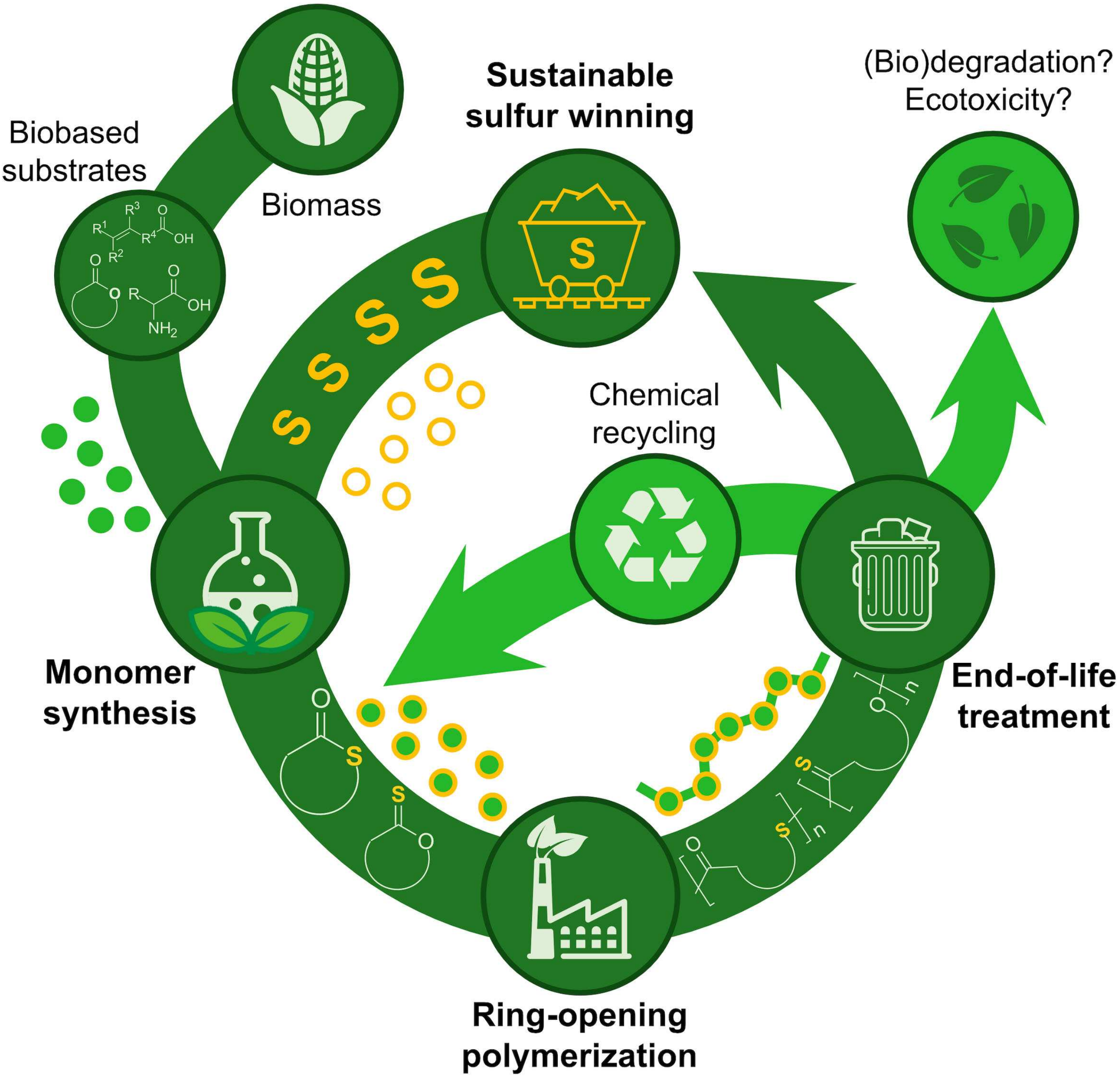
Sustainable Polythioesters via Thio(no)lactones: Monomer Synthesis, Ring-Opening Polymerization, End-of-Life Considerations, and Industrial Perspectives

An Sofie Narmon,[a, b] Christian A. M. R. van Slagmaat,[b] Stefaan M. A. De Wildeman,[b] and Michiel Dusselier*[a]



As the environmental effects of plastics are of ever greater concern, the industry is driven towards more sustainable polymers. Besides sustainability, our fast-developing society imposes the need for highly versatile materials. Whereas aliphatic polyesters (PEs) are widely adopted and studied as next-generation biobased and (bio)degradable materials, their sulfur-containing analogs, polythioesters (PTEs), only recently gained attention. Nevertheless, the introduction of S atoms is known to often enhance thermal, mechanical, electrochemical, and optical properties, offering prospects for broad applicability. Furthermore, thanks to their thioester-based backbone, PTEs are inherently susceptible to degradation, giving them a high sustainability potential. The key route to PTEs is through ring-opening polymerization (ROP) of thio(no)lactones. This Review critically discusses the (potential) sustainability of the most relevant state-of-the-art in every step from sulfur source to end-of-life treatment options of PTEs, obtained through ROP of thio(no)lactones. The benefits and drawbacks of PTEs versus PEs are highlighted, including their industrial perspective.

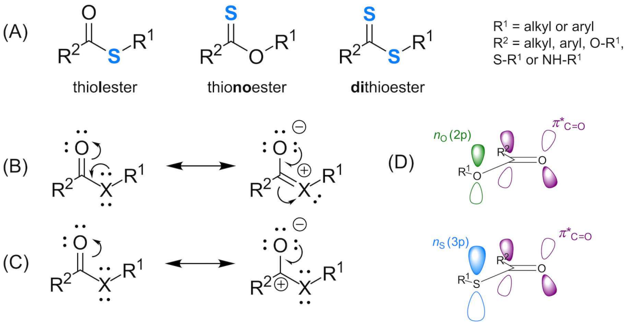
1. Introduction

Although plastics have become an inseparable part of daily life, the rising environmental concerns associated with the use of fossil fuels and the accumulation of plastic debris in the environment prompts the chemical industry in the direction of sustainable biobased, (bio)degradable and/or recyclable polymers, aiming for a closed-loop economy.[1,2] In this context, aliphatic polyesters (PEs), such as poly(lactic acid) (PLA), polybutylene adipate terephthalate (PBAT), and polyhydroxyalkanoate (PHA), have become increasingly popular as (potential) alternatives for conventional plastics, thanks to their biobased and/or biodegradable and often biocompatible character combined with sufficient thermal and mechanical properties as well as industrially viable production processes. Industrial PEs are made by polycondensation of dialcohols with dicarboxylic acids (PBAT),[3] by ring-opening polymerization (ROP) of (di)lactones (PLA),[4] or through microbial synthesis (PHA).[5] Polythioesters (PTEs), the sulfur-containing analogs of PEs, have attracted far less attention and currently no PTEs have been commercialized. However, introducing sulfur in the polymer backbone is known to result in some promising material properties. Sulfur-based polymers are generally known to exhibit high refractive indices, higher melting points and thermal stability, a lower solubility, good mechanical properties, and electrochemical activity.[6–12]

The term thioester refers to esters in which at least one oxygen (O) atom is replaced by sulfur (S). Consequently, three possible thioester structures exist (Scheme 1A). Replacing only the alkoxyl O of the ester by S leads to a thiolester, whereas when only the carbonyl O is changed one speaks of a thionoester. The molecule is called a dithioester when both O atoms are replaced.[6,13] In the rest of this Review, the term 'thioester' will be used as a general term for sulfur-containing esters, whereas the terms 'thiolester', 'thionoester', and 'dithioester' will be used when specifically indicating one of the structures in Scheme 1A.

The larger atomic radius of S provides thioesters with very different reactivities compared to esters. S has a lower electronegativity and electron density, stabilizing its conjugated S^- ion. Therefore, thiols are stronger acids than alcohols, whereas thiolates are stronger nucleophiles than alkoxides. The larger atomic radius of S often results in ineffective orbital overlap [2s, 2p (O) versus 3s, 3p (S)], resulting in less strong bonds compared to those with O (e.g., C–X, X–H, C=X, though not X–X). Thiolesters are abundantly present in metabolism, mainly as acylating agents, of which the most well-known example is acetyl coenzyme A. Owing to the ineffective overlap of orbitals between C (2s, 2p) and S (3s, 3p; Scheme 1D) and the electrons being more stabilized on S, the resonance structures in Scheme 1C are dominant in thiolesters, whereas those in Scheme 1B are more pronounced in esters. Consequently, thiolesters exhibit a more positively charged carbonyl carbon and a reduced double bond character between C and S. The carbonyl carbon of thiolesters will often be a stronger electrophile and therefore more susceptible to attacks of strong nucleophiles (if the steric hindrance of the larger S atom is no limiting factor), whereas the thiolate is a better leaving group. Therefore, nucleophiles will often be easier acylated by a thiolester than by an ester.[10,14]

The high reactivity of thioesters makes PTEs extremely interesting as potentially sustainable, degradable materials in closed-loop economies, as will be discussed in more detail in this review. The effectivity of acylation is amongst others attractive in the context of solvolysis for chemical recycling or



Scheme 1. (A) Chemical structure of different types of thioesters. Adapted from references [13] and [6]. (B) Dominant resonance structure of esters (X=O). (C) Dominant resonance structure of thiolesters (X=S). (D) Orbital overlap in (thiol)esters.

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[a] *A. S. Narmon, Prof. Dr. M. Dusselier*
Department of Microbial and Molecular Systems
Center for Sustainable Catalysis and Engineering (CSCE)
KU Leuven, Celestijnenlaan 200F, 3001 Leuven (Belgium)
E-mail: michiel.dusselier@kuleuven.be
[b] *A. S. Narmon, C. A. M. R. van Slagmaat, Dr. S. M. A. De Wildeman*
B4Plastics BV
IQ-Parklaan 2 A, 3650 Dilsen-Stokkem (Belgium)

hydrolysis in (bio)degradation. However, the high reactivity of S compounds also requires a different approach with regard to polymerization. The nucleophilic nature of thiolates and the strong electrophilicity of the carbonyl carbon of thiolesters and their general instability regularly generates side reactions (e.g., trans-thioesterification, back-biting) during polymerization, resulting in less control over the reaction and thus the final polymer structure.[11] To prevent problems such as unwanted side products, low molar masses, high dispersities ($Đ$s), and racemization, different monomers, reaction conditions, catalysts, and polymerization techniques are needed as opposed to PE syntheses.

In contrast to some PEs, PTEs do not naturally occur, and various synthesis methods are described (Scheme 2). The vast majority of research focused on polythiolesters with only very few examples of polythionoester and polydithioester synthesis. Polycondensation-based methods have been employed since the 1950s[15] in which PTEs were obtained by reactions of various aliphatic and aromatic diacid chlorides with dithiols containing diverse functional groups (Scheme 2A).[16–26] Polycondensation of diesters (instead of diacid chlorides) and dithiols is only illustrated in the presence of enzymes.[27] Polycondensations of different α- or β-mercaptocarboxylic acids (Scheme 2B) and their esters have been attempted as well, but reactions either failed or were extremely slow and only produced short-chain oligomers.[13,28–31] One exception includes the enzyme-catalyzed polycondensation of 11-mercaptoundecanoic acid to relatively high molar mass PTEs.[32] Polyaddition-based syntheses include the radical addition (radical initiator or UV light) of dithiol acids to unconjugated diolefins[15,33] (Scheme 2C) or the polyaddition of diacid chlorides to bicyclic thioethers with quaternary onium salts (Q^+ Y^-; Scheme 2D) resulting in PTEs with pendent chloromethyl groups.[34–37] Next to these chemical methods, the microbial synthesis of poly(3-mercaptoalkanoates) has been described as well.[38] These chemical synthesis methods all involve a step-growth polymerization process, indicating that high molar masses are only obtained at very high monomer conversions. In addition, polymerizations often proceed in a less controlled manner. Another drawback inherently related to polycondensations is the release of condensates (e.g., HCl or H_2O) during the reaction that must be removed to prevent depolymerization by chemical equilibration. As opposed to the synthesis of PEs, the synthesis of PTEs is often performed with the more reactive (and toxic) acyl chlorides instead of carboxylic acids. Nevertheless, from a green chemistry point of view, halogenated compounds should be prevented.

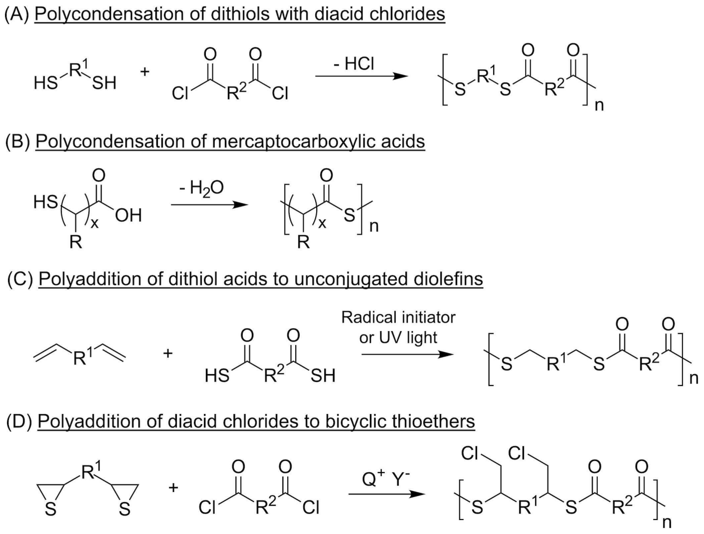
Ring-opening polymerization, being a chain-growth polymerization reaction in which a cyclic monomer is added to a growing polymer chain by ring-opening the monomer, often enables the controlled generation of high MM polymers with low $Đ$ under mild reaction conditions and is therefore of great interest.[4,39] Although the literature on PTE synthesis via ROP is relatively limited, attempts have been described starting from thio(no)lactones (Scheme 3A) and S-carboxyanhydrides (Scheme 3B).[40] More recently, also the ring-opening alternating

An Sofie Narmon obtained her M.Sc. degree in Bioscience Engineering (KU Leuven, Belgium) in 2018 with a major in Catalytic Science and Technology. She is currently performing her Ph.D. research at the Center for Sustainable Catalysis and Engineering (KU Leuven) in collaboration with B4Plastics. Her research focusses on the catalytic synthesis and polymerization of novel lactone monomers for degradable (bio)plastics.

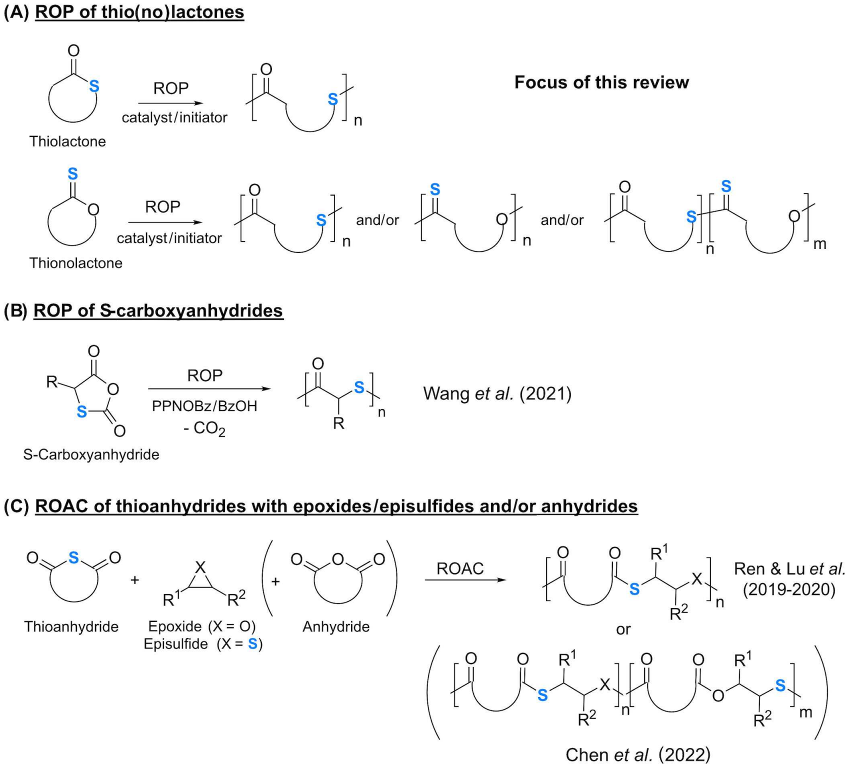
Christian A. M. R. van Slagmaat was born in Utrecht, The Netherlands, in 1991. He received his B.Sc. And M.Sc degrees in Chemistry and Nanomaterials at Utrecht University and performed his Ph.D. research under the guidance of Dr. Stefaan De Wildeman at Maastricht University. His research interests include organic and catalytic chemistry in combination with autoclave, microwave, and flow-reactors to establish sustainable products and processes.

Dr. Stefaan De Wildeman graduated as a Bioscience Engineer (KU Leuven, 1998) and finished his Ph.D. after discovering a new dehalorespiring bacteria (Ghent University, 2002). He joined DSM in 2002 to explore new biobased building blocks for novel materials. Stefaan co-developed the Master "BioBased Materials" and created the Chair of Building Blocks at Maastricht University. In 2014 he founded B4Plastics, a polymer architecture company designing novel polymeric backbones from new BioBased Building Blocks (B4). Since 2020, B4Plastics joined the top 2% league of Green Deal Scale-Ups in Europe and became winner of the 'Food Planet Prize 2021' for its degradable fishing gear.

Prof. Michiel Dusselier obtained his Ph.D. (Bioscience Engineering Catalytic Technology, 2013) at KU Leuven, Belgium, working on catalysis for bioplastics synthesis. In 2014–15, he did postdoctoral work at Caltech, USA, looking into zeolite syntheses. He is now an associate professor at KU Leuven and co-founded the Center for Sustainable Catalysis and Engineering in 2019. He is focusing on zeolite synthesis (subject of an ERC Starting Grant), degradable plastics and heterogeneous catalysis (CO_2). He has authored ca. 75 peer-reviewed papers and 12 patents. In 2022, he received the Young Researcher Award of the International Zeolite Association.



Scheme 2. Polyaddition- and polycondensation-based methods to synthesize polythiolesters. $Q^+ Y^-$ = quaternary onium salt.



Scheme 3. Ring-opening polymerization (ROP) methods for the synthesis of polythioesters: (A) ROP of thio(no)lactones. (B) ROP of S-carboxyanhydrides; PPNOBz = bis(triphenylphosphine)iminium benzoate, BzOH = benzoic acid. (C) Ring-opening alternating copolymerizations (ROAC) of thioanhydrides with epoxides/episulfides and/or anhydrides.

copolymerizations (ROACs) of thioanhydrides with epoxides/episulfides and/or anhydrides to obtain PTEs and copolymers of thiolesters and esters were reported (Scheme 3C).[41–44] While this Review was under preparation, Li and co-workers[12] published a Review paper covering the recent advances in the three ROP methods presented in Scheme 3. This Review will only focus on the ROP of thio(no)lactones (Scheme 3A) and provide a comprehensive summary of the research performed in this area. Although the work by Li et al.[12] gives an excellent and complete overview of the state-of-the-art in ROP chemistry for PTEs, we here offer a more critical look at the sustainable and industrial potential of PTEs as derived by ROP of thio(no)lactones. Critical insights on sulfur as a resource for polymers, the synthesis of thio(no)lactones itself, and their ROP with regard to mechanisms, thermodynamics, and kinetics will be provided. The potential of PTEs as (bio)degradable and recyclable materials is discussed, as well as some future perspectives concerning the industrial production of the materials.

