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Edited by Zhibo Li

Organocatalysts in Polymer Chemistry

Synthesis and Applications

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Editor

Prof. Zhibo Li
Qingdao University of Science and Technology
Qingdao, 266042
China

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Preface

Catalysts not only play a crucial role in increasing the reaction rate, but also have a great impact on the selectivity of desirable reaction over side reactions. In particular, catalysts have been a powerful tools in polymer synthesis, including the ability to control the molecular weight, dispersity, terminal groups, the architecture, stereochemistry and topology of the macromolecule (linear, branched, cyclic, bottle-brush, cross-linking, *etc*) as well as the composition and monomer sequence of the copolymers. Organometallic catalysts consisting of a metal center and organic ligands are the most extensively investigated catalysts for polymer synthesis considering the ability to finely adjust the catalytic activity and selectivity by almost limitless combination of metals and ligands. Organocatalysts have emerged as an alternative to organometallic complexes, especially for the biomedical and electronic applications where metal residues may be detrimental to the material performance. Compared to organometallic catalysts, the advantages of organocatalysts include simple handle, low cost, better stability to oxygen and water, good solubility and easy removal from the polymers. In addition, many organocatalysts are commercially available, thus promoting their widespread applications for polymer synthesis.

Organocatalysis can be traced back to 1894 when Knoevenagel promoted the condensation reaction of formaldehyde and malonate using ethylenediamine as the catalyst [1]. Organocatalysts have been greatly developed, especially in the field of enantioselective organocatalysis. The earliest attempt that can be verified is the enantioselective synthesis of cyanohydrin with quinine alkaloids reported by Bredig and Fiske in 1911 [2]. In 2021, the Novel Prize in Chemistry was awarded to Benjamin List and David W.C. MacMillan for their pioneering contributions in the development of asymmetric organocatalysis. Compared to the organocatalysis on the synthesis of small molecules, the organocatalysis for polymer synthesis is still in its infancy. In 2001, James L. Hedrick *et al*. reported the first organocatalytic "living" ring-opening polymerization of lactide using ethanol as an initiator and 4-(dimethylamino)pyridine (DMAP) or 4-pyrrolidinopyridine (PPY) as the catalyst [3]. Since then, the field of organocatalytic polymerization has undergone a renaissance. In the past two decades, organocatalysts have been greatly developed and achieved extensive applications in various polymer synthesis, including ring-opening polymerization (ROP), ring-opening copolymerization

(ROCP), controlled radical polymerization as well as the depolymerization of commodity polymers.

Some excellent reviews have been published to summarize the recent advancements on organocatalytic polymerization, especially for the ROP of cyclic monomers [4–13]. A book with the title of "Organic Catalysis for Polymerisation" edited by Andrew Dove, Haritz Sardon and Stefan Naumann summarized the achievements of organocatalytic polymerization until 2018 [14]. Given the rapid development of this field, expecially the binary organocatalyst in polymer synthesis, organocatalyst catalyzed photo polymerization, as well as organocatalyst catalyzed depolymerization, we believe it is a suitable time to edit a book to review the state-of-the-art examples for organocatalytic polymerization.

All chapters in this book are written by the outstanding scholars in their field. This book include following topics: ROP of cyclic esters toward degradable polymers, ROCP of epoxide and anhydrides, ROCP of CO_2/COS/CS_2 with epoxides, ROP of cyclicsiloxane, ROP of *N*-carboxyanhydride (NCA) to prepare polypeptides, stereoselective ring-opening (co)polymerization and controlled ATRP and RAFT. We will also cover the applications of organocatalysts in the depolymerization of commodity polyesters such as PET and polycarbonate. Recent progresses of binary organocatalyst and organic Lewis pairs for polymer synthesis will also be discussed. This book will cover the most recent research progresses regarding the applications of organocatalysts in polymer synthesis, particularly in degradable polymers. It will summarize the advances of organocatalysis in polymer chemistry in the past two decades. We hope this book will offer a great guideline for postgraduate students, professors, technicians as well as industrial experts.

December 2024 *Zhibo Li*

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1

Organocatalyzed Ring-Opening Polymerization of Cyclic Esters Toward Degradable Polymers

Feng Li[1], Takuya Isono[1], and Toshifumi Satoh[1,2]

[1]Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan
[2]List Sustainable Digital Transformation Catalyst Collaboration Research Platform (List-PF), Institute for Chemical Reaction Design and Discovery (ICReDD), Hokkaido University, Sapporo 001-0021, Japan

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.

