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Organocatalyzed Ring-Opening Polymerization of Cyclic Esters Toward Degradable Polymers

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1.1 General Introduction

The discovery of ring-opening polymerization (ROP) of cyclic esters to afford polyesters dates back to the 1930s. The hydrolyzable nature of the ester functional group in the polymer chain endows the chain with degradability (e.g. thermal, chemical, bio), rendering polyesters as promising candidates for biomedical applications and as environmentally benign polymer materials. In addition, cyclic esters exhibit polymerizability with an extremely broad scope of catalysts. The ROP of cyclic esters can occur via anionic, cationic, and coordination mechanisms, using different types of catalysts such as transition-metal catalysts, enzymes, and organocatalysts (Figure 1.1). Thus, the ROP of cyclic esters is the first and the most investigated organocatalyst-based polymerization reaction to date.

After extensive investigations over the past two decades, various organocatalysts have been reported to exhibit catalytic activity in the ROP of cyclic esters (Figure 1.2). The typical reaction mechanism for various catalysts is introduced in Section 1.2.

After the numerous initial investigations of novel organocatalysts, driven by the scientific interest in transition-metal-free catalysts, several factors such as catalytic efficiency, selectivity, thermal stability, and safety have been considered in recent works toward meeting the requirement for industrial application. However, metal complexes, such as tin(II) 2-ethylhexanoate ($Sn(Oct)_2$), are still used in industries to produce polyesters. An increasing number of recent studies have indicated the promising future of organocatalysts, even under industrially relevant conditions. In Section 1.3, the paradigm shifts in the organocatalyzed ROP of cyclic esters are illustrated.

β-Butyrolactone (β-BL), lactide (LA), δ-valerolactone (VL), and ε-caprolactone (CL) are among the most studied cyclic ester monomers because of their relatively high ring strain, good polymerizability, biodegradability, and biocompatibility of their corresponding polyesters, poly(β-butyrolactone) (P(β-BL)), poly(lactic acid) (PLA), poly(δ-valerolactone) (PVL), and poly(ε-caprolactone) (PCL) (Figure 1.3a).

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Figure 1.1 ROP of cyclic esters into polyesters.

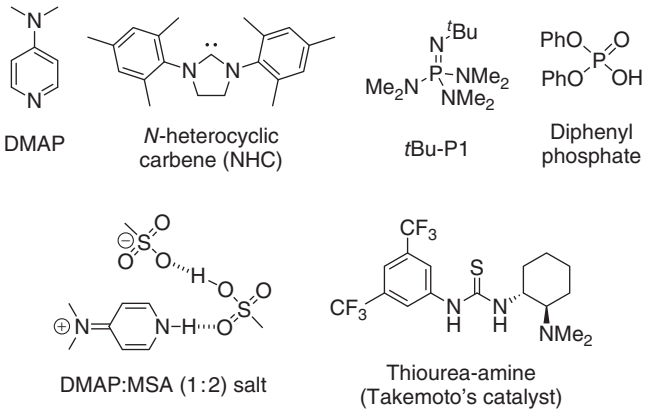

Figure 1.2 Representative organocatalysts for the ROP of cyclic esters.

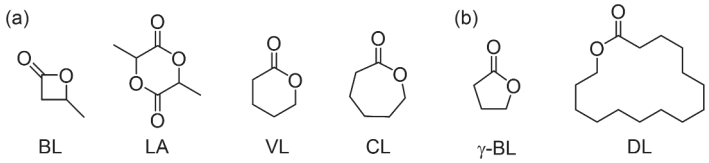

Figure 1.3 Representative cyclic esters with relatively high (a) and low (b) ring strains.

However, five-member and large-ring lactones such as γ-butyrolactone (γ-BL) [1, 2] and ω-pentadecalactone (DL) [3, 4] cannot be polymerized easily owing to their low ring strain (Figure 1.3b). The successful demonstration of controlled polymerization of low ring strain γ-BL under low temperatures by highly active catalysts, including metallic catalysts and organocatalysts, and depolymerization of P(γ-BL) back to γ-BL monomer at an elevated temperature signified the impact of the closed-loop polymerization methodology [1, 2]. Since this seminal work of Hong and Chen, chemically recyclable polyesters with novel monomer designs, especially the ones that can be easily derived from renewable biomass resources, have become an emerging research topic, and the number of research reports has increased rapidly in recent years. Although their research was largely focused on the monomer design, polymer properties, and recyclability, organocatalysts have been used extensively. Polyesters that can degrade easily under environmental conditions are also important, aside from the chemically recyclable polyesters. Therefore, the introduction of other facile functional groups to the main chain of polyesters for enhancing their degradability has also been an important topic in recent years. In Section 1.4, breakthroughs in achieving improved degradability and recyclability are discussed.

This chapter focuses on the features of organocatalysts, cyclic ester monomers, and the corresponding polymers. Utilizing the organocatalyzed ROP of cyclic esters for the synthesis of block copolymers and tailoring a highly complicated polymer architecture design for synthesizing advanced degradable materials are also important research directions; however, they are not the topics of this chapter.

Alkali-metal salts, such as the salts of carboxylic acids, vitamin C, and (thio)ureas, are not completely organic compounds. The reaction mechanisms of these catalysts are similar to those of common organocatalysts, rather than transition-metal catalysts. In addition, sodium and potassium ions are safe and essential for the human body; therefore, they have been categorized as organocatalysts herein.

1.2 Polymerization Mechanism

1.2.1 Nucleophilic Catalysts

Nucleophilic catalysts, e.g. 4-dimethylaminopyridine (DMAP) and *N*-heterocyclic carbenes (NHCs), are widely used in organic chemistry. The ROP of lactide by DMAP, as reported by Hedrick and coworkers in 2001, is recognized as the landmark that initiated the era of organocatalyzed polymerization [5]. Since this seminal work, many other nucleophilic catalysts, such as phosphines [6], amidines [7], and NHCs [8, 9], have been investigated.

The reaction conditions and polymerizable monomers largely depend on the catalysts employed. A quantitative comparison of the nucleophilicities of these catalysts can provide a better understanding. The Mayr reactivity parameters provide a scale for quantitatively evaluating and comparing the nucleophilicities of various nucleophilic catalysts. Four representative nucleophilic organocatalysts are shown in Figure 1.4, whose Mayr nucleophilic parameter *N* increases in the order of triphenyl phosphines, DMAP, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), and NHCs [10].

Regarding the reaction mechanism of nucleophilic catalysts for the ROP of cyclic esters, the catalytic cycle typically commences with a nucleophilic attack from the catalysts on the carbonyl group of the cyclic esters to open the ring and generate a zwitterionic intermediate. If the reaction is conducted in the presence of an alcohol chain-transfer agent, i.e. ROH, the hydroxyl group can be activated by the anionic site of the zwitterionic intermediate, thus inducing an intramolecular nucleophilic

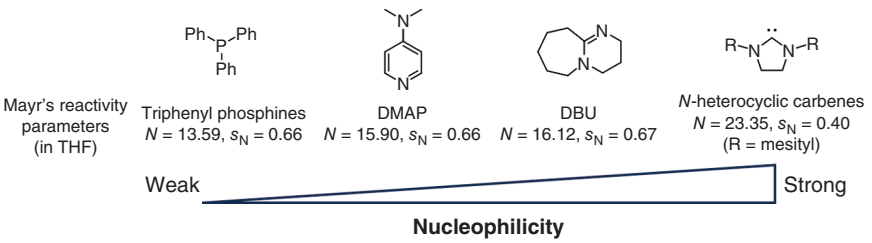

Figure 1.4 Representative nucleophilic catalysts and their nucleophilicities evaluated using the Mayr reactivity parameters.

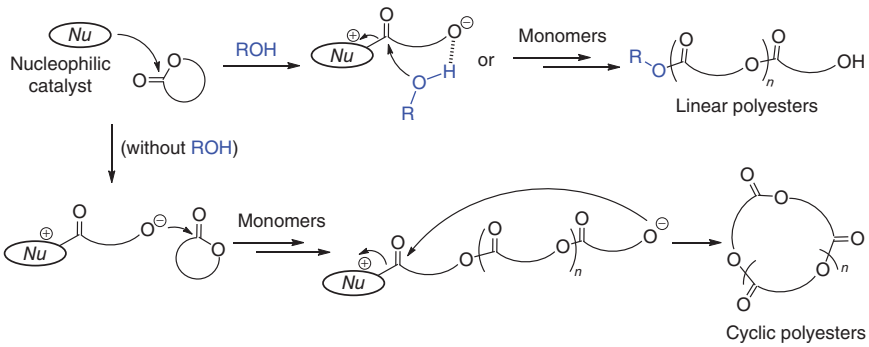

Figure 1.5 General reaction mechanism of the ROP of cyclic esters using nucleophilic catalysts in the presence and absence of alcohol initiators.

attack and releasing the nucleophilic catalyst (Figure 1.5, upper reaction route). The iteration of this process affords linear polyesters. In the absence of ROH, the anionic site, i.e. alkoxide, of the generated zwitterionic intermediate continues to attack other cyclic ester monomers, and at a certain stage, the anionic chain end can nucleophilically attack the cationic activated carbonyl group and release the nucleophilic catalysts, affording cyclic polyesters (Figure 1.5, lower reaction route).

Nucleophilic catalysts typically exhibit a strong basicity; however, their reaction mechanism may not be identified easily. For example, DBU and 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD) are moderate/strong Brønsted bases, but they exhibit relatively high nucleophilicity. Therefore, they could follow the mechanisms of either nucleophilic catalysts [11] or Brønsted base catalysts [12].

