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Recent advances in the ring-opening polymerization of sulfur-containing monomers

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Inspired by the uniqueness of ring-opening polymerization and the ubiquity of sulfur-containing heterocycles, much attention has been paid to the synthesis of sulfur-containing polymers as they can provide novel materials with a broad range of applications ranging from stimuli responsiveness to (bio)degradability. Within this review article an overview is presented regarding various ROP technologies (ROP/rROP/ROMP) which are further categorized by monomer class, detailing significant developments over the previous decades which cement the importance of sulfur-containing monomers in modern polymer chemistry. This article aims to explore the chemistry involved in the ring-opening polymerization of sulfur-containing cyclic monomers by summarizing the state-of-the-art, as well as providing an overview of the fundamental challenges involved in synthesizing sulfur-containing polymers, including potential future directions.

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1. Introduction

The introduction of sulfur atom(s) into chemical compounds is an active area of research, both in the synthesis of new active pharmaceutical ingredients (APIs),[1–3] and in the synthesis of new polymers with enhanced mechanical, electrical, and physicochemical properties.[4] As a consequence, the synthesis of sulfur-containing polymers has received considerable attention due to unique properties that sulfur can instil including optical features, chemical resistance, self-healing capabilities, and heavy-metal capturing abilities, among others.[5,6] In comparison to a parent material, the inclusion of even small quantities of sulfur atoms can significantly alter the physicochemical properties. Even functional groups can be signifi-

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Marlena Pięta

Marlena Pięta completed her Ph. D. in 2018 at Lodz University of Technology (TUL), Poland in the area of organic synthesis, specifically the synthesis of chiral aza-heterocycles with cytotoxic activity. In 2019 she worked as researcher in the process chemistry department in Ryvu Therapeutics, Poland. Since 2020 she has been employed as a post-doctorate at TUL. In 2020–2021 she worked on the synthesis of biologically active compounds and profluorescent probes for ROS in a medicinal chemistry group, and from 2022 onwards she is working on the synthesis of new monomers for radical ring-opening polymerization (rROP) in a polymer chemistry group.

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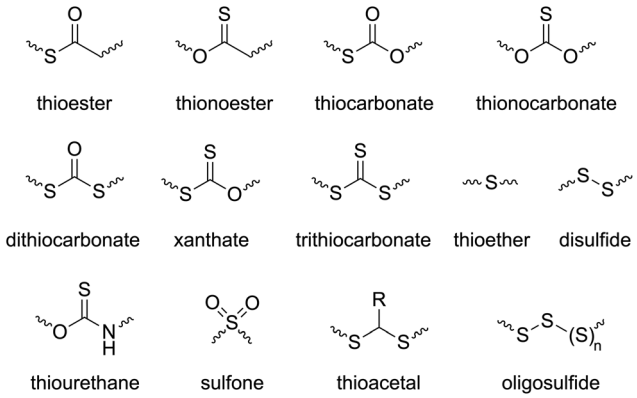
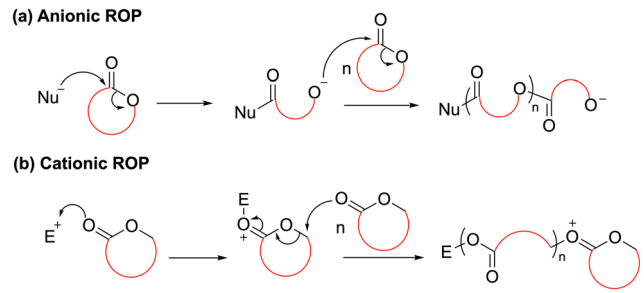
cantly altered by the inclusion of sulfur atoms. For example, a thioester functional group possesses a weak resonance in comparison to its (oxo)ester counterpart, this phenomenon making thioesters relatively electrophilic and therefore more susceptible to nucleophilic attack. Consequently, relative to polyesters, polythioesters can be degraded by additional mechanisms including aminolysis, trans-thioesterification and oxidative hydrolysis.[7]

Ring-opening polymerization (ROP) is a powerful chain-growth polymerization technique that enables the facile incorporation of heteroatoms into a polymer, facilitating access to a broad range of materials. Over the past forty years, various ROP processes including anionic, cationic, coordination–insertion, organocatalytic and radical methods have been explored to target polymers with specific and controllable properties. Based on the polymerization mechanism, ROP can generally be classified into three primary categories: ring-opening polymerization (ROP), radical ring-opening polymerization (rROP), and ring-opening metathesis polymerization (ROMP).[8,9] By the application of ROP and judicious choice of monomer, various sulfur-containing functionalities can be installed into a polymer backbone (Scheme 1).

For ring-opening polymerization (ROP), the mechanism typically involves either a cationic or anionic initiator species performing the ring-opening of a cyclic monomer to ultimately generate an ionic propagating species. In specific, anionic ROP (AROP) proceeds by nucleophilic attack of an initiator species on a polarized bond of a cyclic monomer to generate an anionic propagating species (Scheme 2a). Conversely, in cationic ROP (CROP), the most polarized functionality within a cyclic monomer attacks an electrophilic initiator species to form a cationic initiating species which then undergoes subsequent ring opening *via* either an S_N1 or S_N2 mechanism (Scheme 2b). These processes then repeat until all monomer is consumed or the reaction quenched, forming a polymer. The nature of the initiating and propagating species determines both the rate of polymerization and the control over the macromolecular structure; with carefully tailored conditions allowing



Scheme 1 Sulfur-containing functional groups that can be incorporated into a polymer backbone by the proper choice of monomer and ROP method.



Scheme 2 General mechanism of (a) anionic and (b) cationic (S_N2) ROP. Note that cationic polymerization can also occur by an S_N1 mechanism (not shown).

Joanna Pietrasik

Joanna Pietrasik received her Ph. D. in 2003 at Lodz University of Technology (TUL), Poland; next she spent 2 years at Carnegie Mellon University (CMU), USA, in the group of Prof. Matyjaszewski as a postdoc. She obtained her habilitation degree in 2014. She now holds the position of professor at TUL. Her research activity is dedicated to polymer synthesis, inorganic particles, surface modifications, as well as hybrid materials and nanocomposite properties.

Christopher M. Plummer

Christopher Plummer completed his Ph.D. in 2016 at RMIT University, Australia in the area of organic synthesis, specifically the synthesis of oxygenated heterocycles. Between 2016–2019 he was employed as a post-doctorate at Sun Yat-sen University (SYSU), China working on the post-modification of polyolefins. In 2019–2021 he worked as researcher in an industry-funded position at Aix-Marseille University, France, working on the synthesis of new monomers for radical ring-opening polymerization (rROP). Following this, he took up a position as Junior Principal Investigator at Lodz University of Technology (TUL), Poland, and is a presently a group leader in polymer chemistry.

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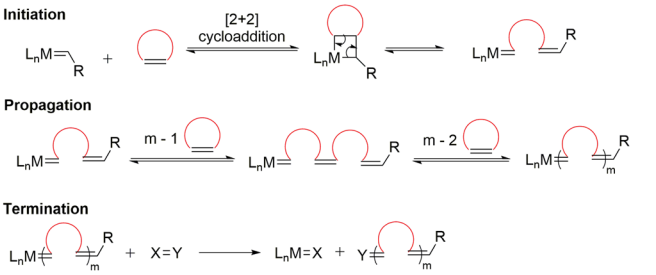
for the synthesis of polymer architectures including star-shaped, branched, statistical and block copolymers. Depending on the initiator system and conditions applied, different degrees of activation of either the monomer or propagating chain-end are obtained.[10,11] For example, the difference in ROP behaviour between ε-caprolactone (ε-CL) and L-lactide (LLA) towards cationic and anionic initiating species: cationic ROP of ε-CL with diphenyl phosphate (DPP) proceeds with good control at a moderate rate, while poor control is reported for LLA. Conversely, the reversed trend is observed with the anionic catalyst, 1,8-diazabicycloundec-7-ene (DBU).[12–14]

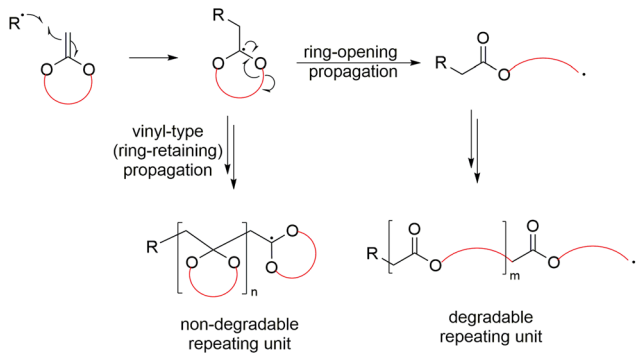
A mechanistic variation named radical ring-opening polymerization (rROP) is a polymerization technique that involves the polymerization of cyclic monomers *via* a free-radical pathway.[15,16] As a radical polymerization methodology, rROP is thereby compatible with free-radical polymerization (FRP), as well as reversible-deactivation radical polymerization (RDRP)[17] methods which provide precise polymerization control. It has been stated that rROP can be considered to combine the advantages of both ROP and FRP in one polymerization system, *i.e.* it can produce polymers incorporating heteroatoms and/or functional groups in the polymer backbone, alongside the robustness and mild conditions of an FRP process.[15,16] A primary challenge of employing rROP monomers is the mechanistic reactivity competition between the radical ring-opening process and the direct radical propagation of the vinylic bond (*i.e.*, propagation without ring-opening). This mechanistic competition frequently gives rise to polymers containing both ring-opened and ring-retained units within the same polymer backbone (Scheme 3).

Another polymerization technique within this family, ring-opening metathesis polymerization (ROMP), is a transition metal alkylidene-triggered process in which cyclic olefins experience ring-opening and are concomitantly joined together to form a polymer chain (Scheme 4).[18] Similar to Ziegler–Natta type polymerizations, ROMP is also a chain-growth polymerization that belongs to the family of polyinsertions. Initiation begins with the coordination of a transition metal alkylidene complex to a cyclic olefin to form a metallocyclobutane intermediate, followed by [2 + 2] cycloaddition, and finally cycloreversion to generate a linear propagating species. In principle, all the steps within ROMP are readily reversible and therefore exist as an equilibrium between polymerization and depolymerization.[19] Recent developments in ROMP provide a versatile strategy for the construction of functional polymers with controlled molecular weights and architectures, including block copolymers.[19–21] Moreover, ROMP displays living polymerization characteristics for many monomer types, particularly strained and bicyclic olefins.[22]



Scheme 4 General mechanism of ROMP.

The ROP of sulfur-containing monomers is a broad research area with several recent developments. Accordingly, there have been multiple excellent review articles published that overlap with the topics discussed herein, including polythioesters,[23,24] thiocarbonyl monomers,[25] sulfur chemistry in polymers,[26] and degradable polymers by rROP.[15] In consideration of the significance of both sulfur-containing polymers and ROP within the field of polymer science, we herein present an overview of the ROP of sulfur-containing monomers, principally those in which the sulfur–containing moiety is part of the heterocyclic unit. This article categorizes monomers by their primary functional group, and by the polymerization methodology applied *i.e.* ROP, rROP, ROMP, and additionally includes some miscellaneous polymerization techniques which are not readily classified. In principle, this review primarily considers the relevant literature from the past two decades, but also includes pioneering research to give a thorough overview of the subject.



Scheme 3 Competition between radical ring-opening and ring-retaining (vinyl type) polymerization.

2. Ring-opening polymerization (ROP)

2.1 Cyclic thioesters

In pioneering work on the ring-opening polymerization of thioesters, in 1968 Overberger and Weise reported the anionic ROP of 7- and 6-membered thiolactones, ε-thiocaprolactone (**M1**) and δ-thiovalerolactone (**M2**), respectively, using potassium *tert*-butoxide (KO*t*Bu) at 155 °C. Interestingly, it was reported that the 5-membered analogue γ-thiobutyrolactone (**M3a**) was not polymerizable under identical conditions (Scheme 5).[27] However, in 2020, Illy *et al.* reported the anionic ring-opening copolymerization (ROCOP) of **M3a** with functionalized epoxides using a *t*Bu-P$_4$/BnOH initiator system to

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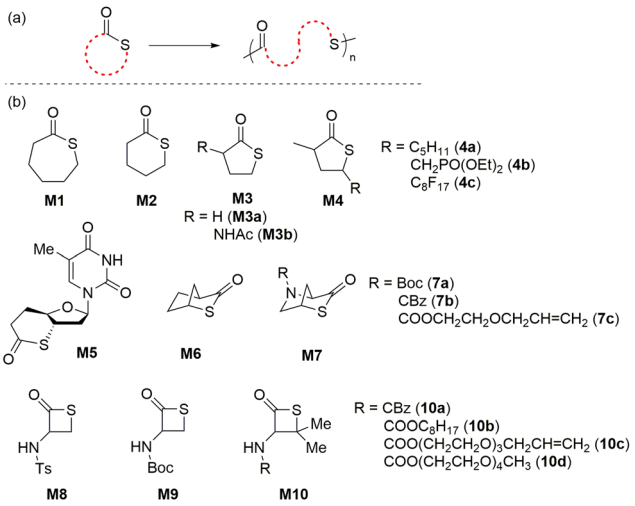


Scheme 5 (a) ROP and (b) monomer structures of thiolactones.

