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Unlocking the Potential of Polythioesters

Adam W. Woodhouse, Azra Kocaarslan, Jennifer A. Garden, and Hatice Mutlu**

As the demand for sustainable polymers increases, most research efforts have focused on polyesters, which can be bioderived and biodegradable. Yet analogous polythioesters, where one of the oxygen atoms has been replaced by a sulfur atom, remain a relatively untapped source of potential. The incorporation of sulfur allows the polymer to exhibit a wide range of favorable properties, such as thermal resistance, degradability, and high refractive index. Polythioester synthesis represents a frontier in research, holding the promise of paving the way for eco-friendly alternatives to conventional polyesters. Moreover, polythioester research can also open avenues to the development of sustainable and recyclable materials. In the last 25 years, many methods to synthesize polythioesters have been developed. However, to date no industrial synthesis of polythioesters has been developed due to challenges of costs, yields, and the toxicity of the by-products. This review will summarize the recent advances in polythioester synthesis, covering step-growth polymerization, ring-opening polymerization (ROP), and biosynthesis. Crucially, the benefits and challenges of the processes will be highlighted, paying particular attention to their sustainability, with the aim of encouraging further exploration and research into the fast-growing field of polythioesters.

1. Introduction

Few chemical advances have had as significant an impact on society as the discovery of plastics. In 1907 the first commercialized synthetic polymer, Bakelite, was produced, heralding the beginning of the plastic age.[1,2] Nowadays, synthetic polymers can be found everywhere: in households, clothes, packaging, and increasingly in the environment as pollution. In 2018, 360 million tons of plastic were produced globally. Approximately one-sixth of these polymers were produced in Europe (62 million tons), of which 7.7% were polyesters and predominantly poly(ethylene terephthalate) (PET).[3] This abundance of plastic is problematic because commercial plastics have a long lifespan. For example, PET bottles can last for decades in the ocean which makes them persistent in the environment, posing hazards to animals and ecosystems.[4] Therefore, significant scientific research efforts have been directed towards improving the sustainability of commodity plastics.[5] However, achieving the design and synthesis of polymers that address consumer needs without eroding the prosperity of future generations, i.e., damaging our environment, health, and economy, is a significant and complex challenge. Strategies to improve polymer sustainability include: (i) the use of alternative (largely bio-based and inexpensive) feedstocks instead of petroleum; (ii) adopting energy-efficient processes that emit fewer CO_2 and greenhouse gas emissions, require less net water and utilize renewable energy sources, (iii) reducing the carbon footprint by replacing carbon-based monomers with new materials based on other elements; (iv) producing less waste; (v) realizing a facile end life (through approaches such as re-/up-cyclability), and (vi) creating materials that are capable of degrading into benign species in the natural environment, even if that is not their intended final destination. Indeed, the development of re-/up-cyclable plastics is imperative for a sustainable environment and future.

The reutilization of elemental sulfur into polymer materials simultaneously incorporates several of these strategies.[6] Sulfur is not only a highly abundant element and a by-product of oil refining and gas-purification processes, but also the oldest fungicide existing in ambient conditions. Recent studies on sulfur-containing polymers have been somewhat sporadic, but importantly have renewed interest in this field. The incorporation of sulfur can significantly modify the properties of a polymer, with a diverse range of sulfur-containing functional moieties opening up access to a broad range of materials (**Figure 1**).[7] For example, polythiourethanes can display enhanced tensile strength and flexibility compared to their oxygenated counterparts (polyurethanes), due to the strong hydrogen bonding ability

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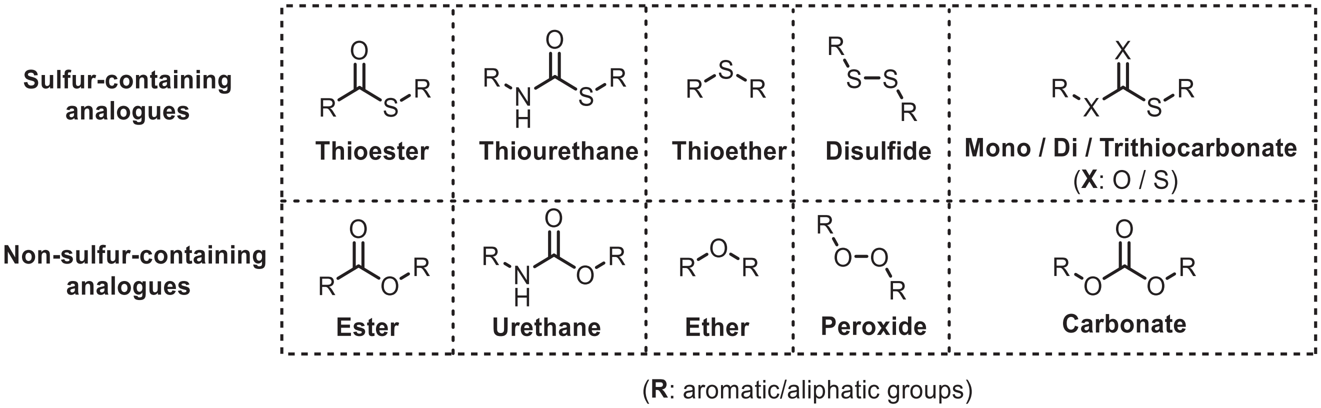


Figure 1. Some of the most common sulfur functional groups and the respective nonsulfur equivalents (R depicts either aliphatic or aromatic functional groups).

of the thiourethane carbonyl oxygen and amide hydrogen.[8] Another example comes from disulfides, in which the S–S bond can reversibly form and degrade in response to stimuli such as redox, thiol nucleophiles, heat, or light.[9,10] Sulfur-incorporated polymers can also have self-healing properties, i.e., the ability to recover from physical damage.[11]

Recently, there has been increasing interest in polymers containing the thioester functional group.[12,13] A polythioester is analogous to a polyester, except one or more of the oxygen atoms has been replaced by sulfur (Figure 1). As the sulfur 3p orbital and the carbon 2p orbital have poorer overlap than oxygen 2p orbitals and carbon 2p orbitals, there is a lower degree of resonance stabilization in a thioester than in an ester. Therefore, a thioester carbonyl bond is weaker and more electrophilic than the carbonyl bond of an ester.[14] This higher reactivity is also exploited in biology.[15] For example, acetyl-CoA is a natural acetylating agent that contains the thioester group. Crucially, the enhanced electrophilicity also makes polythioesters susceptible to nucleophilic attack, and thus attractive prospects as degradable materials through hydrolysis.[16] Furthermore, polythioesters can exhibit higher melting points, lower solubility, and higher heat stability than polyesters.[17]

The dynamic covalent bond and strong thermal characteristics of polythioesters indicate that these materials could be potential alternatives to non-renewable polyesters. Still, to date polythioesters have never been industrially synthesized due to limits imposed by cost, low yield, and toxic by-products.[18] Therefore, it is of scientific interest to design polythioesters that are economically viable and meet the principles of Green Chemistry and sustainability. Indeed, an in-depth literature survey revealed that thioester-decorated polymers have become a significant area of research in the past 5 years. This review provides a perspective of recent advances made in the field of main-chain polythioesters, with insights into step-growth methods, ring-opening polymerization (ROP), and biosynthesis, as well as some key bottlenecks and current challenges. There are three main classes of polythioester (**Figure 2**). The equally significant syntheses of polythionoesters (where the carbonyl O is replaced with S), polydithioesters (when both O atoms are replaced with S), and sidechain polythioesters are omitted. Strategies towards polythionoesters face challenges as carbonyl scrambling can occur, leading to a mixed polymer backbone.[19] Meanwhile, dithioesters can act as reversible-addition-fragmentation chain-transfer (RAFT) agents[20] and they are efficient dienophiles, able to undergo competing Diels–Alder reactions.[21] Therefore, direct approaches to polydithioesters are also challenging.

To aid the reader, in this review the term "polythioester" is used as a general term for polymers in which the alkoxyl O of the ester is replaced by S (Figure 2, left). Representative examples of polythioester syntheses are discussed, along with the chemical characteristics of polythioesters, which governs their application in diverse fields spanning energy storage to biomedicine. Furthermore, the industrial scalability of these syntheses will be covered, as well as different degradation pathways available (chemical, thermal, photo- and biodegradation), to provide a perspective on how to fully unlock the potential of polythioesters.

