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Design of depolymerizable polymers toward a circular economy

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Transition from the traditional linear economy to a circular economy is the key to reducing the amount of plastic that ends up in the environment and recovering value from the waste. However, energy-efficient, environmentally friendly, and economical technologies to recycle the mounting volume of low-grade plastic waste are lacking when compared to the low cost of primary fossil-based plastic production. This led to extensive efforts to identify methods that mitigate the waste that already exists and develop new polymers to eliminate the poor recyclability problem caused by current materials. Polymers capable of depolymerizing back to their own monomers provide a promising solution. This chemical recycling process has the potential to eliminate contaminants, selectively depolymerize a particular polymer from a waste stream, and recover high-purity monomers from contaminated wastes; however, the process must be energy-efficient and economical. This review discusses recent advances in chemical design of polymers that can depolymerize back to their monomers with an emphasis on strategies that shift the monomer–polymer equilibrium to enable reversible depolymerization and polymerization. Novel approaches developed for ring-opening polymerization and ring-closing depolymerization, reversing free radical polymerization, and reversible reactions that enable depolymerization of highly crosslinked thermosets to small molecular monomers are reviewed. Self-immolative polymers, which have a long history of chemistry innovation to realize the balance between stability and rapid depolymerization, are briefly discussed to serve as an inspiration for new polymer designs. Any new materials designed should have at least matching properties and stabilities compared to existing materials. Thus, this review reflects the status of current research that not only demonstrates the reversible polymerization chemistry but also achieves outstanding material properties.

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1. Introduction

The world is drowning in plastic. This is a result of the traditional linear economic model of taking raw materials from nature, making the product, using it, and then discarding the materials as waste. The desirable qualities that make plastic usage so prolific – durability and stability – are the same qualities causing long-lasting plastic pollution problems. Strategies to improve the sustainability of plastics involve but are not limited to four important aspects: finding renewable feedstocks,[1,2] extending the service life of traditional polymers,[3,4] mitigation of the waste that already exists,[5–7] and the development of new materials to eliminate the poor recyclability problem caused by current materials.[8–12] The production of plastics is in fact more energy efficient than non-plastic alternatives such as glass, aluminum, steel, or paper, requiring roughly half the energy, a fraction of the water consumption, and produces a fraction of the smog.[13] Thus, the issue lies in how plastics are handled post-consumption. One approach to address the end-of-life management is transitioning into a circular economy. A circular economy keeps materials, products, and services in circulation for as long possible, minimizing environmental waste. It reduces material use, redesigns materials, products, and services to be less resource intensive, and recaptures "waste" as a resource to manufacture new materials and products.[14]

Plastic recycling strategies that turn wastes into products are being pursued with intensive efforts from both the industry and the scientific community.[15] The recycling strategies can be categorized into three different cycles (Fig. 1):[16] the polymer loop, the monomer loop, and the molecular loop. The polymer loop refers to the most commonly practiced mechanical recycling where the polymer backbone remains unchanged in chemical composition. This is currently the most common method of recycling well-known post-consumer plastics such as polyethylene terephthalate (PET), high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene (PP). This approach is the most technologically mature and most energy-efficient and should be considered as the first choice. However, mechanical recycling is not suitable for low-grade wastes (highly contaminated wastes, mixed waste streams, products that have been downgraded over many mechanical recycling cycles), thermosets, and applications with high requirements for color, odor, and other properties. In these cases, the monomer and molecular loops offer viable solutions. The monomer loop refers to depolymerizing the polymer backbone into monomers. The monomers are purified and reused to make new polymers. The molecular loop refers to breaking the polymers down into small molecules that require additional steps to form monomers before repolymerization. Processes such as pyrolysis and gasification fall into the molecular loop and are the most energy-intensive processes. Advances in the monomer and molecular loop, have the potential to offer scalable and energy efficient solutions to traditionally non-recyclable wastes and have been the focus of recent research.

Over the last two decades, the pursuit of backbone degradable polymers has expanded significantly from biodegradation[17] and partial degradation,[18] to full backbone depolymerization.[19] The field can be split into two broad categories: (1) chemically recycling of preexisting commodity polymers and (2) development of new polymers to replace current commodity polymers that are more easily recycled. Traditional methods such as hydrolysis, glycolysis, alcoholysis, and aminolysis to recover valuable monomers from commercial polyesters, polyurethanes, polyamides, and polycarbonates have been extensively studied and are seeing increasing success on industrial scale.[20–23] Chemical recycling often faces solvent and energy constrains. Thus, new catalytic systems are being developed to improve the conversion and product

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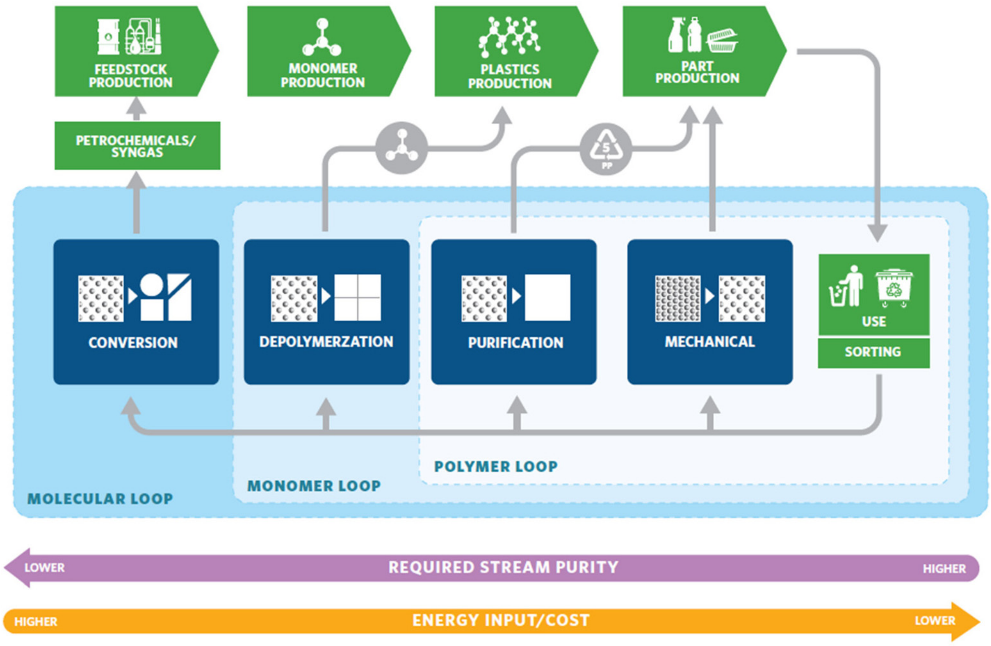


Fig. 1 Diagram for a circular plastic economy. Reproduced from ref. 16 with permission from American Chemical Society, copyright 2020.

selectivity under mild conditions.[24,25] Catalysis and processes such as temperature-gradient thermolysis are paving the way for upcycling of polyolefins.[26–28] Investigations into different solvents,[29,30] and conditions to depolymerize vinyl polymers[31] are also among the forefront of recent progresses. Developing new polymers to replace current ones also have many challenges to be addressed, chief among them is finding materials that have comparable stability and mechanical performances to existing commodity polymers and achieving economic feasibility of scaling up. As mentioned in numerous reviews, we are at an early stage of tackling the plastic waste problem, and therefore multipronged approach should be taken to accelerate the technological advances.[6,10,32]

This review comes at a time when the urge to develop a sustainable polymer economy is at its highest. We will focus our discussion on the redesign of polymer structures capable of the monomer loop *via* depolymerization. Unfortunately, depolymerization is difficult to realize with many existing plastic wastes, especially the widely used polyolefins. New polymers with inherent depolymerizability, repolymerizability, and with performances comparable to various commodity polymers, along with recycling processes that are economically feasible, represent the design goal for the next-generation plastics. This review aims to comprehensively evaluate recent synthetic innovations of depolymerizable polymers focusing on the polymerization and depolymerization chemistries as well as the mechanical performances of the new materials in comparison to commodity plastics. We will first dive into the design methodologies including ring-chain equilibrium, reversing free radical polymers, and depolymerizable crosslinked thermosets. For the ring-chain equilibrium enabled recycling, in addition to the enthalpy-driven ring-opening polymerization (ROP) of strained cyclic monomers, we will highlight entropy-driven ring-opening polymerization (ED-ROP) as an emerging method of chemical recycling, such as polycarbonates and polydithioacetals, which have not been discussed in extent in prior reviews. We also include a brief discussion of self-immolative polymers (SIPs) considering the rich chemistries that have been developed in the field of SIP since its introduction in 2008[33] that offer inspirations for recyclable polymer design. Finishing out this review are design parameters that should be considered moving forward. Due to the rapid progress in polymer recycling in the last five years, we limit the scope of this review to examples of degradable polymers that recycle back to monomers with high yields and exclude the ones that degrade to oligomers.

2. Depolymerizable polymers based on ring-chain equilibrium

In recent years, there has been significant focus on using reversible ring-opening polymerization (ROP) to develop recyclable polymers. Cyclic monomers and their corresponding polymers have the same types of bonding. It follows then that the thermodynamics can be tuned by the ring-strain energy (RSE) and the entropy change of polymerization with high sensitivity to reaction conditions, including temperature and concentration. To understand how the thermodynamics can be tuned, we can start by viewing polymerization as a reversible reaction:

$$M_n^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^* \qquad (1)$$

When the rate of polymerization equals the rate of depolymerization, an equilibrium is reached. For most monomers, the equilibrium greatly favors the product due to the large enthalpic driving force. At higher temperatures, the rate constant of depolymerization (k_{dp}) increases more rapidly than polymerization (k_p), which shifts the equilibrium to the monomer side. This usually occurs above the polymer's decomposition temperature. Therefore, in pursuit of depolymerizable polymers, the strategy is to identify monomer–polymer systems that are near their thermodynamic equilibrium.

The ROP offers several advantages. The ring-closing depolymerization (RCD) and ROP cycles do not generate any side products. Polymers with a variety of heteroatom backbones similar to step-growth polymers can be prepared, but with much higher molecular weights. The ring-opening metathesis polymerization (ROMP) of cycloalkenes form polymers with all hydrocarbon backbones, which are promising replacements for polyolefins. Even being near equilibrium, the ROP polymers sustain high thermal stability in the absence of catalysts. Although we used the term "ring-chain equilibrium" here, the polymer "chain" can also be a cyclic polymer. Cyclic polymers have even higher stabilities than their linear counterparts due to the absence of end groups.[34] Functional groups can be conveniently introduced *via* ring modifications. Thus, ROP offers high control over both the polymer structure and polymerization–depolymerization equilibrium.

2.1 Tuning the thermodynamics of ring-chain equilibrium

There are two types of ROP, enthalpy-driven ROP for small to medium sized rings with ring-strains, and entropy-driven ROP (ED-ROP) of strainless macrocyclic rings (Fig. 2). This section will discuss how to control the equilibrium positions between the monomer and the polymer during the polymerization and depolymerization cycles. For these ROPs, both the enthalpy and entropy terms play a role in determining the equilibrium position.

Enthalpy-driven ROP. Polymerization of small to medium-sized rings is driven by the release of ring strain energy (RSE), resulting in a negative enthalpy change (ΔH_p). The entropy of polymerization (ΔS_p) has two different contributions, translational and conformational entropies. Enthalpy-driven ROP usually has a negative ΔS_p due to the larger loss of translational entropy over the gain of conformational entropy. Thus, the Gibbs free energy of polymerization (ΔG_p) is highly sensitive to the RSE, and RSE can be fine-tuned with ring-size and ring-substitutions. Here we use well-studied cyclic ester monomer as an example to illustrate the general thermodynamics and structural effects that RSE has on the polymerization and depolymerization equilibrium, which are summarized in detail in a review paper by Albertsson *et al.* (Fig. 3).[35] In the next section, we will dive into the specific chemistries and materials.

Fig. 3a shows the differences in ΔG_p as a function of ring size. Compared to the 4-membered ring, 5- and 6-members rings are promising candidates for depolymerizable polymers as they are closer to their equilibrium ($\Delta G_p = 0$) at 25 °C. With near equilibrium systems, they tend to yield a mixture of monomers and low molecular weight polymers. Thus, the questions are, how to push the equilibrium to the polymer side to obtain high monomer conversion and high molecular weight polymers, and conversely how to shift the equilibrium to the monomer side quantitively.

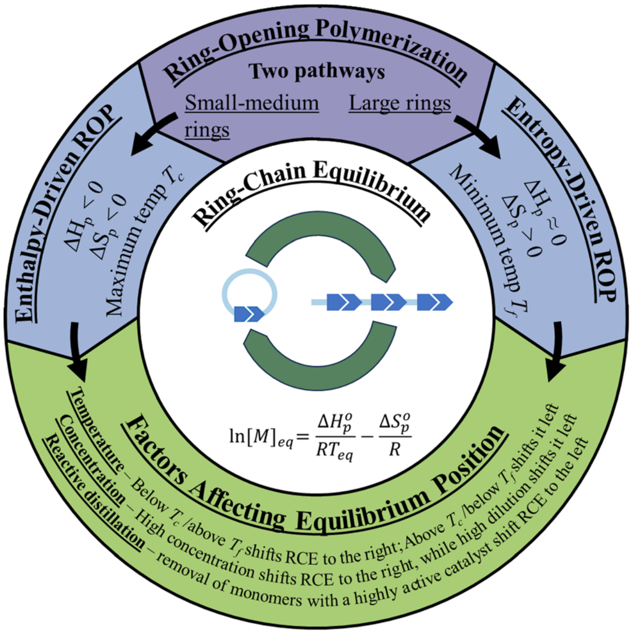


Fig. 2 Graphic depiction of the two pathways of ROP and the factors affecting the ring-chain equilibrium.

The equilibrium control is best described by the Dainton and Ivin equation:[36]

$$\ln[\mathrm{M}]_{\mathrm{eq}} = \frac{\Delta H_{\mathrm{p}}^{\circ}}{RT_{\mathrm{eq}}} - \frac{\Delta S_{\mathrm{p}}^{\circ}}{R} \tag{2}$$

where $[\mathrm{M}]_{\mathrm{eq}}$ is the equilibrium monomer concentration and T_{eq} is the temperature at which equilibrium is reached. Eqn (2) describes the important relationships about how the equilibrium position $[\mathrm{M}]_{\mathrm{eq}}$ changes with temperature, $\Delta H_{\mathrm{p}}^{\circ}$, and $\Delta S_{\mathrm{p}}^{\circ}$. This relationship is derived from the equilibrium condition. At equilibrium, $\Delta G_{\mathrm{p}} = \Delta G_{\mathrm{p}}^{\circ} + RT_{\mathrm{eq}} \ln K_{\mathrm{eq}}$. When $\Delta G_{\mathrm{p}} = 0$, the equilibrium constant $K_{\mathrm{eq}} = \frac{[\mathrm{M}_{n+1}^{*}]}{[\mathrm{M}_{n}^{*}][\mathrm{M}]_{\mathrm{eq}}} = \frac{1}{[\mathrm{M}]_{\mathrm{eq}}}$. Combining these equations gives eqn (2), which can be rewritten as

$$T_{\mathrm{eq}} = \frac{\Delta H_{\mathrm{p}}^{\circ}}{\Delta S_{\mathrm{p}}^{\circ} + R \ln[\mathrm{M}]_{\mathrm{eq}}} \tag{3}$$

Thus, a ceiling temperature (T_{c}) is defined to describe a scenario where the equilibrium lies on the very left side. It is the temperature at or above which the concentration of monomer in equilibrium with its polymer becomes essentially equal to the initial monomer concentration ($[\mathrm{M}]_0$).

$$T_{\mathrm{c}} = \frac{\Delta H_{\mathrm{p}}^{\circ}}{\Delta S_{\mathrm{p}}^{\circ} + R \ln[\mathrm{M}]_0} \tag{4}$$

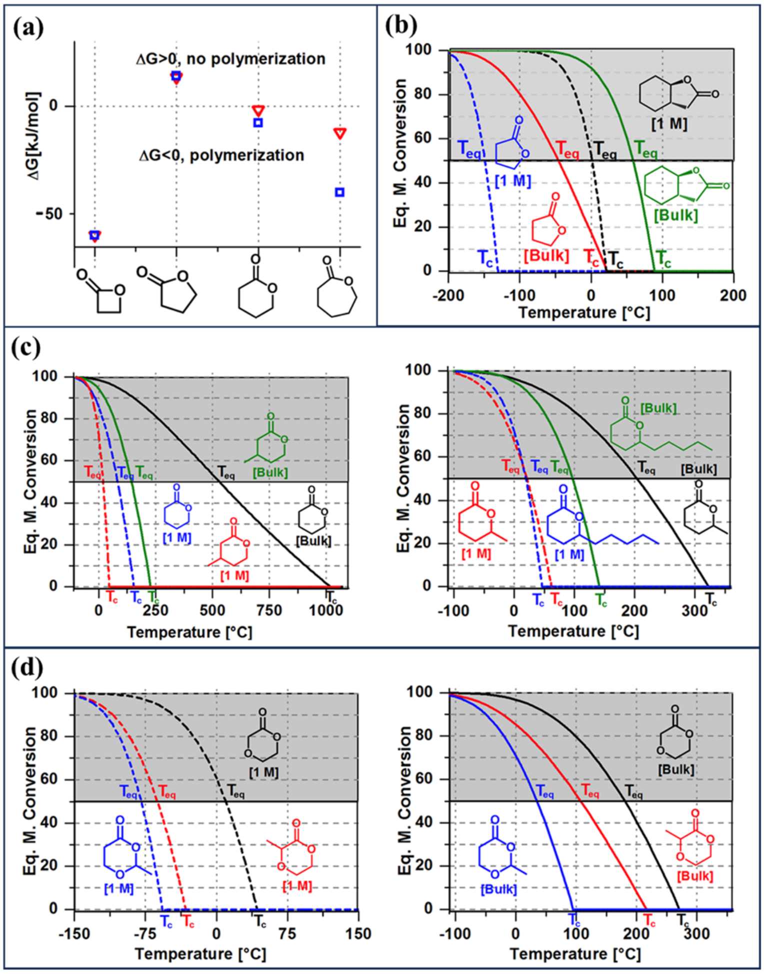


Fig. 3 Thermodynamic considerations for ring opening polymerization. (a) The difference in ΔG_p as a function of ring-size at normal pressure and 25 °C. (b) The effect of fused-ring on the equilibrium monomer conversion as a function of temperature of γ-lactones. (c) The effect of ring-substituents of various lengths on the equilibrium monomer conversion of δ-lactones. (d) The effect of substituent position on the equilibrium monomer conversion of ether-δ-lactones. For each monomer shown in figures (b)–(d), the equilibrium monomer conversion over temperature curves are shown for two starting monomer concentrations, bulk and 1 M. Reproduced from ref. 35 with permission from American Chemical Society, copyright 2016.

