=1.27). ROTERP occurs in approximately 97% selectivity under these conditions, meaning that only 3% thioester links from erroneous co-occurring PTA/BO ROCOP and no thiocarbonate links from CS<sub>2</sub>/BO ROCOP form (Figure S22). After full PTA consumption there is again an excess of unconsumed BO and CS<sub>2</sub> present in the mixture, and this enables a second mechanistic switch back to ROCOP in a last stage of the new polymerisation sequence. Hence continuing the polymerisation after ROTERP at room temperature for 16 h leads to a second ROCOP phase to form another poly(thiocarbonate) block in the same selectivity

as before increasing the molecular weight to M<sub>n</sub>=46.28 kDa (Đ=1.32). This switch cascade from ROP to ROCOP to ROTERP back to ROCOP ultimately generates PDL-*b*-poly(thiocarbonate)-*b*-poly(ester-alt-ester-alt-trithiocarbonate)-*b*-poly(thiocarbonate) with compositionally pure ROP and ROCOP blocks and a ROTERP block in approximately 97% selectivity. The polymer exhibits a T<sub>g</sub> of 13.7 °C (ESI Figure S26) and a stepwise decomposition profile with two T<sub>d,onset</sub> at ca. 130 and 300 °C (ESI Figure S27). To further substantiate our claims, we confirmed switchable catalysis and block polymer formation for the stand-alone εDL ROP to CS<sub>2</sub>/epoxide ROCOP switch (see ESI Section S3). Here, we were able to obtain a micro-phase separated PDL-*b*-poly(thiocarbonate) polymer as shown by SAXS (ESI Figure S20) exhibiting two T<sub>g</sub>'s at -45.7 °C for the PDL ROP block and at 26.2 °C (ESI Figure S18) for the ROCOP block and a similar stepwise thermal decomposition profile with two T<sub>d,onset</sub> at ca. 130 and 300 °C (ESI Figure S19).<sup>[37]</sup> Having established that ROP, ROCOP and ROTERP can be combined in switchable cascades employing CS<sub>2</sub> we were curious to see whether the same holds true for PhNCS/BO ROCOP producing poly(monothioiminocarbonates) and PhNCS/PTA/BO ROTERP producing poly(ester-alt-ester-alt-dithioiminocarbonates). Hence, we attempted mechanistic switching from εDL ROP to PhNCS/BO ROCOP to PTA/PhNCS/BO ROTERP (Figure 4, ESI Section S5). Accordingly, we added PhNCS (500 eq. per LiOBn in 250 eq. BO) to polymerising εDL (50 eq.) in BO (250 eq.) after



**Figure 3.** (a) Schematic of εDL ROP to CS<sub>2</sub>/BO ROCOP to PTA/CS<sub>2</sub>/BO ROTERP to CS<sub>2</sub>/BO ROCOP switchable catalysis sequence and polymer structure. (c) GPC traces of aliquots removed at different stages of switchable catalysis.

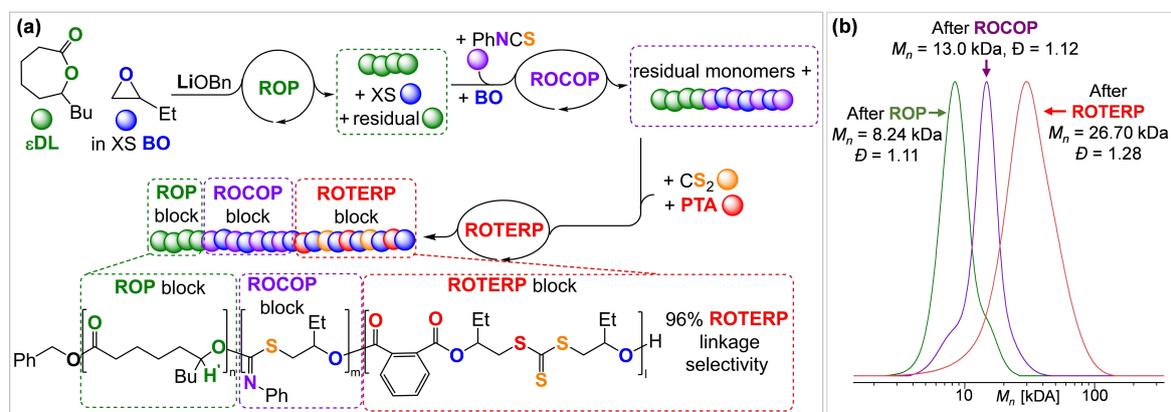


**Figure 4.** (a) Schematic of  $\epsilon$ DL ROP to PhNCS/BO ROCOP to PTA/PhNCS/BO ROTERP switchable catalysis sequence and polymer structure. (b) GPC traces of aliquots removed at different stages of switchable catalysis.