1.2.2 Base Catalysts

Organobase catalysts constitute an important type of organocatalysts for the ROP of cyclic esters. Base catalysts can be divided into Lewis bases and Brønsted bases. This section focuses on Brønsted bases, which function as proton acceptors. Lewis bases with a high nucleophilicity have been categorized as nucleophilic catalysts in Section 1.2.1. In the ROP of cyclic esters, commonly used Brønsted bases catalysts include amines, amidines, guanidines, and phosphazenes [13–15]. Pyridines and other *N*-containing heterocycles are Brønsted bases as well; however, considering their weak basicity and medium-to-high nucleophilicity, they have been introduced in Section 1.2.1 as nucleophilic catalysts (e.g. DMAP).

The basicity of the abovementioned Brønsted bases spans a wide range across 24 orders of magnitude – from the relatively weak triethylamine (pK_{BH}^{+} 18.8 in acetonitrile) to the super strong base *t*-BuP_4 (pK_{BH}^{+} 42.7 in acetonitrile) (Figure 1.6) [16–18]. Hence, the basicity of the catalyst can be tuned according to the requirements of the corresponding polymerization reaction. Catalysts with medium-to-strong basicity, e.g. DBU, TBD, and phosphazenes, are most commonly used.

Regarding the reaction mechanism, the chain end activation mechanism is typically considered in the ROP of cyclic esters with alcohols as initiators

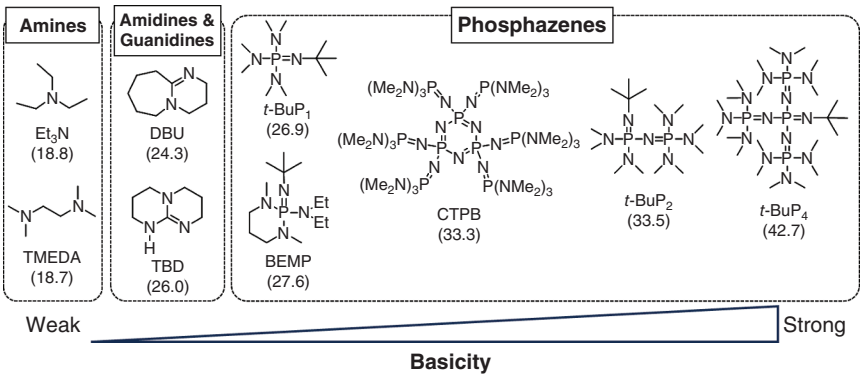

Figure 1.6 Representative Brønsted base catalysts and their basicity (pK_a of the conjugated acid in MeCN).

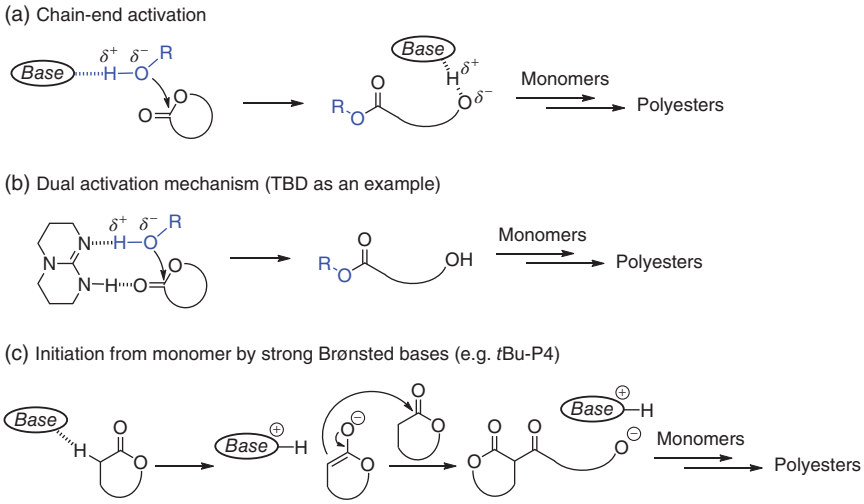

Figure 1.7 General reaction mechanism of the ROP of cyclic esters using Brønsted base catalysts.

(Figure 1.7a) [19]. Through hydrogen bonding, the base activates the –OH group of the alcohol initiators or the propagating chain ends to enhance their nucleophilicity and attack the carbonyl group of the cyclic esters. The higher the basicity of the catalyst, the more prone it is to complete deprotonation toward generating naked alkoxide anions; thus, its reactivity is higher.

When a bifunctional organobase, such as TBD, is used, the dual-activation mechanism via double hydrogen bonding interactions is usually considered (Figure 1.7b) [20]. The Brønsted basic site of the guanidine activates the –OH group, whereas the Brønsted acidic site (N–H) interacts with the carbonyl group of the cyclic esters. When cyclic esters are polymerized without using alcohol initiators, the polymerization could initiate from the monomer via the deprotonation of the α-proton of the

esters, thus forming nucleophilic enolate species (Figure 1.7c). In this case, highly basic catalysts, such as phosphazenes, are commonly used [2].

1.2.3 Acid Catalysts

Acid catalysts are among the most important organocatalysts for the ROP of cyclic esters. Based on their characteristics, acid catalysts can be divided into Brønsted acids and Lewis acids. In terms of the organocatalyzed ROP of cyclic esters, Brønsted acid catalysts have been widely reported. Herein, the representative mechanisms and examples are introduced. Simple strong inorganic acids, such as HOTf and HCl, can catalyze the ROP of cyclic esters; however, these reactions were typically not considered organocatalyzed polymerizations at the time of the study [21–25].

Carboxylic, phosphoric, and sulfonic acids are commonly used in the organocatalyzed ROP of cyclic esters based on Brønsted acid catalysts (Figure 1.8). On the basis of the structure and acidity of the catalyst and the polymerization conditions, the reaction mechanisms can be divided into three categories (Figure 1.9). The activated monomer (AM) mechanism is a typical polymerization mechanism for the ROP of cyclic esters (Figure 1.9a). The Brønsted acid activates the carbonyl group of the cyclic ester, rendering it more prone to a nucleophilic attack from the hydroxyl group of either the initiator or the propagating chain end. The nucleophilic attack could also occur at the sp^3 carbon next to the ester group, thus forming an ion-pair intermediate with the counteranion of the Brønsted acid catalysts (Figure 1.9b) [28, 29]. This chain end structure is highly reactive and can accept a nucleophilic attack from another molecule of the cyclic ester monomer. This polymerization mechanism is usually referred to as the activated chain end (ACE). The activated chain ends are usually terminated by quenching the polymerization using alcohols or other nucleophiles. The AM and ACE polymerization mechanisms were proposed a long time ago; however, the dual-activation mechanism of the ROP of cyclic esters by

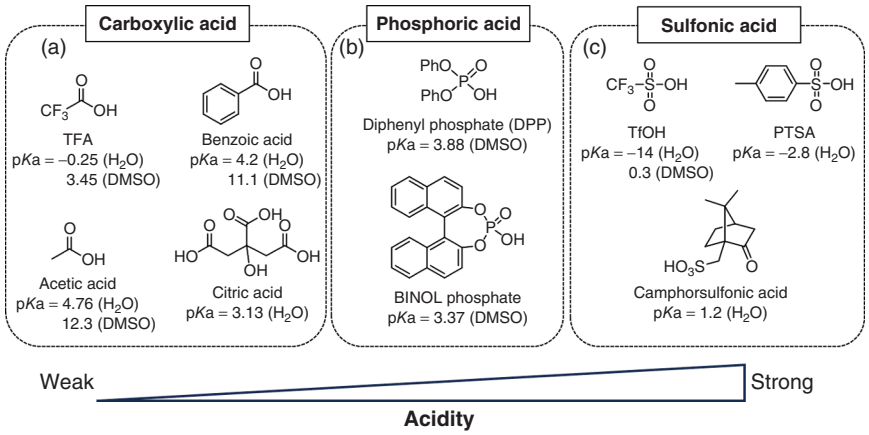

Figure 1.8 Representative Brønsted acid catalysts and their acidities. Source: Bordwell [26] and Christ [27].

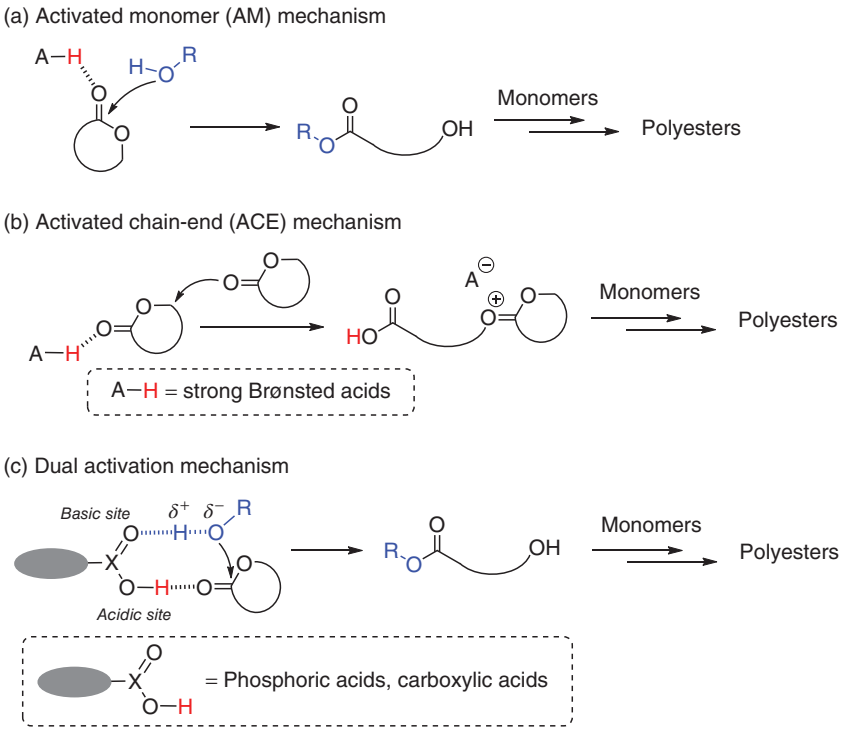

Figure 1.9 General reaction mechanism of the ROP of cyclic esters using Brønsted acid catalysts.

acid catalysts was not recognized until the recent decades (Figure 1.9c) [30, 31]. In the dual-activation mechanism, the Brønsted acidic site of the catalyst activates the carbonyl group of the cyclic ester monomer and renders it more electrophilic; meanwhile, the Brønsted basic site of the catalyst activates the alcohol initiator or chain end, rendering it more nucleophilic. This dual-activation mechanism ensures proximity of the monomer and propagating chain end, thus allowing for smooth progress of the polymerization. Considering the structural features and acidities of the catalysts, the catalysis by sulfonic acids is more likely to proceed via the AM or ACE mechanism because of their high acidities. In the case of carboxylic and phosphoric acids, the polymerization usually proceeds via the dual-activation mechanism because of the weak-to-medium acidities of these two types of catalysts.