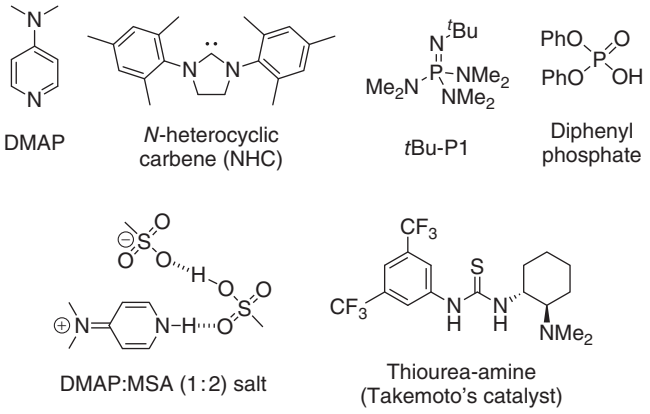

Figure 1.2 Representative organocatalysts for the ROP of cyclic esters.

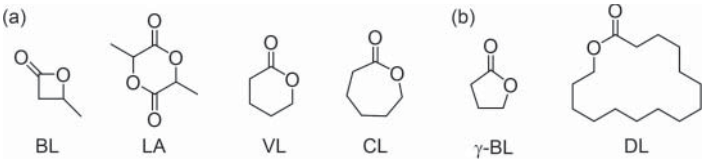

Figure 1.3 Representative cyclic esters with relatively high (a) and low (b) ring strains.

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

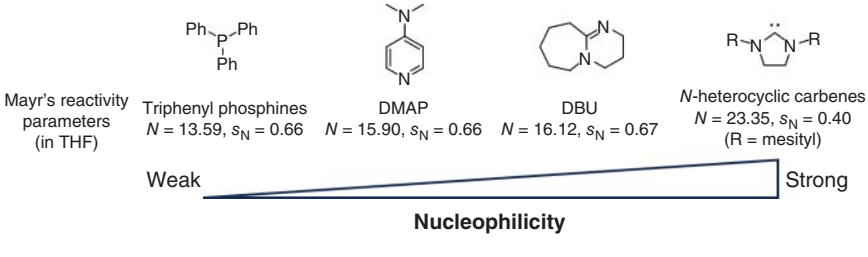

Figure 1.4 Representative nucleophilic catalysts and their nucleophilicities evaluated using the Mayr reactivity parameters.

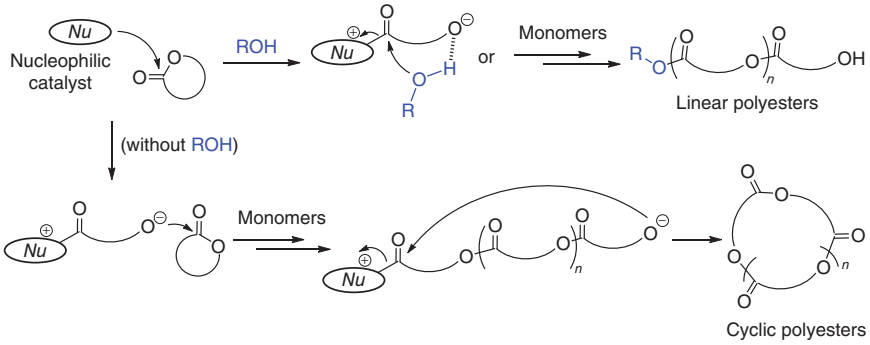

Figure 1.5 General reaction mechanism of the ROP of cyclic esters using nucleophilic catalysts in the presence and absence of alcohol initiators.

