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Polymers

Sequence Control in Sulphur-Containing Ring-Opening Co- and Terpolymerisations

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Abstract: Sulphur-containing polymers uniquely expand the catalogue of accessible material properties compared to current commodity materials, yet their synthesis remains underdeveloped. Combining sulphur- and oxygen-containing monomers in ring-opening copolymerisation leads to a reshuffling reaction of the sulphur centres, which has been challenging to control — a central task for reliably tailoring properties. However, very recent methodologies have emerged that not only suppress but also utilise this phenomenon to precisely access sulphur-containing polymer structures. These structures can exhibit improved degradability, chemical recyclability, refractive indices and crystallinity compared to their all-oxygen analogues. Furthermore, underutilised and even entirely untapped monomer feedstocks can become accessible as a result. This minireview aims to provide a roadmap of the tools currently available to selectively access sulphur-containing co- and terpolymer structures to enable emerging applications that leverage the chemistry of sulphur.

1. Introduction

Associated with the underlying chemistry of sulphur, sulphur-containing polymers exhibit unique material properties.[1] For example, the chemically soft lone pair of sulphur centres allows these polymers to coordinate transition metals, which can be utilised to purify contaminated water.[2,3] Furthermore, the greater lability of sulphur's covalent bonds, compared to elements from the second period (typically used in commodity polymers), not only makes these bonds easier to break but also to exchange. This renders sulphur-based materials capable of forming covalent adaptable networks, which can be thermally reshaped without added catalysts.[4] The ability to oxidise sulphur not only offers potential for chain cleavage but also allows alteration of polymer polarity and solubility.[5] Additionally, sulphur's increased molar refractivity imparts higher refractive indices to these polymers, useful, for example, in reducing the thickness of polymer lenses.[6,7] Sulphur-containing polymers can also exhibit increased semi-crystallinity compared to their all-oxygen analogues, resulting in improved mechanical performance,[8] while sulphur's greater angular flexibility can reduce ring strain in sulphur-containing heterocycles. As a direct consequence of the latter, polymers derived from the ring-opening polymerisation of such heterocycles exhibit decreased ceiling temperatures compared to their all-oxygen analogues, thus facilitating depolymerisation — an important feature in chemical recycling of polymers back to their monomers as well as dynamic and responsive behaviour.[9–18] Taken together, it is clear that incorporating sulphur centers into polymer chains not only enables unique applications but also addresses sustainability challenges that current commodity materials face. Therefore, much effort has focused on developing synthetic access to these materials beyond traditional polycondensation and vulcanization methodologies. In this regard, impressive progress has been made in the fields of inverse vulcanization and ring-opening polymerisation.[19–21] Much progress has also been made in the field of ring-opening copolymerisation (ROCOP), where a strained heterocycle is copolymerised with a second monomer. Figure 1 summarises known monomer combinations and the derived polymer structures based on epoxides and thiiranes that can be selectively assembled by a catalyst C known in ROCOP to date.

The notable advantages of ROCOP include, on one hand, the wide variety of polymer structures that are accessible, and on the other, the diverse monomers that can be used. These monomers include not only industrially relevant epoxides (such as propylene and ethylene oxide) but also many functional derivatives developed in the context of epoxide ring-opening polymerisation.[22] Moreover, ROCOP enables the formation of copolymers from monomers that do not form stable homopolymers, which is particularly relevant in the context of polymerising elemental sulphur, a waste

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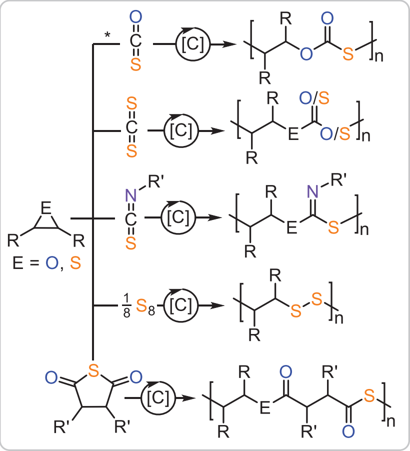


Figure 1. Examples of sulphur-containing ROCOP monomer combinations based on epoxides (E=O) and thiiranes (E=S). *only reported for epoxides. [C] = catalyst.

product of the petrochemical industry. While many sulphur-containing ROCOPs are known (previously summarised by one of the authors in 2021[23]), they can be plagued by numerous side reactions that negatively impact polymer yield, regularity of the polymer microstructure and molecular weight. These side reactions occur to a much greater extent for some monomers than for others. Recent years have seen significant progress in understanding when and why these side reactions occur. These developments not only allowed to avoid these and thereby optimise material performances, but most importantly even utilizing them to develop new classes of sequence selective terpolymerisations. Hence, this minireview aims not only to highlight recent progress in sulphur-containing ROCOP but also to shed light on the factors that govern selectivity, enabling the design of new polymerisation methodologies for degradable and functional sulphur-based materials.

2. The Oxygen–Sulphur Exchange Reaction in Epoxide ROCOP

Considering Figure 1, one might expect the ROCOP of CS_2 and epoxides to yield polydithiocarbonates featuring -O-(C = S)-S- (OSS) linkages (Figure 2a), with the oxygen atoms coming from the epoxide and the sulphur atoms coming from carbon disulfide. However, CS_2/epoxide ROCOP has proven to be more complex than anticipated. Since the first report on carbon disulfide/epoxide copolymerisation, linkages other than the expected OSS from alternating copolymerisation have been observed. Adachi and coworkers first employed Et_2Zn-based catalysts in CS_2/propylene oxide (PO) ROCOP and observed, via IR spectroscopy, significant amounts of $R_2C{=}O$ groups, such as —O—(C=O)—O— (OOO) and —O—(C=O)—S— (OOS) linkages, as part of the polymer.[24] From this point onward, the formation of linkages other than OSS will be referred to as O/S scrambling. Thereafter, both heterogenous and bicomponent transition metal and borane-based catalysts have been employed for the copolymerisation of CS_2 for a range of different epoxides and links from O/S scrambling were always observed in dominant proportions. As part of these explorations Darensbourg, Zhang and others formulated different mechanistic hypotheses on the origin of the scrambling process which all involve nucleophilic attack of an OSS link.[25–28] Although, historically many different nucleophiles (epoxides monomers, cocatalysts, chain ends) have been proposed to lead to this pathway, the following most robust mechanistic hypothesis emerged in recent years.

