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Perspective

Self-Switchable Polymerization: A Smart Approach to Sequence-Controlled Degradable Copolymers
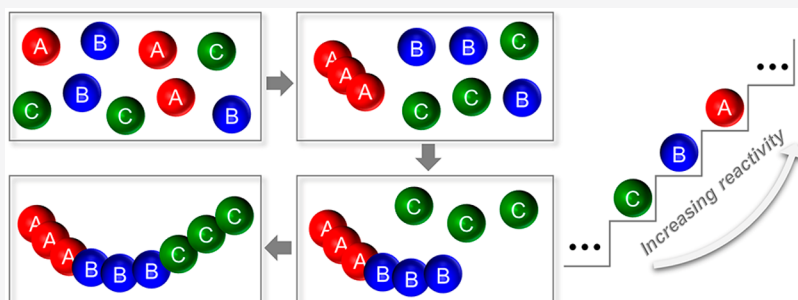
Chenyang Hu, Xuan Pang,* and Xuesi Chen

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ABSTRACT: In the quest for sustainable development, degradable polymers are attractive alternatives to traditional fossil-based plastics. As monocomponent degradable polymers often suffer from unsatisfactory performances, the utilization of corresponding copolymers with tailored block compositions is viable for improved properties. To this end, the emerging field of self-switchable polymerization offers a facile access to the on-demand synthesis of degradable copolymers with controlled sequences, in which the polymerizations were regulated by the monomers themselves. This Perspective outlines state-of-the-art self-switchable polymerization systems based on ring-opening (co)polymerization with various types of monomers. The scope of catalysts and monomer types are summarized. Comprehensive comparison between different types of monomers is offered along with an outlook on possible monomers in the future.

INTRODUCTION

Plastics have brought unparalleled convenience as a unique type of low-cost, resilient, and lightweight materials. The production of plastics has grown continuously over the past 50 years, and it is expected to double in the next 2 decades.[1] However, the vast majority of current plastics are derived from fossil feedstocks and are nondegradable.[2] As most of the plastic products end up as waste, plastic pollution is becoming a major threat to ecosystems particularly in landfills and aquatic environments.[3] As promising sustainable alternatives, degradable polymers are gathering an ever increasing interest among the scientific and industrial communities.[4] Regarding the drawbacks of traditional plastics at end-of-life, degradable polymers offer a way to fundamentally solve plastic pollutions, which are especially meaningful for the application of single-use plastics.