2. Sulfur As a Resource for Polymer Materials

Sulfur (S) is among the most abundant elements on Earth and is estimated to occupy 0.03–0.1 % of the Earth's crust.[45] Sulfur occurs both in its elemental form (e.g., evaporite, volcanic deposits) or as metal sulfides (e.g., pyrite) or sulfates (e.g., gypsum, anhydrite). Despite its wide geological availability, more than 80 % of the sulfur used in industry is obtained from the desulfurization of crude oil and natural gas.[46] To prevent the release of sulfur dioxide (SO_2) into the environment and acid rain by the combustion of fossil fuels, H_2S and covalently bound S are removed from the feedstock and converted to elemental S by hydrodesulfurization and the Claus process. This way, about 70 million tons of sulfur are produced worldwide every year, resulting in a large excess of a relatively cheap elemental resource.[47] Even though elemental S is low in toxicity, it is a flammable and explosive material that is often stockpiled in open deposits.[47,48] In that light, one could argue that using sulfur in sustainable polymer materials would be a great way to valorize the ever-growing sulfur piles. However, the future shift from fossil-based materials and fuels to more sustainable alternatives could cause a drastic drop in the sulfur supply.[49]

Today, the vast majority of sulfur is used in the production of sulfuric acid (H_2SO_4), currently one of the most vital commodity chemicals, for example for fertilizers, ore leaching, batteries, and pulping.[50] Other smaller-scale uses for elemental sulfur include pesticides, cosmetics, and rubber vulcanization,[48,50] whereas it is expected to become important in solid-state batteries (e.g., Li–S).[47,48] With the rise in population and technological development, the demand for sulfuric acid and sulfur will keep rising, whereas the main source of sulfur is expected to disappear.[49] Even though there is an almost unlimited amount of S sources present on Earth,[46] current existing mining processes require large amounts of energy and can have a profound impact on the environment.[49] Therefore, the development of cheap, and eco-friendly technologies for sulfur extraction from the most abundant minerals is of utmost importance. Moreover, research should also focus on other sustainable methods for S-winning, such as sewage mining through sulfur removal and recovery from wastewater.[51]

From a future perspective, sulfur will likely be an indispensable resource for various industrial applications [e.g., solid-state batteries, fertilizers, metal leaching (both in winning and recycling)]. S-containing polymers could become an essential part of this industry. Although the number of commercially available S-containing polymers is limited (mainly polysulfones and polysulfides),[9] the addition of sulfur atoms in the polymer main chain is known to improve or create certain interesting material properties. Depending on the type of functional S-group, S-containing polymers can exhibit a high refractive index, metal coordination and adhesion ability, self-healing properties, high electrochemical activity, ionic conductivity, a high thermal and flame resistance, and better mechanical and processing properties.[9–12] Although functionality is vital, degradability and/or recyclability of plastics is a key feature to prevent inefficient disposal and reduce the need for virgin sulfur sources. For example, the unique chemistry and intrinsic reactivity of thioester bonds in polythioesters, the focus of this review, make this group of polymers susceptible to easy depolymerization for end-of-life treatment. Hence, certain S-containing polymers are very attractive as next-generation, sustainable materials. However, as discussed above, it is vital to consider the recoverability and type of sulfur sources in the future before the large-scale development of new sulfur sink technologies.

3. Synthesis of Thio(no)lactones

Thiolactones are a group of sulfur-containing lactone analogs in which one or both oxygen atoms are replaced by a sulfur atom: thiolactones, thionolactones, and dithiolactones (Scheme 3A). To the best of our knowledge, dithiolactones have not been used in ROP.

The sulfur atoms in thio(no)lactones provide these molecules with a unique reactivity that differentiates them from lactones. Owing to this unique reactivity, thiolactones are often found in (bio)chemical pathways (e.g., homocysteine thiolactone), used as intermediates in the synthesis of biologically active compounds, such as those used in medicinal applications.[52–54] Lately, these molecules have found more use in polymer chemistry. The thiol groups, created by opening thiolactone rings, can react with diverse functional groups and, as a consequence, are used in various ways (e.g., as linkers, pendant groups with functionalization potential, initiating systems, thiolation agents, reactants in step-growth polymerization) to engineer polymer materials.[55–57] Owing to their higher stability, mainly five-membered thiolactones (γ-thiolactones) have been naturally found and described in these applications. However, in the context of ROP – where ring-opened thiolactones compose the polymer backbone – less stable ring structures are key to drive polymerization. Various approaches to synthetically obtain thio(no)lactones have been reported. The most relevant and straightforward methods in the context of small-sized (4–7 membered) thio(no)lactones for ROP will be discussed. For a more complete overview of these and other methods (often in the context of thiolactones as intermediates in (bio)organic synthesis) the reader is referred to other reviews.[52,54]

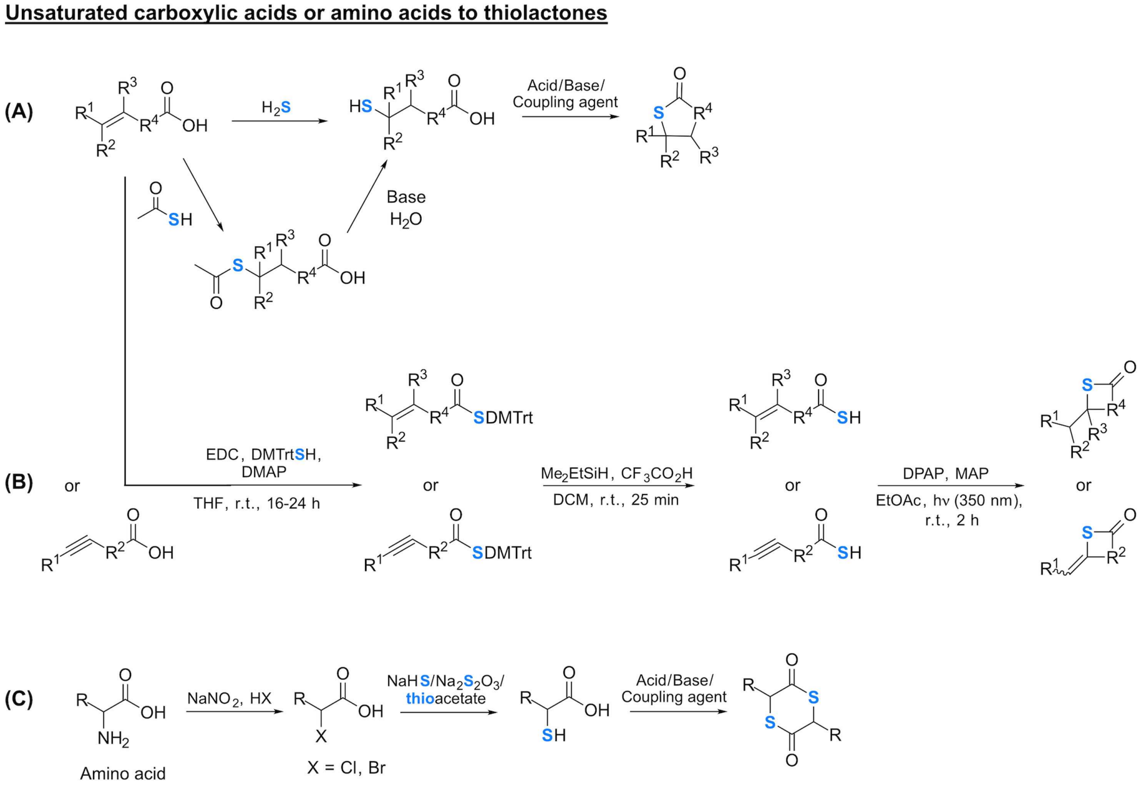
For completion, it must be mentioned that a two-step synthesis method that is often described for lactones and industrially applied for the synthesis of lactide, i.e., the oligomerization of lactic acid followed by the back-biting depolymerization of the PLA oligomers to obtain lactide,[58] is not widely described for the synthesis of thiolactones. Two rather old (1950–1970) studies[59,60] describe this type of method for the synthesis of thiolactide and thioglycolide (see below), but yields are limited. As mentioned in the introduction, polycondensation of mercaptocarboxylic acids is challenging, which might be a reason for the limited usage of this method in the past.

3.1. From unsaturated carboxylic acids or amino acids to thiolactones

The most common route to thiolactones involves the cyclization of mercaptocarboxylic acids (i.e., carboxylic acids with -SH groups at the α, β, γ, etc. position relative to the carbonyl C) or their derivatives. To obtain small ring size (4–7) thiomonolactones, an intramolecular cyclization of β, γ, δ, or ε-mercaptocarboxylic acids or their derivatives is required. However, for thiodilactones, being molecules with two thiolester groups in one ring, an intermolecular cyclization is desired between α and/or β-mercaptocarboxylic acids (6–8 rings) or their derivatives.

Mercaptocarboxylic acids do not naturally occur and are, in turn, made in various ways (Scheme 4A,C). A typical synthesis method includes the addition of H_2S or thioacetic acid ($CH_3C(O)SH$) to an unsaturated carboxylic acid (e.g., acrylic acid to β-mercaptopropionic acid or crotonic acid to α-mercaptobutyric acid; thiol-ene reaction or Michael addition).[61] Another possibility is the substitution reaction of halogenated carboxylic acids (or their salts) with H_2S, alkali metal hydrogen sulfides (e.g., NaHS), sodium thiosulfate ($Na_2S_2O_3$), or alkali metal salts of thioacetate. Halogenated carboxylic acids in turn could readily be obtained from naturally occurring amino acids in the presence of $NaNO_2$ and HCl or HBr, such as performed by Wang et al.[62] for the synthesis of different biobased, substituted α-mercaptocarboxylic acids.

Cyclization or condensation of mercaptocarboxylic acids or their derivatives (e.g., thioether, amide, ester, acyl chloride) to obtain thiolactones is typically performed under reflux conditions in the absence or presence of acids [e.g., trifluoroacetic acid, *p*-toluenesulfonic acid (*p*-TSA)] or bases [e.g., triethylamine (TEA), diisopropylethylamine (DIPEA)].[52] However, many reported methods also employ coupling or dehydrating agents to drive condensation reactions (e.g., $BOP^+ PF_6^-$,[63] P_2O_5,[64] triphosgene,[65] diphenylphosphinic chloride,[66] hexafluorophosphate azabenzotriazole tetramethyl uronium[67]). One, in particular, is the Steglich thioesterification in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) or *N*-(3-(dimethylamino)propyl-*N*′-ethylcarbodiimide hydrochloride (EDC HCl) with DMAP (4-dimethylaminopyridine) under mild reaction conditions. McCourt and Scanlan[61] proved the efficiency of EDC HCl in the synthesis of a broad spectrum of γ- and δ-thiolactones in relatively high yields and confirmed the compatibility of the



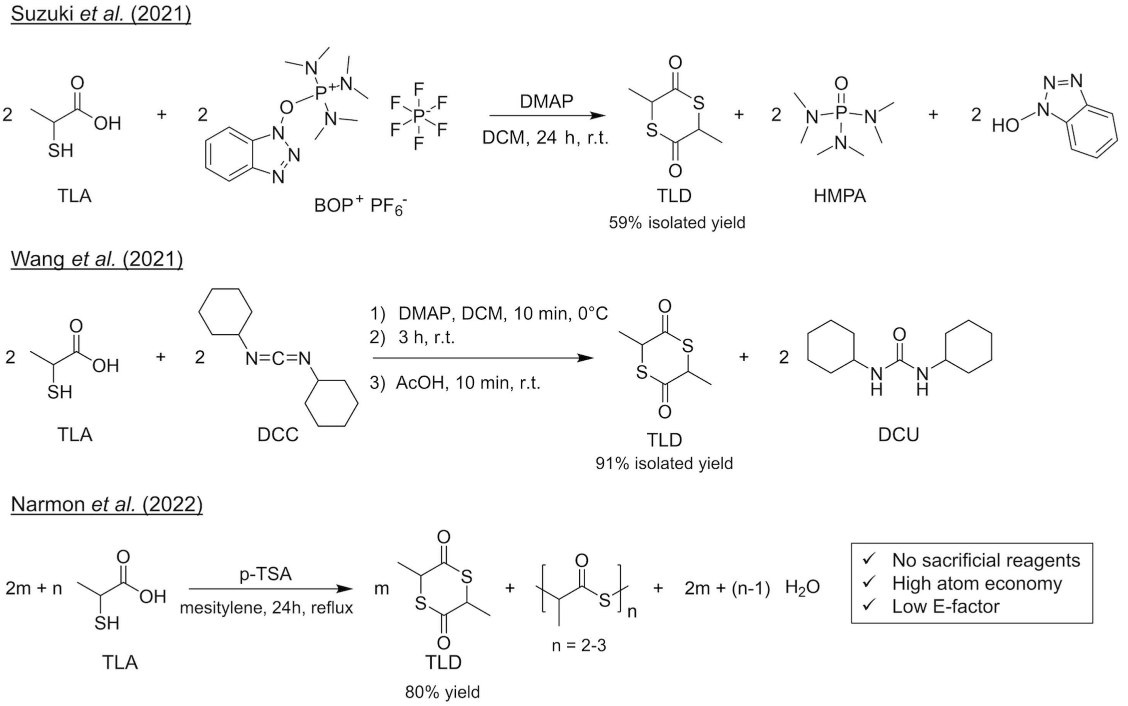
Scheme 4. Methods to obtain thiolactones from unsaturated carboxylic acids or amino acids: (A) Unsaturated carboxylic acid to mercaptocarboxylic acid to thiomonolactone via intramolecular thioesterification, (B) Unsaturated carboxylic acid to unsaturated thiocarboxylic acid to thiomonolactone via intramolecular thiol-ene reaction under UV light (only five- and six-membered rings described). (C) Amino acids to mercaptocarboxylic acids to thiodilactones via intermolecular thioesterification.

method for certain functional groups (halogens, esters, nitro compounds). However, coupling agents, needed in stoichiometric or excessive amounts, significantly reduce atom economies, increase the number of waste products, and with that complicate product purification. Moreover, a lot of these coupling agents and their by-products are hazardous or toxic.

These inherent drawbacks were shown and overcome by our group for the direct condensation reaction of thiolactic acid (TLA) to thiolactide (TLD) in a Dean-Stark setup with refluxing solvent.[68] Our work showed the high efficiency and green chemistry potential of Brønsted acid catalysts in this reaction as compared to coupling reagents used in other reported studies ($BOP^+ PF_6^-$[63] or DCC[62] with DMAP) (Scheme 5).

Sulfonic acid catalysts, such as *p*-TSA (in mesitylene) resulted in a TLD yield of up to 80% and a volumetric productivity of 11.2 g_{TLD} L^{-1} h^{-1}, whereas this method improved the atom economy of the other reported reactions with 63–88% and reduced the ecology factor (E-factor) by 66–97% (Figure 1).[68] Attempts were made to heterogenize the catalytic system and different sulfonic acid ion-exchange resins and Brønsted acid zeolites were tested. However, reaction yields and selectivities were much lower (up to 39% (resin) and 28% (zeolite) yields). Shape-selective Brønsted acid Beta zeolites (H-BEA) were shown to be very successful in the synthesis of lactide (LD) from lactic acid (LA), whereas *p*-TSA merely catalyzed polycondensation toward oligomeric LA species.[69] However, in this S-chemistry, TLA showed a much lower tendency toward polycondensation, and shorter linear oligomers were observed in the presence of Brønsted acids, possibly due to the lower stability of polythiolesters compared to polyesters. This resulted in a higher selectivity toward the cyclic product and reduced the need for a shape-selective zeolite. It was also shown by gas phase FT-IR (Fourier transform infrared) experiments that TLA (compared to LA) interacted very strongly with both the Lewis and Brønsted acid sites in the zeolite, which was believed to lead to poisoning of the active sites and counteract catalytic activity.[68] Whereas condensation reactions with hydroxy acids to obtain lactones often are performed under specific conditions to prevent rapid polycondensation (e.g., low concentration, low temperature-vacuum regimes, shape-selective catalysts),[59] this seems to be less needed for mercaptocarboxylic acids.

Another method to obtain thiolactones (mainly five-membered rings described) starting from unsaturated carboxylic acid is via converting the carboxylic acid into an unsaturated thiocarboxylic acid (−C(O)SH), which can then undergo an intramolecular acyl thiol-ene or acyl thiol-yne cyclization (Scheme 4B). McCourt et al.[70] synthesized unsaturated thiocarboxylic acids by reacting their corresponding carboxylic acids with dimethoxytritylthiol (DMTrtSH) in the presence of EDC and DMAP at room temperature (RT). Subsequently, the protecting group was removed by bringing the thiolester at mildly acidic conditions (Me_2EtSiH, CF_3CO_2H) for 25 min. The silane and acid were removed in vacuo and the intramolecular thiol-ene/thiol-yne reactions were performed under UV light (350 nm) in the presence of a radical initiator [2,2-dimethoxy-2-phenylacetophenone (DPAP)] and photosensitizer [4-methoxyacetophenone (MAP)]. High yields and regioselectivity were observed for the



Scheme 5. Methods for the synthesis of thiolactide (TLD) from thiolactic acid (TLA). $BOP^+ PF_6^-$ = benzotriazol-1-yloxytris(dimethylamino)phosphonium hexafluorophosphate; DMAP = 4-dimethylaminopyridine; HMPA = hexamethylphosphoramide; DCC=*N*,*N*′-dicyclohexylcarbodiimide; DCU = dicyclohexylurea; E-factor = ecology factor. Scheme adapted from reference [68].

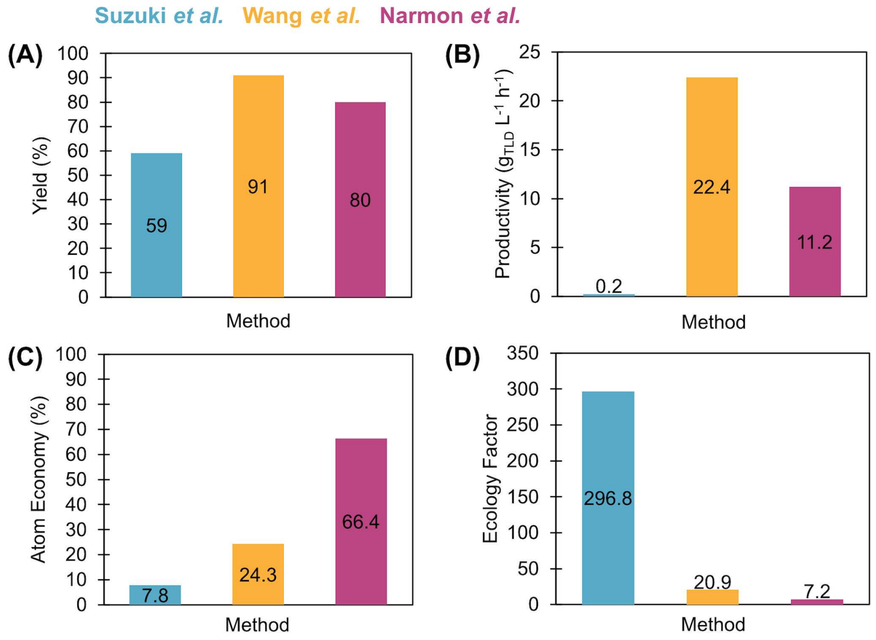


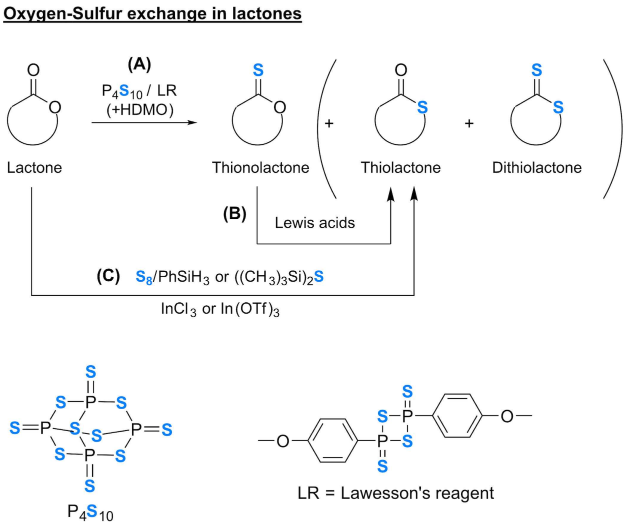
Figure 1. Results of methods for the synthesis of TLD from *rac*-TLA (Scheme 5): (A) Yield (for Suzuki et al.[63] and Wang et al.,[62] this is the isolated yield; for Narmon et al.[68] this is the reaction yield); (B) productivity; (C) atom economy [(molar mass of desired product/molar masses of reactants) × 100]; (D) ecology factor (mass of total waste/mass of product). For data calculations, see reference [68].

thiol-ene reactions, whereas thiol-yne reactions led to slightly lower yields and a mixture of regioisomers. Moreover, the process seemed compatible with certain functional groups (nitro, halogen, and ester). Other examples of radical-based thiolactone synthesis methods can be consulted in another review.[54] However, these methods were also mainly used in the synthesis of γ-thiolactones, which are challenging to ring-open polymerize due to their very low ring strain. In addition, most of these methods use rather complex chemical compounds in multiple reaction steps to often reach low to mediocre thiolactone yields.

