Title: Heterocycle/Heteroallene Ring Opening Copolymerisation: Selective Catalysis Delivering Alternating Copolymers

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Heterocycle/Heteroallene Ring Opening Copolymerization: Selective Catalysis Delivering Alternating Copolymers

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Table of content: Ring opening copolymerisation (ROCOP) is a powerful living polymerisation yielding numerous alternating copolymers with precisely placed heteroatoms in the polymer backbones. In this review we summarize the state-of-the-art for this important methodology, describe the principles of its catalysis and illustrate the potential for the different monomer combinations and resulting polymers. Trends and future challenges in this catalysis and its resulting materials are highlighted.

Abstract:

Heteroatom containing polymers have strong potential as sustainable replacements for petrochemicals, show controllable monomer-polymer equilibria and properties spanning plastics, elastomers, fibres, resins, foams, coatings, adhesives and self-assembled nanostructures. Their current and future applications span packaging, house-hold goods, clothing, automotive components, electronics, optical materials, sensors and medical products. An interesting route to these polymers is the catalysed ring-opening copolymerisation (ROCOP) of heterocycles and heteroallenes. It is a living polymerisation, occurs with high atom economy and creates precise, new polymer structures inaccessible by traditional methods. In the last decade there has been renaissance in research and increasing examples of commercial products made using ROCOP. It is better known in the production of polycarbonates and polyesters but is also a powerful route to make N-, S- and other heteroatom containing polymers, including polyamides, polycarbamates, polythioesters and others. This review presents an overview of the different catalysts, monomer combinations and polymer classes accessed by heterocycle/heteroallene ROCOP. It aims to provide a guide for users.
both to the catalysis and the resulting materials properties as well as highlighting opportunities for future research and applications.

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Introduction

Synthetic polymers are structurally tuneable materials integral to modern life whether for commodity products, like clothing, food packaging or house-hold goods, or for specialist applications, such as microelectronics, renewable energy generation or robotics.\textsuperscript{[1]} With worldwide production volumes exceeding 370 M tonne annually, a polymer free society is at best a vague memory rather than a vision for the future.\textsuperscript{[2]} The success story of last centuries polymers has its origin in close coupling with the liquid fuel industry, optimized production methods, low costs and immense chemical diversity; these features allow for material properties to be precisely tailored to a huge range of different applications. In the coming century, a move away from petrochemical raw materials allows for more widespread consideration of chemistries beyond hydrocarbons. There should be advantages to such chemistries which are closer to monomer-polymer equilibrium and hence should facilitate complete depolymerisation, chemical recycling and even biodegradation.\textsuperscript{[2–4]} Heteroatom containing polymers are
experiencing a renaissance both because of their potential to address such sustainability priorities and to deliver new or better properties targeted to future applications. Currently, sulphur cross-linked polymers are essential as rubbers and engineering thermoplastics, while amide linkages are, of course, integral to the performances of nylon fibres and urethanes to PU foams.\cite{1,5–7} Most of these materials are made by versatile and scalable polycondensations. Future economic, environment and technological challenges may benefit from materials better tailored to application.

One option is to improve structural control and hence provide insight into structure-property relationships into features such as heteroatom placement, functionalised block polymer sequence, architecture, molar mass value and distribution as well as regio- and stereochemistry. Delivering such tunability requires controlled polymerisation methodologies and one interesting and generally applicable option to install heteroatoms is heterocycle/heteroallene ring opening copolymerisation (ROCOP).\cite{8,9} Controlled, or living, polymerization show complete and fast chain initiation followed by uniform propagation rates, limited side-reactions and triggered termination. The resulting polymers show predictable molar mass values, narrow dispersities, compositions dictated by starting monomer stoichiometry and high end-group fidelity; because the growing polymer chain ends are ‘living’ they may be used to make (block) copolymers and more complex architectures with unparalleled selectivity.\cite{10–12} Heterocycle/heteroallene ROCOP typically affords functional polymers such as (thio)esters, (thio)carbonates, carbamates or urethanes.

Heterocycle/heteroallene ROCOP dates from the 1960s and renewed attention is partly driven by sustainability potential as monomers like CO₂, COS, SO₂ or S₈ are industrial wastes and others may be bio-derived.\cite{13,14} Applications for these materials naturally depend upon their polymer chemistry and physics but already low molar mass, ROCOP polyols show promise as surfactants, coatings, adhesives or foams and higher molar mass polymers show promise as high refractive index materials, absorbents, supports and high-performance plastics.\cite{15}
This review presents the principles of heterocycle/heteroallene ROCOP catalysis as a tool for polymer synthesis. It introduces the polymerisation methodology, using better-known monomer combinations such as carbon dioxide/epoxide and anhydride/epoxide ROCOP, and then presents other rarer monomer combinations, with special focus on polymers containing O, N or S heteroatoms. Research is progressing fast using such specialized monomer combinations but prior to optimizations of material properties, reproducible, effective and selective polymer syntheses are essential. In some cases, ROCOP catalysis activity and selectivity is rather low and here areas for future development are highlighted driven by promising initial polymer property data. The review is necessarily focussed on polymerisation catalysis where advances will allow for future explorations of polymer properties, processing and applications.

**Figure 1**: Summary of ROCOP monomer combinations presented in this review.
Recent trends in CO$_2$/epoxide ROCOP

Arguably the most widely investigated ROCOP is that of CO$_2$ and epoxides. Over the last 50 years this reaction has advanced from a lab curiosity to a commercialised technology.[16,17] Here, this monomer combination serves as an exemplar of the conceptual advances both in catalysis and product performances. There are already several other excellent reviews of CO$_2$/epoxide ROCOP and the interested reader is directed to these other reports for comprehensive coverage of this field.[15,18–22] In this work, the characteristics of CO$_2$/epoxide ROCOP are excellent illustrations of principles which are generally applicable to other, more unusual monomer combinations and key developments can also inform upon future research directions for other polymers.

Firstly, the elementary steps of CO$_2$/epoxide ROCOP (Figure 3) are described since most are general to other heteroallene/heterocycle combinations:

1. **Initiation** occurs when a coordinated epoxide is ring opened, by the initiator/catalyst, to form an alkoxide which becomes the propagating species. The initiator can be a metal-ligand, an ionic co-catalyst or a Lewis base.
2. **Propagation** occurs by two alternating processes: (a) CO$_2$ insertion where the alkoxide transforms into a carbonate intermediate. Many catalysts show CO$_2$
insertion kinetics that are considerably faster than epoxide ring-opening. (b) *Epoxide ring opening* where the carbonate intermediate ring opens the epoxide to regenerate the alkoxide. For many catalysts this is the “rate determining step”.

(3) *Termination* occurs when the catalyst is permanently de-activated, usually by irreversible protonolysis achieved by adding excess water, acid or even atmospheric moisture into the polymerisation.

Other processes can also occur and these may or may not be desired:

(1) *Backbiting* occurs when the alkoxide or carbonate intermediates attack the polymer chain rather than a new monomer. This process generates “cyclic 5-membered carbonate” (c5c) instead of progressing chain growth. For most carbon dioxide/epoxide couplings c5c is the thermodynamic product and polycarbonate is the kinetic product.

(2) *Epoxide homopropagation* occurs when the alkoxide intermediate reacts with a second epoxide molecule, rather than with carbon dioxide. It results in the formation of ether, or even polyether, linkages in the polymer chain.

(3) *Chain transfer* occurs when deliberately added protic compounds, typically alcohols, water or carboxylic acids, undergo a rapid and reversible series of exchange reactions with the propagating alkoxide or carbonate intermediates.[23] Catalysts able to undergo controlled chain transfer reactions can be very useful, for example in precise control over polymer molar mass or end-group functionality. These reactions are also exploited to produce multi-functional star or branched materials. In some contexts, a form of chain transfer is applied to ‘start’ polymerisations. In other contexts, chain transfer occurs from 1,2-diols formed by epoxide hydrolysis attributed to low levels of water contamination.[23,24] In such cases, the resulting polycarbonates show bimodal molar mass distributions, due to chains initiated both by catalyst and diol.[25,26] Some catalysts are very tolerant to chain transfer agents delivering precisely controlled molar mass and directing specific applications.[27,28] Low molar mass, hydroxyl end-capped polycarbonates are useful as surfactants, polyols or resin components and for making higher polymers, particularly polyurethanes.[7] Cross-linking reactions either using end- or side-chain substituents deliver coatings, resins or thermosets. Higher molar mass polycarbonates are used as elastomers, films and rigid plastics.[15]
Figure 3: Illustration of the key steps in CO$_2$/epoxide ROCOP. [M] refers to a metal catalyst, “P” to the polymer chain, X the initiating co-ligand.

Figure 4: Illustration of the key difference between mono- and bimetallic pathway.

Heterocycle/heteroallene ROCOP is critically dependent upon the catalyst selection and here an outline of the best performing systems is provided. One widely investigated class are metal(III) salen or porphyrin catalyst systems which comprise Cr(III), Co(III) or Al(III) complexes used with a nucleophilic cocatalyst, often a soluble “onium”-halide salt (consisting of a weakly coordinating cation such as R$_4$N$^+$, R$_4$P$^+$ or Ph$_3$P=N$^+$=PPh$_3$ (PPN) and e.g. Cl$^-$ or Br$^-$) or an organic base (e.g. Diazabicycloundecene (DBU), Triazabicyclodecene (TBD)). These catalyst systems polymerize via bimetallic and/or monometallic mechanisms (Figure 4). Often both mechanisms appear to occur in parallel, differing by epoxide activation at the same or a different metal to the site of carbonate coordination. In either case catalytic activity is lost or severely compromised without the co-catalyst and this means that...
activity also falls rapidly below a critical ion-pair concentration.\textsuperscript{[29]} At high temperatures, such systems typically deliver large amounts of c5c.\textsuperscript{[20]}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{metal_salen_catalysts_with_tethered_cocatalyst.png}
\caption{Metal salen catalysts with tethered cocatalyst; \(X = 2,4\)-dinitro-phenolate.\textsuperscript{[33–36]}}
\end{figure}

To address these difficulties, many catalysts were re-designed to attach the co-catalyst to the ancillary ligand; this strategy led to outstanding activity values, amongst the highest reported in this field (Figure 5). Nozaki and co-workers pioneered this strategy, reporting a piperidinium tethered Co(III) salen which showed excellent activity for CO\textsubscript{2}/propene oxide (PO) ROCOP.\textsuperscript{[33]} Later, Lee and co-workers reported a Co(III) salen featuring two tethered silylammonium dinitrophenolate co-catalysts which showed remarkable activity at low catalyst loading.\textsuperscript{[34]} Even higher rates were achieved by tethering four ammonium(dinitro)phenolate substituents to the Co(III) salen complex, although it should be noted the catalyst syntheses were lengthy.\textsuperscript{[35]}