In the realm of degradable polymers, polyesters and polycarbonates are two types of representative materials with excellent biodegradability and multiple derivations from renewable resources.[4−6] Conventionally, many industrial polyesters and polycarbonates are produced through polycondensation reactions.[7] These processes are typically very energy-intensive and small molecule byproducts need to be constantly removed to reach high conversion. In many cases, the yielded polymers also have limited molecular weights and the harsh reaction condition further triggers inevitably thermal degradation.[8] In comparison, ring-opening (co)polymerization for the synthesis of aliphatic polyesters and polycarbonates emerged to be an advantageous alternative. As appealing chain growth approaches, ring-opening polymerization (ROP)[6] and ring-opening copolymerization (ROCOP)[9,10] of cyclic monomers are atom-economical and require much milder reaction temperature. At the same time, the molecular weight could be precisely controlled with dispersity remaining low. These controlled natures further enable the tailor of polymer composition, architecture and topology.[11]
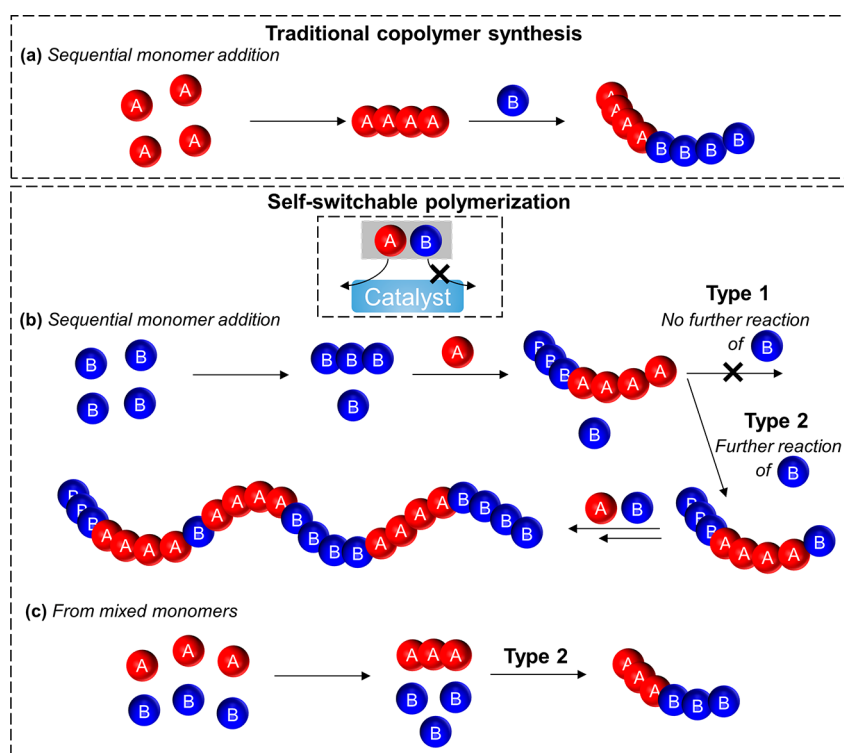
To date, controlled/living polymerizations have facilitated the synthesis of a wide array of sustainable polymers, but many of them are suffering from incomparable performance to traditional plastics. For example, poly(lactic acid) (PLA) is the most commercially successful and largest scale sustainable polymer.[12]
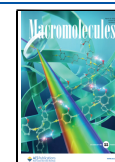
Figure 1. Synthesis of block copolymers under (a) traditional and (b, c) self-switchable protocols.
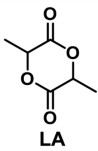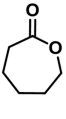
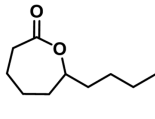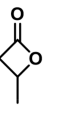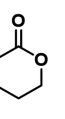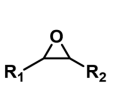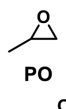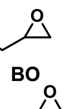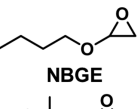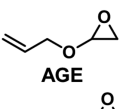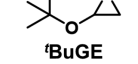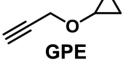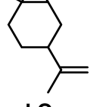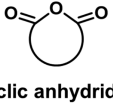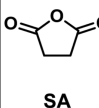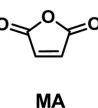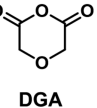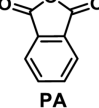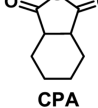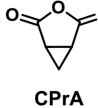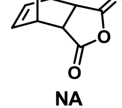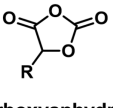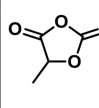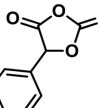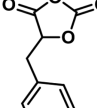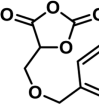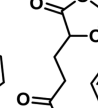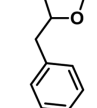PLA derives from renewable feedstocks such as corn and is synthesized through lactic acid from bacterial fermentation. However, the crystalline and brittle nature of PLA (less than 10% elongation at break) limits its potential applications.[13] Because of the restricted source and lack of chemical modification handles, the straightforward variation of PLA backbone to tune its physical properties is very challenging. To meet the demand for practical use, 10−20 wt % of additives are usually needed to be formulated with PLA, yet this would increase the complexity of recycle and risk of toxicant leak.[14] To this end, integrating PLA with other distinct polymer into block copolymers becomes an ideal choice to improve the performance of PLA.[15] Beyond PLA, many other sustainable block copolymers also show significant improvement over pristine homopolymers in the context of morphologies, thermal and elastic properties, etc.[16] In addition, the precise control of monomer sequence is also a central challenge in polymer chemistry and can significantly affect the behavior of polymeric materials.[17−23]