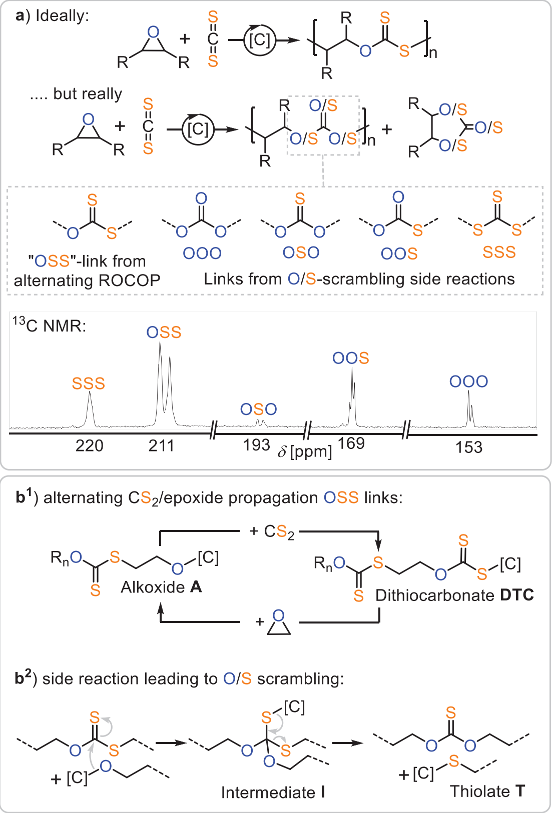
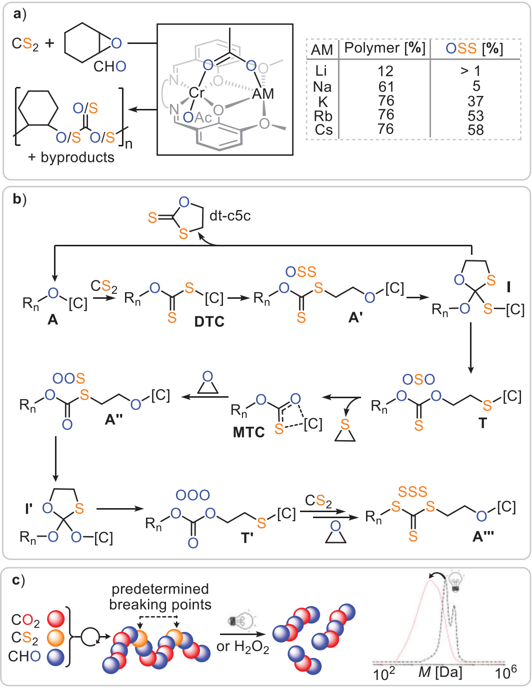


Figure 2. a) Product distribution observed in the reaction of CS_2 with epoxides and various catalysts [C]; the inlay shows zoom into the quaternary carbonyl $R_2C{=}O/S$ region of a typical ^{13}C NMR spectrum of an isolated CS_2/epoxide copolymer. Reaction pathways leading to (b^1) alternating OSS links as well as (b^2) O/S scrambled links. Figure adapted from ref. [24] under CC BY 4.0.

As shown in Figure 2b, alternating CS_2 and epoxide insertion produces catalyst-bound dithiocarbonates **DTC** and alkoxides **A** through alternating insertion, creating the OSS links. However, if an alkoxide **A** reacts with an OSS link from, for example, another polymer chain, a tetrahedral intermediate **I** forms, which then collapses to generate a thiolate **T** and an OSO link. In this reaction sequence, the polymer link is effectively enriched in oxygen, transforming OSS to OSO. Propagation of the thiolate by CS_2 insertion results in a sulphur-enriched —S—(C=S)—S— (SSS) link. Although, this hypothesis provides a solid starting point, it does not explain all observed linkages. To address this, our group recently reported a comprehensive study on CS_2/cyclohexene oxide (CHO) ROCOP using a series of heterobimetallic



AM	Polymer [%]	OSS [%]
Li	12	> 1
Na	61	5
K	76	37
Rb	76	53
Cs	76	58

Figure 3. a) CS_2/CHO ROCOP catalysed by a series of heterobimetallic CrAM catalysts.[29] b) DFT modelled propagation pathway explaining O/S scrambling for ethylene oxide EO to reduce computational cost. c) Statistical CO_2/CS_2/CHO terpolymerisation installing predetermined breaking points into polycarbonate; overlaid GPC traces before and after irradiation. Figure adapted from ref. [24] under CC BY 4.0.

CrAM catalysts (AM = Li, Na, K, Rb, Cs), which completed the mechanistic understanding of O/S scrambling (Figure 3a).[29]

Moving down the periodic table from Li to Cs revealed that an improvement in polymer selectivity (versus cyclic dithiocarbonate dt-c5c) is associated with increased OSS selectivity (i.e., less O/S scrambling), supporting the idea that the reaction pathways leading to dt-c5c and O/S scrambled links are mechanistically related. Importantly, in the all-oxygen ROCOP, cyclic byproducts are known to form via so-called backbiting, in which alkoxide intermediates react with polymer links directly adjacent to the chain end.[30] Model reactions revealed that the reaction between metal alkoxides and organic (di)thiocarbonates results in the formation of oxygen-enriched metal carbonates and thiirane byproducts, which are sulphur-containing analogues of epoxides. The latter could also be identified as byproducts of the CS_2/CHO ROCOP, providing key information to complete the mechanistic picture for the O/S scrambling mechanism shown in Figure 3b.

The key extension of the previous mechanistic hypothesis is that alkoxides **A'** formed following epoxide insertion from **DTC** react with dithiocarbonate OSS links directly adjacent to the chain end to form a cyclic version of intermediate **I**. This then collapses into a thiolate **T** that sits adjacent to an OSO. Furthermore, catalyst-bound thiolates can eliminate thiiranes to form catalyst-bound thiocarbonates **MTC** that propagate and undergo analogous O/S scrambling at the chain end (forming thiolate **T'** sitting adjacent to an OOO link). O/S scrambling is thermodynamically favourable, as indicated by density functional theory, likely due to the accumulation of negative charge on the larger sulphur centers. In the context of O/S scrambling, it should be noted that, Zhang reported for COS/PO ROCOP that scrambling can also stem from catalysed COS hydrolysis into CO_2, which itself serves as a monomer to produce, for example, all-oxygen carbonate (OOO) linkages, highlighting the potential for these pathways to be also at play in CS_2 ROCOP.[31] Due to the mechanistic similarity of all heteroallene/epoxide copolymerisations, CS_2/CHO ROCOP could be combined with CO_2/CHO ROCOP in a CO_2/CS_2/CHO terpolymerisation (Figure 3c). In this case, OOO linkages predominantly form due to kinetically favoured CO_2 insertion. Nevertheless, the scrambled sulphur-containing linkages rendered the polymer oxidatively and photochemically labile—degradability pathways that are not accessible to the all-oxygen polycarbonate analogue. This highlights a larger concept: introducing a few sulphur centers into oxygen-containing polymers can act as predetermined breaking points to enhance degradability.