Usually, T_c is reported for $[M]_0$ at unit molarity or bulk state; however, one can see that T_c is a function of $[M]_0$ and that it decreases with dilution. ΔH_p° can be adjusted by RSE and ΔS_p° can be fine-tuned by the size of the monomer.

Thus, eqn (2) and (4) give us a general guideline to control the equilibrium, an example of which is illustrated in Fig. 3b–d for lactones with different ring-size and substituents. The characteristic behavior of enthalpy-driven ROP is shown in equilibrium conversion *vs.* temperature curves, where increasing the temperature shifts the equilibrium to the left, promoting depolymerization. Conversely, lowering the temperature induces propagation due to the negative ΔS_p°. The T_{eq} shown in Fig. 3 is defined as when $[M]_{eq}$ is 50% of the starting monomer concentration, $[M]_0$. As the temperature continues to increase, T_c is reached and the monomer conversion drops to zero. The concentration dependency of T_c modeled in eqn (4) is shown in Fig. 3 as T_c drops going from bulk polymerization to a starting $[M]_0$ of 1 M.

Equilibrium control that relies exclusively on temperature and concentration is quite limited. For example, γ-butyrolactone is difficult to polymerize as it has an extremely low T_c even in bulk. Thus, design tools that change the ΔH_p° and ΔS_p° values are extremely useful. A fused-ring approach is commonly used to increase the RSE, and thus the T_c, to make the monomer more polymerizable. This is shown in Fig. 3b, where T_c increases by over 100 °C when γ-butyrolactone is fused with a cyclohexane ring. In certain cases a fused-ring strategy can also decrease the ring-strain energy.[37] Ring-substitutions that do not create a fused ring usually decrease the T_c. As shown in Fig. 3c, six-membered δ-lactones have quite high T_c's even though its ΔG_p is slightly below zero; however, a large drop of T_c is observed in ring-substitutions with aliphatic groups of increasing length. The trend can be explained by the Thorpe–Ingold effect: as the steric hinderance of a substituent increase, the molecule will favor ring closure and intramolecular reactions.[38] This effect is more profound at high concentrations but become negligible in certain cases at 1 M monomer concentration (Fig. 3c). The position of the substitute also plays an important role on the thermodynamics as demonstrated by Fig. 3d. Hillmyer *et al.* showed that polymerization rate depends strongly on substituent position and exhibits a more modest dependence on alkyl length (from $-CH_3$ to $-(CH_2)_8CH_3$) under bulk room temperature conditions. However, the physical properties of the resulting aliphatic polyesters depend much more on substituent length than on substituent position.[39]

Entropy-driven ROP (ED-ROP). When the ring-size gets bigger, the RSE disappears, leading to a negligible ΔH_p. The loss of translational entropy decreases as the size of the monomer increases, until it cannot compensate for the increase of conformational entropy, and ΔS_p becomes positive. Polymerization does not involve much heat, but rather is driven by the overall increase of entropy.[40,41] This type of ROP is characterized by a floor temperature (T_f) when ΔH_p and ΔS_p are both positive. While T_f is defined with the same equation as T_c (eqn (4)), polymerization only occurs above the T_f which is characteristic of ED-ROP. The earliest known examples are the polymerizations of elemental sulfur, selenium octamer, and octamethylcyclotetrasiloxane. Their ΔH_p are 9.5, 13.5, and 6.4 kJ mol^{-1}, respectively, with ΔS_p being 27, 31, and 190 J K^{-1} mol^{-1}, respectively.[42] Recently, ED-ROP has been studied as an alternative approach to synthesizing traditional step-growth polymers of high molecular weight, and has been successful for silyl ethers,[43] lactones,[44–47] disulfides,[48] carbonates,[49] hemoglobin,[50] and other new polymerization chemistries.[51] The main challenge has been the synthesis of macrocyclic monomers. In theory, macrocyclic monomers can be obtained from the RCD of the corresponding polymers synthesized from a non-ROP route at temperatures below T_f under dilute conditions. The Odelius group also showed the generation of macrocyclic monomers through sublimation of the corresponding polymers to avoid the use of solvents.[49]

With a negligible ΔH_p, ED-ROP exhibits high sensitivity to temperature and concentration which originates from the $T\Delta S_p$ contribution to the overall ΔG_p. Opposite of the enthalpy-driven ROP, ED-ROP is favored at higher temperatures due to the positive ΔS_p. Reversible ED-ROP systems with near-quantitative depolymerization have been sporadically reported.[40,41,51] There remains an unexplored design space for ED-ROP-based chemically recyclable polymers. Comparatively, enthalpy and entropy driven ROP are similar in that they both utilize the unique chemical environments present in cyclic monomers, albeit of different sizes. They share many attractive features, such as the perfect stoichiometry and no emission of small molecules or volatiles, making them eco-friendly. ED-ROP also exhibits unique advantages.[41] Virtually no heat is evolved during ED-ROP because the mixtures of homologous macrocycles are often strainless. In addition, the macrocyclic monomers are usually solids which are easy to store and transport. Thermal stability is less of a concern even in the presence of catalyst because polymerization is favored at high temperatures. As such, strict requirements for catalyst removal, which can be difficult such as when making thermosets, becomes unnecessary. In comparison, low T_c polymers derived from strained cyclic monomers need strict catalyst removal to avoid depolymerization that can be activated at higher temperatures.

Depolymerization strategies. Depolymerization is conducted with two different approaches, high dilution which lowers T_c or increases T_f, and reactive distillation that drives the reaction to the monomer side. These strategies apply to both enthalpy- and entropy-driven ROPs, although macrocycles are more difficult to be distilled off.

The concentration dependency of the equilibrium is illustrated in Fig. 4. Monomers have higher translational entropy, whereas polymers exhibit higher conformational entropy. Under concentrated conditions, the conformational entropy dominates, shifting the equilibrium to the polymers. At low concentrations, translational entropy dominates and the equilibrium shifts to the monomer side. Thus, high dilution significantly decreases the depolymerization temperature.

The use of solvent can be avoided by reaction distillation, although the trade-off is the higher processing temperature required. Ideally, depolymerization should be carried out at temperatures well below T_c to obtain depolymerization in high yields. However, for polymers with intermediate to high T_c's, depolymerization is possible above the T_c under reactive distillation. Monomers are removed as soon as they are formed, which shifts the reaction out of equilibrium and toward the monomer formation. This process requires a highly reactive catalyst to activate the exchange reactions that enable monomer formation *via* ring-closing depolymerization. Byers group found that $ZnCl_2$, when combined with poly(ethylene glycol), forms a particularly active catalyst that works universally for RCD of a variety of polyesters and polycarbonates.[52] The catalyst induces random chain scissions, allowing monomer recovery under distillation at 160 °C, which is near or below the T_c of the polymers ($153\ ^\circ C < T_c < 261\ ^\circ C$). The use of more reactive catalysts is expected to further lower the distillation temperature.

In the following sections 2.2–2.6, we will introduce specific examples of depolymerizable polymers synthesized from enthalpy- and entropy-driven ROPs.

2.2 ROP of lactones and thiolactones

Polyesters are the world's fourth-most produced synthetic polymer, after polyethylene, polypropylene, and polyvinylchloride, making them the most used heterochain polymer in plastic bottles and fabrics. Polyester is also the most recyclable commodity polymer. Recycled polyethylene terephthalate (PET) bottles are shredded, washed, and then used for remaking the bottles or spinning into fibers. However, low-quality PET waste, such as polyester carpeting wastes, rely on chemical recycling, including hydrolysis, glycolysis, methanolysis, and enzymatic recycling to recover valued products, or otherwise be downcycled. Chemical recycling approaches are being actively investigated to identify energy efficient and environmentally benign processes[53–58] with commercialization efforts from industry on a global scale.[59,60]

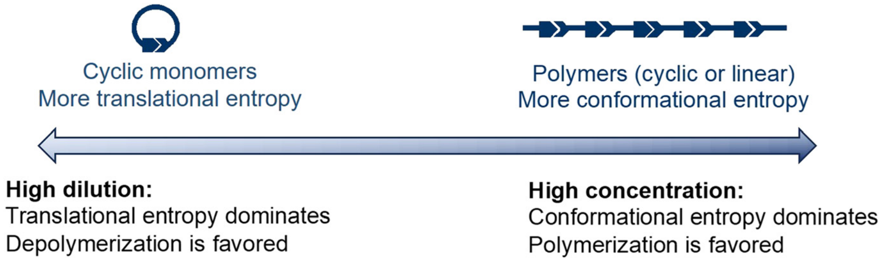


Fig. 4 Graphical depiction of the effect of concentration on the ring-chain equilibrium.

Commercial polyesters are typically synthesized from step-growth polymerization (Fig. 5a). However, new advances in the ROP of lactones have led to high molecular weight polyesters with thermal and mechanical properties that are outperforming polyolefins, while still maintaining their recyclability *via* RCD. The cyclic monomers can be derived from biomass through simple steps, thereby reducing the need for petrochemical starting materials. Two approaches are used to tackle the recyclability. One is to develop new synthetic strategies for cyclic monomers that are usually considered as non-polymerizable due to low RSEs, such as 5-membered γ-butyrolactone (γBL). The corresponding polymers have low thermodynamic stability (low T_c) but can be kinetically stabilized. They easily depolymerize under ambient conditions with a catalyst. The other approach is to depolymerize high T_c polymers, which are traditionally considered as non-depolymerizable. Reaction distillation has thus far been extensively investigated and Fig. 5 summarizes the recent progress, ranging from 4- to 6-membered cyclic esters.

The first example shown in Fig. 5b is a new polyhydroxyalkanoate (PHA) synthesized from substituted four-membered β-lactone. PHAs have long been of interest as sustainable plastics because of their biorenewability, biocompatibility, and biodegradability in the ambient environment. They are typically biosynthesized from microorganisms, or abiotically *via* polycondensation of hydroxyacids. ROP of 4-membered β-lactones or 8-membered diolides are also commonly used. However, despite the extensive research,[61,62] industrial applications of PHAs are limited by the long-standing challenges of lack of melt processability, mechanical brittleness, and unrealized closed-loop recyclability. The Chen group addressed these challenges using α,α-dialkylated β-butyrolactone ($(Me)_2BL$) as the monomer, which eliminates the α-hydrogens in PHA.[63] The backbone α-hydrogen causes the facile *cis*-elimination responsible for PHA's thermal instability. This causes the molecular weight to decrease during melt-processing conditions as often observed for unsubstituted PHA at only 180 °C. ROP of $(Me)_2BL$ proceeds with a superbase catalyst ^tBu-P_4 {1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranyliden-amino]2λ^5,4λ^5-catenadi(phosphazene)}, affording well-controlled molecular weight ranging from 43.0 to 554 kg mol^{-1}. Compared to unsubstituted PHA, this new polymer exhibited 56 to 85 °C enhancement of thermal stability, enabling melt-processing. The polymer showed a rare case of tacticity-independent crystallinity with T_m of 167 and 176 °C for the atactic polymer, and it increased to 243 °C for the isotactic counterpart. The α,α-dialkyl substitution along with the high molecular weights also overcame the brittleness (Fig. 6a). Degradation was most efficient *via* hydrolysis in aqueous lithium hydroxide, affording the hydroxy acid ($3H(Me)_2BA$). The 4-membered monomer can reform from the degradation product *via* a one-step cyclization. Although $3H(Me)_2BA$ can directly polymerize *via* step-growth polymerization, it only yielded oligomers or low molecular weight polymers. Synthesis of the virgin $(Me)_2BL$ monomer was demonstrated on a 200 g scale, and the starting compounds can be bio sourced.

Opposite of the 4-membered β-lactones, 5-membered γ-butyrolactones (γBL) have less RSEs and were considered non-polymerizable. This limitation was tackled by polymerizing γBL at −40 °C.[34] The low temperature compensates for the entropy loss. Solvent was selected so that the polymers formed precipitates from the solution in a crystalline state to further shift the equilibrium toward propagation. Under ambient pressure with a proper catalyst, this approach yielded 90% monomer conversion and polymer molecular weights up to 30 kg mol^{-1}.[34] Although T_c of the poly(γ-butyrolactone) (PBL) is low (−9 and −136 °C for $[M]_0 = 10$ M and 1 M, respectively), the polymer was shown to be kinetically stable up to 300 °C without catalysts. Catalyzed by a strong base such as DBU, depolymerization proceeded rapidly within minutes at just room temperature due to the low T_c. Despite the success in polymerization, PBL suffers from low mechanical robustness and impractically low synthetic temperature. This was addressed by *trans*-ring fusion at the β and γ positions as shown in Fig. 5c, monomer **M1**, which effective increases the ring-strain energy.[64] As a result, the T_c was enhanced by over 100 °C compared to γBL and polymerization of **M1** proceeded at room temperature, reaching a much higher molecular weight of 875 kg mol^{-1} for the resulting polymer. The presence of cyclohexanyl groups in the backbone increased both the T_g and T_m by over 100 °C as well. The mechanical strength was improved; however, the maximum strain did not surpass 20% (Fig. 6b). With a higher T_c, the depolymerization temperature increased to 120 °C catalyzed by $ZnCl_2$, which provides enhanced room temperature stability. It should be noted that the γBL monomer can be produced from succinic acid, a fermentation product from glucose.

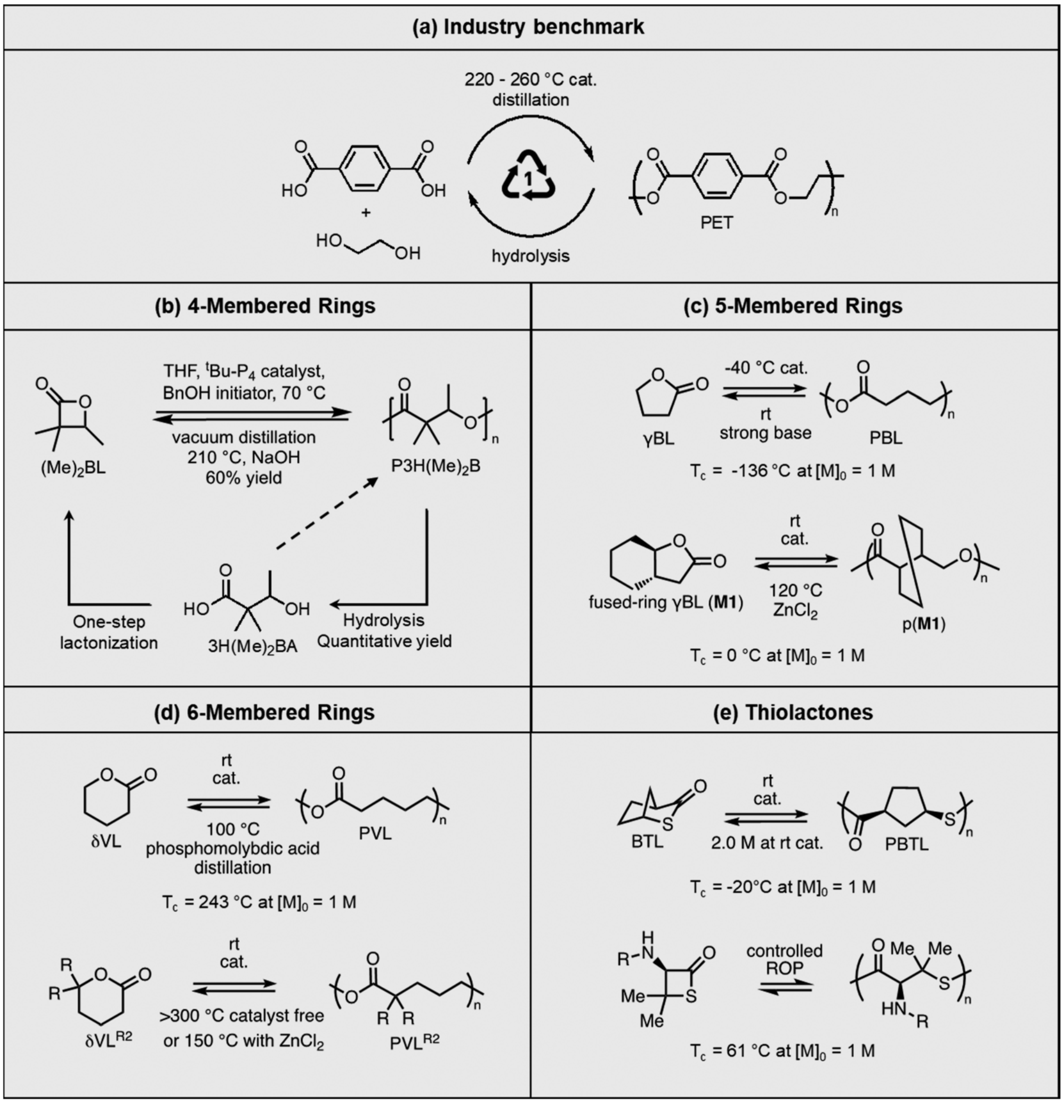


Fig. 5 Polymerization and depolymerization of various polyesters. (a) Chemical recycling of PET currently used in industry. (b) Recycling between α,α-dimethyl-β-butyrolactone ((Me)$_2$BL) and its polymer (P3H((Me)$_2$B) (ductile; T_m = 243 °C; T_d = 335 °C). c) Top: recycling between γ-butyrolactone (γBL) and its polymer (PBL) (brittle; T_g ~ −52 °C; T_m ~ 60 °C; T_c = −9 °C at $[M]_0$ = 10 M); bottom: recycling between fused-ring-γBL (**M1**) and its polymer (p**M1**) (slightly ductile; T_g ~ 50 °C; T_m ~ 188 °C; T_c = 88 °C at $[M]_0$ = 8 M). (d) Top: recycling between δ-valerolactone (δVL) and its polymer (PVL) (ductile; T_g ~ −53 °C; T_m ~ 57 °C; T_d > 300 °C); bottom: recycling between *gem*-dialkyl-substituted δVL (δVL^{R_2}) and its polymer (PVL^{R_2}) (highly variable thermal and mechanical properties depending on the position and length of the R groups). (e) Top: recycling between 2-thiabicyclo[2.2.1] heptan-3-one (BTL) and its polymer (PBTL) (ductile; T_m = 166–213 °C; T_d > 320 °C); bottom: geminal dimethyl substituted penicillamine-derived β-thiolactone (N^R-PenTL) and its polymer (PN^R-PenTL) (brittle at rt; T_g = 50 °C; T_m = 100 °C; T_d = −192 °C).

The 6-membered lactone, δ-valerolactone (δVL) has a higher RSE compared to the 5-memberd γBL. It leads to a tendency towards ROP; however, with a high T_c of 298 °C at $[M]_0$ = 1 M, the polymer is difficult to recycle. In this case, a kinetic approach that shifts the equilibrium to depolymerization by removing the monomer *via* solvent-free vacuum distillation proved to be feasible (Fig. 5d).[65] Its success relies on highly active catalysts. With 2.0 mol% of ZnCl$_2$ under 0.07 Torr pressure at 150 °C, which is below the T_c, the monomer was recovered in 99% yield. When catalyzed by an inorganic polyacid, phosphomolybdic acid (PMA), at 2.0 wt%, the depolymerization preceded at only 100 °C, recovering 98% of the monomer in 3.5 h. The use of more active catalysts allows for vacuum distillation at lower temperatures and improved energy efficiency.