From the examples above it can be seen that complex and high molar mass coupling agents and/or radical initiators are widely described in the synthesis of thiolactones. Even though they often enable rather high thiolactone yields at mild reaction conditions, they result in excessive amounts of waste products and strongly reduced atom economies. In addition, large amounts of waste- and by-products often require extensive or complex purification procedures, making these methods less sustainable and industrially viable. Although condensation reactions in the absence of sacrificial reagents seem possible, mainly homogeneous catalysts are still employed. Sulfur's inherent nature complicates the use of heterogeneous catalysts due to its poisoning effect on a wide variety of metals and typical support materials. Future research should focus on simplifying synthesis methods and preventing the use of high-molar mass coupling agents, as well as searching for heterogeneous support materials that are insensitive to sulfur poisoning.

3.2. Oxygen-sulfur exchange in lactones

Another method to obtain thio-, dithio-, and mainly thionolactones is through oxygen-sulfur exchange in lactones through thionation reactions. Thionations are typically performed in the presence of a thionating agent such, as phosphorus pentasulfide (P_2S_5 or P_4S_{10}), or Lawesson's reagent (LR; Scheme 6A).[52,71]



Scheme 6. Oxygen-sulfur exchange in lactones: (A) Lactones to thiolactones in the presence of a thionating agent [P_4S_{10} or Lawesson's reagent (LR)] with or without hexamethyldisiloxane (HDMO). (B) Isomerization of thionolactones to thiolactones with Lewis acids. (C) Selective conversion of lactones into thiolactones with S_8/$PhSiH_3$ or $((CH_3)_3Si)_2S$ catalyzed by $InCl_3$ or $In(OTf)_3$, respectively.

The main driving force of the reaction is the stronger affinity between P and O compared to P and S, resulting in a more thermodynamically stable product after O–S exchange.[72] Although, thionation of the carbonyl oxygen of lactones to create thionolactones most readily occurs – depending on the reaction conditions, substrate, and thionating agent – a mixture of thio-, thiono- and dithiolactones can be obtained as well (Scheme 6A).

P_4S_{10} is an often-used and versatile chemical in the synthesis of numerous organosulfur compounds.[73,74] It is a crystalline and highly flammable solid that decomposes in the presence of H_2O.[74] LR is obtained by a reaction of P_4S_{10} with anisole or by reacting anisole with sulfur and red phosphorus.[72] Both compounds are known to react as dithiophosphoranes (R-PS_2) with carbonyl compounds (after thermal cleavage) to create thiocarbonyls via a four-membered ring intermediate.[72,73,75] Reactions with these thionating agents are typically performed in refluxing solvents (e.g., toluene, xylene, THF, acetonitrile) for several hours. However, the application of microwaves under solvent-free conditions is described to reduce reaction times to a few minutes.[72,76] Yields obtained with P_4S_{10} are generally lower than with LR, whereas the inherent drawback related to LR is the relatively difficult removal of this compound and its byproducts from the product mixture.[74] Nevertheless, both drawbacks can be overcome by using a combination of P_4S_{10} and HMDO (hexamethyldisiloxane), which is found to strongly increase the thionating activity of P_4S_{10}, reaching yields comparable to or even higher than LR.[77,78] HDMO prevents the formation of undesirable side products by interacting with highly electrophilic species formed by O–S exchange in P_4S_{10} (e.g., polythiophosphates).[74] Combinations of LR with HMDO have also been described.[79] Examples of these agents used to make thionolactones include the synthesis of ε-thionocaprolactone (ε-TnCL) in 75% isolated yield form ε-caprolactone (ε-CL) in the presence of P_4S_{10} and HDMO by Datta and Kiesewetter[80] and the synthesis of γ-thionobutyrolactone (γ-TnBL) in 90% isolated yield from γ-butyrolactone (γ-BL) with LR in refluxing toluene for 5 h by Yuan et al.[81] For a more extended overview of thionation reactions of different lactones by these reagents the reader is referred to other papers.[72,73,79] Next to HDMO, other additives have been used to accelerate reaction rates or increase yields of thionations, but these are outside the scope of this review.

It is worth mentioning that some effort has been made to immobilize P_4S_{10} on solid supports, but no tests on lactones were described. Kaushik and co-workers[82,83] used alumina (Al_2O_3) supported P_4S_{10} in the thionation of amides and ketones under reflux conditions. Compared to reactions with only P_4S_{10}, the supported reagent not only provided for easy separation and a purer mixture, but also a reduced reaction time and a higher product yield were observed. Al_2O_3 was said to not only serve as a support but also to scavenge polythiophosphate electrophiles and prevent side product formation. In addition, a solid-supported reagent is expected to facilitate reaction scale-up and enable safer handling of dangerous or malodorous compounds. Later, the same reagent was also proven to be efficient under microwave irradiation, showing reduced reaction times and improved yields.[84] Comparable advantages were observed with SiO_2 as solid support.[85]

The isomerization of thionolactones to thiolactones has also been shown in the presence of Lewis acids (Scheme 6B). However, the tested substrates were mainly γ-thionolactones and in certain cases, a significant amount of lactones and to a lesser extent of dithiolactones were obtained as side products, certainly when δ-thionolactones were used.[86] Significantly fewer studies focused on the selective conversion of lactones into thiolactones. Sakai et al.[87] proposed the direct conversion of lactones into thiolactones in the presence of S_8 catalyzed by $InCl_3/PhSiH_3$ (Scheme 6C). Thiolactone yields were low to moderate and strongly depended on the substrate used, in which γ-lactones performed better than δ-lactones. Later, the same group performed thiolactone synthesis in the presence of disilathiane ($(Me_3Si)_2S$) with $In(OTf)_3$ to obtain higher yields, but still mainly for five-membered rings.[88] Obtaining thio(no)lactones from naturally available or widely produced lactones seems viable, but remains underexplored.

4. Ring-Opening Polymerization

In the following sections, a short summary will be given of the most important and recent reports on the ROP of thio(no)lactones, divided among thiomonolactones and thiodilactones. The described monomers, their corresponding polymers, the used catalytic systems, and the obtained molar masses and thermal properties of the materials are brought together in Tables 1 and 2. We limit our discussion to polymers with decent molar masses, made from monomers that can be obtained in a reasonable amount of reaction steps and/or are biobased. For a more complete and detailed review, the reader is referred to the very recent work by Li and co-workers.[12]

4.1. Thiomonolactones

4.1.1. Substituted β-Thiopropiolactones

Substituted four-membered β-thiopropiolactone (β-TPL) rings from recent literature are discussed. Suzuki et al.[89] described the ROP of an *N-tert*-butyloxycarbonyl (*N*-Boc) cysteine-derived β-TPL (Table 1, entry 1) in the presence of *N*-Boc-L-cysteine methyl ester as the initiator in NMP (*N*-methyl-2-pyrrolidone) at RT. Owing to possible trans-thioesterification reactions, molar masses were low and *Đ*s were rather broad. Chains seemed to be linear with defined terminal SH groups (acyl-sulfur cleavage mechanism) and molar masses were in line with the amount of initiator added. Benzylamine could also initiate the ROP of the thiolactone, but some side products were seen (oxidation of SH end-groups to disulfides and/or trans-thioesterifications).

The side reactions observed by Suzuki et al.[89] were overcome by introducing two methyl substituents on the β-position of the thiolactone, as shown by Xiong et al.[65] They performed ROP on penicillamine-derived β-thiolactones containing different substituents on the N-group of the amine (Table 1, entry 2).

Table 1. Thio(no)monolactone monomers, their corresponding polymers, the catalyst systems and reaction conditions used, the obtained molar masses, and thermal properties of a selection of reported examples.

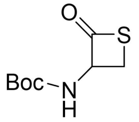
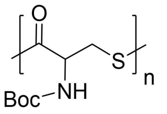
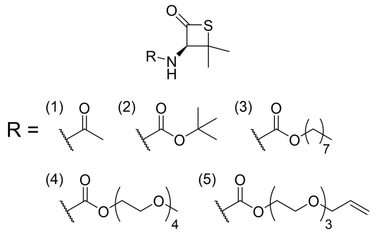
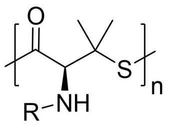
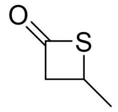
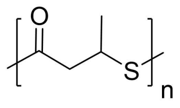
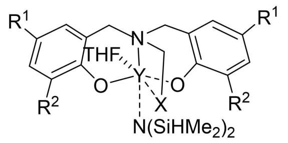
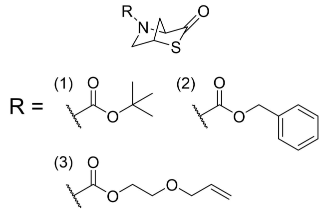
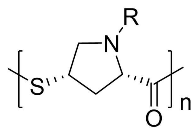
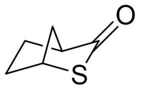
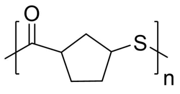
Entry	Monomer	Polymer	Catalyst system (Reaction conditions)	Molar mass [M_n, kg mol^{-1}] (Dispersity) [$Đ$]	Thermal properties	Ref.
1			*N*-Boc-L-cysteine methyl ester (0.98 M, NMP, RT)	2.9–8.8 (1.6–2.4)	–	[89]
2			Catalyst: TEA, DBU, ^{t}BuP$_4$ Initiator: BnSH (Bulk, RT)	6.4–70.6 (1.09–1.30)	**R = (3)** $T_g = 50\,°C$ $T_m = 100\,°C$	[65]
3			 X═CH$_2$NMe$_2$, CH$_2$OMe, CH$_2$NEt$_2$, 2-pyridyl, R^1═R^2═^{t}Bu, CMe$_2$Ph, Me, Cl, CPh$_3$ (0.5–1 M, toluene/THF, −80–18 °C)	1.9–59.2 (1.14–1.83)	**Isotactic and cyclic** $T_g = 4\,°C$ $T_m = 101\,°C$	[90]
4			Catalyst: TEA, DBU Initiator: BnSH (2 M, CDCl$_3$, 25 °C)	6.2–259 (1.03–1.32)	**R = (2)** $T_g = 67\,°C$ **R = (3)** $T_g = 32–37\,°C$	[66]
5			Catalyst: La[N(SiMe$_3$)$_2$]$_3$, DBU, ^{t}Bu–P$_4$ or IMes Initiator: BnOH (6.25–25 M, toluene/THF/DMF, RT)	8.8–170 (1.44–2.78)	$T_m = 166–213\,°C$ $T_g = 112\,°C$	[93]

Table 1. continued

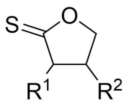
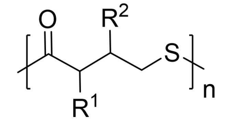
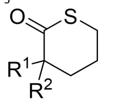
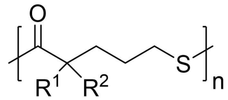
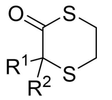
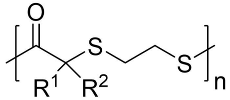
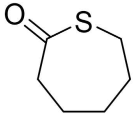
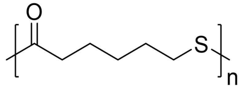
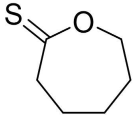
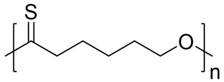
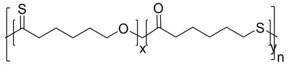
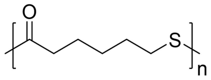
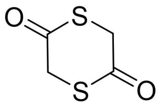
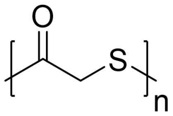
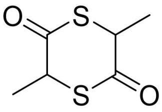
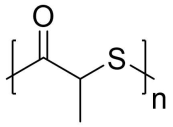
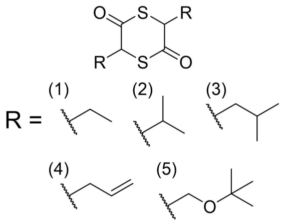
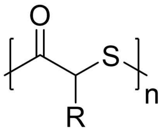
Entry	Monomer	Polymer	Catalyst system (Reaction conditions)	Molar mass [M_n, kg mol^{-1}] (Dispersity) [$Đ$]	Thermal properties	Ref.
6	 (1) R^1=R^2=H (2) R^1=CH_3, R^2=H (3) R^1=H, R^2=CH_3		Catalyst: $^tBuP_4$ Initiator: Ph_2CHOH, BnOH, 1-octanethiol (3.4–6.8 M, toluene/xylene, 80–120 °C)	(1) 23.1–162.6 (1.32–1.66) (2) 108.1–238.6 (1.34–1.48) (3) 97.5–251.0 (1.50–1.56)	(1) T_g = −49 °C, T_m = 100 °C (2) T_g = −30 °C (3) T_g = −30 °C	[81]
7	 (1) R^1=R^2=H (2) R^1=CH_3, R^2=H (3) R^1=R^2=CH_3		Catalyst: DBU Initiator: 1-dodecanethiol (5–7.3 M, $CDCl_3$/THF, −33 °C-RT)	(1) 14.3 (2.1) (2) 15.2 (1.7) (3) 5.6 (1.3)	(1) T_m = 123 (2) T_g = −40 (3) T_g = −34	[67]
8	 (1) R^1=R^2=H (2) R^1=CH_3, R^2=H (3) R^1=R^2=CH_3 (4) R^1=Ph, R^2=H		Catalyst: DBU Initiator: 1-dodecanethiol (3–8.2 M, $CDCl_3$/THF, 0 °C-RT)	(1) 15.8 (1.6) (2) 18.7 (2.2) (3) 18.1 (2.1) (4) 3.7 (1.9)	(1) T_g = −34, T_m = 88 (2) T_g = −25 (3) T_g = −12 (4) T_g = 19	[67]
9			Catalyst: DBU, TBD, MTBD, BEMP/TU Initiator: octadecylthiol (1 M, $CHCl_3$, RT)	6–32 (1.40–1.70)	T_m = 108–109 °C[64] T_g = −40 °C[64]	[100]
10		(1) 	(1) (a) MeLi, ^nBuLi, $^{sec}BuLi$, ^tBuLi, PhLi, MeMgCl, ^tBuMgCl, ^tBuOLi (1 M, toluene, 0–100 °C) (1) (b) Catalyst: DBU, TBD, MTBD, BEMP/TU Initiator: octadecylthiol, 1-pyrenebutanol, BnOH (2–4 M, C_6D_6, RT)	(1) (a) 6.8–19.0 (1.26–2.67) (b) 8.2–22.5 (1.10–1.41)	(1) (b) T_m = 9 °C	[80,101,102]
		(2)  (3) 	(2) ^tBuOK, DBU (2 M, toluene, 100 °C) (3) BF_3OEt_2, TfOH, TfOMe, TfOEt (0.1–1 M, DCM/$MeNO_2$ /benzene/toluene, −78–28 °C)	(2) 3.8–4.5 (1.54) (3) 9.9–57 (1.35–2.56)		

Table 2. Thiodilactone monomers, their corresponding polymers, the catalyst systems and reaction conditions used, the obtained molar mass, and thermal properties of a selection of reported examples.

Entry	Monomer	Polymer	Catalyst system (Reaction conditions)	Molar mass [M_n, kg mol^{-1}] (Dispersity) [$Đ$]	Thermal properties	Ref.
1			(a) Piperidine, DEA, CHA (0.4 M, $CHCl_3$, RT) (b) Catalyst: DBU Initiator: 4-^{t}butylphenyl methanethiol (0.68–1.36 M, DMF, 0 °C-RT)	(a) 14–17 (b) 1.5–1.6 (1.2–1.3)	T_m = 158–169 °C	[13,28–30,63]
2			(a) Catalyst: DBU, DIPEA, PMP, pyridine Initiator: 2-ethylhexyl glycolate (2.28–5.7 M (or bulk), DCM/ACN/THF/toluene, 0–50 °C) (b) Catalyst: DMAP, TEA, TBD, ^{t}BuP$_2$ Initiator: BnSH (5.9 M, DCM, 25 °C) (c) Catalyst: TEA Initiator: BnOH (25 M, DCM, RT)	(a) 0.4–4.9 (1.4–3.1) (b) 4.2–73.3 (1.28–1.55) (c) 11.6–31.1 (1.5–1.8)	T_g=-1–0 °C	[62,63,68]
3			Catalyst: DMAP Initiator: BnSH (5.9 M, DCM, 25 °C)	16.3–100.5 (1.26–1.41)	(1) T_g = −4.2 (2) T_g = 34.6, T_m = 115.6 (3) T_g = 17.0 (4) T_g = −19.2 (5) T_g = 41.9	[62]

Reactions took place in bulk at RT with BnSH (benzyl thiol) as the initiator and organic bases as the catalysts [TEA, DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene), ^{t}BuP$_4$ (1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)-phosphoranylidenamino]-2λ^5,4λ^5-catenadi (phosphazene)], resulting in polymers with M_n values between 6.4 and 70.6 kg mol^{-1}. The dimethyl substituents were described to reduce the activity and conformational possibilities of the chain-end thiolate groups and to stabilize the thiolester linkages in the polymers, reducing uncontrolled side-reactions. Moreover, the substituents reduced the ring strain of the β-TPLs by the Thorpe-Ingold effect, enabling fast depolymerization to the monomer at relatively low temperatures (Table 7, entry 1).[65]

Very recently (2022), Li and co-workers[90] proved the successful ROP of racemic β-thiobutyrolactone (Table 1, entry 3) and with that the first chemical synthesis of poly(3-thiobutyrate) [or poly(β-thiobutyrolactone) (P(β-TBL)]. Only microbial synthesis had been described before of this sulfur analog of poly(3-hydroxybutyrate) (PHB). Unlike previous research on the ROP of thiolactones, they screened a variety of metal-based (Al, Zn, La, and Y) complexes, instead of organic catalysts. Yttrium amido complexes with a diamino-bis-(phenolate) ligand (Table 1, entry 3) did not only show full conversion at RT after 1–5 min, but changing a part of the ligands resulted in syndio- or isotactically enriched chains when starting from a racemic monomer.