2. Advantages and Limitations in the Use of Step-Growth Polymerizations to Produce Polythioesters

Polymers formed by step-growth reactions are essential in industry: many ubiquitous polymers such as PET and Nylon-6,6′ are prepared in this way. Step-growth polymerization generally uses a singular reaction mechanism (e.g., an esterification), involves di-functional monomers and exhibits an exponential increase in molecular weight so that high molecular weights can only be accessed at high conversions.[22] The synthesis of di-functional monomers for step-growth polymerization generally requires fewer synthetic steps than cyclic monomers required for

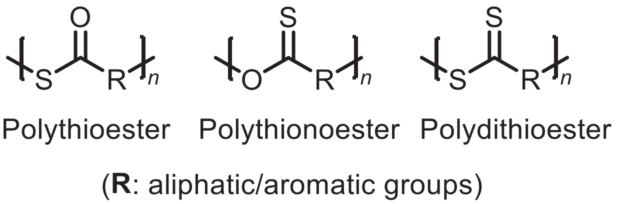
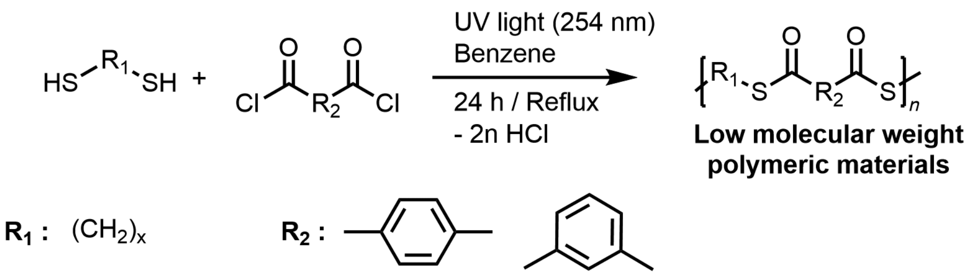


Figure 2. Chemical structures of polythioesters, polythionoesters, and polydithioesters (R depicts either aliphatic or aromatic functional groups).



Scheme 1. Synthesis of polythioester from dithiols and acyl dichlorides, reported by Marvel (adapted from ref. [24]).

ROP,[23] which is an attractive feature from a sustainability perspective.

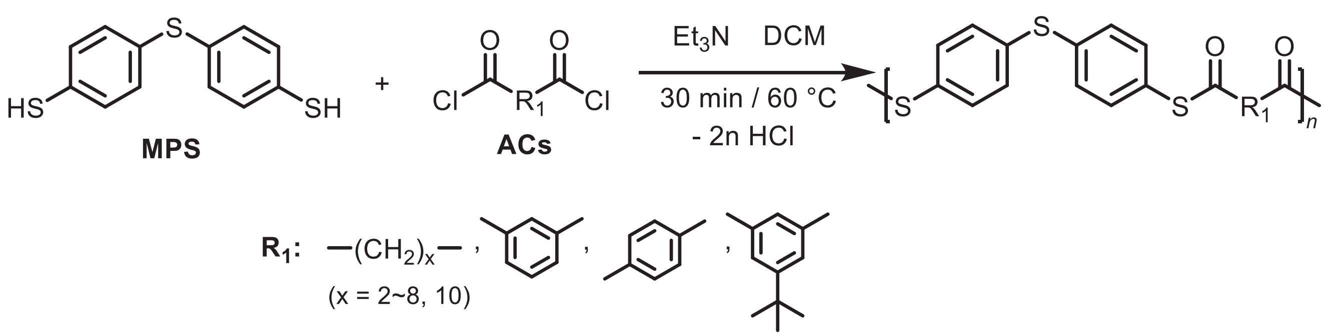
2.1. Polycondensation

The seminal synthesis of a polythioester was reported in 1951 by Marvel (**Scheme 1**),[24] involving a substitution reaction between dithiols and dibasic acid chlorides to yield a polymer with low molecular weight as measured by inherent viscosity (0.07–0.21 dL g^{-1}). The polymerization reactions were performed under 254 nm UV light in highly toxic solvent, i.e., benzene, at moderate temperatures (80 °C), with hydrochloric acid (HCl) produced as a highly corrosive by-product. While this procedure lies far from the principles of Green Chemistry, this pivotal work paved the way for future endeavors.[6]

These efforts were built upon in a series of studies spanning decades, which investigated the synthesis of various semiaromatic polythioesters.[25,29] It was shown that interfacial condensation, where polymerization occurs at the phase interface of the two monomers, provides polymers with satisfactory thermal properties such as high melting points (<240 °C).[25]

The interfacial polycondensation reactions were carried out at 15 °C, and resulted in polymers with higher reduced viscosity values (η_{red} = 0.76 dL g^{-1}) and softening ranges (i.e., the temperature range at which the resin flows under a given load on heating, 125–133 °C) compared to those polymers synthesized through solution polycondensation at 10 °C (η_{red} = 0.46 dL g^{-1}, softening range = 100–130 °C) and 140 °C (η_{red} = 0.62 dL g^{-1}, softening range = 83–136 °C). The higher viscosity values and softening temperatures suggest that polythioesters synthesized by interfacial polycondensation have higher molecular weights and are more thermally resistant than polymers synthesized by solution polycondensation.[29] However, these syntheses were also performed in benzene, and required NaOH to neutralize the harmful HCl by-product generated. While the production of HCl is a key driving force for the polymerization, the use of toxic solvent and strong base is non-ideal from a Green Chemistry perspective.

In the mid-2000s, Hirano et al. employed interfacial condensation to produce polythioesters derived from bis(4,4′-mercaptophenyl)sulfide (MPS) and various acid dichlorides (ACs) (**Scheme 2**).[30] The number-average molecular weight (M_n) of the resultant polythioesters was determined; this is a key metric as higher molecular weight often correlates to improved mechanical properties, up to a specific molecular weight where a plateau in mechanical properties is observed.[31,32] Through the interfacial condensation method, high M_n polymers were obtained (M_n = 11 000–88 100 g mol^{-1}). The respective polythioesters also had a higher oxygen permeability than their polyester equivalents (e.g., 6.2×10^{-15} and 2.4×10^{-15} cm^3 cm (cm^2 s Pa)$^{-1}$, respectively).[33] This high O_2 permeability was explained by the lower crystallinity of the polythioester, caused by the larger radius of sulfur compared to oxygen, and the lower polarity of the S–C bond than the O–C bond. However, the polythioesters had lower decomposition temperature ($T_{d,5\%,}$ as measured via thermal gravimetric analysis (TGA)) than their polyester equivalents (**Table 1**). As will be discussed further in the contents of this review, polythioesters have been shown to have higher melting point (T_m) and glass transition temperature (T_g) values than their polyester equivalents. However, as shown in the latter case, the thermal degradation temperatures of these polythioesters are often equal to or lower than the equivalent polyester. Despite this fact, the benefits of polythioesters generally outweigh the decrease in $T_{d,5\%}$.



Scheme 2. Synthesis of polythioesters with high oxygen permeability and molecular weight values via an interfacial polycondensation approach (adapted from ref. [30]).

Table 1. Thermal properties of MPS polyesters and polythioesters obtained via thermal gravimetric analysis (TGA) and the respective correlation to the acid dichloride derivative employed (adapted from ref. [30]).

Acid Dichloride Derivatives	No. Methylene units	Polyester[33] $T_{d,5\%}$ [°C]	Polythioester $T_{d,5\%}$ [°C]
Succinyl	2	368	290
Glutaryl	3	369	318
Adipoyl	4	360	321
Pimeloyl	5	358	328
Suberoyl	6	366	335
Azelaoyl	7	362	334
Sebacoyl	8	374	330
Dodecanedioyl	10	372	327
Isophtaloyl	–	436	389
Terephthaloyl	–	454	437

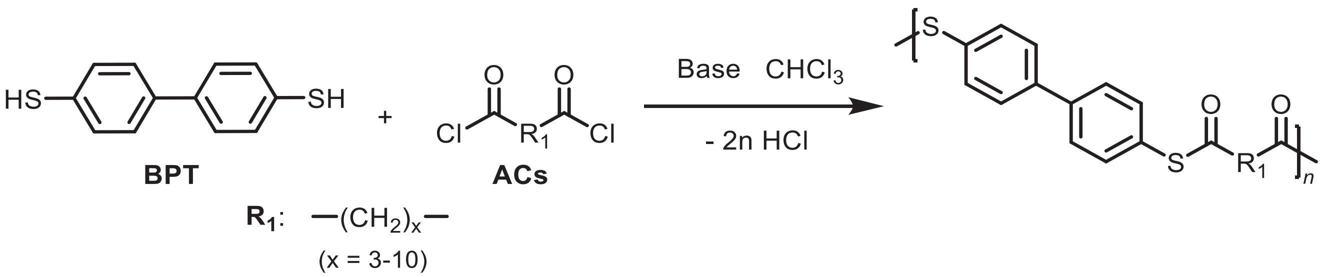
Polythioesters synthesized via polycondensation from 4,4′-biphenyldithiol (BPT) and various ACs were also studied by Hirano and colleagues (**Scheme 3**).[34] The reactions were performed in chloroform and provided quantitative yields. Some of the polymers were insoluble in chloroform, which prevented determination of the M_n values via size exclusion chromatography (SEC) analysis. The analyzable polymers had M_n values of 26 200–38 300 g mol^{-1}; these values are relatively high for polythioesters produced via polycondensation and are in a similar range to the polymers made from MPS. The thermal resistances of the BPT polythioesters were also compared to polyester derivatives derived from 4,4′-biphenyldiol (BPH) and ACs. In contrast to the previous study on MPS polythioesters, the BPT polythioesters exhibited similar $T_{d,5\%}$ values to the corresponding polyesters (e.g., 324 and 334 °C, respectively).

