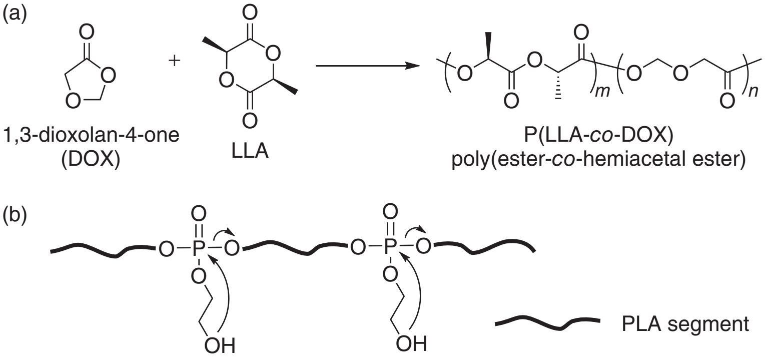
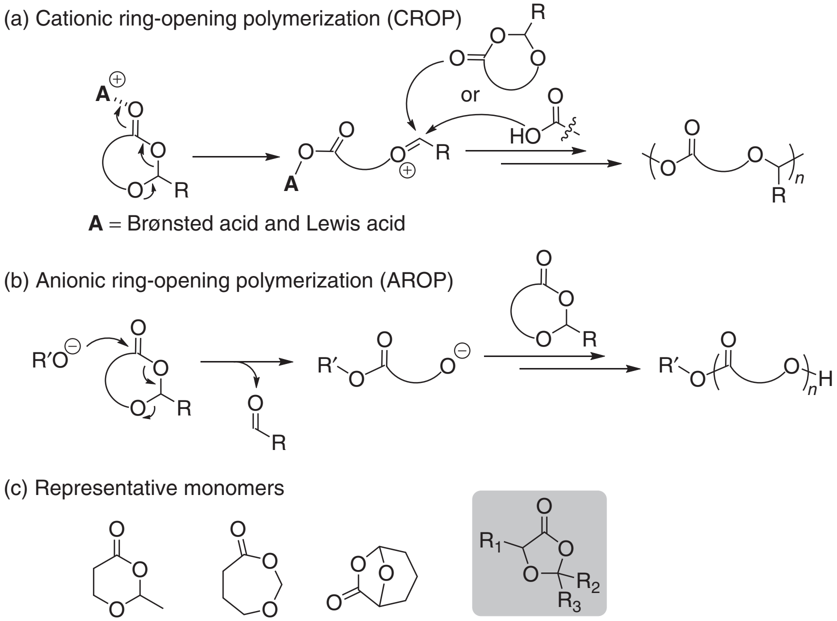


Figure 1.30 (a) Copolymerization of hemiacetal ester DOX with LLA; (b) incorporation of phosphate moiety into PLA.

thermal properties similar to LLA, namely, T_m and T_g. However, the degradability in aqueous environments increases noticeably. Upon 10% incorporation of DOX, the mass loss and reduction in molecular weight of the P(LLA-*co*-DOX) film in seawater are 2% and 35%, respectively, after 45 days; no changes are observed in PLLA during the same period. Another design for a marine-degradable PLA involves the introduction of phosphate moieties into the polymer chain (Figure 1.30b) [127]. The PLA chains undergo rapid cleavage via an RNA-inspired intramolecular attack by the free hydroxyl group, thus transforming into easily degradable lactide oligomers. However, the iterative addition of LA and cyclic phosphate monomers is required for the synthesis. Cyclic acetals, such as 1,3-dioxolane (DXL) and its derivatives, can also copolymerize with LLA [128–130]. Although the degradability, especially under acidic conditions, is significantly enhanced, the material properties differ substantially from PLA. Most of the copolymers become amorphous, with their T_g values at approximately room temperature.