In recent years, there has been a surge of interests in using switching agents to control polymerizations and synthesize tailored block copolymers.[24] Compared with producing diblock copolymers using macromolecular initiators[25,26] or bifunctional initiators,[27,28] this "smart" approach enables reversible modulation of catalytic selectivity from monomer mixtures and real-time control of polymer sequence. And it further shows far-reaching implications including synthesizing sophisticated sequences with exquisite functions.[29] With external switching agents such as water,[30] oxygen,[31] carbon monoxide,[32] redox reagents,[33] etc., block copolymers could be produced through in situ transformation of active propagating species, and insightful reviews can be found elsewhere.[34,35] Modulation by external fields including electrochemical[36,37] and light-controlled[38] polymerizations are also novel and powerful switching techniques, which could produce distinct block copolymers

from monomer mixtures. Summary of polymerization under various external fields can be found in another excellent review.[39] In comparison, self-switchable (or "chemoselective") polymerization is of significant interest as a uniquely facile and atom-economical strategy, where specific monomers could at the same time act as the switching agents by automatically interrupting the original reaction with different catalytic cycles.[40] In the synthesis of well-defined block copolymers, self-switchable polymerization is viable and advantageous compared with traditional approach (Figure 1). Conventionally, the preparation of block copolymer under chain-growth polymerizations is tedious and requires strictly stepwise feeding of monomers (Figure 1a). To avoid tapered microstructures, it is necessary for the first monomer to be fully consumed before addition of the next one.[41] On the contrary, the process becomes much easier when a monomer (A) dominates in insertion and show extremely "strong" reactivity over another monomer B from their mixtures. As shown in Figure 1b, in case of monomer B is polymerized first, addition of monomer A would instantly stop the previous polymerization. Then exclusive insertion of monomer A is proceeded. In this way, distinct diblock copolymer is spontaneously produced over the polymerization systems with minimal side reactions and steps. Further, current self-switchable systems vary in whether the residual monomer B remains active after consumption of monomer A: In type 1, the polymerization would stop and end up with diblock copolymers. In type 2, the leftover monomer B could be converted subsequently. And benefit from the remaining activity of both monomers, multiblock copolymers could further be synthesized through multiple feeding of monomers A and B mixtures. This perspective aims to overview prior documents of self-switchable polymerizations regardless of the remaining activity of monomer B, and further seeks to highlight successful examples of type 2 systems. Moreover, starting from mixed monomers (Figure 1c), type 2 system shows unique advantage as a "one-pot/one-step"
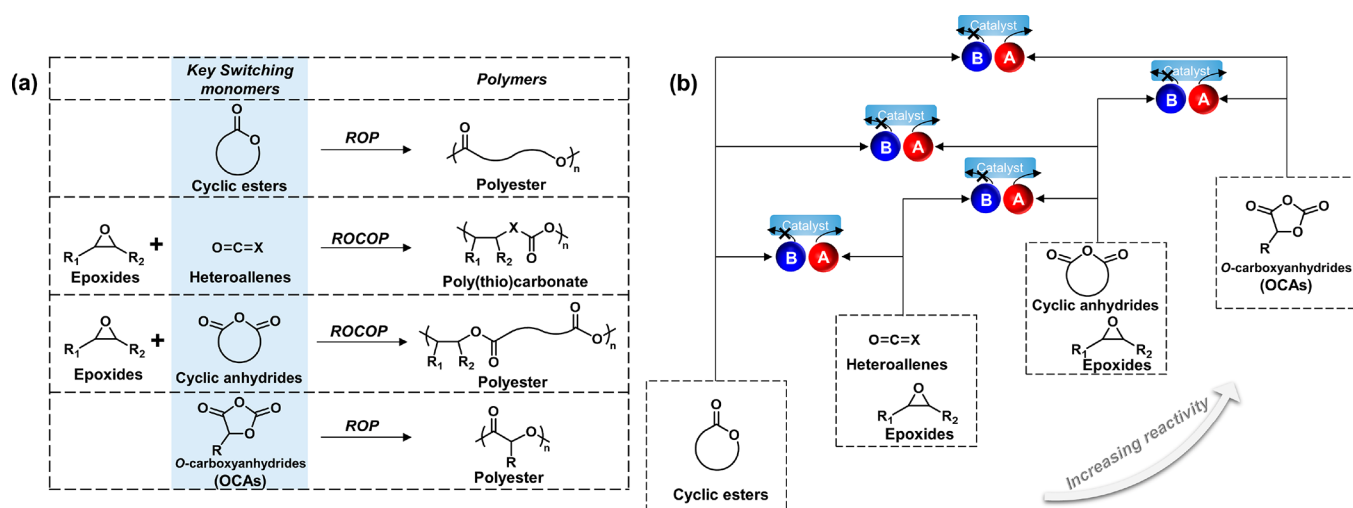
Figure 2. (a) Ring-opening (co)polymerizations and key switching monomers. (b) Successful monomer pairs combined in self-switchable polymerization.