An alternative approach to sulphur-containing copolymers from epoxides is the ring opening copolymerisation with cyclic phthalic thioanhydride (PTA) producing semiaromatic materials comprising ester and thioester links (Figure 4). Although alternating propagation would precisely yield ester-*alt*-thioester, Ren and coworkers also observed the formation of diester and dithioester links in the polymer chain of PTA/PO copolymer from bicomponent catalysis ($M_{n,max.} = 60\ kg\ mol^{-1}$, $Đ = 1.4$) based on the commercial SalCyCr(III)Cl/ nitridobis(triphenylphosphan)chlorid (PPNCl) catalyst pair.[33] This observation is reminiscent of O/S-scrambling in CS_2 ROCOP likewise producing linkages enriched (dithioester) and depleted (diester) in sulphur compared to the perfect sequence. Figure 4c shows the mechanistic hypothesis developed later by our group (see below) featuring an O/S-scrambling mechanism at the propagating chain end via a cyclic intermediate **I** that transforms an alkoxide chain end **A'** into a thiolate chain end **T**. At higher reaction temperatures, other erroneous links that presumably form through thiirane elimination pathways in analogy to CS_2/epoxide ROCOP were also observed. Yet low reaction temperature and catalysts based on ligand scaffolds with tethered cocatalysts could suppress these side reactions for PTA/PO ROCOP ($M_{n,max.} = 50\ kg\ mol^{-1}$, $Đ = 1.2$) and also yielded strictly alternating ester-*alt*-thioester from a range of other epoxides.[34]

Li and coworkers reported a bicomponent catalyst based on an Al(III) complex featuring a bipyridine-based tetradentate N,N,O,O ligand system that also suppressed O/S scrambling in PTA/PO polymerisation ($M_{n,max.} = 54\ kg\ mol^{-1}$, $Đ = 1.4$), allowing the use of a wide range of epoxides.[35,36] Mixtures of PTA, phthalic anhydride (PA), and PO resulted in block copolymer formation, where the PA/PO polyester block formed before the PTA/PO block (Figure 5a), even though the latter reaction occurred faster in the stand-alone ROCOP. This observation can be rationalised by the fact that alkoxide intermediates (which both polymerisations share from PO ring-opening) chemoselectively insert into PA over PTA due to the higher partial positive charge on the carbonyl center

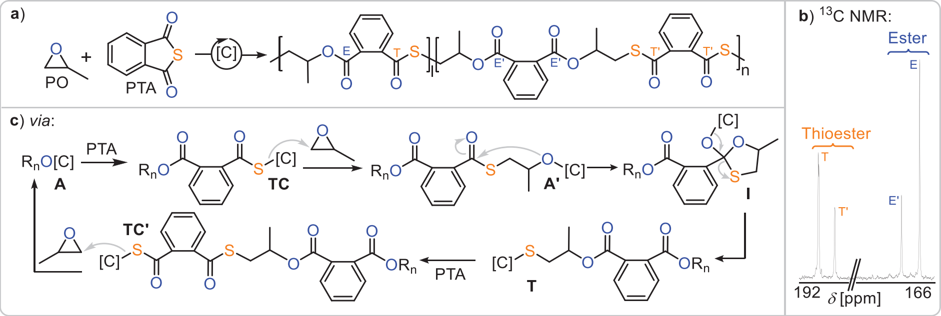


Figure 4. a) Product distribution of PTA/epoxide. b) Zoom into the quaternary carbonyl $R_2C{=}O$ region of a typical ^{13}C NMR spectrum of an isolated PTA/epoxide copolymer. c) Mechanistic hypothesis explaining the resonance distribution observed in the ^{13}C NMR spectrum. Figure adapted from ref. [32] under CC BY 3.0.

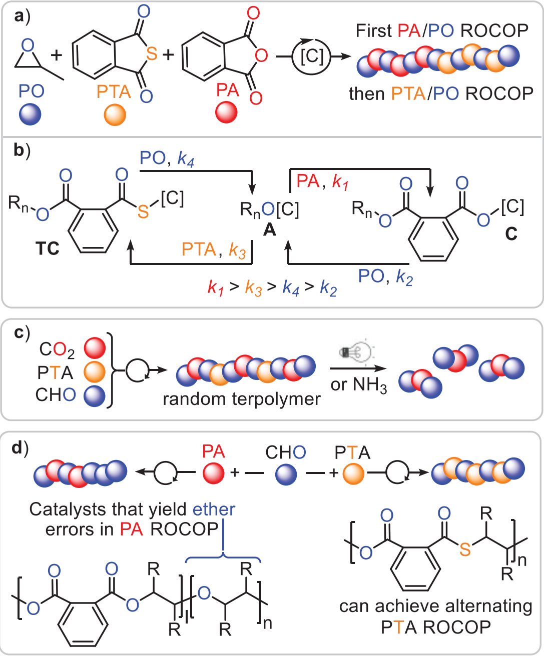


Figure 5. a) Blockpolymerisation from mixtures of PA, PTA and PO. b) Relative rate of individual insertion events explaining the blockpolymer formation. c) Random terpolymer formation CO_2, PTA and CHO. d) Comparing PA with PTA ROCOP employing the same family of heterobimetallic Al(III)M catalysts (M = (Earth)alkalimetal).

of PA, making it more susceptible to nucleophilic attack by alkoxide intermediates (Figure 6a).

In our own research, we terpolymerised PTA and CO_2 with CHO using heterobimetallic catalysts and observed statistical terpolymer formation in which the links from PTA/CHO deviated from strict ester-*alt*-thioester alternation, resulting in more ester than thioester links.[37] We identified this deviation to occur via a thiirane elimination pathway, which led to oxygen-enriched terpolymers. Nevertheless, the randomly distributed thioester links in the polymer main chain enhanced degradability upon UV irradiation as well as through aminolysis with ammonia. Moving from Chromium(III)-based heterobimetallics to Aluminum(III)-based catalysts within the same ligand scaffold led to at least a 10-fold activity enhancement in PTA/CHO ROCOP.[38] Employing 4-vinyl-substituted CHO allowed us to achieve a maximum M_n of 67.2 kDa ($Đ$ = 1.4). Interestingly, comparative assessment of alkali, alkaline earth metals and lanthanum as the second metal in PA and PTA/CHO ROCOP revealed that some catalysts produced ether defects in the polyester from PA ROCOP, resulting from erroneous CHO homopropagation. In contrast, the very same catalysts were able to achieve alternating PTA/CHO ROCOP with minimal amounts of scrambling. While the underlying reasons remain to be fully understood, it appears that moving to sulphur-containing monomers provides intrinsic sequence-selectivity benefits.