In addition to copolymerization, development of novel cyclic ester monomers is an alternative approach for enhancing the degradability of polyesters. Cyclic hemiacetal esters have been studied extensively [131–133]. Although poly(hemiacetal ester)s can be synthesized via condensation polymerization [134], the ROP of cyclic hemiacetal esters has been developed as a more well-controlled method [135]. The resulting poly(hemiacetal ester)s are acid-labile and potentially biodegradable polymers. Therefore, they hold promise as degradable alternatives to current polymer materials in daily applications and for high-end applications such as drug delivery systems [136]. Regarding the polymerization conditions, poly(hemiacetal ester)s can be obtained only via cationic ring-opening polymerization (CROP) using Brønsted acid or Lewis acid catalysts (Figure 1.31a). Through anionic ring-opening polymerization (AROP), polyesters are obtained by eliminating aldehyde (Figure 1.31b). The CROP of exocyclic hemiacetal esters can also produce acid-labile poly(hemiacetal ester)s with different molecular structures (Figure 1.32) [137].

Cationic copolymerization of cyclic hemiacetal esters with other monomers to synthesize degradable polymers has also been widely investigated [138, 139]. The



(a) Cationic ring-opening polymerization (CROP)

(b) Anionic ring-opening polymerization (AROP)

(c) Representative monomers

Figure 1.31 Ring-opening polymerization of cyclic hemiacetal esters via (a) cationic mechanism, (b) anionic mechanism; and (c) representative monomers (the monomer marked in gray was reported in copolymerization only).

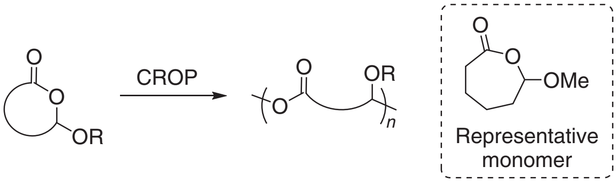


Figure 1.32 CROP of exocyclic hemiacetal esters.

synthesis of poly(hemiacetal ester)s via the copolymerization of cyclic acetals or aldehydes with cyclic anhydrides has been reported recently [140, 141]. However, these examples are not introduced in detail herein.

Other functionalities have also been introduced into the cyclic ester monomers to enhance the degradability of the resulting polymers. 4-carbomethoxyvalerolactone (CMVL), which bears a carbomethoxy group at the 4-position of δ-VL, undergoes ROP to afford poly(4-carbomethoxyvalerolactone) (PCMVL), upon catalysis by DPP (Figure 1.33a) [142, 143]. The resulting PCMVL is tough, easily degradable, and recyclable. Regarding its degradation mechanism, especially under basic conditions, the retro oxa-Michael reaction is the main reaction pathway (Figure 1.33a, right). When a ketone group is introduced at the 4-position of δ-VL, the cyclic ester 4-ketovalerolactone (KVL) can also undergo ROP to yield PKVL in a manner similar to that effected by the DPP catalyst [144]. The polymer structure is similar to that of poly(glycolide) (PGA). The synthesized PKVL shows $T_g = 7\,°C$ and $T_m = 132$

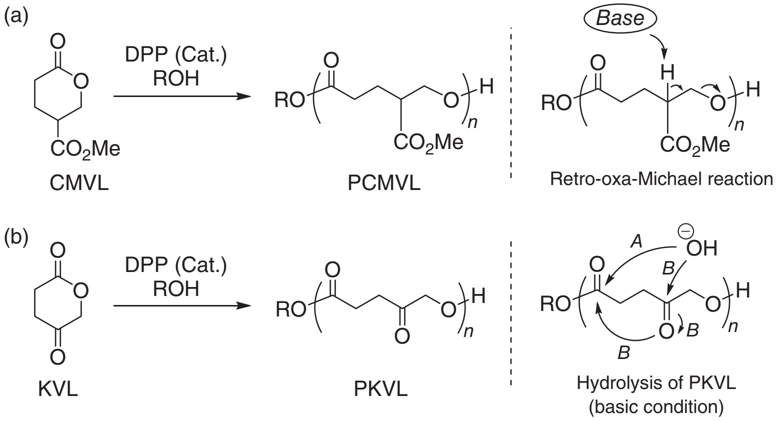


Figure 1.33 ROP of novel cyclic esters.

and 148 °C. The PKVL undergoes facile depolymerization, especially under basic conditions. The hydroxy anion can nucleophilically attack the ester carbonyl (Figure 1.33b, right, path A) and ketone groups, followed by an intramolecular attack on the ester carbonyl group (path B). This mechanism explains the rationale behind PKVL undergoing a faster hydrolysis than PVL, under basic conditions.