The properties of PVL are tunable *via* ring substitutions. Monoalkyl-substituted δVL gives amorphous polymers, allowing for the use in soft elastomers.[39] Racemic carbomethoxy substitution at the γ-position surprisingly gave a semi-crystalline polymer (T_m = −7–95 °C varied by the length of substituents).[68,69] A strategy to further increase the melting transition temperature was demonstrated using gem-dialkyl-substitution that eliminated the stereogenic center. As shown in Fig. 5d, polymers formed from δVL^{R_2} monomer exhibited a

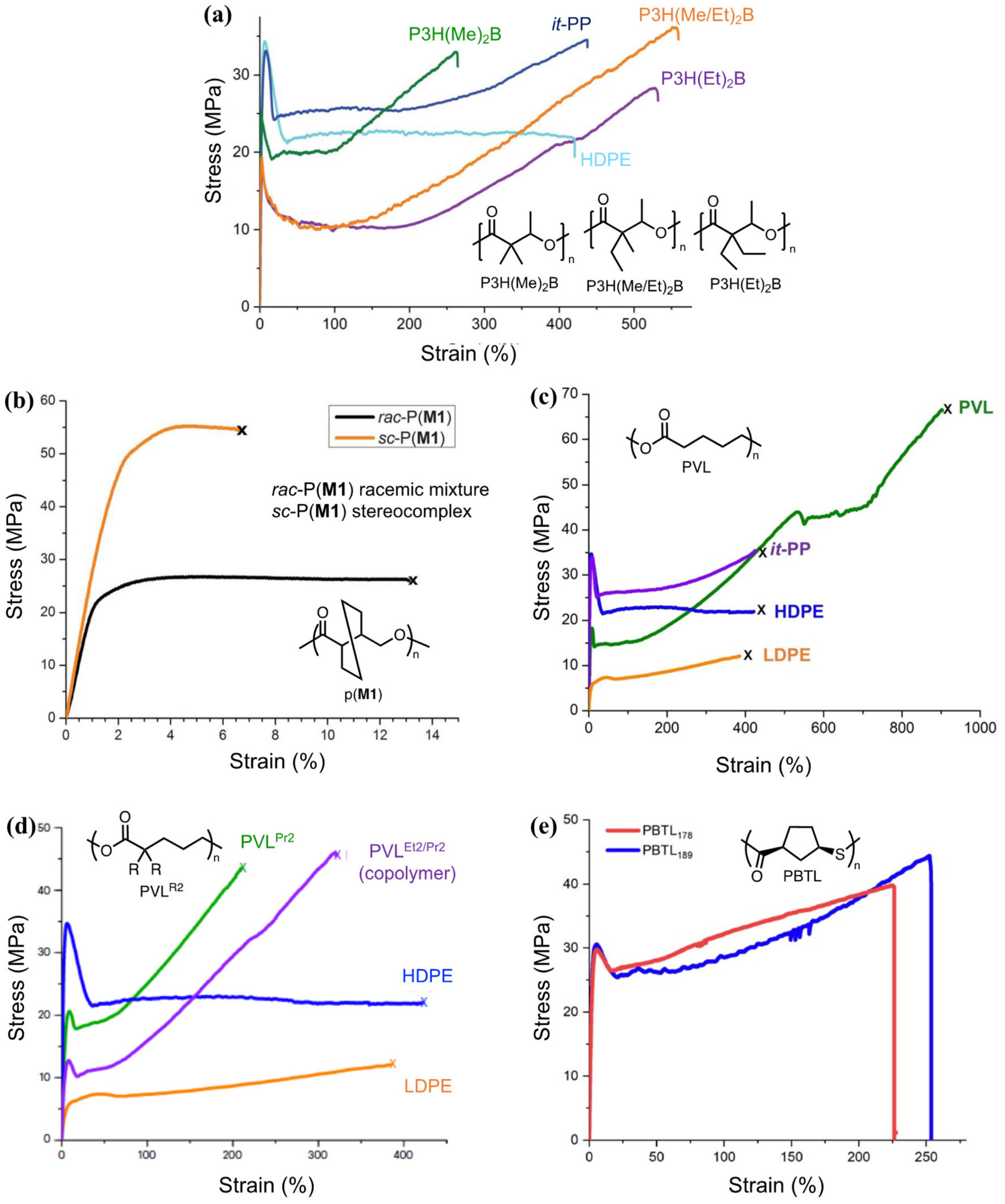


Fig. 6 A side-by-side comparison of the tensile curves of various circular polyesters, polythioester, in comparison to isotactic polypropylene (it-PP), high-density polyethylene (HDPE), and low-density polyethylene (LDPE). Details about their syntheses and recycling properties are shown in Fig. 5. (a) is reproduced from ref. 63 with permission from AAAS, copyright 2023. (b) is reproduced from ref. 64 from AAAS, copyright 2018. (c) is reproduced from ref. 65 with permission from Wiley, copyright 2023. (d) is reproduced from ref. 66 with permission from Springer Nature, Copyright 2023. (e) is reproduced from ref. 67 with permission from AAAS, copyright 2020.

wide range of T_c from 67–115 °C and T_m from 44–140 °C depending on the length of the alkyl substituents, making it a highly tunable circular platform with mechanical properties comparable to polyolefins (Fig. 6c and d).[66]

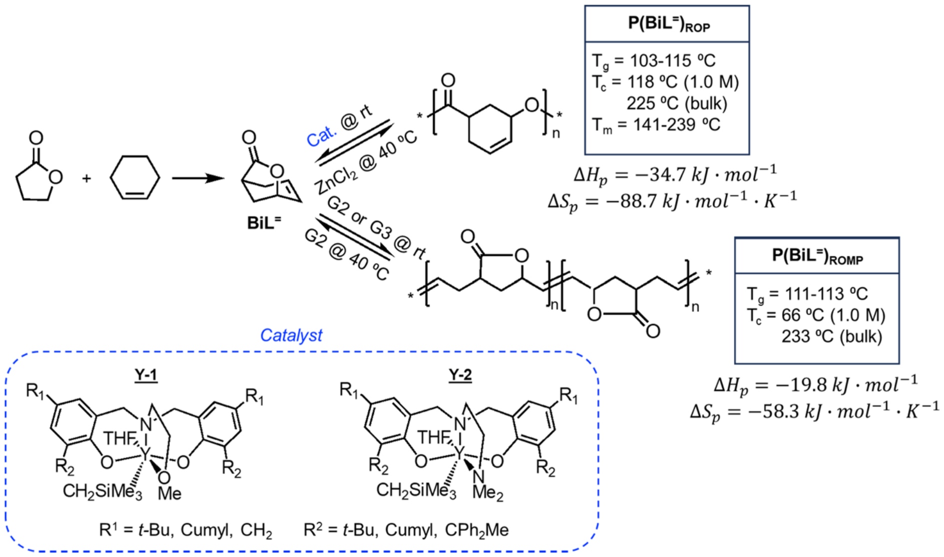
The success of recyclable polyesters inspired the studies on polythioesters. Replacing oxygen with sulfur changes the monomer RSE. The 4- and 7-membered thiolactones readily polymerize *via* anionic[70,71] or free radical initiated ROP,[72] but 5- or 6-membered rings are difficult to polymerize.[73] Thioester is more reactive than ester toward nucleophiles and makes a promising candidate for use in dynamic polymers.[74] Although the 5-memberd γ-thiolactone is reluctant to polymerize, its bridged bicyclic form, 2-thiabicyclo[2.2.1]heptan-3-one (BTL), polymerizes at room temperature to high molecular weight poly(2-thiabicyclo[2.2.1]heptan-3-one) (PBTL) (Fig. 5e, top).[67] With a low T_c of −20 °C at $[M]_0$ = 1 M, PBTL depolymerizes easily at room temperature. PBTL also exhibits unique intrinsic crystallinity. The atactic PBTL has a T_m of 166 °C which increases to 213 °C with 100% tacticity, and the degree of crystallinity and tacticity can be fine-tuned within this range through catalyst control. The tensile properties of PBTL closely resemble polyolefins (Fig. 6e). Fully recyclable polythioesters have also been demonstrated for γ-thiolactone bridged with pyrrolidine, giving an amorphous polymer with relatively low dispersity ($Đ$ = 1.32) even when reaching a molecular weight of 226 kg mol^{-1}.[75] β-Thiolactone (4-membered ring, Fig. 5e, bottom) modified with geminal dimethyl group and a secondary amine group also shown to be easily recyclable although the semicrystalline polymer is brittle.[76] The ultimate advantage of the last two systems is that the amine groups allow for post-polymerization modifications.

There is one more interesting avenue of synthesis using lactones by employing a hybrid monomer. The Chen group developed a bicyclic lactone/olefin hybrid of γ-butyrolactone (γ-BL) and cyclohexene.[77] This hybrid monomer can produce two different polymers depending on the catalyst employed: polyester *via* ROP (P(BiL$^{=}$)$_{ROP}$) and functionalized poly(cyclic olefin) *via* ROMP (P(BiL$^{=}$)$_{ROMP}$) (Scheme 1). The polyester synthesized is semicrystalline with a high T_g (103–115 °C) and a T_m in the 141–239 °C range, while the poly(cyclic olefin) is amorphous with a T_g of 111–113 °C. The tacticity of polymers can be controlled *via* catalyst selection. Both polymers are thermally robust and depolymerize under mild conditions (25–40 °C) with the appropriate depolymerization catalyst. The hybrid monomer can then be cleanly recovered *via* chain unzipping (ROP) or scission (ROMP). The functional groups remain intact post polymerization (double bond in ROP, lactone in ROMP) allowing for further tuning of thermal and mechanical characteristics. The versatility of the hybrid monomer shows promise and demonstrates that it is possible to have a closed polymer system with the application of an orthogonal polymerization/depolymerization strategy and prompts the investigation into other hybrid monomer systems.

The studies discussed above showed similar characteristics for polymers derived from various lactones and thiolactones. They are strong, semicrystalline polymers with high melting transition temperatures. The T_m is adjustable *via* stereocontrol and substitutions. Amorphous polymers form with large substituents. Fig. 6 which summarizes the tensile properties of the various polymers discussed in Fig. 5, shows that their Young's moduli, yield stress, and ductility are comparable or even surpass those of polyolefins, showcasing their potential as polyolefin replacements. The p(**M1**) is not particularly ductile but exhibits high tensile stress under low strain. It is noteworthy that the high mechanical performance is realized through not only the monomer design, but also synthetic techniques that involve the design of the catalyst, initiator, solvent, and reaction conditions to enable well-controlled polymerization leading to high molecular weight polymers. Their low molecular weight counterparts are usually brittle. Chemistry innovation is the key in such material designs even though details about the reaction systems are not discussed extensively in this review.

2.3 Ring-opening metathesis polymerization (ROMP) of cycloalkenes

ROMP of cycloalkenes is particularly attractive for the design of recyclable polymers as it produces all-hydrocarbon backbones without heteroatoms. Upon complete removal of the catalysts, these polymers are suitable for applications where



Scheme 1 Hybrid monomer design and polymerization. Reproduced from ref. 77 with permission from American Chemical Society, copyright 2022.

greater hydrolytic and thermal stability are necessary. ROMP is based on the mechanism of olefin metathesis of strained cycloalkenes catalyzed by a transition metal alkylidene complex, most famously the ruthenium-carbene Grubbs catalysts. This chain-growth polymerization produces stereoregular polymers with low dispersity, high molecular weight, and consequently outstanding mechanical performance being either rigid or flexible. ROMP has been used for industrial production of *trans*-polyoctenamer (a reactive plasticizer used in the rubber industry), polynorbornene elastomer, and poly(dicyclopentadiene) (for reaction injection molding of large engineering parts). Traditionally, ROMP is irreversible due to the release of significant RSE; however, by lowering the ring-strain, a near-equilibrium system that undergoes ring-closing metathesis (RCM) to regenerate the monomer can be realized.

Rings such as cyclopropene and cyclobutene have RSEs that are too high to allow for realistic depolymerization, and the RSE of cyclohexene is too low to enable polymerization at all. With the relative rarity of cycloheptenes, that leaves cyclopentenes and cyclooctenes as promising candidates with the appropriate amount of RSE to enable recyclability.[78]

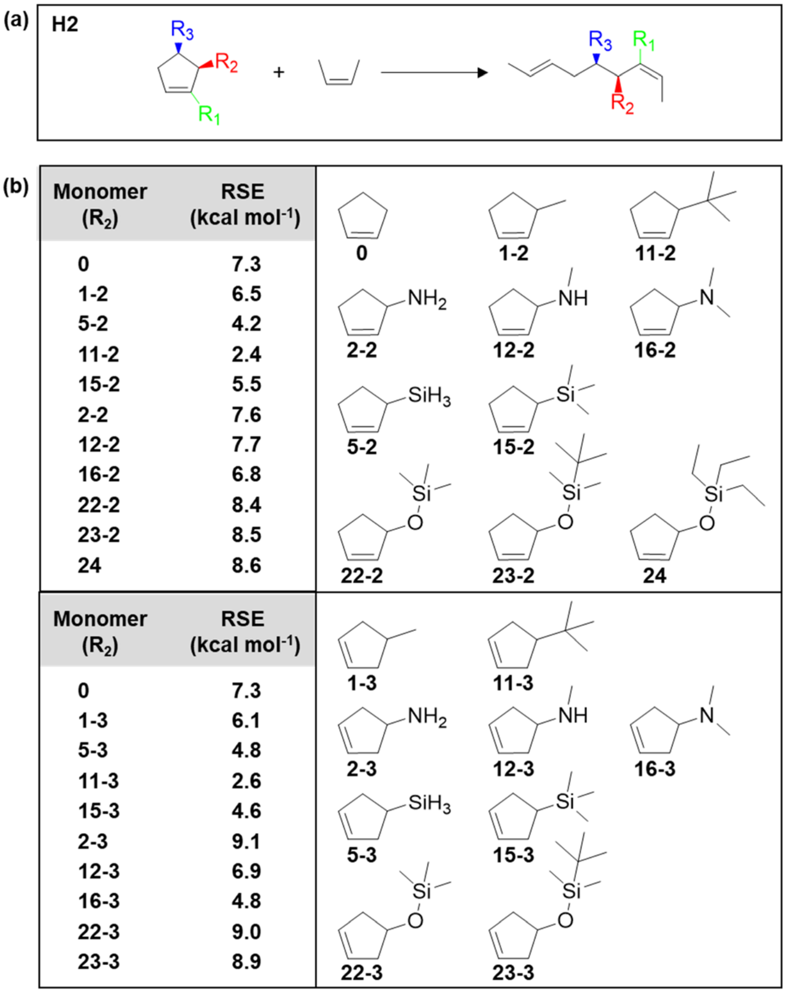
Polypentenamers from cyclopentenes have been shown to depolymerize since 1972.[79] The early work on ROMP of cyclopentenes took place in industry driven by their similarities to natural rubber but was limited by synthetic challenges. Recent advances in synthetic approaches and understanding of the fundamental mechanisms allow the synthesis of polypentenamers with high molar mass, low dispersity, and precise microstructures.[80–82] These polymers exhibit interesting elastomeric properties which strongly depend on *trans*/*cis* content and pendent groups. *trans*-Polypentenamers showed a strain-induced crystallization which provides self-reinforcement effect similar to natural rubber.[83] Precise placement of phenyl pendent groups produced an ethylene–styrene copolymer structure that behaves as a strong elastomer.[84] Polypentenamers synthesized from cyclopentene can depolymerize in solution.[85,86] They have also found their way into bottlebrush copolymers that depolymerize *via* end-to-end unzipping instead of random scission like unmodified polypentenamers.[87] Since polypentenamers are soft and amorphous, they are suggested as recyclable tire additives.[88]

The Xia group discovered that the five-membered enol ether ring, 2,3-dihydrofuran, can undergo ROMP with Grubbs catalysts,[89] even though enol ethers have been used as quenching agents for Grubbs catalysts and thus viewed as terminating agents for ring-opening reactions as opposed to monomers. Thermodynamics for the ROP of 2,3-dihydrofuran is like cyclopentene and rubbery polymers with a M_n up to 127.7 kg mol^{-1} can be obtained at room temperature with a $T_g = -50.5$ °C and a subzero T_c. The deactivation of the catalyst following the metathesis reaction was done by cleaving the catalyst through peroxide oxidation and provides thermal stability up to 320 °C. Depolymerization in the bulk state at 60 °C by 0.01 mol% of Grubbs second-generation catalyst (G2) recovered >90% pure monomer after only 2.5 h. Its polymerizability is promising for a compound previously considered as only a quenching agent.

The ring strain energy of cyclopentene prevents bulk depolymerization of polycyclopentene under ambient conditions. The Moore group addressed this limitation by attaching bulky substituents directly on the cyclopentene ring.[90] The substituents significantly lowered the T_c, with more pronounced decrease for bulker substituents, which can be attributed to a smaller loss of entropy (ΔS_p). Depolymerization in the bulk was achieved in the 50–100 °C temperature range with different substituents. Crosslinked networks were formed with bifunctional and trifunctional monomers which proved to be thermodynamically stable and mechanically robust at room temperature, but readily depolymerizing above bulk T_c to give liquid monomers that can be repolymerized through cooling to room temperature again. Furthermore, degradation temperature can be fine-tuned by copolymerization of monomers that exhibit different T_c's.