3. Reducing O/S Scrambling in Oxetane ROCOP

Although SalcyCrCl-based catalysts yielded heavily O/S scrambled copolymers alongside cyclic six-membered trithiocarbonate byproducts in the first attempt at CS_2/oxetane (OX) ROCOP, a heterobimetallic analogue combining a SalCy pocket for Cr(III) coordination with a 18-crown-6 pocket for K coordination produced a copolymer with up to 96% OSS linkages and 99% polymer selectivity (see Figure 6).[27,39] This led to an up to 7-fold improvement in the maximum obtainable molecular weight (M_n = 100 kg mol^{-1}, $Đ$ = 1.6) over the previous state of the art catalysts. Both, the choice of metals and fixing both metals within the same ligand scaffold were critical in achieving the highest selectivity. The report further emphasised the importance of selective catalysis to enhance material properties, as the polymer microstructure strongly influenced the thermal and mechanical properties of the materials. While the O/S scrambled polymers were amorphous with a T_g of −29 °C, the polymers with high OSS selectivity were semicrystalline with a T_m of 90 °C (and a T_g of −17 °C). Thus, sequence-controlled polymers can be processed into flexible films, whereas scrambled polymers cannot. The semicrystallinity is particularly noteworthy, as the all-oxygen counterpart polytrimethylene carbonate (with all OOO linkages) is also an amorphous polymer, highlighting that replacing oxygen with sulphur centers in otherwise isostructural polymers can lead to improved thermal and mechanical properties.[40,41]

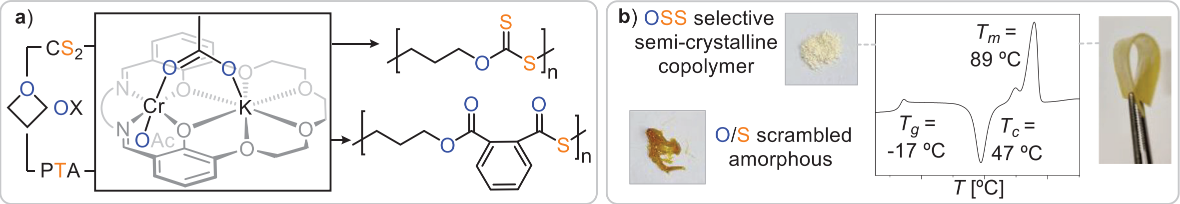


Figure 6. a) Selective OX ROCOPs based on Oxetane (OX). b) Sequence selective CS_2/OX ROCOP resulting in semi-crystalline materials whereas O/S scrambling yields an amorphous material. Figure adapted from ref. [29] under CC BY 4.0.

Furthermore, we found that, compared to all-oxygen polycarbonates, polytrimethylene dithiocarbonate undergoes more facile depolymerisation due to the decreased ring strain exhibited by sulphur-containing heterocycles. In parallel, Zhang reported that triethylborane/PPNCl organocatalysts mediate quantitative polymer formation and up to 98% sequence selective CS_2/OX ROCOP at room temperature ($M_{\mathrm{n,max.}} = 40\ \mathrm{kg\ mol^{-1}}$, $Đ = 1.7$).[42] Computational studies indicated that while CS_2 insertion only requires the aid of one borane, both the catalyst bound dithiocarbonate chain end and the incoming oxetane monomer require borane activation in the rate determining step of the polymerisation which could be confirmed experimentally as such that a 2:1 BEt_3/PPNCl ratio showed superior activity to a 1:1 ratio.

Moving to the synthesis of polythioesters, our group reported that heterobimetallic CrAM catalysts (AM=Na, K, Rb), based on the macrocyclic ligand scaffold mentioned above, deliver alternating poly(ester-*alt*-thioesters) from PTA and OX.[43] In contrast to their performance in CS_2/OX ROCOP, all alkali metals, as well as catalysts where both metals are coordinated by different ligand scaffolds, produced perfectly alternating semicrystalline ($T_m = 88\ °C$) copolymers. Higher maximum molecular weights ($M_{\mathrm{n,max.}} = 139\ \mathrm{kg\ mol^{-1}}$, $Đ = 1.3$) could be achieved than previously reported for PTA ROCOPs alltogether.

Subsequently, we confirmed that PTA/OX ROCOP is highly catalyst-tolerant, as all investigated systems—including bicomponent SalCyMCl (M=Cr(III), Al(III)) or BEt_3 catalysts in combination with PPNCl cocatalysts—yield perfectly alternating copolymers.[32] By systematically comparing PTA ROCOP with oxetanes, epoxides and thiiranes using a heterobimetallic CrK catalyst, we identified factors that lead to high sequence selectivity in OX ROCOP. Backbiting reactions occur to a lesser extent when heterocycles are used that produce primary alkoxide chain ends upon ring opening. This means that ethylene oxide, ethylene sulfide, oxetane and 3,3′-disubstituted oxetanes are particularly suited monomers in sulphur-containing ROCOP. Computational studies revealed that for epoxides, PTA insertion is exergonic for ring-opening by primary alkoxides, while it is endergonic for secondary alkoxides. Furthermore, bicyclic epoxides kinetically disfavour backbiting by leading to strained intermediates. Nevertheless, the ROCOP must be terminated in a timely manner, ideally before complete monomer conversion, as intermolecular scrambling pathways can disrupt polymer chains even after the polymerisation has finished. Capitalizing on this circumstance, we then used BEt_3 in conjunction with KOAc to achieve selective PTA/OX ROCOP, with performance further boosted by coordinating K with 18-crown-6.[44]

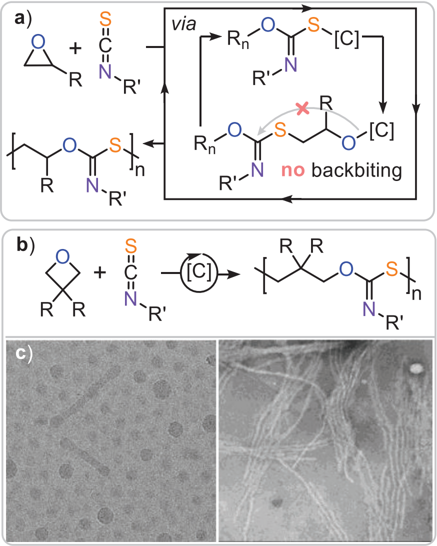


Figure 7. a) Isothiocyanate/epoxide ROCOP selectively yielding thioimidocarbonates without the occurrence of O/S scrambling. b) Isothiocyanate/oxetane ROCOP and c) self-assembled nanostructured by on derived diblock copolymers. Figures adapted from ref. [50] under CC BY 4.0.