4.1.2. *γ-Thiobutyrolactones*

Five-membered thiolactones, of which γ-thiobutyrolactone (γ-TBL) is the unsubstituted structure, are – similar to their lactone counterparts – thermodynamically very challenging to ring-open polymerize due to their low ring strain.[91] Although γ-TBL has not yet been successfully homopolymerized, other methods to drive the polymerization of five-membered thiolactones have been employed (e.g., the use of bicyclic γ-TBLs with higher ring strain, copolymerization).

Yuan et al.[66] described the ROP of 4-hydroxyproline-derived bicyclic γ-TBLs (Table 1, entry 4). Biobased and readily available trans-4-hydroxy-L-prolines were transformed into their corresponding thiolactones via a three-step one-pot procedure (yield = 53–65 %) with S coming from methanesulfonyl chloride. Solution ROPs of the monomers with TEA or DBU as the catalyst and BnSH as the initiator at RT resulted in linear chains with M_n values between 6.2 and 259 kg mol^{-1} (depending on the type of N-substitution and the amount of catalyst) and narrow $Đ$s. High monomer conversions were reached within short reaction times [40 min–24 h (TEA), 5 min (DBU)]. The authors reasoned that the bridged bicyclic structure results in a high reactivity, due to its higher ring strain (compared to normal γ-thiolactones), and in a minimization of trans-thioesterifications. The quantitative recycling of the PTEs to their monomers was possible in the presence of DBU at mild reaction conditions (Table 7, entry 2), in contrast to the more stringent conditions needed in the depolymerization of typical polyesters and polycarbonates, due to the lower ring strain of the monomer and lower ceiling temperature of polymerization (T_c, i.e., the temperature at which the rates of polymerization and depolymerization are equal) as compared to lactones.[92] The industrial availability of the substrate, the possible large-scale (i.e., 1000 kg) synthesis of the thiolactones, their high functionalizability, their interesting ROP kinetics and thermodynamics, and the high chemical recyclability of the polymers make them interesting sustainable materials for commercialization. However, their rather weak thermal properties [i.e., no T_m, low T_g, and low decomposition temperature (T_d)] may limit their applicability and processability.

In 2020, Shi et al.[93] investigated the ROP of an unsubstituted bridged bicyclic γ-TBL, i.e., 2-thiabicyclo[2.2.1]heptan-3-one (Table 1, entry 5). This monomer was synthesized from biobased 3-cyclopentene-1-carboxylic acid, in the presence of thioacetic acid in 80% yield (50 g scale) and only in cis-configuration (Scheme 4A). Depending on the type and amount of catalyst ($La[N(SiMe_3)_2]_3$, DBU, $^tBu–P_4$ or IMes [1,3-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene)] used (with or without BnOH as the initiator), the monomer concentration, and the type of solvent, the polymer structures obtained at RT in solution were cyclic or linear and atactic or (completely) stereoregular (i.e., cis versus trans configuration of cyclopentylene units) and with high M_n values. All polymers were semicrystalline, independent of stereoconfiguration or topology (cyclic or linear), but T_m values increased with increasing stereoregularity up to 231 °C ($T_g = 112$ °C). The tacticity-independent crystallization of the polymers was explained by a high three-dimensional order of the cyclopentylene ring-based chains, even in the presence of stereo-defects. Moreover, the bridged bicyclic structure creates a more rigid polymer backbone with good mechanical and thermal properties. In addition, chemical recycling of the PTEs back to their monomers was thermodynamically favored thanks to the relatively low ring strain of the bicyclic thiolactone (Table 7, entry 3).

Very recently (2022), Yuan et al.[81] published the successful ROP of γ-thionobutyrolactone (γ-TnBL), α-methyl-γ-TnBL, and β-methyl-γ-TnBL to produce poly(γ-**thio**butyrolactone)s [P(γ-TBL); Table 1, entry 6], **not** poly(γ-**thiono**butyrolactone)s, by alkyl-oxygen bond cleavage (instead of acyl-oxygen bond cleavage) ring-opening with S/O isomerization (see below). The monomers were made in one step via the sulfurization of their corresponding lactones in the presence of Lawesson's reagent (Scheme 6A; yield = 80–92%). ROP in the presence of La and Y-based catalysts did not work, possibly due to S-metal interactions. Organocatalysts such as DBU and TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) also seemed inactive at RT. However, phosphazene bases ($^tBuP_{1/2/4}$) were capable of creating P(γ-TBL), but certain side products were observed. By adding Ph_2CHOH as the initiator and increasing temperature, the basicity of the catalyst ($^tBu–P_1 < {}^tBu–P_2 < {}^tBu–P_4$) and the monomer/catalyst ratio, a more rapid and selective ROP was obtained with fewer side products (full conversion). Owing to complete S/O isomerization and exclusive alkyl-oxygen cleavage, an irreversible ROP was obtained without a (de)polymerization equilibrium, making ROP possible at relatively high temperatures (80–100 °C). The S/O isomerization was mentioned to be the most important thermodynamic driving force of the reaction since the five-membered thionolactone did not exhibit a sufficient ring strain. Polymers with high molar masses between 23.1 and 251.0 $kg\,mol^{-1}$ were obtained. P(γ-TBL) showed to be a semicrystalline material with a high T_m (100 °C), a T_g of −49.2 °C, and mechanical properties comparable with low-density polyethylene. In addition, complete depolymerization of P(γ-TBL) was reached in an alkaline aqueous solution or in the presence of TBD (Table 7, entry 4).

4.1.3. δ-Thiovalerolactones

Very little is reported on the ROP of the six-membered thiolactone, δ-thiovalerolactone (δ-TVL). In 1968, Overberger and Weise[64] described the anionic ROP of δ-TVL in the presence of ^tBuOK at 155 °C with a monomer conversion of 21% and low MM. δ-TVL was synthesized by distillation of 5-mercaptovaleric acid.[64,94]

Very recently, Stellmach et al.[67] successfully polymerized δ-TVL, α-methyl-δ-TVL and α,α-dimethyl-δ-TVL (Table 1, entry 7). These monomers were synthesized by substitution of thioacetic acid to (methyl-substituted) 4-pentenoic acid, followed by hydrolysis and a Steglich-type thioesterification (overall yield up to 47%). To also study the effect of sulfur substitution, the ROPs of different 1,4-dithianones (DTNs, i.e., DTN, α-methyl-DTN, α,α-dimethyl-DTN, and α-phenyl-DTN), in which an extra S atom was introduced at the β-position of δ-TVL, were performed (Table 1, entry 8). These monomers were obtained by reacting the desired haloacetyl halide with ethane dithiol (yield = 35–65%). ROP was executed with DBU as the catalyst and 1-dodecanethiol as the initiator in THF at or below RT. It was observed that δ-TVL showed a monomer conversion of 46% at RT while lower temperatures were needed for the methyl-substituted analogs, to only obtain even lower conversions due to a decreased ring strain (Thorpe-Ingold effect). However, introducing an extra S in the ring increased the monomer conversion (e.g., 87% for DTN). The addition of methyl substituents to δ-TVL seemed to decrease T_c, whereas a decrease in enthalpy (ΔH_p) and entropy of polymerization (ΔS_p), and as a consequence an increase in T_c, were observed with the introduction of a second S atom in the ring. However, the series of methyl-substituted DTNs showed different results. Whereas α-methyl-DTN exhibited a lower monomer conversion, a higher conversion was observed for α,α-dimethyl-DTN. DFT calculations showed that bulky substituents seemed to disrupt the geometry of DTN, which resulted in an increased ring strain and a very strong drop in ΔS_p. The authors argued that a strongly negative ΔS_p makes monomers more sensitive to changes in temperature, which allows for an easy shift from polymerization to depolymerization with only a small temperature change. Depolymerization of poly(α,α-dimethyl-DTN) was shown in the presence of DBU (Table 7, entry 5).

4.1.4. ε-Thiocaprolactones

Overberger and Weise (1964–1968)[64,95,96] were the first to describe the synthesis and ROP of ε-thiocaprolactone (ε-TCL). ε-TCL was made by distillation of 6-mercaptohexanoic acid in the presence of P_2O_5 at 190–220 °C (48 % yield). ε-TCL was anionically polymerized, aided by strong bases. The best results were obtained with ^{t}BuOK at 150 °C and ^{n}BuLi at 25 °C, resulting in monomer conversions of 58–100 %. The obtained poly(ε-thiocaprolactone)s (P(ε-TCL)s) exhibited a T_m of 108–109 °C.[64]

Later, Union Carbide Corporation published a patent on the polymerization of various thiolactones (6–9 membered rings, including ε-TCL), in the presence of metal carboxylates of Cd and Mn and primary alcohols or mercaptans as initiators at 120–200 °C in bulk.[97–99]

More recent research by Kiesewetter et al.[100] (Table 1, entry 9) showed the solution ROP of ε-TCL by different organocatalysts at RT. In the presence of strong, nucleophilic amidine bases (i.e., TBD, MTBD (7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene), and DBU) and octadecylthiol as initiator, complete conversions were obtained within 0.5 min to 24 h. Polymers with M_n values between 6 and 32 kg mol^{-1} and narrow Đs were created. Stronger basic, but weaker- or non-nucleophilic catalysts [i.e., BEMP (2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine), DMAP and Me_6TREN (tris[2-(dimethylamino)ethyl]-amine)] did not show any monomer conversion, suggesting a nucleophilic polymerization mechanism. The addition of a thiourea (TU) to BEMP did help the ROP of ε-TCL towards full conversion and M_n values of 10 kg mol^{-1}. Whereas ε-caprolactone (ε-CL) usually needs a combination of a strong base and H-bond donor (e.g., TU, H interacts with the carbonyl O to create a more electrophilic carbonyl C), ε-TCL can polymerize without an H-bond donor, which is explained by the higher electrophilicity of the carbonyl carbon of a thiolester compared to an ester and the stronger nucleophilicity of thiols compared to alcohol.

In 1999, Endo and co-workers[101] described the anionic solution ROP of ε-thio**no**caprolactone [ε-T**n**CL; Table 1, entry 10 (1a) and (2)]. Depending on the catalyst, copolymers with two different repeating units, i.e., (1) thiolesters or (2) thionoesters, were obtained in different ratios of these units. When organolithiums, Grignard reagents (MeMgCl, ^{t}BuMgCl), or ^{t}BuOLi were used, the polymers fully consisted of thionoesters [Table 1, entry 10 (1a)]. ^{t}BuOK and DBU, on the other hand, created polymers predominantly consisting of thiolester units [i.e., 63 or 89 % respectively; Table 1, entry 10 (2)]. Polymerizations were performed in toluene at 100 °C for 20 h and resulted in chains with M_n values of 3.8–19 kg mol^{-1} and monomer conversions between 25 and 100 %. The authors explained the different structures by the mechanisms of polymerization in which the catalyst – an anionic nucleophile – could attack either the thiocarbonyl carbon to create an alcoholate anion as propagating unit (acyl-O cleavage), or the α-methylene carbon of the ether oxygen (alkyl-O cleavage) to create a thiocarboxylate anion as propagating species (see below, Scheme 8). The first mechanism results in thionoester units, whereas the second mechanism results in thiolesters. Whereas very strong nucleophiles (e.g., organolithiums and Grignard reagents) follow the first mechanism, weaker nucleophiles (e.g., DBU) predominantly create thiolester units.[101] Later, the same research group published the cationic solution ROP of ε-TnCL in the presence of BF_3OEt_2, TfOH, TfOMe, or TfOEt [Table 1, entry 10 (3)], all yielding polymers of a thiolester nature. The use of BF_3OEt_2 created the longest chains (M_n of 57 kg mol^{-1}) at almost complete monomer conversion.[102] In 2016, Datta and Kiesewetter[80] described the organocatalytic ROP of ε-TnCL in the presence of organic bases (TBD, DBU, MTBD) and octadecylthiol at RT in C_6D_6 to create pure poly(ε-thionocaprolactone) [P(ε-TnCL)] (M_n up to 22.5 kg mol^{-1}, monomer conversion between 84 and $>$99 %) without the formation of thiolesters [Table 1, entry 10 (1b)]. Whereas in Endo's[101] work DBU resulted in S/O scrambling at 100 °C, in this study it was shown that lowering the reaction temperature to RT resulted in pure P(ε-TnCL).[80] Identical to Kiesewetter's work on ROP of ε-TCL, BEMP did only catalyze the reaction in the presence of TU, again suggesting a nucleophilic polymerization mechanism.

4.2. Thiodilactones

4.2.1. Thioglycolide

The synthesis and ROP of thioglycolide (TG), the thiolactone analog of glycolide (Table 2, entry 1), dates back to the 1950s. Schöberl and co-workers found that TG could be obtained by in vacuo removal during thermal degradation of oligothioglycolides (back-biting depolymerization, cf. lactide synthesis[59]), made by polycondensation of α-mercaptoacetic acid. The isolated TG proved to be useful to create polythioglycolide (PTG) by ROP in the presence of primary and secondary aliphatic amines [piperidine, diethylamine (DEA), and cyclohexylamine (CHA): Table 2, entry 1 (a)]. M_n values of 14–17 kg mol^{-1} (end-group analysis) were reached, and the polymers exhibited a T_m of up to 169 °C.[13,28–30]

Since the first publications by Schöberl and co-workers no further attention had been given to the ROP of TG until the recent research by Suzuki et al.[63] TG was synthesized in 54 % isolated yield by reacting sodium thioglycolate with DMAP and BOP^+ PF_6^- reagent (Scheme 5). ROP of TG was performed in DMF in the presence of DBU and 4-*tert*-butylphenyl methanethiol at 0 °C to RT [Table 2, entry 1 (b)]. At RT a monomer conversion of 21 % was obtained, whereas lowering the temperature to 0 °C and doubling the monomer concentration led to conversions of 29 and 39 % respectively. The resulting polymers had low M_n values of up to 1.6 kg mol^{-1}.

4.2.2. Thiolactide

Thiolactide (TLD) is the sulfur-containing analog of lactide (LD; Table 2, entry 2). LD is a widely studied and industrially used dilactone in ROP for the synthesis of one of the most prominent polyester bioplastics, poly(lactic acid) (PLA). Although Bührer and Elias[60] described the synthesis of polythiolactic acid [or polythiolactide (PTLD)] by ROP of thiolactic acid-*S*-carboxy anhydride and the synthesis of TLD by pyrolysis of their obtained polymers (PTLD) in 1970, the ROP of TLD had not been described until very recently (2021).

Suzuki et al.[63] synthesized TLD by the same method as described above for the synthesis of TG, but starting from *rac*-thiolactic acid (*rac*-TLA), and isolated pure TLD in 59% yield (Scheme 5). NMR analysis showed the ratios of *rac*- to *meso*-TLD to vary around 95:5–98:2, which was explained by the predominant formation of *rac*-TLD due to its higher stability. ROP of *rac*-TLD was conducted in the presence of DBU and 2-ethylhexyl glycolate, both in solution and in bulk [Table 2, entry 2 (a)]. Monomer conversions up to 55% were reached in bulk at RT. The authors found DBU to polymerize TLD even in the absence of an initiator. To improve the reaction control, other base catalysts (DIPEA, PMP (1,2,2,6,6-pentamethylpiperidine), and pyridine) were tested. Only pyridine did not induce polymerization in the absence of an initiator and the amount of initiator determined the MM of the polymers. In general, low M_n values between 0.4 and 4.9 $kg\,mol^{-1}$ were reached. Compared to *rac*-TLD, *rac*-LD showed a higher polymerizability under the same reaction conditions (94% conversion). This was explained by the smaller ring strains of *rac*- and *meso*-TLD (calculated with DFT to be 22.8 $kJ\,mol^{-1}$ and 31.1 $kJ\,mol^{-1}$ respectively) compared to 47.2 $kJ\,mol^{-1}$ for *rac*-LD. This also proved the lower stability of *meso*-TLD versus *rac*-TLD. Alkaline hydrolysis (pH 10) was conducted on PTLD and compared to a racemic polylactide (PLD) sample with a comparable MM. It was noticed that the PTE exhibited a faster degradation compared to its ester counterpart. Moreover, PTLD also degraded faster under UV-light irradiation.

Wang et al.[62] performed the successful ROP of TLD and other alkyl-substituted thiolactides (Table 2, entries 2 (b) and 3). The monomers were synthesized in high yields (75–91%) by cyclization of their corresponding α-mercapto acids by a Steglich thioesterification reaction (DCC with DMAP, Scheme 5). The α-mercapto acids were either commercially available or synthesized from naturally occurring α-amino acids by substitution with NaHS (Scheme 4C). Solution polymerization of *rac*-TLD was performed with various organic base catalysts (DMAP, TEA, TBD, and $^tBuP_2$) and BnSH as the initiator at RT in DCM (5.9 M). As a rule of thumb: the stronger the base catalyst (TBD, $^tBuP_2$) was, the higher the rate of polymerization reached, but the more trans-thioesterification reactions occurred. DMAP/BnSH afforded the highest M_n values up to 73.3 $kg\,mol^{-1}$ (conversions up to 58%). Depolymerization of PTLD was performed in DBU at 25 °C and resulted in complete conversion to the monomer [Table 7, entry 6 (a)]. Comparable results were obtained in bulk with DMAP under vacuum distillation [Table 7, entry 6 (b)]. DFT calculations were conducted to compare the ROP thermodynamics and kinetics of TLD with LD. TLD showed near-equilibrium thermodynamics at room temperature (i.e., ΔG_p (Gibbs free energy of polymerization) is very close to zero) favoring ring-closure depolymerization. In addition, a lower energy barrier for propagation was observed for TLD compared to LD, indicating a kinetically more favored chain growth of TLD than of LD. The DMAP/BnSH catalyst system was also used for the ROP of other substituted thiolactides [all racemic; Table 2, entry 3: thioethylglycolide (1), thioisopropylglycolide (2), thioisobutylglycolide (3), thioallylgycolide (4) and thiohydroxymethylglycolide (5)] and resulted in rapid polymerizations at RT with monomer conversions ranging between 74 and 92% and M_n values of 16.3–100.5 $kg\,mol^{-1}$. All PTEs were atactic and their T_g values ranged between −19.2 and 41.9 °C [$(4) < (1) < (3) < (2) < (5)$]. Although atactic, the PTE of (2) was semicrystalline with a T_m of 115.6 °C, whereas all other PTEs were fully amorphous. Moreover, complete depolymerization happened for all PTEs aided by DBU at 50 °C.