Given the importance of substituents on changing the thermodynamics, the Kennemur group sought computational approaches to predict the RSE for a large set of substituted cyclopentene as a means to guide the monomer design.[91,92] The DFT calculations were based on homodesmotic equations that capture the conformational changes upon ring-opening and side-chain rearrangements, providing the ability to calculate the effects of substituents on the RSE of a monomer. Fig. 7a shows an example of a homodesmotic reaction where the reactants and products contain equal numbers of carbon atoms and have the same hybridization state before and after, as well as the same substituents. By matching the hybridization and substituent groups, the enthalpy of the equation is representative of the ring strain energy in the cyclic monomer. Some of the screened cyclopentenes are shown in Fig. 7b. In general, it was found that the homoallylic (R_3) substitution resultes in slightly larger RSEs than for alkenyl (R_1) or allylic substitution (R_2) across the board. R_3 substituents experience higher repulsions from eclipsing interactions with the hydrogens on C2 and C4 positions. In addition, the RSE is most sensitive to the first atom of the substituent. Increasing atom size increases the bond length, thus decreases the RSE. Electronegativity generally increases the RSE in the R_1 position, while the R_2 and R_3 substituents do not appear to follow a trend. Thus, in addition to developing and solidifying the reliability of a predictive method of RSE, the parameters that need to be considered when selecting monomers would be the size and substitution of the first atom primarily considered, and position (allylic *vs.* homoallylic) of the substituent secondarily considered.[92]

Different from polypentanemers which can serve as strong rubbers, ROMP of fused-ring cyclooctene produces rigid polymers with physical properties comparable to commodity plastics such as polystyrene.[37,93,94] The ring-strain of unmodified cyclooctene is too high to enable efficient depolymerization; however, based on the hypothesis that the ring-strain of cyclooctene can be lowered by a fused-ring, the Wang group calculated RSEs for cyclooctene with 3-, 4-, 5- and 6-membered rings both *cis*- and *trans*-fused at the 5- and 6-positions using density function theory (DFT).[93] The results identified that



Monomer (R_2)	RSE (kcal mol^{-1})
0	7.3
1-2	6.5
5-2	4.2
11-2	2.4
15-2	5.5
2-2	7.6
12-2	7.7
16-2	6.8
22-2	8.4
23-2	8.5
24	8.6

Monomer (R_2)	RSE (kcal mol^{-1})
0	7.3
1-3	6.1
5-3	4.8
11-3	2.6
15-3	4.6
2-3	9.1
12-3	6.9
16-3	4.8
22-3	9.0
23-3	8.9

Fig. 7 (a) Homodesmotic equations used to calculate RSEs. Substituent locations (R) are denoted as alkenyl (R_1), allylic (R_2), or homoallylic (R_3). (b) Calculated RSEs of allylic (R_2) and homoallylic (R_3) monomers. The monomer structures correspond to the monomer RSEs in the table. Reproduced from ref. 92 with permission from American Chemical Society, copyright 2023.

trans-cyclobutane (CB)-fused cyclooctene (Fig. 8a) has the lowest RSE, which was verified experimentally.

The main contribution for the low RSE of *trans*-cyclobutane-fused cyclooctene is the change of tortional strain going from the cyclic to the ring-opened linear form. As shown in Fig. 8b, the non-substituted cyclooctene shows a significant change of dihedral angles H5–C5–C6–C7, H6–C6–C5–C4 and H5′–C5–C6–H6′ after ring-opening. In comparison, for *trans*-cyclobutane fused cyclooctenes (*trans*-CB), since the tortional strains are locked in the acyclic diene, the dihedral angles remain identical between the cyclic and acyclic forms. This leads to an overall reduction in RSE; however, for *cis*-cyclobutane fused cyclooctenes (*cis*-CB) the reduction in tortional strain is offset by the large distortion of the cycloalkane ring, which is released upon the opening of the cycloalkene ring.

A particularly valuable finding from this study is the importance of entropy change in the equilibrium of an enthalpy-driven ROMP. As shown in Table 1, the Wang group studied the structure–polymerization thermodynamics relationships for nine fused-ring cyclooctenes with varying fused-ring sizes and substituents.[94] **M1$_{\text{ester}}$** (5.0 kcal mol^{-1}) and **M1$_{\text{imide}}$** (5.1 kcal mol^{-1}) have lower RSEs than cyclopentene (5.2 kcal mol^{-1}) and thus, lower ΔH_p.[93] One would usually expect them to have lower T_c's and be difficult to polymerize. But their T_c's are much higher than cyclopentene and can polymerize more easily. This is because of their less negative ΔS_p values. The lower decrease in entropy upon polymerization can be attributed to the lower loss in translational entropy for the larger-sized monomers and the higher gain in rotational entropy due to the higher number of freed bonds in the eight-membered ring that were attained through the ring-opening reaction. Over 90% depolymerization into the corresponding monomers was achieved by heating these polymers (25 mM) at 50 °C with G2 (1 mol%) for 2 h. Increasing the fused-ring size from 4 to 5 increases the ΔH_p, which is unfavorable for depolymerization. Interestingly, this can be compensated by substituents, which largely vary the ΔS_p without significant effects on ΔH_p. This is shown in Table 1, **M2** and **M3a–e**. The *gem*-disubstitution of

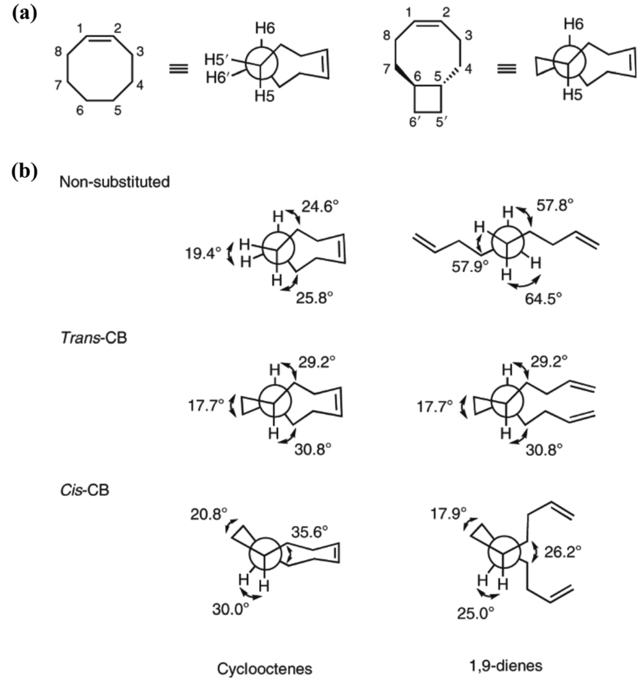


Fig. 8 Dihedral angles of substituted and non-substituted cyclooctene. Reproduced from ref. 93 with permission from Springer Nature, copyright 2021.

M3c and **M3d** reduced the T_c by ~300 °C than the mono-substituted **M3b**, making them more depolymerizable. This Thorpe–Ingold effect which promotes cyclization is entropic in origin as the *gem*-disubstituted **M3c** and **M3d** have more negative ΔS_p. The germinal substituents constrain the conformational freedom of the polymer, meaning less gain of rotational freedom upon polymerization, thus a more negative ΔS_p dominated by the loss of translational entropy.

These polymers showed good thermal stability (Table 1) and strong mechanical properties in addition to their improved recyclability. Varying the substituents from flexible pendant groups such as butyl ester to rigid imide rings, the T_g can be tuned by a range of 155 °C from −55 to 100 °C.[37] The crosslinked polymers made from the low T_g fused-ring cyclooctenes showed tough elastomeric characteristics with a tensile strain upwards of 200% and the tensile stress in the megapascal range. The imide functionalized ring resulted in a glassy polymer with tensile characteristics comparable to polystyrene.[93]

2.4 S$_\mathrm{N}$ArROP

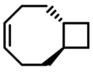
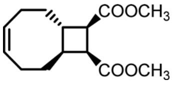
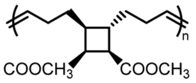
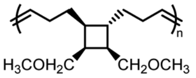
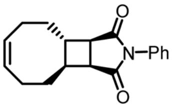
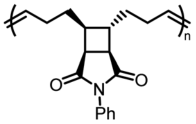
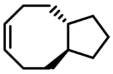
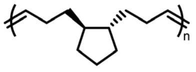
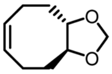
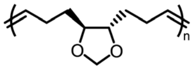
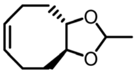
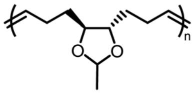
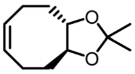
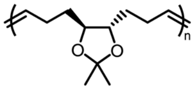
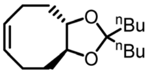
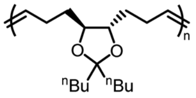
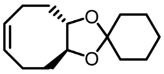
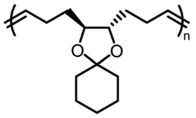
Nucleophilic aromatic substitution (S$_\mathrm{N}$Ar) is a well-known dynamic covalent chemistry.[95–99] In small molecules, S$_\mathrm{N}$Ar is the displacement of a good leaving group, typically a halide, by a nucleophile. This forms an intermediate Meisenheimer complex[100] that facilitates the switch between leaving group and nucleophile. S$_\mathrm{N}$Ar has been utilized to synthesize high-performance industrial materials; however, there are few reported uses of its inherent reversibility.[101,102] Gutekunst and coworkers have taken this idea of S$_\mathrm{N}$Ar reversibility and combined it with ROP to facilitate depolymerizability using a cyclic aromatic thioether denoted as S$_\mathrm{N}$ArROP (Scheme 2).[103] The resulting polythioether has a T_g of 79.5 °C and expressed mechanical properties comparable to commonly used thermoplastics such as polyethylene, poly vinyl acetate, and poly vinyl chloride. The depolymerization proceeded through backbone cleavage with the addition of thiol and DBU followed by backbiting, showing a successful isolated yield of 85% at 90 °C and a concentration of 10 mg mL^{-1}. This was confirmed by depolymerizing iodoacetamide end-capped polythioether, resulting in a 70% isolated yield. The polymers can be tailored with different R groups, possess high recyclability and impressive mechanical characteristics, ultimately showing promise for industrial applications.

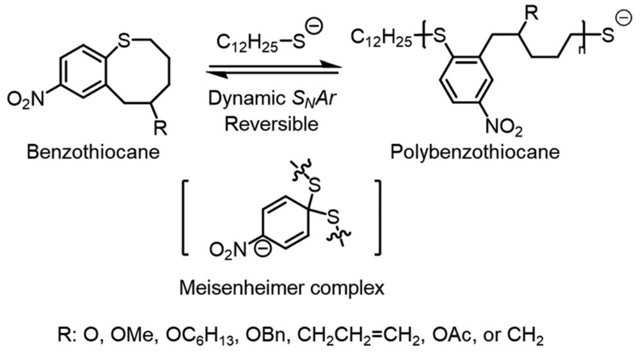
2.5 Polyacetals

Polyacetals are promising candidates for depolymerizable polymers due to the dynamics of acetal bonds in the backbones.[104,105] Acetals undergo rapid exchange reactions under acidic conditions. Hydorlysis of non-cyclic acetal bonds in polymers readily proceeds under a pH of 7.4, leading to numerous biomedical applications.[106] Cyclic acetal units are more resistant toward hydrolysis and provide strong mechanical stability but are still hydrolyzable with a strong acid.[107] Due to their tunable degradability, polyacetals have attracted interest lately in advancing their synthetic techniques;[106] however, a major limitation is the lack of molecular weight control. For example, poly(1,3-dioxolane) (PDXL) can be synthesized *via* ROP of 1,3-dioxolane cyclic monomer catalyzed by either Brønsted or Lewis acids, but its applications as bulk materials were limited by the low molecular weights (up to 44 kg mol^{-1}).[108]

A breakthrough over molecular weight control was made by the Coates group *via* reversible-deactivation cationic polymerization.[109] The reaction uses halomethyl ether as the initiator (MOMX), a Lewis acid catalyst, and 2,4-di-*tert*-butyl pyridine as the acid trap. As shown in Fig. 9a, propagation is mediated by reversible activation of the dormant halide-terminated chain ends by a Lewis acid such as InX_3 or ZnX_2. In choosing the Lewis acid, selectivity toward chain-end activation relative to binding oxygens in the monomer or polymer is critical. $GaCl_3$, $SbCl_5$, $SnCl_4$, and $FeCl_3$ directly activated the monomer even in the presence of the initiator, and thus did not provide any control over the polymerization. The more labile Br leaving group increased the polymerization rate by 25-fold compared to Cl, giving high molecular weight semi-crystalline polymers in minutes at room temperature (Fig. 9b). Material properties improved significantly from brittle to tough as molecular weight increased from 37.9 kg mol^{-1} to 180 kg mol^{-1}, with tensile properties comparable to isotactic polypropylene and high-density polyethylene (Fig. 9c).[110] Dispersity values varied between 1.51–1.74 due to transacetalization, but it did not hinder the living nature of the polymerization or physical strengths of the resulting material. Even though acetals are susceptible to acid hydrolysis, the commercial success of

Table 1 Polymerization thermodynamic data for fused-ring cyclooctene monomers (left) and molecular weight information and thermal properties of their corresponding polymers (right). Reproduced from ref. 94 with permission from American Chemical Society, copyright 2022

Entry	Structure	ΔH (kcal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	T_c at 1.0 M (°C)	Entry	Structure	M_n (kDa)	$Đ$	T_d (°C)	T_g (°C)
M1		−2.1 ± 0.1	−3.4 ± 0.3	335	**P1**		58	1.61	391	−55
M1$_{ester}$		−1.7 ± 0.3	−3.6 ± 0.9	199	**P1$_{ester}$**		142	1.55	401	18
					P1$_{ether}$		293	1.91	372	−34
M1$_{imide}$		−2.8 ± 0.5	−4.9 ± 1.6	295	**P1$_{imide}$**		198	1.96	409	100
M2		−2.9 ± 0.3	−3.2 ± 0.8	614	**P2**		82	1.64	405	−33
M3a		−2.7 ± 0.2	−2.9 ± 0.7	646	**P3a**		171	1.71	360	−30
M3b		−2.6 ± 0.2	−2.7 ± 0.7	675	**P3b**		102	1.78	367	−14
M3c		−3.2 ± 0.1	−4.9 ± 0.3	376	**P3c**		247	1.89	342	−4
M3d		−3.3 ± 0.2	−5.0 ± 0.6	380	**P3d**		164	20.8	327	−27
M3e		−2.8 ± 0.1	−3.3 ± 0.5	571	**P3e**		258	1.86	547	8



Scheme 2 Nucleophilic aromatic substitution of cyclic aromatic thioether. Reproduced from ref. 103 with permission from American Chemical Society, copyright 2023.

polyoxymethylene (POM) as a highly crystalline rigid plastic demonstrates that they sustain sufficient chemical and thermal stability for real world applications. With complete removal of the catalyst, the polymer remained stable up to 350 °C.

Depolymerization took place *via* RCD catalyzed by strong acids such as camphorsulfonic acid and diphenylphosphoric acid. The H^+ activates oxygen in the backbone and initiates the RCD. A representative degradation procedure is shown in Fig. 9d. Monomer of high purity was recovered by distillation from a mixture of different plastics containing various dyes and additives due to the low boiling point of the 1,3-dioxolane monomer. Availability of the monomer, mechanical strength of the bulk polymer, high thermal and chemical stability, and the energy-efficient depolymerization to recover pure monomers from complex mixed waste, make PDXL an outstanding circular system.

2.6 Polydithiolanes

First discovered in the 1950s, ROP of 5-membered 1,2-dithiolanes provides unique opportunities as the polymerization and depolymerization can be conducted in water.[111,112] Lipoic acid, also known as thioctic acid, serves as the monomer (Fig. 10) and it is widely available as a low-cost over-the-counter nutritional supplement. Deprotonation of the carboxylic acid with a base allows the monomer to dissolve in water, and ROP pro-

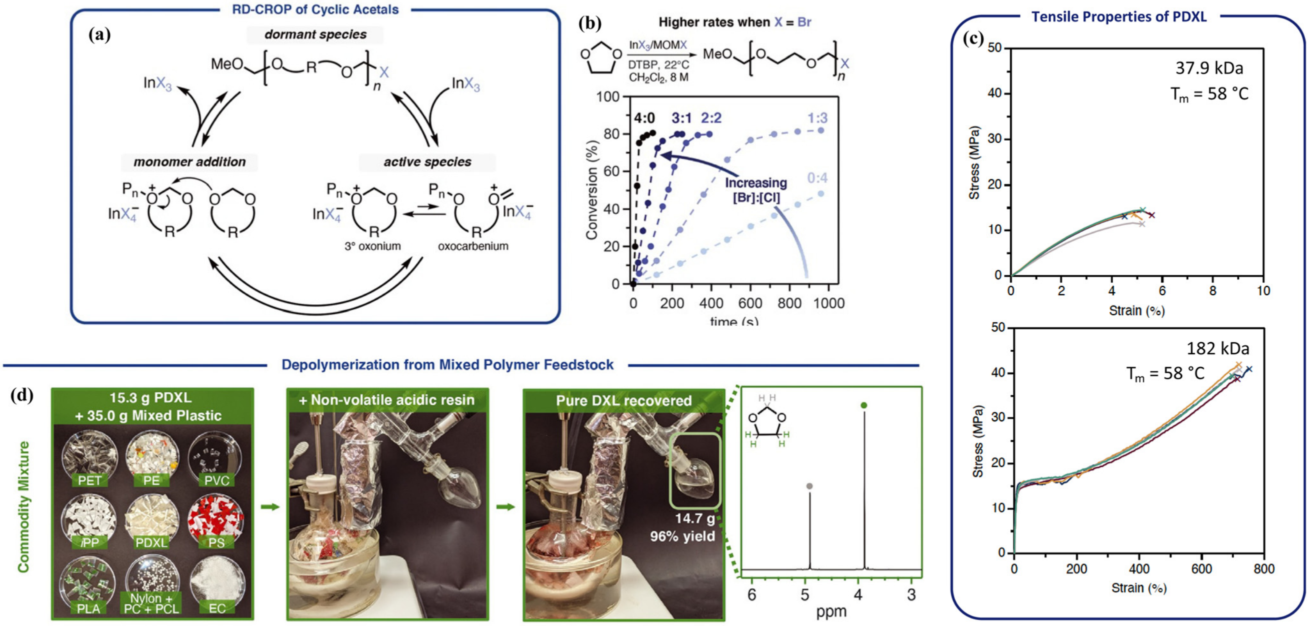


Fig. 9 Poly(1,3-dioxolane) (PDXL) circular system (T_c = 13 °C). (a) Proposed mechanism for the reversible-deactivation polymerization of cyclic acetals. (b) Reaction rate increases when increasing the [Br] : [Cl] ratio in InX_3/MOMX catalyst/initiator system. (c) Tensile properties of PDXL with molecular weight of 37.9 kg mol^{-1} (top) and 182 kg mol^{-1} (bottom). (d) Recovery of the monomer from a mixed commodity plastics feedstock. Recycling condition: PDXL 80–180 kg mol^{-1}, acid resin (Dowex-50, 5 wt%, nonvolatile), mechanically stirred at 150 ± 5 °C, distilled under ambient pressure, monomer recovered in 96% yield and >99% purity. Reproduced from ref. 109 with permission from AAAS, copyright 2021.

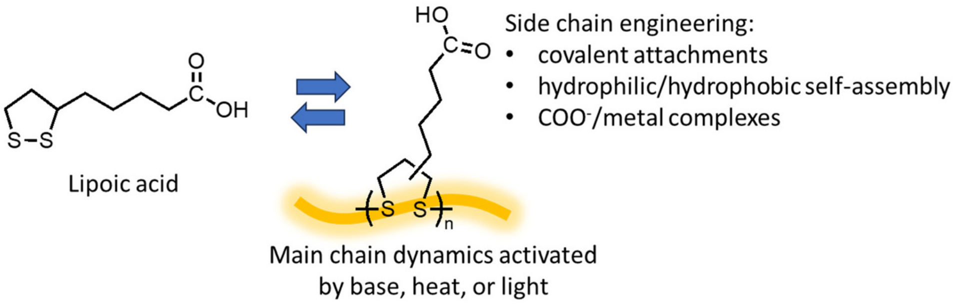


Fig. 10 Graphical depiction of the polymerization of lipoic acid.

ceeds as water evaporates, producing a polymer with disulfide in the backbone and ionic carboxylate pendant groups, which assembles into a mechanically tough and strong material.[111] The ROP can also be carried out by simple solvent-free melt polymerization at 70 °C and retain the carboxylic acid groups.[112] Diluting the polymer to a lower concentration in basic aqueous solution lowers the T_c and induces RCD. Acidification of the solution changes the monomer from hydrophilic to hydrophobic, enabling monomer recovery by precipitation or solvent extraction. The study also demonstrated that depolymerization in water allows for the separation of additives and contaminants such as dyes, reinforcing agents, and flame retardants by simple filtration before the monomer recovery step since they are usually water insoluble. The wide availability of the monomer feed and robust polymerization conditions are promising for scale-up and commercialization.