Polycondensation can also be used to develop polymers with attractive properties for optical applications.[35] The Abbe number (ν_D) is a measure of how much a material disperses light, given by (Equation 1), where n_D, n_F, and n_C are the refractive indices (RI) of the material at wavelengths of the sodium D (589.3 nm), hydrogen F (486.1 nm), and hydrogen C lines (656.3 nm), respectively.[36] A lower Abbe number indicates greater dispersion, which is generally unsatisfactory for an optical material, which should allow light to pass unhindered. Refractive indices for conventional polymers are typically in the range of 1.30–1.70, however for applications such as a polymer microlens a higher value is desired.[37] Aromatic and conjugated groups both generally increase the RI of a polymer, due to the increasing polarizability of the material. However, sulfur atoms can also have a strong positive effect on the RI, even in the absence of conjugation or aromatic groups

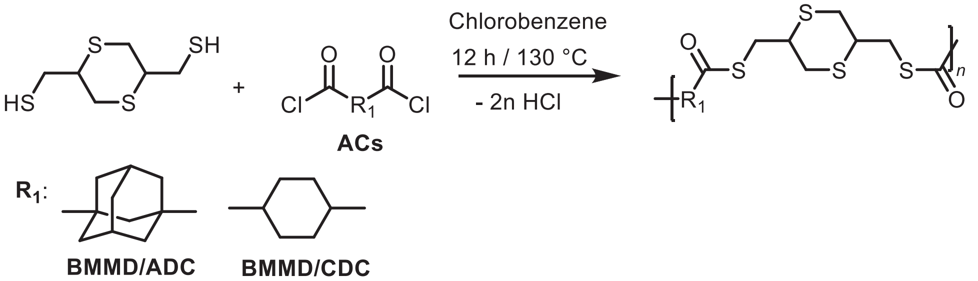
$$\nu_D = \left(n_D - 1\right) / \left(n_F - n_C\right) \tag{1}$$

You et al. synthesized polythioesters by the polycondensation reaction of 2,5-bis(sulfanylmethyl)−1,4-dithiane (BMMD) and adamantanedicarbonyl dichloride (ADC) or cyclohexanedicarbonyl dichloride (CDC) for 12 h in chlorobenzene, without the need of a catalyst (**Scheme 4**).[38] These polymers exhibited high Abbe number values (30.0–32.9) and refractive indices (1.6271–1.6149), indicating that the materials could be useful in optical applications. The thermal stability was very high, with $T_{d,5\%}$ values of 301–307 °C and glass transition temperatures (T_g) values ranging from 65 to 110 °C. The high T_g of the polymers was proposed to be due to the bulky groups on the acid dichloride that provided an increased polymer chain rigidity. Indeed, the polymer containing an adamantane group in the repeating unit had a much higher T_g (110 °C) than the polymer with a cyclohexyl group in the repeating unit (T_g = 65 °C). The study was a significant advance in the field, demonstrating the possibility of synthesizing polythioesters with strong affinity for optical applications.

It is worth noting that all the polycondensation reactions presented involved production of HCl, a generally undesirable byproduct due to its corrosive, harmful and toxic nature. This is a clear limitation of the previously mentioned methods. To overcome these challenges, Kato et al. developed a synthetic method towards polythioester derivatives that uses the immobilized lipase *Candida antarctica* (**Scheme 5**).[39] The monomer 11-mercaptoundecanoic acid (11MU) was polymerized in bulk, which gave a high molar mass polymer with M_n value of 14 800 g mol^{-1}. Remarkably, the polymer could be depolymerized into a cyclic oligomer, and could even be repolymerized again by the lipase, thereby imparting recyclability as a characteristic. This study demonstrates the chemically recyclable synthesis of polythioesters, but in spite of this, the toolbox of polythioesters remains limited. This is in marked contrast to polyesters, which are industrially important and are often prepared via step-growth polymerization, whereas there are relatively few reports on the synthesis of polythioesters via polycondensation and most were published over a decade ago. Still, these studies highlight some of the potential benefits of polythioesters, such as high Abbe numbers, recyclability, and high T_g. These advantages demonstrate that polythioesters are a class of material worth further study.



Scheme 3. Synthesis of polythioesters by polycondensation with high thermal stabilities and molecular weight values (adapted from ref. [34]).



Scheme 4. Synthesis of polythioesters with high Abbe number values, paving the way for this class of polymers towards optical applications (adapted from ref. [38]).

2.2. Polyaddition

Polyaddition can occur through a radical mechanism, requiring an initiator to form a radical species which then polymerizes. It is well known that thiols can undergo addition across an olefin unit.[40] This reaction does not occur with alcohols due to the lower reactivity of alcohols compared to thiols, so the scope of designable thioester-based polymers is high compared to polyesters. In 1953, Marvel reported the first synthesis of polythioesters via such a mechanism, by combining dithiols with nonconjugated diolefin bis-allyls in the presence of 254 nm UV light (**Scheme 6**).[41] Compared to the seminal polycondensation reaction reported by Marvel in 1951 (Scheme 1), the polymers had higher molecular weight values, determined by their inherent viscosity (0.08–1.9 dL g^{-1}).

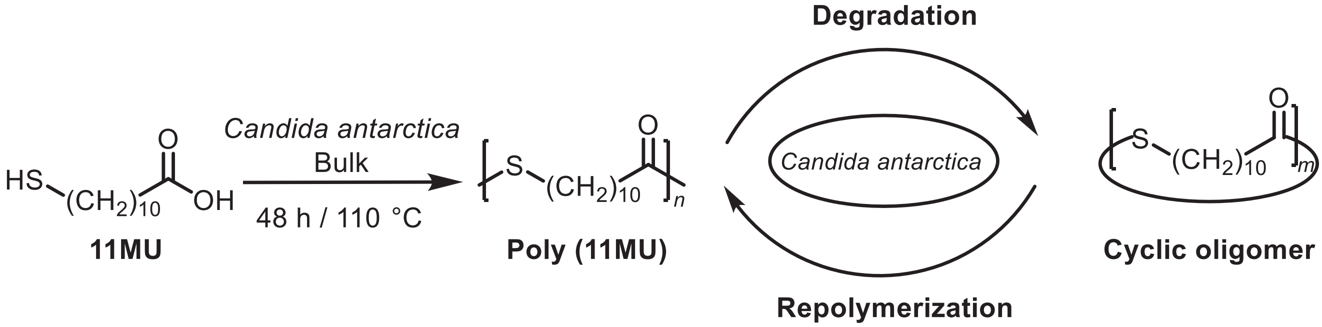
Forty years later, a novel approach to generate polythioesters via polyaddition was developed, which exploited the quaternary onium salt catalyzed addition of diacyl chlorides to bis(thiirane)s to generate high molar mass polymers (M_n = 40 000 g mol^{-1}) as it is shown in **Scheme 7**.[42] The process avoided the production of harmful by-products, despite still utilizing acyl chlorides as comonomers. The quaternary onium salts catalysts employed – such as tetrabutyl ammonium bromide and chloride – are environmentally benign and are reusable,[43] both of which are attractive features for industrial processes.

