Recyclable polythioesters and polydisulfides with near-equilibrium thermodynamics and dynamic covalent bonds

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The accumulation of discarded petroleum-based plastics causes serious environmental crises. Currently, recyclable polymers with neutrality in thermodynamics, such as polyesters, polycarbonates, and polyolefins, have been developed as promising alternatives to traditional petroleum-based polymers. However, the chemical recycle of these polymers usually requires high energy input and expensive catalysts. Dynamic covalent bonds, such as thioester and disulfide bonds, have emerged as building blocks for constructing recyclable polymers that can be rapidly degraded/recycled under mild conditions. In this review, we introduce representative studies on recyclable polythioesters and polydisulfides with respect to their synthetic strategies, thermodynamic manipulation, physicochemical properties, and preliminary applications. We also highlight the important role of kinetic factors played in the design of recyclable polymers. Finally, major challenges, perspectives, and future opportunities in the synthesis and applications of polythioesters/polydisulfides are discussed.

polythioesters, polydisulfides, recyclable, near-equilibrium thermodynamics, dynamic covalent bond

1 Introduction

Traditional petroleum-based synthetic polymers such as plastics play an indispensable role in virtually every aspect of modern society, ranging from commodity products to high-performance functional materials and medical/healthcare products. In one sense, plastics accompany a modern human being every second from cradle to tomb. The statistics in 2020 showed that the global annual production of plastic had reached 370 million tons, with an average annual growth rate of 3%–4%. After service, however, only less than 14% of these plastic products were recycled, with most others being landfilled (40%), incinerated (14%), or directly discarded into environment (more than 32%). Up to 2015, the accumulative amount of discarded plastics was estimated exceeding 8 billion tons [1,2].

The non-degradable nature of most plastics makes them persist on onthe planet with an almost infinite lifetime, causing serious environmental crises, such as fertility decline of soil and water pollution [3,4]. More worrisome, recent studies have shown that the invisible polyolefin-based plastic particles (a.k.a. microplastics) floating in air, land, and water, are more difficult to deal with and may bring greater challenges to human health [5,6]. While physical recycling seems to be the most straightforward approach, it often yields products with deteriorated properties and reduced value, the so-called down-cycling. To realize the opposite up-cycling, one fascinating approach is to chemically degrade or recycle current plastics including polyethylene terephthalate (PET) and polyethylene (PE) into chemicals with added value [7]. Indeed, many efforts from industry and academia have been devoted to this direction and exciting

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advancements have been made in the past few years [8–16]. Nevertheless, due to the inertness of the carbon-carbon bond, the chemical degradation/recycling of polyolefins is often done at the cost of high-energy input, expensive catalysts, and stringent conditions. From the resource point of view, the plastic industry will consume 20% of all fossil fuels in 2050 [17]. In this context, it would make a considerable contribution to reducing petroleum oil consumption if renewable resources can be used for the manufacture of next-generation sustainable polymeric materials [18–24].

Biomass-based novel polymers that could be easily depolymerized into starting monomers at the end of the life cycle have been appealing [25]. This closed-loop monomer-polymer-monomer economy could theoretically establish a sustainable paradigm from both the materials and energy perspectives. For this goal, ring-opening polymerization (ROP) systems with characteristic near-equilibrium thermodynamics emerged as excellent candidates owing to their intrinsic recyclability [26,27]. Presumably, chemists have accumulated mounting experience and physical organic theories manipulating the enthalpy and entropy of the process toward a ΔG_p^o of 0 kJ/mol. This includes strategies such as judicious choice of the ring systems, introducing heteroatoms, and taking advantage of subtle substitution effects [28–30]. From 1950s to 1990s, Höcker *et al.* [31], Wu *et al.* [32], Endo *et al.* [30,33] and Lieser *et al.* [34] have separately noticed the thermodynamic equilibrium of the ROP of 2,2-dimethyltrimethylene carbonate, tetrahydrofuran, spiroorthoester, and 1,3,5-trioxane. Interestingly, the past decade has witnessed the renaissance of this classical approach thanks to the advancement of modern polymerization methods and powerful catalysts for both the forward ROP and backward ring-closing depolymerization (RCDP).

Polyesters are by far the most promising sustainable polymers. Although difficult in recycling monomers and suboptimal in mechanical properties, both polylactide (PLA) and biosynthetic polyhydroxyalkanoates (PHAs) are undergoing rigorous industrial manufacture and commercialization processes. In the meantime, efforts of designing novel polyesters with intrinsical recyclability have never been haltered. Notably, Chen *et al.* [35–39], Hong *et al.* [40], and Li *et al.* [35–41] systematically reported a series of elegant examples of controlled ROP and RCDP of γ-butyrolactone (**1**, GBL), α-methylene-γ-butyrolactone (**2**, MGBL), cyclohexyl-fused butyrolactone (**3**, **4**) and [3.2.1]bicyclic lactone (**5**), affording corresponding polyesters with good thermal/mechanical properties and complete recyclability. Besides those five-membered lactones, recyclable polyesters polymerized from six- (**6–8**) and seven-membered ring (**9** and **10**) lactones have also been reported by Hoye *et al.* [42], Wang *et al.* [43], Li *et al.* [44,45] and Shaver *et al.* [46]. Recyclable polycarbonates (PC) also received considerable attention for their low toxicity, good biocompatibility, and biodegrad-

ability [47–50]. Höcker *et al.* [31] reported PCs with high molecular weight and good thermal properties based on trimethylene carbonate (TMC) derivatives since 1986. However, their depolymerization was unselective for the decarboxylation and the generation of oligomers [51]. Recently, many researchers reported the alternating copolymerization of CO_2 with epoxides, affording regio- and stereoregular polycarbonates (**11**, **13**, **14**) with high molecular weight (M_n) [50,52–58], which can be selectively recycled into pristine epoxide/CO_2 monomer or cyclic carbonate. Ellis *et al.* [59] and Darensbourg [60] revealed the chirality-dependent pathway of depolymerization of epoxide. Apart from polyesters and polycarbonates, polymers made by ring-opening metathesis polymerization (ROMP) [61–64] have also been attempted for RCDP under mild conditions enabled by the powerful Grubbs catalysts. The ROP-RCDP equilibrium of five-membered cyclopentene was early observed by Calderon *et al.* [65] and Grubbs *et al.* [66], which has the potential for the construction of infinitely recyclable polyolefins [67–69]. In 2020, Xia *et al.* [70] reported the controlled ROMP of 2,3-dihydrofuran (**17**), a cyclic enol ether, and the recycling of resulting poly(dihydrofuran) into pure monomer with high conversion (>90%). Apart from those five-membered cyclopentenes, Wang *et al.* [71,72] predicted and realized the reversible ROMP of *trans*-cyclobutane-fused cyclooctenes (*t*CBCO) with low ring strain energy, which experienced efficient RCDP. More representative examples are listed in Figure 1 and have been sufficiently discussed in recent reviews [26,27,73–75].