1.2.4 Ionic Catalysts

During the initial research on organocatalyzed polymerization, catalysts without charges were used in most studies. In the past decade, salt or ionic organocatalysts have been developed for the ROP of cyclic esters [32]. They exhibit better catalytic activities and thermal stabilities than conventional organocatalysts. These aspects are introduced in Sections 1.3.1 and 1.3.3.

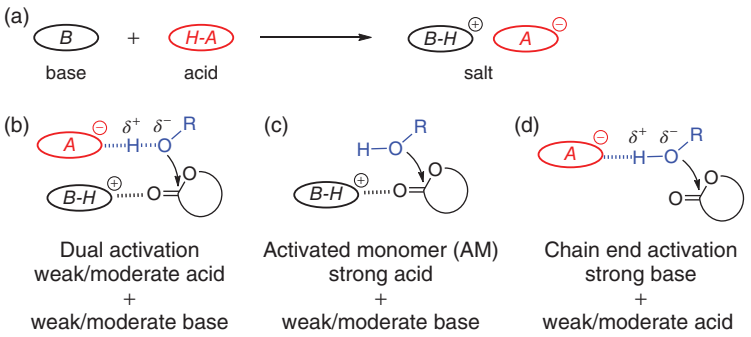

Figure 1.10 Salt catalysts and general reaction mechanism of the ROP of cyclic esters for different types of salt catalysts.

When a Brønsted acid and base are mixed in a ratio of 1 : 1, a salt is formed (Figure 1.10a). However, the produced salt exhibits a different acidity or basicity, depending on the relative strengths of the acidic and basic parts, which in turn determines the reaction mechanism governing the ROP of cyclic esters. A dual-activation mechanism has been typically proposed – The anion activates the alcohol initiator or propagating chain end, whereas the cation activates the cyclic ester monomer (Figure 1.10b). This mechanism is usually observed for a mixture of a weak/moderate acid and weak/moderate base, such as 1 : 1 mixtures of DBU and benzoic acid, DMAP and diphenyl phosphate (DPP), and DMAP and saccharin (Figure 1.11a–c) [33–35]. The conjugated bases and acids of strong acids and bases are weak, respectively; hence, they exhibit weak or negligible interactions with the monomer or propagating chain end. Therefore, the AM mechanism is typically proposed when a salt catalyst constituted by a strong acid and a weak/moderate base is used, e.g. a 1 : 2 mixture of bipyridine and camphorsulfonic acid (Figures 1.10c and 1.11d) [36]. In theory, the chain end activation mechanism can also be considered for combinations of strong bases and weak/moderate acids (Figure 1.10d). However, to the best of our knowledge, this activation has not been reported

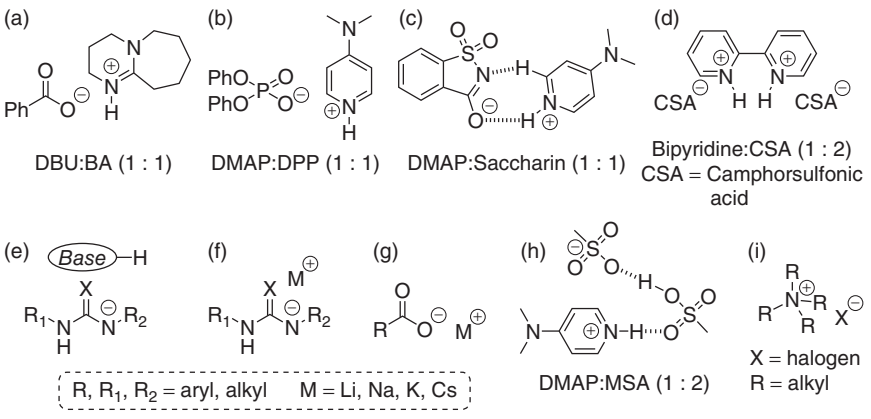

Figure 1.11 Examples of salt and ionic catalysts.

[32]. Ureas, thioureas, and carboxylic acids have relatively weak acidities. Their alkali-metal salts and salts with strong organic bases, such as phosphazenes, have been reported as effective catalysts for the ROP of cyclic esters (Figure 1.11e–g) [37–39]. The dual-activation mechanism has been proposed in these cases because of the bifunctional nature of the anions thereof.

In addition to the salts formed using a 1 : 1 ratio mixture of an acid and a base, mixtures with an unequal ratio, i.e. an excess amount of either an acid or a base, have been used for fine-tuning the reactivity and catalytic performance. For example, the ionic catalyst DMAP: methanesulfonic acid (MSA) (1 : 2) has been used for catalyzing the ROP of L-lactide (LLA) in bulk at an acceptable reaction rate without epimerization (Figure 1.11h) [40]. Tetraalkylammonium halides, which are representative of onium salts, can also function as effective catalysts for the ROP of cyclic esters (Figure 1.11i) [41, 42].

Zwitterions are also referred to as inner salts, in which the cations and the anions are covalently linked together in the same molecule. To the best of our knowledge, zwitterionic organocatalysts have not been used for the ROP of cyclic esters thus far. However, for the ROP of trimethylene carbonate (TMC), trimethyl glycine, which is a natural betaine sourced from sugar beets, has been demonstrated to be an effective and environmentally benign organocatalyst [43].

1.2.5 Bifunctional and Multifunctional Catalysts

Bifunctional and multifunctional organocatalysts are molecules in which two or more catalytically active moieties are linked covalently. Dual-activation is the commonly accepted reaction mechanism by which the ROP of cyclic esters is promoted efficiently. Although the dual-activation model can be realized using monofunctionalized catalysts such as DPP and TBD, the use of bifunctional and multifunctional catalysts could be beneficial for fine-tuning the interactions with both the propagating chain ends and cyclic ester monomers. Thus, both the active propagating chain end and the activated cyclic ester monomer can adopt suitable conformations in the transition state, thereby decreasing the activation energy. Bifunctional and multifunctional catalysts are viewed as the mimicry of enzymes, which catalyze reactions using multiple amino acid residues cooperatively.

Regarding the catalyst design, Takemoto's catalyst, which comprises a thiourea moiety and trialkyl amine group, is one of the most representative bifunctional organocatalysts (Figure 1.12a) [44]. It has been successfully used in the ROP of LA [45]. Because Takemoto's catalyst is chiral, it has also been employed for the stereoselective polymerization of racemic lactides (*rac*-LA) [46].

In the case of Takemoto's catalyst, the weakly acidic thiourea functions as a hydrogen-bond donor that interacts with the carbonyl group of the cyclic esters, thus activating the electrophile; the basic amine group partially deprotonates the –OH group at the propagating chain end or initiators, thus activating the nucleophile (Figure 1.12b). Owing to its efficiency, Takemoto's catalyst has been used as a prototype for developing bifunctional and multifunctional catalysts. Various bifunctional catalysts have been developed by varying the components of either the hydrogen-bond donor or the Brønsted base. For example, upon changing the

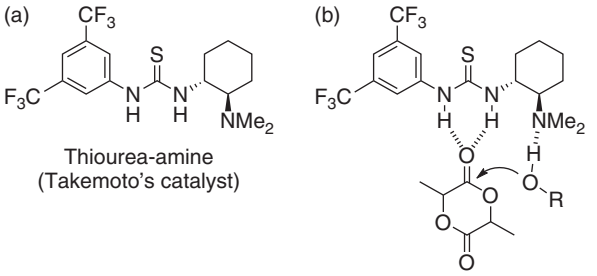

Figure 1.12 (a) Takemoto's catalyst; (b) dual-activation mechanism in the ROP of LA.

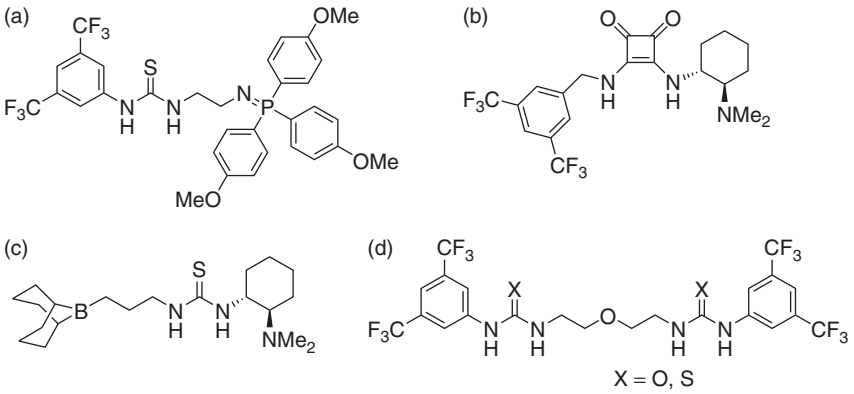

Figure 1.13 Some bifunctional and multifunctional catalysts.

amine moiety in the thiourea–amine catalyst to a more basic iminophosphorane moiety, its catalytic activities in the ROP of LA, VL, and CL are enhanced, while maintaining good control over the dispersity (*Đ*) (Figure 1.13a) [47]. The change in the hydrogen-bond donor moiety from thiourea to squaramide also affords an effective bifunctional catalyst for the ROP of LA (Figure 1.13b) [48]. The borane–thiourea–amine trifunctional organocatalyst can catalyze the synthesis of block copolymers, with PLA as one block, from a monomer mixture in a one-pot, one-step manner (Figure 1.13c), as per a recent report [49]. Mimicry of enzymes by introducing multiple functional groups into a single catalyst molecule could be a promising strategy. However, this approach significantly increases the synthetic complexity of the catalysts and the number of possible structures to be explored to obtain an optimized catalyst candidate. Furthermore, a novel catalyst design concept of using more than one hydrogen-bond donor unit, such as urea or thiourea, has been reported for the ROP of cyclic esters (Figure 1.13d) [50, 51].

