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New sustainable polymers with on-demand depolymerization property

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To combat the crisis of today's synthetic polymers arising from unsustainable production and disposal, it is essential for the synthetic polymer community to reshape the current polymer industry with sustainable polymers. As an emerging class of sustainable polymers, the development of chemically depolymerizable polymers (CDPs), which can undergo closed-loop depolymerization/repolymerization cycles to reproduce virgin polymers without the loss of properties from recovered monomers, offers an ideal solution to preserve finite natural resources, provides a feasible solution to the end-of-life issue of polymer waste, and thereby establishes a circular materials economy. However, two grand key challenges have been encountered in the establishment of practically useful CDPs: how to balance polymerization and depolymerization ability and how to unify conflicted depolymerizability and physical properties. Accordingly, this critical review article presents our vision for summarizing feasible strategies to overcome the above two significant challenges and the design principles for constructing an ideal CDP by highlighting selected major progress made in this rapidly expanding field.

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1 Introduction

Nowadays, synthetic polymers have become an essential material to modern life and the global economy because of their low cost and versatile functions that can meet the very different needs of consumer products. As the largest synthetic consumer product in the world, the global production of plastics continuously increases each year and reaches 400.3 million metric tons (Mt) in 2022 [1]. However, the current production relies on petroleum feedstocks, and the uncontrollable disposal of synthetic polymers follows an unsustainably linear economy model. By 2050, annual production of plastics is predicted to reach 1.12 billion tons, which is predicted to account for 20% of global petroleum consumption [2]. In 2022, the Organization for Economic Co-operation and Development predicted that annual production would increase from 460 Mt in 2019 to 1,231 Mt in 2060 [3]. Moreover, due to the non-degradable nature of the vast majority of synthetic polymers, the polymer wastes, being discarded in landfills and dumped illegally in nature, are incessantly accumulated and persistent in the environment, which bring about enormous material value loss and economic loss, and often difficult to quantify the negative impact on the environment. Up to 2019, the plastics industry has generated approximately 6.3 billion metric tons of plastics, among which 19% were incinerated, only 9% had been recycled, and 81% became waste and accumulated in landfills and the natural environment [4].

To combat today's challenge in synthetic polymers, it is critical significance to develop new polymer chemistry towards more sustainable polymers [5–7], commonly referred to as the next-generation polymer materials. Such polymers have been redefined very recently as materials that would be "derived from nonnutritive, waste, or biobased resources that can be obtained in an economical manner using the principles of green chemistry." Ideally, such materials should be valuable and low-cost but bear a distinct characteristic that they can be infinitely recycled with minimal contributions to climate change [8]. Some elegant examples, including biobased [9–12] and biodegradable polymers [13–16], constitute a traditional class of sustainable polymers, which have been intensively pursued in the past two decades. In contrast to biological recycling in biodegradable polymers that typically lead to low or no recovery of the materials' value while generating neat ultimate CO_2 emission after use, polymer chemists coined a new type of sustainable polymer with on-demand depolymerization property in that the post-use polymers can be chemically converted into pristine monomers or valuable chemicals, which are subject to next round of polymerization to make new polymers [17–26]. In this review, we termed such polymers as chemically depolymerizable polymers for simplicity (CDP, Figure 1), differentiating from the conventional scope of chemical recycling [27,28]. One of the most appealing features of CDPs is that these polymers can undergo closed-loop recycling through a reversible depolymerization/repolymerization cycle, where new polymers are able to be reproduced from recovered monomers, thus offering great potential to preserve finite natural resources, providing a feasible solution to the end-of-

Figure 1 Illustrations of the chemically depolymerizable polymers (color online).

life issue of polymer waste, reducing neat CO_2 emission during polymer using cycle, and ultimately establishing a circular materials economy. Such a strategy establishes a conceptual analog that polymer monomers can mimic metal atoms for performing ideally unlimited or at least multiple life cycles before being converted into CO_2 and H_2O.

As early as the 1990s, investigations into the depolymerization of commodity polymers by thermal or catalytic pyrolysis have been reported [29,30]. However, due to an energy-intensive process accompanied by a variety of side reactions, depolymerization is difficult for many existing polymers. In 2011, Yang and Wang [31], Chinese scientists from Sichuan University, found that biodegradable poly(*p*-dioxanone) can be depolymerized back to monomer when heating at 150–250 °C. Notably, in 2016, Hong and Chen [32,33] from Colorado State University achieved, for the first time, efficient chemical synthesis of poly(γ-butyrolactone) (PBL), a structural equivalent of biomaterial poly (4-hydroxybutyrate) (P4HB), *via* ring-opening polymerization (ROP) of γ-butyrolactone under ambient pressure, and also demonstrated the quantitative depolymerization of PBL into γ-BL. This breakthrough has provoked significant interest in the field of CDPs, and the past eight years have witnessed unprecedented achievements made in this rapidly expanding field [17–24]. Due to the scientific and economic significance of CDPs, the International Union of Pure and Applied Chemistry (IUPAC) has ranked “from plastics to monomers”, “macromonomers for better plastic recycling”, and “depolymerization” as one of ten chemical innovations that will change our world in 2019, 2020, and 2023, respectively [34–36].

In principle, the establishment of an ideal CDP requires a thorough consideration of thermodynamics, namely the reaction equilibrium of polymerization and depolymerization [18,22]. For most polymerizations that are exergonic and driven by enthalpy, there is a critical temperature—known as ceiling temperature ($T_c = \Delta H_p^\circ/(\Delta S_p^\circ + R\ln[M]_0)$, ΔH_p° and ΔS_p°: enthalpy change and entropy change at standard polymerization conditions, $[M]_0$: initial monomer concentration), at which the change in Gibbs free energy (ΔG_p) is zero and the polymerization/depolymerization is at equilibrium. The inherent T_c value is critically important for CDP because it can be utilized to determine and quantify polymerizability (from the monomer’s perspective) or depolymerizability (from the polymer’s perspective). At temperatures below T_c, polymerization is favored, while depolymerization is favored at temperatures above T_c.

For the conventional polymerizations, their T_c values are generally too high, which results in polymers with practically impossible depolymerizability, which makes it difficult to construct polymerization-depolymerization cycles. For example, ethylene polymerization possesses an extremely high T_c value of ~610 °C [22]. As a consequence, the thermolysis of polyethylene not only requires an energy-intensive process but also suffers from low monomer recovery (25%) and low depolymerization selectivity accompanied by a variety of side reactions (*e.g.*, gases, waxes, char) [37]. Although low-T_c (*e.g.*, < 0 °C) polymerizations are inclined to depolymerization, these polymerizations usually either stop at low conversion or must be run at very low temperatures, also hampering the ability to sustain closed-loop cycles. Therefore, to establish an ideal CDP, a delicate balance between the polymerization and depolymerization ability must be achieved, presenting a formidable challenge.

On the other hand, to meet the demands of practical application, CDPs need to compete with or even exceed the physical performance of existing commercial polymers, which usually exhibit excellent durability, stability, processability, and thermomechanical properties. However, the depolymerizability of CDPs is generally achieved at the expense of their physical performance. Therefore, another key challenge in this area is how to create high-performance CDPs that are durable and robust in use yet readily depolymerized on demand under certain conditions instead of inopportune depolymerization, thereby unifying conflicted depolymerizability and physical properties.

This critical review aims to summarize feasible strategies to overcome the above two big challenges as well as the design principles for an ideal CDP by highlighting selected major progress made in this rapidly expanding field. According to the different main chain structures of CDPs, this review is divided into two sections, including heterochain CDPs and carbon-backbone CDPs. Each section is further divided based on the polymerization methods used for synthesizing CDPs. At last, we conclude with our perspective on the ideas and opportunities for the field. Examples of dynamically cross-linked thermosets [38–40], indirect depolymerizations that require multiple transformations/catalytic reactions, or the addition of chemical reactants to recover monomers (*e.g.*, the depolymerization process of poly(ethylene terephthalate) (PET)) [41,42] are not covered in this review, excellent reviews on which can be found elsewhere.

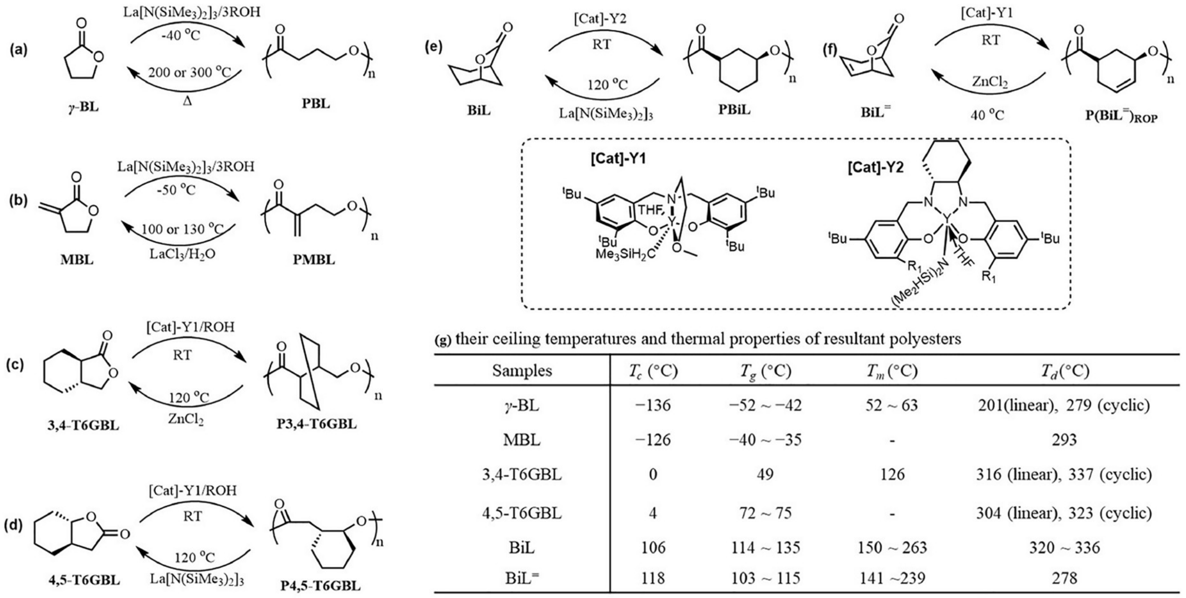
2 Heterochain-based CDPs

2.1 Ring opening polymerization

2.1.1 *Chemically recyclable polyesters from five-membered lactones*

Non-strained five-membered lactones (*e.g.*, γ-butyrolactone (γ-BL), tulipalin A/α-methylene-γ-butyrolactone (MBL)) are ubiquitous in nature and can be commercially produced from biomass, offering great potential as renewable feedstocks for the synthesis of sustainable polymers. However, it has long been a formidable scientific challenge to ring-open polymerize non-strained five-membered lactones because of their low strain energy (*i.e.*, too small a negative change of enthalpy to drive ROP) [43]. In 2016, Hong and Chen [33] achieved, for the first time, an efficient ROP of γ-BL (Figure 2a) *via* the establishment of two crucial strategies, including performing the ROP below the T_c at a given concentration (*i.e.*, T = –40 °C, $[\gamma\text{-BL}]_0$ = 10 mol/L) and modulating the reaction conditions so that the formed polymer precipitates out of solution during the polymerization to shift equilibrium towards polymerization. By utilizing the rare earth metal complexes or organic *t*Bu-P_4 superbase as catalysts, γ-BL can be effectively converted into high-molecular-weight poly(γ-butyrolactone) (PBL) [32]. Importantly, the obtained polymer can be selectively and quantitatively recycled back into γ-BL through thermal- or catalyst-triggered depolymerization (Figure 2a). The remarkable success of this work provoked significant interest from the polymer community in the development of CDPs. The employment of above two strategies has also enabled the successful ROP of MBL (Figure 2b) by carrying out the polymerization at –60 °C below the T_c of –52 °C at $[\text{MBL}]_0$ of 5.0 mol/L, affording functional polyester (PMBL) with complete depolymerizability [44]. Shortly after, several metal-based and organic catalysts, including cyclic triphosphazene superbase (CTPB) [45], *N*-heterocyclic olefins [46], and CTPB (or *t*Bu-P_4, MeONa)/(thio)urea binary systems [47–49], have also been developed for the efficient and in some cases controlled ROP of γ-BL. Subsequently, CTPB/urea binary catalytic system was also utilized by Li *et al.* [50] to realize the chemoselective ROP of MBL. As a potential application, dihydroxyl functionalized PBL can be used to prepare recyclable polyurethane elastomers [51].

Although both PBL and PMBL can fulfill the on-demand depolymerization with or without catalysts under not-so-harsh conditions given their characteristic thermodynamics, ROPs of these low-T_c monomers require energy-intensive low reaction temperature and inhomogeneous conditions, which severely hamper their possibly industrial scale-up applicability. To address this challenge, Hong and coworkers [52,53] established a new polymerization strategy termed



Samples	T_c (°C)	T_g (°C)	T_m (°C)	T_d (°C)
γ-BL	−136	−52 ~ −42	52 ~ 63	201(linear), 279 (cyclic)
MBL	−126	−40 ~ −35	-	293
3,4-T6GBL	0	49	126	316 (linear), 337 (cyclic)
4,5-T6GBL	4	72 ~ 75	-	304 (linear), 323 (cyclic)
BiL	106	114 ~ 135	150 ~ 263	320 ~ 336
BiL=	118	103 ~ 115	141 ~239	278

Figure 2 The ROPs of five-membered ring monomers: (a) γ-BL, (b) MBL, (c) 3,4-T6GBL, (d) 4,5-T6GBL, (e) BiL, (f) $\text{BiL}^{=}$ and their reversed depolymerization as well as (g) their ceiling temperatures (T_c, $[\text{M}]_0$ = 1.0 mol/L) and thermal properties of resultant polyesters.

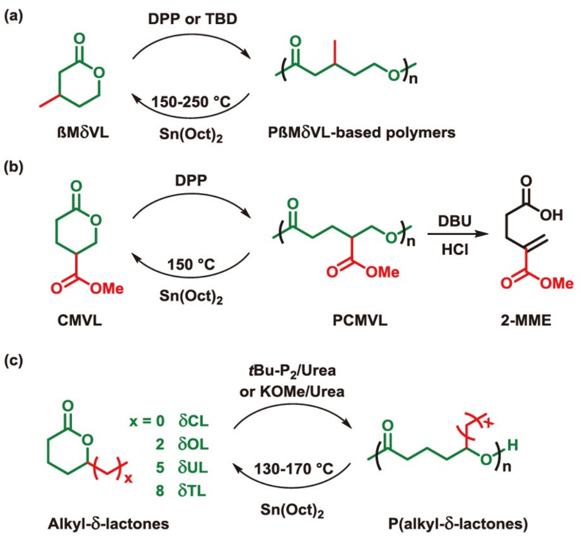
isomerization-driven ROP (iROP) to circumvent the unfavorable thermodynamics for the ROPs of non-strained five-membered lactones by constructing a thionolactone intermediate *via* one-step sulfurization of the corresponding lactone. Different from conventionally ring strain-driven ROPs of lactones, the iROP of thionolactone is thermodynamically driven by S/O isomerization, thus rendering non-strained five-membered rings highly polymerizable for the first time at industrially relevant temperature of 80–100 °C. The development of a robust iROP catalyst provides a unique opportunity for a fascinating opportunity to convert these abundant but underexploited renewable feedstocks (*e.g.*, γ-butyrolactone, γ-valerolactone, peach lactone, dihydrojasmone lactone, whiskey lactone) into new sustainable polymers with their key physical properties well comparable to representative commodity polyolefin plastics.

Moreover, a precise monomer design strategy has also been developed by Chen and coworkers [54,55] through coupling a five-membered γ-BL core with suitable substituents and substitution patterns to tune ring strain, thus facilitating the polymerization thermodynamic while realizing the controllable depolymerization under mild conditions. For example, Chen *et al*. [54,55] creatively established six-five bicyclic lactones through the introduction of a trans-six-membered ring at α and β positions of γ-BL, which rendered five-membered lactone highly polymerizable at room temperature (Figure 2c and d). The resulting poly(3,4-T6GBL) has improved thermal stability (T_d = 340 °C) and crystallinity (T_m = 190 °C) compared with PBL (T_d = 273 °C (cyclic topology) and 201 °C (linear topology), T_m = ~60 °C), while still maintaining the fully tail-to-head depolymerizability [55]. Very recently, Chen *et al*. [56–59] also designed a hybrid lactone with a bridged bicyclic structure by coupling low-T_c γ-BL with high-T_c substructure (*e.g.*, ε-caprolactone) for high polymerizability and performance properties (Figure 2e and f), also providing a powerful approach to unify conflicting (de)polymerizability and performance properties.

2.1.2 *Chemically recyclable polyesters from substituted six-membered lactones*

Compared with the low-strained five-membered γ-BL, six-membered δ-valerolactone (δ-VL) and its derivatives that possess moderate ring strain and T_c may be ideal candidates to prepare chemically recyclable polyesters at mild conditions. Moreover, ring strain and associated (de)polymerizability, as well as the properties of resultant polyesters, can be further adjusted by modulating the structure and positions of substituents to the δ-VL ring [60,61]. For example, β-methyl-δ-valerolactone (βMδVL) can be obtained through direct fermentation of glucose or prepared from the intermediate compound methylhydroxy acid [62]. Hillmyer and coworkers [63] achieved the bulk ROP of βMδVL at room temperature and further synthesized PβMδVL-based thermoplastic polyurethanes and flexible foams (Figure 3a). These polyurethane materials can be chemically recycled to recover βMδVL in high purity (95% by ^{1}H NMR) and high yield (97%) catalyzed by stannous octanoate (Sn(Oct)$_2$) by heating the bulk materials at 200–250 °C.

Furthermore, Hillmyer *et al*. [64] developed recyclable cross-linked polycarbonate (PC) and polyester elastomers based on βMδVL with enhanced solvent resistance and thermal stability. Both elastomers were demonstrated to depolymerize in the presence of Sn(Oct)$_2$ and pentaerythritol ethoxylate at 150 °C overnight under vacuum, resulting in the recovery of the βMδVL monomer in up to 93% yield. In 2018, Hoye *et al*. [65] synthesized a carbomethoxylated



(d) their ceiling temperatures and thermal properties

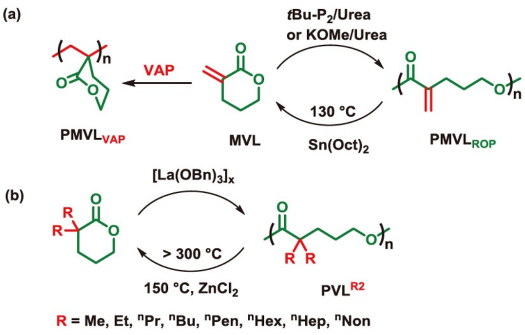
Samples	T_c (°C)	T_g (°C)	T_m (°C)
βMδVL	14~40	-56~-51	-
CMVL	98	-18	86
δCL	42	-39	~40
δOL	28	-52	-
δUL	42	-55	-
δTL	47	-56	-

Figure 3 ROPs of mono-substituted δ-valerolatones: (a) βMδVL, (b) CMVL, (c) alkyl-δ-lactones and their reversed depolymerization as well as (d) their ceiling temperatures (T_c) and thermal properties of resultant polyesters (color online).

polyvalerolactone using malic acid as the feedstock. This semi-crystalline polyester can be chemically recycled in two independent pathways either by backbiting depolymerization at 150 °C in the presence of $Sn(Oct)_2$ to recover 4-carbomethoxyvalerolactone (CMVL) with an 87% yield or by cleaving the polyester in a retro-oxa-Michael fashion catalyzed by a base to afford methacrylate monomer, 2-methyleneglutaric monomethyl ester (2-MME) (Figure 3b). As a commercially available bio-renewable monomer, δ-caprolactone (δ-CL) is a δ-methyl-substituted six-membered lactone that is naturally found in fruits and can be synthesized on a large scale from bio-sourced 5-hydroxymethylfurfural [66]. However, the poor polymerization activity and controllability of δ-CL originating from the less nucleophilic propagating chain end (secondary alcohol species) hampers its application as a material. Recently, Shen and Li *et al*. [67] achieved the first "living"/controlled ROP of δ-CL using a base/urea binary catalytic system (Figure 3c). The addition of urea as a co-catalyst significantly improved the polymerization rate and controllability, producing PδCL with controlled molecular weights, narrow dispersity ($Đ$) and well-defined chain-ends. The detailed thermodynamics investigation suggested the thermodynamic near-equilibrium characteristics for the ROP of δ-CL. The change of enthalpy ($\Delta H_p°$) and entropy ($\Delta S_p°$) was measured as -12.8 kJ mol^{-1} and -40.6 J mol^{-1} K^{-1}, respectively, corresponding to a T_c of 42 °C at $[M]_0 = 1$ mol L^{-1}. PδCL was able to selectively depolymerize to recover δ-CL under vacuum at 130 °C with an almost quantitative yield in the presence of $Sn(Oct)_2$. PLLA-*b*-PδCL-*b*-PLLA triblock copolymers with tunable mechanical properties ranging from tough thermoplastics to thermoplastic elastomers were synthesized by a one-pot sequential ROP of δ-CL and L-lactide (L-LA). Remarkably, these triblock copolymers can be chemically converted into ethyl lactate and δ-CL through cascade alcoholysis and subsequent depolymerization of PδCL.

Telechelic PδCL diols with well-defined terminal hydroxyl groups were then prepared in the presence of an organobase *t*Bu-P_2/urea at a catalyst loading as low as 0.05 mol% in bulk at room temperature (RT). Given the "living"/controlled polymerization characteristics of ROP of δ-CL, a one-pot strategy by cascade ROP of δ-CL and step-growth polymerization of PδCL diol precursors with 4,4′-methylene diphenyl diisocyanate (MDI) was then used to produce polyurethane thermoplastics with excellent mechanical properties. These polyurethane thermoplastics can be chemically recycled to recover high-purity δ-CL with an almost quantitative yield by distillation at 180 °C under reduced pressure in the presence of $Sn(Oct)_2$ as the catalyst [68]. Very Recently, Shen and Li *et al*. [69] have extended the chemically recyclable (co)polyesters to δ-substituted six-membered lactones with different alkyl groups (Figure 3c). Interestingly, the rheological and mechanical properties of the resultant (co)polyesters can be adjusted by changing the alkyl substituent length.