4. Reducing O/S Scrambling in Isothio-Cyanate ROCOP

Some heteroallenes are intrinsically resistant to O/S scrambling, such as carbonyl sulfide (COS), for which many highly selective copolymerisations have been developed and reviewed in the past.[45] However, COS is a toxic gas and, for example, is not commercially available in Europe. In recent years, isothiocyanates, valuable building blocks in thiirane ROCOP as for example demonstrated by *Wu*,[46,47] have emerged as suitable monomers that, like COS, undergo less O/S scrambling with epoxides and oxetanes.

Both simple lithium salts and BEt_3-based bicomponent catalysts yield poly(monothioimidocarbonates) featuring —O—C(=NR)—S— thioimidocarbonate links instead of the theoretically possible —O—C(=S)—NR— thionourethane links (Figure 7).[48,49] This occurs on a kinetic basis, as the formation of thionourethane links is thermodynamically more stable but associated with higher insertion barriers during the epoxide ring-opening step. Maximum molecular weights of $M_{n,max.} = 59$ kg mol^{-1} ($Đ = 1.1$) were achieved from PhNCS and PO, although a variety of other epoxides, as well as different aromatic and aliphatic RNCS, were also successfully copolymerised, yielding amorphous copolymers with glass transition temperatures ranging from −36 °C to 120 °C. Some of the resulting poly(thioimidocarbonates) (EtNCS-co-CHO) could be used as positive resists for electron beam lithography, outperforming commercially used poly(methyl methacrylate) in terms of sensitivity (130 versus 180 µC cm^{-2}). These materials could also be utilised in the construction of two-dimensional photonic crystals. Furthermore, PhNCS/PO ROCOP could be combined with PA/PO ROCOP, where ternary mixtures of PA, PhNCS and PO resulted in block copolymer formation, similar to the previously discussed PA/PTA/PO terpolymerisation. In this process, PA/PO ROCOP occurs first, forming a polyester block, followed by PhNCS/PO ROCOP, which forms imidothiocarbonate blocks.

In our own research, we reported on the ROCOP of RNCS with oxetanes under heterobimetallic CrRb catalysis, which proceeded without O/S scrambling, though minor amounts of the kinetic thionourethane —O—C(=S)—NPh— links were formed alongside the dominant (>90%) thioimidocarbonates —O—C(=NPh)—S—.[50] High maximum molecular weights of $M_{n,max.} = 124$ kg mol^{-1} ($Đ = 1.7$) were achieved for PhNCS/OX, and this monomer combination also exhibited high melting points of 178 °C. While aryl-substituted RNCS yielded semi-crystalline materials, the aliphatic cyclohexyl analogue, produced amorphous materials when copolymerised with oxetanes. PhNCS generally resulted in narrower molecular weight distributions than CS_2 under similar conditions with oxetanes, making this monomer combination particularly useful for constructing block copolymers. By adding mPEG-OH macroinitiators as chain transfer agents, amphiphilic block copolymers were formed, which could be assembled into various morphologies (micelles, worms, cylinders, platelets) through (crystallisation-driven) self-assembly. Analogous block polymers could be formed from aryl substituted isothiocyanates and also PTA as a comonomer forming self-assembled structures in water in which transition metal salts and complex fragments could be coordinated by the sulphur-containing cores.[51] In contrast, CS_2/oxetane ROCOP in the presence of chain transfer agents led to substantial scrambling which, in light of results in oxygenated ROCOP implies that scrambling also occurs via off catalyst pathways via initial decoordination of the chain end.[52]

5. Controlling O/S Exchange in Sequence Selective Terpolymerisation

Although O/S scrambling has mostly been considered a complication, it also presents an opportunity by introducing chemical complexity that, if controlled, could provide access to unique polymer sequences. In this context, a landmark report by *Werner* and *Komber* demonstrated that lithium alkoxide catalysts deliver polymers consisting of alternating

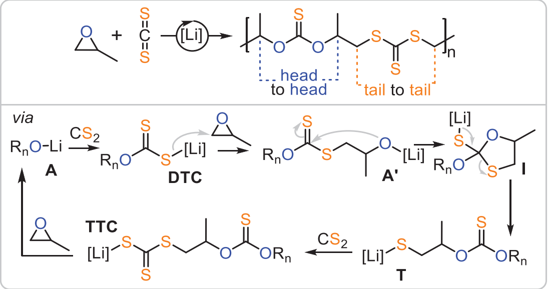


Figure 8. Lithium catalysed CS_2/PO copolymerisation delivering a poly(OSO-*alt*-SSS) sequence.

OSO and SSS links from CS_2 and PO (Figure 8).[28] In these polymers, the OSO links are connected to the CHR_3 "head" positions of the ring-opened PO, while the SSS links are connected to the CH_2R_2 "tail" positions of the ring-opened PO. These links are formed with up to 92% sequence selectivity, reaching molecular weights up to $M_n = 109$ kDa ($Đ = 1.8$). The formation of these links can be rationalised by a propagation pathway in which "tail-selective" PO ring-opening by **DTC** occurs, forming a secondary alkoxide **A'** that rapidly backbites into an adjacent OSS link to create the cyclic intermediate **I**. This intermediate then collapses into a primary thiolate **T**, which propagates by inserting CS_2 and forming a metal-bound trithiocarbonate **TTC**, which tail-selectively inserts PO to complete the cycle. Essentially, this report demonstrated that simple lithium salt catalysts can mediate O/S exchange in a highly selective manner—a feat that other catalysts could not achieve—making it all the more remarkable given their simplicity.