Recently, Nozaki and co-workers reported a four-arm tethered Al(III) porphyrin catalyst showing excellent activity for CO\textsubscript{2}/cyclohexene oxide (CHO) ROCOP (TOF 10,000 h\textsuperscript{-1}, 120 °C, 0.0025 mol\%, 99% PCHC).\textsuperscript{[37]} These catalyst-tethered systems show a first order dependence on overall catalyst concentration, whereas the analogous bicomponent system shows a fractional order in metal complex.\textsuperscript{[36]} Another advantage is the improved selectivity for polymer, attributed to reduced backbiting from uncoordinated
chains by electrostatic attraction ‘holding’ any free anions ‘close’ to the cationic catalyst. Neutral co-catalysts were also tethered to metal complexes delivering rate enhancements, e.g. Lu and co-workers applied a TBD tethered Co(III) salen which was 6 times more active than the bicomponent equivalent and maintained activity low dilution (0.01 mol%).[38]

**Figure 6:** Proposed mechanism for bicomponent organocatalysed CO2/epoxide ROCOP.[39,40]

Organocatalysts (albeit often featuring metals from Groups 1-13) are also active for CO2/epoxide ROCOP and are typically bicomponent systems comprising a Lewis acid/base pair. Some of these organocatalysts may be attractive in terms of small-scale ease of use and lack of colour. Feng and co-workers discovered that Et3B (Lewis acid) and PPNCl (Lewis base) combinations showed good activity for both CO2/PO (TOF 49 h⁻¹, 60 °C, 0.1 mol%, 10 bar, 83% PPC) and CO2/CHO ROCOP (TOF 600 h⁻¹, 80°C, 0.025 mol%, 10 bar, 99% PCHC).[39,41,42] DFT investigations support the rate determining step involving triethylborane epoxide and propagating chain-end coordination; this mechanism closely resembles earlier reports for metal/co-catalyst bimetallic pathways. Very recently, Wu and co-workers reported a quaternary ammonium tethered 9-borabicyclo(3.3.1)nonane, applied at 0.005 mol% loading, which shows high activity for CO2/CHO ROCOP (TOF 4900 h⁻¹, 150 °C, 15 bar).[40] A related quadruply borane tethered ammonium salt achieves CO2/epichlorohydrin (ECH) ROCOP producing white polymer (TOF 7 h⁻¹, 25 °C, 0.1 mol%, 25 bar, 99% polymer) (Figure 7).[43]
Figure 7: CO₂/ECH copolymerisation by ammonium-borane catalyst produces white polycarbonate.[43] Copyright © 2021 American Chemical Society.

Reports proposing bimetallic mechanisms for bicomponent systems motivated preparation of deliberately di- and multi-metallic catalysts many of which operate without co-catalyst.[18] In the best cases, these catalysts are as active as tethered catalyst/co-catalyst systems and may be simpler to make and apply since they maintain high activity at much low CO₂ pressure.[43]

Figure 8: Bimetallic active site for CO₂/CHO ROCOP proposed for zinc diketimide catalysts.[21,44,45]

Coates and co-workers pioneered Zn(II)-diketimide catalysts and through elegant kinetic investigations established the most active were loosely associated dimers; this excellent work has already been thoroughly reviewed.[21] Lee and co-workers reported Zn(II)₂-bis(anilido-aldimide) catalysts for CO₂/CHO ROCOP (TOF 312 h⁻¹, 80 °C, 0.02 mol%, 12 bar, 94% PCHC) and noted that electron withdrawing ligand substituents enhanced activity but reduced selectivity (TOF 2860 h⁻¹, 80 °C, 0.002 mol%, 14 bar, 79% PCHC).[44,46] Later, Rieger and co-workers reported a highly active macrocyclic Zn(II)₂-bis(diketimide) catalyst (TOF 9130 h⁻¹, 100 °C, 0.025 mol%, 40 bar, >99% PCHC).[45] Curiously, it follows somewhat complex carbon dioxide pressure dependent kinetics, with a zeroth order from 5 - 25 bar changing to a first order from 25 - 45 bar. Further studies showed that more rigid macrocycles reduced the activity,[47] whereas
electron-withdrawing substituents increased it (TOF 155,000 h$^{-1}$ 100 °C, 0.0125 mol %, 30 bar, 88% PCHC).[48]

From 2008, our team investigated catalysts feature metal coordination by dinucleating macrocyclic diphenolate tetraamine ligands.[49] The first report described Zn(II)$_2$ catalysts which showed moderate activity at 1 bar CO$_2$ pressure (TOF 18 h$^{-1}$, 80 °C, 0.1 mol%) and were, at that time, a rare example of low pressure catalysts. Subsequently, Mg$_2$ (TOF 35 h$^{-1}$), Co(II)$_2$ (TOF 161 h$^{-1}$) and Fe(III)$_2$ (TOF 6 h$^{-1}$) catalysts all showed activity at 1 bar CO$_2$ pressure (80 °C, 0.1 mol%).[50–52] Detailed investigations of the polymerisation kinetics, DFT calculations, $in situ$ spectroscopy and structure-activity studies supported a chain shuttling mechanism in which the polymer chain moves between the two metals with each monomer insertion.[53] A key outcome from this mechanism was the potential for heterodinuclear catalysts since each metal was attributed a distinct role in the catalytic cycle.

Heterodinuclear Zn(II)Mg(II) catalysts showed greater activity than either homodinuclear analogues, i.e. Zn(II)Zn(II) or Mg(II)Mg(II).[58,59] This work provided the first evidence of catalytic synergy and supported the hypothesis that each metal has a distinct mechanistic function. Variants of this Zn(II)Mg(II) catalyst, featuring organometallic, non-initiating C$_6$F$_5$ co-ligands and applied with alcohol as chain transfer agent, allowed for both high activity and selectivity for telechelic polycarbonates.[60] The organometallic Zn(II)Mg(II) catalysts react with the diols to form the desired alkoxide initiators $in situ$ and deliver accurate control over molar mass and end-group chemistry. These catalysts were used to prepare polycarbonate-b-polyester-b-polycarbonate ABA triblock copolymers from mixtures of CHO, CO$_2$ and
biobased \(\varepsilon\)-decalactone. The catalysts deliver precise control of the bock ratios and carbon dioxide contents (6 - 23 wt%). By controlling the carbonate linkage content, the material properties of the polymers were tuned from adhesives to elastomers to ductile plastics, addressing in particular the brittleness of the parent PCHC segments. In 2018, Mashima and co-workers reported a series of high activity multimetallic catalysts featuring Zn(II)\(_3\)Ln(III) for CO\(_2\)/CHO ROCOP (TOF 300 h\(^{-1}\), 100\(^\circ\)C, 0.05 mol%, 3 bar CO\(_2\)). In 2020 the same ligand produced more active Co(II)\(_3\)Ln(III) catalysts (TOF 1625 h\(^{-1}\), 0.004 mol%, 20 bar).\[56,61\]

![Figure 10: Co(II)Mg(II) synergic heterodinuclear catalyst for CO\(_2\)/CHO ROCOP compared with the Mg(II)Mg(II) and Co(II)Co(II) variants sheds light on the molecular basis for synergy.\[54\]](image_url)

In 2020, our team investigated the phenomena which underpin catalytic synergy in CHO/CO\(_2\) ROCOP using a heterodinuclear Mg(II)Co(II) catalyst.\[54\] This catalyst showed an excellent activity at 1 bar (TOF 1205 h\(^{-1}\), 120 \(^\circ\)C, 0.05 mol%, 99% PCHC), and 20 bar CO\(_2\) pressure (TOF 12460 h\(^{-1}\), 140 \(^\circ\)C, 0.05 mol%, 99% PCHC). It showed four times higher rate than Mg(II)Mg(II) and double that of Co(II)Co(II) catalysts. Detailed kinetic analyses showed that \(|\Delta S^\ddagger|\) is reduced for Mg(II) containing catalysts whilst \(\Delta H^\ddagger\) is smaller for Co(II) containing variants. Hence, the success of the heterodinuclear catalyst is the attributed to Mg(II) coordinating the epoxide with reduced transition state entropy, while the Co(II)-carbonate attacks it with reduced
transition state enthalpy. Synergy arises because each metal has a distinct role in the catalytic rate determining step and the kinetics provide experimental evidence for this proposition. Epoxide ring opening transfers the propagating alkoxyde to the Mg(II) site and carbon dioxide insertion results in the chain “shuttling” back to the Co(II) centre ready for the next cycle of monomer insertions.

In 2020, we also reported a heterodinuclear Co(III)K catalyst, coordinated by an asymmetric diphenolate, diamine macrocycle featuring a tetra-ether moiety, that showed excellent activity in PO/CO₂ ROCOP (TOF 800 h⁻¹, 70 °C, 0.025 mol%, 30 bar CO₂, 93% PPC).[62] Notably this catalyst tolerates up to 250 equivalents of chain transfer agent useful for production of polycarbonate polyols. Another heterotrimetallic catalyst featuring Zn₂Na also shows good activity for CO₂/CHO ROCOP at 1 bar CO₂ pressure and enables adjustable ether contents (TOF = 75 - 956 h⁻¹, 80 – 120 °C, 0.025 mol%, 5 - 33% PCHO links in PCHC); this catalyst even retained good activity at 0.5 bar CO₂ pressure and can switch between CHO ROP and CO₂/CHO ROCOP when changing the reaction atmosphere from CO₂ to N₂ and vice versa.[57]

![Figure 11](https://example.com/figure11.png)

**Figure 11:** Thermally controlled reversible CO₂/epoxide polymerisation and depolymerisation. Copyright © 2017 Wiley.[63]