Newly designed polymers should be intrinsically recyclable while serving as a platform for functionalization. 1,2-dithiolane polymers are such an example. The dynamics of the disulfide bond in the backbone in combination with substitutions *via* the carboxylic acid groups opens opportunities for material applications. Opportunities arise from the dynamic chemistry of 1,2-dithiolane polymers for the design of dynamic smart materials have been discussed in detail in a perspective by Tian.[113] Both light and heat can activate the disulfide bond and induce polymerization, leading to photo and thermally responsive materials.[114] Disulfide metathesis enables efficient self-healing that prolongs the lifespan of materials.[114,115] With reducing agents, disulfide breaks and forms two thiols, providing another approach to depolymerize poly(1,2-dithiolane)[116] and is applicable to removable adhesives.[115,117] The side group modifications produce liquid crystalline elastomers,[118] bottlebrush polymer networks,[114] and cell-penetrating polymers.[119] Covalent and carboxylate-metal noncovalent crosslinks can conveniently tune the polymer viscoelasticity.[120] Synthetic methodologies that provide the control over polymer dispersity and topology (linear *vs.* cyclic) have also been developed.[121] Meanwhile, the labile nature of the disulfide also challenges the durability of the polymers. Reaching a balance between durability and dynamic functionality requires new perspectives and approaches about the materials lifecycle.

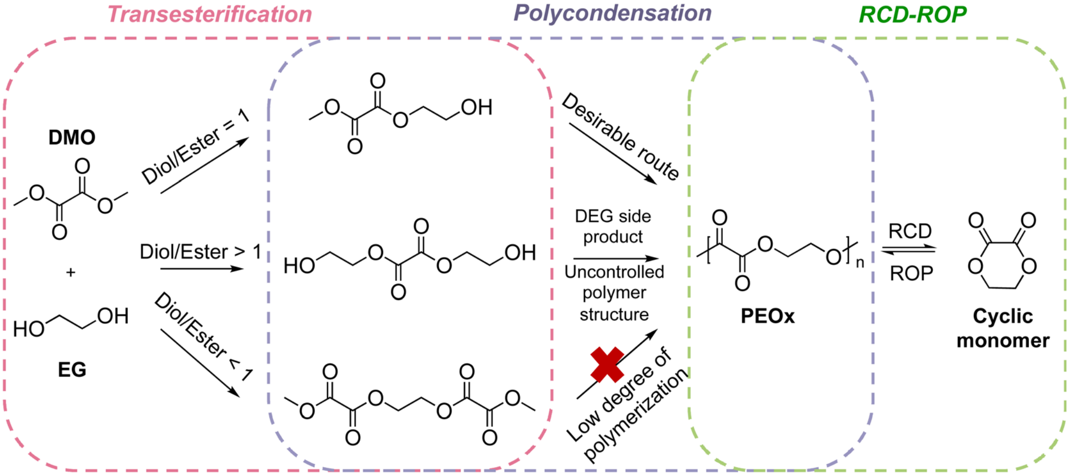
2.7 Polyamides and polycarbonates

Due to the popularity of polyamides in consumer products, it is pertinent to briefly discuss research into potential application of polyamides in a circular economy. However, since many other reviews have covered polyamide synthesis[122–124] and recyclability,[125] this section will be kept brief. In the realm of polyamides, the current research is heavily geared towards depolymerization of post-consumer nylon-6 through RCD and development of its replacement. Several groups over the past few years have taken to finding and developing efficient catalysis to recover ε-caprolactam.[126,127] Recovery yields have been improved through the use of lanthanide catalysts[126] over ruthenium-based catalysts[127] though both provide a method of chemically recycling post-consumer nylon-6. As for development of materials that are easier to chemically recycle, hybrid nylon has become a popular focus. Synthesized from bicyclic lactam with the properties of high T_c ε-caprolactam and low T_c pyrrolidone, hybrid nylon 4/6 shows promising characteristics. A copolymer made of nylon 4/6 and nylon 4 is more thermally stable than nylon 6 with T_g values 40–100 °C higher with the added benefit of accessible chemical recyclability.[128]

Chemical recycling to monomers of polycarbonates has also been more extensively reviewed elsewhere,[10,129,130] and thus much like our discussion on polyamides this will be kept brief. There has been a heavy focus on using renewable sources as feedstocks for polycarbonates made through ROP. Seven-membered fused-ring monomers derived from maleic anhydride, furan, and α-terpinene can undergo ROP to give aliphatic polycarbonates or ROMP to give poly(cyclic olefins) with a wide range of T_g values (80 °C to 200 °C).[131] There has also been investigation into tandem ROP of imidazole carboxylate bearing cyclic carbonate with renewable alcohols of glucose tetraacetate, acetylated isosorbide, lauryl alcohol, and ethanol in the presence of an organocatalyst to generate recyclable functional polycarbonates.[132] The chemical recyclability of these polycarbonates shows extreme promise, as many methods exist and are still being developed to push polycarbonates through RCD back to their cyclic monomers. Recent methods include using seven membered ring carbonates with *trans*-cyclohexyl fused ring.[131] These monomers yielded high molecular weight polymers (M_n upwards of 650 kg mol^{-1}), high thermal stability with degradation temperatures greater than 300 °C, complete depolymerization into dimers that can be repolymerized in moderate yields, and they can be functionalized post polymerization through crosslinking and UV induced "click" reactions. N-Heterocyclic carbene-mediated ring-expansion of cyclic monomers were also used to generate cyclic polymers through zwitterionic ROP. They gave high yield (>90%) and high molecular weight (110–150 kg mol^{-1}) recyclable polymers *via* a "ring to ring" circular approach.[133] Varying catalysts have been a target of method improvement as well with the goal of creating alternatives to toxic metal catalysts. An example of this is the synthesis of poly(cyclopentene carbonate) (PCPC) from copolymerization of CO_2 and cyclopentene oxide (CPO). It is promising but ultimately was a challenging chemically recyclable polymer to make. The Wu group found a work around using metal-free catalysis *via* organoboron catalysts. Their method cuts out low reactivity toxic metal catalysts and increases catalytic efficiency (1 kg PCPC per g of catalyst). In addition, depolymerization returns CPO *via* a combination pathway of random chain scission and chain unzipping in near quantitative yield (>99%).[134] As mentioned earlier, this is a sampling of recent research and there is much more research happening in the realm of polycarbonates that has been extensively covered elsewhere.

2.8 Polyoxalate

Polyoxalate synthesis has been reported since the 1930s by Carothers who found that the poly(ethylene oxalate) (PEOx) can be prepared from ethyl oxalate and ethylene glycol, which under distillation, depolymerizes into 1,4-dioxane-2,3-dione cyclic monomers along with other thermolysis products. The system was described as "the monomer polymerizes spontaneously, and purified polymers are partially depolymerized". Other polyoxalates were synthesized by Carothers but all the polyoxalates synthesized at the time held no practical value as their molecular weights were low with low hydrolytic stability.[135] Later work by Alksnis and McNeill around 1980s confirmed that the equilibrium relationship existed between the cyclic monomer and the polymer.[136,137] Polyoxalates are known to have renewable feedstocks derived from biomass or CO_2, their syntheses have been advanced to reach a molecular weight of ~70 kg mol^{-1}, a broad range of thermal properties can be obtained using different diol feedstocks, and hydrolysis produces nontoxic low molecular weight compounds suitable for biomedical applications.[138] Driven by these advantages, Wei and coworkers investigated the feasibility of scaling up the synthesis of PEOx from dimethyl oxalate (DMO) and ethylene glycol (EG) in a melt polycondensation reaction (Scheme 3) to a 5 L scale, while retaining the chemical recyclability and material characteristics shown on benchtop experiments.[139] The resulting PEOx has T_m up to 176 °C, $T_{d,5\%}$ up to 227 °C, and elongation of break at 2.5%. The PEOx showed degradability *via* hydrolysis in simulated marine environments. After 24 days, 27% of PEOx was hydrolyzed, a characteristic of which is unachievable with most polyesters. Closed-loop recycling was initiated through high temperature thermolysis followed by pyrolysis and produced a white powder of the cyclic monomer



Scheme 3 Synthesis and closed-looped recycling of PEOx.[139] DEG stands for diethylene glycol. Reproduced from ref. 139 with permission from American Chemical Society, copyright 2023.

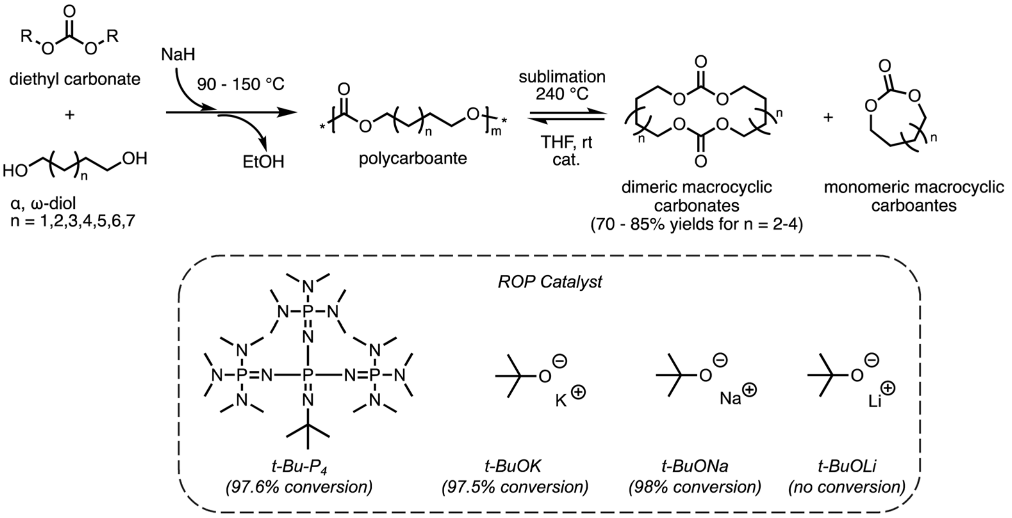
1,4-dioxane-2,3-dione. The recovered monomer polymerized spontaneously without the need for catalyst due to the high activity of the cyclic monomer. The material ultimately shows promise in not only CRM, but also in reducing the environmental impact of polymers that escape from a circular economy.

2.9 Entropy-driven ROP polymers

As discussed in section 2.1, ED-ROP of large strainless cyclic monomers has a unique set of design parameters that allows for the development of novel recyclable materials. Studies of ED-ROP are still in its infancy with regards to chemical recycling. Only a limited number of ED-ROP polymers have been reported so far[40,41,51] and fewer studies on reversible ED-ROP. One such example is ED-ROP of macrocyclic carbonates for a fast and simple method to synthesize and recycle polycarbonates developed by the Odelius group.[49] As shown in Scheme 4, the polycarbonates were first synthesized *via* polycondensation of various diols with diethyl carbonate catalyzed by sodium hydride. Interestingly, distilling the polycarbonate at 240 °C catalyzed by sodium hydride (NaH) formed dimeric macrocyclic carbonates as the primary products which can be collected using a sublimation apparatus in high yield. Monomeric cycles were formed simultaneously in smaller amounts as vapor which did not interfere with the crystallization of dimeric products. To assess the ROP behavior and recyclability of the macrocyclic carbonates, ED-ROP was done in tetrahydrofuran with benzyl alcohol initiator and the catalysts in Scheme 4 at ambient temperatures. The fastest polymerization was observed with sodium *tert*-butoxide (*t*-BuONa) catalyst, giving high monomer conversion (98%) within 3 seconds in ambient temperatures. In order of decreasing conversion, *t*-Bu-P_4 and potassium *tert*-butoxide (*t*-BuOK) showed high monomer conversion within 10 seconds, where lithium *tert*-butoxide (*t*-BuOLi) showed no conversion at all. Thus, the recyclability of the polycarbonates back to monomers was established giving a promising method that can be scaled up for industrial use with relative efficiency.

Polysilylethers can be made *via* ED-ROMP by bifunctional silyl ether-based monomers using a Grubbs 3rd generation bipyridyl complex (G3). Previously, the Johnson group had success with this method making copolymers of cyclic bifunctional silyl ether olefins with a variety of ROMP-active norbornene derivatives.[140–142] Most recently they have taken an interest in the facile deconstruction of the homopolymer, for which the thermal properties are comparable to polydimethylsiloxane.[43] Homopolymerization with 7 and 8-membered bifunctional silyl ether olefins were tested. The 7-membered olefin formed a cyclic dimer without polymerization; however, the 8-membered silyl ether polymerized with a molecular weight upwards of 150 kg mol^{-1} in 2 h (Fig. 11a). The homopolymerization is concentration dependent as demonstrated in Fig. 11b, indicating the sensitivity of the entropy-driven ring-chain equilibrium to concentration. In the depolymerization studies, a solution of the polymer treated with G3 showed a decrease in the chain size by an order of magnitude. The treatment led to the reformation of the monomers with a ~28% yield with this method. The design of the polymer allows for an alternative pathway for depolymerization. When exposed to a Brønsted acid or fluoride ions, the polymer rapidly deconstructed *via* Si–O cleavage into *cis*- and *trans*-isomers of butene, pentene, and hexene. Repolymerizability of the recovered deconstruction products is theoretically possible, enabling them to be reused elsewhere.

Our group demonstrated a new class of polymer, polydithioacetal (PDTA), that undergoes highly reversible ED-ROP cultivated by dithioacetal exchanges.[143] Dithioacetals have been widely used in synthetic organic chemistry as a protective group but has received only limited attention in polymer chemistry. Dithioacetal is formed from the reaction of an aldehyde with two thiol groups. It exhibits higher hydrolytic stability compared to the *O*,*O*-acetal.[144] Although dithioacetals are



Scheme 4 Polymerization pathway of polycarbonates from α,ω-diol and diethyl carbonate and its recycling *via* RCD and ED-ROP. Reproduced from ref. 49 with permission from American Chemical Society, copyright 2022.

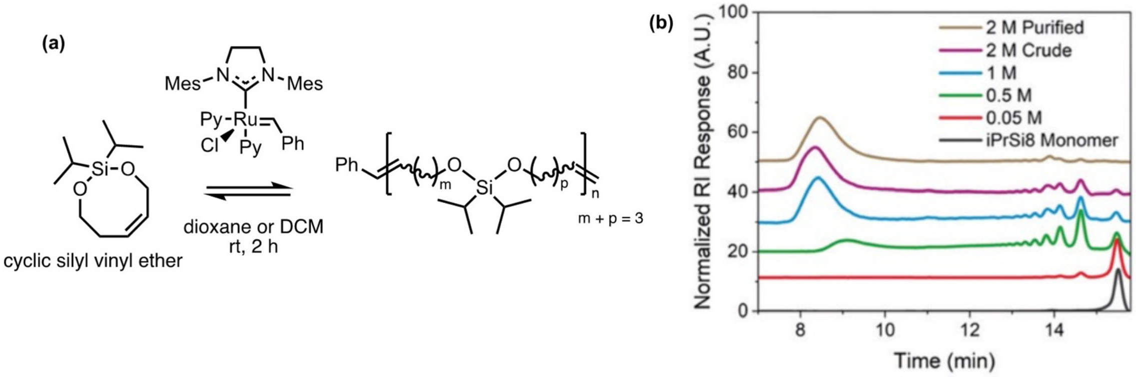


Fig. 11 Homopolymerization of bifunctional 8-membered silyl ethers *via* ROMP.[43] (a) Scheme of 8-membered silyl ether forming high molecular weight polysilylether. (b) Size exclusion chromatography of polysilylether prepared at increasing monomer concentration in dioxane. Reproduced from ref. 43 with permission from Royal Society of Chemistry, copyright 2022.

relatively stable, they can be activated by strong acid catalysts. Given their straightforward synthesis, tunability, and dynamics, we investigated dithioacetal as a reversible bond in developing recyclable polymers. We synthesized PDTAs using 3,4,5-trimethoxybenzaldehyde and alkyl dithiols catalyzed by *p*-toluenesulfonic acid (PTSA) *via* a step-growth mechanism. Chemical recycling is achieved through RCD of the PDTA to generate cyclic monomers which can then be repolymerized *via* ED-ROP (Fig. 12a). RCD takes place by diluting the polymer and refluxing it in toluene for 24 h catalyzed by zinc(II) triflate. The result is a mixture of macrocycles of various sizes, which is characteristic of an entropy-driven ring-chain equilibrium, in the form of a sticky white-yellow powder (Fig. 12b–d). The macrocycles could then be repolymerized back into the polymer at room temperature upon the addition of an acid catalyst. The recyclable PDTA system represents several advantages: (1) easy to synthesize – the polymers are formed *via* a one-step reaction between commercially available aldehyde and dithiol monomers, which then undergo closed-loop recycle *via* RCD and ED-ROP; the macrocycles can be repolymerized at ambient temperatures without isolating specific ring sizes and yield high molecular weight polymers; and the cationic ED-ROP can be conducted conveniently in the fume hood with all starting compounds and solvents used as purchased without further purifications; (2) functionalizable – the benzaldehyde and dithiol starting compounds provide chemical handles for versatile backbone and side-chain engineering, which opens opportunities for functionalization; (3) stability – a unique feature of ED-ROP is that polymerization is favored with increasing temperature and concentration, thus depolymerization at high temperature for bulk materials is not a concern, even in the presence of the catalyst which activates the dithioacetal exchanges. Due to the unique duality of structural stability and local bond dynamics, PDTA can be integrated into crosslinked networks to create recyclable thermosets which will be discussed in section 5.