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

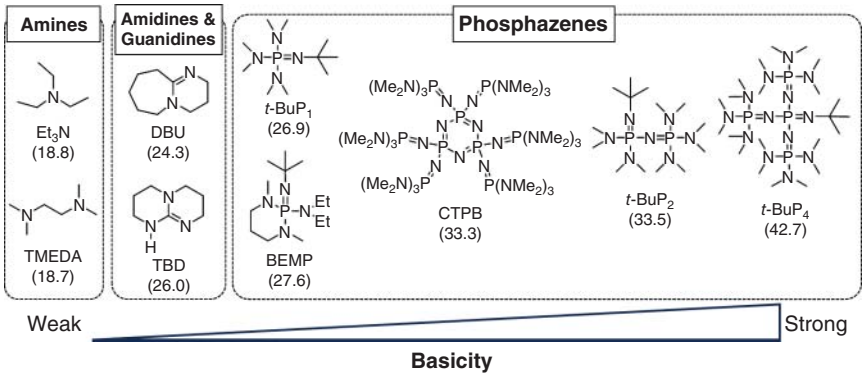

Figure 1.6 Representative Brønsted base catalysts and their basicity (pK_a of the conjugated acid in MeCN).

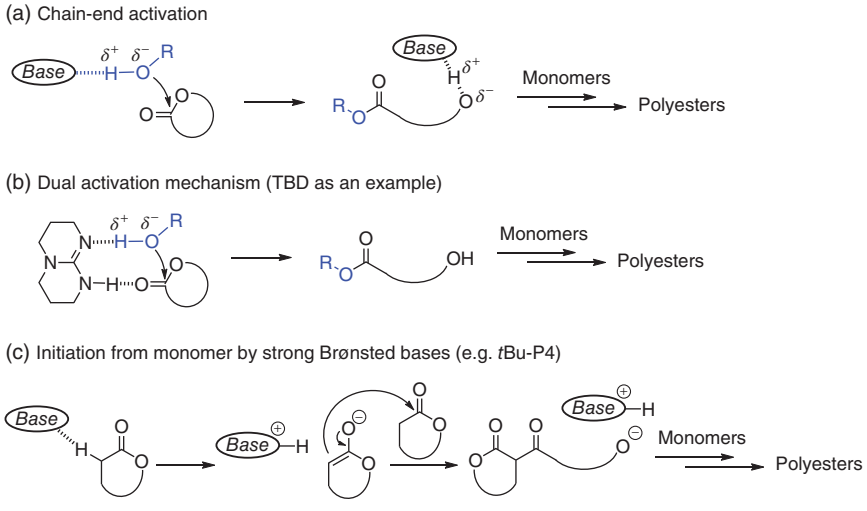

Figure 1.7 General reaction mechanism of the ROP of cyclic esters using Brønsted base catalysts.

(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

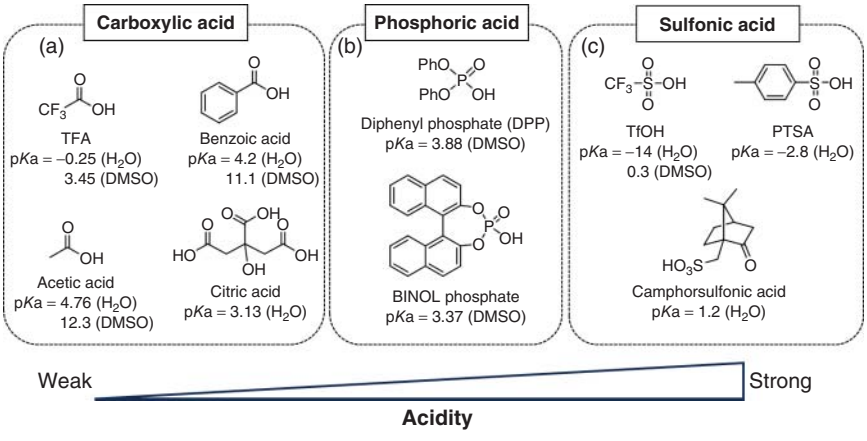

Figure 1.8 Representative Brønsted acid catalysts and their acidities. Source: Bordwell [26] and Christ [27].