The polycarbonates prepared by CO₂/epoxide ROCOP are usually the kinetic reaction product which provides an opportunity to chemically recycle them to either cyclic carbonates or the parent monomers.[3] Lu and co-workers reported a di-Cr(III) catalyst for N-heterocyclic epoxide/CO₂ ROCOP, showing >99% polymer selectivity at 60 °C.[63] Nonetheless, at 100 °C the near quantitative depolymerisation occurred re-forming the epoxide and CO₂. Depolymerisation of the purified polymer back into monomers also occurred in bulk, without any catalyst, at higher temperature (260 – 300 °C). The result illustrates future potential in circular polymerisations/depolymerisations process, although it should be emphasised that such low temperature depolymerisation could be problematic for polymer processing and may need optimization. Fully bio-derived
poly(limonene carbonate), prepared by CO$_2$/limonene oxide (citrus fruit peel) ROCOP, was also depolymerized to limonene oxide and CO$_2$ using either a Zn(II)$_2$ complex or organic bases.[64,65] This depolymerisation chemistry is both monomer and catalyst dependent, since reports of PCHC depolymerisation indicate selective c5c formation.[57,66–68] Although, trans c5c can undergo ring-opening polymerization to form polycarbonates. [69,70] Accordingly, Coates and co-workers reported a neat proof of chemical recycling using isotactic PCHC, synthesized using an enantioselective Zn(II)-bis(diketimide) catalyst. Vacuum thermolysis, at 250 °C, selectively depolymerized it into trans-c5c in 95% yield; the cyclic carbonate was subsequently efficiently repolymerized.[68]

**Recent trends in anhydride/epoxide ROCOP**

Another classic ring-opening copolymerisation is that of cyclic anhydrides with epoxides to yield polyesters.[13] It access many different polyester backbone and side-chain chemistries. In contrast to heterocycle ROP, the ring-strain of epoxides/anhydrides is less impacted by substituents and thus the polymerisation remains thermodynamically feasible using substituted/functionalized monomers.[71] It is also an excellent means to increase backbone ‘rigidity’ through the incorporation of aromatic or strained heterocyclic units. Many epoxides and anhydrides are already large-scale chemical products and this may help accelerate implementation of this polymerisation methodology. There have already been some comprehensive reviews of epoxide/anhydride ROCOP; here only recent developments in catalysis will be described with focus on findings most relevant to other monomer combinations.[8,9] Here, most catalysts are benchmarked by performances using phthalic anhydride(FA)/CHO but so far this field lacks common standards and the multitude of other monomers and reaction conditions complicate catalyst comparisons (Figure 12).
Figure 12: Selection of high performance CHO/PA ROCOP catalysts.\cite{57,58,72–75}

Most catalysts active for CO$_2$/epoxide are also active for anhydride/epoxide ROCOP, yet the reverse isn’t necessarily true. For example, Lewis base catalysts only form c5c for CO$_2$/epoxides, but catalyse anhydride/epoxide ROCOP at appropriate temperatures.\cite{76,77} This reactivity difference stems from the side-reactions: alkoxide terminated polymer chain ends back-bite into adjunct carbonate links to form c5c but such a pathway has a higher barrier in anhydride/epoxide ROCOP. Nevertheless, in the latter polymerisation, alkoxide chain ends can undergo transesterification broadening the molar mass distributions.

Figure 13: Coates and co-workers apply catalyst design to minimize transesterification side-reactions.\cite{78–80}

Tolman, Coates and co-workers reported an excellent ROCOP mechanistic investigations using Al(III) salen/PPNCl bicomponent catalysts.\cite{78} A bis(carboxylate) aluminate resting state was proposed in the initial stages of the catalysis, even when a large excess of epoxide was present. The rate determining step was proposed as epoxide insertion into the aluminium-carboxylate intermediate producing a
mono(alkoxide)-mono(carboxylate) aluminate intermediate. Rapid insertion of an anhydride monomer into this intermediate regenerated the bis(carboxylate) aluminate resting state. The Al(III) salen/PPNCl catalyst forms an ion pair and should be treated as such in any kinetic analyses. As the polymerisation progressed and the anhydride concentration became depleted, the bis(alkoxide) aluminate intermediate accumulated and undesired side-reactions, such as transesterification, became feasible. Inspired by the mechanism, Coates and co-workers reported highly active aminocyclopropenium chloride tethered Al(III) salen catalysts which maintained high activities at low catalyst loading (PO/Norbornene anhydride, TOF 80 h\(^{-1}\), 60 °C, 0.005 mol%, vs. TOF = 10 h\(^{-1}\) for a bicomponent catalyst).\(^{[79]}\) These properly designed tethered catalysts showed much less transesterification, epimerisation and chain-end coupling reactions than bicomponent analogues. The performances were rationalised by control over metallate equilibria avoiding formation of free alkoxide chains. The tethered catalyst was also tolerant to large quantities of chain transfer agent allowing for molar mass control.\(^{[81]}\) In bicomponent systems chain transfer agents reduce the propagating chain nucleophilicity, through hydrogen bonding, and suppress metallate formation via competitive coordination to the metal. The tethered system intrinsically favours metallate formation and hence counterbalances deleterious influences of chain transfer agents and allows to access branched and star polymers.

Coates and co-workers also developed Al(III) salen catalysts with electron-withdrawing para-fluoro substituents which significantly reduced transesterification.\(^{[80]}\) It was proposed that the substituents stabilize the aluminate and prevent alkoxide chain-end dissociation from the catalyst, a hypothesis reminiscent of those rationalizing the enhanced performances of tethered catalysts systems in CO\(_2\)/epoxide ROCOP.

**ROCOP of CO\(_2\) with oxetanes**

![Diagram of ROCOP of CO\(_2\) with oxetanes](image)

**Figure 14:** Copolymerizations of CO\(_2\) and oxetane proceeding either via direct CO\(_2\)/oxetane ROCOP or via intermediate c6c and its ROP into PTC.
The four-membered cyclic ether oxetane shows only a slightly lower ring strain ($\Delta H = 81$ kJ/mol) than its three member cousin, ethylene oxide ($\Delta H = 104$ kJ/mol): its copolymerisation with carbon dioxide should, therefore, be feasible. Following initial reports of low yield ternary catalysts, Baba and co-workers reported bicomponent Lewis acid ($\text{Bu}_2\text{SnI}_2/\text{phosphine, nitrogen Lewis base}$) catalysts (TOF $\sim 7$ h$^{-1}$, 100 °C, 2 mol%, 49 bar, $M_n \sim 1200$ g/mol, 88 - 99% carbonate content). The mechanism was ambiguous with respect to formation of trimethylenecarbonate (c6c) either as an intermediate or by-product because c6c ROP is feasible and forms the same poly(trimethylene carbonate) (PTC). The authors observed an initial increase in c6c concentration correlating with decreasing concentration of oxetane, but followed by a decrease in c6c concentration over longer reaction times with formation of PTC.

**Figure 15:** CO$_2$/oxetane ROCOP catalysed by Cr(III) salen/R$_4$NCl catalyst, with different direct and indirect pathways illustrated. The most active catalyst system is Cr(III) salen /R$_4$NCl (TOF 41 h$^{-1}$, 110 °C, 0.08 mol%, 35 bar, $M_n\sim 10.1$ kg/mol). It’s activity was lower for copolymerisations with oxetane compared with epoxides, but its selectivity for polymer versus cyclic carbonate was much better. It was proposed that c6c ROP and CO$_2$/oxetane ROCOP operate simultaneously with the active catalyst being a chromate species. The overall rate law was first order in catalyst ion pair (i.e. chromate) and oxetane concentrations; the experimental $\Delta G^+_{\text{ROP}} = 101.9$ kJ/mol and $\Delta G^+_{\text{ROCOP}} = 107.6$ kJ/mol. Copolymerisation of 3,3'-substituted oxetanes were also feasible, but slower, than for oxetane and also occurred through c6c ROP. Substituted oxetanes generally formed more c6c in the final product mixtures, likely due to equilibrium constraints on their
ROP. The catalyst also readily depolymerised disubstituted PTC when applied without a CO₂ atmosphere.

**Figure 16:** In situ IR spectroscopy applied to CO₂/3-methoxymethyl-3-methyloxetane ROCOP using Cr(III) salen/R₄NN₃. Data show a maximum c6c concentration (highlighted in red) which supports a parallel c6c ROP mechanism. Copyright © 2011 American Chemical Society. [92]

Ammonium salts, R₄NX (X = Cl, Br, I, N₃, OAc), with a bis-hydrogen bond donor, I₂ or BEt₃ were also active catalysts. [93–96] It was proposed that oxetane activation occurred by borane coordination, hydrogen- or halogen-bonding. Some organocatalysts were effective using unpurified monomers, although the resulting polycarbonates molar masses were very low (< 2 kg/mol) likely due to protic compound contamination. Although readily available, all these organocatalysts required high loadings of 0.5 - 3 mol%, show only modest activities (TOF ≤ 5 h⁻¹, ≥ 90°C) and produced variable c6c:PTC product ratios depending on the reaction conditions.

**Figure 17:** CO₂/oxetane ROCOP using a bicomponent I₂/TBD catalyst. [94]

Improving catalyst performances, as well as tackling monomer purity issues to drive up molar mass values (both of which are lacking behind what has been achieved in CO₂/epoxide), will be essential to yield useful PTC which, when prepared by other means, shows promise as in biomedical applications. [97,98] PTMC (Tₙ ca. −20°C) has been used to form matrices for cell growth with particular focus on regeneration of bone, cartilage, nerve and/or blood vessels. [99–102] PTC undergoes rapid hydrolysis,
under biologically relevant conditions, but unlike aliphatic polyesters does not generate acidic decomposition products which can reduce inflammation side-effects.\textsuperscript{[103]} Such properties are important for any biomedical implants targeted to fully degrade after healing.\textsuperscript{[104]} As a component in block polymers it also allowed for the controlled release of anti-cancer drugs, proteins and gene-therapeutics.\textsuperscript{[105–107]}

Other ROCOPs involving oxetanes and tetrahydrofuran

Cyclic anhydrides and oxetane ROCOP is also feasible but under-investigated. Endo and co-workers described Ti(IV) bis(phenolate) catalysts active using various anhydrides, although in some cases around 40 mol\% ether linkages were observed (TOF < 3 h\textsuperscript{-1}, 1.7 mol\%, 120 °C, \(M_n = 2.8 - 4.9\) kg/mol).\textsuperscript{[108]} Adding a phosphonium co-catalyst resulted in completely alternating polymers from 3,3'-disubstituted oxetanes and succinic/diphenic anhydride (TOF < 1 h\textsuperscript{-1}, 130 °C, 5 mol\%, \(M_n = 2.9 - 11.1\) kg/mol).\textsuperscript{[109]} Alternating copolymers from anhydride/THF ROCOP was achieved with a bistriflimidic acid catalyst (TOF 3 - 10 h\textsuperscript{-1}, 120 °C, 1 mol\%, \(M_n = 2.0 - 3.5\) kg/mol).\textsuperscript{[110]} An organoaluminium catalyst, Al(iBu)\textsubscript{3}, also terpolymerises anhydrides, epoxides, oxetane or THF into (ABC)\textsubscript{n} polymers.\textsuperscript{[111]} Although the properties of the resulting polyesters remain under-investigated, increasing the chain length between ester linkages is expected to accelerate biodegradation and may hold future promise for tailoring degradation rates.\textsuperscript{[112]}
ROCOP of dihydrocoumarin with epoxides