α-Methylene-δ-valerolactone (MVL) is a bifunctional six-membered lactone monomer bearing an exocyclic α-methylene. MVL can be prepared *via* a simple two-step protocol using bio-derived δ-VL and ethyl formate as starting reagents. In contrast to the alkyl mono-substituted δ-VL, the introduction of α-methylene does not generate stereogenic centers. Xu *et al*. [70] reported the chemoselective ROP of MVL using *N*-heterocyclic carbenes (NHC) as the catalyst but only produced oligomers. Later, Shen and Li [71] achieved the chemoselective controlled ROP of MVL using a base/urea binary catalyst (Figure 4a). The resultant PMVL



(c) Ceiling temperatures and thermal and mechanical properties

Sample	T_c (°C)	T_g (°C)	T_m (°C)	σ_b (MPa)	ε_b (%)
MVL	93	3	79	20.0 ± 1.9	291 ± 43
VL^{Me2}	115	-40	75	-	-
VL^{Et2}	78	18	140	29.8 ± 1.7	13.3 ± 0.5
VL^{Pr2}	67	-18	123	44.0 ± 2.6	209 ± 15
VL^{Bu2}	88	-28	77	-	-
VL^{Pen2}	100	-33	68	-	-
VL^{Hex2}	92	-41	80	22.0 ± 1.7	234 ± 8.0
VL^{Hep2}	-	-49	44	-	-
VL^{Non2}	-	-57	50	11.1 ± 0.4	273 ± 12

Figure 4 The ROPs of (a) MVL, (b) VL^{R2} and their reversed depolymerization. (c) The ceiling temperatures and thermal and mechanical properties of resultant polyesters (color online).

was a semi-crystalline polyester with a high crystallinity (X_c = 52%). The high-molecular-weight PMVL (M_n = 74.6 kDa) behaved as a tough thermoplastic with comparable mechanical properties to those of commercial polyolefin materials (σ_b = 20.0 ± 1.9 MPa, ε_b = 291% ± 43%). PMVL can be depolymerized to recover the original monomer with high yield and purity catalyzed by $Sn(Oct)_2$. Notably, the pendent double bond of PMVL provided an opportunity to further tailor the properties by post-modification through thiol-ene click reaction.

Recently, Xu and Chen *et al*. [72] developed a dual catalyst/polymer recycling system in that recyclable inorganic phosphomolybdic acid catalyzes selective depolymerization of high-ceiling-temperature (T_c = 243 °C) PVL in bulk phase, which, upon reaching suitable molecular weight (> 26 kDa of M_c, critical entanglement molecular weight) exhibits outstanding mechanical performance with high tensile strength of 66.6 ± 5.1 MPa, fracture strain of 904% ± 31%, and toughness of 308 ± 27 MJ/mol. However, PVL shows only a low T_m value of 56 °C, which obviously limits the scope of its use. To address this challenge, Xu and Chen *et al*. developed a novel gem-dialkyl substituted VL (VL^{R2}) by introducing two dialkyl substitutions at α position of δ-VL for enhancing recyclability and heat resistance (Figure 4b). These disubstituted δ-VLs showed finely balanced (de)polymerizability, allowing both the facile production of high-molecular-weight polymers under ambient conditions and selective depolymerization of PVL^{R2} to fully recover monomers in pure state under mild conditions (150 °C with a catalyst such as $ZnCl_2$ or >300 °C without a catalyst). PVL^{Et2} and PVL^{Pr2} show high T_m values of 140 and 123 °C, which compare well with the T_m values of HDPE and LDPE, respectively. PVL^{Pr2} is a strong, ductile and tough material, which largely outperforms LDPE in all areas and is even stronger than HDPE. The copolymer $PVL^{Pr2/Et2}$ further outperforms PVL^{Pr2} with a higher ultimate strength (σ_B = 47.1 ± 0.3 MPa), elongation at break (ε_B = 322% ± 1.4%) and toughness (U_T = 79.7 MJ/m^3). PVL^{Pr2} and $PVL^{Pr2/Et2}$ also show excellent barrier performance with low oxygen permeability values and low water-vapor transmission [73].

Poly(p-dioxanone) (PPDO), also known as poly(1,4-dioxan-2-one), is a semicrystalline poly(ether-ester), generally prepared from ROP of p-dioxanone (PDO). PPDO has been demonstrated to have good biocompatibility and biodegradability as well as excellent mechanical strength given its crystallinity with T_m of 110 °C [74]. As biocompatible polymers, PPDO has been approved by the Food and Drug Administration (FDA) of the USA as an absorbable suture under the name of PDS® first introduced by Ethicon in 1981 [75]. The synthesis of PPDO has received extensive interest due to its potential biomedical applications [75–77]. However, PPDO as a degradable and sustainable polymer, did not receive sufficient attention as much as PLA and others. The main reason was probably due to its monomer cost. Recently, Wang *et al*. [78] invented an efficient and highly selective catalytic dehydrogenation cyclization catalyst to one-step synthesize PDO monomer with high yield by using cheap diethylene glycol as raw material. The yield and purity can reach 99%, and the catalyst life exceeds 180 days. Up to now, a wide range of catalysts have been employed to realize the ROP of PDO, including organic metal compounds, metal-free organic catalysts, and enzymes [79–81]. Recently, Tian *et al*. [82] developed novel single-group bifunctional hydrogen-bonding catalysts based on thiazolium for bulk ROP of PDO to achieve the dispersity below 1.4 with high monomer conversion. Besides its great physical properties, PPDO can be completely decomposed into environmentally harmless substances, such as CO_2 and H_2O, in natural environments [83,84]. More importantly, the ROP of PDO exhibits a very suitable balance between polymerization and depolymerization with a moderate T_c of 265 °C [85], not only enabling the achievement of PPDO with high molecular weight and narrow molecular weight distribution under ordinary polymerization conditions, but also realizing the efficient and mild depolymerization to yield high-purity PDO monomer [86,87]. It is obvious that like PPDO, the biodegradable and chemically recyclable polymers which were put forward internationally by Wang *et al*. [31,88] for the first time, meeting the requirement of the green and low-carbon development of polymer materials, is supposed to be one of the ideal candidates for the single-use polymer' products.

Given the presumably stable PDO monomer structure, $\Delta H_p°$ and $\Delta S_p°$ was measured as −14.5 kJ mol^{-1} and −48.1 J mol^{-1} K^{-1}, corresponding to a T_c of 28 °C at $[M]_0$ = 1 mol L^{-1}. In 2000, Nishida *et al*. [86] reported pyrolysis of PPDO to PDO monomer with 99.3% yield after 3.5 h at 230 °C. Unfortunately, such a pyrolysis strategy required high temperature and relatively long depolymerization time, which undoubtedly caused side reactions, such as intramolecular esterification/transesterification to form cyclic PPDO oligomer and *cis*-elimination reaction to generate olefinic products, thus limiting the recycling efficiency [89]. Most recently, Zhang *et al*. [90] developed a Brønsted-Lewis acidic ionic liquid/polyhydroxy-compound system (BLAIL) to attain ultrafast and highly selective depolymerization of PPDO to PDO (Figure 5). As a result, using BLAIL $[Et_3NH][ZnCl_3]$ at 160 °C in 8 min, high molecular-weight PPDO can be almost fully depolymerized to the PDO monomer with a yield of 95%.

The copolymerization of two or more monomers is an effective way to combine the advantages of each corresponding homopolymer and improve their unsatisfied properties while maintaining their inherence depolymerization characteristics. Xiong *et al*. [91] conducted a sequential copolymerization of PDO and various n-alkyl substituted δ-valerolactones ((R)VLs) to poly(p-dioxanone)-*block*-poly(n-

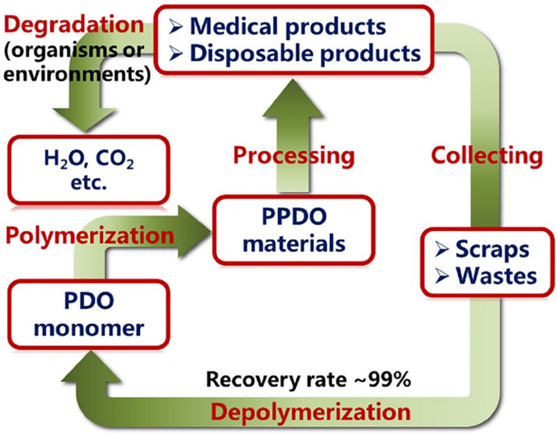


Figure 5 Chemically closed-loop recycling and degradation of PPDO (color online).

alkyl-valerolactones) (PPDO-*b*-P(R)VLs) diblock. By changing the alkyl substituents (R) length and the P(R)VLs content, the physical properties of PPDO-based diblock copolymers can be adjusted effectively to meet the practical application requirements. Using Sn(Oct)$_2$ as a catalyst, these diblock copolymers can be depolymerized to PDO and the respective (R)VL co-monomers at 120 °C under reduced pressure. Moreover, Yan *et al*. [92] prepared poly(γ-butyrolactone)-*block*-poly(*p*-dioxanone) (PγBL-*b*-PPDO) by a one-pot sequential copolymerization of γ-butyrolactone (γ-BL) and PDO (Figure 6). The thermal depolymerization of PγBL-*b*-PPDO copolymers to co-monomers PDO and γ-BL with a yield of 95.4% and an isolated purity of 99% was conducted at 120 °C under vacuum without any catalyst, and subsequently two recycled monomers can be re-copolymerized to regenerate the copolymers with nearly identical structures and properties, realizing the proof-of-concept for the closed-loop recycling from copolymers to co-monomers and back to copolymers.

2.1.3 Chemically recyclable polyesters from seven-membered lactones

In addition to bio-renewable monomers, it is especially attractive to prepare chemically recyclable polyesters using bioplastics as feedstock. Poly(3-hydroxybutyrate) (P3HB) has emerged as the most successful commercial polyhydroxyalkanoate (PHA) due to its renewable feedstock, biodegradability and good mechanical properties. However, P3HB cannot be efficiently chemically recycled to its pristine monomer to recover the material value. Shaver *et al.* [93] developed a seven-membered monomer, 2,3-dihydro-5*H*-1,4-benzodioxepan-5-one (2,3-DHB). In the presence of an aluminum catalyst (MeAl[salen]), a polymer with an aromatic ring in the backbone was obtained that was capable of depolymerization at a low reaction temperature (room temperature) with a high monomer conversion. The equilibrium between the monomer and polymer allows for the establishment of a reversible polymerization-depolymerization cycle by simply adjusting the initial monomer concentration in a one-pot reaction. Recently, Shen and Li *et al.* [94] reported an effective strategy to achieve the upcycling of P3HB to produce a series of chemically recyclable poly (ether-ester)s. Ethyl 3-hydroxybutyrate (HBEt) was first obtained by alcoholysis of P3HB, which was then reacted with cyclohexene oxide (CHO) to produce intermediates that can be finally converted to the bicyclic ether-ester monomer 4-methyloctahydro-2H-benzo [*b*] [1,4dioxolan-2-one (4-MOHB). The controlled ROP of 4-MOHB produced amorphous P(4-MOHB), which can be depolymerized using *p*-toluenesulfonic acid (TsOH) or Sn(Oct)$_2$ in solution or in bulk to recover 4-MOHB monomer (Figure 7a). P3HB can also be converted to an *N*-heterocyclic lactone, 5-methyl-*N*-Boc-1,4-oxazepane-7-one (MeOxP$_{\mathrm{Boc}}$), which underwent controlled ROP to produce amorphous poly(amine-*alt*-ester) [95]. P(MeOxP$_{\mathrm{Boc}}$) could be depolymerized to recover MeOxP$_{\mathrm{Boc}}$ monomer catalyzed by Sn(Oct)$_2$ in dilute solution at 120 °C or by ZnCl$_2$ as a catalyst in bulk at 150 °C. Notably, the corresponding cationic polymer can be successfully prepared by removing the pendent *t*-butoxycarbonyl protecting groups of P(MeOxP$_{\mathrm{Boc}}$) (Figure 7b). Despite these advancements, both P(4-MOHB) and P(MeOxP$_{\mathrm{Boc}}$) exhibited amorphous properties due to their low stereoregularity, which greatly limited their applications.

This problem was recently addressed by using enantiopure bicyclic ether-ester as monomers (Figure 7c). The as-prepared 4-MOHB consisted of two diastereoisomers with distinct polarities, which can be separated by column chromatography to afford two enantiopure monomers. These enantiopure monomers can undergo stereoretention ROP in the presence of Sn(Oct)$_2$ as the catalyst to prepare stereoregular polyesters [96]. In contrast to the amorphous atactic polyesters prepared from racemic monomers, the obtained stereoregular polyesters exhibited excellent crystalline behaviors with melting temperatures up to 176 °C for PM1. These stereoregular polyesters can be depolymerized back to recover enantiopure monomers catalyzed by Sn(Oct)$_2$ in di-

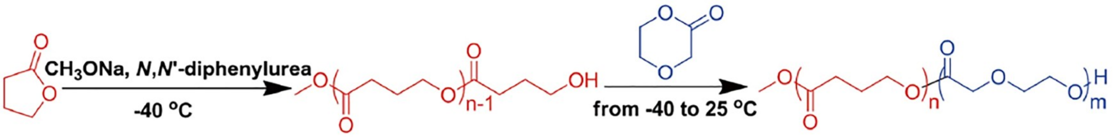


Figure 6 Synthesis of PγBL-*b*-PPDO (color online).

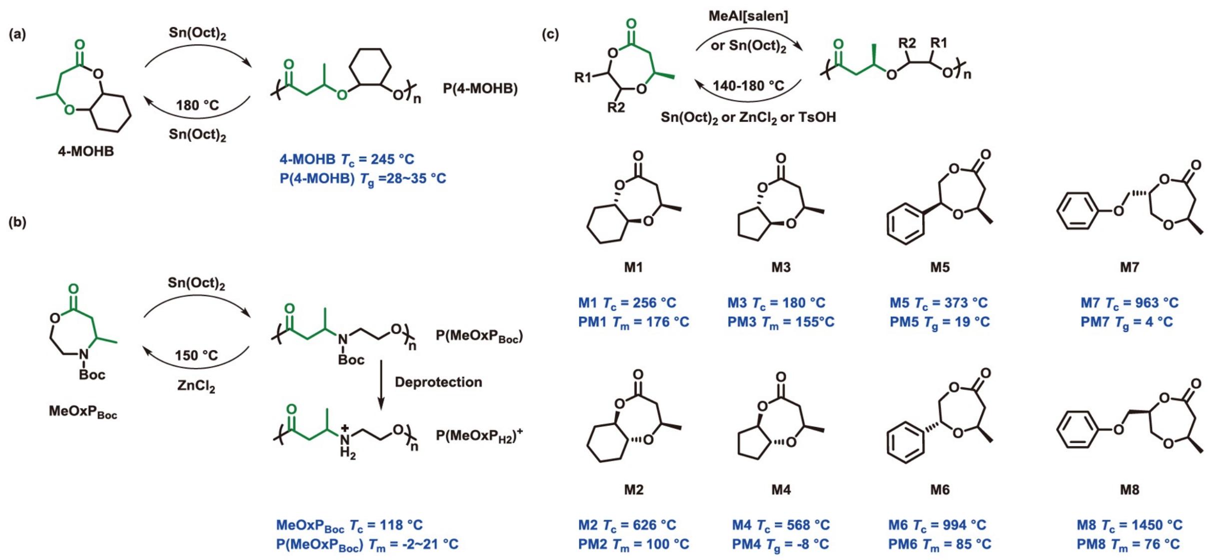


Figure 7 (a) Upcycling of P3HB to prepare closed-loop recyclable poly(ether-*alt*-ester)s. (b) Upcycling of P3HB to *N*-heterolactone and recyclable poly (amino-*alt*-ester). (c) Chemical structures of *O*-heterolactones and their ceiling temperatures as well as the physical properties of resultant polyesters (color online).

luted trimethylbenzene solutions or by distillation under reduced pressure in the presence of $ZnCl_2$ as the catalyst. Enantiopure *O*-heterocyclic lactones bearing with pendent phenyl groups were also prepared using racemic styrene oxide as the starting reagent (Figure 7c) [97,98]. Notably, PM6 behaved as a semi-crystalline (T_m = 85 °C, X_c = 34%) tough thermoplastic with good mechanical properties (σ_b = 7.9 ± 0.7 MPa, ε_b = 170% ± 20%). All four polyesters (PM5–PM8) can be depolymerized in solution catalyzed by $Sn(Oct)_2$ to recover the pristine monomers.

Recently, Cai and Zhu *et al*. [99,100] exploited salicylic acid and its derivatives as natural aromatic building blocks to construct two series of aromatic cyclic esters R^1-DHB-X-R^2 and BDPO-R^1R^2 (Figure 8). A facile synthetic strategy by taking advantage of epoxides and (thio)salicylic acid as starting materials was developed to efficiently prepare aromatic cyclic esters R^1-DHB-X-R with stereo-defined and diverse functionalities. This system illustrated the feasibility of ROP and subsequent ring-closing depolymerization (RCD) back to monomers, indicating a chemically recyclable polymer system. Additionally, isotactic *R*- and *S*-polymers generated by the ROP of enantiopure monomers were able to form stereocomplexed polymers with enhanced thermal properties and crystallinity compared with their corresponding component enantiomers. More importantly, post-polymerization modification, including "click", cross-linking, oxidation, and deprotection reactions, were carried out to enable the fine-tuning and improvement of the thermal and mechanical properties of these pristine polymers toward access to value-added materials (*e.g.*, T_g increased up to 121 °C). Furthermore, the introduction of naphthalene groups in the polymer main chain enhanced the T_g values of P(DHN-R) significantly (T_g > 100 °C).

Considering that the conjugation between aromatic rings and carbonyl groups in R^1-DHB-X-R^2 could diminish its polymerization reactivity, a new class of aliphatic-aromatic monomers R^3-BDPO-R^1R^2 *via* "nonadjacent ester" strategy was prepared from salicylaldehyde (Figure 8). Gratifyingly, this system combined the robust polymerization reactivity of aliphatic esters with the beneficial properties of aromatic linkages, furnishing fully chemically recyclable polymers [101]. BDPO-R^1R^2 underwent rapid polymerization at room temperature, affording polymers with high molecular weight (M_n) up to 438 kDa. Varying the pendant groups R^1 and R^2 on the monomers allowed access to polymers with a broad range of T_gs from −1 to 79 °C and mechanical performance from brittleness to elasticity. Further, installing methoxy and bromo embellishment on the phenyl moiety (R^3-BDPO-R^1R^2) preserved the high polymerizability and recyclability of the pristine BDPO system and demonstrated a slight improvement in T_g [102]. Remarkably, the naphthalene engineering of this system (NDPO-R) led to the appearance of melting transitions based on PXRD analysis. Ultimately, copolymerization study was continuously investigated to construct high-performance polymers. The rigid naphthalene served as a strong and hard building block to toughen the elastomer P(BDPO-Hex), delivering an LDPE-like mechanical performance.

2.1.4 *Chemically recyclable polythioesters*

Polythioesters (PTEs) are polyester analogues in which the non-carbonyl oxygen atoms in the main chain are replaced with sulfur atoms [103]. The introduction of sulfur atoms brings the material with unique properties such as high re-

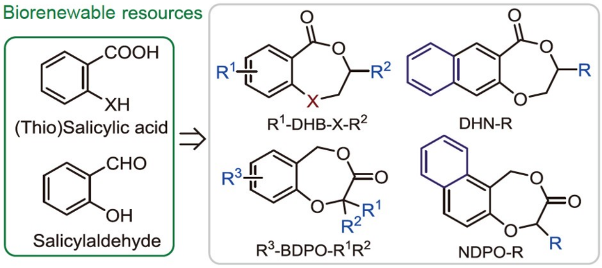


Figure 8 Salicylic-based monomers for CDPs (color online).

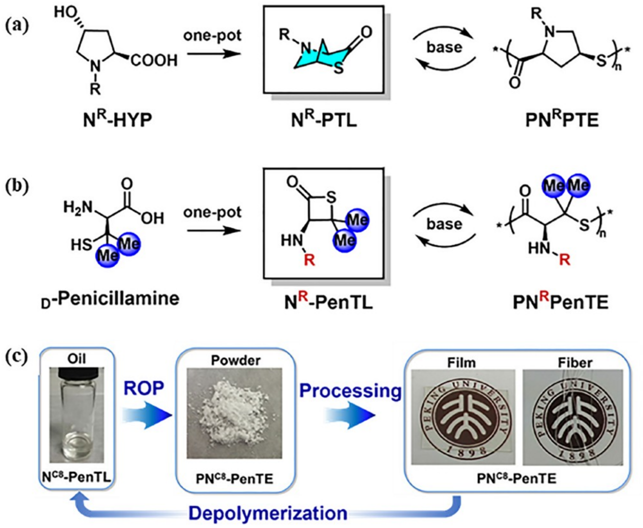


Figure 9 Development of controllable and recyclable PTEs *via* the judicious choice of ring systems and taking advantage of subtle substitution effects. (a) 4-Hydroxy-L-proline derived bridged-ring thiolactone, as well as its controlled ROP and depolymerization. Reproduced from Ref. [107] with permission. Copyright 2019 American Chemical Society. (b, c) D-penicillamine derived β-geminal dimethyl substituted β-thiolactone, and its controlled (de)polymerization. The obtained PTE powder can be easily hot-processed into films or fibers, and the materials can be completely depolymerized to recover monomers. Reproduced from Ref. [109] with permission. Copyright 2020 Elsevier Inc. (color online).

fractive index and excellent crystallinity [104,105]. However, the controllability of thiolactone polymerization is suboptimal, likely due to side reactions of thioesters caused by its enhanced reactivity (*e.g.*, intramolecular or intermolecular transthioesterifications) [106]. To address these problems, Lu *et al.* [107] designed a series of bridged-ring thiolactones ($\mathrm{N^R}$-PTL) with high ring strain from biomass feedstock 4-hydroxy-L-proline (Figure 9a). The ROP of $\mathrm{N^R}$-PTL mediated by benzyl mercaptan (BnSH) and triethylamine (TEA) afforded PTEs with predictable molar mass (M_n), and well-defined chain ends (benzyl thioester on α end and thiol on ω end, respectively). Remarkably, PTEs with M_n up to 259 kDa and low *Đ* of ~1.20 were readily obtained by using weak base TEA as the catalyst. Switching to a stronger base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) dramatically shortened the reaction time to 5 min without compromising too much the controllability of ROP. In addition, employing catalytic amounts of base in diluted solution quantitatively recovered monomer $\mathrm{N^R}$-PTL in 2 min at 50 °C through a head-to-tail depolymerization mechanism. Density functional theory (DFT) calculations elucidated the importance of rational molecular design, presuming that $n\rightarrow\pi^*$ orbital interactions between the side chain urethane and thioester carbonyl reduced the electrophilicity of thioester, while the relatively high steric hindrance effectively suppressed chain transfer side reactions, thus improving the controllability of ROP. Interestingly, a series of bicyclic lactone analogues ($\mathrm{N^R}$-PL) that had similar structures with $\mathrm{N^R}$-PTL were capable of achieving controlled ROP [108]. This drastic difference highlighted the distinct thermodynamic and kinetic features brought about by the differences in bond lengths, bond angles, and electronic effects between lactones and thiolactones.