1.3 Recent Trends in Organocatalyst Development

Regarding the recent trends in organocatalyst development for the ROP of cyclic esters, the following four aspects are considered to be significant: enhancements in

the catalytic efficiency, selectivity, heat tolerance, and safety. These four aspects are introduced in this section.

1.3.1 Higher Catalytic Efficiency

When the ROP of cyclic esters approaches a high percentage of monomer conversion, transesterification can easily occur, leading to a broad dispersity. Before the period of extensive research on organocatalyzed polymerization, strong inorganic bases were used for catalyzing or initiating the ROP of cyclic esters via anionic polymerization. For instance, when the ROP of lactide is initiated by lithium diisopropylamide (LDA) at room temperature in a dioxane solvent, the monomer conversion can reach over 95% within a few minutes, affording PLA with a broad dispersity ($Đ = 1.9$) [52]. In the organocatalyzed ROP of cyclic esters, high selectivity has been considered as a common research objective instead of high reactivity, for a relatively long time.

In recent years, organocatalysts have been successfully developed to achieve fast, selective, and well-controlled ROP of cyclic esters. (Thio)urea anions are good examples. The (thio)urea anions with alkaline-metal cations, such as Na^+ or K^+, were first reported to catalyze the ROP of various cyclic esters in a fast and controlled manner [37, 53]. By fine-tuning the molecular structure of (thio)ureas and the countercation, the ROP of LA, δ-VL, ε-CL, etc., could be completed within seconds, with the monomer conversion reaching >90% and narrow dispersity ($Đ < 1.1$). The reaction proceeds via the dual-activation mechanism, with the (thio)urea anion (N^-) activating the propagating chain end (–OH), whereas the N–H moiety of the (thio)urea anion interacts with the carbonyl group of the cyclic esters (Figure 1.14a). In addition to alkaline-metal bases, various strong organobases, including DBU, MTBD, cyclopropenimine [54], and phosphazene bases, have been investigated in conjunction with (thio)urea for the ROP of cyclic esters (Figure 1.14b). Consequently, when the acidity of (thio)ureas and the basicity of bases attain equilibrium – pK_a of (thio)urea $\approx$ pK_a of base-H^+ – the best catalytic activity is achieved [55]. Regarding the reaction mechanism, the ROP is proposed to proceed via an anionic mechanism when pK_a of (thio)urea < pK_a of base-H^+ (Figure 1.15a). When pK_a of (thio)urea > pK_a of base-H^+, a cooperative mechanism is proposed (Figure 1.15b).

After these pioneering works, investigations have been expanded by further tuning the catalyst structures, synthesizing statistical and block copolymers, and using them in flow chemistry. For instance, the urea salt with the tetra-*n*-butyl ammonium cation is an effective catalyst for the rapid, selective, and versatile ROP of lactides [56]. Further expansion of the investigation scope of the phosphazene bases in forming urea salts enabled the efficient synthesis of poly(γ-butyrolactone) [57], random poly(lactic-*co*-glycolic acid) [58], and poly(lactic acid)-*b*-poly(alkyl-δ-lactone)-*b*-poly(lactic acid) triblock copolymer as thermoplastic elastomers [38] and pressure-sensitive adhesives [59]. Aside from (thio)urates, the 2,2′-bisindole anion can function as an excellent catalyst to promote the rapid ROP of cyclic esters (Figure 1.15c) [60].

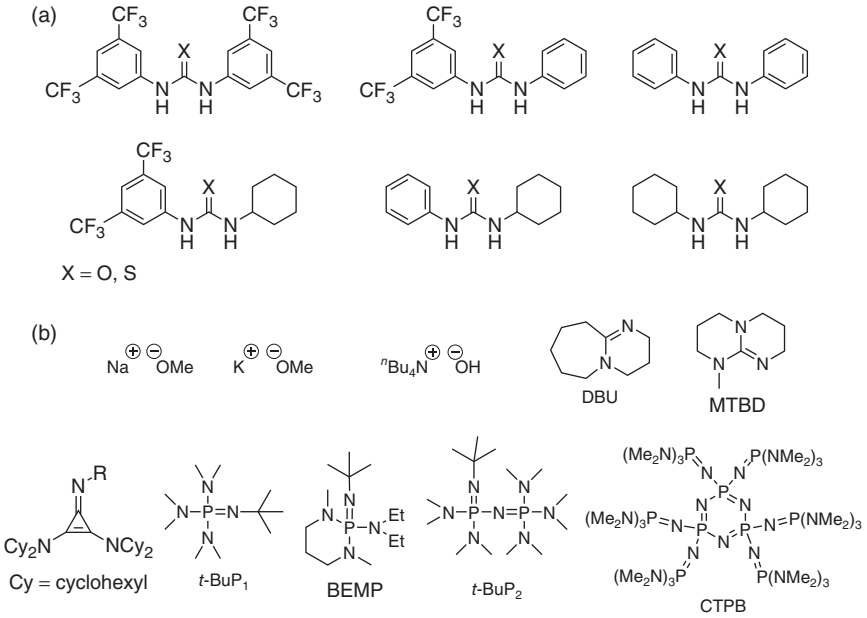

Figure 1.14 Representative structures of (a) ureas, thioureas and (b) bases.

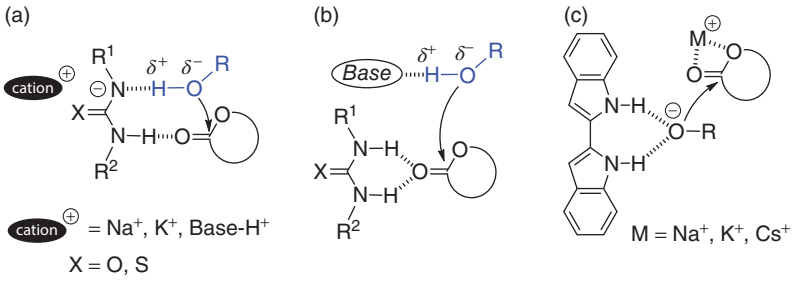

Figure 1.15 (a) Anionic mechanism; (b) cooperative mechanism; (c) reaction mechanism using the 2,2′-bisindole anion.

The progress in rapid and controlled ROP for cyclic esters has opened up new avenues for developing high-throughput synthetic platforms of polymer libraries using flow chemistry techniques [61]. Moreover, by employing continuous-flow reactors, ultrafast ROP of cyclic esters can be achieved using conventional strong inorganic base catalysts, such as KO*t*Bu, affording the polyester products in a well-controlled manner, which cannot be achieved under batch polymerization conditions [62].

1.3.2 Higher Selectivity

High selectivity has been a common, important research goal in the development of novel catalytic reactions and polymerizations. In the ROP of cyclic esters, selectivity

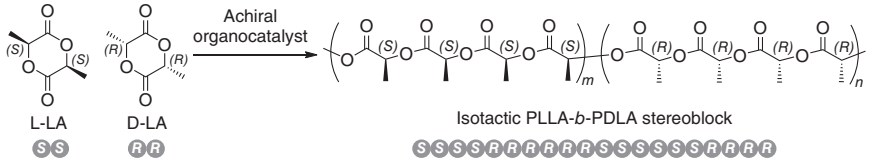

Figure 1.16 ROP of *rac*-LA using achiral organocatalysts.

can include various aspects. This section focuses on enantiomer-selective polymerization and briefly introduces some examples of other aspects.

Among all reports on enantiomer-selective ROP of cyclic esters, the ROP of racemic lactide (*rac*-LA) and racemic β-butyrolactone (*rac*-β-BL) have been chosen as two representative examples [63–66]. Chiral metal-complex catalysts have been extensively investigated for these two ROPs, and highly selective catalysts have been developed. In the past decade, reports on organocatalysts, especially chiral ones, have emerged.

In the early stages, the ROP of *rac*-LA by achiral organocatalysts was mainly reported, wherein isotactic PLA or isotactic-rich PLA was obtained. The selectivity relies on the chirality of the chain end structure that is combined with the achiral catalyst. The L-LA and D-LA molecules were consumed at the same rate, and the obtained isotactic-rich PLA was typically a multiblock copolymer consisting of PLLA and PDLA stereoblocks (Figure 1.16). Therefore, the formation of stereocomplexes was observed in some cases. *N*HCs and phosphazenes are representative achiral organocatalysts used for this polymerization [67–69]. However, to achieve a high level of isotacticity, in which the meso dyads (P_m) ≥ 0.90, the polymerization was usually performed at a low temperature ($\leq -70\,^{\circ}C$).