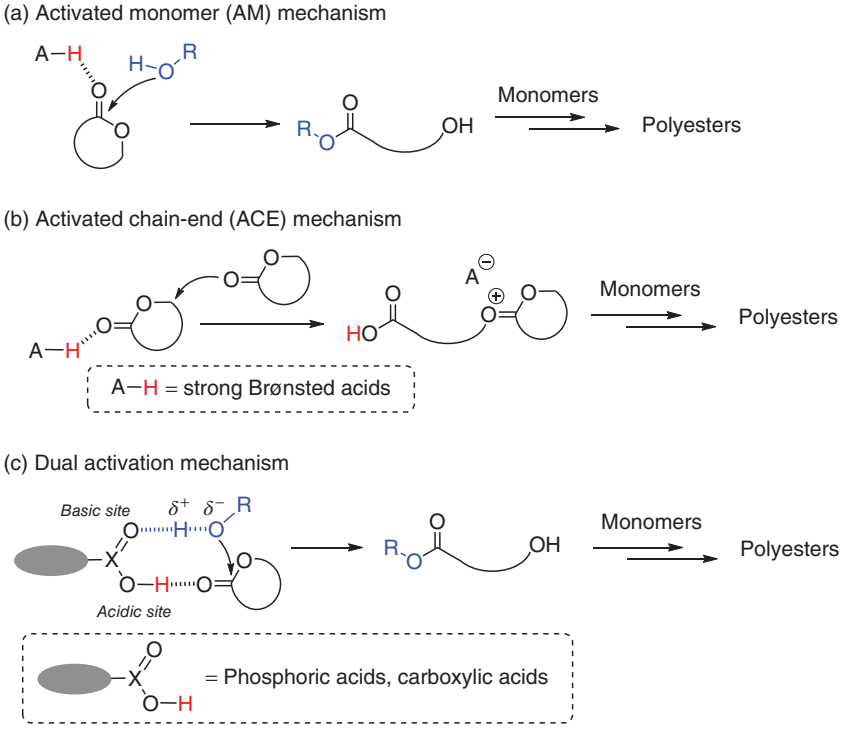

Figure 1.9 General reaction mechanism of the ROP of cyclic esters using Brønsted acid catalysts.

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.

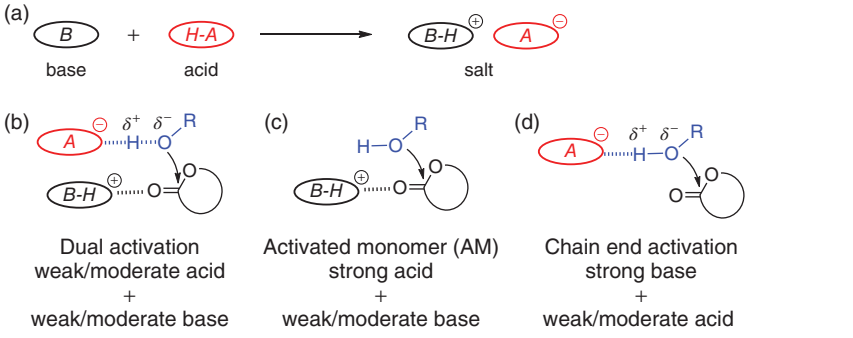

Figure 1.10 Salt catalysts and general reaction mechanism of the ROP of cyclic esters for different types of salt catalysts.

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

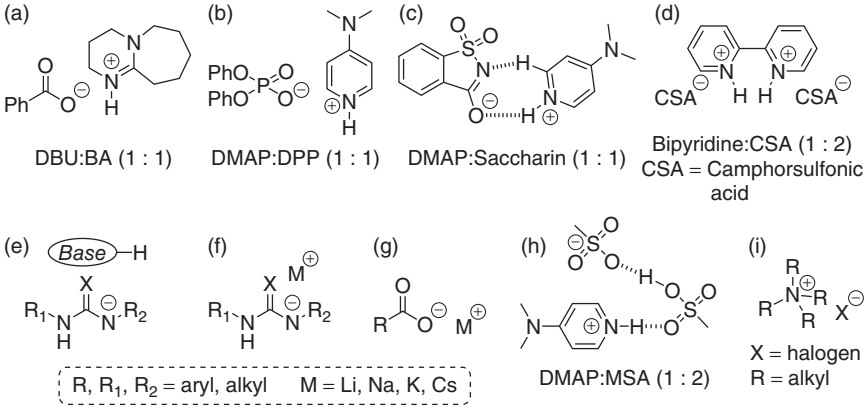

Figure 1.11 Examples of salt and ionic catalysts.

[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

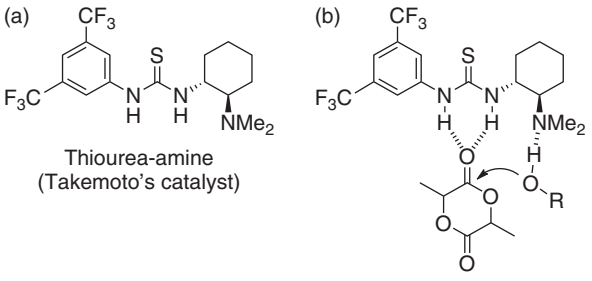

Figure 1.12 (a) Takemoto's catalyst; (b) dual-activation mechanism in the ROP of LA.