In addition to incorporating ring structures (*e.g.*, bridged-rings or fused-rings) into polymer backbones, substituent effects can also effectively modulate the thermodynamics and kinetics of ROP. Lu *et al.* [109] also synthesized β-geminal dimethyl substituted β-thiolactones ($\mathrm{N^R}$-PenTL) from D-penicillamine *via* a one-pot method (Figure 9b). By virtue of the Thorpe-Ingold effect, the ring strain of the four-membered ring monomer was greatly suppressed, which made the depolymerization possible. On the other hand, the large steric hindrance reduced chain transfer and backbiting side reactions during polymerization, thereby improving the controllability of ROP. In contrast, the ROP of cysteine-derived β-thiolactones (which do not have the germinal dimethyl substitution) was less controllable with *Đ* higher than 1.6, while depolymerization of the obtained polymer was not reported [110]. The remarkable differences emphasized the importance of substituent effects. DFT calculations similarly demonstrated that the introduction of geminal dimethyl substitution significantly reduced the ring strain of the β-thiolactones, which made depolymerization thermodynamically feasible. The obtained $\mathrm{PN^R}$PenTE can be easily hot processed into films or fibers, and the materials can be quantitatively recovered to enantiopure $\mathrm{N^R}$-PenTL within 4 h at room temperature with the presence of catalytic amounts of base in dilute solution (Figure 9c). Moreover, the thermal and mechanical properties of resulting $\mathrm{PN^R}$PenTE can be easily tuned by changing the side chain structures.

In certain cases, the replacement of a single atom with another in the cyclic monomer can effectively change the thermodynamics and kinetics of ROP. Tao *et al.* [111] discovered that the ring strain of the monomer could be effectively reduced by a subtle O-to-S substitution, possessing a series of amino acids-based dithiolactones as the “ideal monomers” employed for sustainable polymer preparation (Figure 10a). Dithiolactones maintained polymerization activity under mild conditions, and enabled the synthesis of

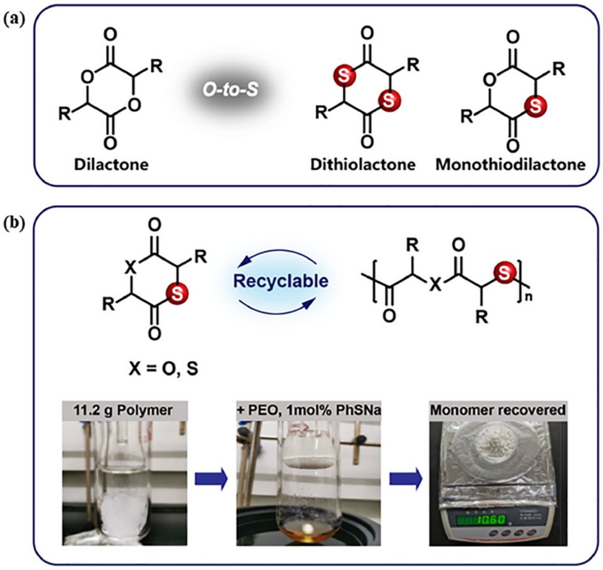


Figure 10 (a) By subtle O-to-S substitution, dithiolactone and monothiodilactone are derived as dilactone analogues. (b) The substitution of oxygen with sulfur facilitates improved polymerization activity and complete chemical recyclability. The resulting polymer can be effectively and selectively regenerated back into the original monomers using a sublimation apparatus with the assistance of an organic base. Reproduced from Ref. [113] with permission. Copyright 2023 American Chemical Society (color online).

functional polythioesters with distinctive characteristics, including controllable molecular weight (up to 100.5 kDa), atactic stereostructures but high crystallinity, and complete chemical recyclability (Figure 10b). The depolymerization process of the resulting polythioester exhibits exceptional selectivity, converting the polythioester into racemic dithiolactone monomers with only 2% *meso*-dithiolactone. The polymerization product of valine-based dithiolactone with pendant isopropyl group, possessing atactic but crystalline unusual characteristics, exhibits a melting point of 115 °C. This polymer can be injection-molded into dumbbell-shaped specimens, exhibiting a tensile strength of up to 21 MPa. Furthermore, the trade-off between the cyclizability/polymerizability, as well as depolymerizability/properties, were successfully addressed in the polythioester materials derived from the ROP of dithiolactones. This ingenious approach offers significant advantages, including the ease of monomer synthesis, the simultaneous presence of controllability and high polymerization activity, high crystallinity, and exceptional activity with selectivity in depolymerization.

Nevertheless, owing to the heightened C–H acidity of dithiolactone, the epimerization side reactions during the polymerization process become unavoidable using organic bases (such as DMAP and TBD) [111]. To address these issues, Tao *et al*. [112] employed aluminum catalysts with meticulously designed ligands to catalyze the stereoselective ROP of dithiolactone, yielding highly isotactic polythioesters with molecular weight up to 45.5 kDa. Both experimental and computational investigations have demonstrated that the aluminum complex exhibits a suitable binding affinity with the sulfide propagating species. This proper binding affinity between the sulfide propagating species and aluminum complex enables the avoidance of catalyst poisoning and minimizes the occurrence of epimerization reactions, which are not achievable with alternative metal catalysts. This material has the ability to form crystalline stereocomplex with a melting point of 94.5 °C, and its mechanical properties are on par with those of low-density polyethylene (LDPE) derived from petroleum. Exposure of the polythioester to the aluminum precatalyst employed in its synthesis triggered the depolymerization process, reverting it back to the original chiral dithiolactone.

This single-atom oxygen-by-sulfur substitution strategy [113] allows for the conversion of "non-recyclable" polyesters into chemically recyclable polymers by reducing the ring strain energy in the monomer (the ring strain energy is decreased from 16.0 to 9.1 kcal mol^{-1}, for dilactone to monothiodilactone). The ROP of monothiodilactone monomers exhibits fast kinetics, remarkable regioselectivity, specifically targeting at the acyl-S bond sites, narrow dispersion ($Đ < 1.1$), and minimal transthioesterifications. As a result, poly(monothiodilactone) with a fully alternating structure of the ester-thioester is obtained, showcasing a highly ordered arrangement. The adjacent thioester and ester in the polymer backbone enhance the "n→π* interaction", thereby stabilizing the thioester bond in the polymer chain, whereas this interaction is not as prominent in the monomer. Thus, the "n→π* interaction" of the polymer backbone suppresses the side reactions during the polymerization, like the transthioesterification, often characterized as "inevitable" in earlier literature, without sacrificing the monomer's activity, thereby enabling controllable ROP of monothiodilactones. The resulting polymer can be effectively and selectively regenerated back into the original monothiodilactones using a sublimation apparatus with the assistance of an organic base (Figure 10b). The impeccably alternating polythioester exhibits comparable mechanical properties to petroleum-based LDPE, particularly in terms of toughness (with an elongation at break exceeding 400%).

2.1.5 *Chemically recyclable polycarbonates*

The aliphatic polycarbonate (APC) can exhibit desired material properties and chemical recyclability *via* a delicate monomer design strategy [18,24,114–118]. Two representative routes from strained heterocycles, *i.e.*, ring-opening copolymerization (ROCOP) of epoxide with CO_2 and ROP of cyclic carbonate, can be envisioned for the synthesis of APCs (Figure 11) [18]. Generally, the ring-opening at the methine C–O bond of the *cis*-ring structure in the epoxide motif results in an inversion of stereochemistry at the methine carbon, thus producing a polycarbonate with a *trans*-backbone configuration. Therefore, it can be inferred that the reverse sequence associated with the alkoxide intermediate to attack the methine carbon atom produces the starting *cis*-epoxide and CO_2 through a ring-closing decarboxylative process (Figure 11). Other alternative backbiting reactions involve the alkoxide or carbonate species attacking the carbonyl or methine carbon, yielding *trans*- or *cis*-carbonate, respectively. Such structures are thermodynamically stable, which impedes ROCOP again, and this represents a big challenge for chemically recycling APCs to epoxides and CO_2.

The first full-cycle depolymerization to epoxide monomers was demonstrated with poly(cyclopentene carbonate)s (PCPC) [119]. For example, NaHDMS catalyzed depolymerization of PCPC at 110 °C slowly produced cyclopentene oxide (CPO) and *cis*-cyclic carbonate with selectivity of 42% and 58%, respectively (Figure 12). A high yield of up to 92% for epoxide formation was obtained when the polycarbonates were treated with Cr^{III}-Salen/$^nBu_4NN_3$ systems under identical conditions. The abnormal result for epoxides formation, rather than *trans*-cyclic carbonates [120], is convinced that the ring strain induced on the resultant five-membered carbonate ring to accommodate the conformational requirements of the alicyclic cyclopentenyl ring makes *trans*-cyclopentene carbonate extremely thermodynamically unstable. The considerable ring strain is also supported by

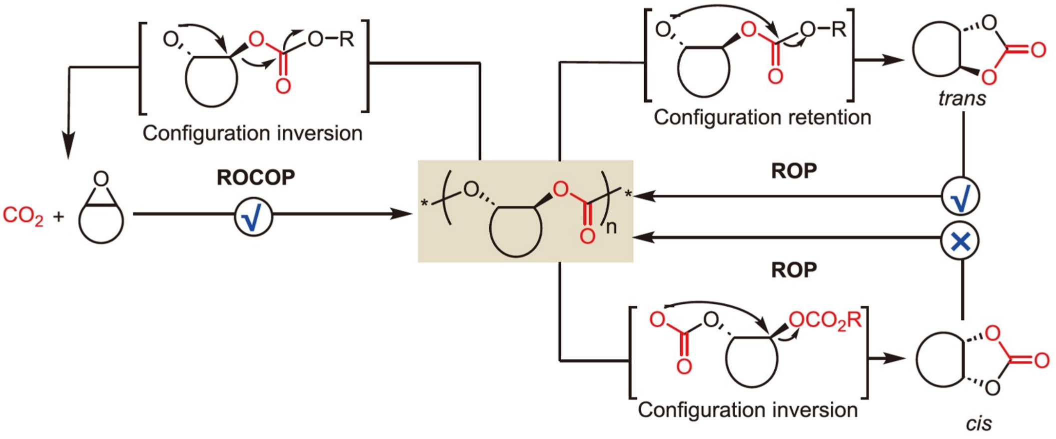


Figure 11 Representative depolymerization modes of APCs to alicyclic epoxides or alicyclic carbonates: the backbiting reactions involve alkoxide and carbonate species. Reproduced from Ref. [113] with permission. Copyright 2020 Springer Nature (color online).

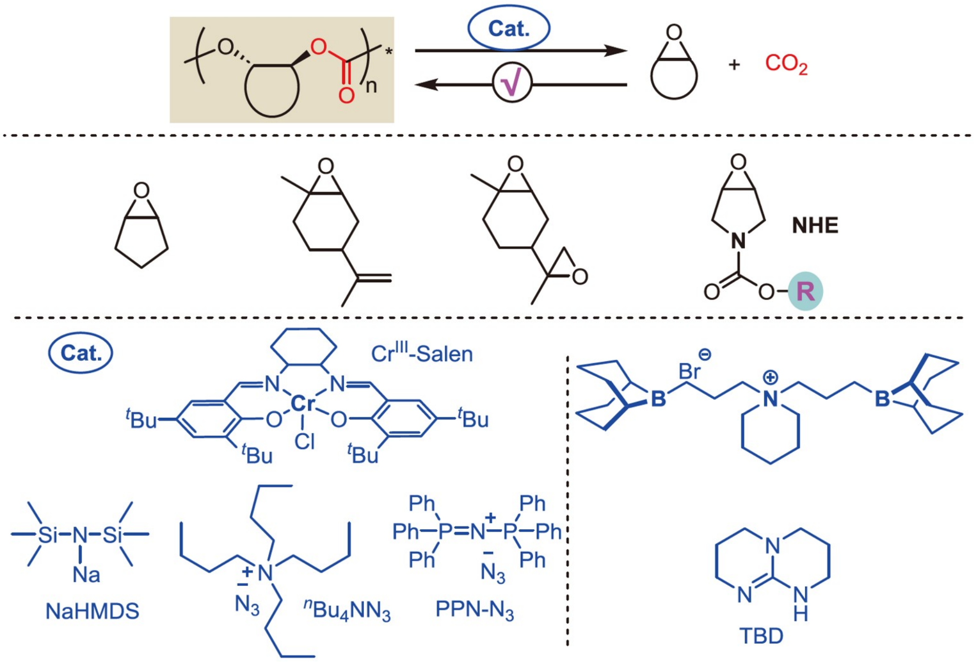


Figure 12 Chemical recycling of representative APCs to epoxide monomers and the used catalysts (color online).

structural simulation, revealing that the *trans* isomer is 20.4 kcal mol^{-1} higher in energy, with a highly distorted bridgehead bond angle (O–CH–CH_2 = 127.2° for *trans versus* 111.5° for *cis*) [121]. The depolymerization to CPO was recently demonstrated by using transition-metal free catalysis, where the combination of organoboron/KOH exhibited superior controllability in the depolymerization of PCPC at 110 °C in toluene, resulting in a nearly quantitative recovery of epoxides (Figure 12) [122].

It is advantageous to keep the five-membered ring core so that the complete chemical recyclability of the designed polymers can be preserved. Therefore, a series of renewable N-hetero-epoxides (NHE) based on a pyrrolidine framework having different substituents on the carbamate group were also designed [123]. Copolymerization of NHE with CO_2 *via* bimetallic catalysis yielded the corresponding APCs with >99% selectivity at 25–80 °C. The APCs can revert to epoxide monomers and CO_2 quantitatively mediated by Cr^{III}-Salen/PPN-N_3 system in organic solution at 110 °C or in bulk thermolysis at 200 °C (Figure 12). Heating the polycarbonates directly to their decomposition temperature (250–350 °C) without a catalyst also selectively yielded the recovered epoxides [124]. In addition to the five-membered ring core, the nitrogen atom further strengthens the recyclability, as demonstrated by density functional theory (DFT) calculations. Moreover, such substituent imparts both functionality and crystallinity. The poly(limonene carbonate)s [21] and their corresponding derivatives can completely depolymerize to limonene oxide and CO_2 at 110 °C in toluene in the presence of TBD [125]. The recyclability and sustainability of these materials highlight the advantages of CO_2-based polycarbonates.

Poly(cyclohexene carbonate)s have exhibited high tensile strength and could be used as sustainable engineering plastics. However, depolymerization of PCHC generally affords *trans*-carbonate, an intermediate that is less efficient toward ROP again [126–129]. Therefore, it is highly desirable to develop a new catalyst or novel catalytic strategy to close the loop for this promising material. The study is initiated by the independent usage of heterogeneous multinuclear Zn^{II} ($Zn\cdot xH_2O$) [130] and bimetallic Mg^{II}–Mg^{II} [131] complexes to quantitatively catalyze the depolymerization of PCHC to cyclohexene oxide (CHO) in toluene. The depolymerization mechanism was disclosed by DFT calculations, revealing that bimetallic catalysis contributed the backbiting reaction to involve an attack by the metal alkoxide species at the methine position for epoxide extrusion ($\Delta G^{\neq}$ = 19.2 kcal mol^{-1}), rather than *trans*-carbonate formation at the carbonyl ($\Delta G^{\neq}$ = 25.5 kcal mol^{-1}) (Figure 13a). This bimetallic process has successfully shifted from chemical recycling to epoxides *via* a metal-bonded alkoxide backbiting reaction from the general metal-free one toward *trans*-carbonates.

Recently, a low loading of Cr^{III}-Salen complex (0.1 mol%) was discovered to catalyze the bulk thermolysis of PCHC at 120–200 °C, yielding the corresponding CHO quantitatively with a high activity of 3,000 h^{-1} (Figure 13c). More importantly, a selectively chemical recycling to CHO (>90% isolate yield) was obtained for the catalytic thermolysis of PCHC in the presence of commercial PET (mineral water bottle), BPA-PC (CD for optical storage), and HDPE (solvent bottle cap) mixed plastic waste, avoiding the need for time- and cost-intensive separation processes [132]. Subsequently, a heterodinuclear Mg^{II}–Co^{II} catalyst was applied for solid depolymerization (bulk thermolysis) of various APCs. An extremely high TOF of up to 26,000 h^{-1} for PCHC depolymerization was obtained at 140 °C with a 0.02 mol% catalyst loading, yielding a recovered CHO with >99% selectivity [133] (Figure 13b).

The depolymerization of CO_2-based polycarbonates to monosubstituted cyclic carbonates with negligible ring strain, *e.g.*, poly(propylene carbonate)s, is considered to be a dead end, which impedes repolymerizaton for chemical recycling [118]. The *cis*-carbonate isomers are generated by undergoing an inversion of stereochemistry at methine car-

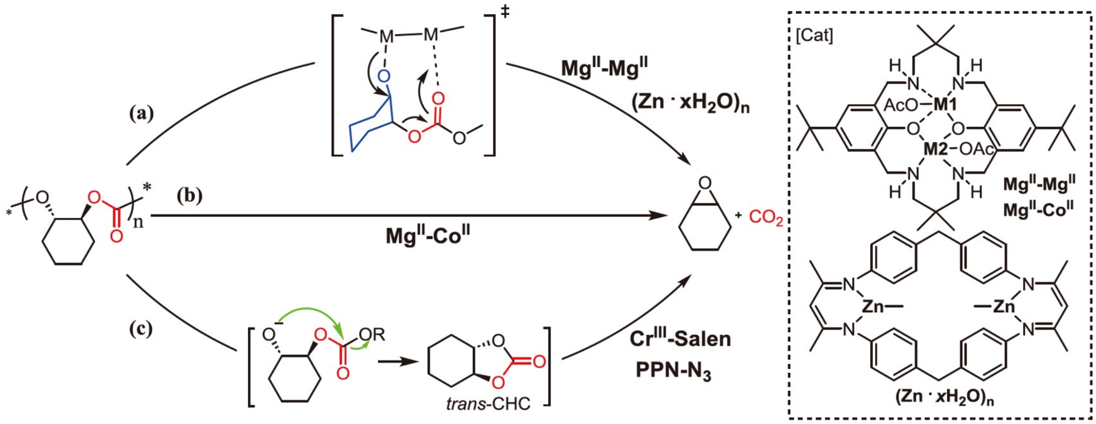


Figure 13 Chemical depolymerization of PCHC to epoxide: solution degradation catalyzed by bimetallic Zn or Mg complexes (a); thermolysis in bulk catalyzed by Mg^{II}-Co^{II} (b) and Cr^{III}-Salen/PPN-N_3 (c) (color online).

bon *via* backbiting of carbonate species in the presence of CO_2 (Figure 11). The acyclic ring fused with a carbonate ring in *trans*-fashion renders such an isomer is kinetically favored *via* alkoxide backbiting toward carbonyls (Figure 11) [115]. While both *cis* and *trans*-carbonate isomers are not ideal monomers for repolymerization to revert chemical recycling, the resultant polymers generally suffer from limited molecular weight values or decarboxylated oligoether units.

Ring-expansion of epoxides using CO_2 yields cyclic carbonate having a five-membered ring structure. Therefore, the design of different carbonates of different sizes with higher ring strains drives the discovery of novel recyclable polycarbonates. For example, trimethylene carbonate and its derivatives have been known for a long time but suffer from monomer-polymer equilibrium during ROP. The powerful metal catalysts and neat conditions are necessary to obtain high conversions and produce poly(trimethylene carbonate) with high molecular weights. In particular, the equilibrium is also responsible for the formation of oligomers and decarboxylated side products upon depolymerization (Figure 14) [134].

The synthetic difficulty is responsible for the less exploration of seven-membered carbonates. The elaborate introduction of *trans*-cyclohexyl fused structure into a seven-membered moiety generates a new class of carbonate monomers, and a representative metal-Y complex exhibited a TOF up to 6 × 10^5 h^{-1} toward ROP. The treatment of the resulting APCs with 5 mol% potassium methanolate also yielded macrocyclic carbonates (MCs) with an isolated yield of ~80%. In particular, those MCs can be repolymerized to generate the parent APCs products [135] (Figure 15a). ROP of MCs has an entropy-driven characteristic requiring high temperature and long reaction time. The ultrafast anionic ROP (<10 s) with *tert*-butoxide enabled a library of MCs with high conversion (>97%), and the resultant polymers were amenable for chemical depolymerization to corresponding MCs catalyzed by ^{t}BuONa with moderate isolate yield (70%–85%) (Figure 15b) [136].

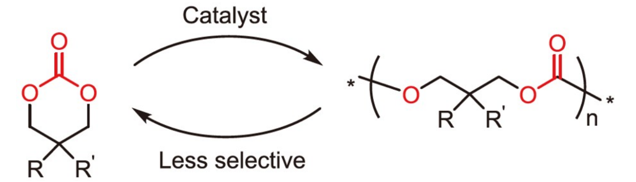


Figure 14 ROP of trimethylene carbonate and corresponding depolymerization (color online).

2.1.6 Chemically recyclable polyamides

Polyamides (PA) are a versatile class of polymers that are employed in a variety of applications, including the production of textiles, high-performance sports equipment, and composite reinforcements. Among PAs, nylon-6 and nylon-66 are the most commonly utilized. The amide bond endows the polymer chain with robust intermolecular hydrogen bonding, conferring upon polyamides a remarkable tensile strength. Amides can be degraded by acid/base-catalyzed hydrolysis or solvolysis. The depolymerization of polyamides requires more harsh conditions than polyesters due to the enhanced conjugation between the carbonyl and nitrogen atoms.