Figure 3. Representative monomers of different classes in self-switchable polymerization (LA, lactide; ε-CL, ε-caprolactone; ε-DL, ε-decalactone; BBL, β-butyrolactone; δ-VL, δ-valerolactone; PO, propylene oxide; BO, 1,2-butylene oxide; NBGE, n-butyl glycidyl ether; AGE, allyl glycidyl ether; ECH, epichlorohydrin; SO, styrene oxide; ^{t}BuGE, $tert$-butyl glycidyl ether; GPE, glycidyl propargyl ether; CPO, cyclopentene oxide; CHO, cyclohexene oxide; LO, limonene oxide; SA, succinic anhydride; MA, maleic anhydride; DGA, diglycolide anhydride; PA, phthalic anhydride; CPA, cyclopentane-1,2-dicarboxylic acid anhydride; CPrA, cyclopropane-1,2-dicarboxylic acid anhydride; NA, norbornene anhydride; OCA, O-carboxyanhydride).

approach where the two monomers would be converted consecutively to directly produce diblock copolymers.

Until now, significant advances have been made in exploiting self-switchable chemistry among various living/controlled polymerizations: In 2007, Lutz et al. reported that N-substituted

maleimides could be sequentially incorporated into the living polymer chain of polystyrene,[42] but the moiety of styrenic-maleimide pair was not ideally alternating. Subsequently, O'Reilly and co-workers took advantage of the vast kinetic gap between $endo$- and exo-norbornenes in ring-opening metathesis
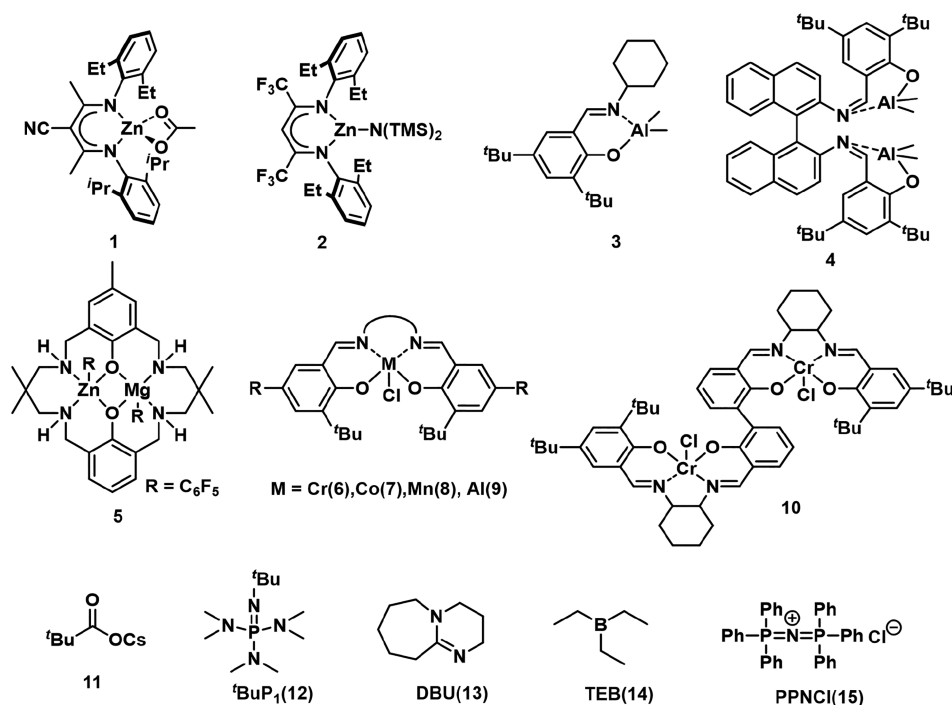
Figure 4. Representative catalysts for self-switchable polymerization.