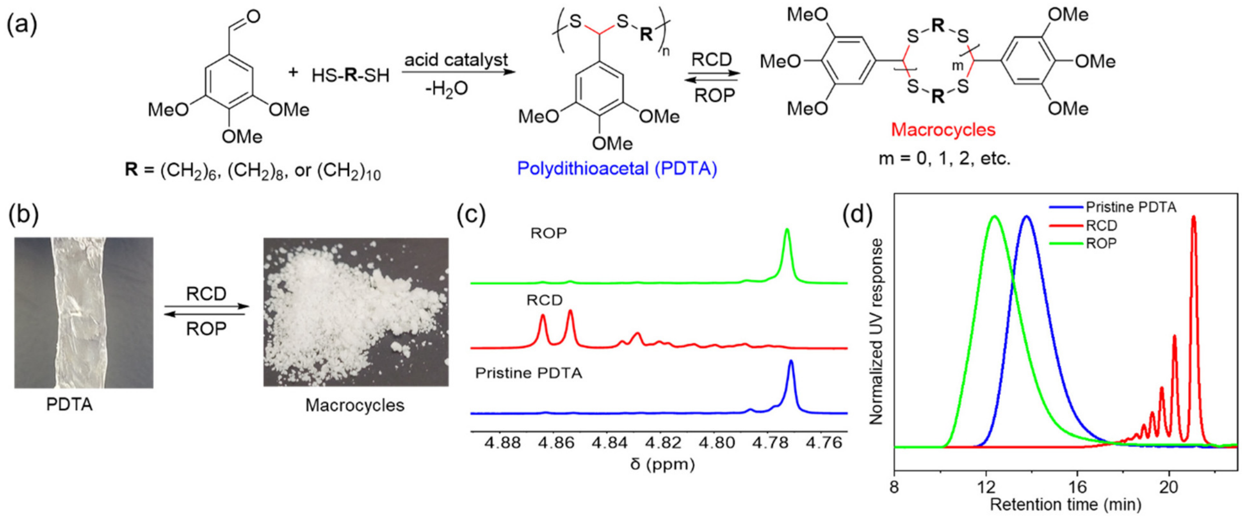


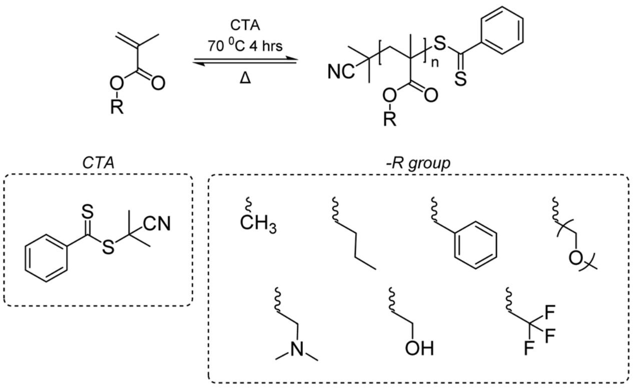
Fig. 12 Chemical recycling of PDTA. (a) Scheme for the formation of pristine PDTA and its recycling *via* reversible RCD and ED-ROP of macrocycles. (b) Representative pictures of the pristine PDTA and macrocyclic mixtures formed after RCD. (c) Partial ^{1}H spectra of pristine PDTA (blue), the crude macrocyclic mixture of various sized rings (red), and after ROP of the RCD mixtures (green). (d) GPC traces showing the normalized UV (254 nm) response as a function of retention time. The color coding is the same as for ^{1}H NMRs. Reproduced from ref. 143 with permission from Wiley, copyright 2023.

3. Reversing free radical polymerization

Vinyl polymers are known to be difficult to depolymerize due to their high T_c's that exceed the decomposition temperature, and the difficulty in activating the highly stable carbon–carbon backbone. In fact, for some, their T_c's are within reach for depolymerization such as disubstituted monomers and monomers with large substituents. For example, poly(methyl methacrylate) (PMMA), a common commodity polymer known as plexiglass, has a T_c of only ~200 °C for $[M]_0 = 1$ M.[145] Thus, there has been a recent focus on developing methods to reverse the radical polymerization of methacrylic polymers to recover the vinyl monomers.

One may question that with such a low T_c, why large-scale recycling of PMMA is still absent. In fact, PMMA synthesized by free radical polymerization must be heated ~200 °C above its T_c to depolymerize. This is due to the high energy barrier to break the carbon–carbon bond to generate a backbone free radical that induces depolymerization.[146] Once the free radical is formed, depolymerization occurs in an end-to-end fashion. An earlier study reported depolymerization of PMMA at lower temperatures during radical addition-fragmentation chain-transfer (RAFT) polymerization[147] and a similar observation was made for atom transfer radical polymerization (ATRP).[148] These depolymerization behaviors were observed under dilute conditions *via* re-activation of their labile end-groups – C–S homolytic cleavage and halogen abstraction.

A near-quantitative depolymerization was reported by Anastasaki group based on the hypothesis that a depolymerizable vinyl polymer should meet two pre-requisites: (1) a relatively low T_c that favors depolymerization thermodynamically, and (2) a labile bond, usually at the chain end, that generates a backbone free radical under mild conditions, to induce the depolymerization.[149] The Anastasaki group addressed these two pre-requisites *via* (1) using dilute conditions to shift the reaction in favor of depropagation and (2) creating weak C–S bond at the chain end. The latter was achieved by synthesizing PMMA and PMMA-derivatives *via* RAFT polymerization with 2-cyano-2-propyl dithiobenzoate as the chain transfer agent (CTA) (Scheme 5). When heated, chain-end radicals are produced and trigger the depolymerization without any catalyst. The catalyst free RAFT reversal depolymerization strategy can be applied to linear, bulk, crosslinked, and functionalized polymethacrylic materials synthesized through RAFT with near-quantitative yield.



Scheme 5 Polymerization and depolymerization of polymethacrylates *via* RAFT. Reproduced from ref. 149 with permission from American Chemical Society, copyright 2022.

While the Anastasaki group demonstrated the feasibility of the depolymerization in dilution, solvent-free and catalyst-free depolymerization of PMMA can be done in bulk reactive distillation enabled by the integration of thermolytically labile endgroups. The Sumerlin group accomplished this using a combination of α-end functionalization with *N*-hydroxyphthalimide esters (Phth) and ω-end functionalization with trithiocarbonates.[150] It was first discovered that PMMA functionalized with only one end group gives only partial depolymerization. Specifically, as shown in Fig. 13, PMMA terminated with Phth at the α-end was synthesized with an ATRP initiator. 65% depolymerization occurred *via* a mechanism of thermally activated decarboxylation of the Phth ester and subsequent loss of isobutylene from the α-chain end. ω-end terminated PMMA with trithiocarbonates was synthesized *via* RAFT polymerization, but only 42% depolymerization was reached from the cleavage of C–S bond at the ω-chain end. Based on these observations, a Phth-modified RAFT agent was synthesized to install thermally labile groups on both chain ends. Activation at both the α- and ω-chain ends significantly enhanced the extent of depolymerization to 92%. Depolymerization was performed at 210–220 °C, 250 °C lower than current industrial methods. This method can be extended to depolymerize ultra-high molecular weight difunctional PMMA (980 kg mol^{-1}) at 41% depolymerization. The lower yield is consistent with highly dilute conditions where it is attributed to the loss of end-group fidelity when reaching ultra-high molecular weight.[149]

Photo assisted RAFT depolymerization can be used to depolymerize polymers with thiocarbonylthio end-groups by leveraging photolysis to drastically increase the radical concentration compared to thermolysis on its own. Within 1 h, depolymerization can reach 87%.[151] Light can be used to accelerate the RAFT depolymerization in the presence of Eosin Y, using a wide range of wavelengths as well.[152]

Depolymerization of ATRP polymers can be accomplished through activation of terminal groups by halogen abstraction. A reaction using an indenyl-based ruthenium catalyst depolymerized a narrowly distributed chlorine capped PMMA.[148] The reaction, performed at 100 °C in solution, allowed the molecular weight to decrease without changing the distribution. Using a copper(II) chloride/tris(2-pyridylmethyl)-amine catalyst ($CuCl_2$/TPMA), chlorine-capped poly(poly(dimethylsiloxane) methacrylate) (P($PDMS_{11}$MA-Cl)) bottle brush polymers[153] and poly(*n*-butyl methacrylate) (PBMA)[154] can also depolymerize into monomers. The efficient atom transfer between the alkyl halide and catalyst enabled 80% monomer recovery of P($PDMS_{11}$MA-Cl) and ~70% *n*-butyl methacrylate within minutes. Increasing the amount of the ligand present during experiments with high catalyst loadings improved the yield and selectivity of depolymerization of P($PDMS_{11}$MA-Cl). When the catalyst loading was decreased, there was better depolymerization selectivity of the monomer over oligomers but this was at the expense of significantly reduced depolymerization rates. By the intrinsic virtue of halogen abstraction, only chains containing chlorine functionalities could be depolymerized enabling selective depolymerization in a mixture of functionalized and unfunctionalized polymers. The depolymerization can also be mediated by iron salts and iron powder, resulting in 75% monomer recovery with a more cost-effective reagent.[155] $CuCl_2$/TPMA mediated depolymerization also

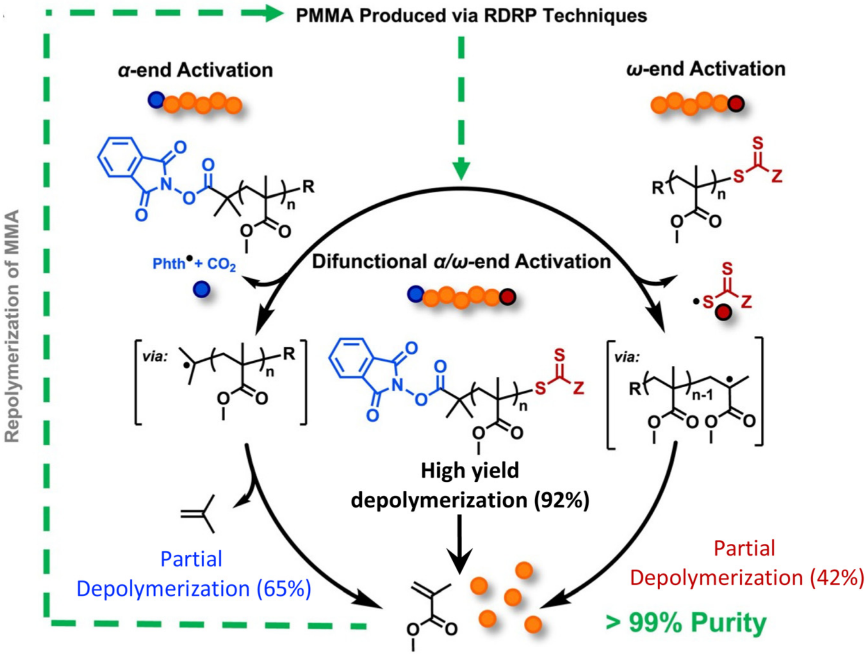


Fig. 13 A scheme depicting the chemical recycling of PMMA to MMA *via* activation of the α-chain ends, ω-chain ends, or a combination of both. Reproduced from ref. 150 with permission from Elsevier, copyright 2023.

showed the ability to quickly depolymerize PMMA and poly(*n*-butyl methacrylate) in under 20 minutes using reactive distillation.[156]

4. Self-immolative polymers

Self-immolative polymers (SIPs) are a unique class of materials that are programmed to depolymerize in a controlled fashion through the removal of a triggering end group upon interaction with external stimuli. Removal of the stabilizing end groups results in domino-like cascade depolymerization. Since their introduction in 2008, the methods of depolymerization of SIPs have expanded from just quinone-methide elimination to include β-elimination of 4-hydroxy-2-butanone, 1,6-eliminations in polyanilines, and pinacol-borate head triggers in the presence of hydrogen peroxide just to name a few.[157] They have been used as stimuli responsive materials and sacrificial layers for surface regeneration in materials sciences. The early developments centered on the concept of self-immolation around room temperature and volatile degradation products. With the latest growing interests in depolymerizable polymers for the purpose of recycling, the two fields certainly merge with a common principle of controlling the monomer–polymer equilibrium.[158] Some of the polymers we have discussed so far depolymerize in an end-to-end fashion, such as the polymethacrylates, but at higher temperatures.

There are two broad categories of SIP: irreversible and reversible.[33] Irreversible SIPs depolymerize into monomers that are different than their starting monomers. They are prepared in a step-wise fashion and depolymerized through elimination or cyclization reactions. The most widely used irreversible SIP is poly(benzyl carbamate)s (PBC) derived from 4-aminobenzyl alcohol.[159] Polycarbonates and variations have also been introduced to the field.[33] Irreversible depolymerization of SIPs has found applications mostly as sensors and in drug delivery where recovery of the initial monomers is not required and sometimes undesirable. Reversible SIPs depolymerize into their original monomers, enabling repolymerization and chemical recycling, much like circular monomers used in reversible ROP reactions. They tend to have low T_c but are kinetically stabilized through their end groups to operate above their T_c. Their T_c's are usually below room temperature to realize rapid depolymerization under ambient conditions. SIPs have been reviewed in several papers.[33,157,160,161] Although SIPs are usually synthesized at very low temperatures due to low T_c and are not all investigated for bulk material applications, the rich chemistry developed in this field over the years can potentially shine light on the design of next generation recycling polymers. Thus, we highlight a few selected examples of reversible SIPs.

4.1 Poly(phthalaldehyde)

Poly(phthalaldehyde)s (PPA)s are high T_g and low T_c (−40 °C) polymers. There are two paths to the synthesis of PPA from phthalaldehyde monomers: anionic polymerization giving linear PPA, and cationic polymerization generating cyclic PPA (cPPA).[162] cPPA depolymerizes using thermally mediated cleavage of the acetal backbone to initiate ring-opening depolymerization (Fig. 14A(a)), thus lowering the kinetic barrier of the thermodynamically unstable polymer chain with a T_c of −42 °C.[163] The low T_c favors rapid depolymerization to the monomer *o*-phthalaldehyde (*o*-PA). The monomer is volatile at the conditions required for depolymerization enabling the recovery of the monomer *via* a cold trap. This allows for cPPA to depolymerize and be separated from mixed waste streams including dyes (Fig. 14A(b)). The mechanical properties of cPPA is characterized with a tensile strength in the 40–50 MPa region and Youngs Moduli around 3.5 GPa; however, it is brittle on its own suffering break around 1.2% strain. Brittleness aside, cPPA has comparable tensile properties to industry standard thermoplastics such as polystyrene.[163] Considering the problems facing the recyclability of fiber-reinforced polymer composites, the White group used cPPA as the bonding polymer matrix to create the composites. This addresses a major issue facing composite recycling, namely that the methods of recovering the fibers from the polymer matrix they are integrated into, such as pyrolysis or solvolysis, require high temperatures (>200 °C) that damage the fibers and alternative mild degradation conditions do not completely remove the polymer matrix, leaving fibers encased in residual resin. With the use of cPPA as the polymer matrix, the matrix can be removed without damaging the fibers or leaving residual polymer matrix on the fibers themselves (Fig. 14A(c)).

Another means to improve the mechanical strength of PPA is crosslinking. One such method is to make a copolymer of phthalaldehyde (PA) and allylated phthalaldehyde (Fig. 14B).[162] The allylated comonomer enables photo induced crosslinking *via* thiol–ene click chemistry. The network showed the same trends of depolymerization with the caveat of showing oligomers once depolymerized which is attributed to the presence of thiol–ene crosslinks. This study also showed that the crosslinked networks can depolymerize with tunable stimuli dependent on the end-cap identity. Using *tert*-butyldimethylsilyl group (TBDMS) as the labile end group, the polymer is sensitive to acid and base, and depolymerized in under 10 minutes when added to either acidic (trifluoroacetic acid) or basic tetrabutylammonium fluoride (TBAF) solutions. Using 2-(2-nitrophenyl)propyl chloroformate (NPPOC) as a photosensitive labile group, the network depolymerized in a few hours after irradiation in a solution of dichloromethane/pyridine mixture.

4.2 Polyglyoxylates

Polyglyoxylates are soft polymers with low ceiling temperatures that can undergo depolymerization through chain end cleavage. The monomers used to make polyglyoxylates are commercially available or can be readily prepared from easy to obtain starting materials such as maleic or fumaric acid. They are recyclable *via* photodegradation of the end cap and the volatile ethyl glyoxylate monomers can be collected and repolymerized (Fig. 14C).[164] It was demonstrated that the mildly

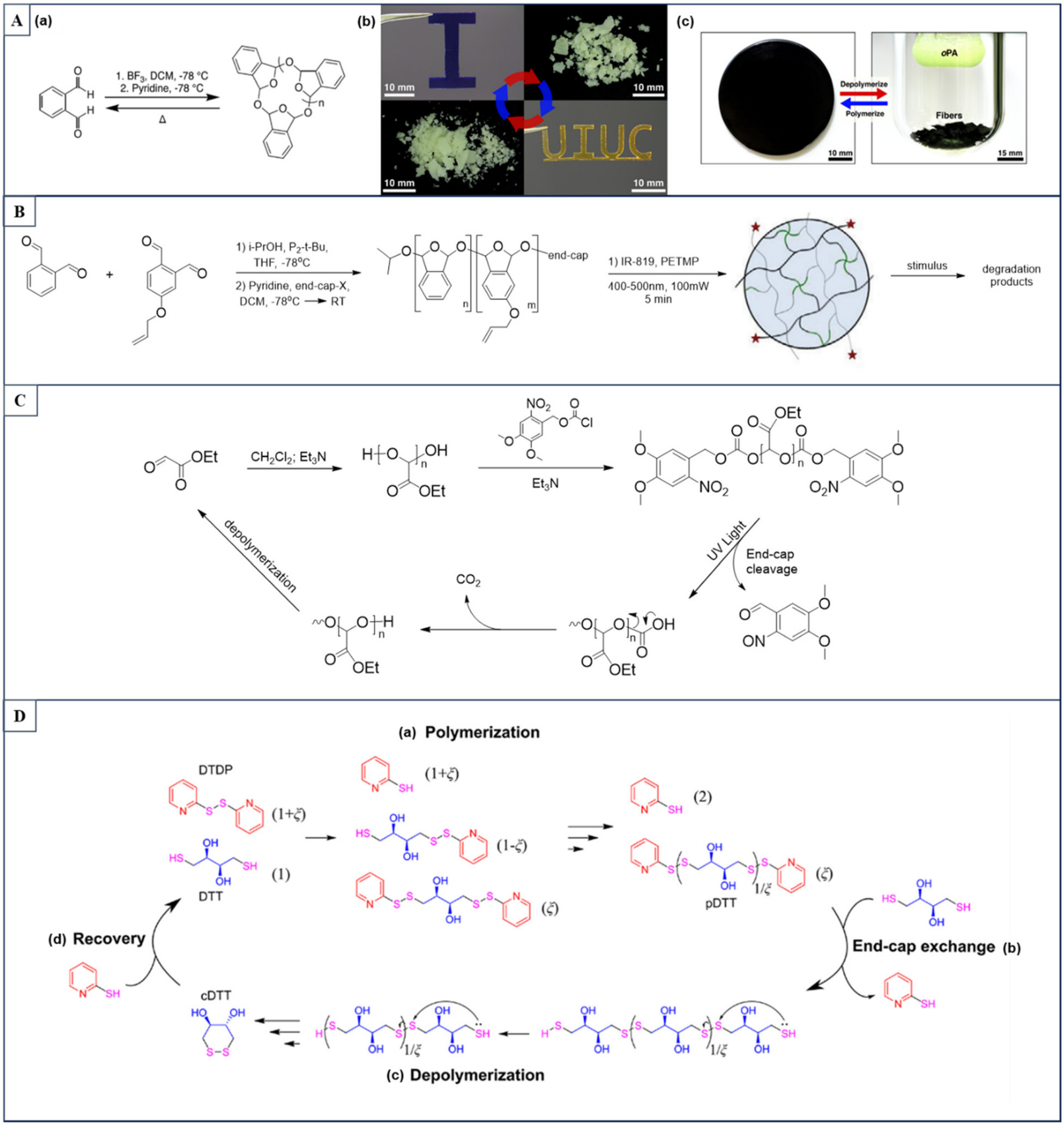


Fig. 14 (A) a. Thermally reversible polymerization of cPPA. b. The solvent cast cPPA films and the monomer (oPA) collected following depolymerization of the dyed films. Blue arrows indicate polymerization and red arrows indicate depolymerization. c. Photographs of a cPPA/carbon nano fiber composite film (left) and sublimation apparatus after heating the composite film to 120 °C for 1 h (right). Reproduced from ref. 163 with permission from American Chemical Society, copyright 2019. (B) Polymerization of a functionalized poly(phthalaldehyde) copolymer and subsequent cross-linking of the self-immolative backbone *via* thiol–ene photopolymerization. The green lines indicate pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) cross-linkers and the red stars indicate removable end-caps. Reproduced from ref. 162 with permission from Wiley, copyright 2021. (C) Polymerization and depolymerization of poly(ethyl glyoxylate). Reproduced from ref. 164 with permission from American Chemical Society, copyright 2016. (D) The solid-state synthesis of pDTT end-capped with pyridinic disulfide. Reproduced from ref. 165 with permission from American Chemical Society, copyright 2020.

acidic conditions used to cleave the backbones of polyacetals instead slow the depolymerization process as the hemiacetals cleave more readily under neutral conditions. In addition, the time to depolymerize was predictably dependent upon temperature and coating thickness and showed no dependency on the presence of water.