Chemical depolymerization represents a compelling strategy for the recovery of nylon-6, enabling the repolymerization of recycled ε-caprolactam (7LM) into the original polymer. In order to reduce the energy demands of nylon-6 depolymerization, significant research efforts have been dedicated to developing more effective catalysts and optimized reaction conditions. This has been achieved through advancements in techniques such as ionic liquids [137] and Ru-catalyzed hydrogenolysis [138]. Recently, Marks *et al*. [139] have exhibited efficient chemical depolymerization of nylon-6 to 7LM at temperatures ranging from 220 to 240 °C, utilizing highly active lanthanide/early-transition metal catalysts, achieving high catalyst turnover frequencies and excellent 7LM recovery yields. Despite these advancements, the inherent recyclability of nylon-6 remains limited due to the high ring strain and ceiling tem-

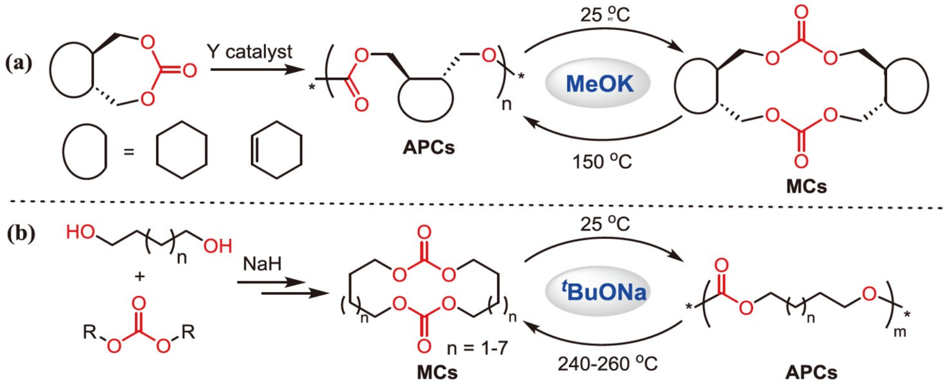


Figure 15 Polymerization and depolymerization of ring fused seven-membered cyclic carbonates (a) and macrocyclic carbonate (b) (color online).

perature (T_c) of 7LM, which have yet to be fully addressed by these methods. Very recently, Chen *et al*. [140] designed a series of novel ε-caprolactam monomers by introducing *gem*-dimethyl groups at different positions (α to ε) of the ε-caprolactam ring. The *gem*-dimethyl disubstitution on the seven-membered lactam ring considerably reduces the T_c (by >700 °C) of these redesigned 7LM monomers (Figure 16), allowing for more efficient chemical depolymerization of the resulting nylon 6 material to the corresponding monomers under milder (60 °C lower temperature) conditions using cheaper and more readily available catalysts. The reactivity of the 7LM monomers is very sensitive to the position of the substitution. The monomers with *gem*-dimethyl substitution at the α, β, and ε positions of the 7LM ring exhibit low polymerization activity due to a combination of steric and RSE factors. In contrast, the 7LM monomers with substitution at the γ and δ positions can be readily polymerized into the corresponding high molecular weight and low dispersibility nylons. The substitution position of the ketodimethyl group also affects the thermodynamic properties of the resulting polymers. δ-*gem*-dimethylated nylon $6^{\delta\mathrm{Me2}}$ is semi-crystalline but exhibits greater brittleness than nylon 6. In contrast, γ-*gem*-dimethylated nylon $6^{\gamma\mathrm{Me2}}$ is an amorphous nylon but exhibits significantly higher T_g (30 °C), yield stress (σ_y, 1.5 MPa), and ductility ($3 \times \varepsilon_B$) than that of nylon 6. The redesigned nylon $6^{\gamma\mathrm{Me2}}$ exhibits desirable properties, including high mechanical properties, closed-loop recyclability, and excellent optical transparency. These characteristics render it a promising candidate for further development.

2.1.7 *Chemically recyclable poly(acetal-alt-ester)s prepared via cationic polymerization*

Aldehydes widely exist in nature, and most of them can be directly obtained from biomass. Due to the low reaction enthalpy, most of the aldehydes are difficult to (co)polymerize. Only several aliphatic aldehydes were reported to undergo cationic or anionic polymerizations at low temperatures [141,142]. Cyclic acetals are derived from the condensation of diols and aldehydes, of which 1,3-dioxolane is a commercially available, low-cost solvent. Previous studies [143–146] showed polyacetals could be synthesized *via* cationic mechanisms using Lewis acid as the catalyst. However, the formation of polyacetal is limited by poor molecular weight control because of the fast and complicated cationic chain growth manner.

Coates *et al*. [144] recently synthesized a high molecular weight poly(1,3-dioxolane), using halomethyl ether (MOMBr) as the initiator and indium(III) bromide ($InBr_3$) as the cationic catalyst for ROP of 1,3-dioxolane. The obtained polyacetals have M_ns as high as 220 kDa. A reversible-deactivation mechanism is proposed through the reversible interconversion of active species and dormant species. These polyacetals have improved thermal stability ($T_{d,5\%} > 337$ °C) and tensile strength (stress σ: 40 ± 1 MPa and strain ε: 720% ± 20%) that are comparable to the typical polyolefins. Of significance, these polyacetals can also be depolymerized to the monomer in the presence of acid as the catalyst in nearly quantitative yield.

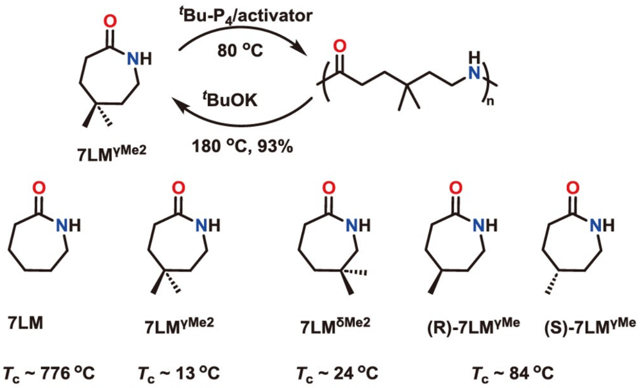


Figure 16 Polymerization and depolymerization of *gem*-dimethyl substitution ε-caprolactam (color online).

Zhang and coworkers [147] successfully realized the alternating copolymerization of aldehydes and cyclic anhydrides through the activation of nucleophilic sites of aldehydes in a cationic manner. By employing 56 aldehydes and 5 cyclic anhydrides as the monomers, 60 poly(acetal-*alt*-ester)s with fully alternating sequences were obtained within several minutes or seconds in one-pot. These polyesters have molecular weights from 2.0 to 22.0 kDa and $Đ$ of 1.2 to 1.6, $T_{d,5\%}$s ranging from 170 to 230 °C, and a broad range of T_gs from −57 to 73 °C (Figure 17). Of significance, the copolymerization of aldehydes and cyclic anhydrides has the typical character of the reversible reaction due to the low enthalpy of the aldehyde. Take the copolymerization of acetaldehyde and glutaric anhydride as an example. The determined $\Delta H_p^\circ = -36.96\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S_p^\circ = -101.46\ \mathrm{J\ mol^{-1}\ K^{-1}}$, and thus the ceiling temperature is ca. 141.9 °C at the monomer concentration of 4.4 M. Therefore, the copolymer (P36A in Figure 17) of 3,5-dichlorobenzaldehyde and glutaric anhydride can be converted to monomers in 94% yield under static vacuum at 180 °C for 8 h. The obtained monomers were also repolymerized to the poly(acetal-*alt*-ester), and thus a closed-loop chemical recycling was realized.

There are also a number of earlier examples of chemical depolymerization where the polymer depolymerizes to produce cyclic oligomers instead of the original monomers. Melchiors *et al*. [148] studied the depolymerization of poly [(R)-3-hydroxybutyrate] (PHB) to the corresponding cyclic trimer (TBL), achieving the highest recycling yields of up to 80%. It was also demonstrated that TBL could be repolymerized to PHB, although subsequent thermodynamic analysis indicated that this was not a viable process.

2.2 Step-growth polymerization

2.2.1 Iterative step-growth for discrete polymers

Discrete polymers mimic natural biomacromolecules such as DNA and proteins, characterized by precisely defined chain lengths, sequences, and chemical compositions [149,150]. This growing field of research is gaining more and more attention because discrete polymers not only possess unprecedented material properties, such as self-assembly, crystalline, and optical properties, but also serve as ideal models for studying fundamental structure-property relationships. However, the synthesis and isolation of discrete polymers are still considered challenging. The synthetic method was exploited by combining organic and polymer chemistries with the aim of reducing time and chemical consumption. Among the synthetic methods that have been developed [151,152], the two synthetic strategies, iterative sequential growth (ISG) and iterative exponential growth (IEG), are the most representative discrete polymer synthesis methods that combine efficiency and reliability (Figure 18). The most typical example of ISG is the solution-phase or solid-supported synthesis of oligopeptides. The IEG is considered the most efficient method for the synthesis of discrete polymers. As shown in Figure 18b, the principle of this method is the use of bifunctional building blocks with orthogonal protecting groups (p_1 and p_2), where the two functional groups (Figure 18a and b) can react with each other upon separate deprotection, leading to coupling. Herein, we propose to classify the ISG and IEG as special step-growth polymerizations in the field of discrete polymer synthesis.

However, discrete polymers bearing on-demand depolymerization characteristics are still rare. The most reported are discrete oligourethanes that undergo cascading 1,6-elimination depolymerizations, releasing each monomer as a 2-oxazolidinone (Figure 19) [153–155]. Such discrete polymers are also called self-immolative discrete polymers. Typically, the depolymerization of discrete oligourethanes occurs following the removal of terminal protecting groups by external stimuli. Moreover, due to the precisely defined structure of discrete oligourethanes, properties of self-immolative oligourethanes, such as self-assembly and molecular recognition, depending on chain length and backbone composition, can be clearly resolved. In addition to discrete oligour-

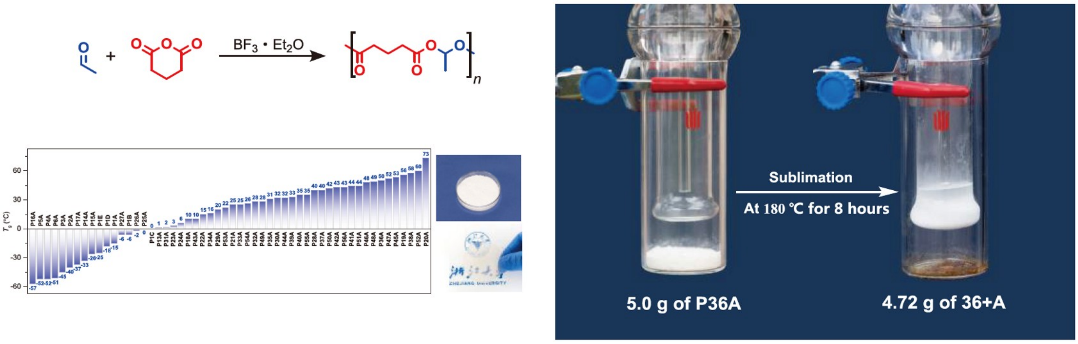


Figure 17 Poly(acetal-*alt*-ester)s with different T_gs synthesized by cationic copolymerization of aldehydes and cyclic anhydrides, and depolymerization of P36A to monomers with the sublimation device (color online).

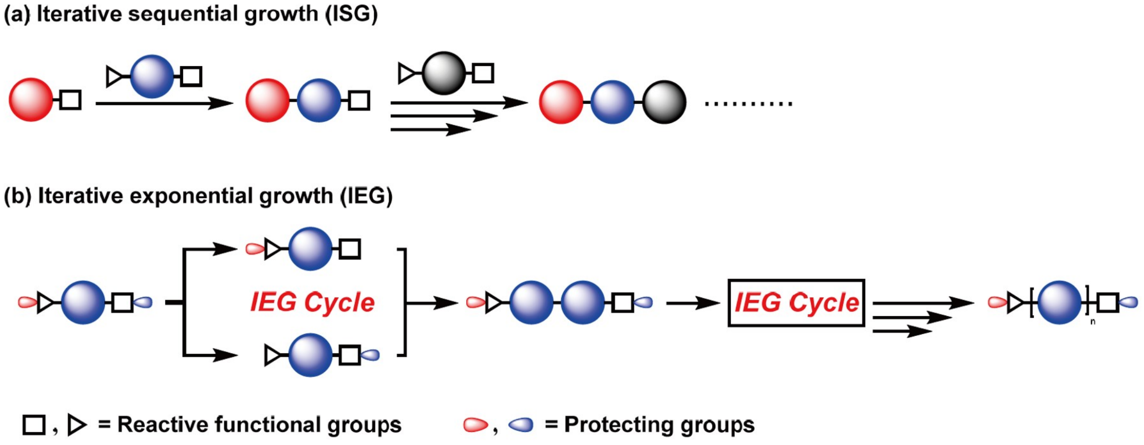


Figure 18 Principles of the ISG (a) and IEG (b) and approaches (color online).

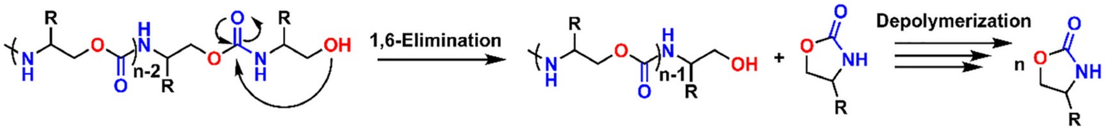


Figure 19 Depolymerization mechanism of discrete oligourethanes (color online).

ethanes, another discrete polymer with depolymerization properties is reported to be discrete oligomeric poly(γ-butyrolactone) (*o*BLs), which was synthesized by Zhang's group [156,157] using the IEG method. In their work, the synthesis method and the crystalline property of *o*BLs were well discussed. On the one hand, discrete polymers can serve as quantitative and refined models to reveal fundamental principles of structure-depolymerization relationships. The discrete polymers with depolymerization properties can also exploit the fundamental depolymerization mechanism as well as developing many other applications.

2.2.2 *Step-growth for recyclable polyesters*

In recent years, methods to obtain recyclable polymers by introducing easy-to-break carbon-heteroatom bonds in the main chain through step polymerization have received extensive attention from academia and industry [9,158–165]. The key to this approach is to create "breaking points" in the resulting polymer chains through the reaction of monomers with ⩾2 functional groups [161], or the monomers themselves have "break points" such as ester linkages, which can be directly introduced into the polymer chains. These breaking points allow the polymer to be chemically recycled back into its monomers, which can then be used to resynthesize the same polymer. For example, Mecking and co-workers [162] used renewable long-chain C_{18} dimethylester and C_{18} diol to synthesize high molecular weight polycarbonates and polyesters, which exhibit polyethylene-like mechanical properties and practical chemical recyclability. Gruter and co-workers [163] used aryl alcohols as solvents, resulting in the *in situ* formation of more reactive aryl esters during esterification, thereby promoting chain growth during polycondensation. The resulting high molecular weight isosorbide-based materials are not only chemically recyclable but also exhibit good mechanical and barrier properties that could surpass common fossil-based materials.

To this end, Xia and Zhang *et al*. [165,166] designed a series of chemically recyclable polymers based on the click reaction of *in situ* generated sulfhydryl groups by cascade polymerization of readily accessible H_2O, carbonyl sulfide (COS), and diacrylates (Figure 20a). This method is tolerance to air, metal- and solvent-free, and can be performed at 60 °C for 4 h, afforded polymers with well-defined ester and thioether sequence, high M_ws of 27.3 to 176.7 kDa, and excellent thermal stability with $T_{d,5\%} \geqslant 289$ °C. Remarkably, the polymers composed of long carbon chains (*i.e.*, low density of in-chain polar groups) demonstrate exceptional mechanical properties comparable to the commodity HDPE. The main chain contains a small number of regularly arranged ester groups as the "break points", which can be chemically recycled and regenerated by two loops: one is *via* hydrolysis, esterification, and polymerization along the original route (Cycle 2 in Figure 20c and d); another is *via* methanolysis and polycondensation (Cycle 3 in Figure 20c).

Very recently, Xia and Zhang *et al*. [166] developed a novel and efficient coupling reaction to connect diols with activated alkenes *via* a bridge molecule of COS (Figure 20b). In the presence of COS and organic base as the catalyst, the less reactive diols (including primary, secondary and tertiary alcohols) were promptly converted to highly active sulfhydryl groups that have almost the same reactivity. Therefore, when COS, diol and diacrylates are used, a series of recyclable polymers with ester and thiocarbonate units is achieved by the step polyaddition of them. This polymerization is atom-economical, efficient, metal-free, and can be performed under mild conditions, afforded unprecedented polymers with abundant sequences in nearly quantitative yields. Of importance, these polymers exhibit excellent melt processing properties and desirable mechanical properties (for example, σ: 21.8 ± 1.9 MPa, ε:17.3% ± 2.5%). Similar to the previous system, the in-chain thiocarbonate and ester polar groups can serve as breakpoints, allowing these polymers to be easily recycled (Cycle 1 in Figure 20c and d). It should be noted that the synthetic method also provides a new strategy to activate alcohols for polymerization.

Starting from the *in-situ* creation of efficient click reactions, Xia and Zhang *et al*. [166] have synthesized a variety of new sulfur-containing polymer materials with well-defined sequences. These polymers are expected to become common plastics in the future, given their large scale of raw materials, facile and versatile synthesis, desirable performance, and chemical recyclability.

2.2.3 *Step-growth polymerization for the synthesis of polyolefin-like polymers*

Polyolefins were mainly made from coordination polymerizations that afforded the all-carbon polymer chain. The chemical inertness of C–C and C–H bonds makes polyolefins extremely challenging for efficient and selective depolymerization towards useful products. In order to make closed-loop recyclable polyolefins or polyolefin-like materials, weakened bonds need to be installed along the polymer

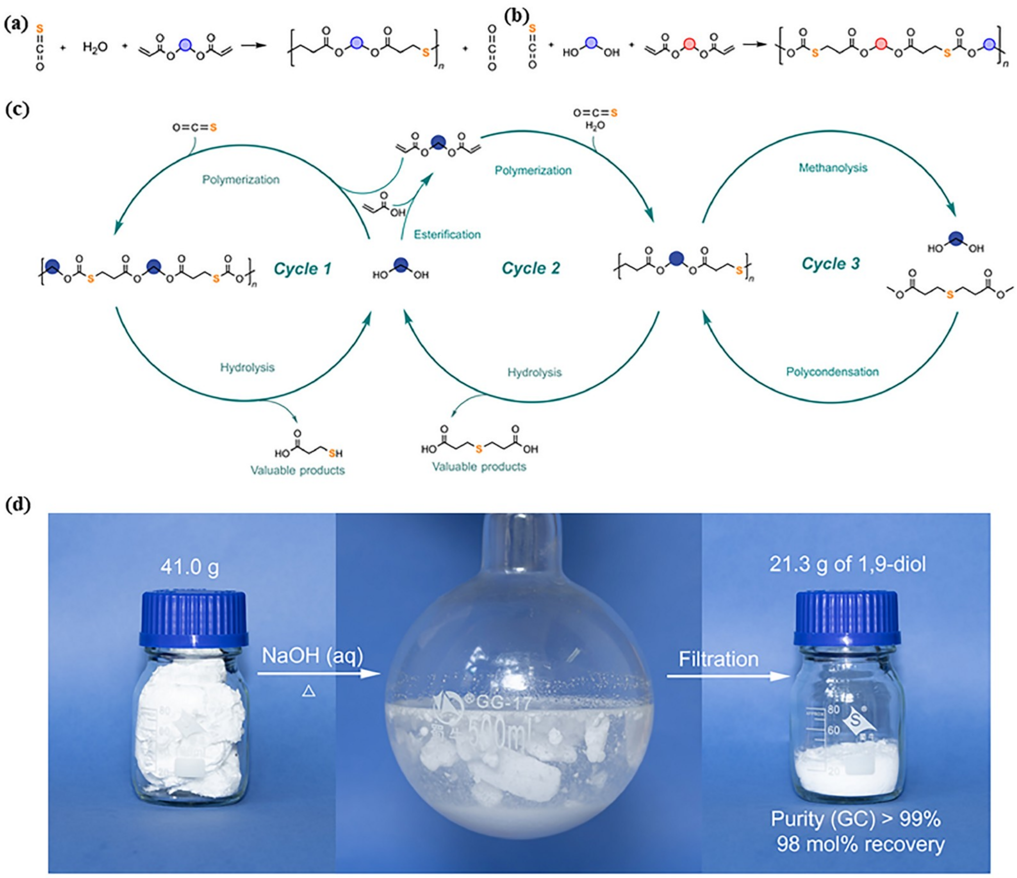


Figure 20 (a) Synthesis of polymers with in-chain ester and thioether groups from polymerization of COS, H_2O, and diacrylates. (b) Synthesis of polymers with in-chain ester and thiocarbonate groups from polymerization of COS, diols, and diacrylates. (c) Schematic diagram of the chemical recycling of the polymers: Cycle 1 shows the cycle of the second system; Cycles 2 and 3 show the cycle of the first system. (d) Chemical recyclability of obtained polymers. Reproduced from Ref. [113] with permission. Copyright 2023 Wiley-VCH GmbH (color online).

backbone. In this regard, step-growth polymerizations are uniquely fit for this process. Ester polycondensation quickly becomes an ideal cleavable linkage as it is one of the most successful types of step growth polymerizations in academia and industry. When the AA- and BB-type telechelic macromonomers (diol; diacid) have a long hydrocarbon chain between the two –OH or –COOH chain end groups, the resulting polymer may show a polyolefin-like structure and properties. This brings advantageous tunability in using the telechelic macromonomers for synthesizing multiblock and graft copolymers [167–169]. Thus, recycling waste polyolefins into polymerizable telechelic macromonomers or making such telechelic macromonomers using olefin (or renewable) feedstocks seems promising solutions for making polyolefins closed-loop recyclable.