**Figure 18:** Dihydrocoumarin (DHC)/epoxide ROCOP by different pathways.

Copolymerizations of aliphatic lactones and epoxides may form copolymers (block/random/gradient) but rarely yields selective alternating copolymers.[113–115] In contrast, the semi-aromatic lactone DHC does not undergo ring-opening polymerisation due to its low ring strain and chain end reactivity (Figure 18). One way to overcome this barrier, would be if DHC were ring opened by an alkoxide chain end, such as that from epoxide ring opening. In such a reaction an aryl-alkyl-lactone becomes an alkyl-alkyl-ester and the chain end is a mesomerically stabilized phenoxide. Hence DHC/epoxide ROCOP is an exergonic process. DHC is an attractive monomer as it is comparatively inexpensive (0.03 $/g), can be sourced from renewable coumarin and is “generally considered safe” by the FDA.[116]

Endo and co-workers pioneered DHC/glycidyl ether ROCOP, using imidazole catalysts, to produce polyesters with 99% selectivity, moderate activity and low molar mass (TOF 30-50 h⁻¹, 120 °C, 2 mol%, \( M_n < 3 \text{ kg/mol, 94-99%} \)).[117–120] Using a bifunctional DHC, in which two lactones are connected through a benzene core, copolymerisation with epoxides resulted in polyesters featuring pendant lactones. These lactones were post-functionalized, using alcoholysis/aminolysis reactions, or provided sites for cross-linking reactions which resulted in materials showing higher \( T_g \) values (60 °C vs 71 – 112 °C, \( M_n = 1.5 - 3 \text{ kg/mol} \)). Furthermore, this DHC/epoxide
based curing system undergoes minimal volume shrinkage – a valuable attribute for bonding materials in electronic devices.\textsuperscript{[121,122]}

Using a Cr(III) salen/PPNCl catalyst system improved rates (TOF 7 - 42 h\textsuperscript{-1}, 80 °C, 0.2 mol\%, $M_n$ = 7 - 20 kg/mol).\textsuperscript{[123]} Strangely many successful CO\textsubscript{2} or anhydride/epoxide ROCOP catalysts, e.g. bis(diketimide)ZnOAc or Co(III) salen/PPNCl, were significantly less active in DHC/epoxide ROCOP. Nonetheless, the Cr(III) salen catalyst system showed broad epoxide scope yielding polyesters with glass transition temperatures from -8 to 57 °C. Most polyesters were amorphous, but DHC/cyclopentene oxide (CPO) or DHC/CHO ROCOP yielded semi-crystalline but atactic polyesters showing moderate melting temperatures ($T_m$: DHC/CPO = 139 °C, DHC/CHO = 173 °C). Lu and co-workers reported the highest activity catalyst - a binuclear [Cr(III) salen]\textsubscript{2}/PPNCl system (TOF 11-115 h\textsuperscript{-1}, 30-100 °C, 0.1 mol\%, $M_n$ = 5-19 kg/mol).\textsuperscript{[124]} Under equivalent conditions, it was significantly more active in CO\textsubscript{2} or PA/CHO ROCOP than DHC/CHO ROCOP. These reactivity differences were exploited to deliver block polyesters (poly((PA-alt-CHO)-b-(DHC-alt-CHO)) from mixtures of PA, DHC and CHO. Organocatalysts, comprising phosphazene bases and alcohols, were also active for DHC/epoxide ROCOP (TOF < 2 h\textsuperscript{-1}, 50 – 80 °C, 2 - 0.2 mol\%, $M_n$ = 2.5 - 12 kg/mol) albeit much slower than Cr based catalysts, and, furthermore, they were less selective showing greater transesterification.\textsuperscript{[125,126]} It was proposed that proton exchange reactions between the chain end and the phosphazene base allowed alcohols to act as a chain transfer agents. Under such conditions, up to 10 equivalents of alcohol (vs. phosphazane base) were used to make branched or brush polymer architectures.

**ROCOP of γ-chalcolactone with epoxides and thiiranes**

γ-Butyrolactone and its chalcogen derivatives, γ-thiobutyrolactone (TBL) and γ-selenobutyrolactone (SBL), have very low ring strain and so ROP is thermodynamically unfeasible under most conditions.\textsuperscript{[127]} This means that these monomers are suitable candidates for ROCOP and, in fact, TBL/epoxide ROCOP was feasible using R\textsubscript{4}N/KCl salt catalysts (TOF 3 - 31 h\textsuperscript{-1}, 90 °C, 3 mol\%, $M_n$ = 7.7 - 9.5 kg/mol) or phosphazene bases with alcohols (TOF < 5 h\textsuperscript{-1}, 25-60 °C, 4 mol\%, $M_n$ = 2 - 6 kg/mol) yielding poly(ester-alt-thioether).\textsuperscript{[128,129]} ROCOP kinetics indicated rapid TBL insertion but slow epoxide ring-opening, resulting in a thiolate resting state.
**Figure 19**: ROCOP between thio/selenolactones and epoxides or thiiranes.

Using the selenium analogue, SBL, resulted in fast ROCOP for many epoxides, using phosphazene bases with alcohol (TOF 68 – 1455 h\(^{-1}\), 25 °C, 1 mol%, \(M_n = 2.1 - 21.1\) kg/mol) or RN-Halide salts (TOF 2 h\(^{-1}\), 80 °C, 2 mol%, \(M_n = 4.6 - 6.8\) kg/mol).\(^{[130,131]}\)

The poly(ester-alt-selenoether) were amorphous with low glass transition temperatures (\(T_g = -59\) to -5 °C, \(T_d = 227 - 275\) °C) and high refractive indices (RI > 1.6). This methodology was also used to make block polymers by sequential epoxide additions.

Thiirane/SBL ROCOP, forming poly(thioester-alt-selenoether), was catalysed by phosphazene bases with thiols (TOF ~ 1200 h\(^{-1}\), -20 °C, 1 mol%, \(M_n = 2.5 - 12.6\) kg/mol, \(T_g = -45\) °C for propylene sulphide (PS); TOF 200 h\(^{-1}\), 25 °C, \(M_n = 3.5 - 12.8\) kg/mol, \(T_g = -4.2\) °C for cyclohexene sulphide (CHS)).\(^{[132]}\) Low polymerisation temperatures were required to avoid homopolymerisation since the barrier to thiirane ROP is quite low (e.g 14.8 kJ/mol for PS).

Polymers containing sulphur or selenium links can be oxidative responsive materials. For example, block copolymers comprising a chalcogen containing hydrophobic block with a hydrophilic block self-assembled into micelles when dispersed in water. Upon oxidation with e.g. \(\text{H}_2\text{O}_2\) the chalcogen centres become hydrophilic causing the micelles to disassemble as demonstrated for a block polymer prepared via SBL/epoxide ROCOP.\(^{[131,133,134]}\) This property was explored for future drug delivery in a recent report of a polymer containing selenoether and PEG blocks. These micelles were loaded with doxorubicin and a photo-oxidant the anti-cancer drug was delivered into upon IR irradiation.\(^{[135]}\)

**ROCOP of bicyclic butyrolactones with epoxides**
**Figure 20:** Bicyclic butyrolactones (left: spiro-butyrolactone (sBL); right: fused bis-butyrolactone (fBL))/epoxide ROCOP by different pathways.

Endo and co-workers also developed a useful methodology to copolymerize bicyclic butyrolactones with epoxides.\(^{[138–144]}\) Accordingly, either fused bicyclic butyrolactones (fBL) or spirocyclic butyrolactones (sBL) were copolymerized with glycidyl ethers. The ring opening of the bicyclic monomer is driven by a thermodynamically favoured isomerisation to a ketone. In terms of catalysts, phosphines were the most active and selective (TOF 1 - 10 h\(^{-1}\), 120 °C, 0.8 mol%, \(M_n = 5.2 - 6.7\) kg/mol). The sBL/phenyl glycidyl ether (PGE) copolymer exhibits a \(T_g\) of 60 °C (\(T_d = 287\)°C) which is significantly higher than the fBL/PGE copolymer with a \(T_g\) of -15 °C (\(T_d = 356\)°C) – these differences were attributed to internal versus pendant ketone groups modulating chain flexibility.

The copolymerisation of either sBL or fBL resulted in volume expansion, a consequence of the double-ring opening of the fused/spiro-cycle, which may be useful for polymer resins.\(^{[140]}\) While epoxide ROP results in volume shrinkage but isopropyl-fBL/PGE ROCOP maintained same volume before and after polymerisation. In resin applications, shrinkage is undesirable, especially for adhesive or filler uses, and may lead to sub-optimal interfaces and performances. Endo and co-workers also reported isoprene substituted bBL which, after ROCOP with PGE, was functionalized via thiol-ene chemistry or radically crosslinked to form networks.\(^{[142]}\) The latter networks showed increased rigidity and the expected improvement in thermal stability (which increased by 50 °C to give \(T_d\) of 326 °C).