12 min at room temperature which stops the occurrence of  $\epsilon$ DL ROP and causes the onset of PhNCS/BO ROCOP. After 3.5 h at room temperature a poly(monothioimidocarbonate) block formed in >99% polymer and sequence selectivity connected to the PDL polymer, and the molecular weight of the polymer increased from  $M_n = 8.04$  kDa ( $\bar{D} = 1.11$ ) to  $M_n = 14.01$  ( $\bar{D} = 1.11$ ). Addition of PTA (50 eq.) in PhNCS (1000 eq.) stops the occurrence of ROCOP and heating to  $80^\circ\text{C}$  initiates ROTERP. After 30 min the molecular weight increased to  $M_n = 21.32$  kDa ( $\bar{D} = 1.12$ ) and a ROTERP block forms that consists of approximately 65% arylester links, 32% dithioiminocarbonate links and 1.5% erroneous thioester and monothioiminocarbonate links, respectively (Figure S33). DSC analysis of the polymer shows an averaged  $T_g = 30.7^\circ\text{C}$  (Figure S37) and TGA analysis shows a stepwise decomposition profile with a  $T_{d,onset} = 175^\circ\text{C}$  for the combined ROCOP and ROTERP block and a  $T_{d,onset} = 300^\circ\text{C}$  for the ROP block (Figure S38). Hence our  $\epsilon$ DL ROP to PhNCS/BO ROCOP to PTA/PhNCS/BO ROTERP cascade ultimately forms a PDL-*b*-poly(monothioiminocarbonate)-*b*-poly(ester-*alt*-ester-*alt*-dithioiminocarbonate) featuring compositionally pure ROP and ROCOP block and a ROTERP block in approximately

97% selectivity. Note that in this cascade stepwise addition of PhNCS is necessary (i.e. ROCOP at 1:1 PhNCS:BO and ROTERP at 3:1 PhNCS:BO). PhNCS/BO ROCOP does not occur at a 3:1 monomer feed while this feed ratio is required to achieve good sequence selectivity during ROTERP;<sup>[23]</sup> this also precludes the occurrence of a final ROCOP stage.

Knowing that both PhNCS and  $\text{CS}_2$  are suitable heteroallenes for our new switches we next attempted changing the heteroallene between the ROCOP and ROTERP stage of our polymerisation cascade (Figure 5). We previously reported that when both PhNCS and  $\text{CS}_2$  are present in a PTA/ $\text{CS}_2$ /PhNCS/BO tetrapolymerisation preferential incorporation of  $\text{CS}_2$  occurs.<sup>[23]</sup> Therefore, we hypothesised that the addition of a sufficient excess of  $\text{CS}_2$  (with PTA) to initiate ROTERP following PhNCS ROCOP could achieve a change of the preferentially incorporated heteroallene between the respective stages of our switchable catalysis. Accordingly, we added PhNCS (500 eq. per 1 eq. LiOBn in 250 eq. BO) to polymerising  $\epsilon$ DL (50 eq.) in BO (250 eq.) after 12 min at room temperature and ROCOP for 3 h at room temperature forms a poly(butylene-monothioiminocarbonate) block from the PDL polymer ( $M_n = 8.24$  kDa before



**Figure 5.** (a) Schematic of  $\epsilon$ DL ROP to PhNCS/BO ROCOP to PTA/ $\text{CS}_2$ /BO ROTERP switchable catalysis sequence featuring different heteroallenes between blocks and polymer structure. (b) GPC traces of aliquots removed at different stages of switchable catalysis.