4.3 Polydisulfides

A major drawback of SIPs is the low temperature required for their syntheses. Pedersen and Daasbjerg developed a method of synthesizing poly(DL-dithiotheritol) (pDTT) in the solid state at room temperature with high yield.[165] Cyclic DL-dithiotheritol (cDTT) is difficult to polymerize *via* ROP due to its low ring strain. Inspired by the step-growth polymerization of aliphatic dithiol to form polydisulfides developed by Ghosh *et al.*,[166] the solid-state synthesis was realized through a sequence of thiol exchanges (Fig. 14D). These exchanges occur at room temperature in the solid state and the molecular weight of these polymers is directly dependent on the excess of the end-cap moiety, 2,2′-dithiodipyridine (DTDP) (ζ) (Fig. 14D(a)). pDTT showed good chemical and thermal stabilities with a shelf life of over 300 days in bulk. Uncapping using DTT itself *via* thiol-disulfide exchange induced depolymerization *via* backbiting to generate the stable cyclic compound cDTT within minutes (Fig. 14D(b and c)). Depolymerization can be quenched at any given time by adding DTDP to reinstall the pyridinic disulfide end-caps. Treating the depolymerization product cDTT with reducing agents recovers the linear DTT monomers, which can be repolymerized to generate a close-looped system (Fig. 14D (d)).

5. Design methodologies for thermoset polymers capable of depolymerization to monomers

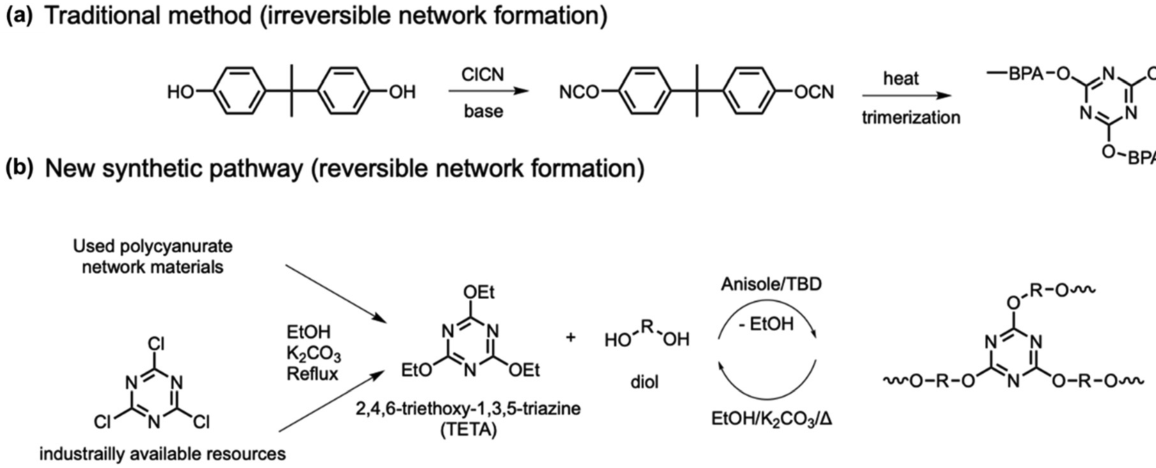
The thermoset market, including mainly unsaturated polyester, epoxy, polyurethane, phenolic resin, and vinyl ester resin, accounts for 15% of the global plastic production.[6] Different from thermoplastics thermosets in the form of composites or foams, serve as long-lasting structural materials used in construction, automotive, aerospace, and wind turbine industries. Their recycling is incredibly difficult due to the highly crosslinked structure. Wind turbine blades, for example, with an average length of 35 meters, are being landfilled or incinerated at their end-of-life. Technologies that rely on chemical recycling that break down thermosets into repolymerizable liquid products are being developed, including acidolysis, solvolysis, and enzymolysis to produce a mixture of monomers and other small molecules. Usually, monomers can only be partially recovered after separation and purification. Recently developed approach is to incorporate cleavable bonds into the network structure, so that crosslinks can be dissociated, and later being reformed, or degrade polymers into oligomers that can be repolymerized.[162,167] Alternatively, chemically recycling to the same monomers offers its own advantage. Production of thermosets relies heavily on the processing, such as liquid molding and foaming. Recycled monomers with the same structures as the virgin ones ensure the same rheological properties suitable for production using the same infrastructure without reformulating or changing the properties of the final products. Herein, we summarize the chemistries that are currently being investigated for fully depolymerizable thermosets.

5.1 Densely crosslinked polycyanurate network

Depolymerizable polycyanurate network developed by Lei group pioneered the idea of redesigning the synthetic route for the same polymer but with reversible chemistry.[99] This approach uses retrosynthetic analysis and it pursues alternative synthetic routes for the existing thermosets. If the alternative route involves reversible chemistry, a traditionally unrecyclable polymer thus becomes recyclable. Scheme 6a shows the synthesis used in industry for the most commercially produced polycyanurate thermoset. The starting compound, bisphenol A, reacts with cyanogen chloride in the presence of a base to produce the cyanate ester, which then trimerize to form a cyanurate ring structure at a higher temperature in the presence of metal salts to form a cross-linked network.[168] The high crosslink density and high aromatic content gives a T_g value that exceeds 250 °C, along with high thermal stability, low water uptake, small dielectric constant, and low dissipation factor, making it suitable for aerospace and electronics industries. However, the trimerization step is irreversible, limiting the polymer's recyclability. The Lei group redesigned the synthetic route by forming the triazine carbon and oxygen single bond *via* reversible nucleophilic aromatic substitution (S_NAr) between alkoxy triazine and alcohol (Scheme 6b). The monomer, 2,4,6-tiethoxy-1,3,5-triazine (TETA) can be synthesized from industrially available cyanuric chloride. Polymerization proceeds *via* the S_NAr reaction between TETA and diol catalyzed by a strong base, triazabicyclodecene (TBD). The use of different aliphatic and aromatic diols provides access for a broad range of glass transition temperatures. For example, when using 1,4-butanediol as the monomer, the network has a T_g of 65.5 °C, exhibiting properties of a tough and strong material with an elongation at break of over 45%, a tensile strength of 45 MPa, and a Young's modulus of 1.1 GPa. At their end-of-life, closed-loop-recycling can be achieved by refluxing in ethanol catalyzed by potassium carbonate (Scheme 6b). Within 16 hours, both monomers are recovered in ~90% isolated yield. Alkyl polycyanurate has not been synthesized before due to side reactions involved in the traditional cyanate ester cyclotrimerization reactions. Thus, in addition to providing a sustainability solution, the chemistry innovation here expands to the library of polycyanurate networks to access more diverse material properties.

5.2 Polydiketoenamines and polytriketoenamines

This group of polymers represents the effort in designing new polymer networks with outstanding mechanical performance and recyclability. Leveraging on the reversible formation of diketoenamine, a series of polydiketoenamines (PDK) capable of depolymerization were developed, allowing recovery of the monomers in their pure states.[169] Diketoenamine bond forms spontaneously from condensation of triketone and amines, while reverse reaction occurs by acidolysis. The polymerization and depolymerization chemistry along with the processes



Scheme 6 Synthetic pathways for polycyanurate networks. (A) Network formation by cyclotrimerization of cyanate ester which is used for industrial productions but is irreversible. (B) Reversible network formation by nucleophilic aromatic substitution of TETA by a diol and removal of ethanol. Adapted from ref. 99 with permission from Springer Nature, copyright 2022.

involved in separating the two monomers from the degradation products are shown in Fig. 15a.[170] Highly crosslinked PDK networks can be conveniently formed by ball milling of a bifunctional triketone and a trifunctional amine crosslinker at room temperature without any solvents or catalysts, producing water as the sole byproduct. The crosslinked polymers in the powder form are then compression-molded into bars and films. This is enabled by the bond exchanges of diketoenamine, allowing it to be thermally reprocessed as a vitrimer. At their end-of-life, treatment with strong acids, such as concentrated HCl or H_2SO_4 aqueous solutions, induces complete depolymerization, producing insoluble triketone monomer which can be separated by filtration with the soluble amine remaining in the acidic solution. The ammonium monomer is then recovered by ion exchange.

The unique processing conditions for monomer recovery, owing to the pH-dependent solubility of the triketone in water, enables PDK recycling in the presence of any water-insoluble contaminants such as dyes, pigments, flame retardant, reinforcing agents, and mixed waste plastics. Specifically, these additives are mostly hydrophobic, so that after depolymerization, they end up in the filtrate along with insoluble triketone monomers (Fig. 15b). Extraction of the triketone into aqueous base allows removal of the contaminants, and subsequent acidification of the basic extract precipitates the pure triketone monomer.

PDK network is a versatile platform with tunable T_gs, mechanical properties, and degradation rates, due to the broad structural design space. Densely crosslinked PDK as shown in Fig. 15a has a high T_g of 125 °C. Crosslink density can be controlled by a combination of diamine monomer and triamine crosslinker, where rigidity of the diamine also dictates T_g and mechanical performances. The use of macromonomers with amine end groups is anticipated to open the door to even more variety of polymers. This is like polyurethanes, for which a broad range of products for different applications, from coatings, rubbers, adhesives, to foams, are developed relying on different polyols. For example, replacing 10 mol% of the triamine crosslinker with poly(propylene glycol) bis(2-aminopropyl ether) (PPG, M_n = 2000 g mol^{-1}) yielded a ductile polymer (Fig. 15c). This showcases the design space in varying the mechanical characteristics based on the PDK platform. Polymers made from recycled monomers exhibit identical mechanical properties compared to the virgin one.

The structural variations also have dramatic impacts on the kinetics of degradation. With heteroatom substitutions on the triketone monomers, diketoenamines formed from TK1 and TK2 hydrolyzes >150 and >25 times faster than the one from TK4, respectively (Fig. 16a).[171] The large rate difference allowed them to be recycled at different temperatures. Increasing the carbon spacing of the amine crosslinker from 2 to 3 also significantly decreases the depolymerization rate (Fig. 16b), which is surprising since the spacer is far from the diketoenamine reaction center.[171] When a triketoenamine is formed from secondary amines and 2,4,6-triformylphloroglucinol, the absence of intramolecular hydrogen bonds further increase the rate of hydrolysis, and depolymerization completes within two hours under otherwise similar conditions (Fig. 16c).[172] NaOH solution also induces complete depolymerization of polytriketoenamine to the monomers at an even faster rate. The underlying mechanisms determining the rate of hydrolysis for these systems were studied in detail using DFT calculations.

5.3 Depolymerization of covalently adaptable networks

Covalently adaptable networks (CANs) are materials that combine the durability and stability of crosslinked thermosets and the reprocessability of thermoplastics. They contain exchangeable bonds that respond to various stimuli (heat, pH, light, *etc.*) and induce inter-chain exchanges, effectively enabling plasticity and reshaping on a molecular

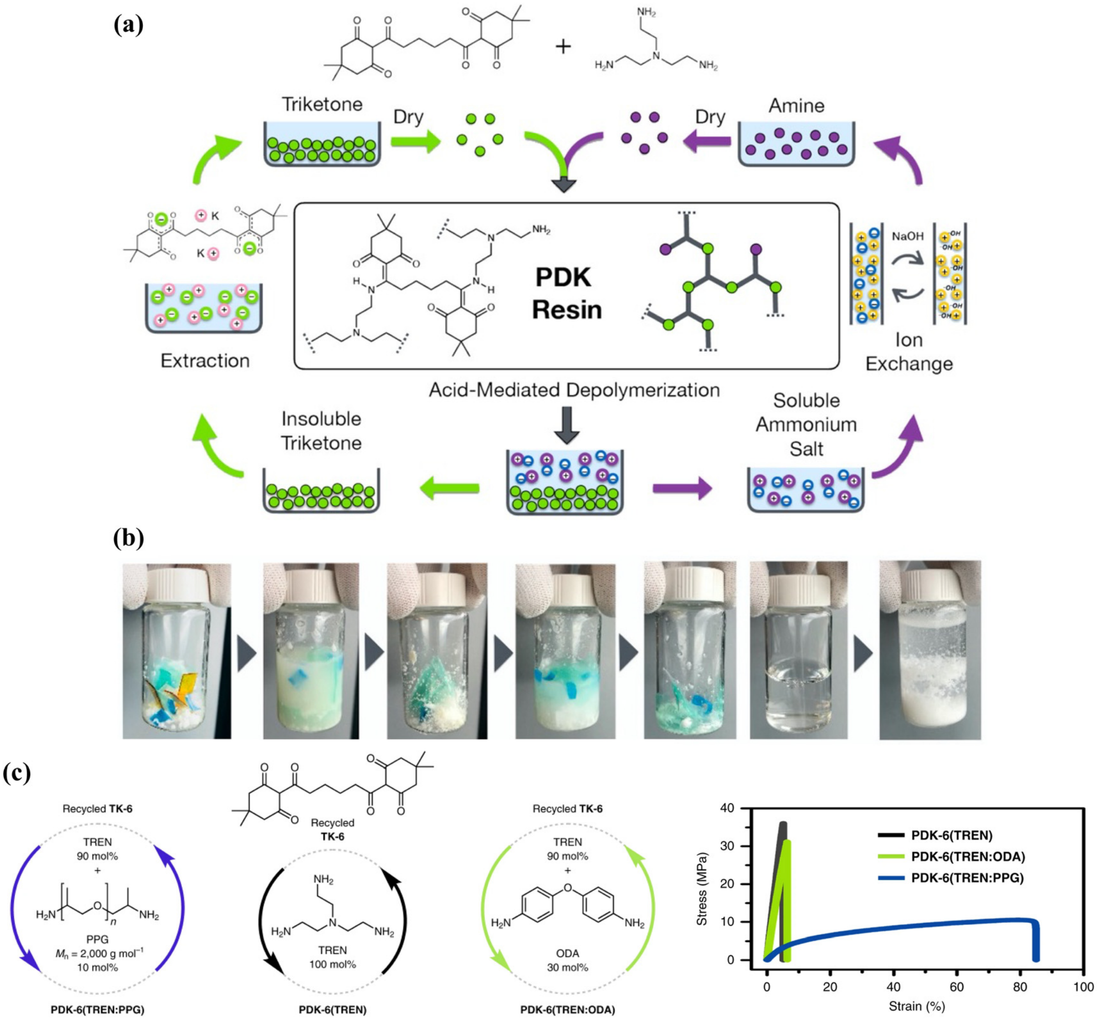


Fig. 15 (a) Schematic illustration for the synthesis of PDK networks from a ditopic triketone (TK-6) and an amine crosslinker (TREN). The polymer depolymerizes back to the monomers *via* hydrolysis in strong acid. The two monomers can be separated based on their different solubilities. (b) Photographs showing orthogonal depolymerization of PDKs and triketone monomer recovery from mixed plastic waste containing poly(ethylene terephthalate) (PET), nylon-6,6 (PA), polyethylene (PE), poly(vinyl chloride) (PVC) and polycarbonate (PC). (c) Reformulation of PEK network using recycled TK-6 and different amines, and their corresponding tensile curves. Reproduced from ref. 170 with permission from Springer Nature, copyright 2019.

level.[99,170,174–183] This can be accomplished in one of two ways: dissociative mechanisms (*i.e.*, elimination–addition mechanism) or associative mechanisms (*i.e.*, addition–elimination mechanism). Dissociative CANs are known as reversible networks and can show a decrease in viscosity while stimuli are applied due to the drop in network connectivity. Associative CANs are known as permanent networks or vitrimers. These preserve their network integrity while stimuli are applied and do not experience a drop in viscosity or gel-to-sol transitions.[184] Since some of the dynamic exchangeable bonds used in CANs are also reversible, complete depolymerization of CANs into the monomers is feasible. As such, thermoset wastes can be mechanically reprocessed and remolded for multiple cycles till significant deterioration of properties occur, they can then be depolymerized to monomers to remake high-quality products. In fact, the depolymerizable networks that as discussed above, including diketoenamine polymers developed by Helms group and the polycyanurate network from the Zhang group, all exhibit such properties. Several studies on vitrimers also reported complete depolymerizability.[175,176,179,185] However, investigations on close-loop recycling of vitrimers, and CANs in general, are lacking. With this consideration, the Weder group selected vinylogous urethane vitrimers as a model study to demonstrate the potential of closed-loop recycling of vitrimers.[185] Vinylogous urethanes are formed from the reaction of bis(acetoacetate)-terminated polyol building block with amine-based crosslinker (Scheme 7a). This material was first developed by the De Prez group[186] and was selected in this model study for its ease of synthesis, high processibility, and broad applicability which have been demonstrated in prior studies.[187–192] Transamination in the presence of excess amines at high