In addition to the aforementioned examples, amine-containing polyesters or poly(amino esters) are an important category of degradable polyesters for biomedical applications [136, 145]. This type of polyester is discussed in detail in Chapter 6.

1.4.2 Development of Novel Chemically Recyclable Polyesters

Chemical recycling of polymer materials converts plastic waste into their starting monomers or other value-added chemicals. This process is considered an important approach for achieving a circular economy of polymer materials. Among these, closed-loop recycling, i.e. converting back into monomers, has attracted considerable research attention in recent years. Among all chemically recyclable polymers, polyesters synthesized via the ROP approach are the most widely studied. Organocatalysts have been used in many reported applications.

According to the fundamental principle of polymerization, most of the polymerization process is enthalpy-driven, i.e. the enthalpy change $\Delta H < 0$. The entropy change of polymerization is always negative ($\Delta S < 0$) because the degrees of freedom decrease during the formation of polymers from monomers. The Gibbs free energy change of polymerization $\Delta G = \Delta H - T\Delta S$ should be negative ($\Delta G < 0$) to allow for the polymerization to occur. When $\Delta G > 0$, the reverse reaction, i.e. the depolymerization, occurs (Figure 1.34). When $\Delta G = 0$, the polymerization and depolymerization reach an equilibrium, and the temperature thereat is called ceiling temperature T_c. In principle, all polymers should have a T_c that can allow for reverse depolymerization to occur. However, most vinyl polymers such as polyolefins decompose via

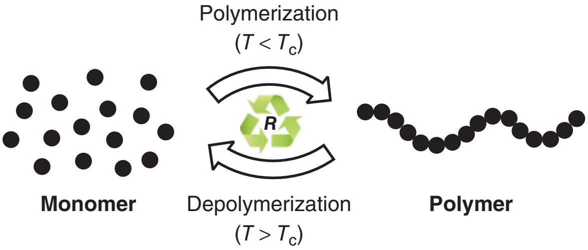


Figure 1.34 Schematic of polymerization and depolymerization.

other reaction pathways before attaining their high theoretical T_c values. Therefore, from a practical viewpoint, T_c needs to be within an appropriate range to facilitate convenient synthesis, use, and chemical recycling of polymer materials. Aside from polymers that can directly depolymerize back to monomers, numerous polymers first degrade to different low-molecular-weight compounds or oligomers, which can then be further transferred back to monomers or polymers. These cases are excluded to narrow the scope of this section.

Five-membered γ-butyrolactone (γ-BL) was considered a nonpolymerizable lactone for a long time because of its low ring strain and small ΔH value. In 2016, Chen and Hong reported the first successful preparation of high molecular weight poly(γ-butyrolactone) (P(γ-BL)) at low temperatures [1, 146]. The isolated P(γ-BL) could withstand high temperatures after the catalyst removal. The polymer could depolymerize back to γ-BL monomers via thermal degradation (Figure 1.35). Although lanthanide complexes were used as the first catalyst, base catalysts, including the organic phosphazene base and the inorganic base *t*-BuOK, also demonstrate excellent catalytic performances for this polymerization [2, 147, 148].

Limited by the theoretical T_c value, the polymerization of γ-BL has to be conducted at low temperatures, which restricts its practical application. Therefore, after Chen and Hong's seminal report, the T_c value and material properties were considered by changing the molecular design of the monomers. Numerous successful examples have been reported to date [149–156]. Here, instead of introducing the novel cyclic ester monomers individually, they are classified into three major categories: (i) bicyclic structures, (ii) substitutions, and (iii) heteroatoms. These three categories are discussed in the following paragraphs.