In 2022, Coates, Delferro and LaPointe *et al*. [170] reported the degradation of HDPE *via* tandem dehydrogenation/cross-metathesis/hydrogenation process to afford ester-terminated telechelic macromonomer for the synthesis of closed-loop chemically recyclable polymers. Dehydrogenation of HDPE was efficiently achieved using an Ir pincer catalyst at 200 °C under a vacuum. Excess 2-hydroxyethyl acrylate (10 equiv.) was then added for cross-metathesis to afford telechelic macromonomer, which was efficiently used for the synthesis of linear closed-loop recyclable polymer (M_w = 33 kDa; T_m = 130 °C) *via* ester polycondensation/glycolysis. When the telechelic macromonomer was reacted with diethanolamine, it afforded a mixture of product, which was polymerized to afford a crosslinked polymer (M_w = 80.3 kDa; T_m = 132 °C, Figure 21). Even though the linear polymer exhibits poor mechanical performance, the crosslinked one shows HDPE-like mechanical properties (yield strength = 18 MPa; strain at break = 970%).

One alternative is to develop new polyolefins that use low-cost commodity fossil-derived or renewable monomers as the primary feedstocks, possess properties analogous to PEs and PPs, have widely tunable microstructure and performance, and are closed-loop chemically recyclable. In 2021, Mecking *et al*. [162] showed that polyesters and polycarbonates bearing a low density of in-chain cleavable linkages are closed-loop recyclable *via* solvolysis (96% yield), and these are HDPE-like materials in terms of structure and properties. The diester and diol starting materials were obtained *via* multistep reactions from renewable feedstocks

(Figure 22a). Polyester-18,18 (PE-18,18) ($M_w \approx 80$ kDa) was synthesized by $Ti(O^nBu)_4$ catalyzed polycondensation with stoichiometric amounts of the biorefinery-sourced C18 diester and diol. Polycarbonate-18 (PC-18) with high molecular weight ($M_w \approx 300$ kDa) was also synthesized by reacting the C18 diol with diethyl carbonate as an auxiliary reagent. The mechanical strength, modulus of elasticity, and ductility of both polymers are comparable to those of commercial HDPE. Besides, they synthesized polyester with ethylene glycol and 1,18-octadecanedicarboxylic acid, which exhibited HDPE-like thermomechanical properties ($T_m = 96$ °C) and can be rapidly and completely degraded by isolated natural enzymes *in vitro* (Figure 22b) [160]. Under industrial composting conditions, the material is biodegraded with a mineralization of over 95% within two months. In 2024, they reported the use of bottom-up and top-down approaches, *i.e.*, nonstoichiometric $A_2 + B_2$ polycondensation and chain scission, for the synthesis of linear waxes with multiple in-chain ester groups as biodegradation break points with these bio-derived diacids and diols as the starting materials [171]. These waxy products contain a low density of multiple in-chain ester groups (8 mol% ester *vs*. methylene for 12, 12 repeat units; 10 mol% for 2, 18 repeat units) and HDPE-like crystalline structures. Their molar mass range ($M_n \approx$ 600–10,000 Da) encompasses the molar mass range of traditional PE waxes as well as Fischer-Tropsch waxes. These attributes render the products promising biodegradable alternatives to conventional petrochemical PE waxes.

In 2022, Coates *et al*. [172] reported hafnium-catalyzed propylene/butadiene copolymerization to afford *i*PP-co-BD with good isotacticity ([*mmmm*] = 0.88) and in-chain olefin double bond *via* butadiene 1,4-insertion (0.25–0.40 mol%).

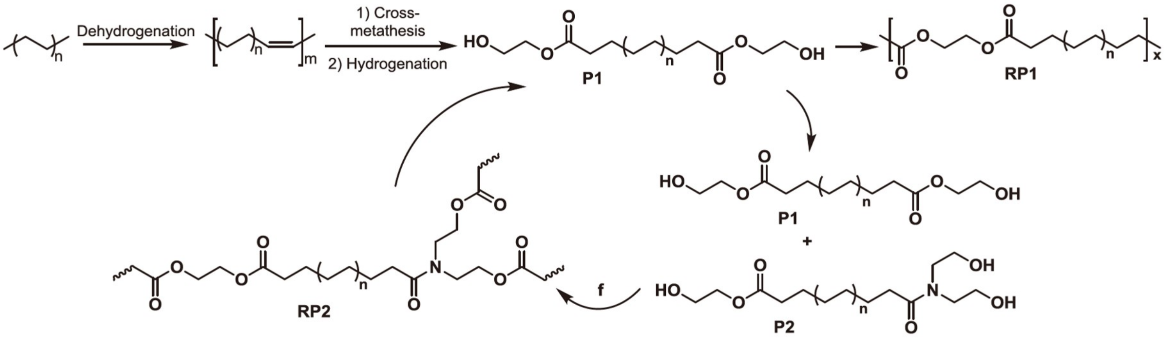


Figure 21 HDPE degradation to telechelic PE macromonomers for the synthesis of closed-loop recyclable polymers. Reproduced from Ref. [170] with permission. Copyright 2022 American Chemical Society.

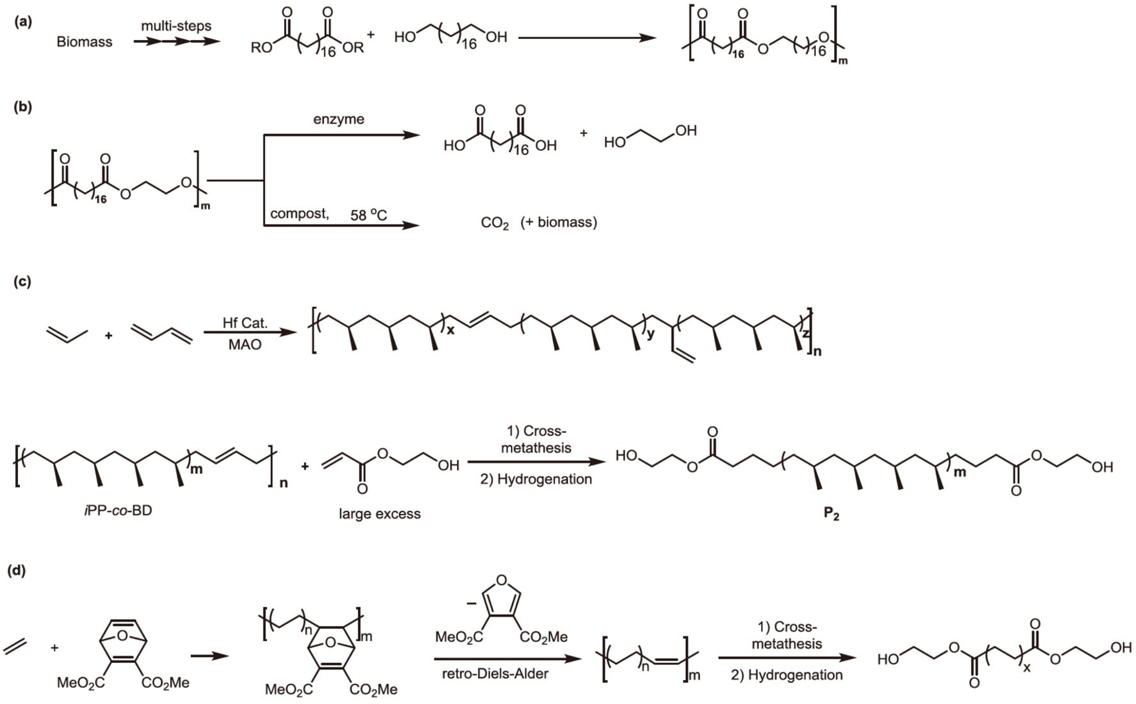


Figure 22 (a–d) The synthesis of polyolefin-like materials from fossil-derived and renewable bulk monomers as primary feedstocks.

The *i*PP-*co*-BD undergoes metathesis depolymerization with 20 equiv. 2-hydroxyethyl acrylate and subsequent olefin hydrogenation to give hydroxy-terminated telechelic macromonomer P_2 (Figure 22c). The neat telechelic macromonomer P_2 undergoes polycondensation to remove the *in situ*-generated ethylene glycol. The resulting polymer can be depolymerized back to P_2-recycled in the presence of ethylene glycol and TBD. The T_m of the polymer remained relatively unchanged (T_m = 90–95 °C) throughout all the transformations. The resulting *i*PP-polyester material exhibited LLDPE-like tensile behaviors, yield points and strain at break. Recently, they reported a new way of obtaining PE with in-chain olefin double bonds *via* a tandem Pd-catalyzed ethylene copolymerization with an oxa-norbornene comonomer, retro-Diels-Alder reaction, and cross metathesis (Figure 22d) [173].

In 2024, Tang, Gao and Chen *et al*. [174] designed and synthesized ester-linked LLDPE-, POE-, and OBC-type copolymers by assembling a series of PE-based AB telechelic building blocks end-capped with –OH and –CO_2Et *via* tandem coordination and condensation polymerization methods, using ethylene and 1-octene as feedstock monomers. Chain end groups of the AB telechelic polyolefins were installed by coordinative chain transfer polymerization (CCTP) of ethylene and 1-octene in the presence of a designer functionalized chain-transfer agent, $Zn[(CH_2CH_2)OTIPS]_2$ (chain head), and quenching reaction of the resulting $Zn(polymeryl)_2$ with $ClC(=O)CH_2CH_2CO_2Et$ (chain end). These new materials' high microstructural similarity to various commercial PE-based materials and tunability bring about similar thermal and mechanical properties, and even additional advantageous adhesion properties to polar surfaces (Figure 23). This AB telechelic building-block strategy paves the way for the design and synthesis of a wide range of circular olefin copolymers and hybrid polyolefin materials with closed-loop recyclability.

Besides using the bio-derived feedstocks and fossil-derived olefin monomers such as ethylene, propylene, and α-olefins, cyclooctene monomers were also used for chain transfer ROMP to synthesize telechelic polycyclooctenes, and these telechelic macromonomers usually have high difunctional purity and can be conveniently used for step-growth polymerizations to synthesize chemically recyclable polyolefin-like polymers. In 2022, Chen *et al*. [175] reported a new strategy for the synthesis of chemically recyclable polyolefin-like polymers *via* a combined ADMET + ROMP approach. Cyclooctene, 3-hexylcyclooctene and functional group-linked *α*,*ω*-diene were used as the starting materials for the cyclic acyclic monomers metathesis polymerization (CAMMP). By changing the ratios and their structures, polyolefin-like polymers with broadly tunable branching structures and functional groups (ester, acetal, silyl, amide, *etc*.) along the main chain can be achieved (Figure 24a). Depending on whether a third monomer (*i.e*., 3-hexylcyclooctene) was introduced, the resulting polymers exhibit polyolefin-like properties typical of thermoplastics and elastomers. Upon treatment with fluoride, acid, or base, some of these polymers also show great degradability.

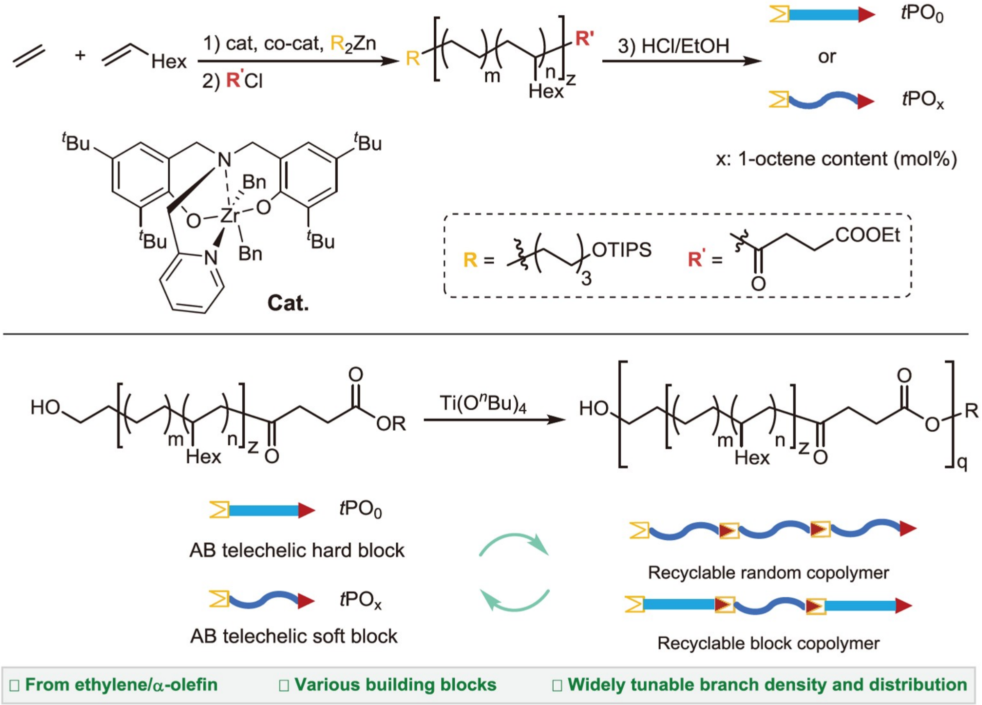


Figure 23 Circular olefin random and block copolymers made *de novo* from ethylene and *α*-olefins. Reproduced from Ref. [174] with permission. Copyright 2024 Springer Nature (color online).

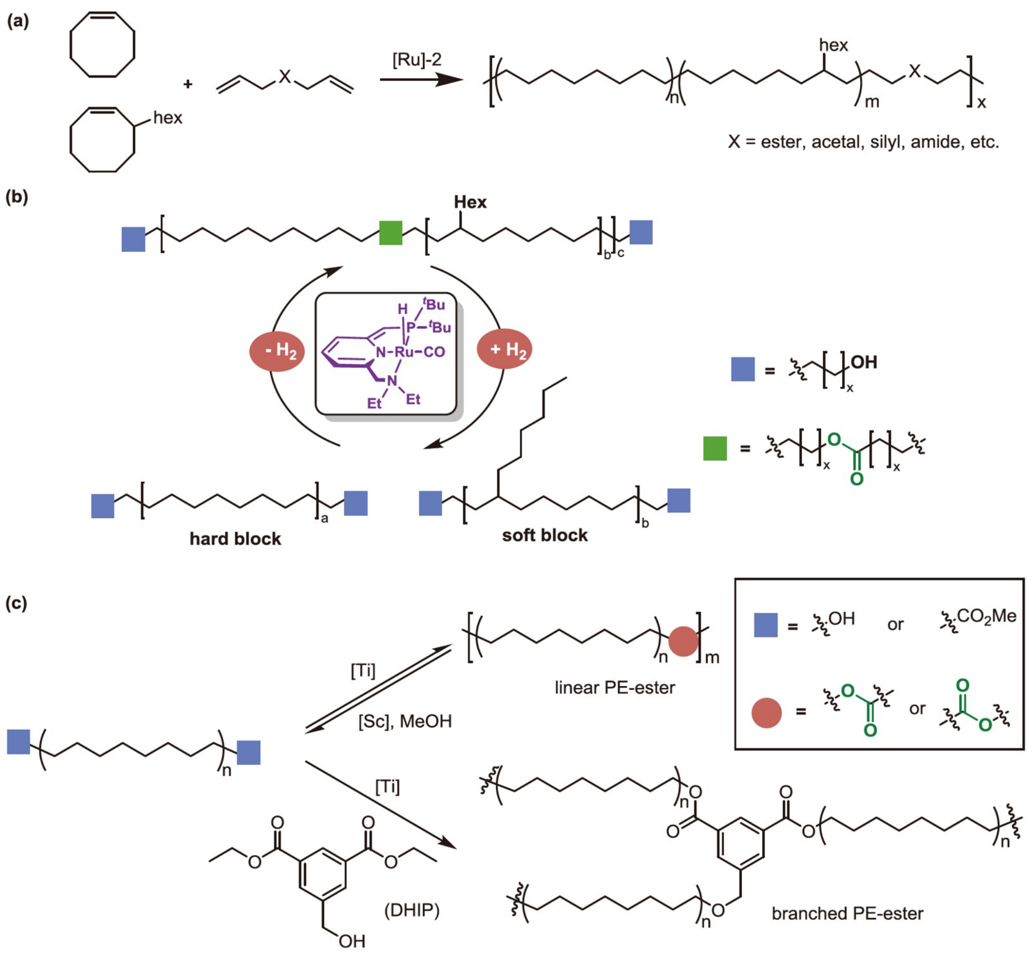


Figure 24 (a–c) The synthesis of chemically recyclable polyolefin-like polymers with telechelic macromonomers derived from ROMP of cyclooctene monomers. Reproduced with adaptation from Ref. [175] with permission. Copyright 2022 Springer Nature (a); Reproduced from Ref. [176] with permission. Copyright 2023 American Association for the Advancement of Science (b); Reproduced with adaptation from Ref. [177] with permission. Copyright 2024 American Chemical Society (c) (color online).

In 2023, Miyake *et al.* [176] reported a new approach for the synthesis of chemically recyclable polyolefin-like polymers using telechelic diols as the starting materials *via* ruthenium-catalyzed dehydrogenation polymerization of alcohols to produce polyesters (Figure 24b). The linear and branched telechelic diols were obtained from the ROMP of cyclooctene and 3-hexyl-cyclooctene, respectively. When both linear and branched telechelic diols were introduced, block copolymers with both soft and hard blocks can be constructed. One notable advantage of achieving ester link *via* two –OH, instead of a more common –OH and –CO_2Me combination, which removes the constraints of precise stoichiometry matching of chain-end groups and allows for deviations in monomer feed ratios. The multiblock polymers exhibit broad mechanical properties similar to typical elastomers, plastomers, and thermoplastics, allowing desirable combinations of both high melting transition temperature and low glass transition temperature (T_m as high as 128 °C and T_g as low as –60 °C). The resulting polymers can be depolymerized back to diol building blocks in the presence of hydrogen using the same approach, making it a closed-loop cycle.

In 2024, Hillmyer *et al.* [177] reported the synthesis of chemically recyclable polymers *via* transesterification polymerization of telechelic polycyclooctenes end-capped with –OH and –CO_2Me. Stoichiometrically self-balanced telechelic polyethylenes underwent transesterification polymerization in the presence of tri-functional diethyl 5-(hydroxymethyl)isophthalate (DHIP) to produce the PE-ester samples with high M_n of up to 111 kg/mol, and tunable branch density can be realized by varying the ratio of the introduced DHIP (Figure 24c). Thermal and mechanical properties of the PE-esters were comparable to those of commercial HDPE and tunable through control of the ester content in the backbone. In addition, branched PE-esters showed higher levels of melt strain hardening compared with linear versions. The PE-ester was depolymerized into telechelic macromonomers through straightforward methanolysis, and the resulting macromonomers could be effectively repolymerized to generate a high molar mass recycled PE-ester sample. This is a new and promising method for synthesizing and recycling high-molar-mass linear and branched PE-esters, which are competitive with HDPE and have easily tailorable properties.

In tackling the polyolefins waste pollution challenges, this combined chain growth and step growth strategy seems very promising. The telechelic products obtained from polyolefins degradation *via* thermal, oxidative and dehydrogenation approaches could, in principle, be used for making closed-loop recyclable polyolefin-like materials. Developing similar non-catalytic or catalytic processes with great efficiency and selectivity under mild conditions is expected to be the focus of the research. So far, the dehydrogenation pathway seems very promising [178,179]. As for the step growth process for making polyolefins or polyolefin-like materials using fossil-derived and renewable monomer feedstocks, there have been only a few reports in the last couple of years. This is mainly due to the challenges in making the telechelic macromonomers. Related catalytic and synthetic challenges will be the focus of the research. This is still an emerging and very preliminary research area that keeps attracting more and more scientists. Last but not least, converting cyclooctene and its substituted version into telechelic macromonomers with very high difunctional purity has become a robust pathway for convenient access to abundant telechelic macromonomers in academic studies. Thus, more related studies aiming at the development of circular processes and polyolefin-like materials will be expected in the following years.

2.3 Multicomponent polymerization

Multicomponent polymerizations (MCPs) involve polymerizations of three or more types of monomers and are featured with mild conditions, high atom economy, high efficiency, simple operation, and, most importantly, the great structural diversity of polymer products [180]. MCP could construct heterochain polymers with various structures and complex groups from simple monomers, and functional groups that enable the development of new sustainable polymers with unique physical and chemical properties as well as on-demand depolymerization property or degradability.

As one of the most extensively explored MCPs, Passerini polymerization of isocyanide, aldehyde and acid has drawn much attention because it could afford various linear, star-shaped, macrocycle, and sequence-defined polymers in high efficiency [181]. Through judicious selection of monomers, some labile functional groups that offered feasible depolymerization reactive sites can be introduced into the polymer chain. For example, polymers with photocleavage moieties possessed high spatial and temporal precision to realize on-demand depolymerization [182,183]. Recently, a Passerini polymerization of 4-pyridinecarboxaldehyde, acid-difunctionalized PEG, and isocyanide difunctionalized PEG was reported by Yu *et al*. [184] to synthesize multifunctional smart materials with double-helical structure and photodegradable moieties (Figure 25a). Under blue-light irradiation (452 nm) with a Ru(II) complex catalyst and ascorbic acid, the photolabile picolyl ester moiety could undergo a photolysis process to lead to a decreasing number of average molecular weight (M_n) from 18 to 0.8 kDa within 2 h.

When the polymer structure was designed with proper distance between functional groups, the tail-to-tail depolymerization by cascade reactions through intramolecular cleavage from the polymer terminus could be achieved [185]. The commonly used intramolecular cleavage reaction involves cyclization to form thermally stable and kinetically favored five- or six- membered rings, which require a particular terminal group and polymeric structure predesigned from monomers. For example, Li *et al*. [186] designed an AB +C-type Passerini polymerization of 4-*oxo*-2-butenoic acid and *tert*-butyl isocyanide, followed by hydrogenation to synthesize poly(4-hydroxybutyrate) (P4HB) (Figure 25b). P4HB degraded almost completely into small molecules, through intramolecular cyclization of terminal hydroxy with ester linkage to form five-membered γ-butyrolactone after 144 h in DCl/$CDCl_3$. In addition to depolymerization through intramolecular cyclization from terminal groups, side chain groups could also play a similar role. For instance, a linear polyester was synthesized through Passerini polymerization involving bio-based L-glutamic acid (Figure 25c) [187]. After deprotection in the presence of HCl, the active amino side groups can react with the ester linkages in the polymer backbone to undergo intramolecular cyclization and degrade into small molecules or oligomers.