Compared to the use of achiral organocatalysts in the synthesis of isotactic PLA, the enantiomer-selective polymerization of *rac*-LA based on chiral organocatalysts is more challenging (Figure 1.17). Cinchona alkaloids were the first organocatalysts reported for this polymerization [70]. However, their stereoselectivity factor is low ($s \leq 4.4$) (Figure 1.18a). 1,1′-Bi-2-naphthol (BINOL)-derived chiral phosphoric acids

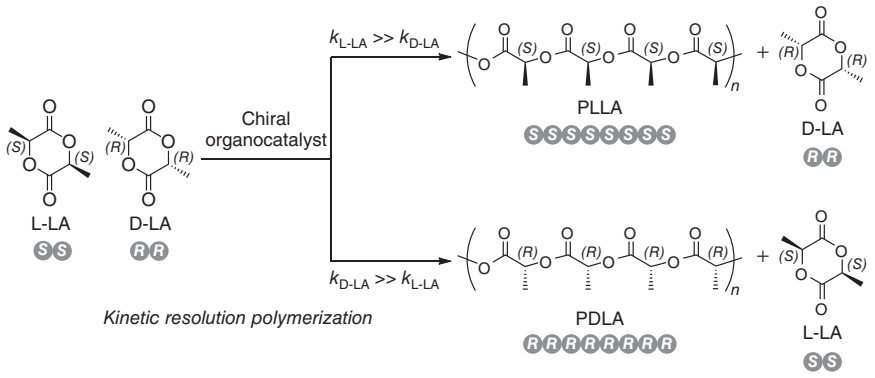

Figure 1.17 ROP of *rac*-LA using chiral organocatalysts: enantiomer-selective polymerization.

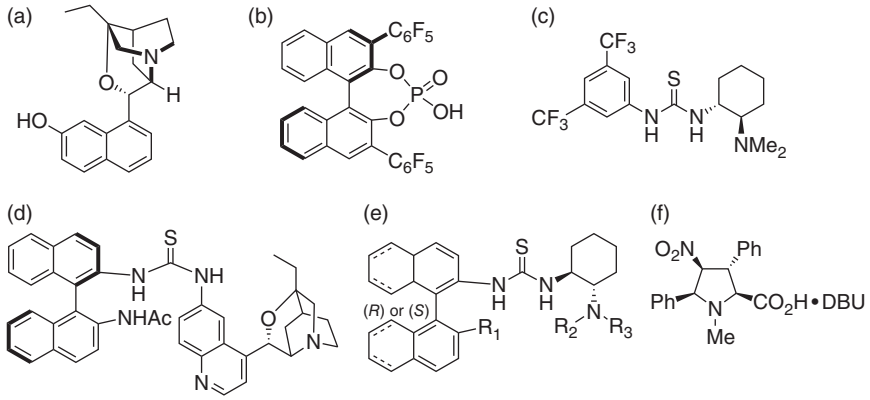

Figure 1.18 Representative chiral organocatalysts for the ROP of *rac*-LA.

are more effective in controlling the enantioselectivity of *rac*-LA. The (*R*)-catalyst polymerizes L-LA prior to D-LA, and the stereoselectivity factor is as high as 28.3 (Figure 1.18b) [71]. Takemoto's catalyst is a commonly used chiral bifunctional organocatalyst for the ROP of LA [45]. The use of enantiopure Takemoto's catalyst in catalyzing the ROP of *rac*-LA results in a relatively high isotacticity ($P_m \geq 0.80$) but low stereoselectivity ($s \leq 5.0$) (Figure 1.18c) [46]. The combination of enantiopure Takemoto's catalyst and a phosphazene base can further increase the isotacticity and reactivity [72]. Other novel chiral bifunctional organocatalysts synthesized by combining the moieties, including cinchona alkaloids, 1,1′-binaphthyl, thiourea, and *trans*-1,2-cyclohexanediamine, have also been reported for the ROP of *rac*-LA (Figure 1.18d,e) [73, 74]. Using these two catalysts shown in Figure 1.18d,e, stereoselectivity factor values of 53 and 17.5, respectively, were obtained, in addition to the high isotacticity of the PLA products. Ionic catalysts consisting of a densely substituted proline-type amino acid and DBU have also been reported to be effective for the ROP of *rac*-LA (Figure 1.18f) [75]. In the abovementioned cases, the highest stereoselectivity factor is 53. Therefore, the obtained PLA should be either L-LA-rich or D-LA-rich, instead of perfect PLLA or PDLA.

Unlike the emerging reports on the organocatalyzed ROP of *rac*-LA, there are no reports on the organocatalyzed ROP of *rac*-*β*-BL, to the best of our knowledge. It can be attributed to the intrinsic difficulties in distinguishing the enantiomers of *β*-BL. The carbonyl group activated by the catalyst is opposite to the chiral center (Figure 1.19a). Therefore, enantiomer-selective polymerization of *rac*-*β*-BL is highly challenging, even when metal-complex catalysts are used [76]. In addition, the ROP of *β*-BL can proceed via two different pathways, which further increases the difficulty in controlling the stereoselectivity in the ROP of *rac*-*β*-BL. A nucleophilic attack on the lactone carbonyl carbon results in stereoretention (Figure 1.19b), whereas that on the methine carbon next to the ester group results in stereoinversion (Figure 1.19c).

Chen *et al*. developed a novel method to circumvent the difficulties in realizing enantiomer-selective ROP of *rac*-*β*-BL using an eight-membered cyclic diolide

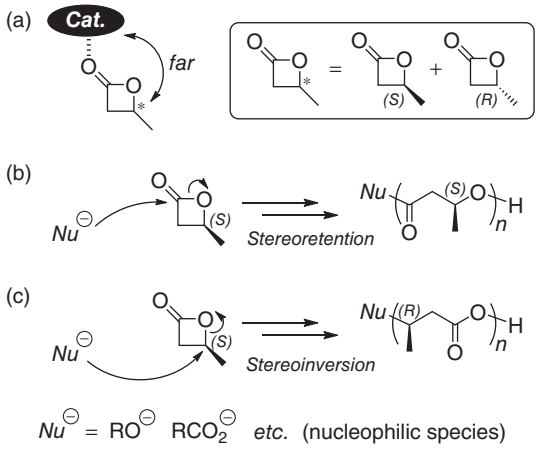

Figure 1.19 (a) Intrinsic difficulty in performing enantiomer-selective ROP of *rac*-β-BL; ROP of β-BL by nucleophilic attack on (b) carbonyl and (c) methine carbons.

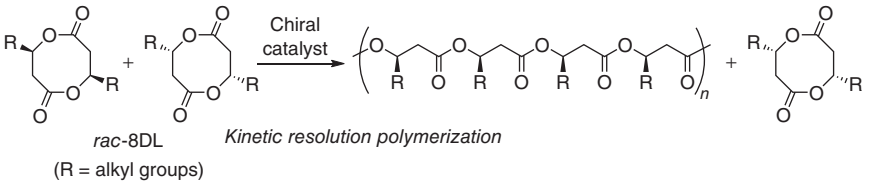

Figure 1.20 Enantiomer-selective polymerization of *rac*-8DL.

(8DL) [77–79]. Although several steps are required for monomer synthesis, near-perfect stereoselectivity in the ROP of *rac*-8DL can be achieved using sterically hindered rare-earth-metal salen complexes as catalysts. Organocatalysts such as BINOL-derived chiral phosphoric acids have also been tested for this polymerization [80]; however, the stereoselectivity factor is low, and stereogradient P(β-BL) is obtained (Figure 1.20).

In addition to enantiomer-selective polymerization, the selectivity includes other aspects such as regioselectivity and chemoselectivity. The highly regioselective ROP of methylglycolide (MG) yields an alternating copolymer of lactic acid and glycolic acid (PLGA), which is a promising biodegradable, biocompatible, and bioresorbable material for medical applications. This polymerization was achieved via a prudent selection of organobase catalysts; the phosphazene base *t*-BuP_2 provided a high regioselectivity. The deprotonated propagating chain ends nucleophilic attack at the lactyl carbonyl group of MG selectively (Figure 1.21) [81].

Regarding the chemoselectivity of the ROP of cyclic esters, copolymerization of different cyclic esters, especially LA and ε-CL, is of significance. Because both PLA and PCL are biodegradable polymers with complementary mechanical properties, their copolymers have been studied extensively. However, because of their drastically different polymerizabilities, statistical copolymers have conventionally been synthesized using metal-complex catalysts [82]. Recently, simple benzoic acid has been reported to catalyze this copolymerization under bulk polymerization conditions at high temperatures [83, 84] (Figure 1.22).

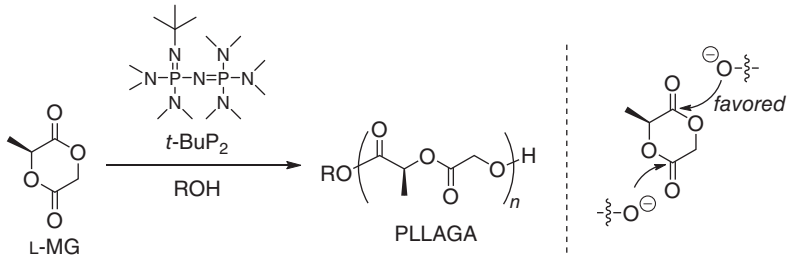

Figure 1.21 Regioselective ROP of MG by the *t*-BuP_2 catalyst.

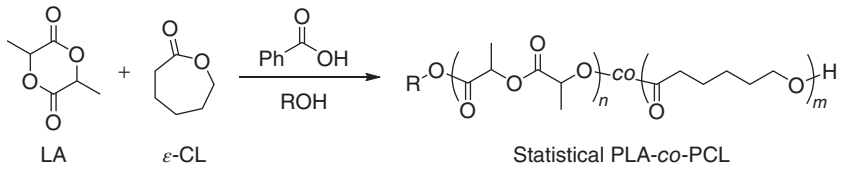

Figure 1.22 Statistical ROP of LA and ε-CL using a benzoic acid catalyst.