As one can tell, most of the above-mentioned systems are based on polymers with relatively strong and inert bonds such as C–C, C=C, and C–O bonds. Of course, it is perfectly reasonable to choose such bonds in the polymer backbone so that the resulting materials can possess high thermal and chemical stability during service. However, the activation of these bonds for both ROP and RCDP usually requires high energy input and expensive catalysts. On the other hand, the lifetime and stability of polymers should match the purposes and context of plastic products. The plastic waste crisis would still not disappear immediately even if we can replace all current petroleum-based polymers with a lifetime of millions of years to polyesters that last for hundreds of years. From this angle, it is sound that some single-use and disposable plastics (*e.g.*, packaging materials) need to be designed more labile and "short-lived". As such, we argue in this review that, apart from the neutrality of thermodynamics, kinetic factors should be taken into consideration in the design of recyclable polymers [76]. It would be necessary and beneficial to further explore dynamic or reactive chemical bonds for polymer construction and destruction. We propose that, ideally, plastics should be designed such that they are durable and stable during usage but could be rapidly or even instantaneously degraded/recycled with low

Recyclable polyesters

Chen et al. **2016**   Li et al. **2020**   Chen et al. **2018**

Chen et al. **2018**   Chen et al. **2021**   Li et al. **2019**

Wang et al. **2015**   Hoye et al. **2018**   Shaver et al. **2016**

Li et al. **2021**

Recyclable polycarbonates

Coates et al. **2014**   Carpentier et al. **2015**   Sablong and Williams et al. **2017**

Lu and Liu et al. **2017**   Darensbourg et al. **2013**
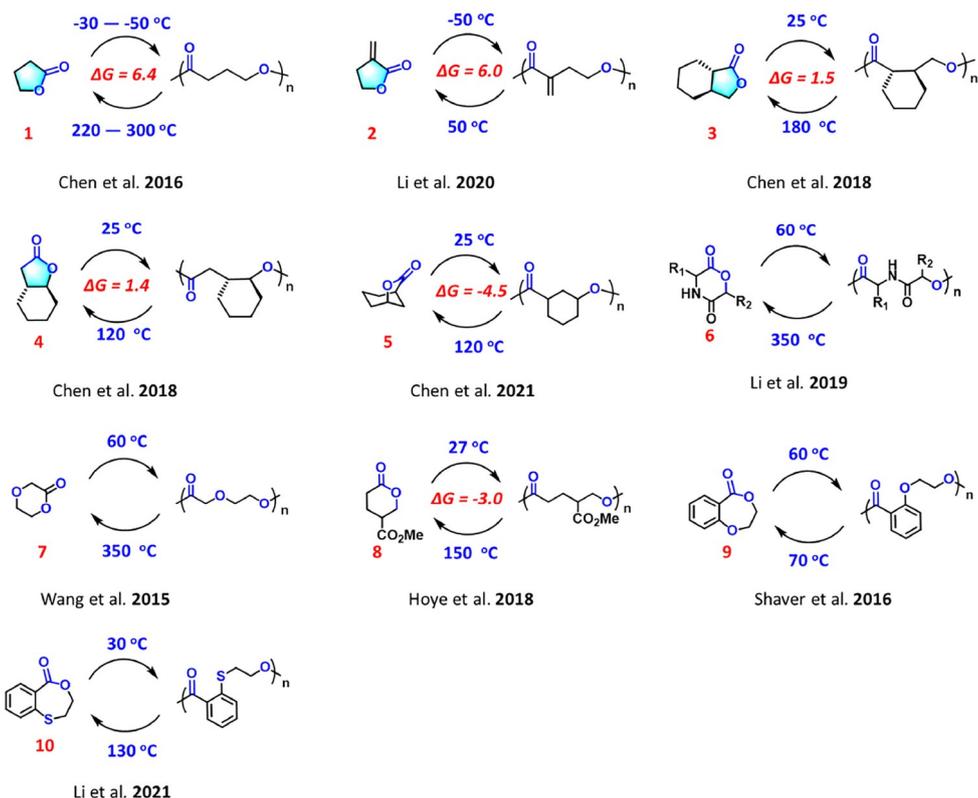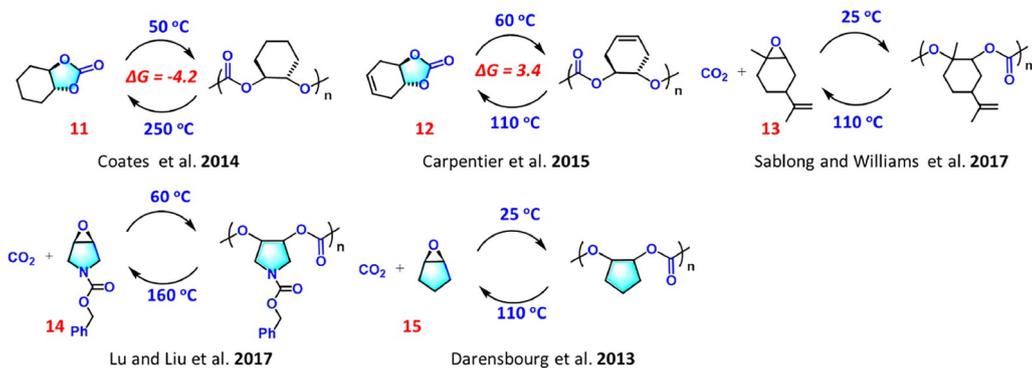
Recyclable poly(cycloolefin)s

Grubbs et al. **2013**   Kennemur et al. **2019**   Xia et al. **2020**   Wang et al. **2021**

Unit of ΔG : kJ/mol

Wang et al. **2021**
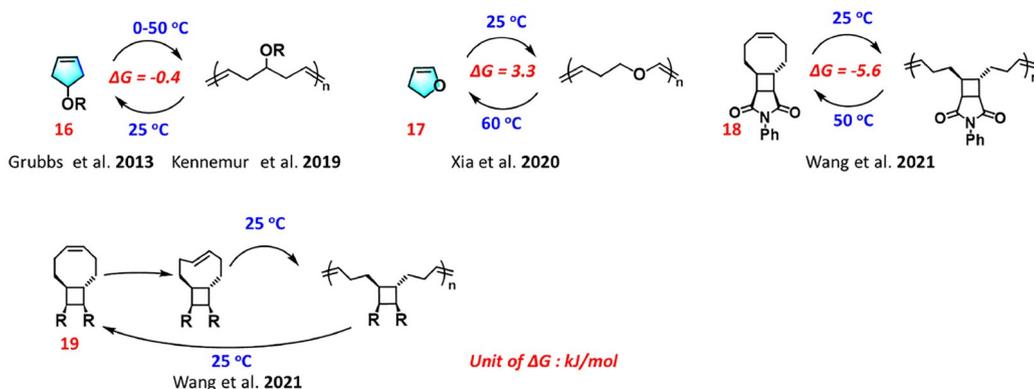
Figure 1   Selected examples of recyclable polyesters, polycarbonates, and ROMP polymers (color online).

cost, low energy input, and in an on-demand fashion. Along this direction, the dynamic thiol-thioster [77,78] and thiol-disulfide exchange [79,80] reactions have emerged as promising handles for constructing covalent adaptive networks (CANs) [81–88]. Moreover, there are also exciting research endeavors exploiting non-crosslinked polymers based on thioester and disulfide linkages, which are the focus of this review (Table 1).