Besides Passerini polymerization, photodegradable polymers were also prepared from other catalyst-free MCPs, including Kabachnik-Fields polymerization of *o*-nitrobenzene containing dialdehyde, diamine, and phosphites [188], the MCPs of diisocyanides, diethyl acetylenedicarboxylate, and bis-anhydrides/1,4-dibromo-2,3-butanedione/halogenated quinones to construct iminofuran-containing polymers [189], and catalyst-free multicomponent cyclopolymerization to access UV-degradable poly(furan-amine)s containing photolabile furan groups [190].

Recently, carbon dioxide (CO_2) was also used as a monomer in MCP, affording polymeric products with depolymerizable or degradable ester moieties. In 2018, Qin and Tang *et al*. [191] reported a facile and efficient three-component polymerization (TCP) involving CO_2, diynes, and alkyl dihalides, conducted under mild reaction conditions to generate poly(alkynoate)s (Figure 26a). Then, they developed a facile and efficient one-pot, two-step, four-component tandem polymerization containing a TCP and an amino-yne click reaction, ingeniously using the monomers of CO_2, diynes, alkyl dihalides, and primary/secondary amines (Figure 26b) [192,193]. Regioregular and tunable stereoregular poly(aminoacrylate)s were generated in high yields, producing polymers with 100% *Z*-isomeric units from pri-

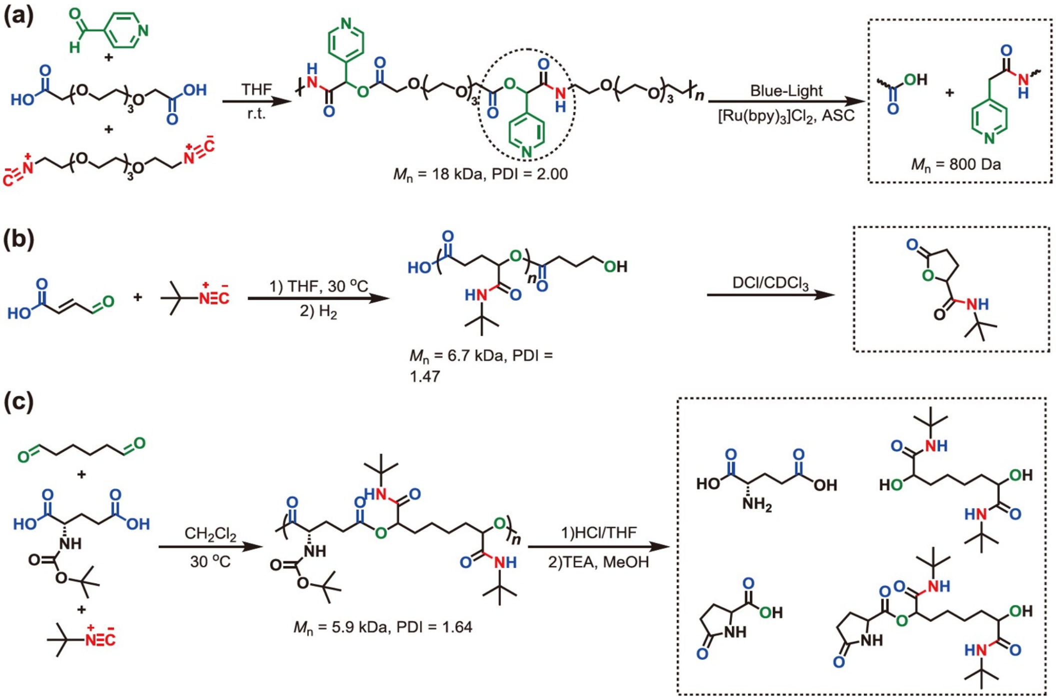


Figure 25 (a) The Passerini polymerizations towards degradable polymers containing photolabile picolyl ester with their photo-degradation process. (b) The AB+C type Passerine multicomponent polymerizations towards poly(4-hydroxybutyrate) with the depolymerization process through intramolecular cyclization. (c) The Passerini multicomponent polymerizations of bio-based monomer towards poly(4-hydroxybutyrate) with the depolymerization process through intramolecular cyclization (color online).

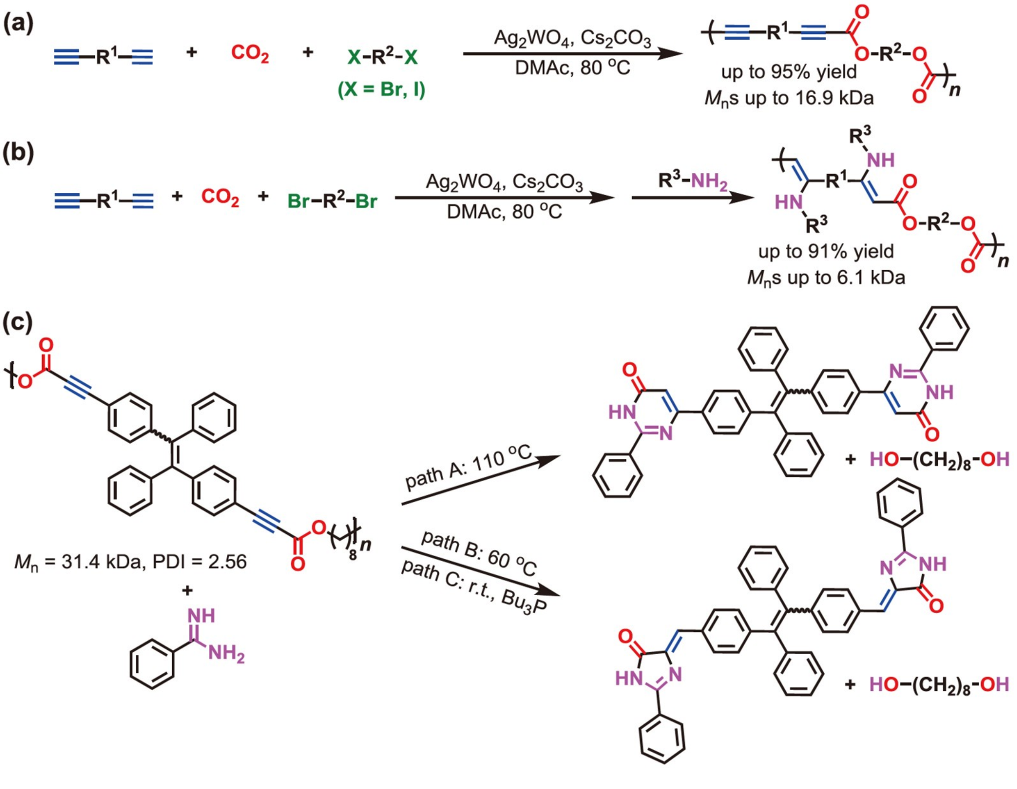


Figure 26 CO$_2$-based MCP for the synthesis of (a) poly(alkynoate)s and (b) poly(aminoacrylate)s. (c) The degradation of CO$_2$-based poly(alkynoate)s (path A: benzamidine, 110 °C; path B: benzamidine, 60 °C; path C: benzamidine, r.t., Bu$_3$P) (color online).

mary amines, and polymers with over 95% *E*-isomeric units from secondary amines. In addition to the conventional linear polymer structures, Qin and Tang *et al*. [194] designed and synthesized tri/tetrayne monomers for the polymerization with CO_2 and alkyl dihalides toward hyperbranched poly(alkynoate)s (*hb*-PAs). Furthermore, they found that CO_2-based poly(alkynoate)s could undergo controlled degradation processes facilitated by benzamidine, involving a sequential addition-heterocyclization-cleavage reaction, yielding diols and high-value-added *N*-heterocyclic compounds [195]. This degradation is temperature-dependent, with the formation of pyrimidone derivative at 110 °C (Figure 26c, path A), and the generation of imidazolone derivative occurring at 60 °C (Figure 26c, path B), or even at room temperature with the inclusion of the Bu_3P catalyst (Figure 26c, path C).

Sulfur-containing polymers have attracted much attention because of their outstanding characteristics, such as high refractive indices, high transparency in the IR region, metal coordination ability, self-healing capability, electrochemical properties, and photocatalytic activity [105]. Hu and Tang *et al*. [196] recently reported a one-pot, two-step tandem polymerization of elemental sulfur, diisocyanides, and dithiols catalyzed by organic bases, affording polydithiocarbamates (Figure 27a). Owing to the dynamic reversibility of the dithiocarbamate group, degradation of the polymer was realized at room temperature. Specifically, dithiocarbamate moiety could react with mercaptan, by which the polymer was converted into oligomers with reduced molecular weight in the presence of DBU. Similarly, Endo *et al*. [197] reported the degradation of polydithiocarbamates upon heating (Figure 27b). The molecular weight of the polymer was reduced from 11 to 1.4 kDa at 150 °C, and the oligomers could be repolymerized at room temperature with the catalysis of Et_3N, suggesting the potential of sulfur-containing polymers as candidates for close-loop recyclable polymers.

Polythioureas are another important group of sulfur-containing functional polymer materials with excellent mechanical and self-healing properties [198]. Hu and Tang *et al*. [199] reported a room-temperature conversion from sulfur to functional polythioureas through a catalyst-free MCP of sulfur, aliphatic diamines, and diisocyanides in the air with 100% atom economy (Figure 27c). Zhang *et al*. [200] both revealed the dynamic characteristics of thiourea bonds, which enabled reprocessing of the thiourea-containing network (Figure 27d) [197]. The controllable degradation of polythiourea was realized by immersing the specimen in DMF containing different contents of amine at different temperatures [201].

Besides heterochain polymers with the above-mentioned examples, MCPs are capable of constructing diverse new functional groups with more complicated structures, rich chemical properties, and new degradation or depolymerization mechanisms. For example, Dong *et al*. [201] reported an organocatalyzed MCP of bis(*N*-sulfonyl aziridine)s, diols, and anhydrides to afford poly(sulfonamide ester)s with diverse structures (Figure 28a). When the linear polymer with plenty of ester moieties along the main chain was treated with an alkaline solution at 100 °C, a bis(hydroxy sulfonamide) compound was isolated in 91% yield, together with the generation of diol and diacid in the aqueous phase as the

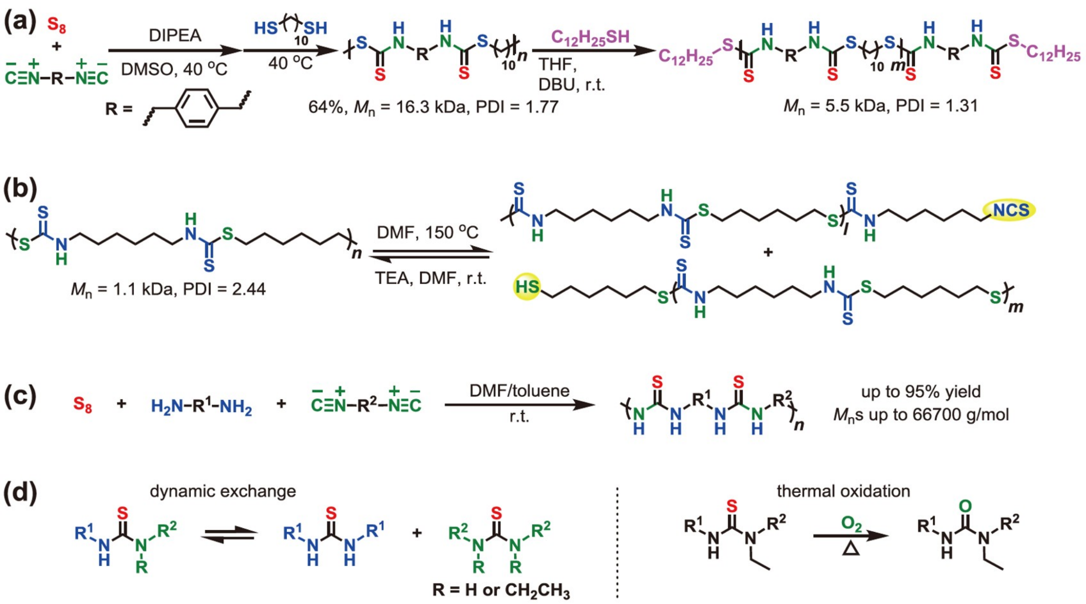


Figure 27 (a) Multicomponent tandem polymerizations of sulfur, diisocyanides, and dithiols toward degradable polydithiocarbamates. (b) Reversible addition reaction of diisothiocyanates and dithiols toward degradable and repolymerizable polydithiocarbamates. (c) MCP of sulfur, aliphatic diamines, and diisocyanides toward polythioureas. (d) Dynamic exchange characteristics of thiourea bond and oxidation characteristics of hindered thiourea bond (color online).

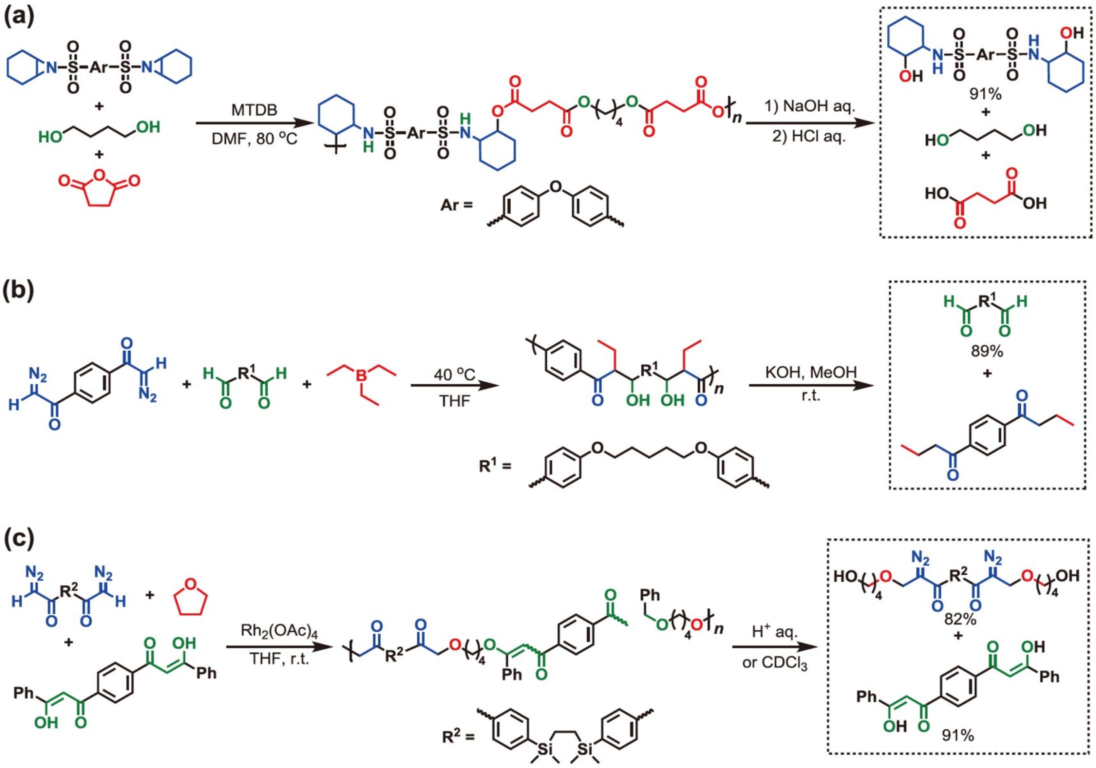


Figure 28 (a) The MCP of bis(*N*-sulfonyl aziridine), diol, and anhydride towards poly (sulfonamide ester) with alkali-trigged depolymerization process. (b) The MCP of bis(diazoketone), dialdehydes and triethylboron towards poly(β-hydroxyketone) with alkali-trigged depolymerization process. (c) The MCP of bis(diazoketone), bis(1,3-diketone) and THF towards poly (β-keto enol ether) with acid-trigged depolymerization process (color online).

depolymerization product. Moreover, the bis(hydroxy sulfonamide) product could be transformed to the original monomer bis(*N*-sulfonyl aziridine) through the mesylation/cyclization reaction, which could be further polymerized.

Similarly, Wang *et al*. [202] reported a catalyst-free multicomponent polycondensation of bis(diazoketone), dialdehydes and triethylboron in tetrahydrofuran (THF) to afford poly(β-hydroxyketone)s (Figure 28b). However, the polymer showed good stability under neutral conditions. According to the retro-aldol reaction, the newly generated C–C bond could be broken under alkalic conditions, which allowed efficient depolymerization in a KOH/MeOH solution to form a dialdehyde monomer with an isolated yield of 89%. Ihara *et al*. [203] reported an Rh-catalyzed three-component polycondensation of bis(diazoketone), bis(1,3-diketone) and THF and poly(β-keto enol ether) was obtained under mild conditions (Figure 28c). The depolymerization of poly(β-keto enol ether) in the mixture of acetone and HCl aqueous solution at room temperature could afford diketone monomer and diol with 91% and 82% isolated yields, respectively.

In summary, MCPs, including Passerini polymerization, CO_2-based MCPs, S_8-based MCPs, and other MCPs, provided powerful tools to access sustainable polymers with diversified and complex structures, unique depolymerization or degradation properties, from simple monomers under mild conditions. The rich polymeric architectures and properties could greatly promote the structural expansion of sustainable polymers with functionalities such as excellent biocompatibility, mechanical strength, fluorescence, and stimuli-response properties.

3 Carbon-backbone sustainable polymers

Most carbon-backbone polymers, such as polyethylene (PE), polystyrene (PS), and poly(methyl methacrylate) (PMMA), are chemically stable. This stability can be beneficial for certain applications, but it makes chemical recycling challenging. Disposing of these polymers through chemical recycling to extract monomers for repolymerization into high-quality plastics is difficult due to their stability. Therefore, this characteristic significantly contributes to environmental pollution and infrastructural strain.

3.1 Metathesis-based depolymerizable polycyclooctenes

Compared with other chemistries used for ROP and RCD, olefin metathesis is unique in that it allows the preparation of polymers with carbon backbone, which is unsusceptible to hydrolytic degradation [204]. Further, olefin metathesis can be performed under mild conditions in the presence of appropriate metathesis catalysts while being kinetically unfavorable in the absence of a catalyst [205]. As a result, undesirable metathesis reactions and depolymerization at elevated temperatures can be avoided, provided that the catalyst is removed judiciously. In addition, olefin-metathesis catalysts are compatible with a wide variety of functional groups, enabling the synthesis of polymers with diverse properties [206].

To ensure suitable thermodynamics for polymerization and depolymerization, the ring strain energy (RSE) of the monomer needs to be regulated appropriately. Among cyclic olefins, the polymerization thermodynamics of cyclopentene (RSE=5.2 kcal mol^{-1}) represents an ideal scenario where the synthesis of high-molecular-weight polypentenamer and the depolymerization of the polymer can both be achieved [207–209]. However, the living polymerization of cyclopentene is challenging due to the comparable rates of propagation and chain transfer [210]. On the other hand, cyclooctene is attractive since the living polymerization of *trans*-cyclooctene has been demonstrated [211,212], and the precursor of cyclooctene, *i.e.*, cyclooctadiene, can be synthesized from dimerization of butadiene [213], which has abundant source including bio-source [214]. However, compared with cyclopentene, the higher RSE (7.4 kcal mol^{-1}) and a smaller loss of entropy during polymerization (−2 cal mol^{-1} K^{-1} for cyclooctene *vs*. −19 cal mol^{-1} K^{-1} for cyclopentene) make the polymerization of cyclooctene much more favorable [215–217]. As a result, depolymerization to monomer is challenging for polycyclooctene.

In order to make polycyclooctene depolymerizable, its RSE needs to be reduced. Inspired by previous ROMP studies done by Grubbs *et al*. [218] and Coates *et al*. [219], Wang and coworkers [220] hypothesized that installing a suitable fused ring at the 5,6-positions of cyclooctene could reduce the RSE of cyclooctene to a level that enables reversible polymerization. They thus calculated the RSEs of cyclooctenes with 3-, 4-, 5-, and 6-membered rings fused at the 5,6-positions, including both *cis* and *trans* isomers (Figure 29a). The calculations showed that *trans*-cyclobutane–fused cyclooctene (*t*CBCO) has the lowest RSE: 4.9 kcal/mol. Notably, the RSE of *t*CBCO is even slightly lower than that of cyclopentene (RSE = 5.2 kcal/mol), the ROMP polymer of which can undergo efficient depolymerization, suggesting that the ROMP polymer of *t*CBCO could also be depolymerizable. Analysis of the computational structures showed that the low strain in the *t*CBCO monomers can be attributed to the fact that the dihedral angles on the fusion site (5,6-positions on the cyclooctene ring) in the monomer and its corresponding ring-opened form are very similar (Figure 29b). In contrast, there is a significant difference in the dihedral angles between the cyclic and acyclic forms for non-substituted cyclooctene and *cis*-cyclobutane fused cyclooctene, which has higher RSEs [220].

Encouraged by the computational results, Wang and coworkers [220] synthesized a series of *t*CBCO monomers and performed polymerization studies (Figure 30a). Interestingly, the enthalpies of polymerization for these monomers were found to be in the range of −1.7–−2.8 kcal mol^{-1} (Table 1, entries 1–3), significantly lower than that for cyclopentene (−5.6 kcal mol^{-1}) [208]. Importantly, the lower enthalpy gain is offset by the lower entropy loss, and polymers of high molecular weight were still made when the polymerizations were conducted at high initial monomer concentrations (>2 M). All of the *t*CBCO polymers underwent depolymerization to form monomers with high conversions (>90%) when the depolymerization was conducted at or below an olefin concentration of 100 mM. The functional group tolerance of the polymerization allowed polymers of various functional groups on cyclobutane to be made (Figure 30b), and their thermomechanical properties tuned, with T_gs ranging from −34 to 100 °C. Further, they demonstrated the synthesis of an elastomeric polymer network by copolymerizing *t*CBCO monomer with a bis-functionalized

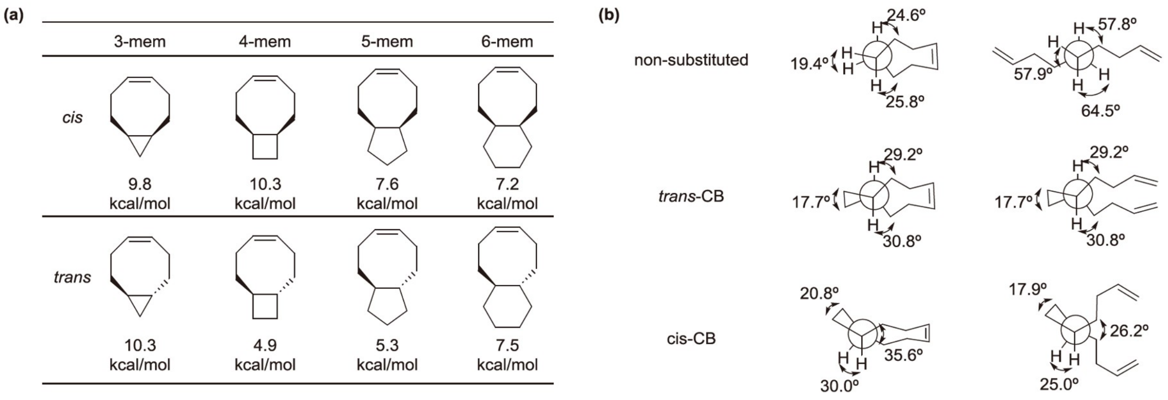


Figure 29 Ring strain energies and Newman projections for fused-ring cyclooctenes. (a) The calculated ring strain energies for cyclooctene with 3-, 4-, 5-, and 6-membered rings that are *cis*- and *trans*-fused at the 5,6-positions. (b) Newman projections along the C5–C6 bond for non-substituted cyclooctene, *trans*-cyclobutane-fused cyclooctene, and *cis*-cyclobutane-fused cyclooctene, along with their corresponding acyclic dienes.