Integration of the ROP of cyclic esters with other types of polymerization, especially the ring-opening copolymerization (ROCOP) of cyclic anhydrides/epoxides and CO_2/epoxides, has attracted much research interest in recent years toward synthesizing degradable block-like copolymers in a one-pot, one-step manner. This type of transformation is referred to as self-switchable polymerization [85–87]. From a mechanistic perspective, self-switchable polymerization is based on catalysts that can catalyze both types of polymerization, namely ROP and ROCOP, and harnesses the intrinsic reactivity differences between the monomers in both catalytic cycles. Self-switchable polymerization was first reported to be catalyzed by metal-complex catalysts; then, organocatalysts were discovered to be effective. Considering the terpolymerization of cyclic anhydrides, epoxides, and cyclic esters as an example, the ROCOP of cyclic anhydrides/epoxides usually occurs prior to the ROP of cyclic esters, affording polyester-based block-like copolymers (Figure 1.23a). Considering the reaction mechanism, the selectivity between the ROCOP and ROP is rooted in the different reactivities of the nucleophilic attack from the hydroxy and carboxylic acid chain ends on the three monomers (Figure 1.23b). The reaction between the hydroxy group and cyclic anhydride is the most favored pathway (k_1), followed by the ring opening of the cyclic ester (k_2) and then epoxide (k_3). The carboxylic acid group preferentially reacts with the epoxide. Therefore, polyester-based block-like copolymers can be obtained by the terpolymerization of a mixture of these three monomers by following the reaction sequence shown in Figure 1.23a. Regarding the use of organocatalysts for this transformation, alkali-metal carboxylates (AMCs) [88], strong organobase catalysts [89, 90], and acid–base catalyst pairs containing triethylborane (TEB) [91] or (thio)ureas [92, 93] are representative examples (Figure 1.23c).

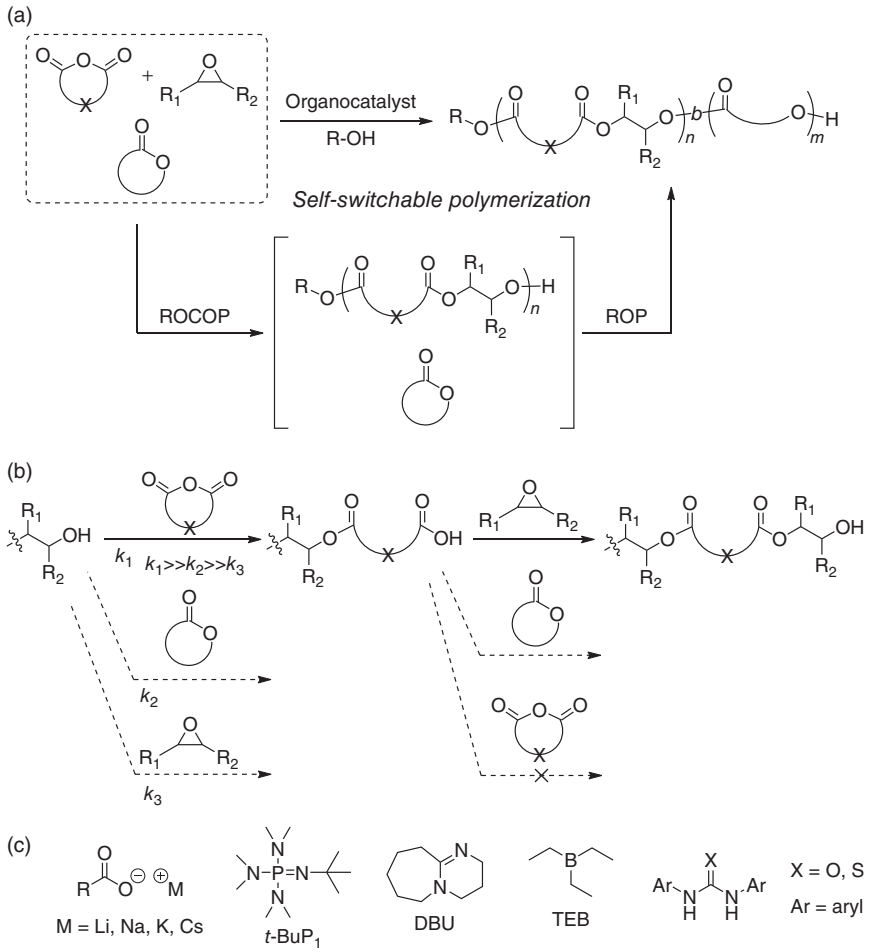

Figure 1.23 (a) Self-switchable polymerization of cyclic anhydrides, epoxides, and cyclic esters; (b) mechanistic consideration of the selectivity; (c) representative organocatalysts.

1.3.3 Higher-Temperature Tolerance

Poor thermal stability is a common feature of most organic compounds. Organocatalyst degradation usually occurs during high-temperature polymerization. Considering the ROP of LA as an example, although numerous environmentally benign organocatalytic systems have been developed, the industrial production of PLA still employs organometallic catalysts such as $Sn(Oct)_2$.

Controlling the ROP of LA using bulk organocatalysts is recognized as a significant challenge because the transesterification and racemization of PLA can easily occur at high reaction temperatures [94]. The melting point of optically pure PLA is approximately 180 °C. Hence, the industrial processing conditions for PLA are set to even higher temperatures [95]. The bulk polymerization of LA can be conducted

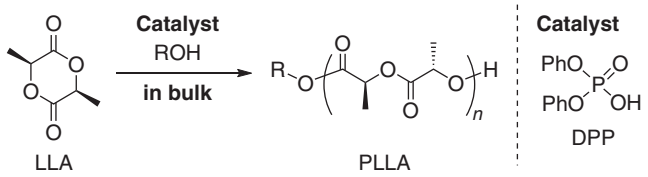

Figure 1.24 ROP of LLA in bulk catalyzed by DPP.

at a temperature above the melting point of LA (95–97 °C). Therefore, the initial organocatalyzed bulk polymerization of LA was commenced from ~100 °C.

Lactide can be catalyzed efficiently using organobase catalysts, including Brønsted bases and Lewis bases (nucleophilic catalysts). However, the bulk polymerization of LA using base catalysts is hindered by base-catalyzed racemization, polymer degradation, and the relatively low thermal stability of the catalysts [94]. Some of these drawbacks can be overcome using organoacid catalysts, although their catalytic activity in the ROP of LA is much lower than that of base catalysts. For example, DPP is an efficient catalyst for the ROP of CL, VL, and TMC in solution, but not for the ROP of LA [30, 96]. When the bulk reaction is performed at 130 °C, well-controlled PLA is obtained without racemization; however, the polymerization warrants a relatively higher catalyst loading than the ROP of other cyclic ester monomers (Figure 1.24) [97].

Acid–base binary catalysts have been extensively studied for the bulk polymerization of LA. Salts usually exhibit higher thermal stabilities than acids or bases alone. For instance, the mixing of TBD and MSA in a ratio of 1 : 1 produces a TBD:MSA (1 : 1) salt, which is calculated to be 37.4 kcal mol^{-1} more stable than free TBD and MSA (Figure 1.25) [98]. Even when the acid–base mixture cannot form crystalline salts because of ionic and hydrogen-bonding interactions, these mixtures still demonstrate an improved thermal stability [99].

A stoichiometric mixture of biogenic creatinine and carboxylic acids, including glycolic acid and acetic acid, was the first reported acid–base mixed organocatalyst for the ROP of LA in bulk (Figure 1.26a) [100]. Acid–base mixtures comprising imidazole and DMAP as the base components and various acid counterparts are also effective catalysts for this polymerization (Figure 1.26b–e) [35, 40, 101, 102]. In addition to 1 : 1 acid–base mixtures, nonstoichiometric mixtures can fine-tune the acidity/basicity, catalytic reactivity, and thermal stability. They have been described as deep eutectic solvents (DES) [103, 104]. Recently, they have been referred to as noneutectic mixture organocatalysts (NEMO), in the context of catalytic reactions [105, 106].

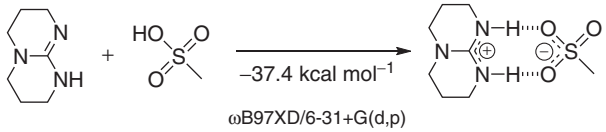

Figure 1.25 Density functional theory calculations of TBD, MSA, and the TBD:MSA (1 : 1) complex.

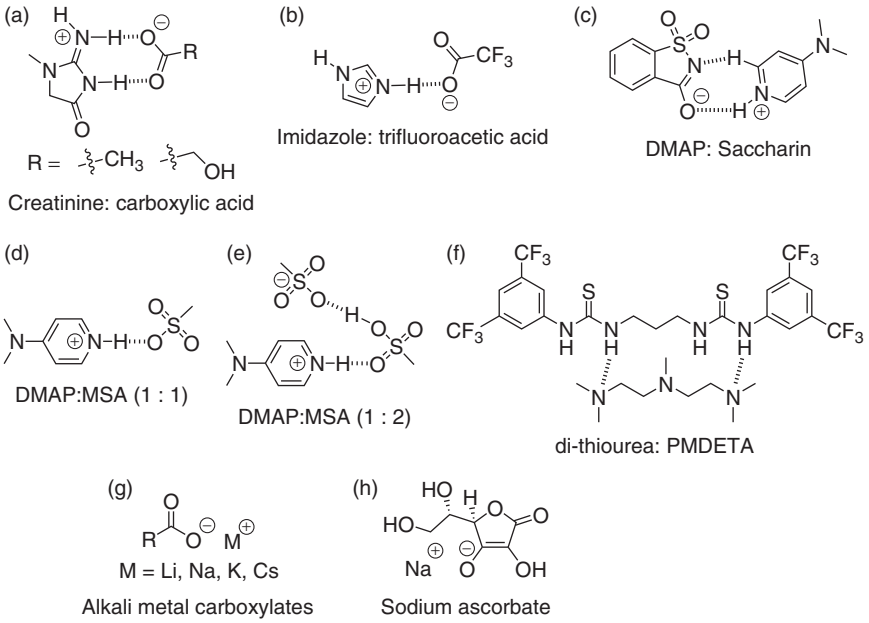

Figure 1.26 Representative acid–base mixed or salt organocatalysts for the ROP of LA in bulk.