2   Recyclable polymers based on the thioester bond

Although sulfur and oxygen belong to the same main group in the periodic table of elements, sulfur has a larger Van der Waals radius than oxygen (R_S (1.80 Å) *versus* R_O (1.52 Å)), resulting in a longer bond length of thioesters over esters (C–S, 1.76–1.83 Å; C–O, 1.36–1.44 Å). The longer thioester bond was expected to fine-tune the ring strain of thiolactone monomers and facilitate the RCDP of corresponding poly-thioesters (PTE) with a stronger thermodynamic tendency

[89]. Moreover, since the conjugation of sulfur p-orbital was not as strong as that of oxygen with the π-orbital of carbonyl, thioesters are well-known as more reactive to nucleophiles than esters, rendering mild conditions for both the forward ROP and backward RCDP. In addition, the introduction of sulfur atoms may give rise to interesting optical, thermal, and mechanical properties [90–99], making them potential candidates as engineering plastics [100,101], dynamic self-healing materials [102–104], and optical sensors [105–107]. As early as the 1950s, Kotch *et al.* [106] and Schöberl [108] reported examples of PTEs prepared by the polycondensation of *p*-benzoyl chloride/ethanedithiol and the ROP of thiolglycolide, respectively. The biosynthesis of PTEs was also realized by feeding 3,3′-thiodipropionic acid to engineered bacteria [109–111]. In the past few years, the chemical synthesis of PTEs flourished partially owing to the advancement of both ROP catalysts for lactones and related characterization technologies [90,112–118]. Since 2015, Kiesewetter *et al.* [113], Suzuki *et al.* [116] and Bowman *et al.* [117] had realized the synthesis of the PTE with low to moderate M_n by the ROP of ε-thiocaprolactone (M_n =

Table 1 Summary of representative thiolactones and dithiolanes monomers [a]
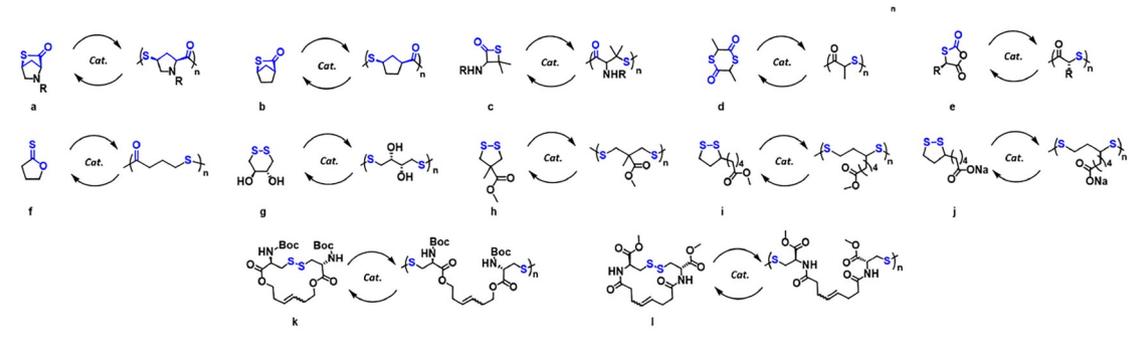
Monomer	T_g (°C)	T_m (°C)	T_d (°C)	T_{poly} (°C)	T_{depoly} (°C)	T_c (°C)	ΔG_{cal} (kJ/mol)	ΔG_{exp} (kJ/mol)	M_n (kDa)	Đ	Stress (MPa)	Young's modulus (MPa)	Elongation at break (%)
a	~32−37	−	196−204	25	50	112	−33.1	−3.56	259	1.24	−	−	−
b	−	166−213	328	R.T.	100	−20	−	2.50	115	1.75	41.4 ± 3.0	2,000 ± 18	233 ± 22
c	~50	~100	~192	25	25	61	3.3	1.0	70.6	1.23	7.0	300	2.8
d	−19.2−41.9	115.6	182−254	25	25	−67	3.3	2.19	100.5	1.36	21.3	−	140.1
e	−2.5−36.5	127.5	202.2−256.4	25	25	Full	−36.0	−	96.2	1.29	9.8	−	40.0
f	−49.2	99.5-102.2	198.0−230.0	80	R.T.	Full	−90.8	−	162.6	1.53	29.8	296.5	412.5
g	44	−	213	25	R.T.	−	−	−	13.5	1.29	−	−	−
h	−	−	−	R.T.	23	−	−	2.7	9.2	2.16	−	−	−
i-Waymouth	−	−	−	R.T.	23	−	−	−0.2	15.3	2.15	−	−	−
i-Moore	−	−	~200	R.T.	65	~27	2.9		630	1.27	−	−	−
j-Lu	−	−	−	−30	37	−	−	−3.31	~55	−	−	−	−
j-Qu	−	−	−	25	25	−	−	−	−	−	~12	168.8	~10
k	31	−	200	60	R.T.	−	−	−	180	1.9	−	−	−
l	39	−	230	85	R.T.	−	−	−	44	3.5	−	−	−

a) T_g: glass transition temperature; T_m: melting temperature; T_d: thermal decomposition temperature; T_{poly}: the temperature of polymerization; T_{depoly}: the temperature of depolymerization; T_c: ceiling temperature; ΔG_{cal}: Gibbs free energy change calculated by density functional theory; ΔG_{exp}: Gibbs free energy change determined from Van't Hoff plots; Đ: dispersity.

6.0–32.0 kg/mol, *Đ* = 1.40–1.70), cysteine-derived β-thiolactone (M_n = 2.9–8.8 kg/mol, *Đ* = 1.6–2.4), and nucleobase-bearing δ-thiolactones (M_n = 2.3–5.7 kg/mol, *Đ* = 1.23–1.36), respectively. In 2019, Lu and Ren [90] reported the alternating copolymerization of thioanhydride and episulfides *via* the catalysis of bis(triphenylphosphine)iminium salt, affording PTEs with high molecular weight (M_n = 29.9–53.6 kg/mol, *Đ* = 1.23–1.72), semicrystallinity, high refractive index, and good machinability. In the same year, Gutekunst *et al.* [114] studied the copolymerization of thionolactone with *tert*-butyl acrylate *via* the free radical mechanism, affording PTE with high molecular weight (M_n = 4.4–32.6 kg/mol, *Đ* = 1.05–1.27). However, these PTEs cannot be recycled as monomers. Overall, the preparation of recycled PTE with high M_n was more difficult than polyesters due to frequent chain-transfer and backbiting processes caused by the thiol-thioester exchange and transthioesterifcation reactions during the ROP.

To address these challenges, Lu *et al.* [89] developed a series of hydroxyproline-derived thiolactones with a bicyclic structural character (N^R-PTL). Interestingly, the ROP behaviors of N^R-PTL mediated by benzyl mercaptan (BnSH)/triethylamine (TEA) were highly controlled, affording PTE (N^R-PTE) with high M_n up to 259 kg/mol, low *Đ* around 1.20 (**a**, Table 1), and well-defined end groups (Figure 2). Moreover, the domino-like RCDP of the uncapped N^R-PTE was triggered by a catalytic amount of base under diluted solution, yielding pristine monomers with high conversions (>95%). Remarkably, compared with most recyclable polyesters, the RCDP of N^R-PTE was significantly faster (within 5 min using TBD as the catalyst) and the conditions were milder. The fast RCDP was partially attributable to both the rigidity of N^R-PTE and the dynamic thioester bond, which allowed chain backbiting with a low energy barrier. The good control in both ROP and RCDP was attributable to the delicate design of the monomer, which was revealed by

density functional theory (DFT) calculation. Presumably, the n→π* orbital interaction between the side urethane and thioester carbonyls within the PTE made the thioester less electrophilic and the relatively high steric hindrance effectively inhibited the undesirable chain-transfer side reaction. Interestingly, Lu *et al.* [119] also reported the synthesis and controlled ROP of a series of bicyclic lactones (N^R-PL) that were structurally analogous with N^R-PTL. Different from PN^R-PTE, the polyesters PN^R-PE were unable to undergo RCDP to recycle monomers. These results vividly underscored the dramatically different thermodynamic and kinetic characteristics of thiolactones and lactones, which were partially consequences of their different C–X (X = O or S) bond lengths (Figure 2). Of note, Chen *et al.* [100] also demonstrated the controlled ROP of a novel thiolactone (BTL) with a similar bridged bicyclic structure to N^R-PTL, affording PBTL with high molecular weight (**b**, Table 1). Consistently with the result of PN^R-PTE, the polymer PBTL could also be depolymerized to recycle monomers. PBTL showed outstanding thermal stability (T_d = 328 °C) and high mechanical properties with a high Young's modulus of 2.00 ± 0.18 GPa, and a breaking elongation of 233% ± 22% (Figure 3). One extra interesting finding is that the topology and tacticity of PBTL were readily tunable by altering the initiator and pK_a of bases, affording products with tacticity-independent semi-crystallinity.