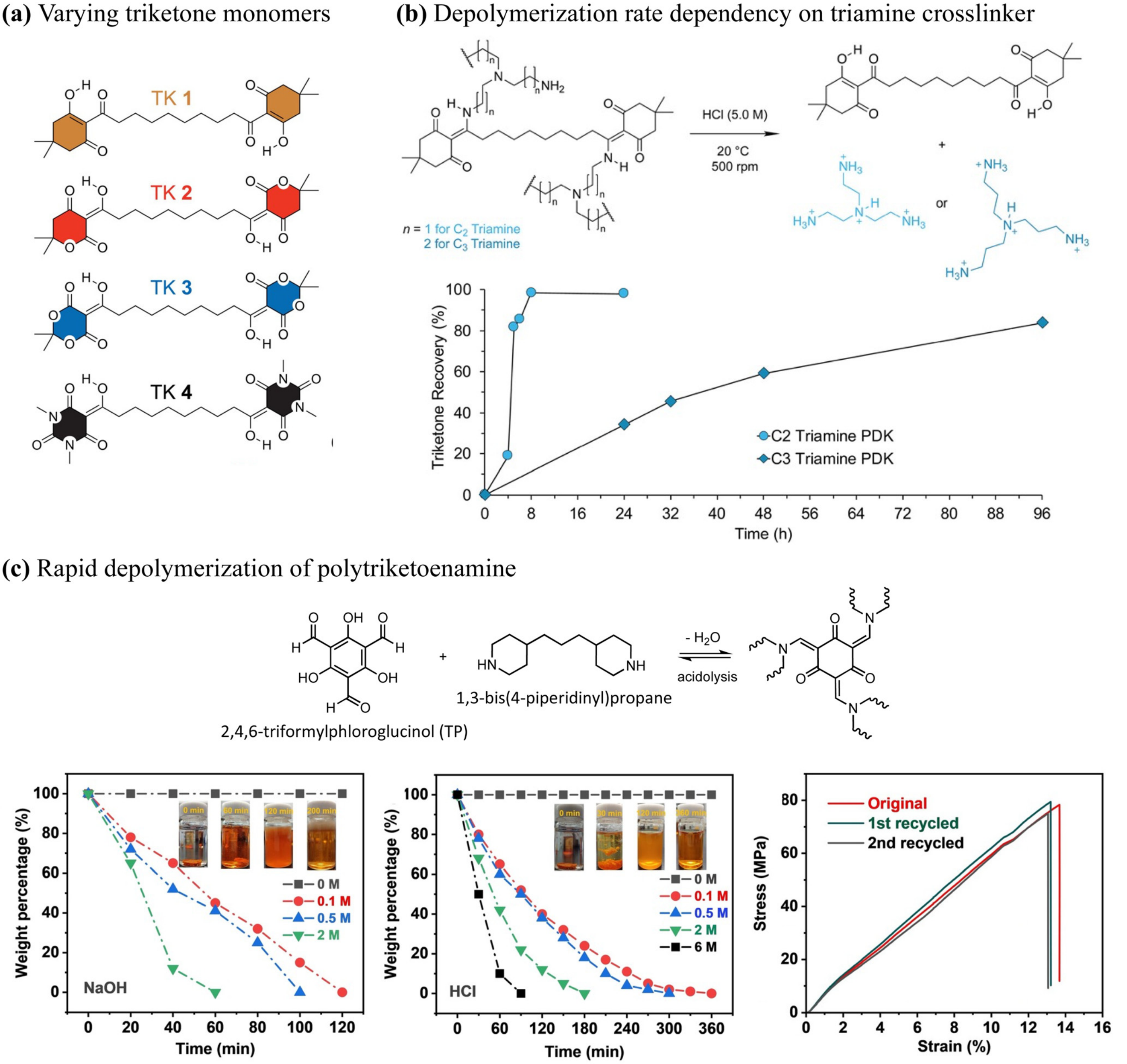
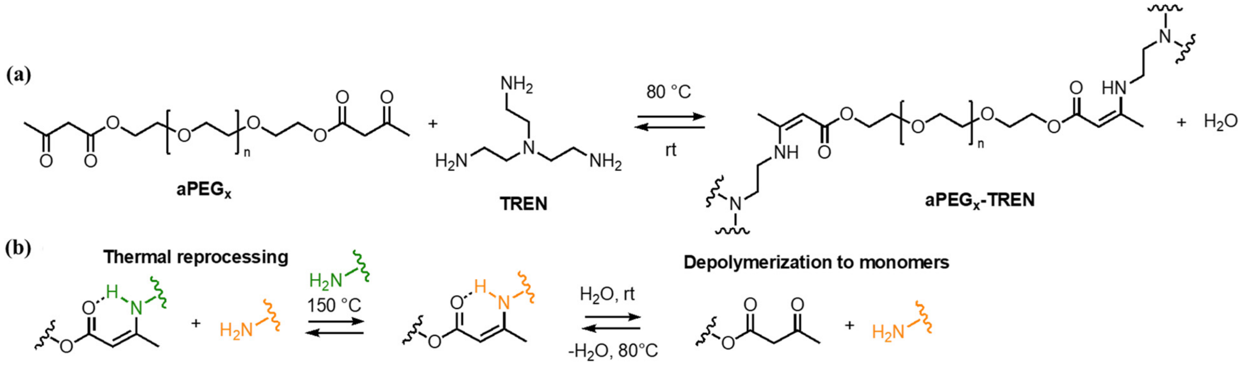


Fig. 16 (a) Structures of triketone monomers with heteroatoms. Adapted from ref. 173 with permssion from AAAS, copyright 2022. (b) Depolymerization scheme with varying structures of the amine crosslinker (top) and their corresponding depolymerization over time (bottom). Adapted from ref. 171 with permission from American Chemical Society, copyright 2023. (c) Synthesis and hydrolysis of polytriketoenamine (top). Their degradation in basic solution (bottom left) and acidic solution (bottom middle). Tensile properties of original and recycled polytriketoenamine (bottom right). Adapted from ref. 172 with permission from American Chemical Society, copyright 2023.

temperatures (60–150 °C) enables the thermal reprocessing without de-crosslinking (Scheme 7b, left). Depolymerization to monomers is realized *via* hydrolysis at room temperature (Scheme 7b, right). If vinylogous urethanes are synthesized from hydrophilic polyol like poly(ethylene glycol), depolymerization proceeds in simply water at rt, allowing 97–99% recovery of the polyol and 88% recovery of the amine crosslinker of high purity after treatment with acidic ion exchange resin. When hydrophobic polyol such as poly(tetrahydrofuran), the polymer remains stable in neutral or basic water, but depolymerizes in 1 M HCl aqueous solution at rt.

5.4 Depolymerization *via* ring-closing depolymerization

As discussed in section 2, numerous depolymerizable polymers have been developed based on reversible ROP and RCD reactions. Hypothetically, crosslinked networks should retain their ability of RCD. This was first demonstrated by the Moore group with the reversible ROMP of cyclopentene derivatives in



Scheme 7 (a) Synthesis of the vinylogous urethane network from bis(acetoacetate)-terminated poly(ethylene glycol) (**aPEG$_x$**) and tris(2-aminoethyl) amine (**TREN**) as the crosslinker. (b) Transamination between an amine and a vinylogous urethane (left) and the reversible hydrolytic depolymerization to the parent monomers (right). Reproduced from ref. 185 with permission from Wiley, copyright 2023.

the bulk state which was discussed in section 2.3.[90] The network reversibly changes between solid crosslinked state at low temperature and liquid depolymerized state at temperatures above T_c. Key findings to note is that compared to monofunctional cyclopentene derivatives which form linear polymers, bifunctional and trifunctional monomers that contain two and three cyclopentene rings linked by a spacer are more polymerizable characterized by higher monomer conversions

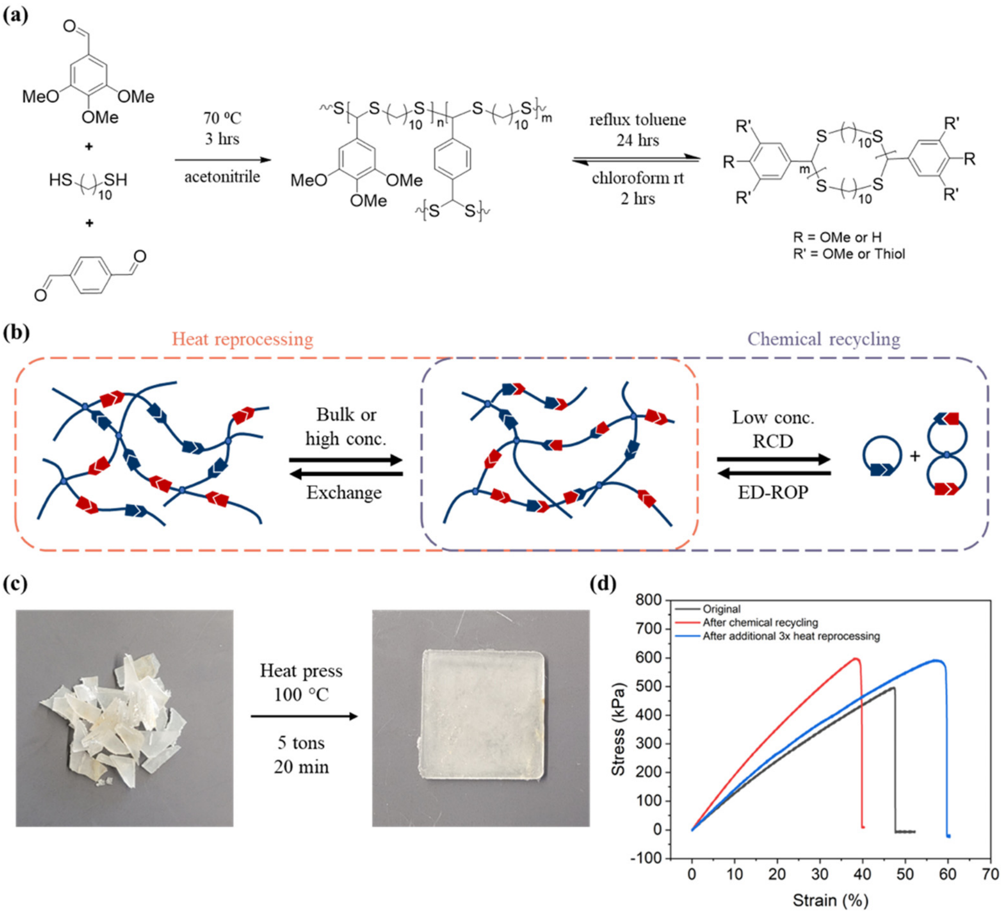


Fig. 17 Reprocessability and mechanical properties of the crosslinked PDTA network. (a) Synthesis of cPDTA and recycling process. (b) Schematic illustration of the reprocessing and recycling mechanisms. (c) Pictures of heat pressing processing. (d) Stress–strain curves of the original network (black), immediately post-chemical reprocessing (red), and 3× mechanical recycling post-chemical reprocessing (blue). Reproduced from ref. 143 with permission from Wiley, copyright 2023.

under the same conditions. This also results in higher depolymerization temperatures. The polymerizability is highly sensitive to the anchoring groups on the rings but not so to the overall length of the spacer.

For entropy-driven systems with a T_f, the crosslinked network behaves differently since polymerization is favored at high temperatures. It forms a different kind of CANs. Activating the bond exchanges without depolymerization should enable thermal reprocessability. The network depolymerizes when needed through RCD *via* dilution or reactive distillation. This was recently demonstrated by our group *via* crosslinked polydithioacetals.[143] Entropy-driven ROPs of the monofunctional macrocyclic dithioacetal rings and their subsequent RCDs are discussed in section 2.9. As shown in Fig. 17a, crosslinked polydithioacetal (cPDTA) was synthesized with terephthalaldehyde crosslinker to form a soft rubbery material. The concept of depolymerizable crosslinked network was demonstrated as illustrated in Fig. 17b,[143] and we expect it to be applicable for many other depolymerizable ROP polymers. The polydithioacetal system is particularly suitable for this application since its polymerization is favored at high temperatures in bulk by virtue of being an ED-ROP polymer. The network will not depolymerize even when dithioacetal exchanges are activated. The network underwent ten cycles of heat reprocessing under pressure (5 tons of pressure at 100 °C) without loss of desirable properties (Fig. 17c). Dithioacetal bonds enabled CANs have also been reported in several other studies.[174,179,193] Complete depolymerization of the cPDTA network into large, strainless macrocyclic monomers *via* RCD was achieved by refluxing in toluene under dilute conditions. The recovered macrocyclic monomers are then able to reform the crosslinked network through ED-ROP in mild conditions, requiring a minimum amount of solvent and 2 h at room temperature, much like their linear counterparts discussed in section 2.9. The chemically recycled network can subsequently be heat reprocessed again. It should be noted that all the chemical recycling and reprocessing processes were catalyzed by zinc(II) triflate which was added to catalyze the synthesis of virgin crosslinked network. It remained in the crosslinked network to activate the dithioacetal exchanges. Purification of the macrocyclic monomers to remove the catalyst or isolation of certain macrocycles based on their sizes is not required for the system to repolymerize back into the crosslinked network. Macrocycles in the solid state do not polymerize at room temperature even in the presence of catalyst. Change of the tensile properties through multiple cycles was observed as shown in Fig. 17d, but we expect that it can be mitigated *via* optimization of the synthetic and reprocessing conditions.

6. Closing remarks

Realizing the circularity is a complex task that requires the engagement of academia, industry, government, and the society at large. Within the scope of research, intensive efforts from the polymer science society have significantly expanded the scope of material design, which is showcased in this review. If the polymer is to be considered for practical applications, its widespread adoption rests heavily on finding polymers that depolymerize and have comparable material characteristics to current commodity polymers and economics. For years the concern has been that the incorporation of degradable bond compromises material stability and performance. As highlighted in this review, recent advancements demonstrated that new recyclable materials can maintain thermal mechanical performance and stability matching those of the existing materials such as polyolefins. Moving forward, application-specific requirements, such as gas permeability for packaging materials, toxicity for food containers, should be met.

While the physical properties and methods are crucial to the polymer design, so is the projected life cycle. Replacing current commodity polymers with recyclable counterparts is one step towards increased sustainability for the industry. However, several questions need to be asked: where are the monomers coming from? Can they be obtained from renewable feedstocks or is it a more efficient use of current petroleum feedstocks? Can the replacements be reused effectively? Or is the recycling of said polymers more detrimental in terms of the energy input needed to recycle them? Do they require high amounts of heat or reaction time? How would that be accomplished on an industrial scale? Replacing current polymers means nothing if what is needed to recycle them puts more pressure on the environment than what we have now.

Many of the chemical recycling processes rely on solvents. The use of large amounts of solvents creates a thermodynamically favorable condition that makes depolymerization possible at lower temperatures. Studies showed that solvents that interact strongly with the monomer can reduce the depolymerization temperature.[194] New types of solvents offer new opportunities, such as ionic liquids whose chemical design can be tailored to target catalytic performance, decomposition temperatures, and polymer solubilities for specific deconstruction applications.[30] These studies confirmed that solvent effects on depolymerization are an important factor, which requires more in-depth studies with green solvents being prioritized. The high costs and challenges in handling high dilution needs to be addressed. Reactive distillation, on the other hand, avoids the use of large amounts of solvents which makes the process greener, but the high depolymerization temperature makes it more energy intensive. It is anticipated that future catalyst development can lower the depolymerization temperatures, as Cantat and coworkers have already shown the feasibility of doing so with the application of hydrosilanes[195] along with numerous other studies.[24,29] Reactive distillation can be more easily adopted with the current industrial infrastructure. To top it off, the distilled products exhibit a high purity.

Another important consideration in material and processing design is the tolerance for contaminants. The depolymerization needs to be selective and efficient so that there is not more energy going into the process than the polymer is worth and selectivity of the depolymerization is extremely important as it is unreasonable to expect that used plastic recycling will be perfectly sorted should the polymer be put to practical use. It then follows that the methods of purification for both the polymer and the depolymerization products also need to be efficient because of the use of additives, specifically modifiers, dyes, plasticizers, catalysts, stabilizers, flame retardants, *etc.* need to be easily removed upon depolymerization. New systems must address these issues to be considered for industrial applications. A lucrative approach to this is using hyperselective depolymerization conditions that are unique to the polymer, enabling mixed plastic waste to be run through various stimuli to recover monomers in stages. Ideally this separation would be selective enough to remove contaminants in as few steps as possible and there are polymers that have demonstrated this ability at a bench-top scale as described in this review.

Optimization is key to convert research into industry. When compared to research, the industry error tolerances can be much narrower. This includes time, materials, and projected loss or error. For example, a reaction that takes 16 h to complete goes from a reasonable time frame in the lab to an eternity in an industrial setting. Production that requires large amounts of solvent, in the hundreds of liters when scaled up, with a 0.5% solvent loss in recycling said solvent becomes an exponentially large amount compared to what 0.5% solvent loss looks like inside a research lab. If there is any hope to transfer an experimental material from a bench top into industry, speed and minimizing loss is crucial. With these things in mind, the path toward a circular economy becomes clearer cut but also faces challenges.

The commonly diagramed circular economy in Fig. 1 is grossly oversimplified with respects to what is typically summarized by the use/sorting aspect. Regardless of the material or application, the circular economy is a complex system that requires coordination between every level of the supply chain, a properly designed regulatory system as well as involvement at the consumer/end user to be successful. A pinch point or failure in any one of these groups can lead to failure of the entire system. For example, in Norway, Infinitum achieved a return rate of 92.8% and 91.5% for PET and aluminum containers, respectively for recycling.[196] These return rates were due to a combination of strong regulatory policy including a deposit return system, infrastructure, collaboration between the grocery and beverage industry and consumer involvement.[197] The collection rates outpaces PET container collection rates for European (average of 61%)[198] and the US (26.6%)[199] where nationwide collection policies are nonexistent and regional policies are fragmented at best. In both regions as well as globally, developing policies such as the Intergovernmental Negotiating Committee on Plastic Pollution,[200] European Union's Plastics Strategy[201] and Packaging and Packaging Waste Directive,[202] and US state-based approach with California's Truth in Labeling (SB343) and EPR Program (SB54), Oregon's Plastic Pollution and Recycling Modernization Act, and Colorado's Producer Responsibility Program for Statewide Recycling Act aim at tackling some of the hurdles of circularity from the regulatory perspective. Similarly, regardless of material and application, once collected, items must be properly designed for sorting through existing and developing infrastructure to reach the proper mechanical, physical, or chemical recycling process. For plastic packaging, the Association of Plastics Recyclers[203] in the US and RecyClass[204] in Europe developed designs for recycling guidelines to ensure that packaging is sortable at Material Recovery Facilities (MRFs) that operate at volumes as high as 300 000 metric tons per year.[205,206] Regardless of recycling technology and tolerance to contamination, effective separation early on ensures the item enters the correct stream, improves quality, reduces yield loss and improves economic viability. Additionally, as the range of incoming streams expands to textiles, automotive, appliance, construction and other durable goods, infrastructure similar to the MRFs that exist for curbside recycling streams will need to be developed and scaled to broaden the range of material available for mechanical and chemical recycling processes.

Lastly, life-cycle analysis and techno-economic analysis that provide preliminary evaluations on the carbon footprints and cost effectiveness associated with new feedstocks, recycling processes such as the use of catalyst, solvent, temperature, pressure, infrastructures for polymer production and recycling, storage, and transportation, must be well-integrated to guide the material and process designs.[207]

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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