Replacement of the acid component with a hydrogen-bonding donor, such as urea or thiourea, also affords tolerance to elevated temperatures, when suitable hydrogen-bonding donors and bases are selected, thus catalyzing the ROP of LA and other cyclic esters in bulk (Figure 1.26f) [107]. The food sweetener saccharin can form an ionic binary organocatalyst with DMAP toward the ROP of LA in bulk (Figure 1.26c) [35]. In addition to the mixtures of organic acids and organic bases, inorganic alkali-metal salts (e.g. AMCs and sodium ascorbate) have been reported for the ROP of LA (Figure 1.26g,h) [39, 108]. These reports indicate the potential of safe food additives as catalysts for polymer synthesis. This discussion is detailed in Section 1.3.4.

Ionic liquids, which typically tolerate high temperatures, can also facilitate the ROP of cyclic esters. However, because they are employed in an excess amount as a solvent or they exhibited low catalytic activity when utilized in the catalytic amounts [109, 110], they are not discussed herein.

1.3.4 Safety Considerations

In numerous works on organocatalyzed polymerization, keywords such as "organic," "metal-free," "heavy-metal-free," or "transition-metal-free" are commonly mentioned to emphasize the nontoxic, safe, and environmentally benign nature of organocatalysts. However, organocatalysts need not mean safe catalysts. For instance, DMAP, the first organocatalyst reported by Hedrick *et al.* is categorized as "Danger" in its safety data sheet [5]. It is highly toxic when ingested or absorbed by

the skin. Phosphazene bases have been reported as effective catalysts for the ROP of cyclic esters. However, the phosphazene-based residue is suspected to be cytotoxic [111]. In contrast, the commonly used organometallic catalyst in industry, $Sn(Oct)_2$, has been approved by the United States Food and Drug Administration (FDA), if the $Sn(Oct)_2$ content does not exceed 1 wt% of the polymer product when applied in coatings that can come into contact with food. However, the regulation for the content of stannous compounds in food is much stricter. The concentration of tin should be lower than 15 ppm, in the case of stannous chloride. The strict regulation of tin also applies to polymers for biomedical applications such as drug delivery carriers, bioresorbable sutures, and implants. To reach this high standard, Evonik Industries AG launched the RESOMER® Zero series of bioresorbable polymer materials, in which the tin concentration was controlled to be less than 1 ppm by the clean removal of tin catalyst residue from the obtained polymers. Therefore, the development of truly safe organocatalysts that meet industrial requirements is significant, especially for polymers related to food and biomedical applications, as it could eliminate the high-cost tin catalyst removal process.

Poly(lactic acid) and poly(ε-caprolactone) are two of the most important biodegradable, biocompatible, and bioresorbable polymers. Here, the ROP of LA and ε-CL are considered as examples to introduce and discuss recent developments in safe organocatalysts for the ROP of cyclic esters. In the early investigation stages of organocatalysts for polymerization, numerous carboxylic acids and amino acids were examined as catalysts for the ROP of ε-CL and δ-VL (Figure 1.27). Many of the tested acids were safe and edible, although their catalytic performances necessitated improvements [112]. For instance, tartaric acid and citric acid are widely used food additives in our daily lives. Benzoic acid, another safe carboxylic acid (whose sodium salt is commonly used as a food preservative) has recently been demonstrated to catalyze the copolymerization of LA and CL in bulk to yield the statistical P(LA-*co*-CL) copolymer, which is a commercially available bioresorbable polymer [83, 84]. In addition to safe carboxylic acids, their alkali-metal salts, such as sodium and potassium salts, are often used as food additives. For example, potassium sorbate and sodium acetate are often used as additives for food preservation and

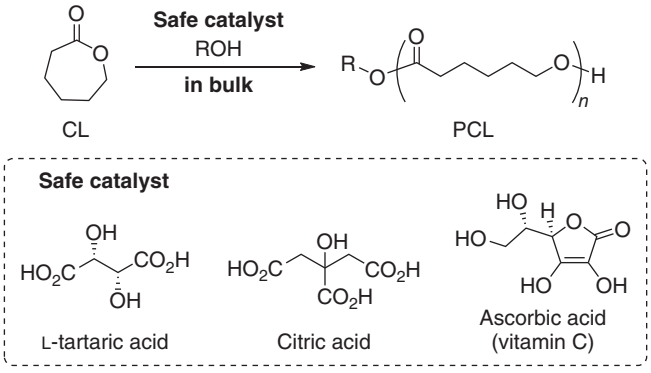

Figure 1.27 ROP of CL and representative truly safe catalysts.

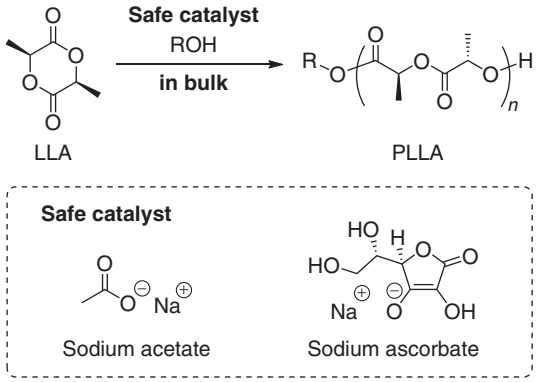

Figure 1.28 ROP of LA and representative truly safe catalysts.

flavor tuning [113]. Satoh *et al*. reported that AMCs, including the abovementioned food additives, can function as simple, effective catalysts for the ROP of cyclic esters under industrially relevant conditions (Figure 1.28) [39, 114]. In addition to the ROP of cyclic esters, the ROP of cyclic carbonates and epoxides and the ROCOP of cyclic anhydrides and epoxides can be catalyzed by AMCs [88, 115–121]. Alteration of alkali-metal cations with organic onium cations can provide new opportunities. Trimethyl glycine, a natural betaine derived from sugar beets, effectively catalyzes the ROP of TMC [43]. In addition to carboxylates, other safe alkali-metal salts have been investigated. Alkali-metal carbonates such as sodium carbonate can catalyze the ROCOP of cyclic anhydrides and epoxides [122]. Ascorbic acid and sodium ascorbate (vitamin C and its sodium salt, respectively) were discovered to be effective catalysts for the ROP of CL and LA (Figures 1.27 and 1.28) [108]. The copolymerization of CL and LA was also facilitated by sodium ascorbate. In addition to polymerization, depolymerization and chemical recycling of PLA can be conducted using sodium ascorbate.

In industrial production, the catalyst residue is commonly not removed to reduce production costs. Therefore, catalyst safety is an important factor when considering their applications. Numerous excellent catalyst designs have been reported after the investigation of organocatalysts for polymer synthesis. However, simple and safe compounds such as sodium acetate and sodium ascorbate have long been overlooked. The aforementioned studies demonstrate the potential of safe and unassuming substances in our daily lives.

1.4 Toward Higher Degradability and Recyclability

The 3R initiative (reduce, reuse, and recycle) aims to build a sound material-cycle society for sustainable development. Global plastic waste is a pressing issue that needs to be addressed. Redesigning current polymer materials toward improved degradability and recyclability is considered an important approach for polymer researchers. Regarding the polyesters synthesized via ROP, significant advancements have been achieved through the development of novel polyesters with higher

degradability and recyclability. In this section, recent advancements are introduced, particularly examples involving organocatalysts.

1.4.1 Incorporation of Chemically Labile Moieties into Polymer Chains for Higher Degradability

Generally, ester bonds undergo hydrolysis. At elevated temperatures, ester hydrolysis reactions can easily occur under strongly acidic and basic conditions in the laboratory. However, under natural environmental conditions, the reaction rate of ester hydrolysis is much lower. In addition, unlike fundamental organic chemistry studies using small molecules, the functional groups on polymers often exhibit different reaction properties because of their high molecular weights. The crystallization or aggregation status of polymers can significantly influence the reaction rate of their functional groups. Regarding the degradation of polyesters via hydrolysis, the hydrolysis of the ester group is typically favored from the chain ends assisted by the free hydroxyl or carboxylic acid groups via backbiting (Figure 1.29a) [123–125].

Incorporation of highly labile moieties into polymer chains, ideally in a random manner, is a representative strategy to facilitate degradation and has been investigated extensively in recent years (Figure 1.29b). After the degradation of the highly active units, long polyester chains are cleaved into short-chain oligomers. After degradation to oligomers, the crystallization/aggregation ability decreases, and the number of reactive chain ends increases drastically, thus facilitating hydrolysis. For example, PLA is one of the most widely used biosourced, biodegradable polymer. Although it can undergo facile biodegradation in compost, its degradation in natural environments, especially in water, can take years. This is ascribed to its semicrystalline nature and the predominant depolymerization mechanism from the chain ends [124, 125]. Introduction of labile moieties randomly into the polymer chain of PLA without altering its material properties is highly desirable. The introduction of highly acid-labile hemiacetal ester functional groups is a widely studied strategy. 1,3-Dioxolan-4-one (DOX), which is synthesized from glycolic acid and formaldehyde, is a representative cyclic hemiacetal ester. The copolymerization of DOX and LLA yields the copolymer P(LLA-*co*-DOX) (Figure 1.30a) [126]. This copolymer has

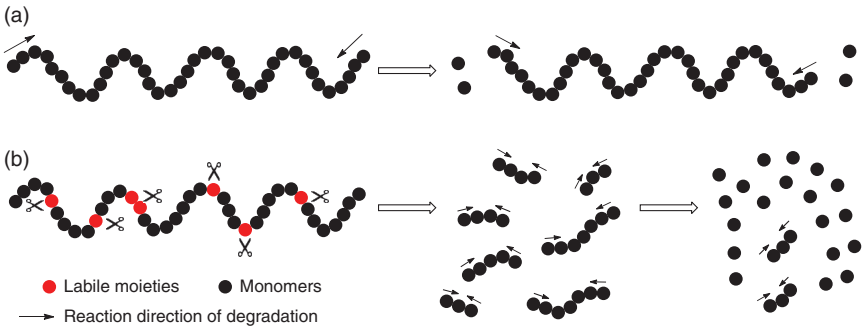

Figure 1.29 Degradation of polymers (a) from the chain ends; (b) from the labile moieties.