switch ( $\bar{D}=1.11$ ),  $M_n=13.01$  kDa after switch ( $\bar{D}=1.12$ ). Addition of  $\text{CS}_2$  (1500 eq.) and PTA (50 eq.) terminates ROCOP and heating to  $80^\circ\text{C}$  causes the formation of a ROTERP block which increases the molecular weight to  $M_n=26.70$  kDa ( $\bar{D}=1.26$ ). NMR spectroscopy shows that the ROTERP block approximately contains 66.5% arylester links, 30% trithiocarbonate links, 2.5% dithioiminocarbonate links and 1% erroneous thioester links (ESI Figure S43). The presence of trithiocarbonate links resulting from a change in the incorporated heteroallene is also seen in the FTIR spectrum  $\tilde{\nu}=1064\text{ cm}^{-1}$  (ESI Figure S48) and the yellow colour of the obtained polymers both indicating the presence of  $\text{C}=\text{S}$  moieties. Therefore,  $\text{CS}_2$  was incorporated in approximately 92% selectivity over PhNCS during the ROTERP phase. DSC analysis of the polymer shows an averaged  $T_g=28.1^\circ\text{C}$  (ESI Figure S45) and TGA analysis shows a stepwise decomposition profile with a  $T_{d,onset}$  of  $175^\circ\text{C}$  for the combined ROCOP and ROTERP block and of  $300^\circ\text{C}$  for the ROP block (ESI Figure S46). Hence, our  $\epsilon\text{DL}$  ROP to PhNCS/BO ROCOP to PTA/ $\text{CS}_2$ /BO ROTERP cascade ultimately forms a PDL-*b*-poly(monothioiminocarbonate)-*b*-poly(ester-*alt*-ester-*alt*-trithiocarbonate) with compositionally pure ROP and ROCOP blocks and a ROTERP block in approximately 96% selectivity.

## Conclusions

In conclusion we have taken switchable catalysis to a new level of complexity combining three distinct mechanisms namely ROP, ROCOP and ROTERP. We could demonstrate that the occurrence of the most complex process suppresses the simpler ones, i.e. *ter*- occurring over *co*- occurring over homopolymerisation. This led us to discover switchable catalysis cascades from ROP to ROCOP to ROTERP, from ROP to ROTERP to ROCOP and from ROP to ROCOP to ROTERP to ROCOP. It furthermore allowed the incorporation of different heteroallenes in the ROCOP and ROTERP phase forming a sequence-controlled block polymer from five distinct monomers.

## Experimental Section

**Materials:** BO, PhNCS,  $\text{CS}_2$  and  $\epsilon\text{-DL}$  (all purchase from Sigma Aldrich) were dried over calcium hydride at room temperature for 3 days and then vacuum transferred or fractionally distilled under static vacuum. BnOH (Sigma Aldrich) was dried over activated 4 Å molecular sieves overnight. All liquids were then subjected to three freeze pump thaw degassing cycles and stored inside an argon filled glovebox prior to use. LiHMDS (Sigma Aldrich) was used as received. Phthalic thioanhydride was synthesized according to the literature procedure.<sup>[26]</sup> PTA was then purified by recrystallisation from  $t\text{-BuOMe}$  followed by recrystallisation from  $\text{CHCl}_3$  and two sublimations under dynamic vacuum at  $90^\circ\text{C}$  and was stored inside an argon filled glovebox prior to use. Polymerisation were performed in oven dried vial closed with a melamine-cap containing a Teflon inlay.

**$\epsilon\text{DL}$  ROP to PTA/ $\text{CS}_2$ /BO ROTERP to  $\text{CS}_2$ /BO ROCOP switch protocol:** In an argon-filled glovebox, LiHMDS (6.4 mg, 1 eq.) was dissolved in BO (0.84 mL, 250 eq.) and BnOH (4.0  $\mu\text{L}$ , 1 eq.) was added. The resulting mixture was stirred for 1 min and  $\epsilon\text{DL}$

(335.5  $\mu\text{L}$ , 50 eq.) was added and ROP was allowed to occur for 12 min. Afterwards,  $\text{CS}_2$  (4.64 mL, 2000 eq.), PTA (316.0 mg, 50 eq.) and BO (2.52 mL, 750 eq.) were added causing an immediate yellow discolouration. The mixture which was reacted at  $80^\circ\text{C}$  until the end of the ROTERP phase (established by aliquot analysis) and was then allowed to react for another 4 h at room temperature. The polymer was isolated by two consecutive precipitations from DCM/MeOH, followed by filtration and drying in a vacuum oven set to  $60^\circ\text{C}$  overnight.