In Lu and Chen's work [120] in 2020, a novel β-thiolactone (N^R-PenTL) derived from penicillamine was utilized to construct PTE (Figure 4). The ROP mediated by both BnSH/DBU and BnSH/*t*BuP₄ (Schwesinger P4 base) showed controlled manners. The ω-end-capped PTE (N^R-PenTE) was thermally stable below 200 °C (5% T_d ~192 °C) and stable against TEA treatment. The ω-uncapped N^R-PenTE, on the other hand, underwent rapid RCDP (~4 h) from the chain end at room temperature as catalyzed by DBU to yield enantiopure monomers. Compared with cysteine-derived
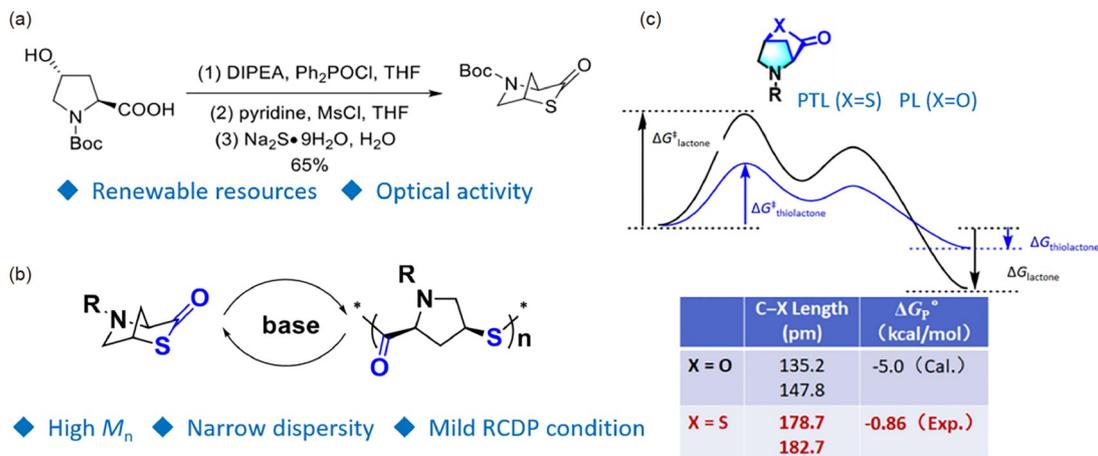
Figure 2 (a) Synthesis of hydroxyproline-derived thiolactones N^R-PTL; (b) the controlled ROP of N^R-PTL and reversible RCDP of PTE; (c) comparison of the bond length and thermodynamics parameters of hydroxyproline-derived thiolactones N^R-PTL and lactones N^R-PL [89] (color online).
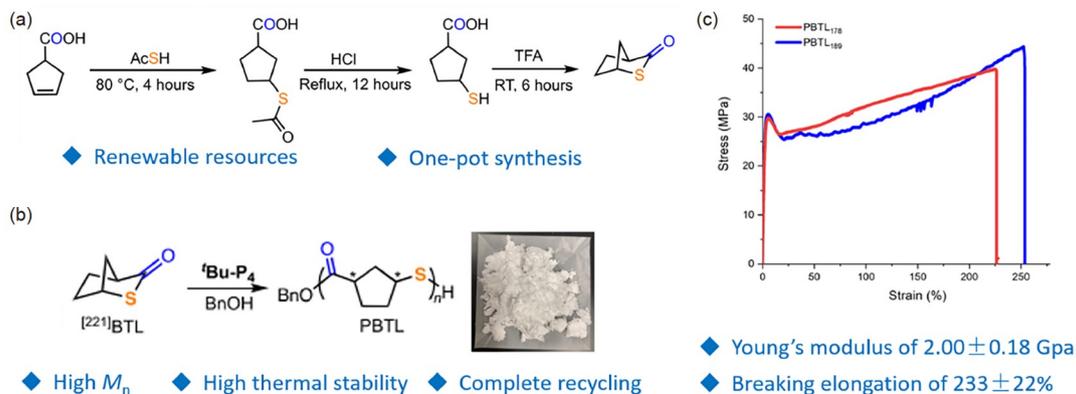
Figure 3 (a) Synthesis of the bicyclic thiolactone monomer BTL; (b) the controlled ROP of BTL and reversed RCDP of PBTL; (c) stress-strain curve of PBTL [100] (color online).
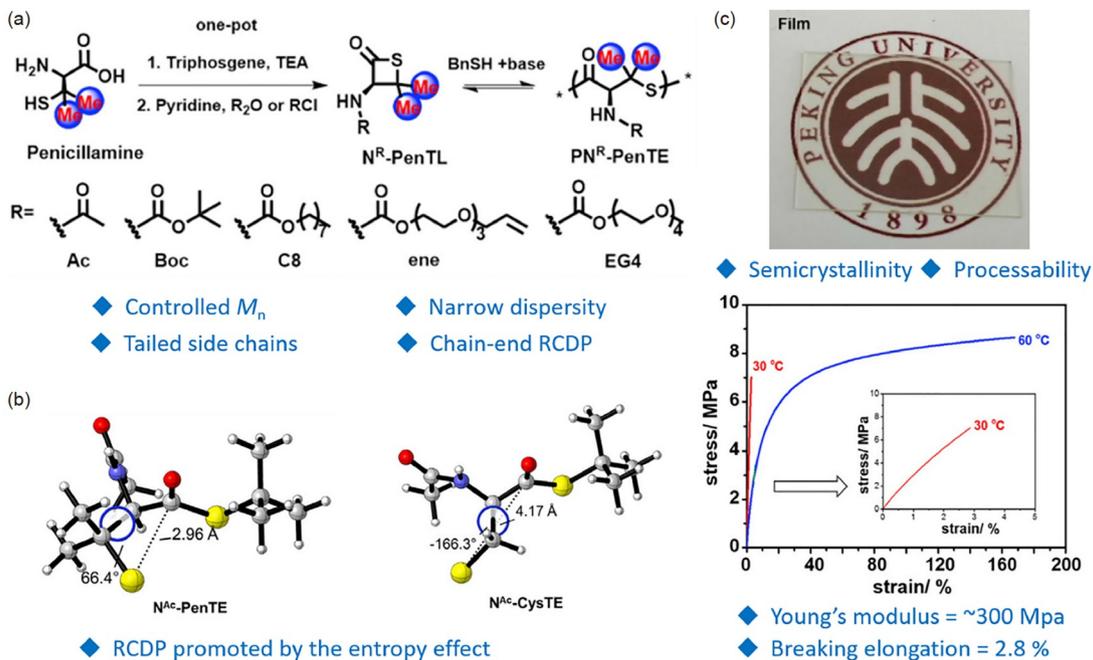
Figure 4 (a) Synthesis and ROP of the penicillamine-derived β-thiolactones and the reversible RCDP of the polymers PN^R-PenTE; (b) DFT calculation of the stable conformation of N^{Ac}-PenTE and N^{Ac}-CysTE showing different thiol-carbonyl distances; (c) a photograph and stress-strain curve of the PN^R-PenTE film [120] (color online).