Building upon the concept of accessing unique polymer sequences through O/S exchange, our group serendipitously discovered that LiX (X=OCH_2Ph, $N(SiMe_3)_2$) achieves the formation of poly(ester-*alt*-trithiocarbonates) from mixtures of PTA, CS_2 and PO (Figure 9) with up to 98% sequence selectivity and high maximum molecular weights ($M_{n,max.} = 111$ kg mol^{-1}, $Đ = 1.8$). These polymers are amorphous ($T_g = 34$ °C), yellow (due to the C=S chromophore) and exhibit good refractive indices around 1.6.[53] Resembling *Werner*'s and *Komber*'s copolymer, the oxygen-rich ester groups are connected to the CHR_3 head positions of the ring-opened PO, while the sulphur-rich trithiocarbonate groups are connected to the CH_2R_2 tail positions, forming a head-to-head-*alt*-tail-to-tail microstructure. The mechanism, as shown in Figure 8, necessitates near-complete O/S scrambling of lithium alkoxides adjacent to thioesters, as well as selective CS_2 over PTA insertion by lithium thiolates **T** and selective PTA over CS_2 insertion of lithium alkoxides **A** adjacent to trithiocarbonates. A combined experimental and computational study demonstrated that although both PTA and CS_2 can be inserted by both lithium alkoxide **A** and thiolate **T**, selective insertion occurs on a kinetic basis.[54] Alkoxide **A** inserts PTA orders of magnitude faster than CS_2, while the reverse is true for thiolate **T**. Furthermore, lithium acts as a true catalyst rather than a spectator counterion, as attempts to employ sodium or potassium instead led to poor performance. This can be rationalised by single crystal XRD analysis of

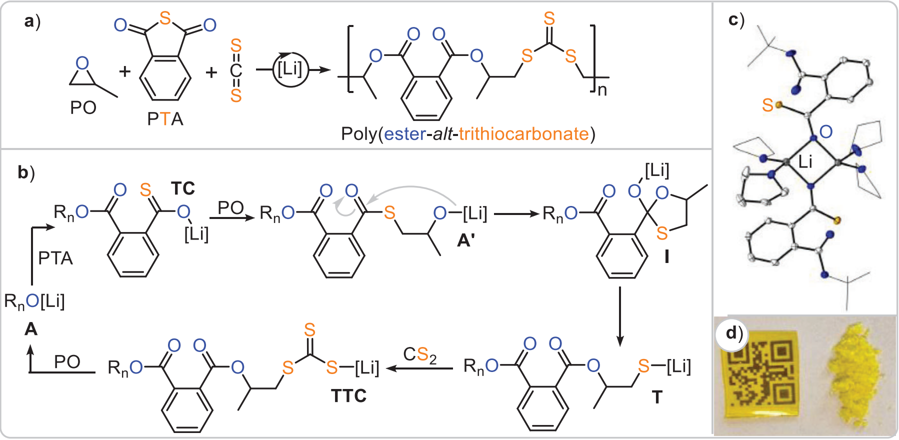


Figure 9. a) Lithium catalysed PTA/CS_2/PO ROTERP delivering poly(ester-*alt*-trithiocarbonates) in a head-to-head-*alt*-tail-to-tail regioselectivity. b) Experimentally and computationally substantiated mechanistic hypothesis. c) Crystal structure of the suspected lithium thiocarboxylate resting state. d) Photograph of the obtained polymer as a free-standing film and powder. Figure adapted from ref. [53] under CC BY 3.0.

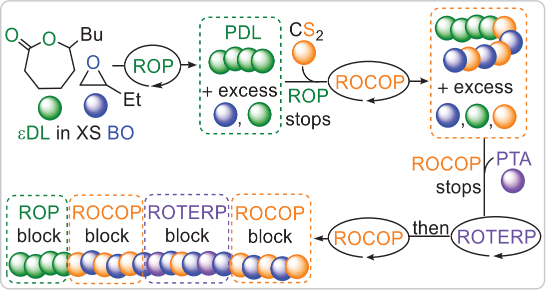


Figure 10. One-pot block polymerisation combining ROP, ROCOP, and ROTERP for multiblock polymer synthesis. Figure adapted from ref. [56] under CC BY 4.0.

model thiocarboxylate intermediates **TC**, identified as the catalytic resting state, which revealed dimeric structures where the sulphur centers remain uncoordinated and accessible for propagation. Additionally, the high oxophilicity and flexible coordination chemistry of lithium enable monomeric, dimeric and charge-separated transition states, all active in various propagation steps, explaining the unique role of the lithium catalyst. As it turned out a series of monomer combinations and blockpolymerisations on the basis of this sequence selective ring-opening terpolymerisation (ROTERP) could be identified.

Similarly, mixtures of PTA, PhNCS, and butylene oxide (BO) selectively formed poly(ester-*alt*-dithioimidocarbonates) ($M_{n,max.} = 14$ kg mol^{-1}, Đ = 1.5), featuring and —S—(C=NPh)—S— link albeit with a reduced sequence selectivity of ca. 90%. These new sequence-selective ROTERPs could then be employed for the design of one-pot block polymerisation.[55,56] For example, lithium alkoxide-catalysed ε-decalactone (εDL) polymerisation in BO as a solvent could be continued with CS_2/BO ROCOP by the addition of CS_2, followed by PTA/CS_2/BO ROTERP with the subsequent addition of PTA, which switched back to ROCOP once PTA was depleted, ultimately forming tetrablock polymers (Figure 10).

Importantly in the above mentioned ROTERPs, the monomers which are combined in the terpolymerisation are mutually compatible meaning that the ROTERP effectively represents the combination of two ROCOPs, e.g. CS_2/PTA/PO ROCOP combining CS_2/PO and PTA/PO ROCOP which can be both achieved individually by the lithium catalyst. Going beyond that, we hypothesised that the lithium thiolate intermediates generated during O/S exchange could facilitate the incorporation of monomers in terpolymerisation with epoxides that otherwise wouldn't undergo ROCOP with epoxides. In this regard, elemental sulphur S_8, a megaton waste product from the oil refining process, serves as a suitable ROCOP monomer when combined with thiiranes but not with epoxides (Figure 11a).[57,58] As originally demonstrated by *Penczek* and *Duda*, and refined by *Lu* and *Ren*, thiolate intermediates generated from the ring-opening of thiiranes can activate elemental sulphur, ultimately forming polysulfide polymers of the form $[CR_2CR_2S_x]_n$, where the sulphur rank x can be controlled by adjusting the amount of initially supplied sulphur. Since thiolates are also generated during O/S scrambling, they should, in principle, allow for the activation of S_8 as well. Realizing this concept, we reported the lithium-catalysed ROTERP of S_8 with CS_2 and epoxides, producing poly(OSO-*alt*-S_x) ($M_{n,max.} = 30$ kg mol^{-1}, $Đ = 1.5$) with up to 99% sequence and 90% polymer selectivity (Figure 11b^1).[59] While S_8 ROCOP requires expensive thiirane comonomers, ROTERP enables polymer formation of S_8 using industrially available epoxides and CS_2. Carbon disulfide is 84 wt% sulphur and obtained from elemental sulphur waste itself. Compared to the parent reaction of CS_2 with epoxides, the addition of sulphur led to increased polymer yields, particularly at higher reaction temperatures, where, without S_8, no polymer and only cyclic dithiocarbonate was obtained. Concerning the mechanism, although CS_2 insertion by thiolate intermediates **T** to yield lithium trithiocarbonates, **TTC** was thermodynamically more favourable than S_8 insertion to form polysulfide intermediates **PS**, propagation from the latter showed lower energy barriers in its reaction with PO (Figure 11b^2).