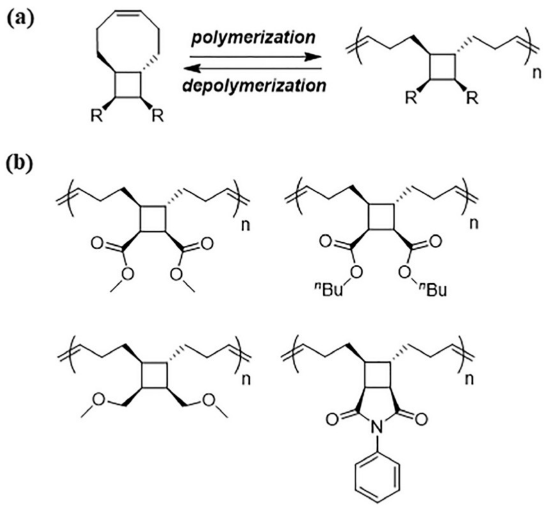
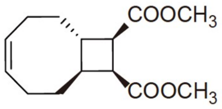
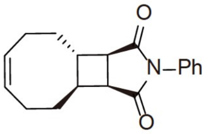
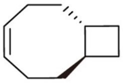
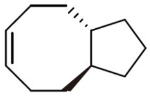
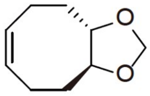
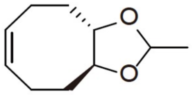
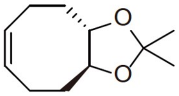
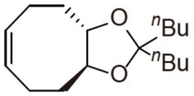
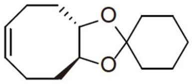


Figure 30 *Trans*-cyclobutane fused cyclooctene (*t*CBCO) based chemically recyclable polymers. (a) A *t*CBCO monomers can be polymerized at high monomer concentrations to yield a high molecular weight polymer, and the resulting polymer can be depolymerized to form the tCBCO monomer. (b) Polymers with various functional groups attached to the cyclobutane ring.

*t*CBCO crosslinker, and remarkably, the polymer network also underwent quantitative depolymerization to form the monomer and the crosslinker [220].

In addition to the *trans*-cyclobutane-fused cyclooctene, the RSE calculations showed that *trans*-cyclopentane-fused cyclooctene (RSE=5.3 kcal/mol) could also be a candidate for making depolymerizable polymers. In a follow-up study, Wang and coworkers compared the thermodynamics of polymerization for polymers based on cyclooctenes with *trans*-fused cyclobutane, cyclopentane, and 5-member cyclic acetals fused at the 5,6-position (Table 1, entries 3–9) [221]. It was found that the cyclopentane and unsubstituted cyclic acetal fused monomers have significantly higher ceiling temperatures (T_c = 614 and 646 °C respectively) than that of the cyclobutane fused monomer (T_c = 335 °C). This was attributed with the higher enthalpy of polymerization for these monomers compared to the cyclobutane fused monomer. When comparing the acetal fused monomers with different alkyl groups, it was observed that while the addition of a single methyl group to the acetal did not lead to a drastic

Table 1 Thermodynamics parameters for the polymerization of trans-fused cyclooctenes

Entry No.	Monomer structure	ΔH_p° (kcal mol^{-1})	ΔS_p° (cal mol^{-1} K^{-1})	T_c @ [M] = 1 M (°C)	Ref.
1	 COOCH$_3$ COOCH$_3$	−1.7	−3.6	199	[206]
2	 O N−Ph O	−2.8	−4.9	295	[206]
3		−2.1	−3.4	335	[207]
4		−3.2	−3.2	614	[207]
5	 O O	−2.7	−2.9	646	[207]
6	 O O	−2.6	−2.7	675	[207]
7	 O O	−3.2	−4.9	376	[207]
8	 O ^{n}Bu ^{n}Bu O	−3.2	−5.0	380	[207]
9	 O O	−2.8	−3.3	571	[207]

change in the T_c (675 °C), geminal substituents on the acetal ring resulted in a significant drop in the T_c (376 and 380 °C for the dimethyl- and di-*n*-butyl functionalized monomers), similar to the Thorpe-Ingold effect [222,223]. The effect was found to be largely entropic—a more negative entropy of polymerization for the *gem*-disubstituted monomers. Replacing the dimethyl- or di-*n*-butyl groups with a spiro cyclohexane group increased the T_c (575 °C). Notably, these substituents were not attached to the cyclooctene ring but rather separated by the acetal ring; the effect was termed a remote *gem*-disubstituent effect. This effect affected the polymerization kinetics—while all the acetal fused monomers were slower to polymerize than the cyclopentane fused monomer, the di-methyl substituted monomer showed slower kinetics than the monomethyl and unsubstituted acetal fused monomers (Figure 31a). Depolymerization studies also demonstrated that the di-*n*-butyl- and dimethyl-disubstituted monomers had higher conversions of depolymerization than other polymers (Figure 31b).

A unique feature of the cyclooctene system is that the *cis*-alkene can be isomerized to *trans*-alkene to substantially increase the ring strain energy and provide a high polymerization driving force (Figure 32a) [224]. This is an important feature, since most reversibly depolymerizable systems are characterized by a low driving force for polymerization, which poses difficulties in accessing diverse functionalities and chain architectures in these polymers. Wang and coworkers [224] demonstrated the photochemical isomerization of *cis*-alkene *t*CBCO into the *trans*-akene isomers using a flow chemistry setup previously reported by Fox and coworkers [225] (Figure 32b), which gave yields up to 80%. With the *trans*-alkene tCBCO monomers, they showed that polymers with controlled molecular weights and low *Đ* can be made (with initial monomer concentration $[M]_0$ as low as 0.025 M and PPh_3/Ru ratio ⩾ 20) and that block copolymers can be prepared (Figure 32c) [224]. Remarkably, both the homopolymers and the block copolymers can undergo quantitative depolymerization to form low-strain *cis*-alkene cyclooctene monomers.

3.2 Chemically recyclable vinyl-addition polymers from bio-renewable γ-methyl-α-methylene-γ-butyrolactone and its derivatives

Vinyl addition polymers are highly stable due to the energy released during polymerization. There are two challenges to the chemical recycling of these polymers: large energy input and multiple competing depolymerization pathways. For instance, PMMA undergoes thermal depolymerization through two different mechanisms [226]. At low temperatures, chain-end scission is the main occurrence, leading to the generation of tertiary radicals at the end of the polymer chain. This initiates the depolymerization of the polymer and generates monomers (Figure 33a). At high temperatures, random scission is more likely to occur, generating two types of macromolecular free radicals: a primary and a tertiary radical. Both types can undergo depolymerization, but primary free radicals generate more by-products, which reduces the recovery rate of monomers (Figure 33b). The use of more complex fixed and fluid bed reactors at temperatures above 400 °C (usually around ~450 °C) is favorable for the random chain scission mechanism, which can reduce the resonance time of PMMA within the reactor and prevent primary free radical species from undergoing unproductive side reactions

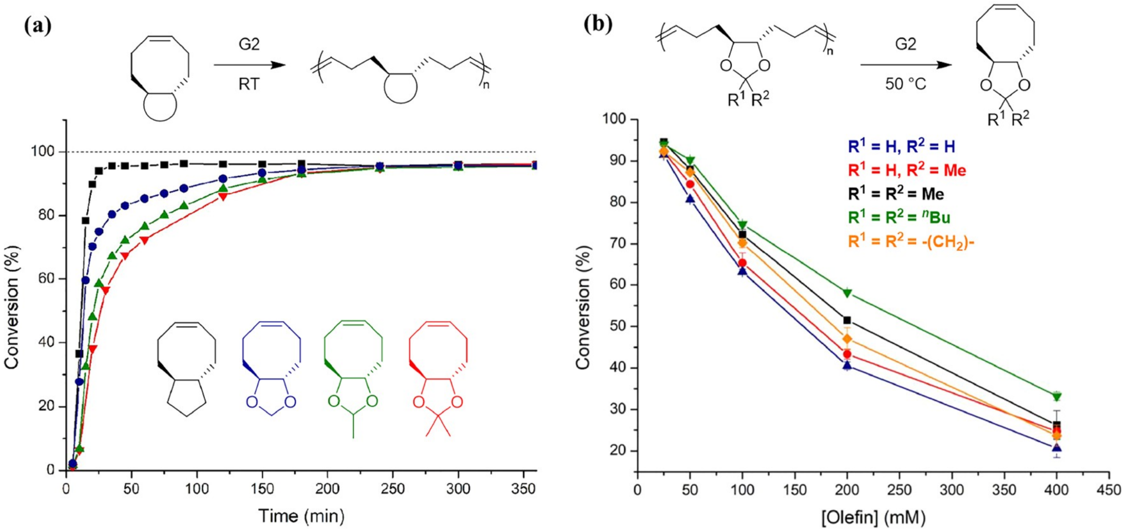


Figure 31 Understanding substituent effects on the polymerizability of chemically recyclable polycyclooctenes. Reproduced from Ref. [221] with permission. Copyright 2022 American Chemical Society. (a) Conversion *vs*. time for the polymerization of different *trans*-cyclopentane fused cyclooctene and 5-membered cyclic acetal fused cyclooctene monomers ($[M]_0$ = 1 M in xylenes, $[M]_0/[G2]$ = 100). (b) Depolymerization of different 5-membered cyclic acetal fused polycyclooctenes at different concentrations ([G2] = 0.01 equiv., $CDCl_3$) (color online).

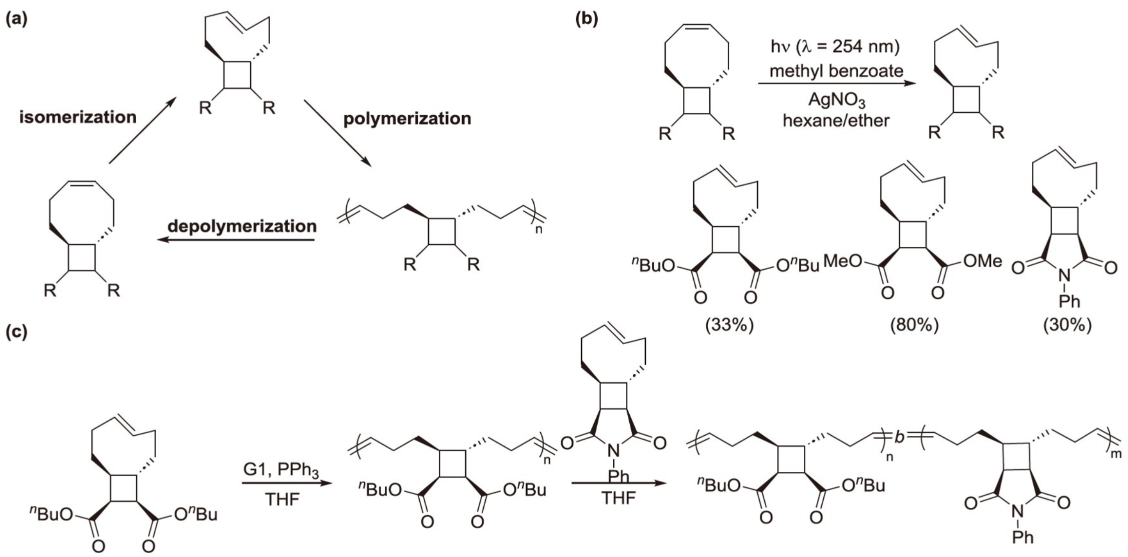


Figure 32 *Trans*-alkene *t*CBCO monomers used in making depolymerizable polymers. Reproduced from Ref. [224] with permission. Copyright 2021 Wiley-VCH GmbH. (a) Schematic showing conversion of *cis*-alkene-*t*CBCO monomer into its *trans*-alkene isomer, polymerization of the *trans*-alkene monomer, and depolymerization of the resulting polymer back to the *cis*-alkene *t*CBCO monomer. (b) Photochemical isomerization of the *cis*-alkene *t*CBCO monomers into their *trans*-alkene isomers; the yield for each product is shown in parentheses. (c) Synthesis of homopolymer and block copolymer using the *trans*-alkene *t*CBCO monomers.

that can lower the overall yield and purity of recovered MMA [227]. Finally, PMMA is depolymerized to methyl methacrylate (MMA) with high to quantitative conversion.

α-Methylene-γ-butyrolactone (MBL) and γ-methyl-α-methylene-γ-butyrolactone (γ-MMBL, usually as MMBL) derived from the renewable resources (white tulips) or itaconic acid and levulinic acid have attracted much attention, as they can be considered as the cyclic analogues and potentially sustainable alternatives of methyl methacrylate (MMA). The rigid cyclic units in the methylene butyrolactones can significantly enhance the polymerization reactivity and improve the polymer properties compared to MMA [228], such as higher glass transition temperature (T_g, PMMA: ~100 °C, PMBL: 200 °C, PMMBL: 221 °C), increased optical properties, resistance to solvent, heat and scratching, and better thermal depolymerization performance. In 2020, Chen *et al.* [229] found that the vinyl lactone repeat unit in P(M)MBL plays a critical role in reducing the side effects caused by primary free radical species generated during random chain breakage. Under the conditions of 400 °C, 50 mTorr, and 3 h, 53% impure MMA was recovered, and the remaining 47% PMMA was carbonized. The recovery conversion of PMBL has been improved to 65%, and the residue has not undergone carbonization, indicating incomplete depolymerization of oligomers. The recovery rate of MMBL has been further increased to 76%, and the purity of the recovered monomers has also been further improved. The residue is an oligomer that is not fully depolymerized. It is predicted that a more effective device or oligomer recovery process can achieve a near-quantitative recovery rate. For PγMMBL, the rigid five-membered lactone ring structure and the methyl substitution on the lactone ring can stabilize the primary free radical by hyperconjugation, allowing it to produce monomers along with the tertiary free radical, suppressing side reactions and producing pure monomers (Figure 33c).

A series of biomass-derived methylene butyrolactones (HMBL, CitMBL, CinMBL, and PeMBL) with substituents varying at γ-position were synthesized *via* a one-pot zinc-mediated allylation-lactonization reaction. $(BHT)_2AlMe/I^iPr$ LP can realize the efficient and living/controlled polymerization of these monomers (Figure 33d) [230]. It is noted that through thermal depolymerizations, PHMBL, PCitMBL, and PCinMBL can be quantitatively (99.8%) or near-quantitatively (94%) converted back to the monomers with high purity, thus demonstrating the complete thermal recyclability of these polymers. With the deep understanding of cooperative and synergistic catalytic effects between LA and LB in the LPP mechanism, a covalently tethered B-P-B intramolecular trifunctional FLP catalyst/initiator composed of two acidic B sites and one basic P site was synthesized and employed to achieve an authentic biobased cyclic PMMBL [231]. The cyclic topology was confirmed by MALDI-TOF MS, as well as the intrinsic viscosity of the resulting polymers. Mechanistic studies uncovered an unprecedented chain initiation reaction that incorporated the features of synthetic strategies for cyclic polymers, including ring-expansion polymerization (REP) and ring-closing polymerization (RCP). In such system, two B-P-B catalysts with two monomer molecules generated a bimolecular cyclic intermediate to serve as the cyclic template for ensuing REP with

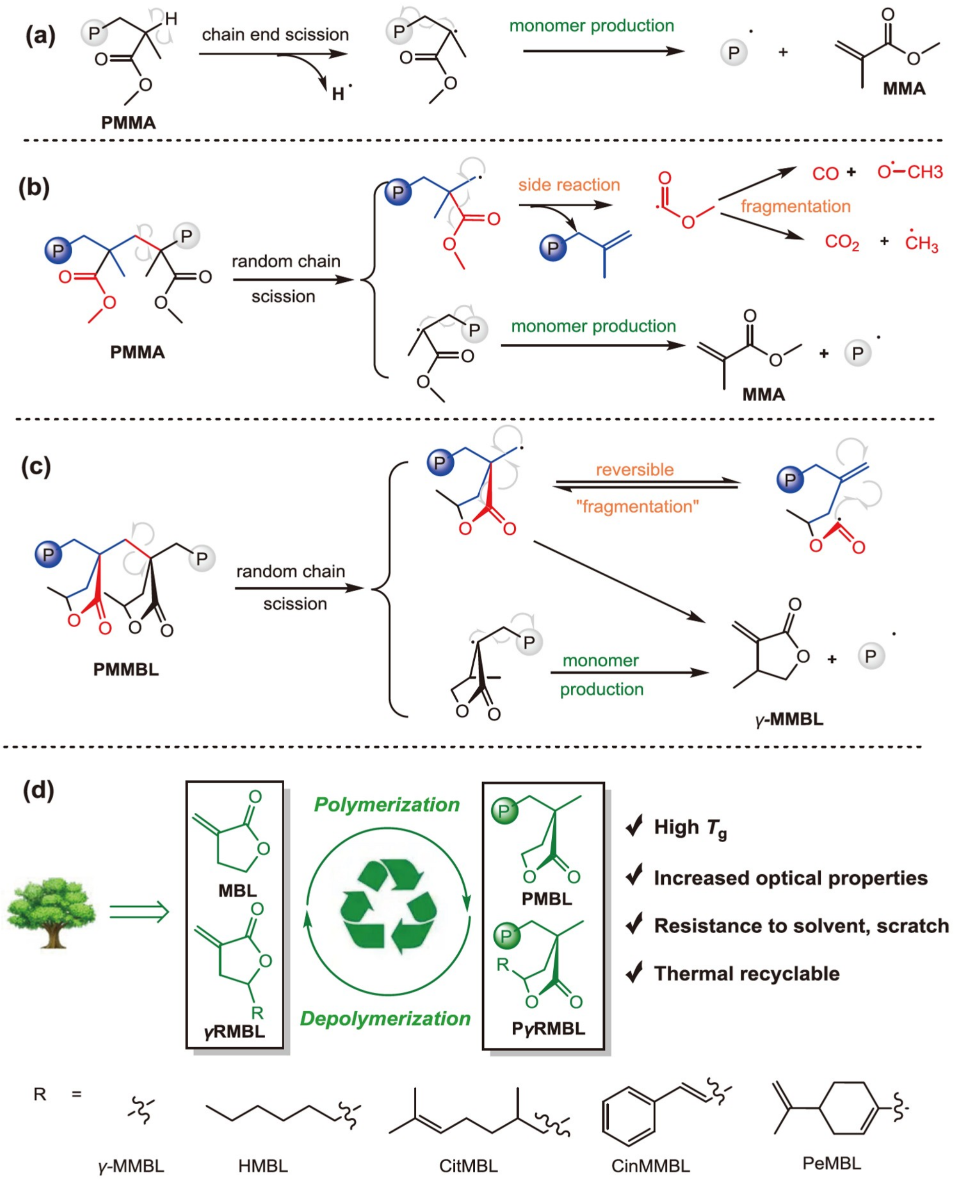


Figure 33 (a) Proposed chain end scission mechanism of PMMA depolymerization. Proposed random chain scission mechanism of PMMA (b) and PMMBL (c) depolymerization. Reproduced from Ref. [220] with permission. Copyright 2020 Royal Society of Chemistry. (d) Chemically recyclable polymers prepared from biomass-derived methylene butyrolactones and their derivatives (color online).

two polymer chains growing from the two catalyst sites *via* pairwise monomer enchainment, and eventual cyclization occurs *via* nucleophilic attack of the α-terminus of one chain by the ω-terminus (nucleophilic enolate) of the other chain, resulting in ring closure to form authentic *c*-PMMBL, along with the release of B-P-B catalysts from the chains. The term "pairwise monomer enchainment" was employed to indicate that two monomers can be enchained at once due to the presence of the two catalyst sites in the biocatalyst REP template. In principle, the probability for the formation of odd-numbered MMBL units is higher than that for the formation of even-numbered MMBL units, which can be confirmed by the MALDI-TOF MS analysis. It is also noted that the cyclic topology in *c*-PMMBL imparts an enhanced initial decomposition temperature and a much narrower degradation window compared with linear PMMBL possessing similar molecular weights and *Đ* values while maintaining high chemical recyclability.

3.3 Controlled radical depolymerization

Controlled radical polymerization (CRP) has been widely used as a powerful and user-friendly synthetic tool to synthesize a wide range of polymers with precisely controlled molecular weight and architecture [232,233]. Among various CRP techniques, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization are considered to be the two most widely utilized polymerization methods [234]. Vinyl polymers prepared by CRP typically have highly stable all-carbon backbones, which provide the polymer materials with excellent strength and mechanical properties. Since all-carbon backbone polymers consist of highly stable and equal-reactivity carbon-carbon bones, depolymerization strategies have to date focused on backbone scission into lower molecular weight polymers [235]. However, it is possible for polymers prepared by CRP with high end-group fidelity (carbon-halogen bond for ATRP and R-S-C(=S)-Z for RAFT) to depolymerize into monomers under suitable conditions by means of reversible generation of active species at polymer chain ends [236].