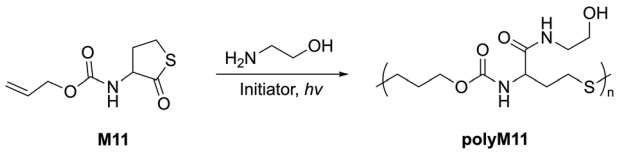
obtain poly(ester-*alt*-thioether)s.[28] Upon performing the polymerization at low temperatures (35–50 °C), the ROCOP featured controlled polymerization characteristics and narrow dispersities ($Đ$ < 1.22). This methodology was later extended for the preparation of renewable poly(ester-*alt*-thioether)s using bio-based thiolactone monomer **M3b** and various functionalized epoxides.[29,30]

In 2015, Kiesewetter *et al.* described the thiol-initiated organocatalytic ROP of **M1** to obtain polymers with broad molecular weight distributions ($Đ$ = 1.4–1.7) but with unsatisfactory M_n values generally lower than 33.0 kg mol^{-1} due to trans-thioesterification side reactions.[31] The suppression of such undesired trans-thioesterification was later reported achievable using fused or bridged-ring thiolactone monomers. In 2017, Avérous and coworkers reported the enzymatic ROP of **M1** mediated by Novozyme 435, yielding the corresponding polythioester with low molar mass and narrow dispersity (M_n = 4.4 kg mol^{-1}, $Đ$ = 1.10).[32] The methodology was extended to the ROCOP of **M1** with ε-caprolactone by applying the lipase in toluene at 70 °C, yielding statistical copolymers with M_n values ranging from 2.9 to 10.8 kg mol^{-1}. In 2018, Destarac and coworkers studied the alcohol initiated and tin(II) octoate ($SnOct_2$) catalyzed ROCOP of substituted γ-thiolactones (**M4a–c**) with trimethylene carbonate to synthesize new functional poly(carbonate-*co*-thioester)s.[33] Nevertheless, copolymers with very low molecular weights (M_n = 1.6–6.2 kg mol^{-1}) were obtained, providing evidence to support the hypothesis of ring stability for γ-thiolactones towards ROP.

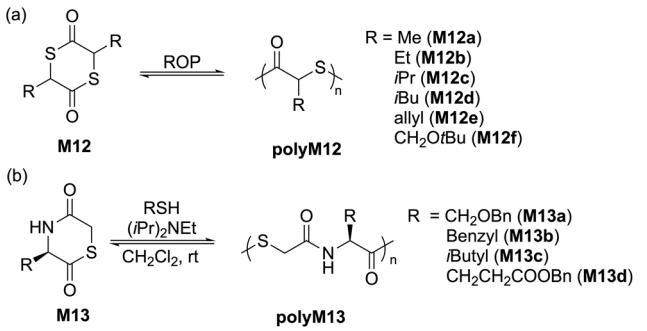
In an unusual report, Bowman *et al.* demonstrated the ROP of fused-ring thiolactone **M5** to furnish DNA-mimicking polythioesters which displayed dynamic and responsive properties, depolymerization capability, and narrow dispersities in the range of 1.2–1.3.[34] However, the highest M_n of the prepared **polyM5** was merely 7.6 kg mol^{-1}, with a poor monomer conversion of 27%. Bridged bicyclic thiolactone **M6** was also reported to be active towards ROP, providing polymers with crystallinity values that could be readily tuned by polymerization conditions to provide samples with T_m values ranging from 166 to 213 °C, this value being directly related to tacticity which modulates the crystallinity.[35] **PolyM6** was found to be chemically recyclable (*i.e.* depolymerizable) in both bulk and solution, and as a proof of concept a recycled **M6** sample was successfully repolymerized. Interestingly, the topology of the resulting polymers was also found to be dependent on the catalyst system. For example, MALDI-TOF indicated that linear polymers were obtained using mixed catalyst systems such as *t*Bu-P_4/BnOH and IMes/BnOH, while cyclic polymers were exclusively obtained using IMes alone. Later, Lu *et al.* carried out the base-catalyzed controlled ROP of bridged-ring thiolactone monomer series **M7a–c** to afford chemically recyclable polymers with M_n values as high as 259 kg mol^{-1} with dispersities generally below 1.15.[36] Upon treatment with DBU at 50 °C, **polyM7** analogues showed quantitative depolymerization in <2 min.[37]

A literature survey revealed that only six reports are available describing the ROP of β-propiothiolactones (*i.e.*, **M8–10**). Their ROPs were carried out with nucleophilic initiators such as amine, thiol, ammonium carboxylate,[38–40] as well as transition metal catalysts.[41] Initial attempts at the polymerization of β-thiolactone monomer **M8** were reported to be complicated by the uncontrolled nature of the polymerization. Suzuki and coworkers reported the synthesis of polythioesters *via* the ROP of a cysteine-derived β-thiolactone **M9**,[42] but the resulting polymers were of relatively low molar mass (M_n < 10.0 kg mol^{-1}) with relatively broad dispersities ($Đ$ = 1.6–2.4), and were also reported difficult to depolymerize. Xiong *et al.* hypothesized that the introduction of geminal dimethyl groups to the four-membered scaffold could accelerate the ring-closure step of the depolymerization, by the so-called "Thorpe–Ingold effect".[43] To this effect they synthesized a series of monomers from naturally occurring amino acid D-penicillamine, differing only in amine substitution (**M10a–d**). The corresponding polymers were found to readily depolymerize in the presence of DBU at 65 °C by a domino-like "zipper" process. Interestingly, **PolyM10c** was reported to depolymerize to a racemic monomer mixture at high temperature (>65 °C), but could also depolymerize to give enantiopure samples of **M10c** at reduced temperatures (*i.e.* 25 °C).

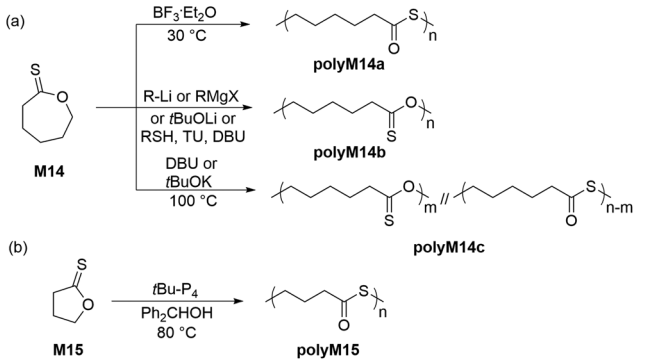
Another 5-membered thiolactone derivative **M11** was polymerized by Du Prez *et al.* by the application of a one-pot amine-initiated ROP and thiol–ene conjugation polymerization. In this way, the polymerization is initiated when γ-thiolactone **M11** is ring-opened by a primary amine, which thereby releases the thiol group to further react with the alkene functionality of another monomer unit, ultimately yielding **polyM11** (M_n = 22.0 kg mol^{-1}, $Đ$ = 1.6) (Scheme 6).[44] Suzuki *et al.* synthesised and polymerized thiolactide (**M12a**), the thioester analogue of lactide which is the precursor to commercially available polylactic acid (Scheme 7a).[45] The polymerization was found to exist as an equilibrium, with monomer conversions reaching only 50% even under forcing bulk conditions. MALDI-TOF experiments revealed that the product



Scheme 6 ROP of γ-thiolactone derivative *via* one-pot amine–thiol–ene conjugation.



Scheme 7 ROP of (a) dithiolactones and (b) 1,4-thiazine-2,5-diones.



Scheme 8 (a) ROPs of ε-thionocaprolactone (**M14**); (b) ROP of γ-thionobutyrolactone (**M15**).

contained cyclic impurities, and that thiol–thioester exchanges had also taken place during polymerization. Controlled polymerizations were then successfully performed using pyridine as a catalyst, however extended reaction times were reported to decrease the M_n which was ascribed to back-biting processes forming cyclic polymer. The authors also homopolymerized thioglycolide (**M12b**), as well as copolymerized thiolactide (**M12a**) and thioglycolide (**M12b**). In comparison to polylactide, polythiolactide (**polyM12a**) showed a lower glass transition temperature (48 °C *versus* −0.5 °C, respectively), and was additionally reported relatively more degradable by alkaline hydrolysis and UV photolysis.

Later, Tao and coworkers improved upon this protocol by performing the controlled ROP of various substituted dithiolactones **M12a–f** mediated by 4-dimethylaminopyridine (DMAP)/BnSH.[46] Structurally diverse polythioesters with controlled molecular weights (M_n values up to 100.5 kg mol^{-1}, $Đ$ = 1.2–1.4) were obtained alongside desirable features such as high crystallinity, enhanced polymerizability and chemical recyclability. Noteworthy, the synthesized polythiolactide samples (**polyM12a–f**) were readily depolymerizable to their corresponding thiolactide monomers in quantitative yield. A variety of amide analogues *i.e.* 1,4-thiazine-2,5-diones (**M13a–d**) were also examined for their polymerizability, providing polymers with M_n values up to 15.5 kg mol^{-1} ($Đ$ = 1.4–2.0) (Scheme 7b).[47]

2.2 Cyclic thionoesters

Endo and coworkers were the first researchers to investigate the anionic and cationic ROP of ε–thionocaprolactone (**M14**) (Scheme 8a). Interestingly, under cationic polymerization conditions (1 mol% $BF_3{\cdot}Et_2O$ in DCE), the ROP of **M14** proceeded with quantitative monomer conversion *via* an inversion of substitution at the thionoester group to generate polythioester **polyM14a** exclusively with an M_n of 57.0 kg mol^{-1} ($Đ$ = 1.95), with the M_n values rising alongside solvent polarity.[48] Conversely, the anionic polymerization mechanism was reported to be dependent on the nature of the initiator.[49] Polythionoesters (*i.e.* **polyM14b**) were exclusively obtained when organolithiums, lithium *tert*-butoxide and Grignard reagents were applied, whereas, KO*t*Bu and DBU yielded mixed copolymers (*i.e.* **polyM14c**), which primarily consisted of thioester repeating groups. As an example, homopolymer **polyM14b** (M_n = 13.0 kg mol^{-1}, $Đ$ = 1.65) could be obtained using 2 mol% *tert*-BuLi at 100 °C, with almost quantitative monomer conversion. Mechanistic investigations suggested that the formation of the mixed copolymer backbone was due to S/O scrambling *via* an S_N2 pathway owing to the considerably high polymerization temperatures (100 °C).

In 2016, Datta and Kiesewetter reported the alcohol (or thiol) initiated ROP of **M14** at ambient temperature without carbonyl scrambling in the presence of DBU and thiourea (TU),[50] leading to homopolymer poly(ε-thionocaprolactone) with M_n values between 12.7–22.5 kg mol^{-1} ($Đ$ = 1.10–1.41). The ROP of **M14** was hypothesized to be operative by dual activation *i.e.* H-bond activation of the thionoester group by thiourea and chain-end group activation by the base (DBU), thereby proceeding without carbonyl scrambling independent of the reaction conditions. More recently, Hong *et al.* demonstrated a *t*Bu-P_4 catalyzed ROP of γ-thionobutyrolactone (**M15**) to obtain the corresponding **polyM15**, the polymerization being driven by a thermodynamically irreversible S/O isomerization (Scheme 8b).[51] This was the first report describing such irreversible ROP, coined "IROP", which rendered the five-membered ring highly polymerizable at 80–100 °C. Quantitative monomer conversion was accomplished within only 4 h, providing **polyM15** in 94% yield with M_n values up to 162 kg mol^{-1} ($Đ$ = 1.47–1.66).