In the first category, bicyclic structures are used. Following the successful polymerization of γ-BL, the structure of five-membered lactone has been integrated

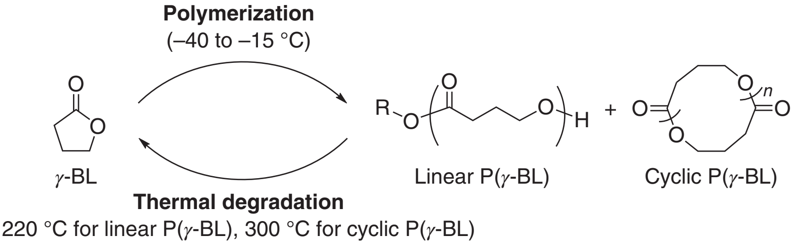


Figure 1.35 Polymerization of γ-BL and depolymerization of P(γ-BL).

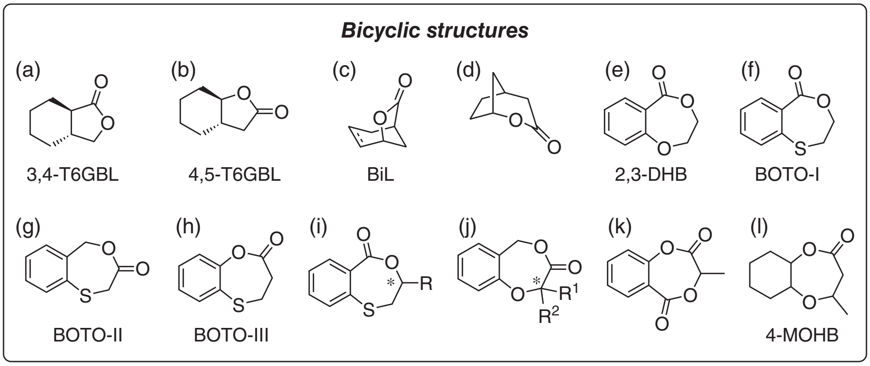


Figure 1.36 Cyclic ester monomers with bicyclic structures.

into bicyclic compounds to tune the polymerizability and material properties of the polymers. As shown in Figure 1.36a–c, the *trans*-fused bicyclic and bridged lactones contain the substructure of the five-membered γ-BL [157–159]. Compared to the normal γ-BL, the bicyclic structure endows the polymer with a higher ring strain; thus, the polymerization can be conducted at room temperature while ensuring the recyclability back to monomers. In addition to the increased polymerizability, the introduction of rigid cyclic structures into the polymer chain drastically increases the glass transition temperature and melting point of the obtained polyesters. This strategy of introducing bicyclic structures has been proven successful for seven-membered lactones (Figure 1.36d–l) [41, 160–166]. Unlike the γ-BL, the seven-membered ε-CL possess good polymerizability; however, the depolymerization process usually requires harsh conditions owing to the less favored ring-closing reaction [167–169]. The development of mild and highly selective PCL depolymerization method remains an important research topic. By introducing bicyclic structures together with heteroatoms, such as oxygen and sulfur, into the seven-membered ring, the ring-closing depolymerization process becomes more favorable, thus allowing for the chemical recycling back to the monomer under milder conditions ($\leq$ 200 °C). In addition to lowering the T_c value to enable facile chemical recycling, the incorporation of cyclic structures and heteroatoms into the polymer chain can also tune the thermal and mechanical properties of the polyester products. Furthermore, side-chain substituents, such as atactic, isotactic, and stereocomplexes, have been introduced to further fine-tune the material properties by altering the functional group and tacticity [163, 165].