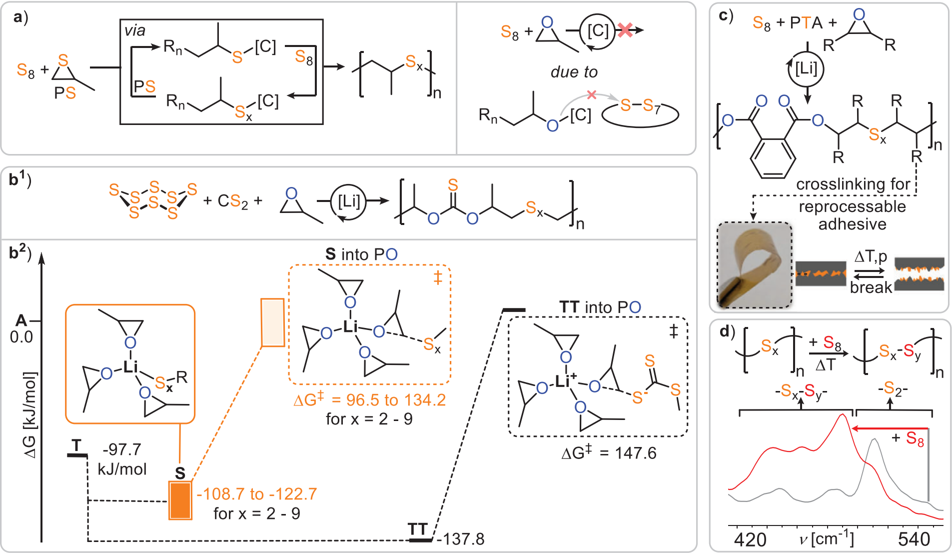


Figure 11. a) S_8/thiirane ROCOP involving catalyst bound thiolate and polysulfide intermediates. Hypothetical S_8/epoxide ROCOP prevented by thermodynamically unfavourable alkoxide insertion into -S—S- bond. b^1) S_8/CS_2/PO ROTERP as well as (b^2) energetics of selectivity determining step. c) S_8/PTA/PO ROTERP and example applications of crosslinked derivatives as thermally reprocessable adhesives. d) Thermally activated S_8 insertion into polyester backbone with associated Raman spectra of the -S_x- region before and after S_8 insertion. Figures adapted from ref. [59] under CC BY 4.0. under and ref. [60]

Thereafter, a substantial improvement in scope and material properties was achieved through the terpolymerisation of PTA with S_8 and a wide range of epoxides, again enabled by O/S exchange (Figure 11c).[60] Poly(ester-*alt*-S_x) with up to quantitative polymer and sequence selectivity ($M_{\mathrm{n,max.}} = 33$ kg mol^{-1}, $Đ = 1.7$) could be prepared. This process tolerated a wide range of epoxides, including challenging monomers such as industrially relevant epichlorohydrin, geminally and vicinally disubstituted epoxides, and natural product-derived vanillin glycidyl ether.

Capitalising on the large monomer scope the glass transition temperatures of the resulting polymers could be tuned from ca. −40 °C up to 130 °C. Furthermore, the good thermal stability of the polymers, enabled the thermal activation of the S_x links to insert additional S_8 (Figure 10d). Even lipoic acid carrying carboxylic acid functionalities which would be intrinsically incompatible with the ROTERP methodology could be introduced via thermal insertion post-polymerisation. Crosslinking the pendant aldehyde groups in the vanillin-derived terpolymers with diamines produced mechanically robust and thermally processable covalent adaptable networks. These networks could be applied as adhesives for stainless steel and wood, whereas addition of lipoic acid into the network via sulphur–sulphur bond metathesis substantially improves adhesive performances on aluminum.

6. Sugar Derived Oxetanes

Clearly, sulphur-containing ROCOP and ROTERP are establishing themselves as useful methodologies. However, the monomers outlined above, including elemental sulphur itself, are petrochemically derived. Given the projected necessity of transitioning to bio-based monomer feedstocks, achieving copolymerisation with such monomers is an intermediate requirement. In this context, bicyclic oxetanes can be obtained from acetal-protected xylose in two synthetic steps. Turning these into sulphur-containing copolymers (Figure 12), *Buchard* reported the ROCOP with CS_2, yielding a polymer with an poly(OSO-*alt*-SSS) microstructure in 95% sequence selectivity and 90% polymer selectivity ($M_{\mathrm{n,max}} = 14$ kg mol^{-1}, $Đ = 1.8$) using a SalcyCrCl/PPNCl bicomponent catalyst.[61] Both temperature and catalyst choice drastically affected the selectivity, with OSS and thioether linkages also being observed. These polymers were UV-degradable, and the degradation process was accelerated by the addition of silanes. *Wooley* and *Darensbourg* found that temperature-controlled O/S scrambling could be achieved