2.3 Sulfur-containing carbonates

Cyclic carbonates are a remarkable monomer class that display volume expansion during ROP,[52] leading to biodegradable

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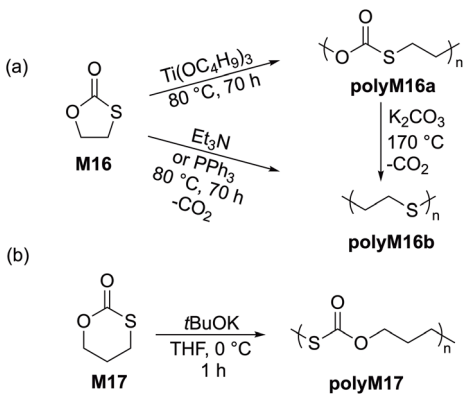
polycarbonates which are applied commercially for biomedical applications.[53] Substitution of one or multiple oxygen atoms with sulfur atoms can potentially result in enhanced physical (*e.g.* increased crystallinity), chemical, thermal, mechanical, electrical and optical properties. In this regard, cyclic thiocarbonate monomers have thereby been designed for the synthesis of thiocarbonate-containing polymers. Depending on the nature of the covalent bonds and the number of sulfur atoms within the carbonate functionality, cyclic thiocarbonate monomers can be divided into three classes: (a) cyclic monothiocarbonates (–S–CO–O–), (b) cyclic xanthates (–S–CS–O–) and (c) cyclic thionocarbonates (–O–CS–O–). It should be noted that no reports are presently available within the literature regarding the ROP of monomers containing cyclic dithiocarbonate (–S–CO–S–) or trithiocarbonate (–S–CS–S–) functionality.

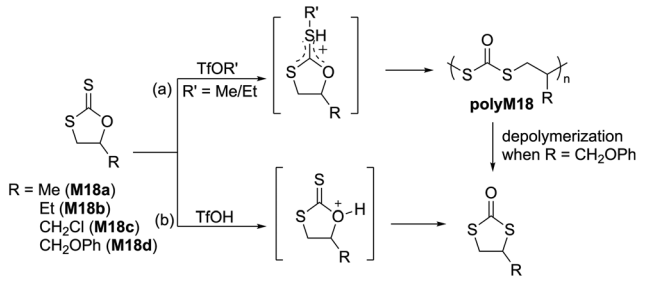
2.3.1 Cyclic monothiocarbonates. In 1975, Soga *et al.* reported the first ROP of a cyclic monothiocarbonate, 2-oxo-1,3-oxathiolane (**M16**) to obtain **polyM16** by the application of titanium butoxide as a catalyst (Scheme 9a).[54] The synthesized polymer was reported to be soluble only in hot DMSO and *p*-chlorophenol. Upon treatment of this polymer with K_2CO_3 at 170 °C, considerable amounts of ethylene sulfide and carbon dioxide are evolved to give poly(ethylene sulfide) (**polyM16b**). To target **polyM16b** directly, the decarboxylation reaction could be performed simultaneously during polymerization by the use of Et_3N and PPh_3. Later, Endo and coworkers reported the first anionic ROP of a six-membered monothiocarbonate, 1,3-oxathian-2-one (**M17**) (Scheme 9b).[55] When initiated by KO*t*Bu, the anionic ROP of **M17** in THF at 0 °C proceeded *via* selective bond cleavage through an thiolate anion to afford **polyM17** with an M_n of 18.0 kg mol^{-1} ($Đ$ = 1.5).

2.3.2 Cyclic xanthates. Endo and coworkers reported that a series of cyclic xanthates (**M18a–d**) undergo ROP with cationic triflate initiators *via* a cyclic carbenium cation intermediate, leading to the corresponding polydithiocarbonates (Scheme 10).[56–58] Both cationic and anionic quantitative depolymerizations were reported using a sample of **polyM18d** (M_n = 11.0 kg mol^{-1}, $Đ$ = 1.2).[59] Unusually, the anionic depolymerization of **polyM18d** by 5 mol% *t*BuOK at 20 °C resulted in the quantitative formation of 4–phenoxymethyl-1,3-dithiolan-2-one, a constitutional isomer of the monomer (Scheme 10). Similar isomerization was additionally observed when monomers **M18a–d** were treated directly with TfOH, likely due to catalytic rearrangement. Later, the same authors demonstrated two strategies to provide the controlled cationic ROP of xanthate monomers **M19a–b** based on neighboring group participation (NGP) initiated by TfOMe (Scheme 11a).[60,61] This approach was later extended to the ROP of xanthate monomer **M20**.[62] However, mixed backbone polydithiocarbonate **polyM20** with M_n values up to 36.0 kg mol^{-1} were obtained, hypothesized by NMR evidence to be due to the formation of a transient aziridinium ion intermediate by NGP (Scheme 11b).

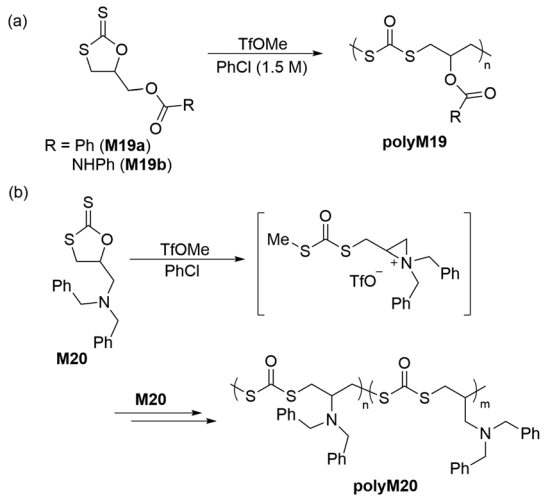
In 2018, Buchard *et al.* reported the ROP of cyclic xanthate monomers **M21** and **M22**, both derived from the natural sugars 2-deoxy-D-ribose and D-xylose, respectively, using triazabicyclodecene (TBD) as an organocatalyst and 4–methylbenzyl alcohol as an initiator (Scheme 12).[63] Polymers **polyM21** and



Scheme 9 ROP of (a) five and (b) six-membered cyclic monothiocarbonate monomers.



Scheme 10 (a) Cationic ROP of five-membered cyclic xanthate monomers (**M18a–d**) and the depolymerization of **polyM18d**; (b) catalytic isomerization of cyclic xanthates (**M18a–d**) when treated directly with TfOH.



Scheme 11 Cationic ROP of cyclic xanthates (a) involving neighboring group participation (NGP); (b) specific example showing the synthesis of mixed backbone polydithiocarbonate **polyM20** obtained upon the polymerization of **M20** initiated by TfOMe.

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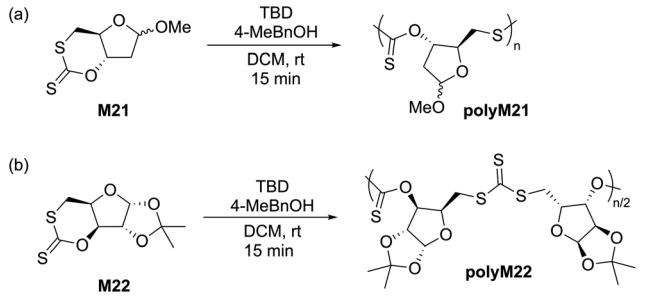
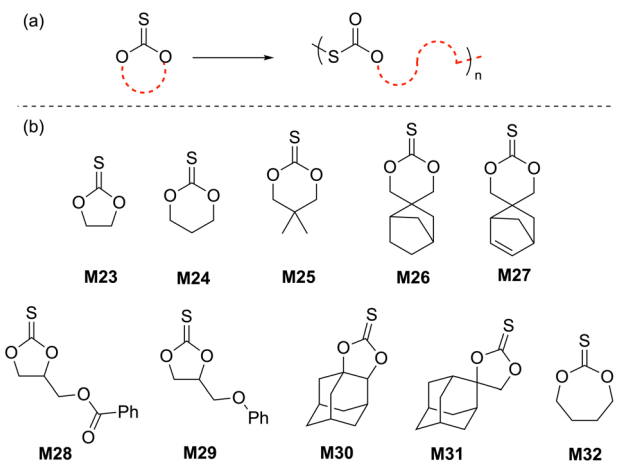


Scheme 12 ROP of cyclic xanthate monomers (a) **M21** and (b) **M22** both derived from the natural sugars 2-deoxy-D-ribose and D-xylose, respectively, in the presence of triazabicyclodecene (TBD) as an organocatalyst and 4-methylbenzyl alcohol as an initiator.

polyM22 with M_n values as high as 11.3 kg mol^{-1} ($Đ$ = 2.2) and 15.7 kg mol^{-1} ($Đ$ = 1.7) were obtained, respectively. MALDI-TOF analysis revealed the presence of both linear and cyclic topologies, in agreement with the limited polymerisation control. Moreover, NMR spectroscopic investigations on the ROP of xanthate monomer **M22** suggested the occurrence of alternating ring-opening mechanisms, ultimately forming regioregular polymers with alternating $C(S)S_2$ and $C(S)O_2$ linkages (Scheme 12b).

2.3.3 Cyclic thionocarbonates. In 1969, Jones and Andreades reported the first ROP of a cyclic thionocarbonate, 1,3-dioxolane-2-thione (**M23**), which was reported to polymerize in the presence of trifluoroacetic acid (TFA) to provide a polythiocarbonate (Scheme 13).[64] **PolyM23** was reported stable up to 200 °C, however no further analysis was performed. Kricheldorf and Damrau later synthesized a polythiocarbonate by the cationic ROP of 1,3-dioxane-2-thione (**M24**).[65] Unfortunately, the obtained polythiocarbonate was reported to be poorly soluble in common organic solvents, and therefore its polymerization behavior was not examined in detail. Nevertheless, DSC measurements confirmed the crystalline character of the resulting polymer, in stark contrast to its oxo-analogue poly(trimethylene carbonate) which is reported to be amorphous. Later, Endo and colleagues explored both the cationic and anionic ROP of diversely substituted monocyclic, spiro- and fused-thionocarbonates with 5-, 6- and 7-membered scaffolds (**M25–M32**, Scheme 13).[66]



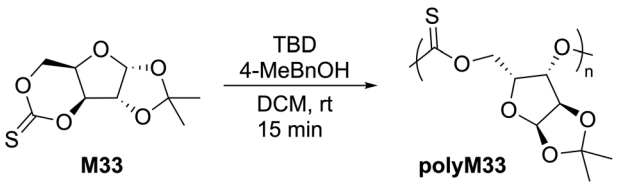
Scheme 13 (a) ROP and, (b) structures of cyclic thionocarbonate monomers.

The cationic ROP of 5,5-dimethyl-1,3-dioxane-2-thione (**M25**) using various initiators such as TfOH, TfOMe, Et_3OBF_4 and $BF_3{\cdot}Et_2O$ all showed controlled polymerization behavior, giving the corresponding polythiocarbonates with M_n values ranging from 11.2 to 31.0 kg mol^{-1} with narrow molecular weight distributions ($Đ$ = 1.04–1.15). It was reported that the cationic ROP of monomer **M28** proceeded *via* NGP of the ester group to provide a homopolymer with an unexpected polymer backbone analogous to cyclic xanthate **M19a/b** (from Scheme 11a). Interestingly, the $BF_3{\cdot}Et_2O$ initiated ROP of **M29** occurred without NGP to afford the expected corresponding polythiocarbonate with M_n = 11.0 kg mol^{-1} and $Đ$ = 1.5.[66]

The anionic ROP of **M32** in the presence of KO*t*Bu provided the corresponding polythiocarbonate (M_n = 8.8 kg mol^{-1}, $Đ$ = 1.07) in quantitative yield, demonstrating the controlled nature of polymerization.[67] The molecular weight of **polyM32** was reported to increase linearly with monomer conversion, retaining a narrow molecular weight distribution. The cationic ROP of monomers **M30** and **M31** bearing fused- and spiro-adamantane moieties was also reported; for example the M_n and dispersity value obtained by the ROP of **M30** with $H_2O/BF_3{\cdot}Et_2O$ were 10.6 kg mol^{-1} and 1.44, respectively.[68] However, **M31** failed to undergo cationic ROP presumably because of the steric hindrance of the bulky adamantane moiety.[69] Nevertheless, this monomer underwent cationic copolymerization with **M23**, **M24** and **M25** when initiated by $BF_3{\cdot}Et_2O$ or Et_3OBF_4 to afford the corresponding, albeit low molecular weight, copolymers. Buchard and coworkers also reported the ROP of *cis*-fused cyclic thionocarbonate **M33** derived from 2-deoxy-D-xylose (Scheme 14).[63] **PolyM33** samples with an M_n values up to 10.6 kg mol^{-1} ($Đ$ = 1.5) were obtained, with close agreement between theoretical and experimental molecular weights. However, MALDI-TOF studies of **polyM33** revealed the formation of a non-negligible quantity of cyclic polymer impurity, ascribed to backbiting of the polymer chain.

2.4 Thiiranes

Since the 1920s it has been reported that thiiranes readily polymerize.[70] Since then, there have been a multitude of methods reported for synthesis of polythioethers, with the most suitable



Scheme 14 ROP of a *cis*-fused cyclic thionocarbonate derived from 2-deoxy-D-xylose.