**ROCOP of COS with epoxides and oxetane**

Carbonyl sulphide COS, the monosulphur analogue of \(\text{CO}_2\), is a both naturally occurring gas (e.g. released by marine plants or volcano eruptions) and an anthropogenic environmental pollutant emitted by burning fossil fuels.\(^{[145,146]}\) It is a
major source of acid rain as it can be oxidized to SO$_2$ in the troposphere and furthermore damages the ozonosphere. Therefore, its use as a monomer could redress some environmental impacts and valorise an industrial waste.$^{[147, 148]}$

**Figure 21:** COS/epoxide ROCOP illustrating different chemo- and regioselectivities.$^{[149]}$

In 2013 Zhang and co-workers successfully achieved both chemo- and regioselective COS/PO ROCOP using a Cr(III) salen/PPNCl catalyst system to produce monothiocarbonate (TOF 288 - 332 h$^{-1}$, 25 °C, 0.1 mol%, $M_n = 21.9 - 25.3$ kg/mol).$^{[149]}$ The selectivity for monothiocarbonate, -(S-)C(=O)-O-, linkages was attributed preferential sulphur (rather than oxygen) coordination at Cr(III). The increased nucleophilicity of the Cr(III)-thiolate intermediate (compared with Cr(III)-alkoxides) was attributed to the higher activities compared to those for CO$_2$/PO ROCOP. The thiocarbonate linkage is asymmetric so copolymerisation with monosubstituted epoxides may form four regioisomeric linkages: HT, TH, TT and HH. The notation describes whether the CH$_2$ (T) or CHR (H) group sits adjacent to the respective sides of the monothiocarbonate links (Figure 21); the Cr(III) salen catalyst system showed remarkably high selectivity for TH linkages (>98%). Polymerisation conditions needed to be quite finely balanced since moderate increased to temperature (60 °C) or adventitious moisture formed cyclic carbonate, dithiocarbonate -SC(=O)S- and carbonate -OC(=O)O- linkages by O/S scrambling.$^{[150]}$ The Cr(III) salen/PPNCl catalysts also showed good activity in COS ROCOP with other epoxides, e.g. COS/CHO (TOF 325 h$^{-1}$, 40 °C, 0.1 mol%, $M_n = 12.3$ kg/mol), COS/PGE (TOF 7300 h$^{-1}$, 25 °C, 0.1 mol%, $M_n = 22.6$ kg/mol) or COS/styrene oxide (TOF 83 h$^{-1}$, 20 °C, 0.1 mol%, $M_n = 77.2$ kg/mol).$^{[151–153]}$

The glass transitions temperatures for the poly(monothiocarbonates) are similar to the polycarbonate analogues and easily controllable over a wide temperature range by changing the epoxide ($T_g = 3 - 115$ °C). Many polymers are optically transparent, with high refractive indices, e.g. RI = 1.63 for COS/PO or 1.70 for COS/CHO.$^{[147]}$ To avoid
chromatic aberration in optical applications, the RI should remain constant with changing refracted light wavelength, a property expressed by the Abbe number $V_d$ (i.e. higher $V_d$ values are better for uses as lenses, prisms, or waveguides).\[154] In COS/epoxide ROCOP, $V_d$ was controlled, and could be increased, by forming random polymers through terpolymerisation. For example, COS/PO/CHO ROCOP leads to tuneable $V_d$ (32.1 - 43.1), high RI (1.52 - 1.56) and $T_g = 44 - 93 \, ^\circ C$, depending on the CHO/PO feed ratios.\[152] CHO/CO$_2$/COS ROCOP, using an [Al(III) salen]/PPNCl catalyst, gave polymers with the highest $V_d$ of 48.6 for randomized equimolar carbonate:thiocarbonate links while maintaining high glass transition and decomposition temperatures ($T_g = 111 \, ^\circ C$ and $T_d = 260 \, ^\circ C$).\[155]

As was also observed for CO$_2$/epoxide ROCOP, tethered catalysts showed field-leading activity: selectivity: catalyst loading values. For example, a DBU-tethered Cr(III) salen catalyst operates at high polymerisation temperatures resulting in very high activity without compromises to O/S scrambling or polymer selectivity (TOF 4670-271000 h$^{-1}$, 25 – 80 °C, 0.005 - 0.00005 mol%, 27.1 - 220.0 kg/mol).\[156] In direct contrast to CO$_2$/PO ROCOP where Co(III) catalysts were usually more active than Cr(III) systems, the reverse was observed for COS/PO ROCOP. The Cr(III) salen catalyst was also active for other COS/monosubstituted epoxide ROCOP – always showing high activity (TOF $> 20,000 \, h^{-1}$). Two slower copolymerisations, COS/CHO (260 h$^{-1}$) and COS/CPO ROCOP (1360 h$^{-1}$), were accelerated when 1 mol% PO was added (TOF = 15,800 h$^{-1}$). The heterogeneous Zn/Co(III) DMC catalysts were also active in COS/CHO ROCOP (190 g/g/h, 110 °C, $M_n = 6.5 - 25.0 \, kg/mol$), forming colourless polymers (c.f. the Cr(II) salen/PPNCl catalysts yielded pale yellow polymers even after repeated washing), albeit with 10% O/S scrambled linkages.\[157]
Figure 22: Semicrystalline graft polymers produced by two stage COS/ECH ROCOP.\textsuperscript{158}

Recently semicrystalline poly(monothiocarbonates), from COS/epoxide ROCOP, were made by polymerizing enantiopure ECH with COS, using a DBU-tethered Cr(III) salen catalyst (TOF 19 h\textsuperscript{-1}, -25\degree C, 0.1 mol\%, $M_n = 3.1$ kg/mol, $T_g = 16\degree C$, $T_m = 97\degree C$).\textsuperscript{159} The polymerisation suffered from termination reactions as molar mass values were very low and these occurred by nucleophilic substitution reactions between the growing polymer chain and the chloride substituent of ECH. Nonetheless, these epoxides underwent a second COS/epoxide ROCOP to yield semicrystalline graft polymers.\textsuperscript{158}

In a two-step process, the length of the substituent of the epoxide terminated “macromonomer” was initially determined by the reaction temperature (-20 to 0 \degree C). In the second step, the temperature was increased to 25 \degree C and the macromonomer underwent ROCOP forming graft polymers ($M_n = 32.9$ - 37.8 kg/mol, with 1.5 - 1.8 kg/mol branches). Both ROCOP processes were well controlled and \textapprox 90\% ECH was converted before graft polymer formation. Naturally, the graft polymer showed different thermal properties to the starting macromonomers ($T_g = 11\degree C$, $T_m = 113\degree C$, $T_d = 262\degree C$). As graft polymers could be readily formed via ROCOP, either with multi-functional chain transfer agents or through temperature switching, this might be a promising future direction for these polymers.\textsuperscript{23} Generally, graft polymers show different rheology and viscosity compared to their linear components because of changes to chain entanglement. Therefore, branched polymer solutions are often much less viscous than their linear counterparts, which may facilitate processing and applications. For example, in the administration of liquid drug formulations which are then easier to inject by syringe.\textsuperscript{160,161} Branched polymers can host a guest molecules through non-covalent encapsulation within the cavities between chains a relevant feature for the delivery and controlled release of pharmaceuticals.\textsuperscript{162}
Isotactic COS/PO and COS/PGE copolymers, prepared from enantiopure epoxides, were amorphous but the COS/EO polymer was semicrystalline ($T_m = 128 \, ^\circ \text{C}$, $T_c = 66 \, ^\circ \text{C}$; note that the all oxygen variant poly(ethylene carbonate) from CO$_2$/EO ROCOP is amorphous ($T_g = 0 - 10\, ^\circ \text{C}$). The catalyst system was a DBU-tethered Cr(III) salen and it showed very high activity (TOF 84900 h$^{-1}$) producing a high molecular weight polymer ($M_n = 193 \, \text{kg/mol}$). An ABA triblock polymer (COS/EO-b-COS/PO-b-COS/EO), featuring a semicrystalline-soft-semicrystalline combination (30% COS/EO units, 70% COS/PO units), with a moderate molecular weight ($M_n = 13 \, \text{kg/mol}$) showed a stress at break of $11.2 \pm 0.1 \, \text{MPa}$ and an elongation at break of $575 \pm 52\%$. The thermoplastic elastomer showed ca 90% elastic recovery from five 300% strain cycles, although the performance cannot match existing thermoplastics, e.g. styrene/butadiene SBS (28 MPa stress-, 800% elongation at break) or polyurethanes PU (25 to 75 MPa stress-, 500% elongation at break), it serves as proof of potential.

Lu and co-workers employed an assymetric catalyst to make semicrystalline poly(monothio carbonates) from achiral meso-epoxides and COS. For COS/CHO ROCOP, [Cr(III) salen]$_2$ yielded atactic polymer but the Co(III) analogue produced highly isotactic polymer ($P_m = 90\%$). The extent of isotactcity of course controlled the maximum melting temperature, with values up to 201°C observed at 99% isotactcity [$M_n = 29.5 \, \text{kg/mol}$]. The same stategy was also successful for the stereoselective ROCOP of cyclopenteneoxide or 3,4-epoxytetrahydrofurane, all forming highly isotactic polymers ($T_m = 141$ and 232 °C).

Organocatalysts for COS/(PO/CHO/PGE) ROCOP include Et$_3$B/Lewis-base which showed lower activity, but slightly higher TH selectivity (TOF 61 - 119 h$^{-1}$, 25 °C, 0.1 mol%, $M_n = 14.4 - 92.5 \, \text{kg/mol}$) than Cr(III) salen catalysts. Bifunctional Lewis bases, such as N,N,N',N' tetraethylethylene diamine, with Et$_3$B showed higher activity (TOF = 8000 - 22500 h$^{-1}$, 0 – 80 °C, 0.1 mol%, $M_n = 46.6 - 81.0 \, \text{kg/mol}$) and maintained high selectivity for polymer at 80°C. A mechanistic switch from ROCOP to ROP was achieved in which COS/PO ROCOP was followed by PO homopolymerisation to form block polymers. Thiourea/Lewis base (/alcohol) systems were effective COS/PO ROCOP (TOF 10 - 112 h$^{-1}$, 25 °C, 0.05 - 0.1 mol%, $M_n = 11.3 - 98.4 \, \text{kg/mol}$) which is surprising given that the same systems fail in CO$_2$ ROCOP.
Figure 24: (Top): Elastomeric COS/oxetane copolymer wafer. (Bottom): Polarized light microscopy image of the crystal growth of the molten COS/oxetane copolymer at 96°C.[170]

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Oxetane/COS ROCOP using Cr(III) salen/PPNCl (TOF 4 - 62 h⁻¹, 40 – 130 °C, 0.4 mol%, $M_n = 4.9 - 40.9$ kg/mol) or Et₃B/PPNCl catalyst systems both yield perfectly alternating polymers, without O/S scrambling.[170,171] Minor amounts of cyclic by-product, thio-c6c, formed at the polymerization end suggesting reactions occurred by direct COS/oxetane ROCOP rather than thio-c6c ROP. The polymers show high crystallinity ($T_m = 128$ °C, $M_n = 30$ kg/mol) which contrasts with the amorphous all-oxygen analogue PTC ($T_g = -20$°C). Furthermore $T_m$ values of related aliphatic polycarbonates (180 – 275 °C) are close to their decomposition.[172–175] In contrast, the thiocarbonate from COS/oxetane ROCOP showed $T_m = 128$ °C and $T_d = 229$ °C, giving a reasonable processing temperature range. This allowed for hot-press processing to produce an elastomeric material (Figure 24), although its tensile properties remain to be reported.

**ROCOP of CS₂ with epoxides, oxetane and thirane**
Figure 25: CS₂/epoxide ROCOP and $^{13}$C{¹H} NMR spectrum illustrating polymer chemistries accessible when O/S scrambling occurs.