N-Boc β-thiolactone (CysTL), a four-membered cyclic monomer structurally analogous to N^R-PenTL, the authors found the introduction of the geminal dimethyl in N^R-PenTL can greatly improve the M_n of the obtained PTE (**c**, Table 1). Moreover, the 'Thorpe-Ingold' effect of the geminal dimethyl substitution forced the chain end of N^R-PenTE to adopt the gauge conform with a short distance of the terminal thiol-carbonyl, which promoted the ring-closing reaction *via* the entropy effect (Figure 4b). DFT calculation also suggested a significant decrease in the ring strain of β-thiolactone by the introduction of geminal dimethyl, rendering the monomer recycling thermodynamically feasible. The semi-crystalline polymer N^{C8}-PenTE with *n*-octyl urethane side chain gave a moderate mechanical property with Young's modulus of ~300 MPa, and a breaking elongation of 2.8%.

Polylactide (PLA) is a classical biodegradable polyester, however, the depolymerization of PLA triggered by metal catalysts often unselectively affords a mixture of *rac*-LA and *meso*-LA [121]. Recently, Tao and Wang *et al.* [122] reported the synthesis of thiodilactone monomers *via* the cyclization reaction of several α-mercapto acids derived from natural α-amino acid. Impressively, the cyclization yields of the *S*-substituted dilactones were much higher than that of lactide. Compared with the ROP system reported by Suzuki using DBU as the catalyst (M_n = 26.9 kg/mol, Đ = 3.34) [123], the

ROP of thiodilactone mediated by weak bases such as DMAP and TEA demonstrated higher controllability (**d**, Table 1). The resulting polythiolactides with tailored side chains have tunable thermal properties and showed semi-crystallinity despite the atactic backbone. Similar to previously mentioned PTE examples, the fast RCDP of poly-thiolactide can be realized under mild conditions, affording thiolactide monomer with quantitative conversion. The author speculated the *O*-to-*S* substitution led to a significant release of the ring strain, which was partially evidenced by the lower ΔG_p^0 of thiodilactone (~0.8 kcal/mol) as compared with that of dilactone (~−10.2 kcal/mol) according to the DFT calculation. Moreover, the RCDP of PLSA selectively afforded *rac*-thiolactide with an ultra-high ratio of 98:2 in a mixture of *rac*/*meso*-thiolactides due to the epimerization catalyzed by DBU (Figure 5). In addition, PLSA was processed into a dumbbell-type spline with a stress of 21.3 MPa and a breaking elongation of 140.1% by injection molding. The same group also reported a class of novel enantiopure *S*-carboxyanhydrides (SCA) monomers derived from α-mercapto acids *via* the triphosgene-mediated cyclization reaction [112]. Compared with thiolactone, the reaction species of SCAs is the more reactive anhydride, which endowed high selectivity for the chain propagation process over trans-thioesterification during ROP. Benefiting from the optimized system using organic ammonium salt and benzoic acid as catalyst and chain transfer agents, respectively, the ultrafast and controlled ROP of SCAs was finished in minutes, affording various PTEs with high M_n, narrow dispersity, and good stereoregularity (**e**, Table 1). Driving by the liberation

of CO_2, the ROP of SCAs was thermodynamically more favorable and the obtained PTE could be potentially recycled in the form of cyclic dithioester.

Since the controlled ROP of the non-strain GBL [124] in 2016, many efforts have also been devoted to the ROP of its analogous γ-butyrolactone to make poly(γ-thiobutyr-olactone) (PTBL). Unfortunately, efforts of making a homopolymer out of γ-butyrolactone have all failed even under extremely low temperatures. This is presumably because the ring strain of γ-thiobutyrolactone is even smaller compared with that of γ-butyrolactone. Recently, Hong *et al.* [125] reported a novel irreversible ring-opening poly-merization (IROP) system affording PTBL with high M_n up to 162.6 kg/mol under industrial benign conditions (80 °C). Differing from traditional approaches to polymerizing γ-thiobutyrolactone, instead, the authors prepared thionobu-tyrolactone (TnBL) in a single step from GBL with an almost quantitative yield (Figure 6). One unique feature of the system was the exothermic S/O isomerization during the ROP, which shifted the thermodynamics favoring ROP with a complete monomer conversion and at mild conditions. It should be mentioned that, although the ROP of TnBL was previously attempted by Endo using scandium tri-fluoromethane-sulfonate catalysts [126], those studies ended up with PTBL with low M_n less than 6.0 kg/mol and low yield due to undesired side reactions. As such, the thermal and mechanical properties of PTBL were suboptimal and not reported previously. In Hong's study, the authors optimized the catalysis system as well as the ROP conditions, which not only largely avoided those side reactions but also improved
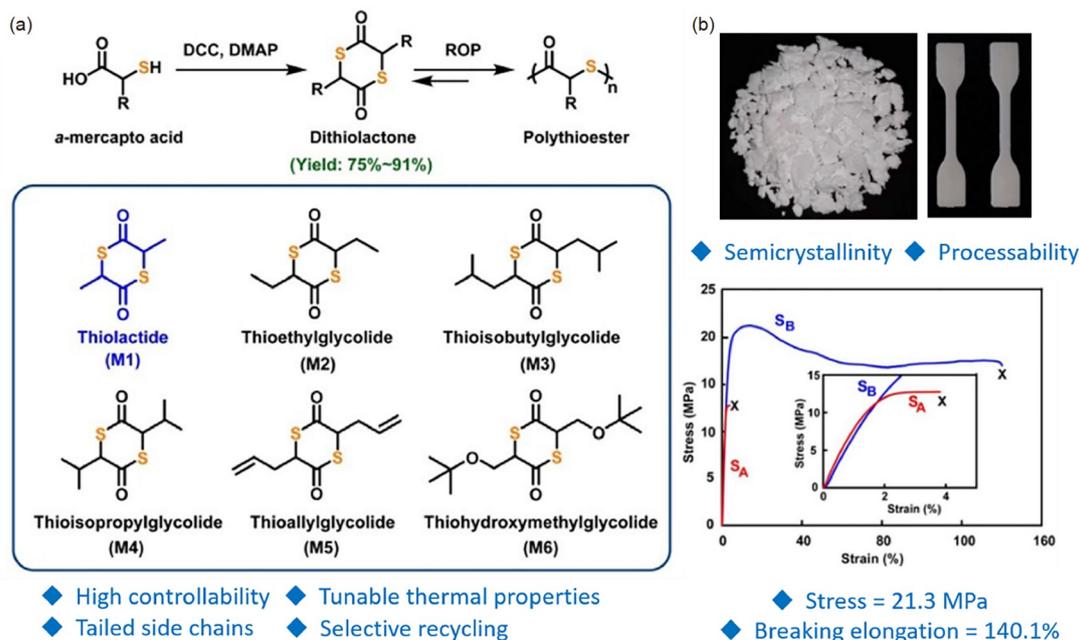
Figure 5   (a) The controlled ROP of amino acid-derived thiodilactone and the reversible RCDP of PLSA; (b) a photograph and stress-strain curve of dumbbell-type spline of PLSA [122] (color online).
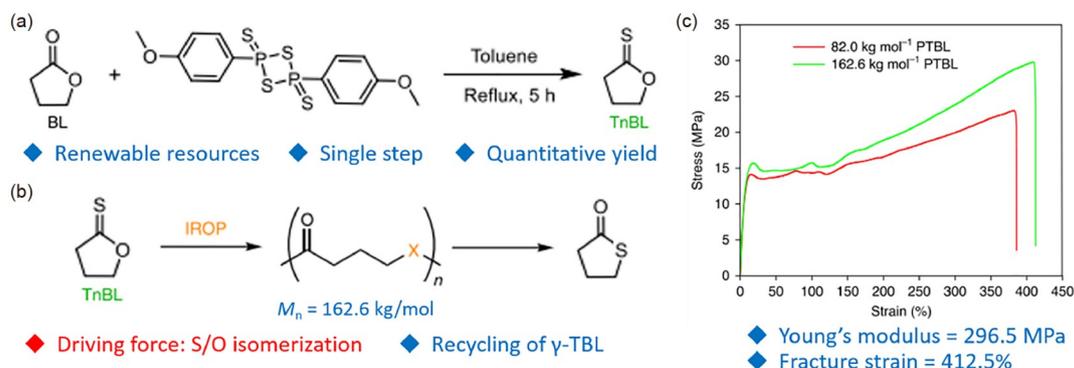
Figure 6 (a) Synthesis of succinic acid-derived thionobutyrolactone (TnBL); (b) irreversible ROP of TnBL and the reversible RCDP of PTBL; (c) stress-strain curve of PTBL [125] (color online).