**$\epsilon\text{DL}$  ROP to  $\text{CS}_2$ /BO ROCOP to PTA/ $\text{CS}_2$ /BO ROTERP to  $\text{CS}_2$ /BO ROCOP switch protocol:** In an argon-filled glovebox, LiHMDS (6.4 mg, 1 eq.) was dissolved in BO (0.84 mL, 250 eq.) and BnOH (4.0  $\mu\text{L}$ , 1 eq.) was added. The resulting mixture was stirred for 1 min and  $\epsilon\text{DL}$  (335.5  $\mu\text{L}$ , 50 eq.) was added and ROP was allowed to occur for 12 min. Afterwards,  $\text{CS}_2$  (4.64 mL, 2000 eq.) and BO (2.52 mL, 750 eq.) were added causing an immediate yellow discolouration and the mixture which was then reacted for 35 min at room temperature. PTA (316.0 mg, 50 eq.) was added, and the mixture was reacted at  $80^\circ\text{C}$  until the end of ROTERP (established by aliquot analysis). Finally, the reaction mixture was allowed to further react at room temperature for 16 h. The polymer was isolated by two consecutive precipitations from DCM/MeOH, followed by filtration and drying in a vacuum oven set to  $60^\circ\text{C}$  overnight.

**$\epsilon\text{DL}$  ROP to PhNCS/BO ROCOP to PhNCS/PTA/BO ROTERP switch protocol:** In an argon-filled glovebox, LiHMDS (6.4 mg, 1 eq.) was dissolved in BO (0.84 mL, 250 eq.) and BnOH (4.0  $\mu\text{L}$ , 1 eq.) was added. The resulting mixture was stirred for 1 min and afterwards  $\epsilon\text{DL}$  (335.5  $\mu\text{L}$ , 50 eq.) was added and ROP was allowed to occur for 12 min. Afterwards, PhNCS (2.3 mL, 19.2 mmol, 500 eq.) and BO (0.84 mL, 250 eq.) were added, and the mixture was then reacted for 3 h at room temperature. Then PhNCS (4.6 mL, 1000 eq.) and PTA (316.0 mg, 50 eq.) were added causing an immediate yellow discolouration of the mixture which was then reacted for 30 min at  $80^\circ\text{C}$ . The polymer was isolated by two consecutive precipitations from THF/pentane and DCM/MeOH, followed by filtration and drying in a vacuum oven set to  $60^\circ\text{C}$  overnight.

**$\epsilon\text{DL}$  ROP to PhNCS/BO ROCOP to  $\text{CS}_2$ /PTA/BO ROTERP switch protocol:** In an argon-filled glovebox, LiHMDS (6.4 mg, 1 eq.) was dissolved in BO (0.84 mL, 250 eq.) and BnOH (4.0  $\mu\text{L}$ , 1 eq.) was added. The resulting mixture was stirred for 1 min and afterwards  $\epsilon\text{DL}$  (335.5  $\mu\text{L}$ , 50 eq.) was added and ROP was allowed to occur for 12 min. Afterwards, PhNCS (1.1 mL, 250 eq.) and BO (0.84 mL, 250 eq.) were added, and the mixture was then reacted for 2 h at room temperature. Then,  $\text{CS}_2$  (3.5 mL, 1500 eq.) and PTA (316.0 mg, 50 eq.) were added causing an immediate yellow discolouration of the mixture which was then allowed to react for 30 min at  $80^\circ\text{C}$ . The polymer was isolated by two consecutive precipitations from THF/pentane and DCM/MeOH, followed by filtration and drying in a vacuum oven set to  $60^\circ\text{C}$  overnight.

## Acknowledgements

The VCI is acknowledged for a Liebig Fellowship for A. J. P. Prof. Dr. Christian Müller and Prof. Dr. Rainer Haag are thanked for continuous support and valuable discussions. Thomas Rybak and Prof. Dr. Bernhard Schartel (Bundesanstalt für Materialforschung Fachbereich 7.5) are thanked for DSC measurements. Glen J. Smales, Brian R. Pauw and Franziska Emmerling (Bundesanstalt für Materialforschung Fachbereich 6.3) are thanked for SAXS measurements. Open Access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** alkali metal · block copolymers · ring-opening polymerisation · sulfur-containing polymers · switchable catalysis

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Manuscript received: July 11, 2022

Revised manuscript received: August 17, 2022

Accepted manuscript online: September 16, 2022

Version of record online: October 20, 2022