Given the industrial significance of step-growth polymerization reactions for polyesters, in the past 15 years there have been remarkably few studies into step-growth polymerization to create polythioesters. There is thus a strong potential for new, greener methods to be developed. For example, instead of utilizing the chlorine atom as a leaving group on the dicarboxylic acid derivative, a more environmentally friendly alternative could be used such as imidazole-functionalized diacids. Indeed, a recent study has shown that imidazole-functionalized diacids can be combined with dithiols to produce polythioesters.[44] An advantage of this method is that DBU-imidazole ionic liquid was produced as a by-product, which is environmentally benign and could potentially sequester CO_2.[45]

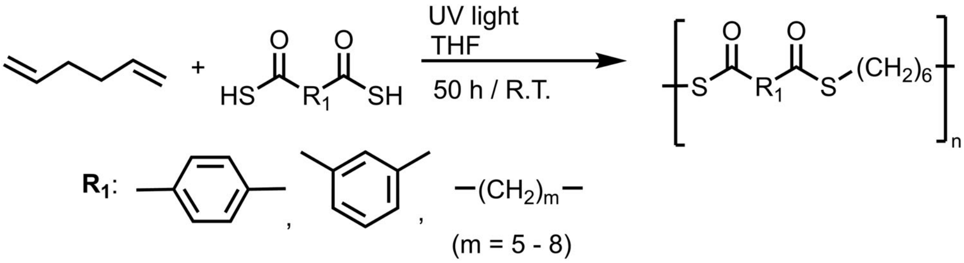
3. Advantages and Limitations in the Use of Ring-Opening Polymerization (ROP) Towards the Synthesis of Polythioesters

An alternative method of producing polythioesters is through ROP of cyclic monomers containing a thioester unit. ROP, a chain-growth polymerization reaction where a cyclic monomer is incorporated into a growing polymer chain by ring-opening the monomer, is often preferable to step-growth methods because it allows good control over molecular parameters such as molar mass, dispersity, and stereoregularity.[46] Such polymerization reactions are often performed under mild reaction conditions and are therefore of great interest. Indeed, a substantial number of manuscripts utilizing ROP methods (with a diverse range of monomers and catalysts) to synthesize polythioesters have been published recently compared to step-growth methods.[47]

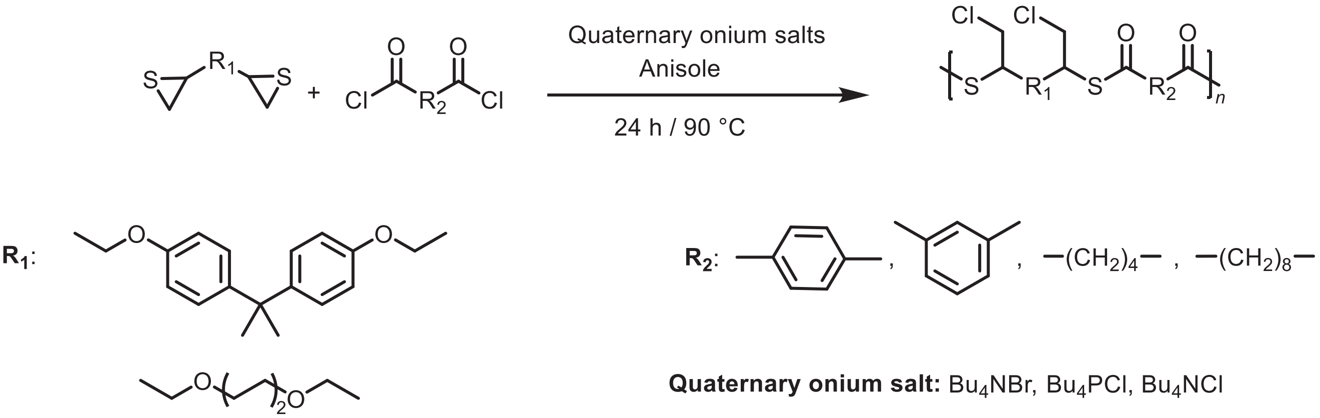
Recently, several reviews have been published providing a comprehensive overview of the state-of-the-art in the synthesis of polythioesters via ROP, including key mechanistic insights.



Scheme 5. Lipase-catalyzed polymerization of 11-mercaptoundecanoic acid (11MU) using the enzyme *Candida antarctica*, followed by degradation and repolymerization (adapted from ref. [39]).



Scheme 6. Radical polyaddition of non-conjugated diolefin bis-allyl with various dithiols at 254 nm UV light to form polythioester (adapted from ref. [41]).



Scheme 7. Synthesis of polythioester via polyaddition of diacyl chlorides and bis(thiirane)s using quaternary onium salts as catalysts (adapted from ref. [42]).

In this section, we will compare the advantages and disadvantages of chain-growth versus step-growth pathways to further emphasize the benefits of step-growth approaches to polythioesters. Accordingly, within the following sub-sections the ROP of thiolactones, thionolactones, and the ring-opening copolymerization (ROCOP) of cyclic thioanhydrides will be discussed as alternative methods for the synthesis of polythioesters.

3.1. Ring-Opening Polymerization of Thiolactone and Dithiolactone Monomers

As monosulfur analogues of lactones, thiolactones are a class of heterocyclic monomers that can be converted to polythioesters via ROP (**Figure 3**). Replacing oxygen with sulfur in a lactone influences the reactivity by decreasing the ring-strain. For example, the ring strain energies of the 5-membered γ-lactone and γ-thiolactone are 7.8 and 3.8 kcal mol^{-1}, respectively, resulting in a unique reactivity that differentiates these monomers from each other.[48] The first synthesis of a polythioester by ROP was reported in 1964, where the 7-membered ϵ-thiocaprolactone underwent anionic ROP with KO^{t}Bu at 155 °C to generate high molar mass polymers as measured by viscosity (0.5–1.0 dL g^{-1}).[49,50] The polymerization was effective with a strong base (potassium t-butoxide), at high temperature (155 °C). While ϵ-thiocaprolactone was efficiently polymerized, δ-thiolactone gave lower yields of 21%, and the γ-thiolactone yielded no polymer at all. This observation aligns with trends in lactone polymerization, where γ-lactones have low ring-strain and are challenging to polymerize.

It took almost 40 years until the first ROP of γ-thiobutyrolactone was performed (**Scheme 8**).[51] By using metal triflates based on Sc, Y, Yb, or La as cationic initiators, yields of 30–50% were achieved. In 2015, the ROP of ϵ-thiocaprolactone to produce a polythionoester was achieved using organic bases 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) as depicted in **Scheme 9**.[52] Importantly, the addition of an equimolar amount of thiourea-containing compound increased the polymerization rate, which was attributed to H-bonding interactions

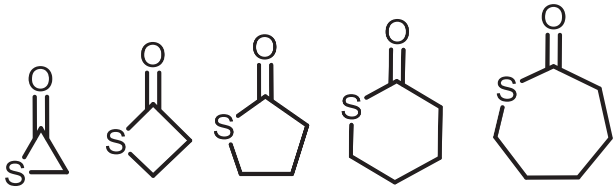
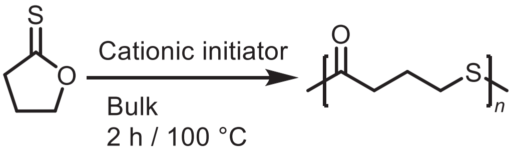
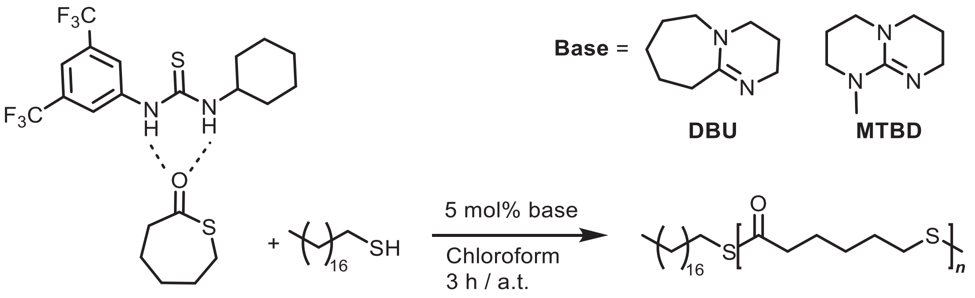


Figure 3. The structures α-, β-, γ-, δ-, and ϵ-thiolactones (left to right), utilized as monomer precursors to polythioesters.



Scheme 8. ROP of γ-thiobutyrolactone using metal triflate initiator, to produce a polythioester derivative (adapted from ref. [51]).



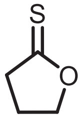
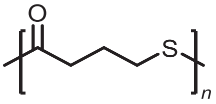
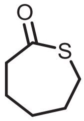
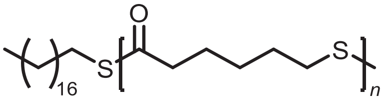
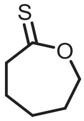
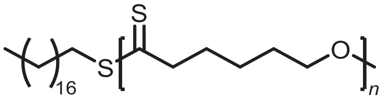
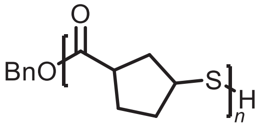
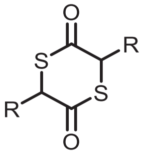
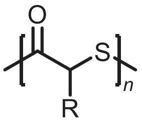
Scheme 9. ROP of ϵ-thiocaprolactone using organocatalytic bases, showing the activating H-bonding interactions of thiourea with the monomer (adapted from ref. [52]).