CS₂/PO ROCOP was first reported in the 1970s, by Adachi and co-workers, using a mixture of Et₂Zn and HMPA (TOF <1 h⁻¹, 25 °C, $M_n = 0.6$ kg/mol).[176] Two key findings resulted: (a) O/S scrambling formed -S-C(=S)-O- linkages as well as other linkage chemistries (see Figure 25); (b) CS₂:Epoxide dramatically influenced catalytic activity and selectivity. This latter observation is different to CO₂/epoxide ROCOP, where catalytic performance is commonly independent of CO₂ pressure.

Heterogeneous DMC catalysts for CS₂/PO ROCOP yielded polymers with low molecular weights and with moderate/good activities (52-182 g/g*h, $M_n = 1.2 - 5.4$ kg/mol).[177] The resulting polymers were oxygen enriched (~ 35% theoretical max. S) and exhibited nearly all the possible permutations of linkages. Moreover, carbonyl sulphide, COS, was detected in increasing quantities as the reaction progressed. This was attributed to COS being more easily, or perhaps rapidly, incorporated rationalizing the observation that -S-C(=O)-O- linkages were the most prevalent.

Darenbourg and co-workers reported CS₂/CHO ROCOP using Cr(III) salen/PPNCl showing better catalytic performance but again linkage scrambling (TOF 124 h⁻¹, 50 °C, 0.08 mol%, $M_n = 26.5$ kg/mol).[178] Polymers showed all linkages forming simultaneously indicating that linkage exchange was faster than propagation. The resulting polymer was semi-crystalline ($T_g = 122$ °C; $T_c = 152$ °C, $T_d=220$ °C) in contrast to amorphous PCHC ($T_g = 110-130$ °C). The crystallinity was reinforced by weak attractive interchain S⋯S interactions. CS₂/CPO ROCOP was also feasible using this
catalyst (TOF 146 h⁻¹, 80 °C, 0.067 mol%), even though the same catalyst produces only c5c for CO₂/CPO reactions.[179,180]

CS₂/oxtane ROCOP, using Cr(III) salen/PPNCl, yielded polymers with high sulphur contents (TOF 83 h⁻¹, 80 °C, 0.1 mol%, $M_n = 13.7$ kg/mol, >95% max. S).[181] Increasing the CS₂ concentration, increased both molar mass and desired -S-(C=S)-O- linkage selectivity. Linkage selectivity decreased with increasing temperature suggesting scrambling is entropically favoured. The presence/absence of cocatalyst also influenced the extent of scrambling suggesting off-metal origins for some exchange reactions.

Clearly, controlling the O/S scrambling side-reactions is a significant challenge in CS₂/epoxide ROCOP. Understanding pathways forming particular linkages remains more hypothetical than proven; nonetheless if in future it were possible to control these processes it might be feasible to produce polymers featuring (ABC)$_n$ or (ABCD)$_n$ monomer sequences instead of the expected, and more common, (AB)$_n$.

![Figure 26: CS₂/epoxide ROCOP, catalysed by LiO'Brien, producing (ABAC)$_n$ copolymer; R = Me, Et.[182]](image)

In 2016 Werner and co-workers realized an (ABAC)$_n$ copolymer, in 92% sequence selectivity, from CS₂ with PO or butylene oxide with LiO'Bu as the catalyst (TOF 50 h⁻¹, 25 °C, 0.125 mol%, $M_n = 132$ kg/mol).[182] The catalyst enchains with a somewhat unusual HH-TT selectivity and a tentative mechanism was proposed (Figure 26). Accordingly, the propagating alkoxide may attack an adjacent -O-(C=S)-S- linkage leading to a -O-(C=S)-O- linkage and concomitant formation of a thiolate chain end. The same lithium alkoxide catalyst also produced isotactic polymer from CS₂/R-PO ROCOP which has a higher $T_g$ than the atactic form ($T_g = 30$ °C for isotactic vs 13 °C for atactic). Organocatalysts, comprising Et₃B/lewis Base, were also effective for
CS₂/PGE ROCOP yielding only trithio- or monothiocarbonate linkages, albeit with worse overall performance than metal systems.\[183\] CS₂/EO ROCOP using bicomponent Et₃B or Cr(III) salen catalysts revealed that the extent of O/S scrambling changed the material properties from completely amorphous (\(T_g = -18.6\) to \(-35.1\) °C) to highly crystalline (\(T_g \sim -34\) °C, \(T_m = 118 - 211\) °C).

![Figure 27](image1)

Figure 27: XRD data for CS₂/EO copolymers from bicomponent catalysts show different degrees of crystallinity.\[184\] Copyright © 2020 Wiley.

While sulphur rich segments tend to be crystalline, the all-oxygen carbonate linkages form amorphous regions. Another interesting feature of these copolymers is their facility for degradation by oxidants. Immersion of solid polymer in 30% \(\text{H}_2\text{O}_2\) for 12 h degraded resulted in degradation to oligomers (\(M_w = 1.8\) kg/mol) with formation of sulphones (\(R_2\text{SO}_2\)) and sulphonic acids (\(RSO_3\text{H}\)).\[184\]

![Figure 28](image2)

Figure 28: CS₂/thiirane ROCOP forming poly(trithiocarbonate).

Early investigations of CS₂/ES or PS ROCOP used highly toxic CdEt₂ or Hg(SBu)₂ catalysts or, in the case of CO₂/PS ROCOP, metalphenolate catalysts, and formed large quantities of thioether as well as heterocarbonate links.\[185–187\] Nozaki and co-workers reported CS₂/PS ROCOP, using Cr(III) salen/PPNCl, producing highly alternating trithio-PPC with high polymer selectivity (92%) and good activity (TOF 76 h⁻¹, 25 °C, 0.2 mol%, \(M_n = 44.6\) kg/mol, \(T_g = 25\) °C, \(T_d > 200\) °C).\[188\] The poly(trithiocarbonate) was only sparingly soluble in common organic solvents but was
highly soluble in CS₂ highlighting future processing challenges for highly heteroatom rich polymers. The polymers showed high refractive indices (RI = 1.78 for CS₂/PS, 1.73 for CHS/PS; in comparison RI of PPC is 1.46 and PCHC is 1.48). In general high RI polymers are investigated for optoelectronic applications such as lenses in image sensors, optical layers in LCD displays, encapsulants for LEDs and anti-reflection coatings.\textsuperscript{[154,189]} Compared to alternative inorganic compounds, the ROCOP polymers may benefit from mechanical flexibility, impact strength, processability by moulding or casting, show light-weights and potentially have lower costs. Although S-containing ROCOP polymers have not been explored in these applications, the broad monomer scope and potential for terpolymerisation may allow future property optimisation.

Both CS₂/PS and CS₂/CHS copolymers exhibited antimicrobial activity against \textit{Escherichia coli} and \textit{Staphylococcus aureus}.\textsuperscript{[190]} Bacterial cultures contacted with polymer films were assessed for cell viability by counting surviving colonies. While the poly(cyclohexene thiolcarbonate) was more effective against \textit{E. coli} (20\% cell viability for CS₂/PS and >10\% for CS₂/CHS after 24 h contact time), the biocidal performance was reversed for \textit{S. aureus} (25\% cell viability for CS₂/PS and 50\% for CS₂/CHS after 24 h contact time).

\textbf{ROCOP of thioanhydrides with epoxides or thiiranes}

Very recently the sulphur analogues of anhydride/epoxide ROCOP were reported to deliver poly(thioester) structures inaccessible by conventional routes.\textsuperscript{[191–193]}

![Figure 29](image)

\textbf{Figure 29:} ROCOP of thioanhydride with epoxides or thiiranes.

Lu and co-workers reported ROCOP of thiiranes with stearic (STA) or glutaric thioanhydride (GTA) using Lewis base/PPNX catalysts.\textsuperscript{[191]} The most effective was PPNOAc which delivered polymers quickly with molar masses close to theoretical expectations (TOF 787 h\textsuperscript{-1}, 25° C, 0.4 mol\%, $M_n = 53.6$ kg/mol, for STA/PS).
Polymerisation control was good, and block polymers were prepared via addition of a second thioanhydride after consumption of the first. The copolymer showed a high refractive (RI = 1.79) and moderate melting temperature ($T_m = 80$ °C), this latter value increased to 90 °C when R-PS is used. The onset of thermal decomposition occurred from 230-300 °C ($T_g = -22 - 60$ °C) depending on the thiirane employed, suggesting the materials have a reasonable processing window.

Phthalic thioanhydride (PTA)/PO ROCOP using Cr(III) salen/PPNCI catalysts showed good performance (TOF 30 – 1420 h⁻¹, 25 - 100°C, 0.1 - 0.001 mol%, $M_n = 18.2 - 60.1$ kg/mol).[192] The polymer showed thioester, ester and thioether linkages, was regio-random and lacked long-range order. The linkage scrambling was attributed to intramolecular and/or intermolecular transesterification reactions akin to CS₂/epoxide ROCOP. Scrambling increased with temperature and influenced the polymer’s glass transition temperature ($T_g = 62$ °C from reactions at 100 °C, $T_g = 70$ °C from reactions at 25 °C, both with $M_n \approx 18$ kg/mol). A tethered lewis base-Cr(III) salen catalyst showed fewer transesterifications (TOF 94 - 567 h⁻¹, 0.1 - 0.01 mol%, 25 – 70 °C, $M_n = 15.9 - 49.7$ kg/mol).[193] Highly regioregular poly(ester-alt-thioester) formed at 25 °C but, once again, higher temperatures resulted in scrambling. This catalyst also successfully copolymerized thioanhydrides with other epoxides, yielding amorphous polymers with glass transition temperatures from 35 to 161 °C, albeit with low molar masses ($M_n = 5.7 - 17.5$ kg/mol). Some poly(thioesters) are biosynthesised by *Escherichia coli* which suggests alternative metabolic pathways based on sulphur.
chemistry which might be relevant to the biological compatibility and biodegradation.[194]

**ROCOP of S₈ with thiiranes**

The ring opening polymerisation of elemental sulphur, i.e. S₈, is thermodynamically disfavoured at temperatures below 159 °C but occurs readily at higher temperatures.[195] This unusual phenomenon arises because S₈ ROP is entropically favoured, i.e. $\Delta S(\text{Polymerisation}) > 0$.[196] Elemental sulphur is a waste product of petrochemical refining, with 70-Mt produced annually, most of it via hydrodesulphurisation.[197] Although a significant portion is used to make sulphuric acid, rubber, and fertilizer, excess of sulphur accumulates in large over-ground storage facilities.