polymerization to achieve the control of monomer sequence.[43] Following elegant contributions were made separately on polyaziridine- (Wurm et al.),[44] polyethylene- (Nozaki et al.),[45] and polyether-based (Williams et al.)[46,47] block copolymers through self-switching polymerizations. Meanwhile, self-switchable ring-opening (co)polymerizations for production of polyesters and polycarbonates have arguably attracted the most attentions[24] thanks to distinctly reactive monomers and the rich scope of catalysts.[48] Herein, this Perspective covers self-switchable polymerizations by focusing on the precise synthesis of degradable copolymers, and seeks to give a comprehensive picture taking together each individual polymerization systems. Statistical copolymers obtained in the polymerizations from monomer mixtures are not to be addressed, although these are also important family of degradable polymers.[14,49−52]

GENERAL MONOMER SCOPE

In the realm of monomers, their distinct chemical natures are essential to achieve perfect kinetic resolution in self-switchable polymerizations. As a key factor, the intrinsic structural difference facilitates one monomer to be exclusively inserted and inhibits the polymerization of the other(s). Ideally, this exclusive insertion should be maintained even in the presence of little leftover "strong" monomer. In the synthesis of degradable polymers, self-switchable polymerization generally requires the use of different types of monomers.[53] On the contrary, self-switchable polymerization among the monomers with similar structures is relatively difficult due to the insignificant structural gap, albeit the discrepancy of insertion rate has been observed from monomer mixtures. For example, lactide (LA) and ε-caprolactone (ε-CL) are both prevailing cyclic esters and show different coordination abilities;[54] In the copolymerization from mixture of them, the reactivity ratio of LA was generally higher than ε-CL.[55] Although LA is inserted preferentially over ε-CL, direct self-switchable polymerization from LA/ε-CL mixtures to produce discrete block copolymer is inaccessible.[56] Through the

modulation of catalytic systems, only statistically blocky,[50] random,[54,57] and tapered[58] copolymers could be obtained.