the M_n control significantly. With its high M_n (**f**, Table 1), the obtained PTBL showed good mechanical properties including Young's modulus of 296.5 MPa and a fracture strain of 412.5% after yielding, which resembles low-density polyethylene (LDPE). Moreover, despite the ROP of TnBL being irreversible, the RCDP of PTBL is intrinsically favored to recycle γ-thiobutyrolactone due to its low strain. Overall, this study demonstrated the elegant chemistry of the IROP of TnBL and the immense application potential of PTBL as next-generation sustainable plastic (Figure 6).

3 Recyclable polymers based on disulfide bond

The ROP of cyclic disulfides such as dithiolanes can be traced back to 1948 [127–129]. A series of classical works were done by Whitesides [130], who systematically studied the thiol-disulfide exchange reaction and calculated the strain of cyclic disulfides with molecular modeling in the 1980s–1990s. It is now well recognized that the driving force for the ROP of cyclic disulfides is mainly derived from the torsional strain of the –C–S–S–C– bond angle. Specifically, the author summarized the quantitative relationship between the CSSC dihedral angle and the enthalpy of the disulfide bond, concluding that a 90° CSSC dihedral angle has the lowest torsional strain [131,132]. For this reason, the five-membered 1,2-dithiolanes with a dihedral angle less than 35° were usually more strained than other cyclic disulfide compounds.

The ROP of lipoic acid (LA), a biosynthesized 1,2-dithiolane found in protein post-translational modification, attracted extensive attention in biomedicine and polymer sciences. Since 2013, Matile *et al.* [133–136] pioneered the aqueous ROP of LA derivative for the intracellular delivery of fluorescence probes and drugs. By using a high monomer concentration and small molecular thiol initiators, they produced poly(disulfide)s (PDS) with moderate M_n ~9.9 kg/mol. The PDS was reported to deliver cargos with a

unique mechanism involving a thiol-mediated covalent translocation on the cell membrane through the thiol-disulfide exchange reactions [137]. In 2020, Lu *et al.* [138] reported the *in situ* preparation of protein-poly(disulfide) conjugates *via* the cryopolymerization of LA derivatives using cysteine-containing proteins as macro-initiators. Interestingly, they showed that the cryopolymerization was successful even at monomer concentrations lower than the equilibrium concentration, which was attributed to the augmented local concentration effect under frozen conditions. Furthermore, by taking advantage of the near-equilibrium character of the 1,2-dithiolane systems (ΔG_p^o ~−3.31 kJ/mol in water), they demonstrated that native proteins could be released through the RCDP of PDS.

Because of its redox-responsiveness and moderate ring strain, PDS polymers have also been considered good candidates for the construction of recyclable polymers in materials science [139]. In 2017, Waymouth *et al.* [140] reported the fabrication of dynamic disulfide-crosslinked hydrogels with tunable properties. To understand how the chemistry of different 1,2-dithiolane monomers affects the performances of the materials, they carefully studied the thermodynamics and kinetics of the ROP of two types of dithiolane monomers namely methyl asparagusic acid (MAA) and methyl lipoate (MLA), respectively. The thermodynamic and kinetic parameters of the polymerization of MLA and MAA were measured based on the Van't Hoff equation (Table 2). According to these results, the author concluded that the number and site of substituents on the five-membered ring greatly affected the thermodynamics and kinetics of the ROP. Specifically, the ROP of MMA demonstrated a higher rate but a lower monomer conversion than that of MLA due to different substitution effects.

Schlaad *et al.* [141,142] designed and synthesized a disulfide/olefin-containing 16-membered macrocycle monomer derived from L-cystine. The novel enantiopure monomer was able to be transferred into high molar mass poly(disulfide)s *via* both ROMP catalyzed by the Grubbs catalyst (M_n

= 60 kg/mol) and ROP mediated by methyl thioglycolate (M_n = 53 kg/mol) with similar monomer conversions (~80% at $[M]_0$ = 1.2 M and T = 85 °C). Moreover, the obtained PDS materials showed a wide process window (T_g = 31 °C and T_d = 200 °C) and could be depolymerized into monomer when diluted in a polar solvent at ambient temperature.

Moore and Liu *et al.* [143] reported the highly effective ROP of methyl lipoate with various initiators, concluding that the linear or cyclic topology of the afforded PDS was tunable by the leaving tendency of the initiator. PDS with M_n ~630 kg/mol, $Đ$ ~1.27, and T_d ~200 °C were obtained with ~10 min. According to DFT computation of the ΔG_p^o of ring-opening reaction of methyl lipoate initiated by PhSH and BuSH, the former was ~9–11 kcal/mol higher than the latter, which promoted the backbiting of the PDS to give the cyclic topology. All those works demonstrated fast recyclability of PDS into monomers with >95% conversions (Figure 7).

Daasbjerg and Pedersen *et al.* [144] reported the synthesis of poly(dithiothreitol) via the condensation polymerization of DL-dithiothreitol (DTT). Interestingly, the polymerization was conducted in the solid state triggered by grinding the monomers with 2,2′-dithiodipyridine (DTDP) as the end-capping agent. Although the polymerization followed a step-growth manner, the author demonstrated that M_n can be

regulated by altering the quantity of DTDP to give M_n ~13.5 kg/mol and $Đ$ ~1.29. The poly(dithiothreitol) capped with DTDP showed a T_d ~213 °C but experienced a degradation under UV irradiation via electron transfer from the end-caps. Moreover, the RCDP of poly(dithiothreitol) into cyclic DTT could be triggered by a catalytic amount of TEA and DTT in the solid state via a backbiting mechanism and was quenched by the addition of excess DTDP (Figure 8). By modifying the poly(dithiothreitol) backbone with pendant catechol units and followed by curing with metal ions, they further fabricated a dual-responsive gel crosslinked by the catechol-metal interaction. The gel exhibited self-healing properties due to the dynamic nature of both the catechol–metal and disulfide bonds. The crosslinked gels can be degraded via two different approaches, namely DTT-triggered self-immolative depolymerization of the PDS backbone and pH-responsive cleavage of the catechol-metal crosslinks, respectively [145].