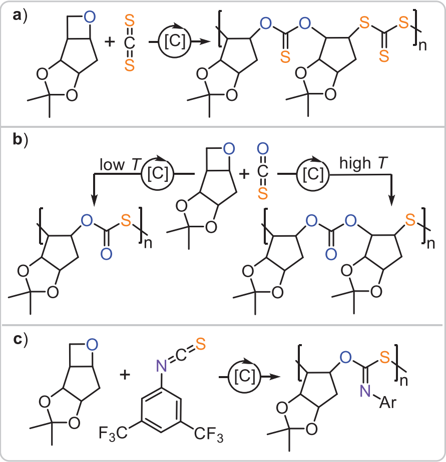
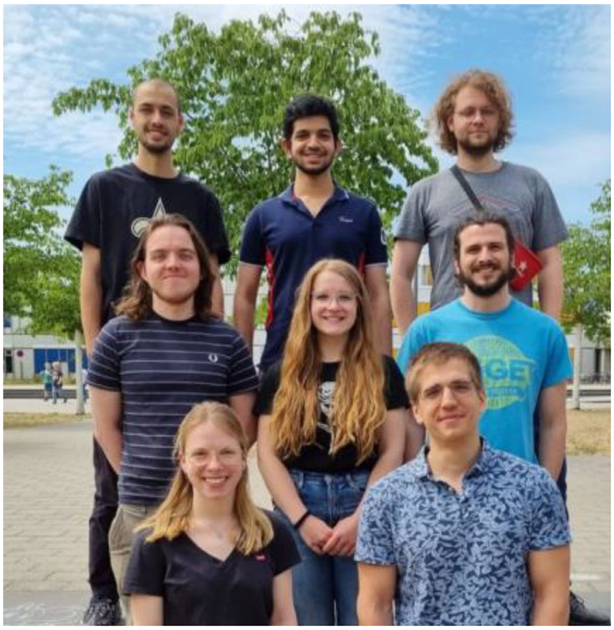


Figure 12. ROCOP of bicyclic Xylose derived oxetane with a) CS_2, b) COS with and c) 3,5-$(CF_3)_2$PhNCS.

in SalcyCrCl/PPNCl-catalysed COS copolymerisations.[62] At 40 °C alternating poly(monothiocarbonates) ($M_n = 3$ kg mol^{-1}, $Đ = 1.2$) featuring OSO links were produced. Increasing the reaction temperature to 120 °C yielded poly(carbonate-*alt*-thioethers) ($M_{n,max} = 28$ kg mol^{-1}, $Đ = 1.2$). Compared to their oxygen-only polycarbonate counterparts, the polymer produced by complete O/S scrambling substantially increased thermal stability achieving a $T_{d,onset}$ of around 310 °C. This enhanced stability may result from the suppression of depolymerisation pathways to cyclic six-membered heterocarbonates, with thioether groups intercepting the carbonate moieties, underscoring the potential for controlled scrambling to even enhance material properties. Relatedly, *Zhang* thereafter reported PPNCl/BEt$_3$ bicomponent catalysis to facilitate alternating COS ROCOP without O/S scrambling at temperatures below 60 °C ($M_{n,max} = 17$ kg mol^{-1}, $Đ = 1.8$).[63] *Buchard* reported the ROCOP with 3,5-bis(trifluoromethyl)-substituted PhNCS under bicomponent aluminium trisphenolate/PPNCl catalysis, selectively yielding poly(monothioimidocarbonates) ($M_{n,max.} = 35$ kg mol^{-1}, $Đ = 1.7$). This polymerisation approach also allowed the ROCOP with aliphatic RNCS, terpolymerisations with bifunctional RNCS to produce crosslinked materials, and block polymers via either a macroinitiator or a stepwise monomer addition strategy.[64]

7. Conclusion and Outlook

In summary, sulphur-containing ROCOP and ROTERP enables the efficient and selective formation of entirely new and complex polymer microstructures from relatively simple monomers through controlled O/S scrambling reactions. Key future objectives must prioritise achieving greater control over molar mass and chain-ends, as none of the polymerisations presented above, despite being anionic, are strictly living. Broadened polydispersities, multimodal distributions, and significant deviations from theoretical molecular weights are common. Additionally, methodologies granting control over tacticity require further attention.[65–70] Achieving such control would not only maximise thermal and mechanical properties but also enable precise access to diverse polymer architectures for applications in, e.g., self-assembly, elastomers, compatibilisers and more.[71–75] At a more fundamental level, this requires a deeper understanding of how catalysis is affected by the transition from traditional oxygen-based to sulphur-containing monomers, as the discovery of sequence-selective methodologies currently relies more on serendipity than rational development. In this regard many performant catalytic strategies for sulphur-free polymerisations remain to be explored and understood in sulphur-containing ROCOP and ROTERP.[76–81] Furthermore, insights on sequence selectivity generated in this filed could be leveraged to enable new polymerisations via cationic, radical or condensation methodologies.[82–87] Ultimately, this will allow for precise tailoring of polymer microstructures to meet the specific properties required for desired applications, as well as the combination of sulphur with all-oxygen-based polymers. As these materials are introduced to the market, it is important to recognise that directly competing with commodity plastics derived from petrochemical sources is likely to be difficult—if not unrealistic—at the outset. Therefore, to maximise the chances of commercial success, efforts should not be focused on replacing materials such as polyethylene for applications like plastic bags. Instead, the unique properties of sulphur should be leveraged in applications that cannot be easily achieved—or only with significant difficulty—without it. One promising example is the development of high-refractive-index polymers for use in optical lenses. Sulphur-rich polymers can readily achieve refractive indices above 1.7, significantly exceeding the market standard, especially for materials that are compatible with injection molding. This enables the production of thinner lenses and provides greater design flexibility for optical components. In addition, the high affinity of sulphur for transition metals should be exploited in applications beyond the scavenging of contaminants for purification. For instance, this property could be used to facilitate the controlled formation of polymer–metal composites, enhancing thermal and electrical conductivity while preventing phase separation through favorable interactions between the polymer matrix and the metal particles. Other potential uses include the immobilization of metal catalysts or, in a more academic context, promoting polymer self-assembly in solution via metal–ligand coordination. This could lead to the formation of catalytically active environments reminiscent of enzyme active sites. In commercial settings, sulphur's affinity for metals is also relevant for the development of coatings and sealants for metal components, offering added functionality and durability. Of course, the degradable nature of sulphur-containing polymers can help alleviate some pollution concerns, particularly with regard to the accumulation of microplastics. Finally, it should be noted that not every application may require full sulphur incorporation in every repeat unit; in some cases, random or block copolymers may be more suitable for optimising performance, shelf-life and processability.



From top left to bottom right: M. R. Stühler (B.Sc. + M.Sc., FU Berlin; current joint Ph.D. with A. J. P.), B. R. Manjunatha (B.S./M.S., IISER Thiruvananthapuram; current Ph.D. with A. J. P.), D. Battke, C. Fornacon-Wood (B.Sc., Sheffield; M.Sc., FU Berlin; current Ph.D. with A. J. P.), J. Stephan (B.Sc. + M.Sc., FU Berlin; current Ph.D. with A. J. P.), C. Gallizioli (B.Sc. + M.Sc., Pavia; current Ph.D. with A. J. P.), Marie Kreische, A. J. Plajer.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analysed in this study.

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