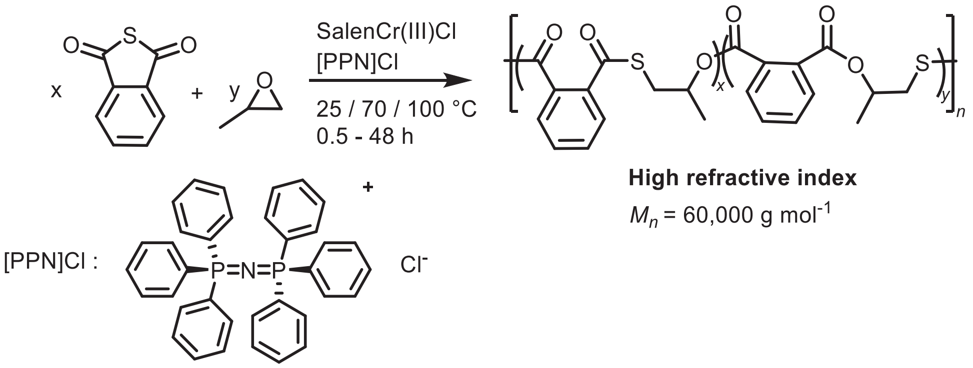
activating the ϵ-thiocaprolactone and reducing transthioesterification. The same approach was later shown to be effective at producing polythionoesters through the controlled ROP of ϵ-thionocaprolactone (**Table 2**).[53]

It is worth noting that none of the aforementioned ROP methods provided polymers with particularly high molar masses, especially compared to the analogous polyesters generated via ROP (Table 2). Thioesters and thiols are more likely to undergo transesterification processes than esters and alcohols, which can result in lower molar masses. Recently, Shi et al. synthesized a polythioester from 2-thiabicyclo[2.2.1]heptan-3-one (BTL, Table 2), a bridged bicylic thiolactone that can be derived from a biobased olefin carboxylic acid.[54] The resultant poly(BTL) (PBTL) possessed qualities such as intrinsic crystallinity, high molar mass and a very high melting point (<213 °C). The presence of such properties is very beneficial for high-performance applications (such as in the aerospace, medical, marine, and chemical industries) where polymers need to have high durability and be able to withstand high temperatures.

Furthermore, PBTL was hard, strong, ductile, and tough, with high Young's modulus (2.00 ± 0.18 GPa) and tensile strength (41.4 ± 3.0 MPa). Remarkably, the polymer also showed intrinsic recyclability: in 10 min and at ambient temperature, PBTL could be depolymerized into the pure monomer with quantitative yield in the presence of a catalyst. This synthesis is a remarkable advance in Green polymerization chemistry; however, it is not without its drawbacks. Obtaining the monomer required a 4-step synthesis, which introduces a significant energy consumption to

Table 2. List of various thiolactone, thionolactone, and dithiolactone monomers, showing the M_n and $Đ$ of the corresponding ROP-formed polymers.

Monomer	Polymer	M_n [g mol^{-1}]	Dispersity $Đ$	Ref.
		3400–6300	2.2–2.9	[51]
		9000–10 000	1.5–1.6	[52]
		22 500	1.14	[53]
 **BTL**	 **PBTL**	49 800	1.4	[54]
		16 300–100 500	1.3–1.4	[55]



Scheme 10. Synthesis of a polythioester with potential optical applications via ROCOP of epoxide/thioanhydride monomers (adapted from ref. [57]).

synthesize the polymer. The process also used harsh reagents such as HCl and tetrafluoroacetic acid. Indeed, this is a common problem among ROP reactions: the cyclic monomers often require lengthy syntheses compared to step-growth reactions that can take advantage of simpler monomer structures.[23]

Dithiolactones can also be utilized as monomers to synthesize recyclable polythioesters (Table 2).[55] *Rac*-thiolactide was polymerized in dichloromethane (DCM) with the organobase catalyst 4-(*N,N*-dimethylamino) pyridine (DMAP) and the initiator benzyl mercaptan. The obtained polythiolactide was capable of undergoing bulk depolymerization into the corresponding monomer at 95 °C under vacuum, with >90% yield. Notably, the depolymerization showed strong selectivity, favoring the production of *rac*-thiolactide over the *meso*-thiolactide isomer at a ratio of 98:2. The methodology was then expanded to a wide range of other monomers, producing recyclable polythioesters with $T_{d,5\%}$ and T_g values ranging from 182–254 and −19.2–41.9 °C, respectively. The depolymerizability and strong thermal properties demonstrates the ability to synthesize polythioesters with customizable end-of-life options for various applications.

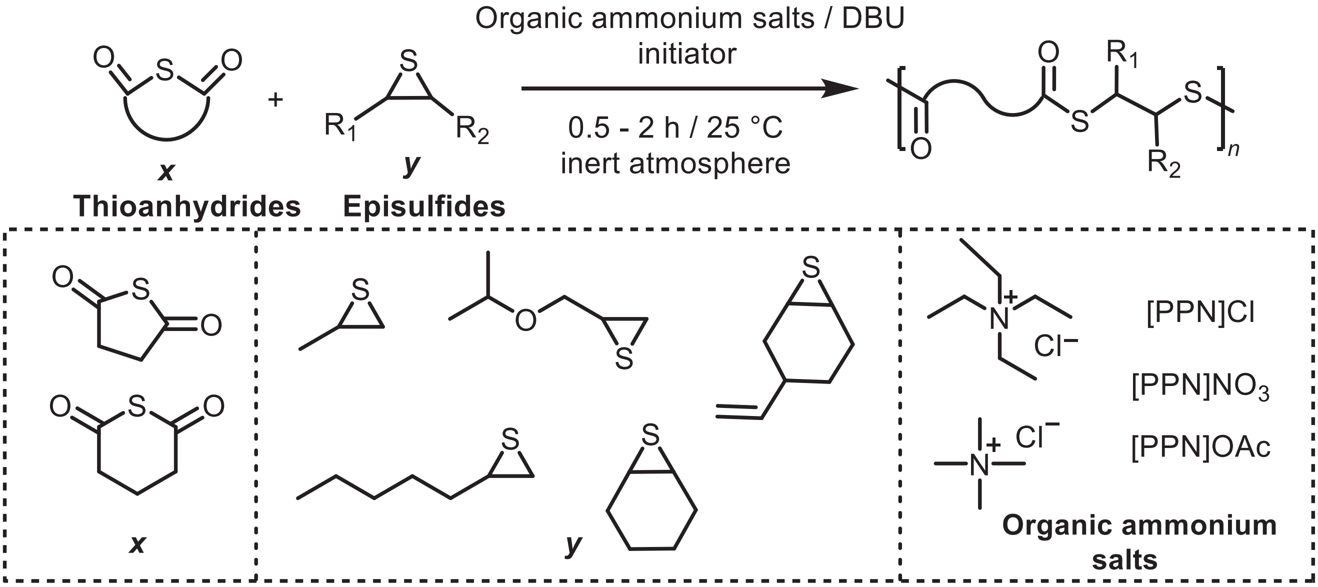
3.2. Ring-Opening Copolymerization of Cyclic Thioanhydride Monomers

Cyclic thioanhydrides are a class of monomer that can be readily synthesized from thioacids and display a wide range of interesting chemistry. For example, in the presence of a suitable nucleophile they can undergo ring-opening to produce thioacids.[56] By taking advantage of this reaction, the ring-opening copolymerization (ROCOP) of thioanhydrides opens access to a broader range of polythioesters. Unlike ROP, which involves just one variety of thiolactone monomer, cyclic thioanhydride copolymerization makes use of two types of monomer. This can lead to greater structural variation through the use of different anhydrides and episulfides/epoxides, each of which can be decorated with different functional groups. In 2019, Wang et al. synthesized a polythioester via ring-opening copolymerization of phthalic thioanhydride and propylene oxide (**Scheme 10**), with very high molar mass (M_n = 60 000 g mol^{-1}).[57] Interestingly, the presence of a larger number of thioester linkages resulted in a higher T_g value (69.5 °C) when compared to equivalent polymers containing more ester and thioether-ester linkages, which suggests that thioester groups have a positive effect on the thermal properties of this polymer. Furthermore, the high refractive index of 1.60 suggests the polymer may be suitable for optical applications. While a chromium salen catalyst/bis(triphenylphosphine)iminium cocatalyst (PPNCl) system was used because this effectively activated propylene oxide, the use of chromium is disadvantageous due to the toxicity of heavy metals, which limits their industrial applications.