The second category involves the introduction of substituents into the cyclic monomer. In particular, gem-disubstitution can significantly improve the chemical recyclability of cyclic esters through the Thorpe–Ingold effect [170]. Similar to ε-CL, δ-VL exhibits a high polymerizability and high T_c of 298 °C at $[M]_0 = 1\,\mathrm{mol\,l^{-1}}$ [171]. Reduction in the T_c value and chemical recycling of the monomer at 140–170 °C have been demonstrated via single substitution at the β-, γ-, and δ-positions (Figure 1.37a–c) [38, 59, 142, 143, 172, 173]. When di-alkyl substitution is performed at the α-position, the T_c value decreases further to 67–115 °C at $[M]_0 = 1\,\mathrm{mol{\cdot}l^{-1}}$, depending on the alkyl group (Figure 1.37d) [171]. Aside from

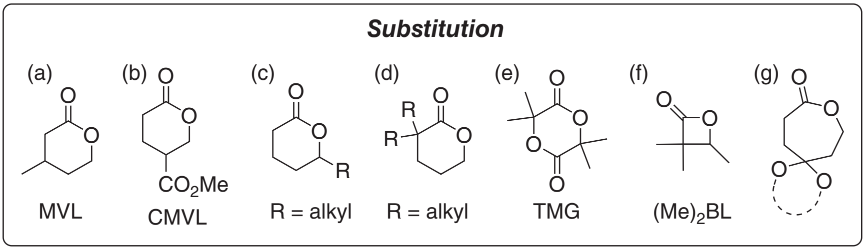


Figure 1.37 Cyclic ester monomers with various substituents.

tuning the T_c, the introduction of different substituents can alter the material properties of the resulting substituted PVLs to adapt to various applications, including plastics [143, 171], polyurethane foams [172], elastomers [38, 173], and pressure-sensitive adhesives [59]. Lactide is a representative six-membered cyclic ester monomer, and PLA is one of the most widely used biopolymers. The T_c of PLA is as high as 343 °C in bulk. The effective depolymerization of PLA to LA by zinc catalyst at approximately 200 °C has been reported. However, racemization occurs partially [174], which can be overcome by dissolving in a dilute, highly polar aprotic solvent, such as DMF and γ-valerolactone (GVL), to reduce the T_c value and suppress racemization [175]. Tetramethyl glycolide (TMG), a cyclic dimer of α-hydroxyisobutyric acid, can be polymerized to PTMG, which shows a high T_m of 185–190 °C (Figure 1.37e). Although the thermal degradation of PTMG conventionally affords methacrylic acid, when $Sn(Oct)_2$ is used as the catalyst at 265 °C, TMG can be recovered with a yield of 80.8% [176]. Polyhydroxyalkanoates (PHAs), represented by poly(3-hydroxybutyrate) (P3HB), are important biorenewable and biodegradable polymers. However, PHAs exhibit a relatively low degradation temperature of $T_{d,5\%} \approx 250$ °C. Moreover, PHAs can easily undergo elimination to form α,β-unsaturated carboxylic acids under thermal conditions. This challenge has been successfully addressed by introducing α,α-disubstituents to the four-membered β-lactone structure (Figure 1.37f) [177]. The gem-disubstitution significantly promotes the ring-closing process toward recovering the monomer under thermal depolymerization at 210 °C; however, the gaseous byproduct 2-methyl-2-butene is generated. In addition to the recyclability, the α,α-disubstituted PHAs show similar melting points, enhanced toughness, and a higher degradation temperature ($T_{d,5\%} = 322$–335 °C), compared to the normal PHAs. The gem-disubstitution strategy has also been reported to be effective in seven-membered lactones. By introducing a spirocyclic acetal-functionality at the γ-position, the chemical recyclability improves considerably along with tunable thermal and mechanical properties, depending on the chemical structures of the acetal units (Figure 1.37g) [178].