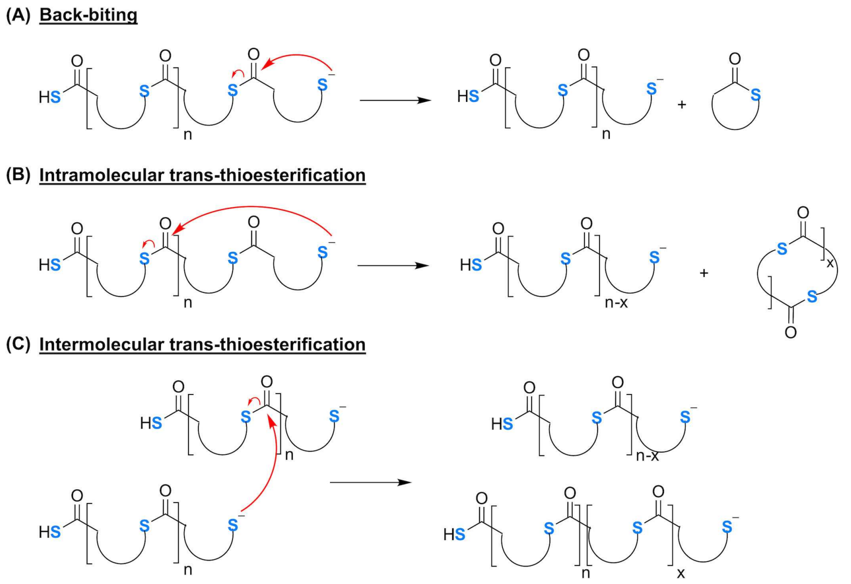
Our group performed the ROP of *rac*-TLD in the presence of TEA and BnOH at room temperature in highly concentrated solutions (25 M) in DCM. Monomer conversions between 36 and 45% were obtained and M_w values increased from 17.4 to 56.0 $kg\,mol^{-1}$ when reducing the amount of catalyst and initiator. Cationic ROP was attempted in the presence of strong organic acids [DPP (diphenylphosphate), *p*-TSA, or TfOH (trifluoromethanesulfonic acid)] with or without BnOH, but no monomer conversions were observed at RT after 48 h. Furthermore, Sn^{II} 2-ethylhexanoate ($Sn(Oct)_2$) with 1-dodecanol was tested in bulk at 40 and 80 °C, but again no reaction occurred, possibly due to strong interactions of S with Sn.[68]

5. Mechanistic Insights into ROP of Thiolactones

5.1. Reactivity and kinetics

The high electrophilicity of the carbonyl C of thiolesters, the high acidity of thiols and the strong nucleophilicity of S^- have a profound impact on the reactivity of thiolactones, thioesters, and thiol end-groups during ROP. It is well known that thiols and thiolesters regularly exhibit a higher reactivity and lower stability than their alcohol and oxoester counterparts.[10,11] This reactivity has an important effect on polymerization kinetics, in which thiolactones and thiolesters seem to exhibit faster ROP kinetics than their lactone and ester counterparts. Faster kinetics can allow very fast polymerizations at mild reaction conditions, thanks to lower activation energy (E_a) barriers. For example, Wang et al.[62] (Table 2, entries 2–3) calculated the energy barrier for propagation in thiolactide ROP, compared it to lactide, and found the barrier for thiolactide to be 26.8 $kJ\,mol^{-1}$ lower, proving a faster chain growth.

However, a higher reactivity also regularly results in more side reactions and an increased presence of trans-thioesterifications and back-biting in growing PTE chains (Scheme 7). This often leads to unwanted phenomena, such as shorter chain lengths, higher $Đ$ values, changes in stereochemistry, or the presence of cyclic polymers, and consequently limited control over the ROP reaction and final chain structure. Nevertheless, certain techniques are described to alleviate side reactions. For example, the introduction of geminal dimethyl groups on the ring, such as shown by Xiong et al.[65] (Table 1, entry 2), stabilizes the thiolester bonds in the polymer and reduces the



Scheme 7. Side reactions in PTE synthesis: (A) Back-biting; (B) intramolecular trans-thioesterification; (C) intermolecular trans-thioesterification.

activity of the chain-end thiolate groups, so that trans-thioesterifications and back-biting reactions are suppressed. Another example includes the ROP of the 4-hydroxyproline-derived bicyclic γ-TBL, as published by Yuan et al.[66] (Table 1, entry 4), in which the steric hindrance of the proline moieties and the orbital interactions between the urethane and thiolester carbonyls minimized trans-thioesterifications. Besides these specific examples, the reaction conditions and the catalyst system used can have a major impact on the extent of side reactions. Some possibly beneficial reaction conditions include lower temperatures, less catalyst, less polar solvents, and lower concentrations.

Considering the studies summarized in Table 1, the use of strong base and/or strong nucleophilic catalysts with or without an alcohol or thiol initiator (e.g., BnOH, BnSH, octadecylthiol) seems to be the popular choice to polymerize thiolactones. This can be attributed to the high electrophilicity of the carbonyl carbon of thiolactones as compared to lactones, promoting nucleophilic attacks. Moreover, Kricheldorf and Schwarz[13] discussed – in the context of poly(thio)ester hydrolysis – the presence of a repelling effect of the large S atom in thiolesters on weak nucleophiles (such as water or alcohols in acidic environments) and said this effect was less pronounced on strong nucleophiles. Meanwhile, studies on metal complex catalysts, readily used in the ROP of lactones, are limited. This could be due to the deactivation of these catalysts by the strong coordination ability of S compounds to metals. However, specific Y and La-based complexes did catalyze certain polymerization reactions.[11] Metal complexes could allow for a more controlled polymerization, as they are known to generally provide for higher chemo-and stereo-selectivity (e.g., Table 1, entry 3).

5.2. Thermodynamics

Owing to the entropically unfavorable character of polymerizations, the ROP of small ring monomers is most often enthalpically driven. The enthalpy of polymerization (ΔH_p) is strongly dependent on the ring strain of the monomers. Ring strain, in its turn, is determined by the repulsion (Van der Waals or transannular), angle, and conformational (torsional) strain of the cyclic molecule, which depend on the functional groups, the degree of substitution, and the size of the rings.[4,103] Although thermodynamical data on the ROP of thiolactones are limited, in general, it seems they exhibit a lower ring strain than their lactone counterparts, which translates to thermodynamically more stable rings. As a consequence, they are expected to have a higher (less negative) ΔH_p, which is indeed observed for all reported examples, when comparing ΔH_p values of thiolactones with the values of their corresponding lactones (Table 3, entries 4–12). Although much less pronounced, also ε-TnCL shows a rise in ΔH_p compared to ε-CL (Table 3, entries 11–12). The same trend was observed by Dugarte et al.[104–107] and Suzuki et al.[63] when calculating and comparing ring strain energies of lactones and thiolactones by means of DFT (Table 4). Both types exhibit the same trend of the ring strain energy significantly dropping from four to five-membered rings and subsequently increasing from five to seven-membered rings. In addition, it is well described in prior reports that, although the introduction of a carbonyl group, in general, has little to no impact on ring strain, the addition of an O atom within the ring significantly increases the strain. However, according to prior reports, the introduction of S reduces or only slightly increases ring strain (depending on ring size).[104–107] This indicates that the addition of S changes the conformational molecular flexibility of the ring so that its molecular conformation and bond angles more strongly approach the geometry of

Table 3. Thermodynamic values for ROP of [thio(no)]lactones at 1.0 M monomer concentration: enthalpy of polymerization (ΔH_p, kJ mol^{-1}), entropy of polymerization (ΔS_p, J mol^{-1} K^{-1}), Gibbs free energy of polymerization at 25 °C (ΔG_p, kJ mol^{-1}) and ceiling temperature (T_c, °C). All data are experimentally obtained.

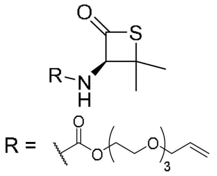
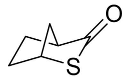
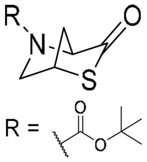
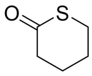
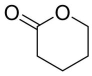
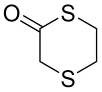
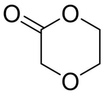
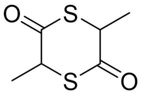
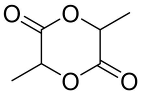
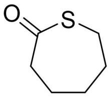
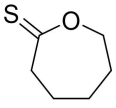
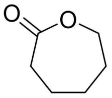
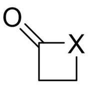
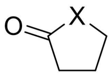
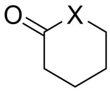
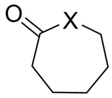
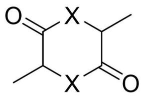
Entry	Monomer	ΔH_p [kJ mol^{-1}]	ΔS_p [J mol^{-1} K^{-1}]	ΔG_p (25 °C) [kJ mol^{-1}]	T_c [°C]	Ref.
1		−9.4	−28.1	−1.0	61	[65]
2		−14.1	−55.7	2.4	−20	[93]
3		−15.6	−40.4	−3.6	112	[66]
4		−4.9	−23.7	2.2	−66	[67]
5		−12.2	−28.6	−3.7	155	[103]
6		−9.5	−30.8	−0.3	34	[67]
7		−15.7	−49.7	−0.9	43	[103]
8		−4.9	−23.9	2.2	−67	[62]
9		−22.9	−41.1	−10.7	284	[108]
10		−10.17 ± 2.9	−1.46 ± 0.9	−9.7	6,727	[100]
11		−24.2 ± 1.3	−56.5 ± 4.2	−7.4	156	[80]
12		−28.8	−53.9	−12.7	261	[108]

Table 4. Ring strain energy of lactones (X=O) and thiolactones (X=S) [kJ mol^{-1}]. Data derived from Dugarte et al.[104–107] and Suzuki et al.[63]

					
Lactone	95.0	32.6	42.7	44.8	47.2[a,b]
Thiolactone	68.6	15.9	31.4	36.4	22.8[a,b]

[a] Racemic (thio)lactide. [b] Obtained from another reference[63] than rest of table[104–107].

a non-strained, acyclic molecule. One could argue that the presence of S increases molecular mobility and reduces repulsion forces by introducing larger bond distances (C–S vs. C–O) and reducing the partial double bond character of the (C=O)–S compared to the (C=O)–O bond. However, when looking at the values in entries 6 and 7 it can be seen that the introduction of a second S or O atom to δ-TVL or δ-valerolactone (δ-VL) respectively shows a more pronounced decrease in ΔH_p of the thiolactone, even though it still exhibits a lower general ring strain.

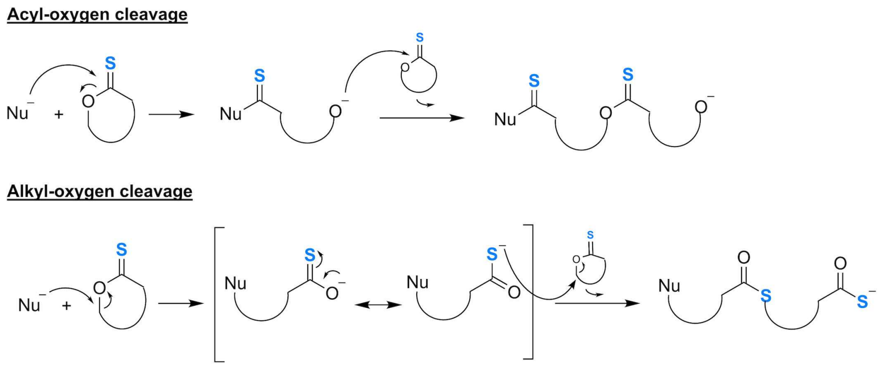
A similar trend is seen when comparing the entropy of polymerization (ΔS_p), in which the introduction of S seems to increase the values as compared to lactones for all examples in Table 2 (entries 4–12). However, a very strong rise is observed for ε-TCL compared to ε-CL (Table 2, entries 10 and 12). The increase of entropy as a function of increasing ring size is well-known and explained by Duda and Kowalski[108] as due to an increase in flexibility (and thus degrees of freedom) in the resultant polymer chain composed of long sequences of monomer units. This effect is also seen in the T_g value of PEs dropping with increased sequence length. One could argue that changing ester groups by thiolesters in a polymer backbone probably increases chain flexibility and thus ΔS_p. As discussed before, whereas esters are stabilized by resonance delocalization of the electrons on the single bonded O atom, thiolesters exhibit much less delocalization of the lone pair on their S atom. As a consequence, the partial double bond character of the C–O unit in PEs is more hindered in its movements and rotation,[10] while PTEs could be called more 'flexible' chain structures. However, this effect is not clearly seen when comparing the T_g values of PEs and PTEs (Table 5), which could also be attributed to differences in chain interactions (e.g., hydrogen bonding), degree of crystallinity, stereochemistry, or MM.

Changes in enthalpy and entropy will have important implications for the equilibrium of (de)polymerization in the ROP of PTEs. A rise in both ΔH_p and ΔS_p results in an increase in Gibbs free energy of polymerization (ΔG_p), approaching equilibrium values or even reaching positive values depending on the monomer concentration and temperature. In addition, lower T_c (see above for definition, $T_c = \Delta H_p / \Delta S_p$) values are often observed. Consequently, ROPs must be performed at low reaction temperatures ($< T_c$), sometimes even below RT to reach sufficiently high monomer conversions and molar masses. On the other hand, depolymerization to chemically recycle thiolactone monomers can generally be performed energy-efficiently at relatively low temperatures ($> T_c$), making PTEs important candidates for chemical recycling.[109,110] In addition, this also implies that the synthesis of thiolactones could be thermodynamically easier than the synthesis of lactones. It is also important to mention here that the size of ΔS_p determines the temperature sensitivity of the (de)polymerization equilibrium. As a result, even if the T_c value is low due to for example a very low $|\Delta H_p|$, if the $|\Delta S_p|$ is insufficiently small still rather large changes in temperature will be necessary to reach complete depolymerization.[67]

The main drawback of the thermodynamic nature of thiolactones is thus related to the low reaction temperatures needed for sufficient monomer conversion due to the thermodynamic equilibrium. However, certain techniques have been applied, as described above, to increase the ring strain and T_c of thiolactones, including bridged (Table 1, entry 4–5) bicyclic ring structures and the addition of extra functional groups within the rings [e.g., N (Table 1, entry 4), S (Table 1, entry 8)]. Although these techniques have also been applied to lactones, a novel approach is the polymerization of **thiono**lactones (Table 1, entries 6 and 10) instead of thiolactones.

Since thionolactones have an O atom in their ring structure instead of S, they are expected to exhibit a higher ring strain (e.g., Table 3, entries 11 and 12) comparable with their lactone counterparts. As a consequence, ring-opening of thionolactones is thermodynamically easier and two possible mechanisms could occur leading to either thiolester or thionoester moieties in the resulting polymer backbone (Scheme 8). When rings are opened by alkyl-oxygen cleavage, the S and O atoms can be interchanged by a S/O isomerization reaction. In addition, the S/O isomerization itself can be an important thermodynamic driving force to polymerize low ring strain monomers, as described above for the ROP of the five-membered thionolactone γ-TnBL (Table 1, entry 6).[81]

However, as exemplified by the research on ROP of TnCL (Table 1, entry 10), the choice of the catalytic system and reaction conditions can have a profound impact on the final polymer structure, consisting of either thiono- or thiolester units



Scheme 8. ROP mechanisms for thionolactones in the presence of nucleophilic initiators through either acyl-oxygen cleavage or alkyl-oxygen cleavage.

Table 5. Thermal properties (T_g and T_m) comparison of polythiolesters, polythionoesters, and polyesters.

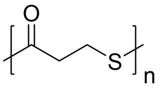
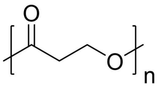
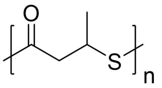
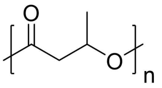
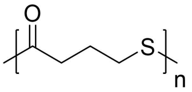
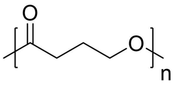
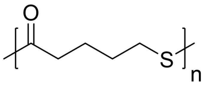
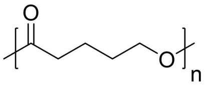
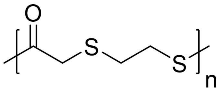
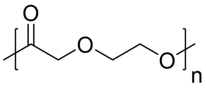
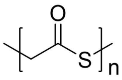
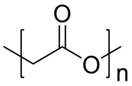
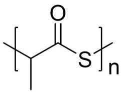
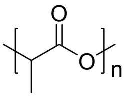
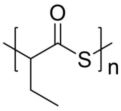
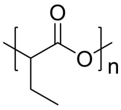
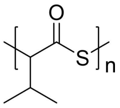
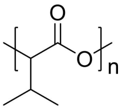
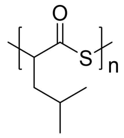
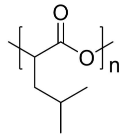
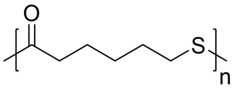
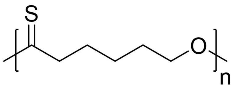
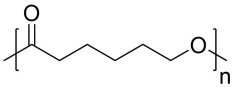
Polymer	Name	T_g [°C]	T_m [°C]	Ref.
	P(β-TPL) Poly(β-thiopropiolactone)	n.d	170	[7]
	P(β-PL) Poly(β-propiolactone)	−20–−10	77–80	[7,112–115]
	P(β-TBL) Poly(β-thiobutyrolactone) (isotactic)	4–8	100	[7,90]
	P(β-BL) Poly(β-butyrolactone) (isotactic)	−4–1	175–180	[116–118]
	P(γ-TBL) Poly(γ-thiobutyrolactone)	−49	100	[81]
	P(γ-BL) Poly(γ-butyrolactone)	−51–−48	53–60	[119,120]
	P(δ-TVL) Poly(δ-thiovalerolactone)	n.d.	123	[67]
	P(δ-VL) Poly(δ-valerolactone)	−67–−60	57–60	[120–123]
	PDTN Poly(dithianone)	−34	88	[67]
	PDX Poly(dioxanone)	−30–−1	110	[4,124]
	PTG Polythioglycolide	n.d.	158–169	[28]
	PG Polyglycolide	35–40	225–230	[125,126]
	PTLD Polythiolactide (racemic)	−1–0	amorphous	[62]
	PLD Polylactide (racemic)	50–60	amorphous	[125,126]
	Polythioethylglycolide	−4.2	amorphous	[62]
	Polyethylglycolide	15	amorphous	[127]
	Polythioisopropylglycolide	35	116	[62]
	Polyisopropylglycolide	56	amorphous	[111]

Table 5. continued

Polymer	Name	T_g [°C]	T_m [°C]	Ref.
	Polythioisobutylglycolide	17	amorphous	[62]
	Polyisobutylglycolide	22	amorphous	[127]
	P(ε-TCL) Poly(ε-thiocaprolactone)	−40	109	[100]
	P(ε-TnCL) Poly(ε-thionocaprolactone)	n.d.	9	[80]
	P(ε-CL) Poly(ε-caprolactone)	−65–−60	56–65	[128]

or a combination of both, depending on which mechanism will preferably take place.[80,101,102] Even though the ROP of thionolactones asks for some reaction optimization efforts, great potential exists concerning improved ROP thermodynamics and chain structure possibilities. Moreover, thionolactones can quite efficiently be synthesized from their lactone counterparts by sulfurization of O to S (vide ante).

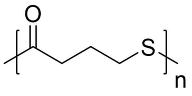
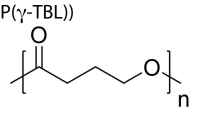
In summary, thiolactones often exhibit superior kinetics (faster polymerization at lower temperatures) as compared to lactones because of their lower E_a of ROP in the presence of strong bases and/or nucleophilic catalysts and initiators. However, this higher reactivity also often generates more side reactions (e.g., trans-thioesterification, backbiting). On the other hand, thiolactones are thermodynamically more stable due to their lower ring strain compared to lactones and thus often require (very) low temperatures to drive the reaction equilibrium towards complete polymerization. Nevertheless, both the low ring strain of thiolactones and the high reactivity of the thiol end-groups and thiolester units in PTEs enable fast and energy-efficient depolymerization, making PTEs very interesting polymers for chemical recycling.

6. Polythiolester Material Properties

The material properties of plastics play a major role in their possible application area and processing methods. Table 5 shows the thermal properties (i.e., T_g and T_m) of some PTEs and their corresponding PE analogs. These thermal properties can (strongly) depend on factors such as the analysis method, the MM, the tacticity, the sample history, or the crystallinity,[111] and therefore one should be careful when comparing data across different studies. With that in mind, it seems that PTEs often have higher melting points [e.g., P(γ-TBL) (100 °C) vs. P(γ-BL) (53–60 °C)] than their corresponding PEs, which would indicate the presence of stronger (chain interactions in the) stacked crystalline structures. However, data on the thermal properties of alkyl-substituted PTEs is very limited, since most examples are amorphous due to the stereo-irregular nature of the PTE chains, which makes it hard to draw general conclusions. Furthermore, the T_g values of the PTEs seem to be often, but not always, lower compared to their PE analogs [e.g., PTLD (−1–0 °C) vs. PLD (50–60 °C)]. This could mean that PTEs may be less stiff chains and/or that they exhibit less and/or weaker chain-chain interactions (e.g., H-bonding).[111] However, again, these examples do not allow general conclusions to be drawn.