The ROCOP of thioanhydrides with episulfides instead of epoxides generates polythioesters with twice as many thioester linkages (**Scheme 11**).[58] Due to the relative ease of activating an episulfide compared to an epoxide, the ROCOP of episulfides with thioanhydrides has been reported where a metal-free organocatalyst was used instead of a chromium-based catalyst. Specifically, organocatalysts such as DBU or organic ammonium salts (e.g., [PPN]Cl) were used as initiators. Notably, the resultant polythioester had a very high refractive index of 1.78, implying strong potential for optical applications. Various thioanhydride and episulfide monomers could be incorporated using this method, achieving polymers with high M_n values (42 300–53 600 g mol^{-1}) and showcasing the versatility of this method to generate diverse polythioesters. A benefit of ROCOP is that it gives access to a larger range of polymer structures than ROP, due to the use of two different monomers. However, the ROCOP of episulfides/thioanhydrides to generate polythioesters is currently more limited than the ROCOP of epoxides/anhydrides to generate polyesters, due to the lesser variety of sulfur-containing monomers available. Therefore, research into the synthesis of episulfides and thioanhydrides could assist further advances in this area.

3.3. Ring-Opening Copolymerizations of Thionolactones

Lactones are a very common class of material that can be found in nature and are produced from biomass.[59] Thionolactones can be conveniently produced from the corresponding lactone through a one-step thionation with Lawesson's reagent, making thionolactones an attractive sustainable option as a monomer for ROP.[60] Spick et al. reported the reversible addition-fragmentation chain-transfer (RAFT) mediated copolymerization of a thionolactone monomer (**Scheme 12**).[61] Specifically, dibenzo[c,e](oxepin-5(7*H*)-thione (DOT) was copoly-



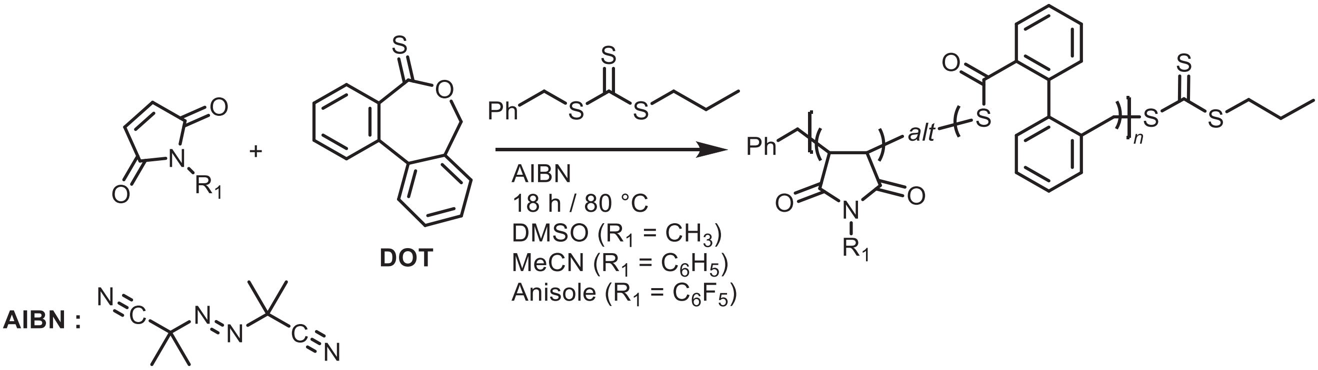
Scheme 11. Metal-free copolymerization of cyclic thioahydrides and episulfides to generate a wide variety of polythioesters (adapted from ref. [58]).

merized with *N*-methylmaleimide, *N*-phenylmaleimide, or *N*-2,3,4,5,6-pentafluorophenylmaleimide, using azobisisobutyronitrile (AIBN) as an initiator. This approach produced a copolymer with a M_n of 12 600 g mol^{-1}, which could be degraded in an excess of *n*-isopropylamine or *n*-propanethiol and DBU into different small molecules depending on the copolymer composition. This was the first reported synthesis of this class of polythioester using a radical ring-opening polymerization (RROP) technique.

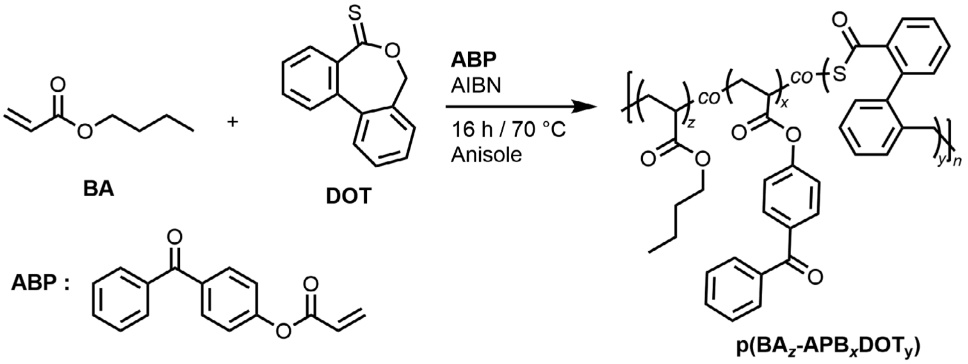
The above method was used very recently to develop a thionolactone-based copolymer of *n*-butyl acrylate (BA), 4-acryloyloxy benzophenone (ABP), and DOT, with the copolymer containing thioester backbone functional groups (**Scheme 13**).[62] The inclusion of the photo-crosslinker ABP allowed for the crosslinking of the polymer under 365 nm UV light. The key feature of this polymer was that it displayed adhesive properties, owing to the crosslinking of polymer chains. The strongest tack and peel strength (i.e., the polymer's ability to form adhesive bonds, and the force required to peel apart the bonded materials) was shown at just 0.25 mol% incorporation of DOT. The authors also demonstrated that the polymer could be selectively degraded in *n*-propylamine. Under these conditions, the thioester backbone was dissolved while maintaining the crosslinking networks, resulting in a decrease in adhesivity. This degradability is comparable to the polymer studied by Spick et al. (Scheme 12), which was degradable under the same conditions. This highlights the potential utility of polymers containing thioester functionalities in the development of recyclable packaging labels, as a large problem in recycling adhesive polymers is their persistence and the associated difficulties in removal. Overall, ROCOP is an effective method of creating polythioesters with favorable properties like high strength, thermal stability or adhesivity. However, a key limitation when compared to step-growth polymerization is the lower customizability of the monomers, as they are limited to certain cyclic structures.

4. Advantages and Limitations in the Use of Biosynthesis to Synthesize Polythioesters

Biosynthesis is an alternative approach to the formation of polymers which avoids traditional fossil-based feedstocks.[63]



Scheme 12. Copolymerization of DOT with various maleimide monomers to produce different backbone-thioester-containing copolymers (adapted from ref. [61]).



Scheme 13. ROCOP of DOT and BA to produce a copolymer with thioester groups in the backbone. AIBN was used as initiator and ABP as a photo-crosslinker unit (adapted from ref. [62]).

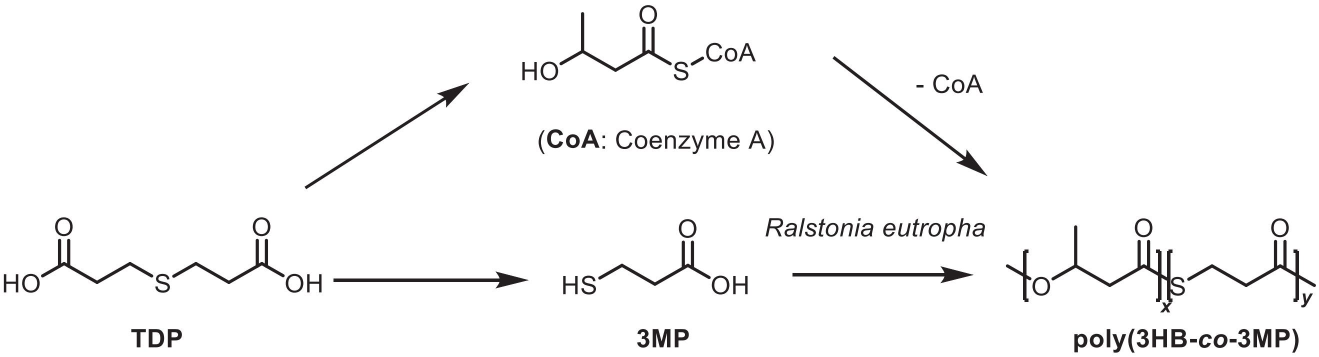
Bacteria produce natural biopolymers serving a wide range of biological functions; therefore, the biochemical pathways of some bacteria can be exploited to synthesize polythioesters. Polythioester biosynthesis has been relatively underexplored compared to the step- and chain-growth methods,[64–66] still, some notable studies have been reported.