In radical addition polymerization, σ-bonds are formed in the polymer at the expense of π-bonds of the monomers, and therefore the enthalpy ($\Delta H_p°$) is usually negative. As the monomers are converted into polymers, both the number of molecules and the degrees of freedom also decrease during the polymerization reaction, leading to a negative enthalpy change ($\Delta S_p°$) of polymerization. The Gibbs free energy of polymerization is thus mainly determined by the polymerization temperature for a given monomer at a specific concentration. However, at temperatures above T_c, not all polymers can undergo depolymerization and regenerate monomers. An important prerequisite for depolymerization to occur is that all polymer chains are capped with reactivatable functional groups (high-end-group fidelity). When sufficient energy is provided, the dormant polymer chains capped with functional groups will break bonds to be reactivated into active polymer chains and regenerate into monomers. Properties of the monomer structure are also critical to the onset of depolymerization, with the number of vinyl substituents directly affecting the depolymerization temperature (*e.g.*, T_c = 397 °C for polystyrene and T_c = 65 °C for poly-α-methylstyrene). That is, vinyl monomers with bisubstitution at the α-carbon have milder depolymerization conditions compared to those with monosubstitution, so much so that current research on depolymerization has focused on the depolymerization of methacrylate polymers.

3.3.1 Depolymerization of polymers prepared by ATRP

ATRP has developed into one of the most commonly used methods for controlled radical polymerization due to its characteristics, such as a wide range of applicable monomers. ATRP realizes precise control of the molecular weight of the polymer and its distribution through a reversible termination mechanism. Polymerization is completed with the participation of a transition metal catalyst, which abstracts a halogen atom from alkyl halide (initiator) during the polymerization process and forms a higher oxidation state and carbon-centered radicals, which can initiate the monomer to form propagating radicals [237–241]. Propagating radicals acquire halogen atoms from oxidized complexes to form dormant species, which reduces the radical concentration and establishes an equilibrium between propagating radicals and dormant species. The labile bonds at the chain ends of polymethacrylate synthesized by ATRP could be used to induce depolymerization through halide abstraction.

Depolymerization of methacrylate monomers with large substituents is easier because of more steric hindrance around the active center, which would make polymerization unfavorable while supporting its reverse process, depolymerization. Polymers with large substituents prepared by ATRP were found to undergo depolymerization during polymerization, which was further corroborated by the apparent deceleration of polymerization in kinetic studies and the 15% monomer regeneration upon elevated temperature (60 to 90 °C) [242]. The low ceiling temperature of depolymerization is entirely attributable to the large substituents due to its low enthalpy of polymerization and more negative entropy. Matyjaszewski's group [238] reported the depolymerization of bottle brush polymers prepared by ATRP capped with –Cl (P(PDMSMA)-Cl), with a depolymerization conversion of 80% at 170 °C in the presence of a $CuCl_2$/TPMA catalytic system in 1,2,4-trichlorobenzene. The conditions of the depolymerization were effectively optimized, and excess TPMA ($[TPMA]_0/[CuCl_2]_0$ = 6) accelerated the depolymerization due to the fact that excess ligand promoted the reduction of Cu^{II}/L to Cu^{I}/L, which is the catalyst of ATRP that can further catalyze the formation of chain radicals from P(PDMSMA)-Cl (Figure 34a).

In 2019, Ouchi's group [237] conducted depolymerization studies on a more challenging polymer (poly(methyl methacrylate) (PMMA)], reactivating Cl-terminated PMMA in the presence of a ruthenium catalyst and depolymerizing it at 100 °C for 24 h at a depolymerization conversion of 6.6%. The authors investigated the depolymerization conditions of PMMA and demonstrated that a lower initial concentration of Cl-terminated PMMA gives higher depolymerization conversions and that the depolymerization conversions can be improved by the timely removal of monomers from the system. Although the conversion to depolymerization was low, this is the first example of depolymerization occurring in purified polymers prepared by ATRP and inspires subsequent depolymerization studies.

Matyjaszewski's group [239] reported the depolymerization of challenging polymers (poly(*n*-butyl methacrylate)) (P*n*BMA)) in the presence of $CuCl_2$/TPMA catalyst, where a 750 mM concentration of repeating units of P*n*BMA in 1,2,4-trichlorobenzene at 170 °C could be depolymerized to a conversion of 67% in the presence of ATRP catalyst, which essentially did not occur in the absence of the ATRP catalyst. The SEC traces shift to low molecular weight during depolymerization accompanied by an increase in dispersity, indicating that the majority of the polymer chains regenerate as monomers after the formation of polymer chain radicals and that lactonization of the polymer chain ends is the main reason for preventing depolymerization from occurring. The group utilized the same depolymerization system to carry out bulk depolymerization of Cl-terminated poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA), and the conversion of depolymerization was 74% and 84%, respectively, when the temperature was raised to 230 °C (Figure 34b) [241]. To date, the majority of research on depolymerization strategies for polymers prepared by ATRP has been directed towards Cl-terminated polymethacrylates rather than Br-terminated ones due to the fact that Br-terminated polymethacrylates produce more pronounced lactonization byproducts, as has been demonstrated by Matyjaszewski's group [239,241].

3.3.2 Depolymerization of polymers prepared by RAFT polymerization

RAFT polymerization is achieved through a degenerate transfer mechanism that allows effective control of the molecular weight of the polymer and its distribution, which is different from the atom transfer mechanism in the ATRP process. Polymers prepared by RAFT polymerization efficiently switch between active center and dormant species during polymerization, which ensures no (or minimal) propagating radical inactivation during polymerization and high-end group fidelity of the polymer. RAFT polymerization is almost considered to be the most robust controlled radical polymerization method by virtue of this characteristic. Current research on the development of degradation strategies for RAFT polymers has focused on thermolysis or photolysis of polymer chain ends. In contrast to the highly stable C–C bonds, the relatively weak C–S bonds preferentially cleave when supplied with a sufficient amount of energy (heat or light), forming polymer chain radicals and inducing depolymerization.

The illuminating work on depolymerization of polymers prepared by RAFT polymerization was reported in 2018 by Gramlich and co-workers [243] on the depolymerization of purified POEGMA and PODMSMA bottle brush polymers capped with a trithiocarbonate end-group. The large substituents of PODMSMA, which give it a low ceiling temperature, resulted in a 35% depolymerization conversion of the bottle brush polymer after 56 h of heating at an initial repeat unit concentration of 28 mM in dioxane at 70 °C. The clear depolymerization mechanism has not been established, and the authors emphasize that for the polymerization of monomers with large substituents similar to ODMSMA, special attention should be paid to the polymerization conditions to avoid depolymerization. In 2022, Anastasaki's group [244] conducted a more in-depth study on the depolymerization of polymers prepared by RAFT polymerization, and a 92% depolymerization conversion could be achieved by depolymerizing polymers capped with dithiobenzoate groups at a repeat unit concentration of 5 mM in dioxane at 120 °C. The relatively low initial concentration gives the depolymerization a relatively low ceiling temperature and achieves high depolymerization conversions. The same group further indicated that the chain end functional group (dithiobenzoate, trithiocarbonate, and pyrazole carbodithioate) and the solvent have a significant effect on the depolymerization conversion and that the depolymerization conditions can be adjusted to obtain the maximum depolymerization conversion [245]. 1,4-Dioxane is often used as a common solvent for depolymerization due to its high depolymerization conversion and less end-group degradation. However, how different solvents affect the functional groups at the end of the polymer chain is still not clearly demonstrated, and this should be further investigated. In 2023,

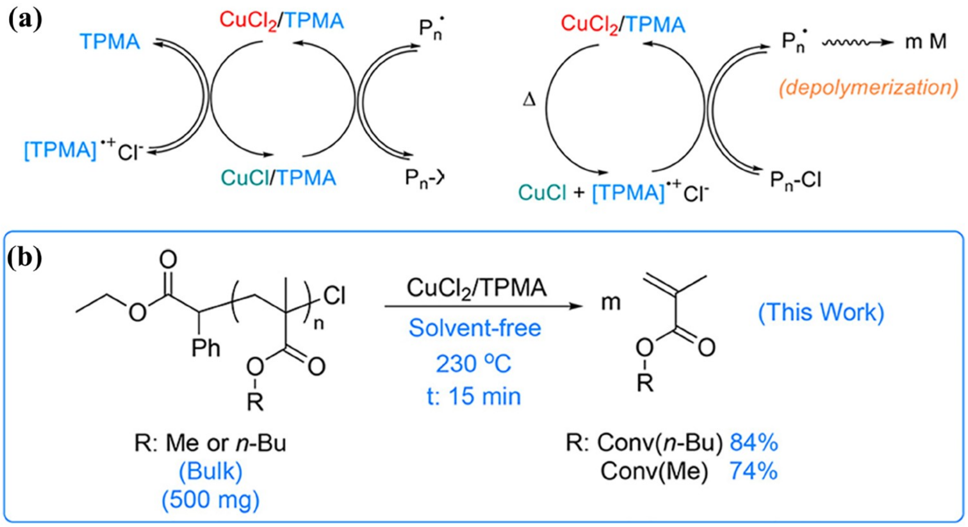


Figure 34 (a) Classical ATRP mechanism using $CuCl_2$/TPMA, (b) depolymerization of polymethacrylates prepared by ATRP in the presence of $CuCl_2$/TPMA. Reproduced from Ref. [232] with permission. Copyright 2023 American Chemical Society (color online).

Anastasaki's group [246] reported a strategy for the bulk depolymerization of polymers prepared by RAFT polymerization and ATRP, in which the functional groups at the end of the polymer chains are first facilely and quantitatively modified before depolymerization (Figure 35). Depolymerization of polymers prepared by RAFT polymerization and ATRP can occur at low temperature (150 °C) after converting the terminal functional groups to double bonds and ultimately obtaining a 90% depolymerization conversion. This solvent-free and low-temperature depolymerization strategy can effectively avoid side reactions due to high temperatures compared to other depolymerization conditions.

Another very effective method of inducing depolymerization is the use of light to directly photolyze the terminal C–S bond of the polymer chain to form polymer chain radicals, which is equivalent to the inverse process of photoiniferter RAFT polymerization. Sumerlin and co-workers [247] developed photoassisted depolymerization of polymers prepared by RAFT polymerization and found that CTAs with lower light absorption wavelengths have higher depolymerization conversions and that light forced the C–S bonds to cleave to produce polymer chain radicals, which facilitated lower depolymerization temperatures. Anastasaki's group [248] utilized a photocatalyst (Eosin Y) to accelerate the depolymerization of polymethacrylate capped with dithiocarbonate and ultimately obtained high depolymerization conversions (~82%). This depolymerization strategy is also applicable to solvents other than 1,4-dioxane, and a depolymerization conversion of about 82% was also obtained in dimethyl sulfoxide (DMSO).

The majority of current research into the depolymerization of polymers prepared by RAFT polymerization utilizes the relatively weak C–S bonds at the ends of the polymer chains (*ω* chain-ends), which is thermally or photocleaved to form polymer chain radicals and then induce depolymerization to occur. Sumerlin's group [249] introduced functional groups at both ends of the PMMA, and the synergistic effect of *α*-end *N*-hydroxyphthalimide esters and *ω*-end trithiocarbonates could lead to near-quantitative bulk depolymerization of difunctional polymethacrylate (Figure 36). This solvent- and catalyst-free depolymerization strategy allows efficient depolymerization at temperatures lower than those required by industrial methodologies.

All preliminary work on depolymerization of polymers prepared by CRP relies on labile bonds at the end of the polymethacrylate chains, which are reactivated into polymer chain radicals prior to depolymerization. Dependent on thermodynamically favorable conditions such as dilution of the initial concentration and elevated temperature to achieve depolymerization under relatively mild and efficient conditions. Depolymerization of CRP will further advance in the coming years in more aspects, such as efficiently elevating the initial concentration of depolymerization and milder depolymerization conditions.

4 Summary and outlook

As an emerging class of sustainable polymers, the development of CDPs represents a landmark achievement in the field of polymer science, which has brought about remarkable success in the precise control of polymer synthesis and, more importantly, transformed the design principle of polymer materials from "polymerization for performance and durability only" to "polymerization for a sustainable polymer with practically-use and on-demanding depolymerization properties".

Highlighted success achieved so far in this critical review has provided several feasible solutions to address two big key challenges——how to balance polymerization and depolymerization ability and how to unify conflicted depolymerizability and physical properties, and also led to formulations of a set of the guiding principles for designing ideal CDPs. Firstly, in terms of thermodynamic perspective, the choice of ergoneutral polymerizations with T_c value in the range of −60–200 °C is necessary for realizing complete conversion of monomer to polymer and complete reversion of polymer to monomer, thereby reaching a fine balance between polymerization and depolymerization ability and endowing the establishment of CDPs with infinite recyclability. Secondly, the thermodynamic favorability is, however, insufficient to construct ideal CDPs. In terms of kinetic perspective, the use of a highly effective catalyst is indispensable, as it can accelerate the polymerization rate by

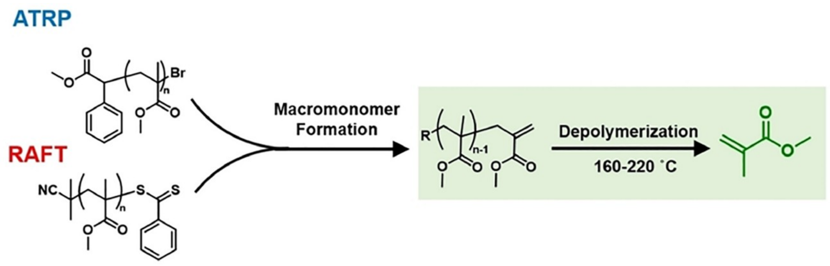


Figure 35 A scheme illustrates the converting of the terminal functional groups to double bonds and the subsequent depolymerization. Reproduced from Ref. [246] with permission. Copyright 2023 Wiley-VCH GmbH (color online).

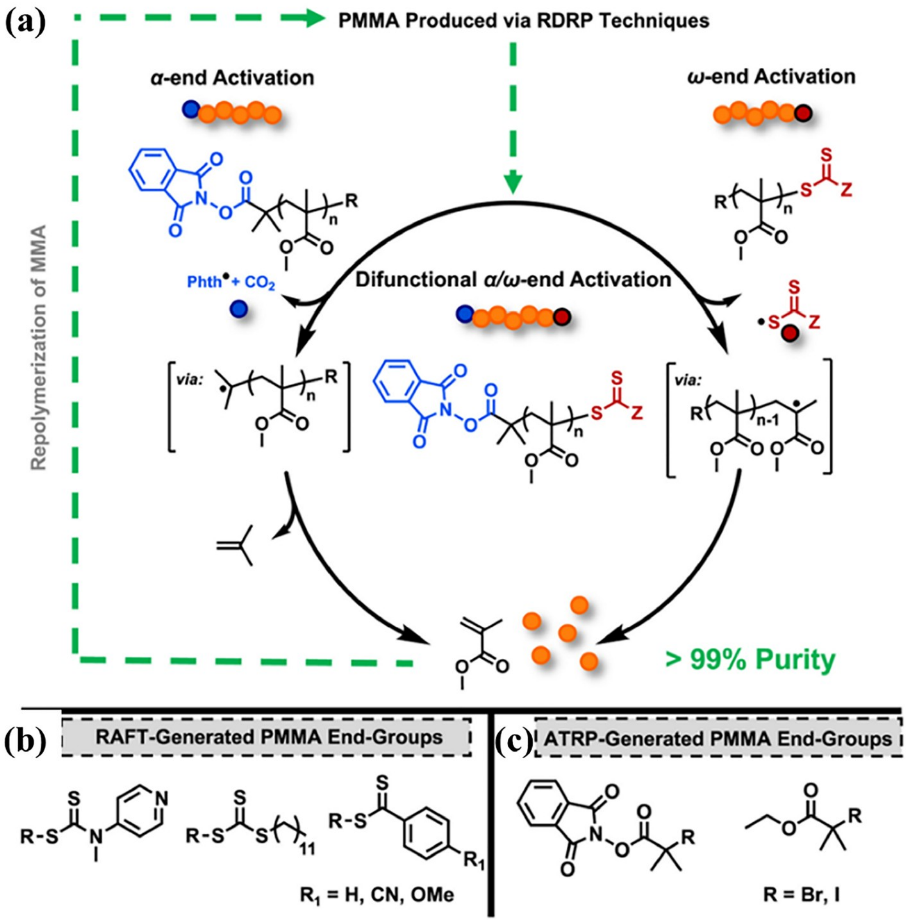


Figure 36 Chemical recycling of PMMA to MMA utilizing labile end-groups. (a) Initiation of depolymerization from *α*-chain ends, *ω*-chain ends, or a combination of the two. This strategy can be applied to polymers derived from (b) RAFT polymerization and (c) ATRP. Reproduced from Ref. [249] with permission. Copyright 2023 Elsevier Inc. (color online).

significantly lowering the energy barrier and thus render the polymerization within an operable time. Thirdly, to unify conflicting depolymerizability and physical properties, monomer design has been accepted as a powerful tool to lead to novel CDPs with excellent performance and chemical recyclability. In addition, the development of CDPs that are "thermodynamically unstable but kinetically stable or kinetically trapped" is another feasible solution to notably enhance the thermal stability of CDPs well above its T_c. Under specific conditions, such polymers can undergo depolymerization readily and selectively, thus furnishing on-demand depolymerization properties.

The development of future CDPs should focus on the following aspects: Firstly, from a monomer's perspective, the current monomers for successful CDPs usually lack commercial availability and/or demonstrated cost-competitiveness synthesized at a small laboratory scale. Therefore, for further industrial consideration, the development of the most readily available, abundant monomers (especially those from bio-based renewable feedstocks or recaptured intermediates from the deconstruction of today's waste plastics) will undoubtedly continue to be a major focus in future research. The theoretical calculation of monomer structure, as well as its thermodynamics and kinetics, would be a valuable complement to experimental design and synthesis. Secondly, at present, the chemical recycling of CDPs mainly depends on energy-intensive thermal processes or the use of acidic or basic conditions, which is also highly material-dependent. The innovation of polymerization catalysis has brought about significant accomplishments in the field of CDPs, but depolymerization catalysis, in contrast, has attracted much less attention. Therefore, we anticipate that the tailored depolymerization catalysts would be crucial to define the reaction temperature and product selectivity of depolymerization. Thirdly, another aspect that needs to be addressed is that the material properties of CDPs need to compete with presently available commodity polymers. Meanwhile, it would be highly desirable if the CDPs used for disposable plastic products could be completely and harmlessly degraded by microorganisms as they are disposed of in natural environments. Besides the design of novel monomers that can impart enhanced properties and functionality, in our opinion, there is also a great future in controlling polymer microstructure and architecture to enable the desired properties of CDPs. Lastly, from a green chemistry perspective, it would be of great interest to design and develop environmental-friendly, energy-efficient, and cost-effective CPR synthesis processes by using green catalysts (*e.g*., reusable catalysts, organic catalysts, nontoxic metal-based catalysts) and solvents.

Some important new advancements in CDPs have been continuing to emerge. For example, Tang *et al*. [250] established five-membered lactones with a bridged [2.1.1] bicyclic structure and *α*-substituted. The resulting polyester backbone comprises a conformationally rigid 1,3 cyclobutane ring, which exhibits superior thermostability ($T_{d,5\%}$ = 376–380 °C) and excellent hydrolytic resistance while still maintaining full depolymerizability. Furthermore, the polymer properties can be modified by the substituents at the *α*-position. The thermal and mechanical performance of the polymers with phenyl and butyl substituents is comparable to that of syndiotactic polystyrene (SPS) and LDPE. Chen *et al*. [251] rationally designed a bicyclic lactone with a pendent hydroxyl group (BiL^{OH}). The resulting hyperbranched polyester (HBPE) exhibits full chemical depolymerizability despite its architectural complexity, showing quantitative selectivity for the regeneration of pristine monomers *via* a unique cascade depolymerization mechanism. Chen *et al*. [252] also developed a remarkable bifunctional monomer that is capable of undergoing orthogonal polymerization into distinct polymers. These polymers include lactone-based polyester and CO_2-based polycarbonate. Notably, these resulting polymers and their admixtures can be effectively depolymerized back to the original monomer through catalytic means. Li *et al*. [253] proposed a paradigm that leverages a "chaperone"-assisted strategy to establish closed-loop circularity for a "non-polymerizable" *α*,*β*-conjugated lactone, 5,6-dihydro-2*H*-pyran-2-one (DPO). Li *et al*. [254] also established a rare example of floor temperature (T_f) regulated closed-loop circularity in poly(ketal-ester). This poly(ketal-ester) was synthesized through entropy-driven ring-opening polymerization (ROP) of the macrocyclic diester HOD, exhibiting remarkable thermostability ($T_{d,5\%}$ up to 353 °C). Notably, this polymer can be quantitatively depolymerized back to its monomer at room temperature within just 1 min with the simple base catalyst ^{t}BuOK. Hu and Tang *et al*. [255] recently reported a robust multicomponent polymerization of three abundantly available, inexpensive monomers: elemental sulfur, CH_2Cl_2, and aromatic diamines. This process enables the direct conversion of sulfur to a series of functional aromatic polythioureas with high molecular weights (M_n up to 50 kDa) in excellent yields (up to 98%). Moreover, the functional aromatic polythiourea can be chemically depolymerized through aminolysis with $NH_3 \cdot H_2O$ to afford a diamine monomer in an isolated yield of 83%. Ren *et al*. [256] reported a universal synthetic strategy for producing polytrithiocarbonates *via* the polycondensation of dithiols and dimethyl trithiocarbonate. This strategy has excellent compatibility with a wide range of monomers, including aliphatic, heteroatomic, and aromatic dithiols, enabling the synthesis of polytrithiocarbonates with diverse structures. Notably, these polytrithiocarbonates can be easily depolymerized *via* solvolysis into the corresponding monomers, which can be repolymerized to virgin polymers without changing the material properties.

In conclusion, at present, the majority of CDPs developed so far cannot be considered mature for commercial applications and reshaping the current polymer industry with CDPs is a considerable challenge that will not be achieved in the near future. To address the challenge, cross-disciplinary research (*e.g*., polymer chemistry, physics, processing, engineering, and organic chemistry, even information technology and artificial intelligence) is highly desirable and collaboration between both the polymer industry and academic researchers is also essential.

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Conflict of interest The authors declare no conflict of interest.

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