Qu *et al.* [146,147] took an elegant pre-organization approach before the ROP of the amphiphilic sodium thioctate, which afforded a PDS film with a long-range-ordered assembling structure spontaneously induced by the evaporation-induced interfacial confinement effect. During the aqueous ROP, the sodium thioctate first assembled into a

Table 2 The thermodynamic and kinetic parameters of the polymerization of MLA and MAA [140]

Monomer	$[M]_{eq}$ (M), 23 °C [a]	K_{eq} (M^{-1}), 23 °C [b]	ΔH_p (kJ/mol) [c]	ΔS_p (J/(mol K)) [c]	k_{obs} (min^{-1}) [d]
A	2.95	0.339	−9.99	−43.35	1.384
B	0.93	1.075	−15.44	−50.84	0.308
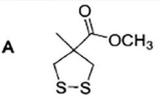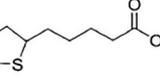
a) $[M]_{eq}$: equilibrium monomer concentration; b) K_{eq}: equilibrium constant of the ROP; c) ΔH_p: standard enthalpy; ΔS_p: standard entropy; d) k_{obs}: observed rate constants of the polymerization.
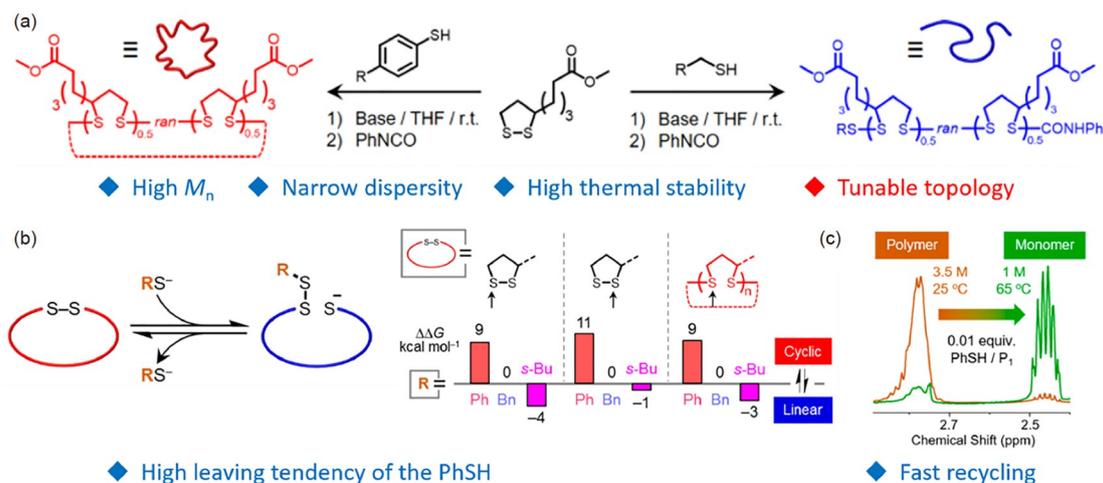
Figure 7 (a) The selective synthesis of PDS with linear or cyclic topology *via* ROP of methyl lipoate; (b) the Gibbs free energy of different initiators; (c) the reversible RCDP of PDS [143] (color online).

relatively ordered supramolecular structure, in which the hydrophobic disulfide-containing ring was preorganized in the core to trigger the dynamic exchange of the disulfide bonds. Then the polymer gradually oriented and assembled to an ordered structure along with the evaporation of the edge of the droplet, endowing the polymer film with birefringence property and humidity-responsive capability (Figure 9). The polymer network could be depolymerized into mixed monomer/oligomer when dissolved in water, and the recycled monomer could be reprocessed into film with considerable mechanical properties (Young's modulus: $E = 168.8$ MPa; tensile stress: $\sigma = \sim 12$ MPa). The same group also reported the controlled bulk ROP of LA in the existence of metal ion additives. The coordination of ions with the side carboxyl of poly(thioctic acid) led to a dynamic network, which can be processed into stretchable and self-healing elastic films with high mechanical robustness. The mechanical property of the thermoplastic elastomer was conveniently tunable by the type and feeding ratio of the metal

salts. Moreover, the metal ion-crosslinked network could be chemically recycled into monomers with high conversion in dilute NaOH solutions and the ferric ions could be removed in the form of suspended $Fe(OH)_3$ by filtration.