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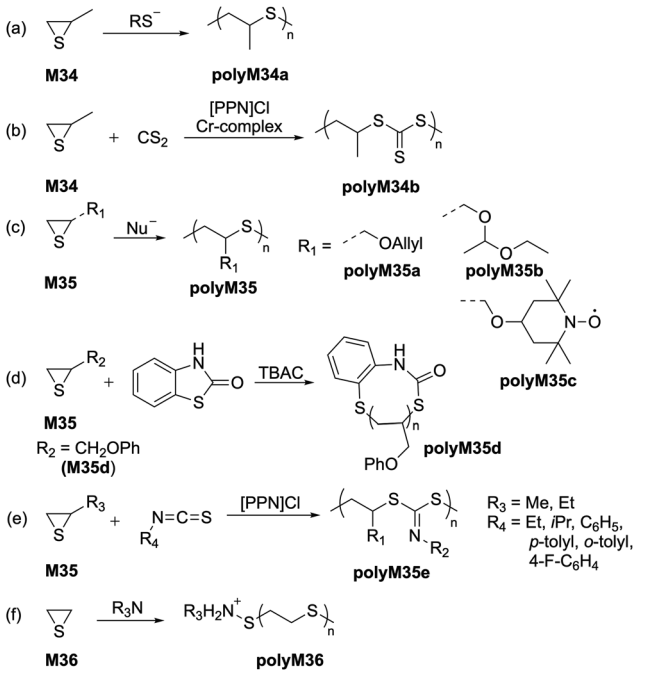
being anionic in nature.[71,72] However, high crystallinity and thereby insolubility in organic solvents have hampered any real-world applications of this polymer series, and thus further development to obtain polythioethers with improved properties remains ongoing. Polymerization experiments focused on the anionic ROP of thiirane derivatives revealed that simple and diverse nucleophiles can be utilized as initiators.[73] In particular, thiolate species derived from thiols have been demonstrated as promising initiators for the ROP of propylene sulfide (**M34**) (Scheme 15a), resulting in pure regiochemical regulation (*i.e.*, head-to-tail microstructure) within the polymer backbone.[74–76] Interestingly, anionic ROP initiated by thiolates has been demonstrated to follow first order kinetics, hence possessing 'living' character.[77] Similarly, the use of the naphthylsodium as an initiator has also demonstrated living character towards the ROP of propylene sulfide (**M34**) in THF, resulting in high molecular weight polymers (**polyM34a**) with M_n values up to 320 kg mol^{-1}.[78] Nishikubo reported the ROP of propylene sulfide (**M34**) initiated by quaternary tetraphenylphosphonium salts, with molecular weights of *ca.* 3000 g mol^{-1} ($Đ$ = 1.18) being successfully obtained.[79] Well-defined block copolymers of poly(styrene-*b*-**M34**) and poly(DMAA-*b*-**M34**) with M_n values of 3.9 and 3.8 kg mol^{-1}, respectively, were also synthesized.

Nozaki and coworkers later reported the ROCOP of propylene sulfide (**M34**) with carbon disulfide using a bis(triphenylphosphine)iminium chloride ([PPN]Cl) and chromium initiator system to obtain alternating polytrithiocarbonates (**polyM34b**) (Scheme 15b).[80] The anionic ROP of various thioglcidyl ether monomers (type **M35**) has also been reported to obtain polythioethers possessing distinct properties (Scheme 15c/d).[81–84] For example, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)-substituted polythioether **polyM35c** has demonstrated potential applications in energy storage (Scheme 15c),[81] while phenyl thioglcidyl ether (**M35d**) underwent ring-expansion polymerization using benzothiazol-2-one (BT) as a cyclic initiator in the presence of tetrabutylammonium chloride (TBAC) as a catalyst (Scheme 15d).[82] The polymerization proceeded in a well-controlled manner to afford **polyM35d** (M_n = 6.15 kg mol^{-1}, $Đ$ = 1.18) with one BT moiety per macrocycle, as confirmed by MALDI-TOF analysis.

Recently, Zhu *et al.* reported similar ROCOPs of episulfides (**M35**) with isothiocyanates in the presence of [PPN]Cl (Scheme 15e).[85] Using this methodology, a distinct class of sulfur-rich polymers (**polyM35e**) with varying substitutions were synthesized with M_n values between 27–78 kg mol^{-1}. Spectroscopic investigations by ^{13}C NMR confirmed the presence of S(C=N)S units in the polymer backbone, rather than S(C=S)N units. Moreover, TGA and DSC analysis of these polymers revealed tuneable glass transition temperatures (T_g) over a range of 31–108 °C. Tertiary amines such as 1,4-diazabicyclo[2.2.2]octane (DABCO) were additionally reported to facilitate the ROP of ethylene sulfide (**M36**) to produce high molecular weight polymers through a zwitterionic mechanism (Scheme 15f), while polyamine-based initiators were reported to produce only oligomeric **polyM36**.[86] Other nucleophiles were examined, however most of these resulted in the formation of oligomers in poor yield due to a slow initiation rate coupled with poor solubility in the reaction media.[26,87–89]



Scheme 15 (a) Thiolate-initiated ROP of propylene sulfide; (b) ROCOP of propylene sulfide with CS_2; (c) anionic ROPs of various thioglcidyl ether monomers; (d) REP of phenyl thioglcidyl ether (**M35d**); (e) ROCOP of episulfides with isothiocyanates and (f) tertiary amine-initiated ROP of ethylene sulfide.

2.5 Cyclic thiourethanes

The ROP of five-membered cyclic thiourethanes, in particular 1,3-oxazolidine-2-thiones, was first reported in 1966, however, these early studies did not report proper characterization for the obtained polymers.[90] In 2003, the cationic ROP of cyclic thiourethane derivatives was re-revisited Endo and coworkers; they reported the living cationic ROP of an enantiopure cyclic thiourethane (**M37**) derived from L-serine using TfOMe in DCM at 30 °C (Scheme 16). The resulting chirally pure polythiourethane (M_n = 13.3 kg mol^{-1}, $Đ$ = 1.06) was obtained in quantitative yield with a head-to-tail structure.[91,92] These results prompted the authors to examine the scope and limitation of this ROP system by exploring new monomer structures (**M38–M43**) and initiator systems (*e.g.* $BF_3{\cdot}Et_2O$).[93–95] For instance, the cationic polymerization of 1,3-oxazinane-2-thione (**M42**) in CH_2Cl_2 at 30 °C resulted in a polymer that was poorly soluble in organic media due to intermolecular H-bonding, while its *N*-benzyl analogue (**M43**) yielded a soluble polymer for which SEC analysis revealed a bimodal distribution. To eliminate this phenomenon, polymerization in nitrobenzene at 50 °C was performed, providing the corresponding polythiourethane in an excellent yield with a M_n of 20.4 kg mol^{-1} ($Đ$ = 1.04).[93]

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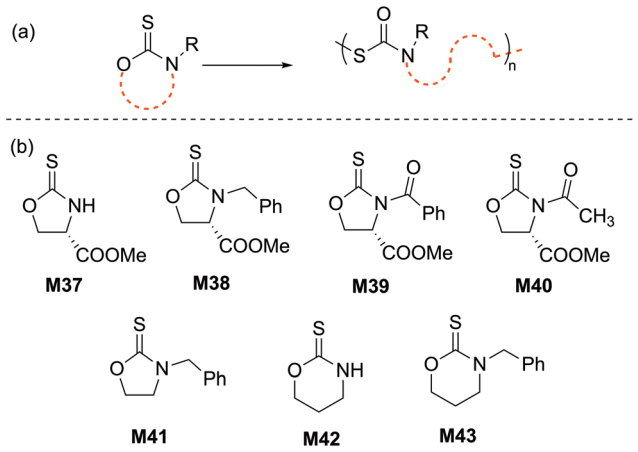
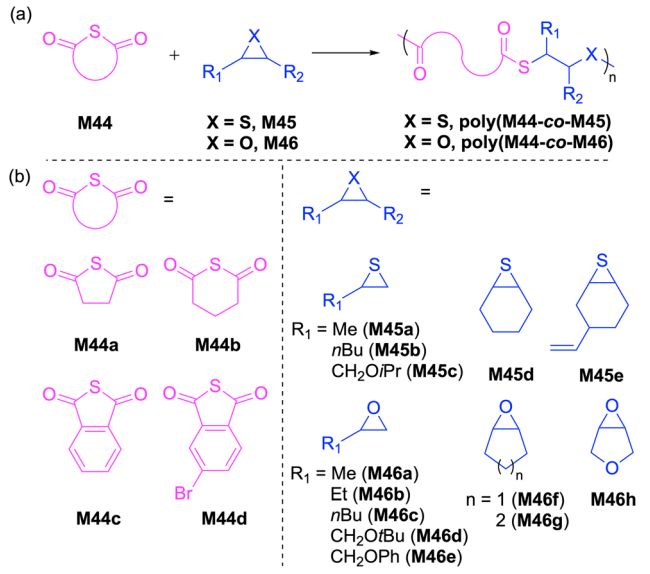


Scheme 16 (a) ROP and (b) monomer structures of cyclic thiourethanes.

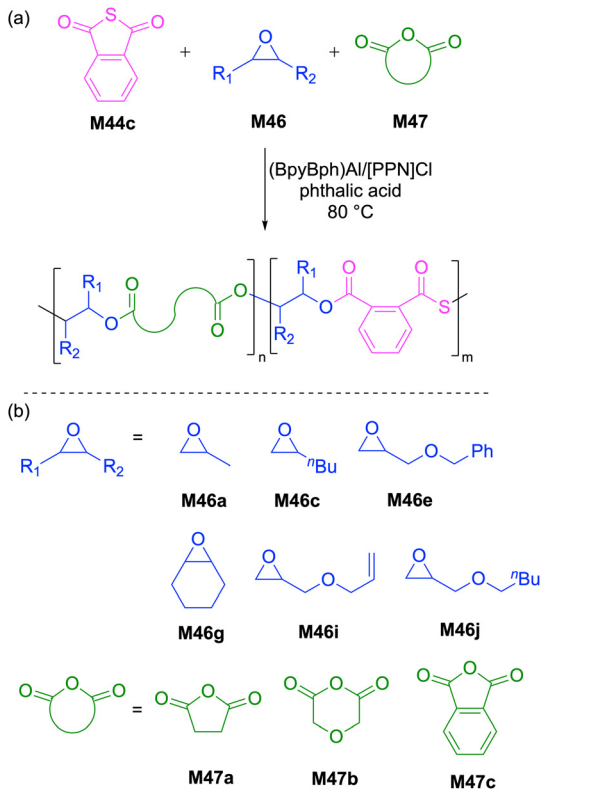
2.6 Thioanhydrides

Ren and coworkers reported extensively the ROCOP of various substituted thioanhydrides with epoxides and episulfides to synthesize aliphatic and semiaromatic polythioester copolymers (Scheme 17). They initially reported the synthesis of well-defined aliphatic polythioesters by the controlled alternating copolymerization of a variety of cyclic thioanhydrides (**M44a/b**) and episulfides (**M45**), yielding copolymers of the type **poly(M44-*co*-M45)** with controlled molecular weights (M_n = 42.3–53.6 kg mol^{-1}) and narrow dispersities ($Đ$ = 1.25–1.35).[96] Later, they explored the synthesis of semiaromatic polythioesters *via* the copolymerization of phthalic thioanhydrides (**M44c/d**) and epoxides (**M46**), catalyzed by a Cr(III)-complex to give polythioesters with M_n values up to 60.1 kg mol^{-1} ($Đ$ = 1.29–1.94).[97] However, NMR spectroscopic analysis revealed that the backbones of the resultant copolymers were composed of multiple repeating units including thioester, ester, and thioether–ester linkages owing to transesterification reactions. This difficulty was successfully overcome by the use of a bifunctional acid–base catalyst system composed of a Cr–salen complex with a covalently tethered TBD (*i.e.* a sterically hindered Lewis base), which significantly suppressed transesterification thereby yielding entirely alternating polythioesters.[98]

Recently, Chen *et al.* reported the synthesis of sequence-controlled polyester-*b*-poly(ester-*alt*-thioester)s *via* a one-pot copolymerization of phthalic thioanhydride (**M44c**), epoxides (**M46**) and anhydrides (**M47**) using phthalic acid as a bifunctional chain transfer agent (CTA) (Scheme 18).[99] Spectroscopic investigations by ^{1}H NMR indicated that the polymerization proceeded *via* two different polymerization mechanisms, namely, the ROCOP of anhydride/epoxide (high priority) and ROCOP of thioanhydride/epoxide (low priority). These observations suggest that the anhydride/epoxide copolymerization occurred initially, while the copolymerization of thioanhydride/epoxide did not proceed until after the full conversion of anhydride monomer. ABA type-triblock copolymers with M_n values ranging from 4.6 to 20.5 kg mol^{-1} ($Đ$ = 1.27–1.50) were obtained with excellent chemoselectivity in presence of phthalic acid as a CTA, demonstrating the significant reactivity difference between anhydride and thioanhydride monomers.