Penczek and Duda demonstrated S₈/thiirane ROCOP (ES, PS, 2-Me-PS) using sodium thiophenolate crown-ether or CdCO₃ catalysts (Figure 31).[198–202] Altering S₈/thiirane from 1:1 to 10:1, modulates sulphur uptake and maxims at 85 wt% (with PS). $^{13}$C NMR spectroscopy shows a range of polysulphide ($S_x$) linkages and their formation was attributed to a linkage scrambling process akin to the transesterification reactions discussed earlier.

![Figure 31: S₈/thiirane ROCOP and linkage scrambling forming polysulphides, $S_x$.](image)

Initial rates analysis demonstrated that the sulphide chain end attacked S₈ about 10 times faster than thiirane. The $-S_9$ intermediate attacked thiirane ca. 100 times faster than it formed S₈. Curiously, the anionic polysulphide chain ends became less reactive the longer the preceding $S_n$ group, suggesting some negative charge delocalisation along the chain. Just like for other ROCOPs, small cyclic by-products formed including cyclic tri, tetra and pentasulphides. These cyclics reached a maximum concentration and then decreased over time, suggesting they undergo ring-opening polymerization which was later confirmed by homo- and copolymerisation with S₈.[201]
Sulphur/heterocycle ROCOP reactions yielded polymers which are amorphous elastomers ($M_n = 10 - 100 \text{ kg/mol}$). In contrast to polysulphides $S_n$, the polymers were stable with respect to depolymerisation as well as to extrusion of sulphur under ambient conditions. Films, cast from polymer solutions, retained transparency after storage for 4 years. Poly(styrene-alt-sulphur), from $S_8$/styrene sulphide ROCOP, showed that increasing the sulphur content (although not quantified) decreased the $T_g$ from 58 to 43 °C which matched previous reports that increasing the sulphur wt% reduced brittleness.[203]

It is emphasised that sulphur-sulphur bonds are often dynamic, a property exploited in autonomously self-healing polyurethane elastomers where macroscopic damage was healed through dynamic disulphides.[204] By simply bringing two ends of the cut specimen bar into contact mechanical properties were nearly completely restored after 24 h. In future, these ROCOP polymers should be explored as self-healing materials.

**ROCOP of SO$_2$ with epoxides**

Sometimes ROCOP occurs spontaneously because the two monomers, A and B, first form an activated monomer adduct A-B which then enchains by step growth or other mechanisms.

![Spontaneous pathway](image)

![Lewis base initiated pathway](image)

**Figure 32**: Base initiated SO$_2$/epoxide ROCOP versus spontaneous copolymerisation.

Such an activated monomer mechanism was reported for SO$_2$/epoxide ROCOP forming low molar mass polymers, enriched with ether linkages.[205–209] Higher molar masses, sulphate incorporation and reaction rates were achieved using Lewis base initiators such as N-heterocycles, phosphines or salts (TOF 20 - 35 h$^{-1}$, 50 °C, 0.1 – 1 mol% pyridine, $M_n = 11.9 - 14.2 \text{ kg/mol}$). Initiation occurred from zwitterions,
LB⁺CR₂CR₂OSO₂⁻ and activity depended on the initiator ionization. Propagation occurs when SO₂ activates the epoxide and generally rates depend on epoxide, SO₂ and Lewis base. Cyclic and linear polymer form which limits molar masses (e.g. SO₂/EO ROCOP = 9.2 - 14.2 kg/mol). Using poly(vinyl pyridine) as initiator, allows for separation of the linear and cyclic polymers which were bound to the macro-initiator. Thermal decomposition of the SO₂/EO copolymer, at relatively low temperature (Td = 216°C), formed mixtures of cyclic five-membered sulphite and EO which were recovered in ~44% yield. The depolymerisation was catalysed by Brønsted or Lewis acids, which reduced the degradation temperature to 50 °C, and was also accelerated by UV irradiation. Lu and co-workers reported PPNX (X = OAc, Cl) intitated SO₂ ROCOP with a range of epoxides (TOF 13 - 1116 h⁻¹, 25 – 50 °C, 0.2 mol%, Mₙ = 3.1 - 19.8, 88 - 99% sulphite content).[210] The authors noted that chain transfer reactions with trace ammounts of water limit the Mₙ of the linear polymers (Figure 33).

Using zinc glutarate for SO₂/PO ROCOP yielded polymers with molar masses upto 42 kg/mol, with 90% sulphite contents (Tg = 14 °C).[211] Using a Cr(III) salen, without co-catalyst, for SO₂/CHO ROCOP gave higher molar masses and sulphite contents compared to the spontaneous path (TOF 80 h⁻¹, 60 – 90 °C, 0.1 mol%, Mₙ = 9.3 - 27.7 kg/mol, Tg = 53 °C, Td = 205 °C, 64 - 77% sulphite).[212] Similar catalysts immobilized on cellulose supports enabled catalyst recycling up to three times with little performance loss.[213] Cr(III) salen/PPNCl catalysts undergo random terpolymerisation of CO₂, SO₂ and CHO which may be relevant to some petrochemical waste streams where CO₂ is contaminated with SO₂.[214] Terpolymers were sulphite enriched reflecting the higher electrophilicity of SO₂ compared to CO₂.

Figure 33: MALDI-TOF MS spectrum SO₂/CHO copolymer showing chains initiated from trace H₂O.[210] Copyright © 2020 American Chemical Society.
ROCOP of RNCO with epoxides and RNCS with thiiranes

Early work demonstrated slow alternating ArNCO/EO ROCOP employing 2 AlEt₃:1 H₂O catalyst system (TOF 0.3 h⁻¹, 25 °C for PhNCO).[215,216] The isocyanate addition to the epoxide occurred with retention of the C=N bond forming an acetal linkage or with retention of the C=O bond, forming a urethane linkage (Figure 34); the semi-crystalline polymer comprised two thirds acetal linkages (ₘₚ = 1-2.1 kg/mol, Tₘ = 80-83 °C). In comparison an isomeric polymer synthesized via ROP that only contains urethane linkages showed a Tₘ = 192 °C. These findings emphasize the importance of linkage connectivity in moderating material properties. It should be noted that alternating polyurethanes, such as formed through ROCOP, are totally different to the polyurethanes currently produced through the condensation of polyols and di-isocyanates.[7] These commercial products contain a much lower wt% of urethane linkages and combine hard and soft domains which are integral to their properties.

![Figure 34: RNCO/epoxide ROCOP led to multiple different linkages.](image)

Faster and more selective ArNCO/CHO ROCOP (TOF >1000 h⁻¹, 80 °C, 0.2 mol%, ₘₚ = 3-8 kg/mol) was achieved using a Mg(II)₂ catalyst [LMg₂OAc₂], but curiously the di-Zn(II), di-Co(III) derivatives, Co(III) or Cr(III) salen/PPNCl catalysts were each completely inactive.[217] Depending on the conditions the polymer contained either mostly urethane, RO-(C=O)-NR₂, or allophanate, RO-(C=O)-NR-(C=O)-NR₂, linkages (the latter from two consecutive ArNCO insertions). The polymers decomposed (Tₜ = 180 – 210 °C) before any phase transitions could occur, with the exception of the p-fluoro substituted polyurethane with Tₜ = 181°C.
Polymerisation of PO, EO, octene oxide or allyl glycidyl ether with tosyl isocyanate, TsNCO, using Et3B/(PPN/R4N)Cl catalysts, resulted in polyurethane materials showing moderate-high molar masses (TOF 10,000 h⁻¹, 25 °C, 1 – 0.1 mol%, \( M_n = 15 – 225 \) kg/mol). Using monofunctional chloride initiators yielded polyurethanes showing monomodal molar mass distributions, whilst phosphazene and diol catalysts, yielded the more useful telechelic polyurethanes. The TsNCO/PO copolymer was amorphous with a \( T_g \) of 107 °C (\( M_n = 20 \) kg/mol, \( T_d = 242 ^\circ \text{C} \)) significantly higher than the related polycarbonate PPC (\( T_g = 22 – 40 ^\circ \text{C}, T_d \sim 242 ^\circ \text{C} \)). By changing the epoxide, it was feasible to control \( T_g \) in the resulting polyurethanes to give values as low as -24°C; it was also noted that TsNCO/EO yields a semi-crystalline polyurethane, with \( T_m = 61 ^\circ \text{C} (T_c = 44 ^\circ \text{C}) \). In related work Oct4NB/((iBu)3Al was investigated for ArNCO/butylene oxide ROCOP, albeit with poor polymer and linkage selectivity. Using \( n^\text{BuLi} \) as the initiator, resulted in successful RNCS/ES ROCOP to produce semi-crystalline poly(imino dithioacetal), \([-\text{CH}_2\text{CH}_2\text{-S-C(=NR)-S}-]\) \( n \) (\( T_m = 63 – 128 ^\circ \text{C} \) depending on \( R \); \( M_n = 25 – 60 \) kg/mol). Polymerisation rates were increased using coordinating solvents, e.g. THF or \((\text{Me}_2\text{N})_3\text{P}=\text{O}\), which enhance the dithiocarbamate chain end nucleophilicity via its coordination to lithium. Terpolymerisation of different RNCS with ES followed reactivity ratio trends, where aryl-NCS are more reactive than alkyl-NCS. For example, PhNCS/EtNCS/ES ROCOP selectively formed the PhNCS/ES block first followed by the EtNCS/ES block. When ES was used in excess it was also consumed by ROP, forming a final poly(thioether) block, albeit alongside slow degradation of the polymer. The RS-(C=NPh)-SR repeat units are hydrolysable, upon contact with dilute aqueous acids, resulting in aniline (PhNH2) release and formation of semi-crystalline polymers comprising RS-(C=O)-SR linkages which are much less soluble than the starting polymer. Wu and co-workers reported strictly alternating RNCS/thiirane ROCOP, with PPNCl initiators, achieving good to excellent activity and molar masses (TOF 21 - 1162 h⁻¹, 0.4 - 0.1 mol%, 25 – 100 °C, \( M_n = 19.9 – 142 \) kg/mol). The different monomer substitution patterns highlight the wide range of structures accessible using this ROCOP methodology (Figure 35).
**Figure 35:** Polymers formed from RNCS/thiirane ROCOP with thermal properties.[221]