Studies on mechanical and rheological properties of PTEs obtained by ROP of thiolactones are even more limited and only a few works determined the Young's modulus and elongation at break of certain S-based materials [i.e., Table 1 entries 2 (R=(3)), 5 and 6; Table 2 entry 3 (R=(2))].[62,65,81,129] Older (1976–1996) studies by Podkościelny and co-workers[16–26] describe the syntheses of PTEs obtained by polycondensation of various diacid chlorides with dithiols of which they determined different mechanical and electrical properties, including the rupture strength, impact strength, binding strength, Brinell hardness, and dielectric constant. Nevertheless, to the best of our knowledge, none of these studies compared the properties of PTEs with the properties of their corresponding PEs. In addition, comparisons of mechanical properties of materials over different, independently performed studies are rather difficult, since the final outcomes are strongly dependent on the MM of the polymers, the type and parameters of the analysis techniques, and the pretreatment and shaping methods of the polymer. However, one relatively reliable, comparative example was worth mentioning here and is presented in Table 6. Table 6 exhibits the tensile strength, Young's modulus, and elongation at break of high MM poly(γ-thiobutyrolactone)

Table 6. Comparison of the mechanical properties of poly(γ-thiobutyrolactone) and its polyester analog poly(γ-butyrolactone).

Polymer (Name)	Tensile strength [MPa]	Young's modulus [MPa]	Elongation at break [%]	Ref.
 (P(γ-TBL))	29.8	297	413	[81]
 (P(γ-BL))	50	70	1000	[119,120]

and its microbially derived PE analog [poly(γ-butyrolactone)]. From these data it can be carefully concluded that the PTE analog is a stiffer and more brittle material than its PE analog, exhibiting a higher Young's modulus, lower tensile strength, and lower elongation at break (along with a higher T_m, see Table 5). However, the data are too limited to draw a general conclusion for all PTE materials.

7. Sustainable Degradation Potential of Polythioesters

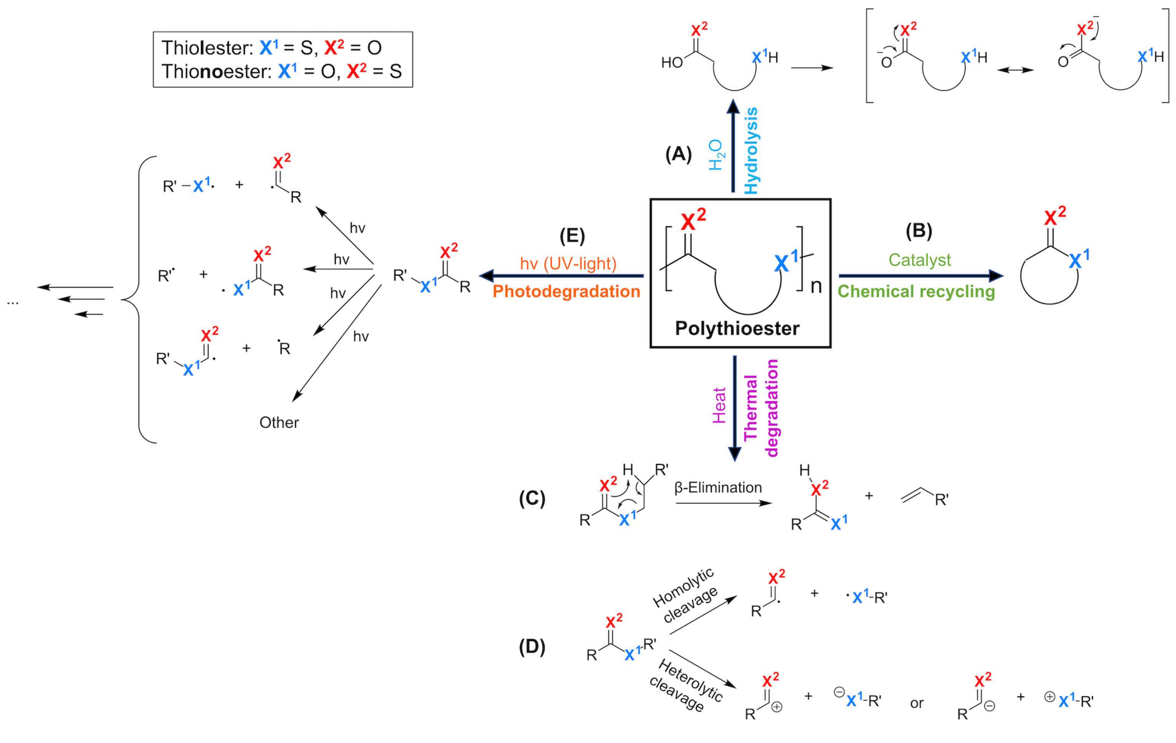
In the following sections a summary will be given of the different degradation options (chemical degradation, thermal degradation, photodegradation, and biodegradation) for end-of-life treatment of PTEs. Scheme 9 provides a graphical summary of these with (possible) degradation products.

7.1. Chemical degradation

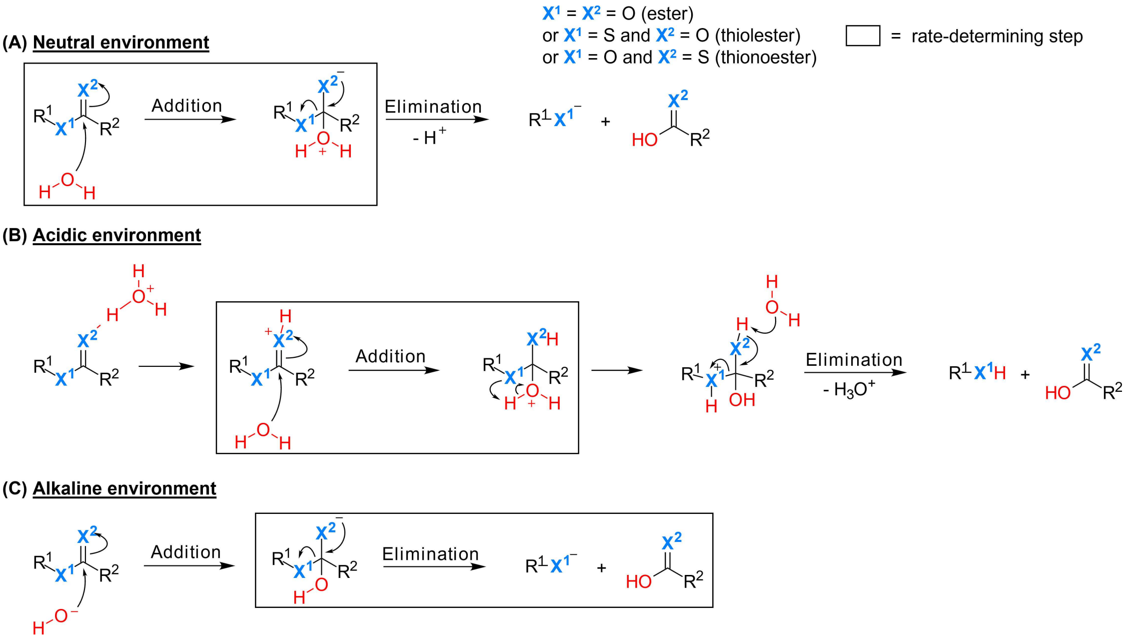
7.1.1. Hydrolysis

The ease of polymer degradation by aqueous hydrolysis (Scheme 9A) strongly depends on reaction conditions and the molecular structure and shape of the materials.

Kricheldorf and Schwarz[130] explained the rate of (thio)ester hydrolysis to be determined by the rate-determining step (RDS) of hydrolysis, being either the addition of a nucleophile (H_2O or OH^-) or the elimination of the SR/SH or OR/OH group (Scheme 10). The RDS, in its turn, depends on the pH (acidic,



Scheme 9. Representation of the different degradation methods for polythioesters and the possible degradation reactions and products: (A) Hydrolysis; (B) chemical recycling; (C) β-elimination; (D) homo- and heterolytic cleavage; (E) photodegradation.



Scheme 10. Mechanisms of (thio)ester hydrolysis in (A) neutral environment, (B) acidic environment, and (C) alkaline environment.

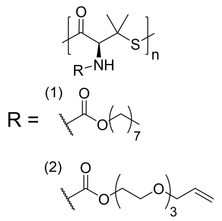
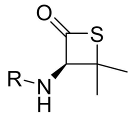
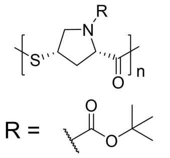
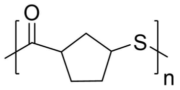
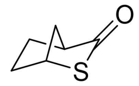
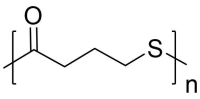
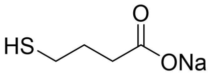
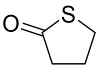
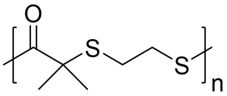
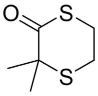
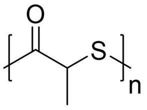
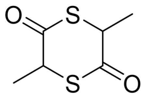
neutral, or alkaline) of the reaction. In neutral or acidic environments (weak nucleophiles) the RDS is the addition step. The authors explained that weak nucleophiles do more readily hydrolyze esters than thiolester. Even though the carbonyl carbon of thiolesters is more electrophilic, S with its larger diameter will probably repel the nucleophile more strongly than O. However, in alkaline conditions (strong nucleophilic OH^-) the RDS is the elimination step, which is faster for thiolesters due to SR/SH being a stronger leaving group than OR/OH. For example, Suzuki et al.[63] performed the hydrolytic degradation of PLD and PTLD in alkaline pH (10) at RT in which the MM of PTLD started declining after 3 h while no changes were noticed for PLD. Yuan et al.[81] tested the hydrolytic degradation of P(γ-TBL) and observed the polymer to be quite stable under neutral and acidic conditions (1 M H^+), whereas complete degradation was observed in alkaline conditions [Table 7, entry 4 (a)]. For thionoesters, however, the repelling effect of S on the nucleophile is not present anymore, and since the C=S bond is more polarized, both types of nucleophiles promote the addition step.[130] This suggests an easier hydrolysis of thionoesters in neutral and acidic environments.

7.1.2. Chemical recycling

Chemical recycling is of utmost importance in the future circular closed-loop economy, thereby reducing the environmental impact of the polymer industry and the need for virgin feedstock input.[131] As discussed above, PTEs in general seem to be very interesting candidates for chemical recycling (less the case for PEs), in which the polymer chains are broken down back to their thiolactone monomers in the presence of a depolymerization catalyst (Scheme 9B). Owing to the relatively low ring strain of thiolactones, compared to lactones, the structures are thermodynamically more easily obtained from their corresponding PTEs by back-biting (Scheme 7A) depolymerization. Moreover, the relatively low T_c of thiolactone ROP enables the reversed reaction to be performed under mild conditions.

Table 7 shows a summary of reported methods for the chemical recycling of PTEs, including the polymer structures and their recycling products, the catalysts and reaction conditions used, and the yield of the recycling product. Most examples are performed in solution (e.g., $CDCl_3$, DCM, toluene) and, depending on the catalyst and concentration, depolymerization can often be performed at RT. Mostly strong organic bases and nucleophiles (e.g., DBU,[65,66] TBD,[81] IMes[93]) are used, which regularly provide for (almost) complete (quantitative) recycling of the monomers, sometimes only after a few minutes or seconds. Besides the high energy efficiency of RT reactions, another advantage of low-temperature depolymerization is the possible prevention or reduction of racemization in the case of enantiopure monomers and polymers, amongst others shown by Xiong et al.[65] (Table 7, entry 1) and Wang et al.[62] (Table 7, entry 6). The main challenge related to a low depolymerization temperature would be the prevention of depolymerization during the processing of PTE materials at temperatures above their melting point. In this regard, removal and/or deactivation of any remaining ROP catalyst is key. It must be mentioned that, in addition to the temperature, other factors will also determine the sustainable potential of chemical recycling, such as the type and amount of solvent used, the monomer yield, and the ease of monomer purification from the remaining polymer and catalyst. However, research on the optimization of chemical recycling and purification of the recyclate of PTEs is limited.

Table 7. Literature summary of chemical recycling/hydrolysis reactions of polythioester, including the polymer structures, recycling products, catalysts, reaction conditions, and recycling product yield [%].

Entry	Polymer	Recycling product	Catalyst	Reaction conditions	Yield [%]	Ref.
1			(a) DBU (b) PhSNa	(a) 0.005 g mL^{-1}, CDCl$_3$, 9.1 mol% catalyst[a], 25 °C, 4 h (b) 0.005 g mL^{-1}, CDCl$_3$, 50 mol% catalyst[a], 25 °C, 2 h	(a) (1) > 95 (2) > 95 (b) (1) > 95	[65]
2			DBU	0.010 g mL^{-1}, CDCl$_3$, 4.4 mol% catalyst[a], 50 °C, 2 min	quantitative	[66]
3			(a) La[N(SiMe$_3$)$_2$]$_3$ (b) IMes	(a) 2 g mL^{-1}, toluene, 1 mol% catalyst[a], 100 °C, 24 h (b) 0.26 g mL^{-1}, toluene, 1 mol% catalyst[a], RT, 10 min	(a) quantitative (b) quantitative	[129]
4		**(a)**  **(b)** 	(a) NaOH (b) TBD	(a) 0.025 g mL^{-1}, 1 M [NaOH]/D$_2$O, RT, 12 d (b) 0.054 g mL^{-1}, DCM, 0.2 mol% catalyst[a], RT, 15 s	(a) quantitative (b) quantitative	[81]
5			DBU + 1-dodecanethiol	0.5 M, THF, 1 mol% DBU[b], 1 mol% 1-dodecanethiol[b], 80 °C, 1 h	90	[67]
6			(a) DBU (b) DMAP	(a) 0.1 g mL^{-1}, CDCl$_3$, 1 mol% catalyst[b], 25 °C, 2 min, (b) Bulk, 1 mol% catalyst[b], 95 °C, vacuum distillation	(a) quantitative (b) > 90	[62]

[a]Mol% of catalyst relative to mol of polymer. [b]Mol% of catalyst relative to mol of monomer units in the polymer.

7.2. Thermal and photo-degradation

According to Kricheldorf and Schwarz, the thermal stability of PTEs depends on the degradation mechanisms. When thermal degradation occurs through β-elimination (Scheme 9C), one could expect thioesters to be more stable than esters, since the reverse reaction through the addition of S onto the double bond of the elimination product should be faster (e.g., thiol-ene reaction). However, the authors argue that in the case of thermal (thiol)ester bond splitting (homolytic or heterolytic, Scheme 9D) thiolester cleavage is probably more favored over ester cleavage due to the higher stability of S anions or radicals.[130] In addition, C–S bonds are in general weaker than C–O bonds and in the case of (thiol)esters, a difference exists in double bond character as well. Thermal degradation could also occur via trans-(thio)esterification or back-biting reactions, which are, as discussed before, more prominent in PTEs than in PEs (Scheme 7). For example, Yuan et al.[66] performed thermolysis at 160 °C under high vacuum (with a condenser to condensate monomer sublimation) for 45 h on their PTEs and recovered 79 % of the monomer [Table 1, entry 4 (R = (1)]. Huang et al.[132] studied the thermal degradation of microbially derived poly(3-hydroxybutyrate-co-3-mercaptopropionate) (see below). Thiolester bonds in the polymer were observed to exhibit a higher thermal stability than the ester linkages, of which crotonic acid was the main degradation product, indicating β-elimination to be the dominant cleaving mechanism in inert (He) conditions. Thermogravimetric analysis, performed on a selection of poly(hydroxyalkanoates) (PHAs) and their S-containing analogs by Kawada et al.,[7] showed both higher and lower degradation temperatures (i.e., $T_{d,5\%}$, temperature at 5 % weight loss) for different PTEs as compared to PEs, possibly depending on the main thermal degradation mechanism and the polymer structures. However, small differences can also be caused by variations in MM or water content of the materials.

Even though oxidative degradation of PTEs does not seem to be (extensively) studied, S-containing molecules are well-known to be more readily oxidizable into more possible oxidation states than their O-containing counterparts.

Photodegradation, by irradiation of photons to trigger the release of radicals that will further react leading to polymer chain cleavage (Scheme 9E), could also be more prominent in PTEs than in PEs. According to Suzuki et al.,[63,89] the π–π* transition in thiolesters occurs at lower UV wavelengths than in oxoesters (Scheme 1D). This was experimentally shown by comparing the photodegradation of PTLD and PLD in which PTLD already showed a decrease in MM after 1 h, whereas PLD remained unchanged.

7.3. Biodegradation

As mentioned before, certain PTEs [poly(3-mercaptoalkanoates)] and copolymers of thiol- (3-mercaptoalkanoates) and oxoesters (3-hydroxyalkanoates) can be microbially synthesized by specific bacterial strains in the presence of sulfur-containing substrates.[38] However, far less is known about the enzymatic and/or microbial degradation of PTEs. Since poly(hydroxyalkanoates) (PHAs) are readily biodegradable by various microorganisms in natural environments, the biodegradability of their sulfur analogs [i.e., poly(3-mercaptoalkanoates)] has been studied by Steinbüchel and co-workers.[133]

In 2003, Elbanna et al.[134] isolated a thermophilic bacterium (*Schlegelella thermodepolymerans*) from activated sludge, which was found to degrade both microbially derived poly(3-hydroxybutyrate) PEs and copolymers of 3-hydroxybutyrate (3HB) and 3-mercaptopropionate (3MP), albeit biodegradation of PHB [or P(β-BL) (Table 5)] was significantly faster. Later the same group studied the biodegradation of both microbially derived poly(3-mercaptopropionate) [poly(3MP) or P(β-TPL) (Table 5)] and poly(3-mercaptobutyrate) [poly(3MB) or P(β-TBL) (Table 5)] homopolymers and copolymers of 3HB and 3MP by PHA degrading bacteria and PHA depolymerases. The bacteria are known to excrete the depolymerases to extracellularly hydrolyze the polymers to products that can be assimilated by the micro-organisms. 22 aerobic bacteria were isolated that were capable of growing in the presence of poly(3HB-co-3MP). However, the same strains did not show any growth in the presence of only the homo-PTE poly(3MP). Different PHA hydrolyzing enzymes were isolated and tested on the co- and homo-PTEs. Even though hydrolysis activity was observed on poly(3HB-co-3MP), the activity decreased with an increasing amount of thiolester, and no enzyme activity was seen for poly(3MP) and poly(3MB). During hydrolysis of the copolymers (by depolymerase of *S. thermodepolymerans*), the enzyme selectively cleaved ester- instead of thiolester bonds, and incomplete degradation of the copolymer was confirmed.[135] Similar results were observed by Zhu et al.,[136] who saw that PHA depolymerases did not cleave 3MP–3MP thiolester bonds. Kamei et al.[137] also studied the microbial degradability of poly(3HB-co-3MP) and again observed the preferential degradation of the ester units. Kim et al.[138] tested the biodegradability of poly(3MP) homopolymers by various microbially enriched samples from 74 different environments (e.g., soil, compost, sludge, fresh water, seawater). However, for none of the samples growth was observed with poly(3MP) as the carbon source, showing the very high resistance of this polymer to biodegradation under both aerobic and anaerobic conditions. Nevertheless, the authors concluded that the analyzed PTEs do not seem to exhibit negative effects on the organisms.