Scheme 17 (a) ROCOP of cyclic thioanhydrides with epoxides/episulfides and (b) monomer structures.



Scheme 18 (a) One-step ring-opening copolymerization of various mixtures of heterocyclic monomers and (b) monomer structures.

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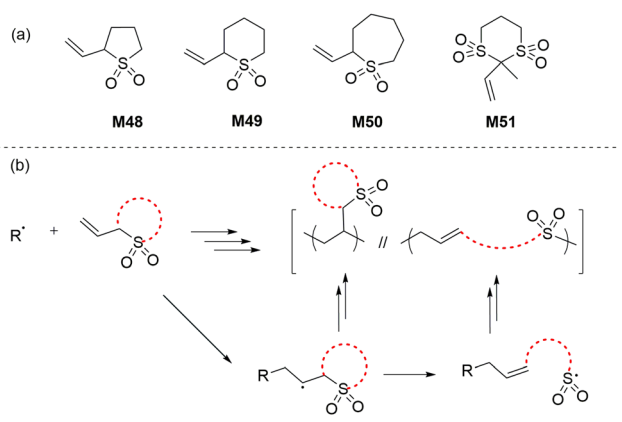
3. Radical ring-opening polymerization (rROP)

3.1 Cyclic vinylsulfones

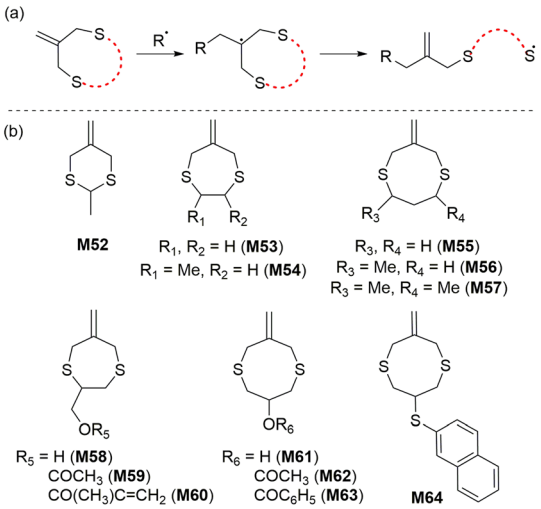
In 1986 Cho and co-workers reported a new class of monomers, the cyclic vinylsulfones, that were able to polymerize by radical ring-opening polymerization (rROP) to give polyalkene sulfones (Scheme 19b).[100–102] The AIBN/BPO-initiated polymerization of monomers **M48–M51** was reported to be dependent upon the ring strain and steric bulk of the monomer (Scheme 19a). It was reported that complete ring-opening polymerization occurred for monomers **M48** and **M51**, while monomers **M49** and **M50** underwent both ring-retaining and ring-opening propagation to give mixed copolymers. Among the six-membered monomers, **M51** was reported to be comparatively more reactive due to the presence of additional functionalities (*i.e.* sulfonyl and methyl) which imparted additional ring-strain. Unfortunately, the resulting polymers were only soluble in concentrated H_2SO_4 and TFA (and DMSO in the case of **polyM51**), these properties preventing their full chemical analysis.

3.2 Cyclic allylic sulfides

In 1996, Evans and Rizzardo reported the rROP of cyclic allylic sulfide monomers to produce polysulfides containing 1,1-disubstituted alkene units along the backbone.[103] The radical ring-opening process of these monomers produces an unusual thiyl radical which can propagate without significant competition from side reactions such as H-abstraction (Scheme 20). Bulk polymerizations of **M53** and **M55** were reported to proceed with complete ring-opening at 70 °C to give crystalline homopolymers of high molecular weight (M_n = *ca.* 6×10^5 kg mol^{-1}).[103] Complete monomer conversion was observed, although the polymers were reported insoluble in all organic solvents, with the exception of pyridine. It was reported that the introduction of methyl substituents (*e.g.*, **M56** and **M57**) provided mostly amorphous polymers which had improved solubility in organic media.[104,105] The monomer **M56** was also reported able to copolymerize with common acrylic and vinylic monomers such as methyl methacrylate and styrene.[105] Yamada and Goto[106] later investigated the photopolymerization of **M62** in the presence of oxygen, demonstrating the robustness of this polymerization system towards oxygen inhibition.



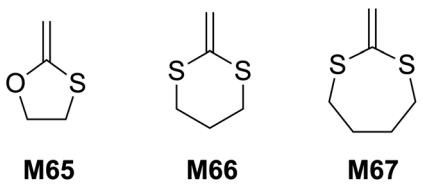
Scheme 19 (a) Cyclic vinylsulfone monomers and (b) rROP mechanism of cyclic vinylsulfones.



Scheme 20 (a) Radical ring-opening and (b) structures of cyclic allylic sulfides.

3.3 O,S/S,S-cyclic ketene acetal (CKA)

In 1984 Bailey and co-workers reported that the rROP of 5-membered O,S-CKA monomer **M65** at 120 °C formed the corresponding thioester-containing polymer with 45% ring-opened units (Scheme 21).[107] The copolymerization of styrene and **M66** also provided a thioester-containing copolymer, which upon hydrolysis produced oligomeric fragments end-capped with a mercaptan and carboxylic acid groups as expected. The polymerization of 2-methylene-1,3-dithiane (**M66**) at 80 °C yielded a low molecular weight (700–1500 g mol^{-1}) polymer possessing almost exclusively dithioacetal units by direct vinyl-type polymerization (*i.e.* without ring-opening).[108] Similarly, its copolymerization with styrene and methyl methacrylate (MMA) proceeded without ring-opening.[109] The homopolymerization of 2-methylene-1,3-dithiepane (**M67**) was reported not successful, for reasons unknown.[108]



Scheme 21 Structures of O,S-/S,S-CKA monomers.

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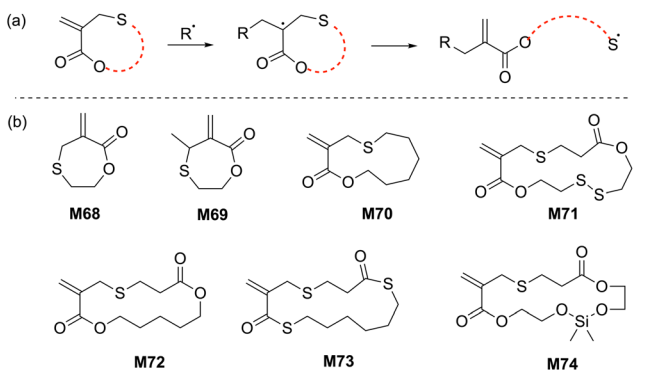
3.4 Sulfide cyclic methacrylates

Reported by Rizzardo in 1994, a new class of sulfur-containing cyclic monomers named the sulfide cyclic methacrylates emerged as promising candidates for radical polymerization.[110] As for the cyclic allylic sulfides, their propagation mechanism involves a thiyl radical (Scheme 22a). Exclusive ring-opening polymerization (*i.e.* with no ring-retaining propagation) and high reactivity were reported for this monomer class during both homopolymerization and copolymerization, although cross-linking was reported for the homopolymerization of **M68** after 20% monomer conversion. However, this phenomenon was not observed for **M69** due to the production of a trisubstituted alkene during the radical ring-opening process, thereby inhibiting radical addition to the alkene.

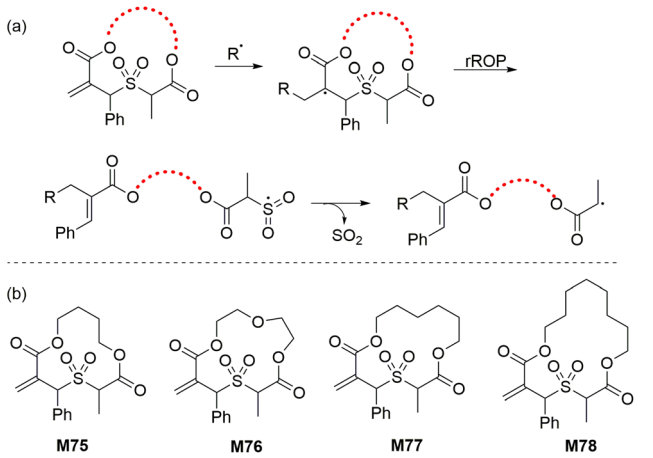
Copolymerizations of **M69** and **M70** with styrene and MMA were reported to proceed with high monomer conversions (70–85%), producing their respective copolymers with M_n values between 1.7–19.2 kg mol^{-1} ($Đ$ = 1.8–1.9). Later, Hawker extended this research by developing macrocyclic sulfide methacrylate monomers having ester, thioester, and disulfide functionalities within the monomer scaffold (Scheme 22b).[111] RAFT copolymerizations of **M70–M73** and MMA displayed good control over molecular masses (M_n up to 30 kg mol^{-1}) and tuneable, but limited incorporation of macrocyclic allylic sulfide units into the copolymer ($F_{\mathbf{M71}}$ = 0.01–0.10). Different potential degradation modes of the copolymer backbone (such as basic/acidic, reductive, thiolate, and even enzymatic) can be envisioned by the proper choice of macrocyclic sulfide methacrylate monomer.

3.5 Macrocyclic allylic sulfones

To overcome the difficulties associated with the rROP of sulfide cyclic methacrylates, a new strategy named radical cascade-triggered ring-opening polymerization (RCT-ROP) was developed. Allylic sulfone groups were thus applied as "ring-opening triggers" *via* a radical cascade sequence that forms a sulfonyl radical which subsequently expels SO_2 to generate a stabilized secondary alkyl radical (Scheme 23). The produced



Scheme 22 (a) General scheme for radical ring-opening of sulfide cyclic methacrylates and (b) structures of the cyclic/macrocyclic allylic sulfides used in rROP.



Scheme 23 (a) RCT-ROP mechanism of a macrocyclic allylic sulfone and (b) structures of the various monomers polymerized by RCT-ROP.

secondary alkyl radical is functionally analogous to that of polyacrylates and is therefore readily suited for controlled polymerization *via* RDRP techniques. In this way, Niu and co-workers[112] synthesized a series of 12–16 membered macrocyclic allylic sulfones (**M75–M78**, Scheme 23) and successfully performed their RAFT polymerization to generate well-defined homopolymers and copolymers. For example, the AIBN initiated RAFT homopolymerization of **M75** in toluene at 100 °C resulted in 62% monomer conversion within 2 h (M_n = 12.1 kg mol^{-1}, $Đ$ = 1.15) while its copolymerization with methyl acrylate (MA) ($f_{\mathbf{M75}}$ = 0.05) proceeded with 92% conversion to yield a copolymer with 12 mol% cyclic monomer incorporation (M_n = 10.2 kg mol^{-1}, $Đ$ = 1.17). However, unfavourable reactivity ratios were observed due to the faster incorporation of the macrocyclic allylic sulfone monomers in comparison to MA.

To overcome reactivity complications, the same group recently reported a photoinduced electron transfer-reversible addition fragmentation chain transfer (PET-RAFT) approach.[113] For instance, the homopolymerization of **M78** mediated by an iridium complex under 450 nm irradiation yielded **polyM78** with an M_n of 9.8 kg mol^{-1} ($Đ$ = 1.11), thereby showing excellent control over the polymerization. A diblock copolymer **polyM75-*b*-M78** (M_n = 13.0 kg mol^{-1}, $Đ$ = 1.20) was also synthesized under similar conditions. It was demonstrated that propagation completely halted when the light source was removed, and then resumed efficiently after the light source was reintroduced. The photocontrolled copolymerization of **M78** with MA at a feed composition of $f_{\mathbf{M78}}$ = 0.05 yielded a copolymer **poly(M78-*co*-MA)** with an M_n of 44.0 kg mol^{-1} ($Đ$ = 1.28). Interestingly, fitting of the polymer compositional data into the Beckingham–Sanoja–Lynd integrated model[114] determined the reactivity ratios of **M78** and MA remained close to unity during the entire range of the monomer feed compositions ($f_{\mathbf{M78}}$ = 0–1). Furthermore, the copolymerization of **M78** with other acrylic monomers at $f_{\mathbf{M78}}$ = 0.09 all exhibited excellent polymerization control and

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near-unity reactivity ratios, suggesting the general applicability of this method to a wide range of acrylates and acrylamides.