**ROCOP involving aziridines**

Aziridines are more nucleophilic than epoxides or thiiranes by virtue of the lone-pair on the N-atom. Hence, they form stable carbamate adducts with carbon dioxide, effectively the reverse of reactivity with SO$_2$ where adduct formation resulted from its increased electrophilicity. For example, ethyl aziridine (EI), reacted with CO$_2$ at -27 °C to form the salt [EICO$_2$][EIH]$^+$. Upon heating this salt, in mixtures of EI and CO$_2$, the anion [EICO$_2$]$^-$ attacked and ring opened the activated aziridine cation, [EIH]$^+$ resulting in copolymerisation by an activated monomer mechanism (Figure 36).[222,223] Two competitive polymerisation pathways were observed in parallel: (i) Formation of polyamine linkages by cationic aziridine ROP and (ii) Branching from these amine links.
Ikeda and co-workers first described catalyst-free CO\(_2\)/EI ROCOP yielding polymers with low urethane contents (<31 mol%), but using propylene imine (PI) resulted in polymers showing up to 70% urethane linkages.\(^{222,223}\) The potential for these monomers to undergo spontaneous ROCOP did not rule out the need and possible benefits for catalysed pathways.\(^{224}\) For example, CO\(_2\)/N-Ph-EI ROCOP using a metal catalyst showed higher polymer yield, urethane content and molar mass to uncatalyzed controls; the best catalysts were MnCl\(_2\)(H\(_2\)O)\(_4\) and Mn(acac)\(_2\). Catalyst systems comprising mixtures of Et\(_2\)Zn with polyphenols/phenylamines formed perfectly alternating oligourethanes (\(M_n < 0.6\) kg/mol).\(^{225}\) Similarly, a ternary Y(Cl\(_3\)CCO\(_2\))\(_3\)/ZnEt\(_2\)/glycerine catalyst for CO\(_2\)/PI ROCOP resulted in polymers with 80% urethane linkages (70 °C, 40 bar, \(M_n \leq 30\) kg/mol).\(^{226}\)

Ikariya and co-workers investigated supercritical CO\(_2\) (up to 220 bar) for CO\(_2\)/PI ROCOP.\(^{227,228}\) While the aziridines were soluble in supercritical CO\(_2\), the polyurethanes precipitated from it, presumably due to intermolecular hydrogen bonding. Using dimethylacetamide as co-solvent prevented precipitation and homogenized the mixture, allowing isolation of polymers with higher molar masses (\(M_n\) 210 kg/mol, 74% urethane linkages).
Figure 37: Aziridine/CO$_2$ ROCOP data (Left) pH dependent water solubility of poly(urethane-ran-amine). (Right) Temperature dependent light transmittances of aqueous poly(urethane-ran-amine) solutions with pH.$^{[229]}$ Copyright © 2005 RSC.

The polymers contain hydrophilic polyamine and hydrophobic polyurethane sequences, in various proportions, and so, depending on the reaction conditions (CO$_2$ pressure, solvent, etc), they show differing lower critical solution temperatures (LCST) in water. The LCST arises from unfavourable entropy of mixing between polymer and solvent and is observed for other polymers, a common example being poly(N-isopropylacrylamide).$^{[230]}$ In the case of these CO$_2$/aziridine copolymers, the amine linkages are susceptible to protonation/deprotonation and thus the solution pH also controls the LCST: under acidic conditions there is no LCST and its value decreases with increasing pH.$^{[229]}$

Figure 38: ROCOP between aziridines and CS$_2$, COS, COSe or cyclic anhydrides.

Ikeda and co-workers reported that water catalysed CS$_2$/N-cyanoethyl-EI ROCOP formed a poly(dithio carbamate) which was semi-crystalline ($T_m = 155^\circ$C) and poorly soluble in all solvents except for DMSO.$^{[231]}$ The rate law showed dependencies of: [N-EtCN-EI][CS$_2$][H$_2$O] and was interpreted by a rate determining step involving attack
by of an N-C(=S)-S group, from an activated monomer complex, upon a protonated aziridine (protonation from water). The CS$_2$/aziridine copolymer showed high alternation irrespective of the starting quantities of each monomer suggesting that the aziridine ROP was significantly less favourable compared to other CO$_2$/aziridine ROCOPs.

**Figure 39:** Thermally induced depolymerisation of neat COS/PI copolymer at 200 °C followed by GPC and NMR spectroscopy.$^{[232,233]}$ Copyright © 2020 American Chemical Society.

COS/aziridine ROCOP is also spontaneous via an activated monomer mechanism.$^{[234]}$ Using COS pressures of 10 to 20 MPa results in the formation of polymers showing molar masses up to 15 kg/mol, within 2 hours at room temperature.$^{[232,233]}$ The highly alternating polymers were macrocyclic, as determined by MALDI-TOF mass spectrometry, and were cleanly depolymerized, at 200°C, into the five membered cyclic thiourethane. These polymers were shown to effectively absorb heavy metal salts, such as HgCl$_2$ and PbCl$_2$, from aqueous solutions. The absorbed metal salts were isolated following thermal depolymerisation and removal of the small molecule cyclics by distillation (Figure 39). While the COS/PI copolymer was amorphous ($T_g = 90^\circ$C), the COS/(N-ethyl-EI) ($T_m = 170^\circ$C) and N-butyl-Az ($T_m = 137^\circ$C) copolymers are semi-crystalline. There is also tentative precedence for spontaneous COSe/aziridine copolymerisation.$^{[235]}$

Poly(ester-amine)s, the formal products of anhydride/aziridine ROCOP, combine the biodegradability of polyesters with the thermal and mechanical properties of polyamides - these desirable features have resulted in applications ranging from drug delivery systems to hydrogels, composite matrices and tissue engineering.
In some cases, anhydride/aziridine ROCOP was spontaneous, but was characterized by poor molar mass control and amine linkages. Quantitative monomer alternation was achieved with Lewis base/alcohol organocatalysts. Cyclic polymers were isolated in some cases where mono/bicyclic anhydrides and N-benzyl substituted aziridines were applied (TOF 1 - 10 h\(^{-1}\), 70 °C, 0.2 - 1 mol%, \(M_n = 4.4 - 34.1\) kg/mol, \(T_g = 41 - 126\) °C, \(T_d = 258 - 311\) °C). As cyclic polymers formed by macrocyclisation during termination, applying higher BnOH loadings resulted in more linear chains.

**Figure 40:** Anhydride/aziridine ROCOP data. (Left) In situ FTIR spectroscopic analysis of PA/N-Ts-EI ROCOP. (Right) DSC thermogram of the copolymer. Copyright © 2020 Wiley.

Good molar mass control was achieved for PA/N-Tosyl-EI ROCOP (TOF 14-27 h\(^{-1}\), 50°C, 0.3 - 2 mol%, \(M_n = 5.1 - 35.7\) kg/mol, \(T_g = 114\) °C, \(T_d = 265\) °C). The authors rationalised the better control by suppression of transacylation side-reactions arising from the electron-withdrawing tosyl substituent which increased the selectivity for linear polymers. Compared to the closest epoxide/anhydride ROCOP analogue poly(propylene oxide-alt-PA) (\(T_d = 269\)°C, \(T_g = 55\)°C), the incorporation of amide linkages increases the \(T_g\) (Figure 40). When excess aziridine was employed, a mechanistic switch to N-Ts-EI ROP was feasible forming a polyamine block after the poly(ester-amide) block. The finding than homogenous organocatalysts greatly improve control in anhydride/aziridine ROCOP might imply that similar catalysts could achieve living heteroallene/aziridine ROCOP (improving upon the spontaneous pathways investigated so far). If successful, such an approach could allow for regularly
placed urethane and amide linkages in the resulting polymers, via terpolymerisation methodologies, which may deliver properties closer to current industrial polyurethanes.

Conclusions and Outlook

Heterocycle/heteroallene ROCOP allows efficient and selective formation of many completely new and sophisticated polymer microstructures from comparatively simple monomers. By optimizing the catalysis, tailoring of both polymerization kinetics and delivery of useful materials for future applications should be prioritized. Although great improvements in carbon dioxide/epoxide ROCOP catalysis have been achieved, in many other cases the catalysis is really early-stage. Key targets are increased reaction rates and control over tacticity, molar mass, linkage and chain end chemistries. One strategy is to seek inspiration from the demonstrated successful approaches in CO₂/epoxide ROCOP catalysis. These include developing co-catalyst tethered metal complexes/organo-catalysts, exploiting heterodinuclear synergy and applying chiral or non-initiating organometallic catalysts to properly control chain stereo- or end-group chemistry. There are, however, some monomer combinations for which optimized carbon dioxide ROCOP catalysts are unsuccessful and, in these cases, the field needs better understanding of the kinetics and mechanisms so as to rationally improve performances. The polymerization catalysis community should feel optimistic in these endeavours since the range and scope of ROCOP catalysts is still very narrow, with many Lewis acid and labile metal/organo-catalysts remaining to be explored. Another priority are tolerant catalysts and processes using impure monomers or mixtures – such systems would be highly attractive for large-scale deployment but could also accelerate uptake by the broader polymer chemistry community.

Here, we have tried to highlight the immense potential for many under-explored monomer combinations to deliver functionalised polymers and materials. The polymer chemistry and physics of these materials is very early-stage and the field will benefit from the attention of those with expertise in processing, properties and applications. One area worth immediate investigation is to use multi-functional chain transfer agents to target new polymer architectures and topologies, most obviously with explorations of star and brush polymers. Another is to exploit recently discovered switchable polymerization catalysis to deliver block sequence selective copolymers.\textsuperscript{[241]} The precise monomer placement within polymer chains afforded by switch catalysis has already shown promise in delivery of ductile plastics, adhesives or thermoplastic
In future, its application with heteroatom functionalized polymers can be used to broaden into sectors including engineering plastics, fibre-compatible resins, soft robotics, ionic conductors and medical materials.

The ring-opening copolymerization processes and polymers may be of interest to tackle UN SDG. Overall, polymer sustainability can only be assessed through life cycle assessments and are application specific but there are some features of these polymers that meet criteria for sustainable polymers. For example, many monomers are existing industrial wastes and others could be bio-derived. It is recommended that catalysis and polymer chemistry research should target such non-petrochemical materials for development. The ROCOP process has high atom economy and may be suitable for retro-fit into existing manufacturing and processing infrastructure. Polymer properties are well-matched with growth industries in renewable energy generation, increased use of biomaterials like wood/paper or in delivering self-repairing products. In terms of end-life options, some of these polymers show promising characteristics for circular chemical recycling. These heteroatom containing backbones appear to facilitate depolymerisation to monomers or small cyclic molecules suitable for repolymerization under accessible conditions. Nonetheless, such properties must be carefully balanced with processing and application performances. Other heteroatom polymer scaffolds are biodegradable and are already finding application in medical sectors, indicating that degradation by-products are not toxic. Taken as a whole such features highlight the potential for this interesting class of polymers in helping tackle the problems of today's materials. Much more research is needed to improve their production, better understand their properties and fully assess life cycle impacts.

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Conflict of Interest

CKW is a director of econic technologies.
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