The third category involves the introduction or alteration of the heteroatoms in cyclic esters. This strategy involves replacing the methylene unit (–CH_2–) with heteroatoms, such as oxygen, nitrogen, and sulfur, and replacing the ester moiety with a thioester. Poly(1,4-dioxan-2-one) (PPDO) is a biodegradable, biocompatible, and bioresorbable polymer that is used as a biomedical material. Compared to δ-VL, it has a lower T_c value of 265 °C, allowing for easier chemical recycling

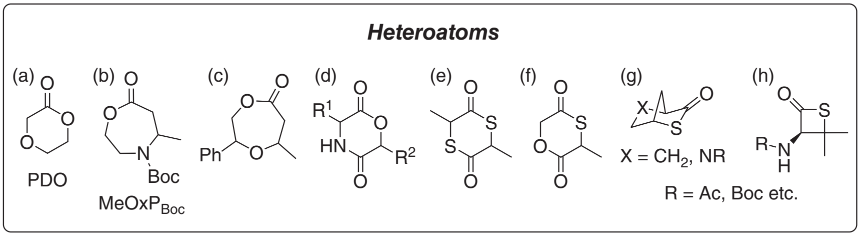


Figure 1.38 Cyclic ester monomers with heteroatoms.

(Figure 1.38a) [179, 180]. The introduction of oxygen and nitrogen atoms together with other substituents into the seven-membered lactone structure could also enable chemical recycling of the polyesters under relatively mild conditions (Figure 1.38b,c) [181, 182]. In addition, these monomers can be synthesized via the chemical upcycling of P3HB. This strategy of altering the heteroatoms can be applied to LA-like monomer structures as well. By changing one ester moiety of LA to an amide, the resulting poly(ester–amide) can be chemically recycled with ease in a closed-loop manner (Figure 1.38d) [183]. Because of the hydrogen-bonding interactions between the amide groups and the tunable side-chain functionality, the thermal and mechanical properties of poly(ester–amide)s can be adjusted over a wide range. For other novel LA-like monomers, changing the ester to a thioester group (i.e. O-to-S) is an effective approach to address the trade-off between the polymerizability of the monomer and depolymerizability of the polymer (Figure 1.38e,f) [184, 185]. More importantly, enhanced mechanical properties, particularly a higher toughness, can be achieved by a simple O-to-S substitution, without deteriorating the thermal properties. A similar O-to-S substitution strategy has been reported for five-membered cyclic thioesters fused in bridged bicycles and for four-membered β-thiolactones with a geminal dimethyl substitution. Both these monomers exhibit excellent polymerizability and recyclability (Figure 1.38g,h) [186, 187].

In summary, this section discusses different design strategies for cyclic esters, especially novel compounds, whose corresponding polyesters can be chemically recycled with ease. Further, for some cyclic ester monomers, more than one strategy has been employed to adjust the polymerizability of the monomer and depolymerizability of the polymer, while considering the material properties.

Closed-loop chemical recycling is a promising solution to the current global plastic problem. In real-world applications, wherein different types of plastic waste are collected together, closed-loop chemical recycling may encounter challenges associated with separating the polymers or recycled monomers.

1.5 Summary and Outlook

Among all types of organocatalyzed polymerization, the ROP of cyclic esters has been studied most extensively. Over the past two decades, a large variety of organocatalysts has been developed to meet the requirements of various cyclic ester monomers under different polymerization conditions. Among the novel organocatalysts, facets related to industrial applications are being increasingly considered.

This chapter discusses the aspects of reactivity, selectivity, thermal stability, and safety. In addition, the ROP of cyclic esters based on external-stimuli-responsive organocatalysts is an emerging research area [188–191]. Several representative examples, particularly those controlled by light, have been reported [192–200]. However, this research area is still in its infancy. We look forward to further improvements, especially at the levels of spatial and temporal control, to enable their application in highly sophisticated material production. In addition to the novel organocatalysts, the recent development of polyesters with excellent chemical recyclability and degradability is introduced in this chapter. In this part of the research, several aspects, including monomer synthesis, polymerization, material properties, and recyclability/degradability should be considered. With the advancements in catalyst development and monomer design, the organocatalyzed ROP of cyclic esters holds great promise for the environmentally benign production of degradable and recyclable polymeric materials.

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