The first polythioester biosynthesis was reported by Lütke-Eversloh et al. in 2001.[66] A copolymer of 3-mercaptopropionic acid (3MP) and 3-hydroxybutyrate (3HB), poly(3HB-*co*–3MP), was synthesized using the *Ralstonia eutropha* bacterium (**Scheme 14**). 3,3′-dipropionic acid (TDP) and 3MP was provided to the bacteria as a carbon source to yield the copolymer. The M_n values of poly(3HB-*co*-3MP) were high, ranging from 112 900 to 1 020 000 g mol^{-1} with polydispersity indices from 1.1 to 7.0. The study demonstrated the proof of concept for polythioester biosynthesis, opening the field to future developments.

Polythioester biosynthetic methodology was subsequently expanded to include the stepwise addition of monomers 3MP, 3 MB or 3-mercaptovaleric acid (3MV) to the engineered *E. coli* bacterium, which allowed the production of three novel homopolymers (**Table 3**).[64] The polymer poly(3MV) had a lower M_n value (81 500 g mol^{-1}) than the copolymer obtained in the previous study. Additionally, the polymers' melting points were relatively high: poly(3MP) had a higher melting point (170 °C) than the analogous polyester, poly(3HP) (121 °C). However, both poly(3MV) and poly(3MB) had lower melting points (84 and 100 °C, respectively) than their nonsulfur-containing analogues (115 and 175 °C). The addition of sulfur to the linear aliphatic polymer thus appears to lead to a higher T_m, whereas for the methyl substituted aliphatic polymer this same alteration leads to a large decrease in T_m. This difference in T_m decreases when the substituted group is larger (i.e., an ethyl group.) The authors postulated that these lower T_m values could be due to low molecular weight and poor crystalline organization in the polythioesters.

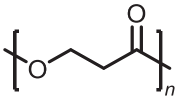
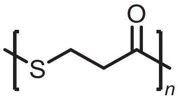
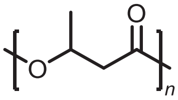
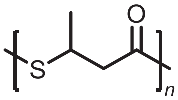
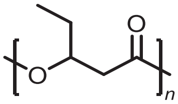
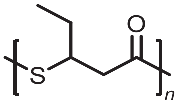
Very recently, Ceneviva et al. used bioengineered *E. coli* to polymerize 3-mercapto-2-methylpropionate (3M2MP) into the homopolymer poly(3M2MP) as well as its copolymer with 3-hydroxybutyrate, poly(3HB-*co*-3M2MP) (**Scheme 15**).[67] The M_n value of the homopolymer was measured to be 576 000 g mol^{-1} while the copolymer values ranged from 183 000 to 442 400 g mol^{-1}, higher than for most other polythioesters obtained by biosynthesis.[65,66] Poly(3M2MP) showed amorphous properties, such as a negative T_g (−3.1 °C) and no melting or cold crystallization peaks. Therefore, poly(3M2MP) was the first reported amorphous polythioester synthesized via biosynthesis. Notably, the homopolymer showed extraordinary elasticity with 2605% elongation at break. This level of elasticity was far higher than those of typical commercial elastomers, which have 100–800% elongation at break.[57] Similar properties were observed for poly(3HB-*co*-3M2MP), which exhibited 1500% elongation at break with 53.9 mol% of 3M2MP. Therefore, the study showed that biosynthesis can be effective at producing high-performance polythioesters.

Overall, the biosynthesis of polythioesters is still a relatively niche corner of polythioester production. Only four biosynthesized polythioesters have been produced to date, showing the limited extent of the research. While there are many opportunities

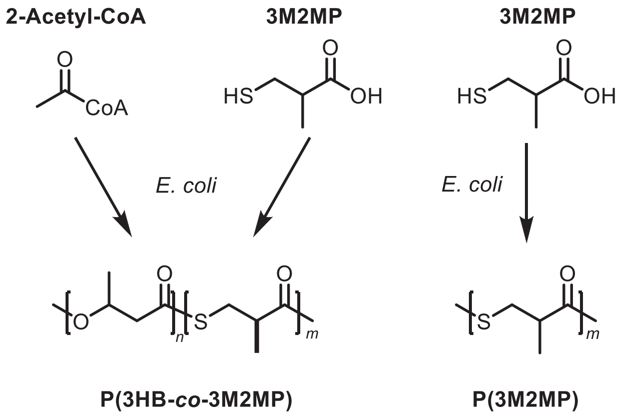


Scheme 14. Biosynthesis of the thioester-containing copolymer poly(3HB-*co*-3MP) using the bacterium *Ralstonia eutropha* (adapted from ref. [66]).

Table 3. Melting points (T_m) and glass transition temperature (T_g) values of different biosynthetic polythioesters and their polyester equivalents (adapted from ref. [64]).

Polymer Name	Polymer Structure	T_g [°C]	T_m [°C]
Poly(3HP)		−10	121
Poly(3MP)		–	170
Poly(3HB)		4	175
Poly(3MB)		8	100
Poly(3HV)		−10	115
Poly(3MV)		−1	84

for new advances in the field, polymer biosynthesis are generally limited for industrial application by their high cost. Equipment can require a substantial capital investment, especially if special separation processes are required to obtain the polymer.[63] For example, all routes described above produce the polymer on the interior of the cell; this means that the bacteria must be lysed, which adds extra energy requirements. Clearly a trade-off between sustainability and cost is required.



Scheme 15. Biosynthesis of the backbone-thioester-containing copolymer P(3HB-*co*-3M2MP) and the polythioester P(3M2MP), utilizing *E. coli* (adapted from ref. [67]).

5. Future Outlook

5.1. Light-Induced Reactions as an Effective Tool for Polythioester Synthesis

Shaping a green and sustainable future is closely tied to the minimization of waste at the source by modifying existing processes at the molecular level. Light, due to its noninvasive nature, ease of application, and exquisite temporal and spatial control, upholds the credentials of sustainable chemistry, thus is a particularly appealing tool for the synthesis of polymers.[68] Indeed, a number of polymerizations have been modified to make use of light in both the visible (400–800 nm) and ultraviolet (254–400 nm) spectrum.[69,70] The large variety of existing photoinitiators affords a broad spectrum of light for photoinduced polymerization, resulting in many opportunities for sustainable polythioester synthesis. The light-induced ROP of cyclic monomers, such as lactones, has received an increase in research interest over the past decade.[71,72] Using a similar light-induced approach, there could therefore be potential to polymerize thio/thionolactones into their corresponding thio/thionoesters. Furthermore, the visible light-induced synthesis of aromatic small molecule thioesters has been shown to be possible, meaning that future polythioester syntheses could be explored taking advantage of this chemistry.[73,74] Therefore, the toolbox of photochemistry to produce polythioesters has great potential to be expanded. Last but not least, photoinduced reactions are especially desirable in industrial settings due to the previously mentioned benefits of using light, making this a promising avenue for the large-scale synthesis of polythioesters.

5.2. Industrial Production of Polythioesters

For any industrial synthesis, it is desirable to optimize the reaction conditions to improve energy efficiency, reduce operational costs, and enhance the overall sustainability. Many methods of synthesizing polythioesters use mild reaction temperatures (>25 °C) with short reaction times (>30 min). However, since polythioesters offer a promising class of degradable or chemically recyclable materials, advances in their production should aim to create a balance between efficiency and environmental considerations, by reducing the production of toxic by-products and/or the use of harmful solvents while still creating industrially scalable processes.

While most step-growth polymerization routes reported to date form harmful hydrochloric acid as a by-product (HCl), alternative routes have been reported utilizing benign catalysts such as enzymes or quaternary ammonium salts, which avoid producing such by-products. Such developments are positive for the future of step-growth polythioester synthesis. Furthermore, polymerization methodologies could be designed to use green solvents such as ionic liquids or water, or to even avoid the use of solvents entirely. The polymerization of 11-mercaptoundecanoic acid (11MU) by the lipase enzyme is one such example of a step-growth/ROP-formed polythioester synthesized in bulk conditions.[39]

Current methods for the microbial production of polythioesters do not require harsh conditions. However, biosynthesis faces its own challenges when scaling to the industrial level.