Although it seems PTEs are non-biodegradable according to most enzymatic degradation studies, a study by Kato et al.[32] showed the lipase-catalyzed synthesis of poly(11-mercaptoundecanoate) (34 kg mol^{-1}), and this PTE was degraded by the same enzyme into small cyclic oligomers (400 g mol^{-1}). It was confirmed that lipase was capable of specifically cleaving the thiolester bonds in the polymer based on mass spectrometric analysis of the degraded samples. However, the biodegradation studies applied a thermophilic enzyme on a diluted polymer in nonane at temperatures up to 110 °C, which is above the melting point of the polymer (i.e., 104.5 °C). Although steric accessibility of the enzyme to the thiolate functionality is significantly increased upon liquifying and dissolving the polymer (or even in general by transcending the T_g), such physiological relations to the observed profuse biodegradation were not considered by Kato et al.[32] To the best of our knowledge, no other studies on enzymatic or microbial degradation of PTEs have been performed.

Even though studies by Steinbüchel and co-workers strongly indicate PTEs are non-biodegradable, only microbially obtained PTEs [i.e., poly(3-mercaptoalkanoates)] were studied. In contrast, the lipase-catalyzed degradation of poly(11-mercaptoundecanoate) was successful, but under significant thermal agitation beyond the melting point of the polymer. This implies that there is no general certainty that all PTEs are non-biodegradable and more research on a larger variety of PTE structures, chemo-physical conditions, as well as enzymes and micro-organisms of notably the thermophilic types is necessary.

8. Industrial Scale-Up Potential and Future Prospects

8.1. Feasibility assessment of industrial PTE synthesis

Polyesters are among the oldest and commercially most abundant polymers that have been studied intensively for well over 80 years and have received tremendous industrial developments into famous plastic grades such as Terylene for textiles, PET for drinking bottles, and P(ε-CL) in the medical field.[139–141] However, their sulfur-containing analogs – PTEs – were discovered later[7] and received rather modest scientific interest until the last decade. Consequently, PTEs are still to find specific commercial applications, and not much is known about their ongoing or anticipated industrial production. Nevertheless, PTEs display many beneficial characteristics in terms of material properties, efficacy of synthesis, and substantial accordance with the principles of green chemistry, which render PTEs admissible for applied research and scale-up studies prospective towards commercialization.

Perhaps the single PTE at present time that is most eligible to breach into industrialization and commercialization is the P(β-TBL) polymer developed by Shi et al.[93] (Table 1, entry 5) Their work has received much attention and made headlines in several online news journals as “the infinitely recyclable polymer”.[142–145] It describes the promising concept of a biobased polymer with formidable and tunable material properties, which can be depolymerized back into its original building block. Importantly, the depolymerization is conducted under controlled conditions in the presence of IMes as the catalyst, which ensures material stability during the lifetime and use of envisioned consumer products thereof. However, the 'infinite' recyclability of this polymer can only be achieved upon complete sorting from other polymers and materials in the waste stream, which is the most challenging obstacle for establishing a circular plastics economy on a commercial level.

In terms of material properties and degradability, PTEs in general display a remarkable difference compared to their PE analogs, offering a broadened scope of commercial applications. As shown in Table 5, most unbranched aliphatic PTEs exhibit a significantly higher melting point in the range of 100–170 °C, which is well suitable for compounding and melt-injection processing, and compatible with the human household 'climate'. Especially since PTEs are probably not biodegradable, but can be rapidly depolymerized under controlled catalytic conditions, their implementation in multi-use plastic products with a limited life span is recommended for consideration. For example, clothing, textiles, and certain kitchen equipment are typical end-user products that must have chemical resistance against biological contact (e.g., food, sweat, mud) as well as frequent sanitation (e.g., washing machine/dishwasher up to 60 °C, detergents), but will inevitably still end up as waste through physical wear-and-tear. At this end-of-life stage, if chemical recycling as demonstrated by Shi et al.[93] is indeed feasible on a commercial scale, the industrialization of PTEs could serve as a groundbreaking development toward circularity and sustainability in commercial plastic products.

From an industrial manufacturing perspective, the generic methodology for synthesizing PTEs via ROP offers some considerable advantages compared to the methodologies for synthesizing normal PEs. Although polycondensation strategies typically require high temperatures (>150 °C) and deep vacuum to afford substantially high molar masses,[146] the ROP of lactones is often conducted at moderately elevated temperatures (RT to ≤ 150 °C) for multiple hours,[108,128,146] but may also take place at low temperatures (-50–0 °C) to drive the polymerization toward high molar masses through thermodynamic control,[147,148] depending on the lactone ring size.[108] However, the catalyzed ROP of thiolactones is often very well feasible at RT due to their thermodynamic and kinetic properties, which effectively leads to rapid polymer chain growth and reaction completion within sometimes even mere minutes. Being able to perform large-scale chemical operations under ambient conditions is a tremendous advantage from a techno-economical perspective, whereas both thermal and (super)chilled processes as well as mechanically stirring viscous polycondensation reactions require huge amounts of energy.[149,150] Also from an ecological perspective this is highly relevant since energy consumption for thermal heating is known to be a major contributor to the environmental impact of the process.[149]

In closer detail to the ROP parameters for PTEs that are reported (Tables 1 and 2), it can be seen that generally high substrate concentrations (>1 M) are applied, and some examples are successfully performed in bulk,[62,65,93] which is a great advantage in terms of space-time yields and omission of solvent to reduce down-stream processing (DSP) efforts and costs. However, when solvents are necessary for ROPs of certain thiolactones, highly undesirable solvents are usually applied – notably DCM, chloroform, toluene, and DMF – which are subjected to strict legislation or even banned from industry at present time. THF (tetrahydrofuran) was also successfully applied,[62,90,93] which offers potential for using related biobased solvents such as 2-methylTHF and 2,5-dimethylTHF instead. Likewise, when solvents are applied for polymer precipitation in the DSP, an eclectic selection of biobased and recyclable solvents is promoted as well, if effective. Perhaps most favorable, the use of supercritical carbon dioxide (scCO_2) as an emerging green industrial tool could address the solvent issue for PTEs in synthesis as well as in DSP, via automatic evaporation and facile scCO_2 recycling for the latter stage.[151] Furthermore, thiolactone ROPs can be performed using organo-catalysts, homogeneous metal catalysts, as well as enzymes. Taking into consideration the fine balance between catalyst activity versus price in combination with the fact that all the reported catalysts for these ROPs are not recyclable, the green industrial choice tends to lean towards metal-free concepts, of which organo-catalysts such as DBU, TBD, and DMAP are the most practical, affordable, less toxic,[152] and commercially available choice.[108] Nevertheless, concerning the chemistry of thiolactone ROP, a lot of discoveries and improvements are still to be made, certainly within the context of sustainable chemistry. These are expected to pave the way to industrial PTE production trials soon.

On the other hand, the concomitant criterium to this prediction is that the corresponding monomers for PTEs can be produced sustainably as well. As discussed before, the exchange of oxygen for sulfur in lactone substrates using P_4O_{10} or LR with specific co-agents is currently the most straightforward methodology because of its use of inexpensive, commercially available chemicals and its appreciable yield range (75–90 %).[72] In addition, the biobased origin, low toxicity, and generally affordable purchase costs of numerous γ-, δ-, ε-, and ω-lactones,[153] as well as the broad structural modularity of synthesizing γ-lactones through radical addition of fatty alcohols to acrylic acid,[154] are particularly attractive features for emerging green industries. In sharp contrast, the critical drawback of these reagents is the lack of product selectivity between thiolactones, thionolactones, and dithiolactones, and intense purification such as industrial chromatography is then required for product separation as well as the removal of inorganic side products. Unfortunately, rigorous synthesis and purification protocols are not viable for the modern bioplastic industry, in which a high production through-put, one-digit sales prices in € kg^{-1} of polymer, and strict conformity to environmental legislature are key to breaching commercialization of novel plastic products. Regarding the challenges of industrial monomer purification for thiolactones, a more promising concept for sulfur exchange was reported only recently by Sakai et al., who developed an alternative S-donor system based on disilathianes in the presence of an indium catalyst.[87,88] These disilathiane reagents are obtainable from cheap and abundant elemental sulfur and can be prepared in situ. Although the most prominent advantage of this novel synthesis relies on its excellent selectivity towards thiomonolactones, in contrast to LR, for example, the fact that small volatile siloxanes are here the side products instead of cumbersome phosphorus derivatives enables the more feasible option for industrial vacuum-distillation of the thiolactone product. Albeit the work in these two reports employs predominantly 1,2-dichlorobenzene as the solvent, some appreciable results in non-chlorinated aromatics were acquired as well, which indicate that extended screening of suitable green solvents (e.g., anisole, 2-methylTHF, cyclopentyl-methyl ether) could be worthwhile. Hence, a tentatively green prospect for the industrial synthesis of bio-derived thiolactone monomers is in the pipeline.

8.2. Environmental considerations for 'end-of-life'

Unlike normal lactone-derived polyesters, PLA grades, and several other polymers with cleavable functional groups, PTEs are not considered naturally biodegradable according to presently available studies. Despite the single reported example of enzymatic depolymerization of poly(11-mercaptoundecanoate),[32] it should be noted that the applied high temperature and hydrophobic conditions are absolutely not representative of nature. Although the recollection and recycling of any plastic material – or other appropriate waste management such as controlled landfill or incineration – is currently strived for to reduce environmental pollution, the unintended release of microplastics into nature through wearing of products and exposure to natural circumstances will probably always remain a challenging obstacle.

Regarding the tentatively envisioned future of PTEs as a commercially available material, strict policies facilitating a tightly closed-loop plastic economy should be applied, to avoid the accumulation of non-biodegradable PTE in the environment. For any traces of PTE micro-plastics that inevitably would still end up in the environment, it is paramount to perform ecotoxicity studies, and to determine the effect of sulfur-rich materials in terms of environmental impact. Secondly, the potential incineration of PTE waste fractions that are not suitable for further recycling anymore should be performed in combination with intensive sulfur recovery technologies (e.g., hydrodesulfurisation)[47] to suppress sulfoxide exhausts into the atmosphere, thereby avoiding the reoccurrence of acid rain.

9. Conclusion and Outlook

This review critically discussed the (potential) sustainability of polythioesters (PTEs) as derived by the ring-opening polymerization (ROP) of thio(no)lactones. The most important and recent state-of-the-art in every step from sulfur source to monomer synthesis to ROP and end-of-life treatment options was scrutinized.

Although sulfur (S) is often seen as an unlimited source, the current, dominant methods of S-winning are not sustainable and are expected to disappear in the future. Therefore, promoting research on more sustainable S-winning techniques and considering the recoverability and circularity of S for polymer materials before large-scale industrialization could be key.

The most important state-of-the-art in the synthesis of thio(no)lactones was summarized (Schemes 4 and 6). Bio-derivable unsaturated carboxylic acids, amino acids, and lactones can be readily converted into thio(no)lactones in one to three reaction steps aided by a sulfur source. Ideally, this S-source is safe and abundant and can be obtained without extensive synthesis steps, making elemental S (currently) the most promising option. Unfortunately, for the sulfurization of unsaturated carboxylic and amino acids, no attempts have been described to use S_8, even though it is generally used in addition reactions to unsaturated bonds or substitution reactions with halogens.[155] The cyclization of these sulfurized compounds to thiolactones is most often described in the presence of various sacrificial reagents (coupling agents, radical initiators, photosensitizers), which have a strong negative effect on both the atom economy and waste production. The direct condensation of mercaptocarboxylic acids in the presence of acids or bases seems more sustainable and interesting from an industrial point of view (i.e., avoiding the cost and viability of coupling agents; Scheme 5 and Figure 1).[68] Heterogeneous catalysts would even be more preferable, but catalytic sites or supports are regularly sensitive to S-poisoning and therefore future research could focus on S-insensitive, efficient, and reusable heterogeneous acids or bases.

Remarkably, very little has been described on the direct conversion of lactones to thiolactones. Since many lactones are widely available, affordable, and biobased, converting them in one step, preferably with S_8, is of great interest. Some success was shown with $InCl_3/PhSiH_3$ as the catalyst.[87,88] However, a limited number of lactone substrates (mainly γ-lactones) were tested and yields were low to moderate. Studying reusable heterogeneous S/O exchange catalysts, with minimal S_8 excess could be very rewarding. Lactones can also be converted to thionolactones in high yields in the presence of a thionating agent (e.g., P_4S_{10} or LR). However, the number of studies on monolactones is limited, whereas dilactones were completely omitted. Moreover, dithiolactones have only been described as side products and, to the best of our knowledge, no research has been conducted on their selective synthesis or ROP. The main drawback of thionating agents is their laborious removal from the reaction mixture. However, this problem can be overcome by using solid-supported P_4S_{10}, but again research on lactones is missing.

Next, a short overview was given of the state-of-the-art in ROP of these monomers. The unique chemistry of S provides in general for higher reactivities as compared to their O-based analogs. High reactivities enable very fast polymerization reactions at mild conditions, but also often lead to more unwanted side reactions (Scheme 7) and limited control, which ask for specific monomer structures, catalytic systems, or reaction conditions. Catalysts for thiolactone ROP almost only consist of strong organic bases and/or nucleophiles, which was explained by the strong electrophilicity of the carbonyl carbon and the repelling effect of the S atom on weak nucleophiles. On the other hand, thionolactones have been polymerized in the presence of acids. Except for some Y and La-based complexes,[90,93] no successful thiolactone ROPs have been conducted by metal-based catalysts, even though they could enable a more controlled and/or stereo-selective polymerization. Strong sulfur coordination with metals is thought to counteract catalytic activity. Nonetheless, successful thionolactone ROP has been shown in the presence of organolithium or -magnesium compounds.

Thiolactones exhibit lower ring strains than thionolactones or lactones (higher ΔH_p), whereas the higher mobility of polythiolesters, as compared to PEs, leads to a higher ΔS_p. Consequently, thiolactone ROPs must often be performed at low temperatures (low T_c). Usually, this means both polymerization and depolymerization can be performed energy-efficiently, making PTEs very interesting candidates for chemical recycling. However, in certain cases, ROP needs to take place below RT, which could be overcome by changing monomer structures and adding functional groups or by the ROP of thionolactones, which can interestingly, depending on reaction conditions and the catalytic system, create both thiono- and/or thiolester moieties in the polymer backbone (Scheme 8).

Although the prior reports on the degradation potential of PTEs are rather limited, certain remarks of interest can be made. No real proof of polythiolester biodegradability has been shown yet, whereas no biodegradation studies have been performed on polythionoesters. Furthermore, an excellent degradation of polythiolesters is observed by hydrolysis in alkaline media or by very fast chemical recycling at mild reaction conditions with strong base and/or nucleophilic catalysts. Chemical recycling could facilitate the development of closed-loop economies and reduce the need for virgin sulfur sources.

Since PTEs are a rather recently developed class of materials, no commercial applications or industrial productions exist. However, promising concepts in terms of material properties and recyclability are emerging. The synthesis procedure for PTEs generally features industrially relevant reaction conditions (e.g., mild temperatures, short reaction durations, high monomer concentrations, compatibility with organocatalysts), which could significantly contribute toward the cost-efficiency and sustainability of the process. On the other hand, further development toward the use of green solvents in the monomer and polymer synthesis, and in the DSP thereof, must still be established. When envisioning the commercialization of PTEs, more information regarding the ecotoxicity of S-rich materials and a strong waste management policy for PTE-based products will be key. In addition, there is still a need for research on the optimization of recycling processes concerning downstream monomer purification and re-use of the monomers in ROP. In this light, the use of efficient heterogeneous depolymerization catalysts can be of high value.

Lastly, as widely mentioned in prior reports on S-based polymers, the unique chemistry of S often creates interesting material properties which are not seen in O-based polymers. However, reports on the material properties of PTEs, except for thermal properties, are extremely limited. Although these unique features are often mentioned as an important reason to perform research on PTEs in the first place, more data are necessary to confirm these assumptions and determine structure-property relations.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: lactones · polythioesters · recycling · ring-opening polymerization · sulfur

[1] T. Iwata, *Angew. Chem. Int. Ed.* **2015**, *54*, 3210–3215; *Angew. Chem.* **2015**, *127*, 3254–3260.
[2] J.-P. Lange, M. Dusselier, S. De Wildeman, in *Biodegradable Polymers in the Circular Plastics Economy*, **2022**, pp. 1–16.
[3] J. Stouten, K. V. Bernaerts, in *Biodegradable Polymers in the Circular Plastics Economy*, **2022**, pp. 113–144.
[4] A. S. Narmon, L. M. Jenisch, L. M. Pitet, M. Dusselier, in *Biodegradable Polymers in the Circular Plastics Economy* (Eds.: M. Dusselier, J.-P. Lange), Wiley-VCH GmbH, **2022**, pp. 205–271.
[5] M. Koller, A. Mukherjee, in *Biodegradable Polymers in the Circular Plastics Economy*, **2022**, pp. 145–204.
[6] H. Mutlu, E. B. Ceper, X. Li, J. Yang, W. Dong, M. M. Ozmen, P. Theato, *Macromol. Rapid Commun.* **2019**, *40*, 1800650.
[7] J. Kawada, T. Lütke-Eversloh, A. Steinbüchel, R. H. Marchessault, *Biomacromolecules* **2003**, *4*, 1698–1702.
[8] H. F. Mark, *Encyclopedia of Polymer Science and Technology*, John Wiley & Sons, **2014**.
[9] A. Kausar, S. Zulfiqar, M. I. Sarwar, *Polym. Rev.* **2014**, *54*, 185–267.
[10] S. Aksakal, R. Aksakal, C. R. Becer, *Polym. Chem.* **2018**, *9*, 4507–4516.
[11] T.-J. Yue, L.-Y. Wang, W.-M. Ren, *Polym. Chem.* **2021**, *12*, 6650–6666.
[12] H. Li, S. M. Guillaume, J.-F. Carpentier, *Chem. Asian J.* **2022**, *17*, e202200641.
[13] H. R. Kricheldorf, G. Schwarz, *J. Macromol. Sci. Part A Pure Appl. Chem.* **2007**, *44*, 625–649.
[14] W. Yang, D. G. Drueckhammer, *J. Am. Chem. Soc.* **2001**, *123*, 11004–11009.
[15] C. S. Marvel, A. Kotch, *J. Am. Chem. Soc.* **1951**, *73*, 1100–1102.
[16] H. Hirano, S. Watase, M. Tanaka, *J. Appl. Polym. Sci.* **2005**, *96*, 508–515.
[17] H. Hirano, J. Kadota, Y. Agari, T. Harada, M. Tanaka, K. Hasegawa, *Polym. Eng. Sci.* **2007**, *47*, 262–269.
[18] W. Podkościelny, A. Kultys, *J. Polym. Sci. Polym. Chem. Ed.* **1976**, *14*, 655–662.
[19] W. Podkościelny, A. Kultys, *J. Appl. Polym. Sci.* **1981**, *26*, 1143–1148.
[20] W. Podkościelny, W. Kowalewska, *J. Appl. Polym. Sci.* **1990**, *39*, 1649–1656.
[21] W. Podkościelny, A. Kultys, *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*, 2265–2273.
[22] W. Podkoscielny, W. Rudz, *Eur. Polym. J.* **1993**, *29*, 1115–1118.
[23] W. Podkościelny, W. Rudź, *Eur. Polym. J.* **1993**, *29*, 69–73.
[24] W. Podkoscielny, W. Kowalewska, *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 2961–2972.
[25] W. Podkoscielny, D. Wdowicka, *J. Appl. Polym. Sci.* **1985**, *30*, 1579–1585.
[26] W. Podkościelny, W. Rudż, *J. Appl. Polym. Sci.* **1994**, *53*, 815–824.