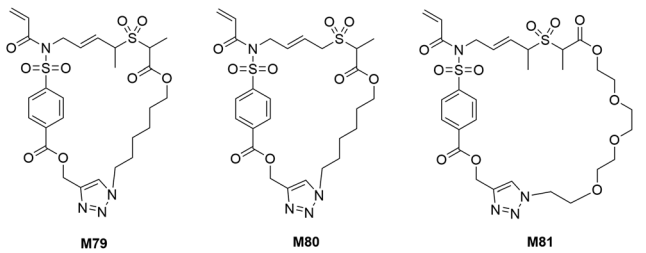
Following the success of RCT-ROP, Niu *et al.* developed a new series of monomers with even larger ring sizes (26- to 31-membered) which were also capable of undergoing radical-initiated cascade polymerization (**M79–M81**) (Scheme 24).[115] It was proposed that a 1,6-diene-fused allylic alkylsulfone could undergo efficient SO_2 extrusion during the cascade process to thereby form a stabilized alkyl radical to enable controlled chain growth. The synthesized macrocyclic structures (**M79–M81**) were successfully homopolymerized using RAFT at 85 °C for 40–45 h, displaying good control over molecular weights and dispersities (M_n = 4.1–20.1 kg mol^{-1}, $Đ$ = 1.21–1.39). The prepared polymers exhibited good thermal stability (~5% mass loss at 310–340 °C), variable glass transition temperatures (T_g = 48–138 °C), and high susceptibility to degradation by sodium methoxide *via* cleavage of the ester and pyrrolidinone groups.

3.6 Thionolactones

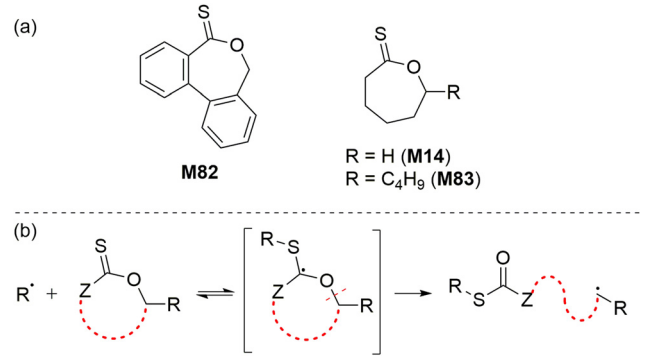
Reported independently by Roth[116] and Gutekunst[117] in 2019, a new class of thionoester-containing rROP monomer recently emerged as good candidates to prepare degradable polymers. The polymerization of such cyclic thionolactone monomers leads to the insertion of thioester linkages into a polymer backbone *via* what was termed "thiocarbonyl addition-ring opening" (TARO) polymerization (Scheme 25).[116] The introduction of thioester groups is advantageous when compared to their (oxo)ester counterpart as thioesters can be degraded by additional mechanisms including hydrolysis, aminolysis, trans–thioesterification and oxidative hydrolysis. Among the various thionolactone monomers reported, only dibenzo[*c*,*e*]oxepane-5-thione (**M82**), ε-thionocaprolactone (**M14**), and ε-thionodecalactone (**M83**) were successfully polymerizable by rROP.[116–119]

Roth *et al.* performed the AIBN-initiated homopolymerization of **M82** in acetonitrile, finding negligible conversion after heating at 80 °C overnight.[116] Later, they improved the conversion up to 22% (M_n = 4.9 kg mol^{-1} and $Đ$ = 2.0) by performing the polymerization in DMSO with the sequential addition of fresh AIBN over 27 days at 60 °C.[120] However, it was noted that this method was impractically slow and failed to produce a well-defined homopolymer. When compared to CKA monomers, **M82** is reported to be relatively stable under ambient conditions, however, heating **M82** in DMSO at 150 °C was reported to lead its isomerization to the thioester (–C(=O)S–) derivative.[116] Attempted RAFT homopolymerizations of **M82** also failed, having only <2% **M82** conversion.[116] Due to the stabilization of the propagating radical by the aromatic ring, **M82** was reported to readily copolymerize with a variety of monomers including acrylates, acrylamides, acrylonitrile and maleimides (Scheme 26). Surprisingly, **M82** was found to inhibit radical polymerizations of vinyl acetate and *N*-vinylcarbazole, and to retard the radical polymerization of styrene without being incorporated.[116,117]

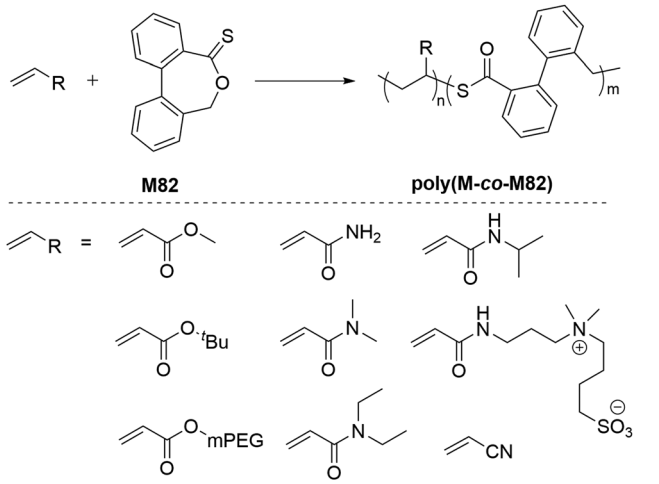
Roth and coworkers investigated the copolymerization of **M82** and MA as a model monomer, which was reported to form alternating sequences of both monomers although it was noted that retardation (*i.e.* a lower-than-expected monomer consumption at a given time) was observed with an increased quantity of **M82** within the feed.[116] During the same period, Gutekunst[117] published the RAFT copolymerizarion of **M82** and *tert*-butyl acrylate (*t*BA) using a 5% DOT feed ratio. A variety of polymer molecular weights (M_n = 4.4–32.6 kg mol^{-1})



Scheme 24 Structures of the macrocyclic allylic sulfone monomers.



Scheme 25 (a) Structures and (b) radical ring-opening of thionolactone monomers.



Scheme 26 (a) Copolymerization of DOT (**M82**) with a vinyl monomer and (b) structures of various vinyl monomers.

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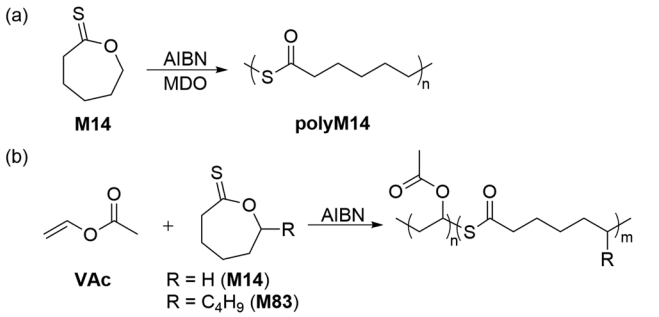
with relatively low dispersities ($Đ$ = 1.05–1.27) were obtained by varying the monomer-to-initiator ratio. It was reported that lower monomer conversions of **M82** were obtained at 50% feed as a result of polymerization retardation. A well-defined diblock copolymer poly(*t*BA-*co*-**M82**)-*b*-poly(*n*BA-*co*-**M82**) was also prepared by RAFT polymerization from a poly(*t*BA-*co*-**M82**) macro-CTA to provide evidence of the livingness of the system. To verify the presence of thioester linkages within the copolymers, degradation experiments were performed by methanolysis (with NaOMe) and thiol–thioester exchange reaction (with cysteine methyl ester), giving broad low molecular weight oligomers (1.7–2.1 kg mol^{-1}).[117]

Interesting, the RAFT copolymerization of **M82** (50% feed ratio) with *N*-substituted maleimides produced well-defined alternating copolymers.[120] The tendency to form alternating sequences was reported to be increased in the order of R = CH_3 < Ph < C_6F_5. Interestingly, when *N*-phenylmaleimide and *N*-(pentafluorophenyl)maleimide were used as comonomers, defects in the alternating structure were more likely caused by faster incorporation of **M82** leading to **M82–M82** (degradable) sequences rather than MI–MI (nondegradable) sequences. **M82** was also reported to copolymerize with a range of neutral and zwitterionic acrylamides to give copolymers that displayed temperature-responsive aqueous solubility behavior, tunable through the comonomer composition, as well *via* degradation.[7] Roth also investigated the radical copolymerization of **M82** with acrylonitrile but reported the copolymer was only soluble in DMSO and therefore difficult to analyse.[116]

After the reported success of thionolactone **M82**, other monomers in this series such as ε-thionocaprolactone (**M14**) were also investigated. Destarac and Harrisson reported well-defined copolymers of **M14** and vinyl esters such as vinyl acetate (VAc) and vinyl pivalate (VPiv) using *via* both free-radical and RAFT polymerization.[118] Using a 10% **M14** feed, copolymerization with VAc was carried out to high conversion, producing poly(VAc-*co*-**M14**) copolymers having M_n values up to 22.8 kg mol^{-1} with good incorporation of **M14**. Spectroscopic investigations revealed that the majority of the incorporated **M14** was present as the ring-opened thioester, while 36.5% of was incorporated in ring-retained form. The copolymerization **M14** and *N*-vinyl pyrrolidinone was reported to result in polymerization retardation, low molar mass, high dispersity and little thionolactone incorporation, while attempts to homopolymerize **M14** were reported completely unsuccessful.

Guillaneuf and co-workers also reported that two thionolactone monomers, **M14** and ε-thionodecalactone (**M83**) were capable of performing rROP with VAc (Scheme 27).[119] It was observed that at 10% feed of **M14** the amount of thioester-linkages within the polymer became enriched, while above 20% feed the polymerization did not occur. In this way, the copolymerization of **M83** with VAc (10 : 90 feed, respectively) provided a copolymer with 20% thioester repeating units (M_n = 16.6 kg mol^{-1}). The authors later identified the initiation phase as the main hindrance to successful polymerization, hypothesizing that **M14** was sequestering the AIBN-derived initiating radicals.



Scheme 27 (a) Radical homopolymerization of **M14** and (b) radical ring-opening copolymerizations of **M14**/**M83** with VAc.

In this way, copolymerizations of **M14** with the CKA monomer 2-methylene-1,3-dioxepane (MDO) were performed, successfully providing homopolymer **polyM14** (M_n = 16.8 kg mol^{-1} and $Đ$ = 3.2), ascribed to its initiation by MDO-derived radicals. Interestingly, spectroscopic analysis of the copolymers revealed the presence of exclusively ring-opened units within the polymer backbone.[118] To extend the scope of this protocol, block copolymers such as poly(DMMA)-*b*-(VAc-*co*-**M14**) and poly(DMMA-*co*-**M82**)-*b*-(VAc-*co*-**M14**) were synthesized *via* RAFT and demonstrated to be selectively degradable, thereby demonstrating the effectiveness of thionolactone monomers in preparing degradable polymers.

4. Ring-opening metathesis polymerization (ROMP)

ROMP is a chain-growth strategy widely applied for the controlled synthesis of π-conjugated functional polymers. The mechanism of the ROMP process is based upon olefin metathesis which was initially proposed by Y. Chauvin and later significantly explored by R. H. Grubbs. A significant number of reports on the ROMP of a broad range of cyclic olefins are available in the literature, however, reports of the incorporation of sulfur-containing monomers are relatively scarce. Attempts to homopolymerize sulfur-containing cyclic olefins by ROMP failed due to the negative neighbouring group effect of sulfur.[121] It was speculated that the coordination of sulfur to the transition metal within the catalyst (*e.g.* ruthenium) is more pronounced when the sulfur-containing linkage is present within the cyclic olefin due to the ease of formation of a five/six-membered ruthenocycle during the propagation step which may lead to catalyst decomposition. Nevertheless, disulfides and thioacetal groups have been successfully incorporated by ROMP into a polymer backbone.