Bates and de Alaniz *et al.* [148] reported the synthesis of mono-PDMS-LA and bis-PDMS-LA as the macromonomer and crosslinker *via* the chain-end modification of poly(dimethylsiloxane) (PDMS) by LA, respectively. The macromonomer mono-PDMS-LA was capable of experiencing an ultraviolet (UV)-mediated bulk ROP *via* the so-called "grafting-through" strategy, affording dynamic bottlebrush PDS without initiator or catalyst (Figure 10). Moreover, using bis-PDMS-LA as a crosslinker, elastomers with tunable low-frequency shear moduli (~ 20–200 kPa) could be constructed within minutes. By taking advantage of the UV-mediated disulfide-exchange reaction, the materials exhibited an effective self-healing property with $\sim 70\%$ and $\sim 50\%$ recovery of shear modulus and toughness, respectively. The elastomers were conveniently recycled as pristine
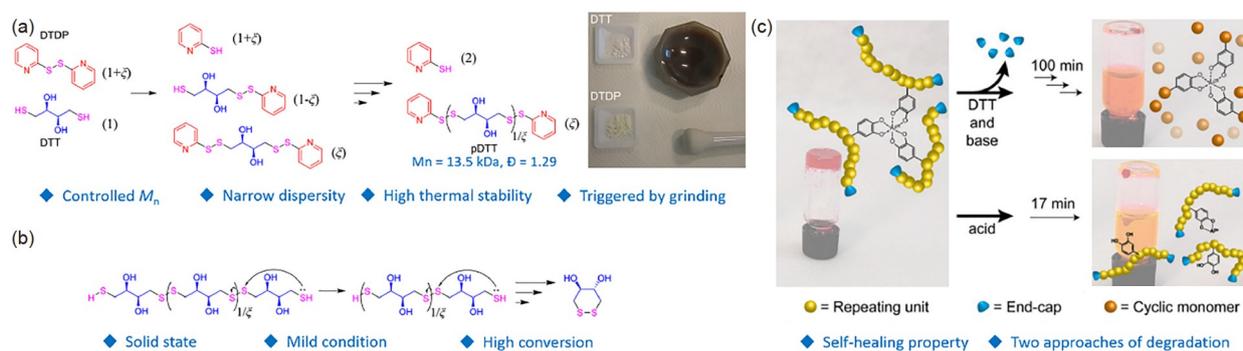
Figure 8 (a) Condensate polymerization of DL-dithiothreitol; (b) the RCDP of poly(dithiothreitol); (c) a photograph and diagram of dual-responsive gel crosslinked by the catechol-metal interaction [144,145] (color online).
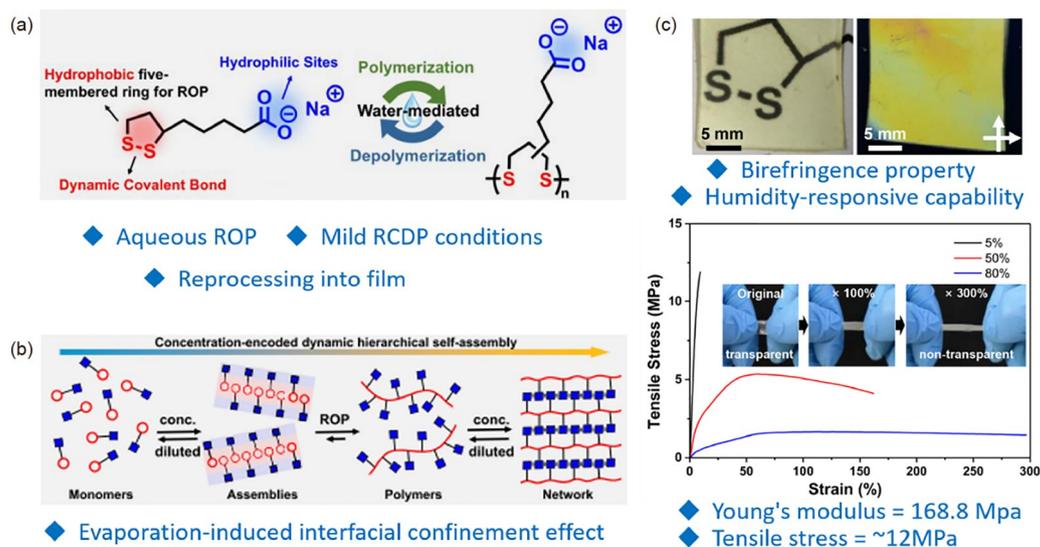
Figure 9 (a) The fabrication of dynamic PDS films *via* ROP of sodium thioctate and the reversible RCDP of PDS; (b) the synthesis of PDS film induced by the evaporation-induced interfacial confinement effect; (c) a photograph and stress-strain curve of PDS film [146,147] (color online).
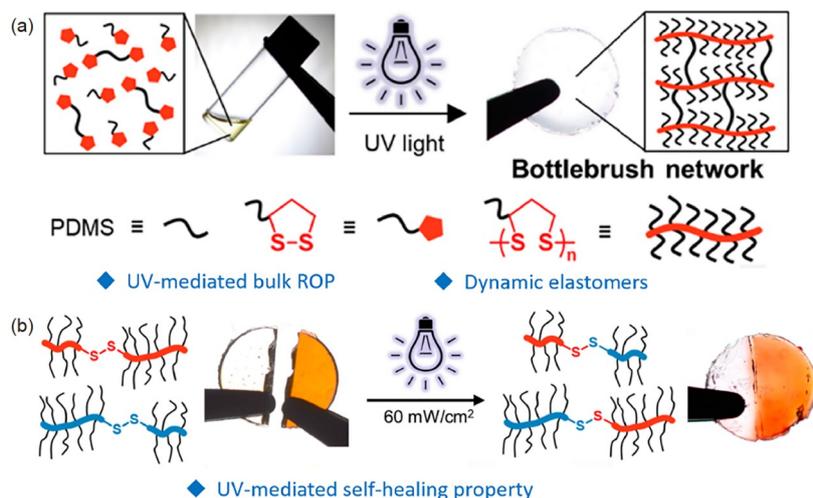
Figure 10   (a) The fabrication of dynamic bottlebrush PDS elastomers *via* ROP of sodium thioctate and the reversible RCDP of PDS; (b) the self-healing of PDS elastomer induced by the UV irradiation [148] (color online).

monomers with a conversion of ~30%–40% when heating to 180 °C, which could be reprocessed into elastomer after UV treatment.

4   Conclusions and perspective

Toward a more sustainable planet, governments across the world have all made ambitious goals in controlling carbon consumption. Polymers, as a form of condensed matter with high carbon contents, can contribute to the control of carbon emissions and in the meantime offer valuable materials. However, this proposal is valid and appealing only when a circular economy of polymers can be established. To generate a closed loop of the carbon economy, the source of polymers should use as less traditional petroleum-based chemicals as possible and the fate of the polymers need to be fully recyclable and reusable. Moreover, both the fabrication and recycling processes of these polymers should be ideally low and green in energy consumption. In this review, we summarize recent progress in the development of controlled near-equilibrium ROP systems in the past decade, with an emphasis on those with thioester and disulfide bonds. Increasingly, polymers with such thermodynamic characters and dynamic covalent bonds have been considered promising recyclable polymers for their intrinsic properties. Nevertheless, the introduction of dynamic bonds could also be a double-edged sword. Often, dynamic bonds lead to low controllability of polymerization and moderate durability of the materials. To date, these problems have been partly overcome by the delicate design of the ROP system. As mentioned earlier, introducing substituent groups with suitable steric hindrance or specific electron effects could increase the stability of polymers by fine-tuning the activity of dynamic bonds [89]. In addition, manipulating the topology

of polymers is also a common strategy to adjust the durability of the materials [67]. Copolymerization with other types of monomers was another way to increase the resistance of polymer by optimizing the ratio of dynamic bonds in the backbone of polymers [114]. Another challenge for the near-equilibrium ROP systems is incomplete monomer conversion, which is an intrinsic trade-off of recyclability. To tackle this problem, some inspiring strategies have been proposed. For example, Chen *et al*. [35] demonstrated the precipitation of PγBL during the ROP, which provided additional driving force shifting the thermodynamic equilibrium toward the ROP direction. Wang *et al*. [72] cleverly improved the monomer conversion by converting the less strained *cis*-cyclooctene to the highly strained *trans*-cyclooctene, while the closed-loop recyclability of the corresponding polymer was retained. Finally, growing insight and knowledge for the manipulation of ROP-RCDP systems are being generated and accumulated with the aid of quantum chemistry simulations, which are indispensable guidance and tools to the rationale design of future monomer/polymer structures.

One ultimate goal of making recyclable plastics is to optimize their thermomechanical properties to a level comparable to polyolefin. Once achieved, they are expected to replace current disposable plastics such as packing materials and mulching plastic film [26,149]. As an important step toward this goal, the semi-crystalline PTE developed by Hong *et al*. [125] demonstrated excellent thermal and mechanical properties resembling commercial LDPE. However, extra considerations such as cost, processing method, and mass manufacturing need to be considered. Moreover, barrier and transport properties including gas penetration and water vapor resistance need to be optimized for package purposes. For food packing and mulching film, biosafety is the utmost factor even before degradability. Apart from

package materials, the PTE and PDS are also promising self-healing materials [150] and triggerable self-immolative polymers by the choice of suitable end-capping reagents [151,152]. Taking advantage of the dynamic nature, the application of PDS in biomedicine, such as cell-penetrating polymers, nanocarriers, and protein-polymer conjugates has been extensively studied [134,138,153]. Compared with conventional biodegradable polyesters, the cascade depolymerization of PTE and PDS may afford a more controllable degradation rate and well-defined degradation species, which could give rise to safer metabolism and clearance of the materials.

Overall, the researches on PTE and PDS are still in the infancy stage, with equal opportunities and challenges lying ahead. With more researchers and efforts devoted to the field, nevertheless, we believe more interesting structures and fascinating material properties are achievable toward more sophisticated applications.

Conflict of interest   The authors declare no conflict of interest.

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