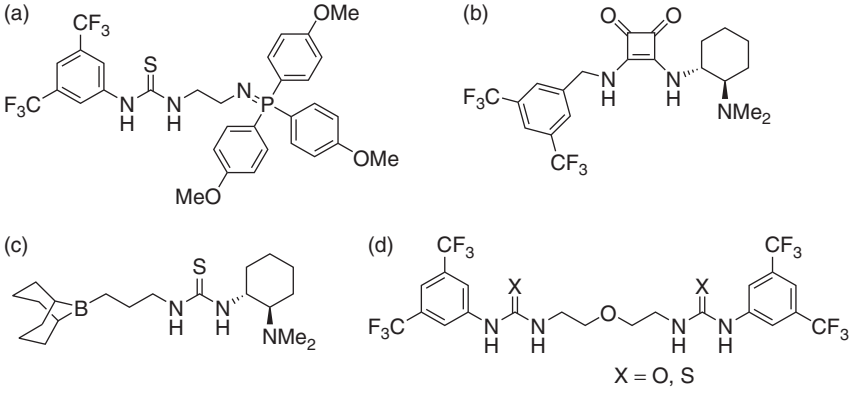

Figure 1.13 Some bifunctional and multifunctional catalysts.

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].

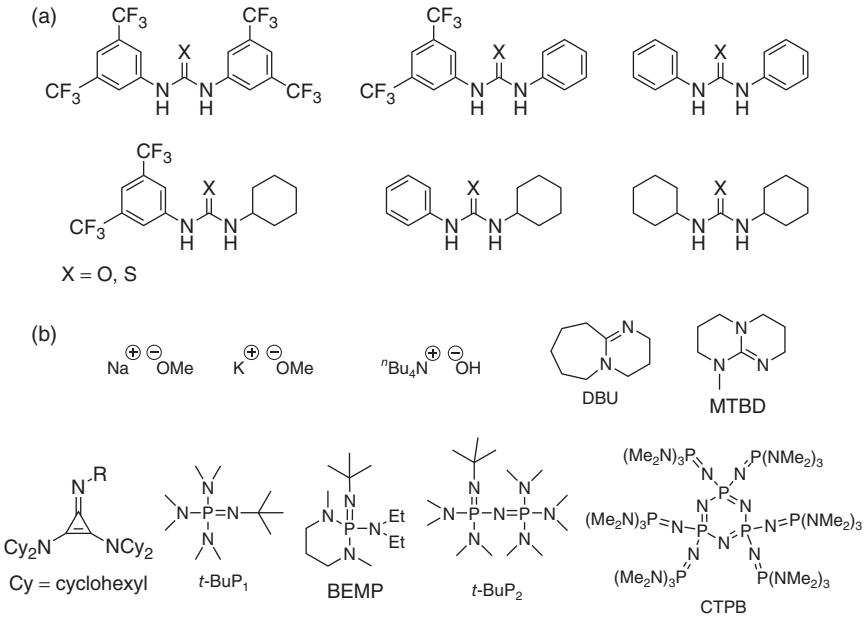

Figure 1.14 Representative structures of (a) ureas, thioureas and (b) bases.

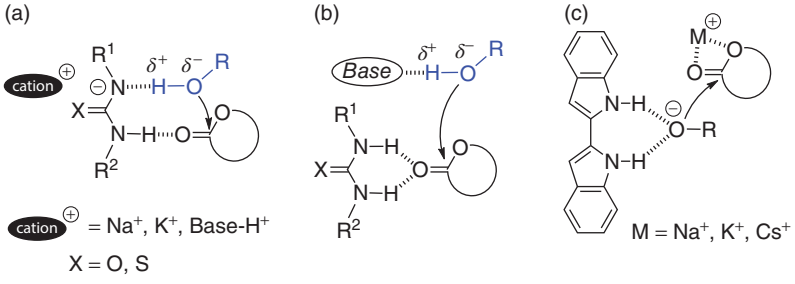

Figure 1.15 (a) Anionic mechanism; (b) cooperative mechanism; (c) reaction mechanism using the 2,2′-bisindole anion.

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