[27] M. Kato, K. Toshima, S. Matsumura, *Macromol. Rapid Commun.* **2006**, *27*, 605–610.

[28] A. Schöberl, *Die Makromol. Chem.* **1960**, *37*, 64–70.

[29] A. Schöberl, G. Wiehler, *Liebigs Ann. Chem.* **1955**, *595*, 101–130.

[30] A. Schöberl, G. Wiehler, *Angew. Chem.* **1954**, *66*, 273.

[31] H.-G. Elias, H. G. Bührer, *Die Makromolekulare Chem.* **1970**, *140*, 21–39.

[32] M. Kato, K. Toshima, S. Matsumura, *Biomacromolecules* **2005**, *6*, 2275–2280.

[33] C. S. Marvel, E. A. Kraiman, *J. Org. Chem.* **1953**, *18*, 707–7014.

[34] A. Kameyama, M. Kiyota, T. Nishikubo, *Tetrahedron Lett.* **1994**, *35*, 4571–4574.

[35] A. Kameyama, Y. Kimura, T. Nishikubo, *Macromolecules* **1997**, *30*, 6494–6497.

[36] A. Kameyama, T. Nishikubo, *Polym. J.* **2009**, *41*, 1–15.

[37] A. Kameyama, Y. Murakami, T. Nishikubo, *Macromolecules* **1999**, *32*, 1407–1412.

[38] J. H. Wübbeler, A. Steinbüchel, *Curr. Opin. Biotechnol.* **2014**, *29*, 85–92.

[39] E. Takeshi, in *Handb. Ring-Opening Polym.*, **2009**, pp. 53–64.

[40] Y. Wang, M. Li, S. Wang, Y. Tao, X. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 10798–10805.

[41] T. J. Yue, M.-C. Zhang, G.-G. Gu, L.-Y. Wang, W.-M. Ren, X.-B. Lu, *Angew. Chem. Int. Ed.* **2019**, *58*, 618–623; *Angew. Chem.* **2019**, *131*, 628–633.

[42] L. Y. Wang, G. G. Gu, B. H. Ren, T. J. Yue, X. B. Lu, W. M. Ren, *ACS Catal.* **2020**, *10*, 6635–6644.

[43] L. Y. Wang, G. G. Gu, T. J. Yue, W. M. Ren, X. B. Lu, *Macromolecules* **2019**, *52*, 2439–2445.

[44] X. L. Chen, B. Wang, D. P. Song, L. Pan, Y. S. Li, *Macromolecules* **2022**, *55*, 1153–1164.

[45] U. S. Department of the Interior, U. S. Geological Survey, J. A. Ober, *Materials Flow of Sulfur*, **2002**.

[46] U. S. Geological Survey, *Mineral Commodities Summaries 2022*, **2022**.

[47] M. J. H. Worthington, R. L. Kucera, J. M. Chalker, *Green Chem.* **2017**, *19*, 2748–2761.

[48] W. J. Chung, J. J. Griebel, E. T. Kim, H. Yoon, A. G. Simmonds, H. J. Ji, P. T. Dirlam, R. S. Glass, J. J. Wie, N. A. Nguyen, B. W. Guralnick, J. Park, Á. Somogyi, P. Theato, M. E. Mackay, Y.-E. Sung, K. Char, J. Pyun, *Nat. Chem.* **2013**, *5*, 518–524.

[49] M. Maslin, L. Van Heerde, S. Day, *Geogr. J.* **2022**, *188*, 498–505.

[50] J. Wagenfeld, K. Al-ali, S. Almheiri, A. F. Slavens, N. Calvet, *Waste Manage.* **2019**, *95*, 78–89.

[51] X. Shao, S. R. Johnson, W. A. Tarpeh, *ACS ES&T Engg.* **2022**, *2*, 807–818.

[52] Z. Paryzek, I. Skiera, *Org. Prep. Proced. Int.* **2009**, *39*, 203–296.

[53] K. Y. Palate, R. G. Epton, A. C. Whitwood, J. M. Lynam, W. P. Unsworth, *Org. Biomol. Chem.* **2021**, *19*, 1404–1411.

[54] R. O. Mccourt, E. M. Scanlan, *Eur. J. Org. Chem.* **2021**, *2021*, 5320–5334.

[55] N. Illy, E. Mongkhoun, *Polym. Chem.* **2022**, *13*, 4592–4614.

[56] D. Frank, P. Espeel, S. Claessens, E. Mes, F. E. Du Prez, *Tetrahedron* **2016**, *72*, 6616–6625.

[57] D. Frank, P. Espeel, N. Badi, F. Du Prez, *Eur. Polym. J.* **2018**, *98*, 246–253.

[58] V. Botvin, S. Karaseva, D. Salikova, M. Dusselier, *Polym. Degrad. Stab.* **2021**, *183*, 109427–109478.

[59] P. Van Wouwe, M. Dusselier, E. Vanleeuw, B. Sels, *ChemSusChem* **2016**, *9*, 907–921.

[60] H. G. Bührer, H.-G. Elias, *Die Makromol. Chem.* **1970**, *140*, 41–54.

[61] R. O. McCourt, E. M. Scanlan, *Org. Lett.* **2019**, *21*, 3460–3464.

[62] Y. Wang, M. Li, J. Chen, Y. Tao, X. Wang, *Angew. Chem. Int. Ed.* **2021**, *60*, 22547–22553.

[63] M. Suzuki, A. Watanabe, R. Kawai, R. Sato, S. ichi Matsuoka, S. Kawauchi, *Polymer* **2021**, *215*, 123386.

[64] C. G. Overberger, J. K. Weise, *J. Am. Chem. Soc.* **1968**, *90*, 3533–3537.

[65] W. Xiong, W. Chang, D. Shi, X. Zhou, E.-Q. Chen, H. Lu, *Chem* **2020**, *6*, 1831–1843.

[66] J. Yuan, W. Xiong, X. Zhou, Y. Zhang, D. Shi, Z. Li, H. Lu, *J. Am. Chem. Soc.* **2019**, *141*, 4928–4935.

[67] K. A. Stellmach, M. K. Paul, M. Xu, Y.-L. Su, L. Fu, A. R. Toland, H. Tran, L. Chen, R. Ramprasad, W. R. Gutekunst, *ACS Macro Lett.* **2022**, *11*, 895–901.

[68] A. S. Narmon, E. Leys, I. Khalil, G. Ivanushkin, M. Dusselier, *Green Chem.* **2022**, *24*, 9709–9720.

[69] M. Dusselier, P. Van Wouwe, A. Dewaele, P. A. Jacobs, B. F. Sels, *Science* **2015**, *349*, 79–81.

[70] R. O. Mccourt, F. Dénès, G. Sanchez-Sanz, E. M. Scanlan, *Org. Lett.* **2018**, *20*, 2948–2951.

[71] H. Khatoon, E. Abdulmalek, *Molecules* **2021**, *26*, 1055.

[72] T. Ozturk, E. Ertas, O. Mert, *Chem. Rev.* **2007**, *107*, 5210–5278.

[73] T. Ozturk, E. Ertas, O. Mert, *Chem. Rev.* **2010**, *110*, 3419–3478.

[74] V. Polshettiwar, M. P. Kaushik, *J. Sulfur Chem.* **2006**, *27*, 353–386.

[75] L. Pawel, T. Witteler, F. Dielmann, *ChemCatChem* **2021**, *57*, 5043–5046.

[76] J. J. Filippi, X. Fernandez, L. Lizzani-Cuvelier, A. M. Loiseau, *Tetrahedron Lett.* **2003**, *44*, 6647–6650.

[77] T. J. Curphey, *J. Org. Chem.* **2002**, *67*, 6461–6473.

[78] T. J. Curphey, *Tetrahedron Lett.* **2002**, *43*, 371–373.

[79] J. Filippi, X. Fernandez, L. Lizzani-Cuvelier, A.-M. Loiseau, *Flavour Fragrance J.* **2006**, *21*, 175–184.

[80] P. P. Datta, M. K. Kiesewetter, *Macromolecules* **2016**, *49*, 774–780.

[81] P. Yuan, Y. Sun, X. Xu, Y. Luo, M. Hong, *Nat. Chem.* **2022**, *14*, 294–303.

[82] V. Polshettiwar, M. P. Kaushik, *Tetrahedron Lett.* **2006**, *47*, 2315–2317.

[83] V. Polshettiwar, M. P. Kaushik, *Tetrahedron Lett.* **2004**, *45*, 6255–6257.

[84] H. R. Lagiakos, A. Walker, M.-I. Aguilar, P. Perlmutter, *Tetrahedron Lett.* **2011**, *52*, 5131–5132.

[85] M. Zarei, *J. Sulfur Chem.* **2013**, *34*, 370–376.

[86] J.-J. Filippi, X. Fernandez, E. Duñach, *Tetrahedron Lett.* **2006**, *47*, 6067–6070.

[87] N. Sakai, S. Horikawa, Y. Ogiwara, *Synthesis* **2018**, *50*, 565–574.

[88] Y. Ogiwara, K. Takano, S. Horikawa, N. Sakai, *Molecules* **2018**, *23*, 1399.

[89] M. Suzuki, K. Makimura, S. Matsuoka, *Biomacromolecules* **2016**, *17*, 1135–1141.

[90] H. Li, J. Ollivier, S. M. Guillaume, J. Carpentier, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202386.

[91] M. Hong, E. Y. X. Chen, *Nat. Chem.* **2016**, *8*, 42–49.

[92] F. S. Danton, K. J. Ivin, *Nature* **1948**, *162*, 705–707.

[93] C. Shi, M. L. McGraw, Z. C. Li, L. Cavallo, L. Falivene, E. Y. X. Chen, *Sci. Adv.* **2020**, *6*, 1–12.

[94] F. Korte, K. H. Büchel, *Chem. Ber.* **1960**, *93*, 1021–1025.

[95] C. G. Overberger, J. K. Weise, *Polym. Lett.* **1964**, *2*, 329–331.

[96] C. G. Overberger, J. K. Weise, *J. Am. Chem. Soc.* **1968**, *90*, 3538–3543.

[97] P. E. Fritze (Union Carbide Corp., Houston, TX), US3755268 A, **1973**.

[98] C. G. Seefried, J. V. Koleske, *Polym. Eng. Sci.* **1976**, *16*, 526–528.

[99] C. G. Seefried, J. V. Koleske, *J. Macromol. Sci. Phys.* **1974**, *B10*, 579–589.

[100] T. J. Bannin, M. K. Kiesewetter, *Macromolecules* **2015**, *48*, 5481–5486.

[101] F. Sanda, D. Jirakanjana, M. Hitomi, T. Endo, *Macromolecules* **1999**, *32*, 8010–8014.

[102] F. Sanda, D. Jirakanjana, M. Hitomi, T. Endo, *J. Polym. Sci. Part A* **2000**, *38*, 4057–4061.

[103] P. Olsén, K. Odelius, A. C. Albertsson, *Biomacromolecules* **2016**, *17*, 699–709.

[104] N. Y. Dugarte, M. F. Erben, R. M. Romano, R. Boese, M. F. Ge, Y. Li, C. O. Della Védova, *J. Phys. Chem. A* **2009**, *113*, 3662–3672.

[105] N. Y. Dugarte, M. F. Erben, R. M. Romano, M.-F. Ge, Y. Li, C. O. Della Védova, *J. Phys. Chem. A* **2010**, *114*, 9462–9470.

[106] N. Y. Dugarte, M. F. Erben, R. Boese, M.-F. Ge, L. Yao, C. O. Della Védova, *J. Phys. Chem. A* **2010**, *114*, 12540–12547.

[107] N. Y. Dugarte, M. F. Erben, E. Hey-hawkins, P. Lo, S. Stadlbauer, M. Ge, Y. Li, O. E. Piro, G. A. Echeverr, C. O. Della, *J. Phys. Chem. A* **2013**, *117*, 5706–5714.

[108] A. Duda, A. Kowalski, in *Handb. Ring-Opening Polym.* (Eds.: P. Dubois, O. Coulembier, J.-M. Raquez), **2009**, pp. 1–51.

[109] C. Shi, L. T. Reilly, V. S. P. Kumar, M. W. Coile, S. R. Nicholson, L. J. Broadbelt, G. T. Beckham, E. Y. Chen, *Chem* **2021**, *7*, 2896–2912.

[110] G. Xu, Q. Wang, *Green Chem.* **2022**, *24*, 2321–2346.

[111] G. L. Baker, E. B. Vogel, M. R. Smith III, *Polym. Rev.* **2008**, *48*, 64–84.

[112] M. Watanabe, M. Togo, K. Sanui, N. Ogata, T. Kobayashi, Z. Ohtakilb, *Macromolecules* **1984**, *17*, 2908–2912.

[113] Y. Kumagai, Y. Doi, *Polym. Degrad. Stab.* **1992**, *37*, 253–256.

[114] V. Crescenzi, G. Manzini, G. Calzolari, C. Borri, *Eur. Polym. J.* **1972**, *8*, 449–463.

[115] E. Shimamura, M. Scandola, Y. Doi, *Macromolecules* **1994**, *27*, 4429–4435.

[116] K. Sudesh, H. Abe, Y. Doi, *Prog. Polym. Sci.* **2000**, *25*, 1503–1555.

[117] R. W. Lenz, R. H. Marchessault, *Biomacromolecules* **2005**, *6*, 1–8.

[118] P. Strong, B. Laycock, S. Mahamud, P. Jensen, P. Lant, G. Tyson, S. Pratt, *Microorganisms* **2016**, *4*, 11-30.

[119] D. P. Martin, S. F. Williams, *Biochem. Eng. J.* **2003**, *16*, 97–105.

[120] T. Moore, R. Adhikari, P. Gunatillake, *Biomaterials* **2005**, *26*, 3771–3782.

[121] M. Aubin, R. E. Prud'homme, *Polymer* **1981**, *22*, 1223–1226.

[122] K. I. Kasuya, T. Ohura, K. Masuda, Y. Doi, *Int. J. Biol. Macromol.* **1999**, *24*, 329–336.

[123] K. I. Kasuya, Y. Inoue, Y. Doi, *Int. J. Biol. Macromol.* **1996**, *19*, 35–40.

[124] J. A. Martins, A. A. Lach, H. L. Morris, A. J. Carr, P. A. Mouthuy, *J. Biomater. Appl.* **2020**, *34*, 902–916.

[125] H. Tsuji, *Macromol. Biosci.* **2005**, *5*, 569–597.

[126] M. Hirata, Y. Kimura, in *Poly(Lactic Acid) Synth. Struct. Prop. Process. Appl.*, **2010**, pp. 59–65.

[127] M. Yin, G. L. Baker, *Macromolecules* **1999**, *32*, 7711–7718.

[128] M. Labet, W. Thielemans, *Chem. Soc. Rev.* **2009**, *38*, 3484–3504.

[129] C. Shi, M. L. Mcgraw, Z. Li, L. Cavallo, L. Falivene, E. Y. Chen, *Sci. Adv.* **2020**, *6*, 1–12.

[130] H. R. Kricheldorf, G. Schwarz, *J. Macromol. Sci. Part A Pure Appl. Chem.* **2007**, *44*, 625–649.

[131] J. Payne, M. D. Jones, *ChemSusChem* **2021**, *14*, 4041–4070.

[132] P. Huang, S. Furutate, S. Mizuno, T. Tsuge, *Polym. Degrad. Stab.* **2019**, *165*, 35–42.

[133] C. Andreeßen, A. Steinbüchel, *Appl. Microbiol. Biotechnol.* **2019**, *103*, 143–157.

[134] K. Elbanna, T. Lütke-Eversloh, S. Van Trappen, J. Mergaert, J. Swings, A. Steinbüchel, *Int. J. Syst. Evol. Microbiol.* **2003**, *53*, 1165–1168.

[135] K. Elbanna, T. Lütke-Eversloh, D. Jendrossek, H. Luftmann, A. Steinbüchel, *Arch. Microbiol.* **2004**, *182*, 212–225.

[136] B. Zhu, S. Tanaka, L. Feng, N. Ishii, K. Kasuya, Y. Doi, Y. Inoue, *Polym. J.* **2005**, *37*, 711–715.

[137] Y. Kamei, A. Nagai, H. Nishida, H. Kimura, T. Endo, *Macromol. Biosci.* **2007**, *7*, 364–372.

[138] D. Y. Kim, T. Lütke-Eversloh, K. Elbanna, N. Thakor, A. Steinbüchel, *Biomacromolecules* **2005**, *6*, 897–901.

[139] G. Loasby, *The Development of the Synthetic Fibres*, **1951**.

[140] M.-O. Christen, F. Vercesi, *Clin. Cosmet. Investig. Dermatol.* **2020**, *13*, 31–48.

[141] N. C. Wyeth, R. N. Roseveare, *Biaxially Oriented Poly(Ethylene Terephtalate) Bottle*, **1973**, US3733309 A.

[142] Phys Org (Colorado State University), "' Infinitely' recyclable polymer shows practical properties of plastics," **2018**, https://phys.org/news/2018-04-infinitely-recyclable-polymer-properties-plastics.html.

[143] Sakharkar, A. (Tech Explorist), "A new kind of plastic that maintains its orignial qualities when recycled - High performance circular polymers with both intrinsic chemical recyclability and crystallinity," **2020**, https://www.techexplorist.com/new-kind-plastic-maintains-original-qualities-recycled/34831/.

[144] Klein, A. (NewScientist), "A new type of plastic may be the first that is infinitely recyclable," **2020**, https://www.newscientist.com/article/2252265-a-new-type-of-plastic-may-be-the-first-that-is-infinitely-recyclable/.

[145] PlasticsToday, "New Plastic Can Be Recycled Multiple Times Without Losing Original Properties" **2020**, https://www.plasticstoday.com/advanced-recycling/new-plastic-can-be-recycled-multiple-times-without-losing-original-properties.

[146] F. Stempfle, P. Ortmann, S. Mecking, *Chem. Rev.* **2016**, *116*, 4597–4641.

[147] Q. Song, J. Zhao, G. Zhang, F. Peruch, S. Carlotti, *Polym. J.* **2020**, *52*, 3–11.

[148] M. A. F. Delgove, A. A. Wróblewska, J. Stouten, C. A. M. R. van Slagmaat, J. Noordijk, S. M. A. De Wildeman, K. V. Bernaerts, *Polym. Chem.* **2020**, *11*, 3573–3584.

[149] M. Bachmann, A. Marxen, R. Schomäcker, A. Bardow, *Green Chem.* **2022**, *24*, 9143–9156.

[150] M. A. Schaffer, E. K. Marchildon, K. B. Mcauley, M. F. Cunningham, *Chem. Eng. Technol.* **2001**, *24*, 401–408.

[151] C. Jérôme, P. Lecomte, *Adv. Drug Delivery Rev.* **2008**, *60*, 1056–1076.

[152] A. Nachtergael, O. Coulembier, P. Dubois, M. Helvenstein, P. Duez, B. Blankert, L. Mespouille, *Biomacromolecules* **2015**, *16*, 507–514.

[153] R. Silva, E. Coelho, T. Q. Aguiar, L. Domingues, *Appl. Sci.* **2021**, *11*, 8500–8522.

[154] I. Toshiya, K. Kiyobumi, *Method for Producing Radical Addition Reaction Product*, **2002**, JP2002338563 A.

[155] T. B. Nguyen, *Adv. Synth. Catal.* **2017**, *359*, 1066–1130.