Hilf and Kilbinger reported the synthesis of thiol-functionalized ROMP polymers *via* 'sacrificial synthesis' using the unsaturated thioacetal monomer, 2-phenyl-1,3-dithiepine (**M84**).[122] Diblock copolymers of *exo*-*N*-hexyl-2,3-norbornene dicarboximide (HNI) and *exo*-*N*-phenyl-2,3-norbornene dicarboximide (PNI) with unsaturated thioacetal monomer were synthesized

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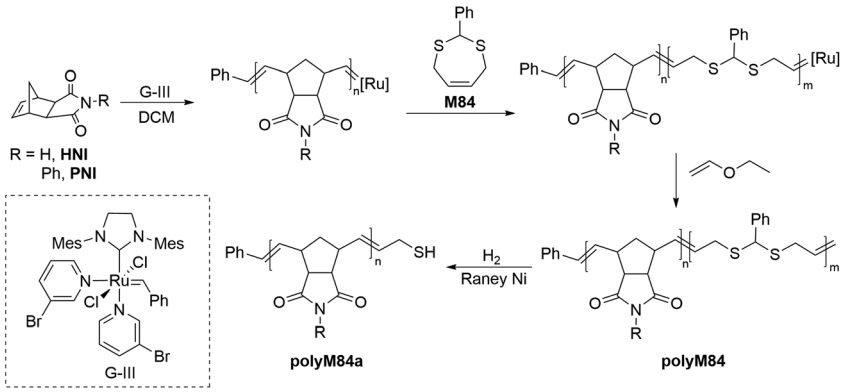
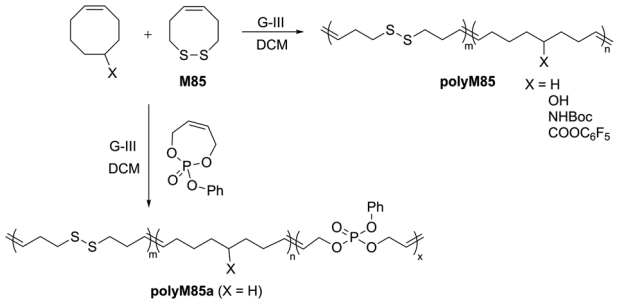


Scheme 28 Sacrificial synthesis of thiol-functionalized polynorborneneimides.

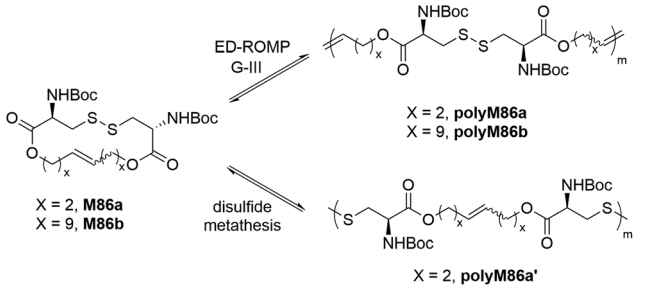
by third-generation Grubbs catalyst (GIII)-catalyzed ROMP (Scheme 28). The thioacetal block of copolymer **polyM84** was then cleaved by hydrogenation using RANEY® Ni to access the thiol functionalized polymer **polyM84a** (M_n = 5.9–33.0 kg mol^{-1}, $Đ$ = 1.09–1.28) which were then successfully employed for the coating of the gold nanoparticles.

Chang and Emrick prepared disulfide-containing polyolefins by the ROMP of disulfide-containing cyclic olefin **M85** with substituted cyclooctene monomers using G-III catalyst.[121] This strategy allowed for the synthesis of a series of degradable block-copolymers (**polyM85**) with disulfide linkages within the polymer backbone, along with functional cyclooctene comonomers bearing pendent hydroxyl, amino, and pentafluorophenyl ester groups (Scheme 29). The disulfide monomer incorporation in the copolymer samples ranged from 5 to 27 mol%, with molecular weights between 12–34 kg mol^{-1}. A significant decrease in the molecular weight of the copolymers was reported upon degradation with tri-*n*-butylphosphine (*n*-Bu_3P) and 1-dodecanethiol, confirming the presence of the disulfide linkages. This ROMP strategy was further extended to terpolymerization with a phosphoester containing cyclic olefin monomer, providing **polyM85a** containing both disulfides and phosphoesters functionalities, which was also reported to exhibit degradability.

Behrendt and Schlaad synthesized 16- and 30-membered macrocycles (**M86a/b**) based upon L-cystine which were polymerized by entropy-driven ROMP (ED-ROMP) to produce



Scheme 29 Synthesis of disulfide containing polyolefins by ROMP.



Scheme 30 ED-ROMP and disulfide metathesis of macrocycles based on L-cystine.

polyM86a/b containing disulfide and ester linkages within the polymer backbone (Scheme 30).[123] Polymers with molar mass values of up to 80 kg mol^{-1} ($Đ$ = 2) were obtained with *ca.* 80% monomer conversion using G-III as a catalyst. The synthesized polymers were successfully demonstrated to be degradable by reductive cleavage of the disulfide linkages. Subsequent kinetic studies on the synthesis of **polyM86a** revealed that the ruthenium catalyst (G-III) was deactivated during the polymerization, thereby limiting the achievable polymer molar mass. Such limitations were overcome by performing disulfide metathesis of the same macrocycle **M86a** to yield the polymer **polyM86a′** (M_n = 180 kg mol^{-1}) with an identical repeating unit structure, but with thiol chain ends.[124]

Gutekunst and Hawker synthesised two 20- and 23-membered sulfonamide-containing macrocycles (**M87** and **M88**, respectively) designed in such a way that a polymerization trigger was attached to a series of glycolate (Gly), (*S*)-lactate (Lact), (*S*)-phenyllactate (PhLact), and β-alanine (β-Ala) units to give ABCD(E)-type sequences which are then displayed in the polymer backbone post-ROMP (Scheme 31).[125] The ROMP of **M87** and **M88** thereby produced sequence-defined polymers with accurate control over molecular weights and low dispersities. For example, G-III catalyzed ROMP of **M88** provided a polymer having an M_n value of 32.6 kg mol^{-1} ($Đ$ = 1.26), with the polymer chain consisting of *ca.* 250 perfectly sequenced units. Upon degradation with TBD, SEC analysis of **polyM88**

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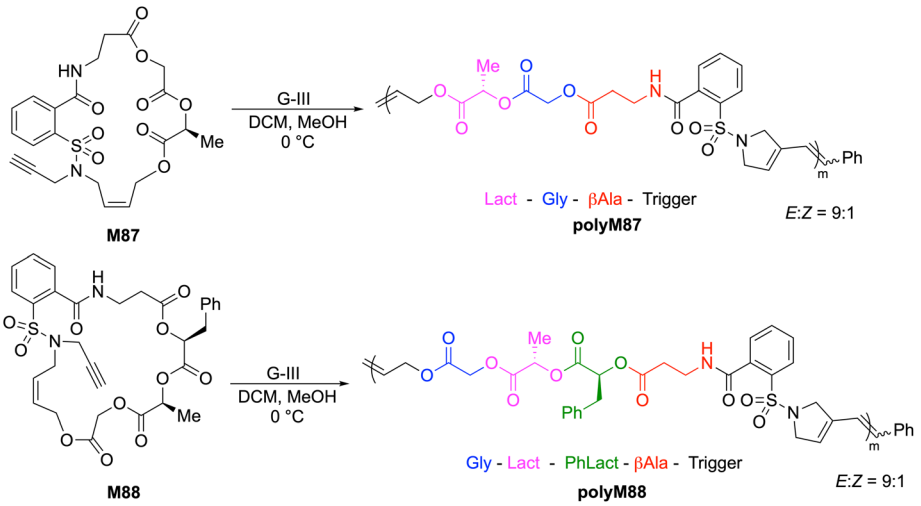


Scheme 31 ROMP of sequenced sulfonamide-containing macrocyclic monomers.

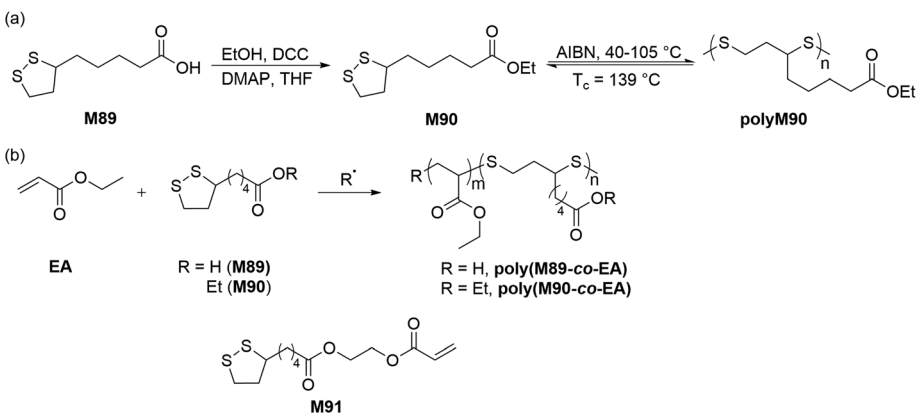
revealed a dramatic decrease in the molecular weight after only 30 seconds, and complete conversion to oligomeric methyl esters with M_n values of *ca.* 200 g mol^{-1} after 2 h.

5. Miscellaneous

5.1 ROP of 1,2-dithiolanes

Calvin and coworkers were pioneers in the photoinduced ROP of 1,2-dithiolanes, demonstrating that the disulfide bond can be activated by the ring strain of the five-membered scaffold to obtain poly(1,2-dithiolane)s.[126] More detailed studies to prepare poly(1,2-dithiolane)s with unambiguous molecular structures were later reported by Endo.[127] They reported the synthesis of copolymers (M_n = *ca.* 5.0 kg mol^{-1}) of lipoic acid (**M89**) and six-membered 1,2-dithiane. NMR spectroscopy of the resulting polymer confirmed a cyclic structure for the copolymer, and dynamic viscoelasticity measurements suggested mechanical entanglements of the cyclic polymer chains. Combined with other structural evidence as well as photodecomposition studies, the authors concluded that the resulting polymers featured mechanically cross-linked polycatenane-type networks. Cyclic disulfide monomers are of particular interest in polymer chemistry as they can provide polymers with disulfide groups within the polymer backbone which can be readily degraded by reduction.

5.1.1 rROP of 1,2-dithiolanes. The attack of a free-radical initiator on a cyclic disulfide monomer leads to the ring-opening of the disulfide-containing heterocycle, yielding sulfur-centered radicals which can then further propagate ring-opening polymerization. In this regard, Raeisi and Tsarevsky identified ethyl lipoate (**M91**), a 5-membered cyclic disulfide derived from naturally occurring lipoic acid (**M90**), as a promising monomer to synthesize degradable polymers by radical polymerization (Scheme 32).[128] The rROP homopolymerization of **M90** was studied at various temperatures in both bulk and solution, but monomer conversion was observed to plateau in all cases, with the plateau being lower at higher



Scheme 32 (a) Synthesis and polymerization of ethyl lipoate (**M90**) and degradation of **polyM90**; (b) radical copolymerizations of lipoic acid (**M89**) and ethyl lipoate (**M90**) with ethyl acrylate.

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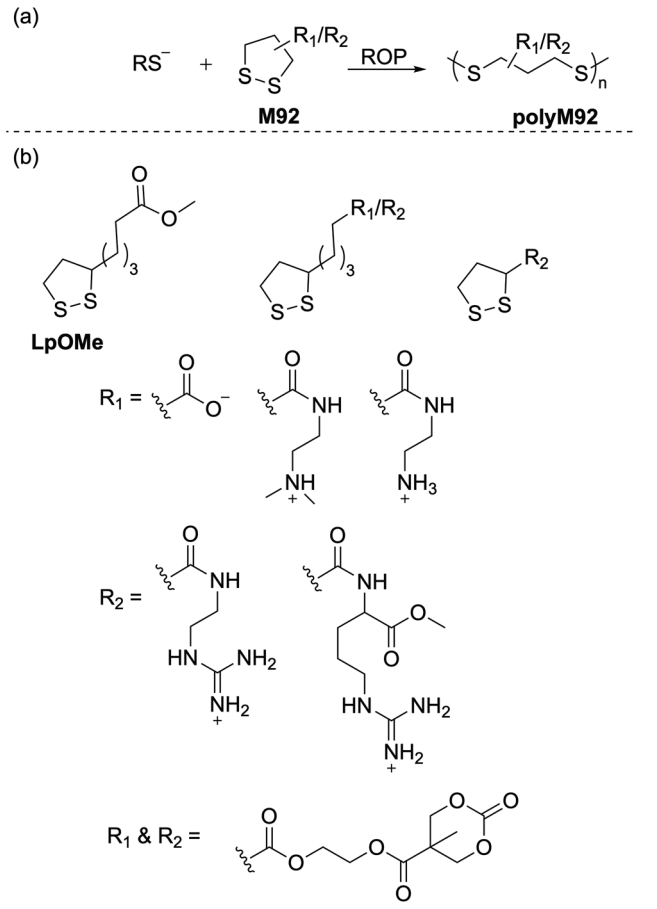
temperatures and/or higher dilutions. At higher temperatures, the molecular weight distributions of the synthesized polymers (**polyM90**) were reported to be in a narrow range due to the fast thiyl radical-disulfide exchange reactions. It was also reported that a monomer–polymer equilibrium existed with a ceiling temperature (T_c) of 139 °C. The SEC traces of AIBN-induced degradations of **polyM90** at 60 °C indicated a significant decrease in molecular weight (from 44.9 to 1.8 kg mol^{-1}) confirming the presence of disulfide linkages within the polymer backbone. Radical copolymerizations of **M89** and **M90** with ethyl acrylate (EA) (1 : 1 feed ratio) readily produced their respective copolymers **poly(M89-*co*-EA)** and **poly(M90-*co*-EA)** (Scheme 32).[129] The radical polymerization of an LPA derivative, 2-acryloyloxyethyl lipoate (**M91**) having both cyclic disulfide and vinyl functionalities was also performed to prepare highly branched sulfur-containing degradable polymers.