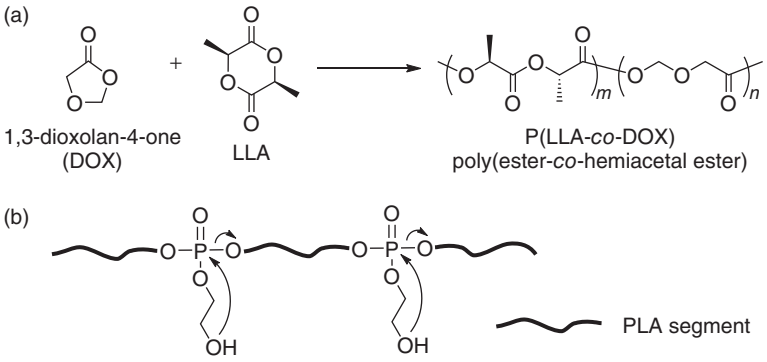

Figure 1.30 (a) Copolymerization of hemiacetal ester DOX with LLA; (b) incorporation of phosphate moiety into PLA.

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

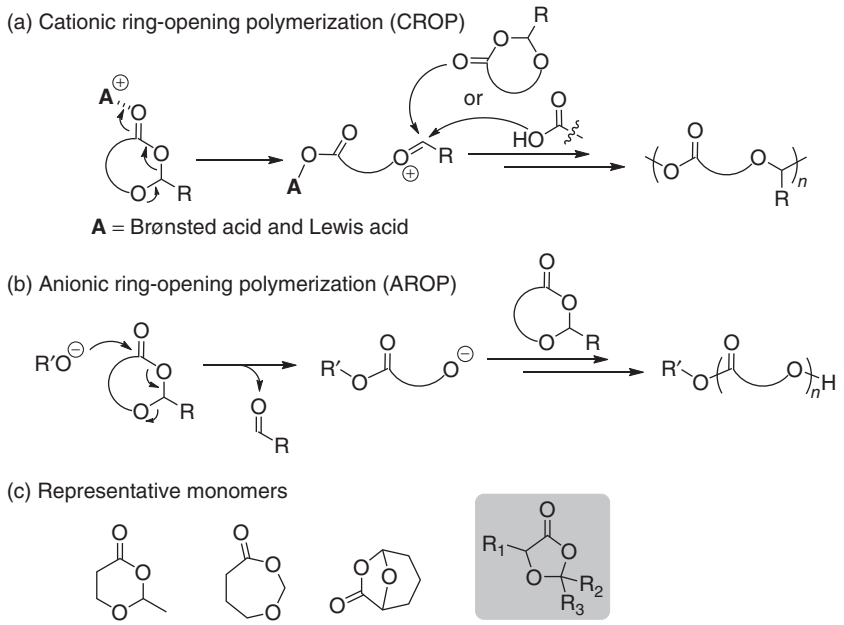

Figure 1.31 Ring-opening polymerization of cyclic hemiacetal esters via (a) cationic mechanism, (b) anionic mechanism; and (c) representative monomers (the monomer marked in gray was reported in copolymerization only).

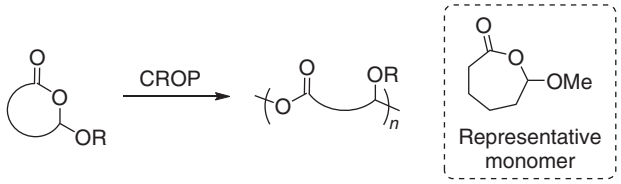

Figure 1.32 CROP of exocyclic hemiacetal esters.

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

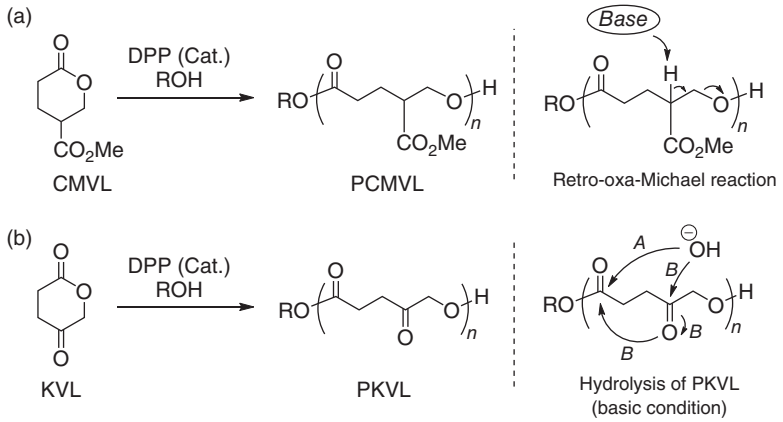

Figure 1.33 ROP of novel cyclic esters.

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

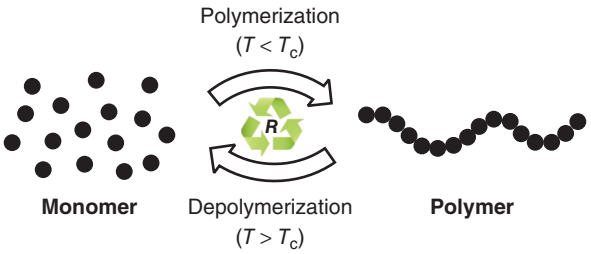

Figure 1.34 Schematic of polymerization and depolymerization.

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

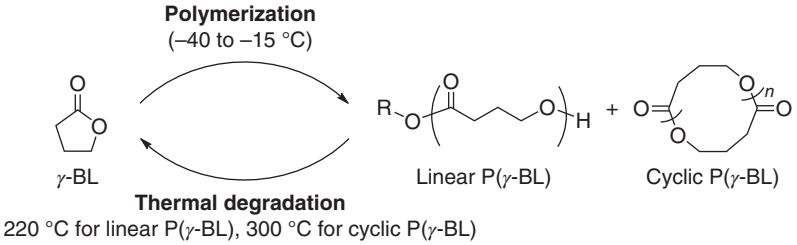

Figure 1.35 Polymerization of γ-BL and depolymerization of P(γ-BL).

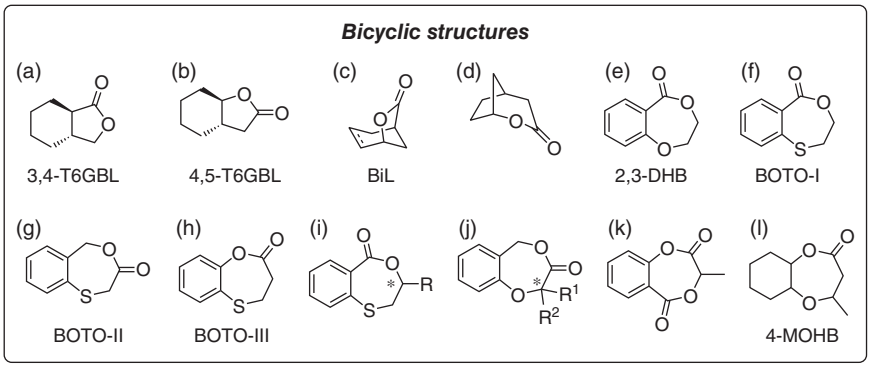

Figure 1.36 Cyclic ester monomers with bicyclic structures.

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

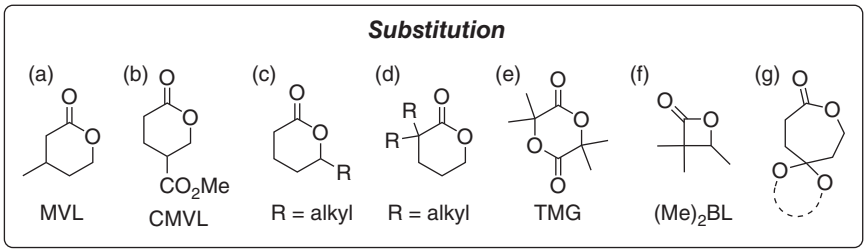

Figure 1.37 Cyclic ester monomers with various substituents.

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

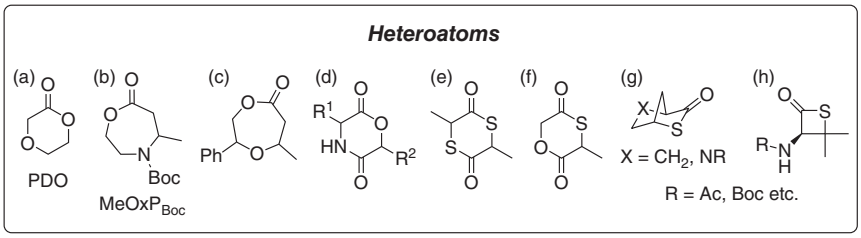

Figure 1.38 Cyclic ester monomers with heteroatoms.

(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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