For example, the industrial production of polyhydroxyalkanoates (PHAs), which are the polyester analogues of polythioesters, may require special considerations such as the use of specialist techniques to isolate the product; this adds complexity to the process. Scaling up polythioester biosynthesis to the industrial level would not be straightforward; however, it has been shown to be possible for PHA, albeit with a relatively high cost (7–10 € kg^{-1}).[75]

5.3. Circular Chemistry of Polythioesters

For any prospective polymer material, it is important to consider its potential for contributing to a circular economy. The framework of the "resource hierarchy," showing eleven levels of strategies for waste avoidance, has been proposed to guide chemists towards such a sustainable future.[6] Polythioesters exhibit properties that are in line with many of these principles. The semicrystalline nature of polythioesters allows for facile reshaping and repurposing of the polymers. High degradation temperatures (e.g., the polymer created by You et al., with a $T_{d,5\%}$ of 301–307 °C) show durability and suggest the potential for long-term reuse. Furthermore, owing to the increased reactivity of the thioester carbonyl bond, some polythioesters have exhibited potential for recyclability. For example, the copolymer synthesized by Spick et al. (Scheme 12) was degradable through aminolysis and thiolysis, producing different small molecules depending on the composition of the copolymer. Another example is the ROP-formed PBTL (BTL: 2-thiabicyclo[2.2.1]heptan-3-one), which could be quantitatively degraded into its monomers and repolymerized. Such a process is effectively the gold standard of circular chemistry as it allows for the infinite and efficient recycling of a polymer material. Meanwhile, the step-growth-formed poly(11MU) could be degraded to its cyclic oligomer and repolymerized.[39] While there has not yet been any reports of a step-growth polythioester that can be fully degraded to its monomers and then repolymerized, this could be a promising area for future research.

The chemical recycling of polyesters has been extensively studied with the aim of creating reprocessed polymers of the same quality as virgin material. For example, polylactic acid is a degradable polyester that can undergo hydrolysis, photodegradation, microbial degradation, and enzymatic degradation, with most research attention being dedicated to the latter two options.[76] However, polyesters alone cannot fulfil all the functions required by a fully circular economy, and the unique degradation pathways of the sulfur-containing polymers suggest they may have an important role to play in the future. As identified in a recently published review, such a circular economy can only be achieved when landfill polymers are effectively sorted from other polymers and waste materials, which is challenging.[18] In light of these considerations, if recyclable polythioesters are to become commonplace, their implementation must go hand-in-hand with significant policy changes that enable efficient waste management practices.

5.4. Future Applications of Polythioesters

In addition to their numerous sustainability benefits, sulfur-containing polymers may be able to perform unique functions because of their highly versatile properties, including optical, thermal, and mechanical characteristics. Polythioesters with high refractive index could be used in optical contexts,[36,37] for example in anti-reflective coatings applied to the surface of the lenses of cameras and eyeglasses (as well as other devices such as television screens) to reduce reflection.[77] Another application could be in microlenses, which require materials of specific refractive indices for use in devices such as cameras and microscopes.[78,79] Indeed, many of the polythioesters outlined in this study exhibited high refractive index values (ranging from 1.6 to 1.8), which illustrates their applicability in these areas.

Furthermore, high T_g and thermal stability is another desirable trait in polythioesters. For example, polythioesters with large $T_{d,5\%}$ values (vide supra) could allow for applications in certain industries with high operating temperatures, such as high-performance gas separation.[80] In addition, amorphous polymers with high T_g values could lead to other applications, for example in optical contexts where fewer crystallites in amorphous polymers provides superior optical transparency.[81]

The mechanical properties of a material are of key importance when identifying the potential applications. Polymers with high strength and toughness can find applications in industries that require high performance, such as the aerospace and construction industries.[82] For example, PBTL is a polythioester with a high Young's modulus and tensile strength; these are favorable characteristics for high-performance materials. Other properties, such as elasticity and adhesivity, are also important, and open up a variety of applications. Notably, biosynthetically produced poly(3M2MP) exhibits extraordinary elasticity (2605% elongation at break), which could be modified by incorporating 3HB to create copolymers. Some DOT-incorporated cross-linked copolymers have shown adhesivity,[62] which could be removed by degrading the thioester backbone via aminolysis or thiolysis. Reversible adhesivity is of great interest in the packaging industry, where the simple and effective removal of adhesive labels is desired. While those aforementioned studies have emphasized that polythioesters have the potential for a wide range of applications due to their mechanical properties, still one should keep in mind that comparison of mechanical properties of materials over different, independently performed studies are rather difficult, since the final outcomes are strongly dependent on the molecular weight of the polymers, the type and parameters of the analysis techniques, and the pretreatment and shaping methods of the polymer.

5.5. Machine Learning

Traditional research methods into polymer synthesis typically use trial and error based on experience and chemical intuition. However, these systematic approaches are often ineffective at creating innovative solutions, as well as being time, cost, and labor intensive.[83] Machine learning (ML) holds great potential for advancing sustainable efforts. ML methods have been successfully utilized to predict various key properties of potential polymers, for example structural properties,[84] dispersion performance,[85] or T_g.[86,87] Application of ML techniques could therefore improve the efficiency of polythioester design by decreasing the time spent in the lab. Polymer informatics research has expanded beyond property prediction, now encompassing aspects of characterization. For example, a ML model was able to accurately classify polymers (including polyesters) into amorphous or semicrystalline groups based on polymer stiffness data.[88] Hence, ML not only offers various opportunities to enhance the production and development of polythioester materials but also to accelerate the decision-making process regarding which polymer structures should be targeted, based on the properties required. However, current challenges in the area arise from the complex nature of polymers and the lack of a large, high quality, publicly available dataset.[89] Overcoming these challenges would help to expedite the wider use of ML methods in polymer design and synthesis.

6. Conclusions

This mini review has given an overview of the methods available to synthesize polythioesters, including polycondensation, polyaddition, ROP, ring-opening copolymerization (ROCOP), and biosynthesis. Using these methods, polythioesters have been made with a variety of beneficial properties, for example strong thermal characteristics, high molecular weight, and high refractive indices. Of the methods outlined, ROP has received the most attention in recent years. ROP allows the creation of high molecular weight polymers displaying features such as recyclability, reversible adhesivity, and elasticity. These features could lead to many interesting applications for polythioesters, for example, in the packaging industry. Still, the methodology generally uses a restricted range of monomers (e.g., thiolactones, thionolactones, and cyclic thioanhydrides). Some of the reactions discussed use toxic catalysts such as those based on heavy metals, which greatly reduce the sustainability impact of the processes and may limit potential applications, for example in food packaging. Furthermore, ROP could be less attractive from a Green Chemistry perspective due to the cost and energy requirements to acquire the monomers, which often require multiple synthetic steps to prepare. Looking forward, efforts could be made to increase the greenness of ROP methodologies by limiting the use of toxic reagents and using bio-based monomers.

Biosynthesis, on the other hand, avoids the use of toxic chemicals, instead using bacteria to produce the polymer. However, only a few polythioesters have been successfully synthesized using this method. The most recent synthesis in 2022 achieved an amorphous polymer with very interesting features such as extraordinarily high molecular weight and elasticity, which could trigger a renewal in interest for polythioester biosynthesis. Nevertheless, challenges are faced in scaling up the biosynthesis process to the industrial level.

Finally, while step-growth polymerization has delivered polythioesters with desirable properties such as high molecular weight, high oxygen permeability, and high Abbe numbers (which could lead to polymers with interesting optical applications, or uses in paints, adhesives and sealants[90]) it has been under-studied in the past 15 years. Unfortunately, there has been a lack of innovation in this area and research has mostly focused around polycondensation of thiols and diacyl chlorides, which produces HCl as an undesired by-product. Notably, polycondensation with the lipase enzyme avoided this by-product, but recently there has been an absence of enzymatically produced polythioesters in the literature. Future research could be directed towards other methods of polycondensation that avoid the usage of acyl chlorides. The relative lack of research into step-growth polymerization approaches to polythioesters, and the diverse range of (potentially bio-based) monomers that can be used in such a reaction, suggests that the area holds a lot of promise. Indeed, the 2019 "Science to enable sustainable plastics" report from the Royal Society of Chemistry highlights polythioesters as interesting and disruptive materials due to the incorporation of chemical break points.[91] As well as this, polythioesters offer sustainability advantages through the replacement of solely carbon-based materials. Nonetheless, to realize these potential benefits, significant technical advances need to be made, allowing a future to be attained where polythioesters make up an essential part of the global polymer portfolio.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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