5.1.2 Thiolate-initiated ROP of 1,2-dithiolanes. Thiolate-initiated ROP of functionalized 1,2-dithiolane derivatives (type **M92**) was also developed to obtain poly(1,2-dithiolane)s with various macromolecular architectures such as polymer brushes,[130] drug carriers,[131] polymer hydrogels,[132] protein–polymer conjugates,[133] and others (Scheme 33). For instance,



Scheme 33 (a) Thiolate initiated ROP and (b) monomer structures of 1,2-dithiolanes.

Moore and coworkers demonstrated a high dependency on the type of thiolate initiator used for the polymerization of methyl lipoate (LpOMe).[134] It was reported that alkyl thiolates led to linear poly(LpOMe)s, while aryl thiolates produced macrocyclic species, hypothesized to be due to differences in the nucleophilicity of the initiators. This ROP approach afforded high molecular weight cyclic poly(1,2-dithiolane)s with M_n = 630 kg mol^{-1} ($Đ$ = 1.27), along with precise architectural control. Both cyclic and linear poly(LpOMe) samples were successfully recycled to the corresponding monomer (up to 95% recovery) by heating at 65 °C in the presence of their respective thiolate initiators. Nevertheless, the majority of these reports focus significantly on the applications of poly(1,2-dithiolane) architectures in the fields of nanotechnology and bio-medicinal chemistry, and therefore lack the detailed spectroscopic characterization valued by synthetic and polymer chemists.

5.2 ROP of elemental sulfur (S_8)

The incorporation of a high content of sulfur atoms into a polymer backbone can provide materials with several exotic and useful properties. For this reason, several research studies have been performed with the aim of utilizing elemental sulfur (S_8, **M93**) for the preparation of new polymeric materials. Polymeric sulfur (**polyM93a**) has been synthesized by performing the ROP of orthorhombic α-S_8 above its floor temperature (159 °C) (Scheme 34a).[135] Under this temperature (*i.e.*, under equilibrium polymerization conditions) the reaction becomes reversible, forming cyclic monomeric sulfur (S_8) due the backbiting depolymerization by terminal sulfur radicals (Scheme 34a). Rapid quenching (using alkene or polyene derivatives) of the equilibrium melt polymerization of **M93** has been applied to preserve the polymeric form of sulfur for prolonged durations. As displayed in Scheme 34, a variety of polymers have been synthesized by employing diverse polymerization strategies including anionic, cationic and free-radical copolymerizations of elemental sulfur (**M93**) with various comonomers. Four excellent reviews are available discussing such copolymerizations in detail,[5,26,135,136] and thus this section merely intends to give a short overview of the research topic.

Bordoloi and coworkers reported the base-catalyzed ROCOP of **M93** and ethane-1,2-dithiol to synthesize polysulfides (**polyM93b**) *via* a thiol–ene type reaction (Scheme 34b).[137] Notably, as the molecular weight of the synthesized polymers increased during polymerization, the sulfur rank (a measure of flexibility and rigidity of inverse vulcanized polymers) was found to plateau. Later in 1981, Boscato *et al.* reported the synthesis of poly(phenylene polysulfane)s (**polyM93c**) through the alkali-mediated reaction of **M93** and *p*-dichlorobenzene (Scheme 34c).[138] High molecular weight linear polymers (M_n = 12.0 kg mol^{-1}) with high sulfur content were obtained by this protocol. However, the post-polymerization removal of by-products (*e.g.*, Li_2S_n, LiCl) was reported problematic. The free-radical ROCOP of **M93** and a variety of unsaturated monomers including vinylics, cyclic olefins and terpenoids was also reported (Scheme 34d).[26,135] Spectroscopic characterization

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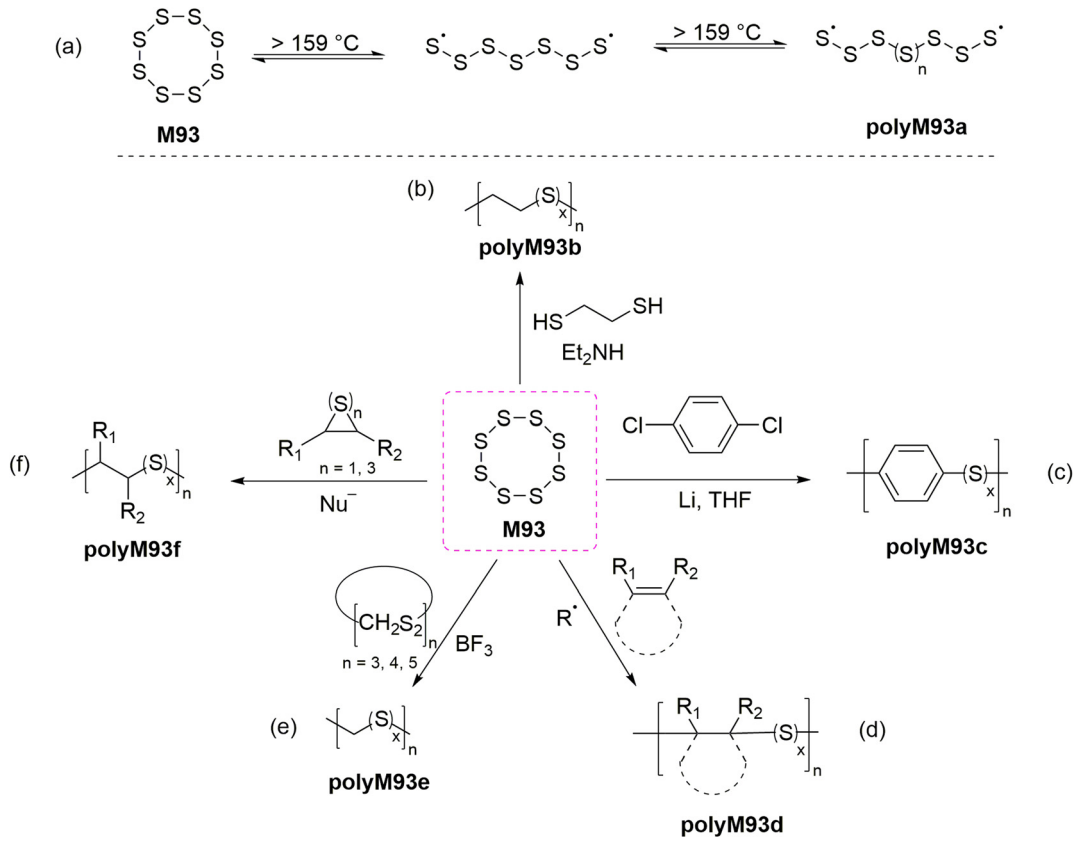
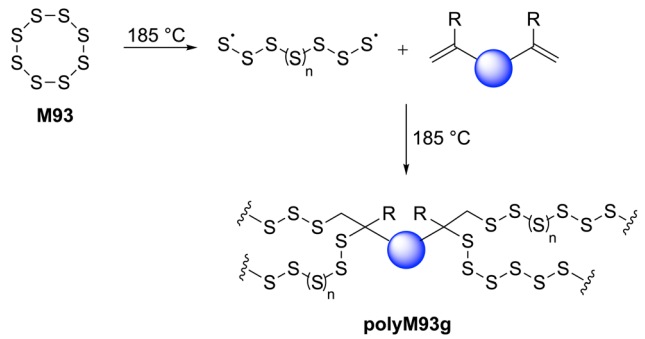


Scheme 34 (a) Ring-opening homopolymerization of elemental sulfur (**M93**, S_8) and ROCOP reactions of **M93** (S_8) with (b) ethane-1,2-dithiol, (c) *p*-dichlorobenzene, (d) olefins, (e) cyclic thioformaldehydes, and (f) cyclic sulfides.

revealed that in-solution copolymerization produced polymers that had relatively low molecular weight and sulfur content, while bulk polymerization gave moderate molecular weight polymers ($M_n \leq 7000$) and comparatively high sulfur content.[139] Schmidt and Weissflog demonstrated the cationic ROCOP of **M93** with cyclic thioformaldehydes using a Lewis acid (*i.e.*, BF_3) to obtain linear, semi-crystalline and colourless polysulfides (**polyM93e**) which were noted to partially decompose upon melting (Scheme 34e).[140,141] The nucleophilic ring-opening of **M93** has also been reported for the synthesis of linear polymers (**polyM93f**) by a ROCOP involving cyclic sulfides (thiiranes and trithioles) (Scheme 34f).[142–144] These copolymers were found to have moderate sulfur rank and molar mass ($M_n < 10^4$ g mol^{-1}).

During the past decade, the synthesis of polysulfide copolymers *via* inverse vulcanization between **M93** and alkene cross-linkers has emerged as an important approach to valorize sulfur, which is generated as a by-product on a huge scale by the petrochemical industry.[5,136,145] During inverse vulcanization, the S–S bonds within **M93** first undergo homolytic cleavage to generate thiyl radicals which then initiate the ROP of other molecules, or undergo a thiol–ene reaction with the alkene additive (Scheme 35). Since its pioneering discovery by Pyun and co-workers in 2013,[146] inverse vulcanization has been extended to a wide class of organic comonomers including styrenes, alkynes, naturally occurring olefins, allylics, maleimides, and nitriles.[5,135] The polysulfide copolymers generated by this approach have found use in lithium–sulfur batteries,[147] dye-sensitised solar cells,[148] transparent IR lenses,[149] controlled-release fertilizers,[150] adhesives,[151] antibacterial surfaces,[152] and adsorbents for environmental remediation *i.e.* to remove heavy-metals from water.[153] However, high reaction temperatures (typically 160–200 °C) are required for this transformation, generating polymeric products with irregular structures and poor solubility.



Scheme 35 Ring-opening copolymerization of elemental sulfur (**M93**) with vinyl monomer (*i.e.* inverse vulcanization).

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6. Conclusion

For next-generation materials, there is an urgent need to develop new polymers containing chemical diversity within the polymer backbone. The introduction of non-conventional functional groups into the polymer backbone offers the possibility to engineer materials that can respond to chemical stimuli and modulate their physicochemical properties. Recent developments in the ROP of sulfur-containing monomers have provided new routes to synthesize sulfur-containing polymers with specific targeted and controllable properties (*e.g.*, refractive index). Polymers containing sulfur-based functionality within the backbone chain are also of great interest due their potential degradability, as well as wide usefulness in the fields of medicinal, biochemical, and material sciences.

Despite excellent properties and immense applications, most conventional polymers suffer from limited degradability or chemical recyclability. Ring-opening polymerization is a powerful strategy to incorporate cleavable linkages into the backbone of polymers. Sulfur-containing functional groups can be selectively cleaved through multiple mechanisms and are therefore also promising candidates for nanotechnology applications such as drug delivery. In addition, polymers with disulfide linkages are also reported to show both degradable and self-healing behaviour. As an example of recent progress in the field, cyclic thionoester-containing rROP monomers have recently emerged as promising candidates to prepare (bio)degradable polymers. The rROP of these monomers has an advantage over conventional rROP systems in that it can selectively insert thioester linkages into a polymer backbone which can be selectively cleaved under mild and specific conditions.

The majority of polymers reported within this article have only been demonstrated on a bench scale and therefore remain at a proof-of-concept stage. For the widespread usage and commercialization of new sulfur-containing polymers, certain important factors will need to be considered including feedstock source, catalyst availability, and that prohibitive energy and material costs are avoided. Moreover, it could be considered advantageous if new monomer feedstock could be bio-sourced and therefore renewable. The development of purpose-driven catalysts that avoid the use of toxic and/or rare transition metals, are efficient, and readily removable from the final material is also paramount. Taking such factors into account, it can be predicated that further exploration of novel systems will lead the efficient preparation of new functional sulfur-containing polymers for use in next-generation materials.

To conclude, the ring-opening polymerization of sulfur-containing monomers is an incredibly productive field, and we hypothesize that the coming decade will be the theatre of important innovations in the design of sulfur-containing polymers with fascinating properties. Nonetheless, there remains much work to be performed in order to obtain this target of next-generation polymers.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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