In chain-growth polymerizations, ROP and ROCOP are the two main strategies for synthesizing degradable polymers.[4,9] As the classes of monomers are continuously expanded, there has been an increasing interest in revisiting the original reactions with distinct class of comonomers to achieve self-switchable polymerizations. Until now, numerous monomer pairs from different classes were discovered with self-switchable features under appropriate catalytic systems (Figure 2). Therefore, the comparison and integration of involved monomer classes is believed to be significantly important in guiding the design of self-switchable systems. Although in some cases judicious selection of catalysts and reaction conditions are also necessary, the existing pairs of "strong" and "weak" monomer classes are informative for potential monomer selection. And the same monomer pairs are often applicable to many other catalytic systems.[59−61] Currently, four major types of polymerizations have been extensively studied for self-switchable polymerizations (Figure 2), including ROP of cyclic esters, ROCOP of epoxides/COX (heteroallenes) as well as epoxides/cyclic anhydrides, and ROP of O-carboxyanhydrides (OCAs) (Figure 2a). While epoxides usually acted as a simple comonomer with COX or cyclic anhydrides and do not directly influence the self-switching, cyclic esters, COX, cyclic anhydrides, and OCAs are the key switching monomers that determine the direction of polymerization. Representative structures of different monomer classes in self-switchable polymerization are summarized in Figure 3. For the polymers, poly(thio)carbonates are synthesized under the ROCOP of epoxides/COX, and polyesters are obtained from the other three approaches. The corresponding poly(thio)carbonates and polyesters are variable building blocks to be constructed into sequence-controlled degradable copolymers. Figure 2b illustrates the overall comparison of switchable monomer pairs between different classes in Figure 2a. The strong monomer (as monomer A, red sphere) could stop the
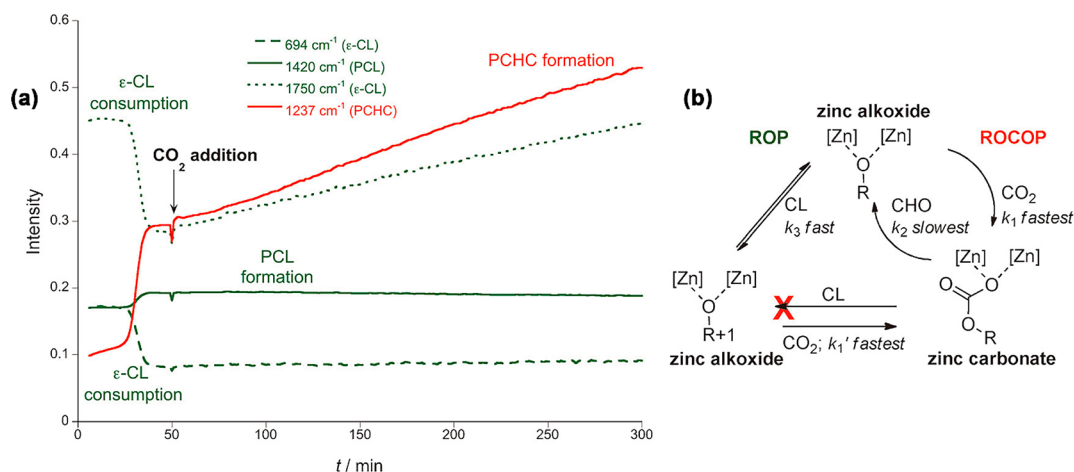
Figure 5. (a) Sequential reaction of CO_2/CHO and ε-CL monitored by in situ IR spectroscopy. (b) Self-switchable polymerization mechanism illustrating the transformation of zinc−oxygen chain end groups. Reproduced with permission from ref 83. Copyright 2014 Wiley-VCH.

polymerization of weak one (as monomer B, blue sphere), at the same time proceeds its own reaction exclusively until full consumption. And one could conclude that switchable monomer pairs follow the order of cyclic esters < hetero-allenes/epoxides < cyclic anhydrides/epoxides < OCAs. Notably, for monomers like heteroallenes and cyclic anhydrides, these same monomers could be both the strong or weak types in self-switchable polymerization depending on the comonomers used. Meanwhile, a progressive fashion could be found when comparing monomer classes with increasing reactivity, and the trend is the same for "nonadjacent" monomer pairs. For example, COX's reactivity falls in the middle of cyclic anhydrides and cyclic esters, and cyclic anhydrides could be successfully used in the control of cyclic esters polymerization as a pair of "nonadjacent" monomers. Similarly, OCAs exerted well control over the polymerization of cyclic ester monomers. Collectively, self-switchable systems facilitate the control over the monomers of (1) cyclic esters and (2) heteroallenes/cyclic anhydrides with epoxides. Detailed examples are as follows.

◼ CATALYSTS

To achieve self-switchable polymerization, a versatile catalytic system that is active for different polymerization cycles is also fundamental. Figure 4 summarizes representative catalysts for self-switchable polymerization, which largely stemmed from the previously well-established catalysts for related pristine polymerizations, and additionally required the catalysts with capability on multiple tasks. For example, catalyst **1**, a highly active β-diiminate ZnOAc complex, was reported by the Coates group to mediate the first self-switchable polymerization from epoxides, cyclic anhydrides, and CO_2.[62] Before that work, the same group separately discovered that catalyst **1** (or very similar structures) could facilitate the alternating copolymerization of epoxides and CO_2[63−65] or cyclic anhydrides.[66] It is believed these preliminary results were crucial for the selection of catalysts. Thereafter, numerous other metal-based catalysts (**2**−**10**) were applied in self-switchable polymerizations, many of which were also efficient catalysts in prior homopolymerizations.[67−72] Detailed polymerization examples with various monomers are to be elucidated below. Specifically, important structural factors (including ligand structure,[4] central metal species,[73] axial group,[74] mononuclear vs dinuclear framework,[75,76] etc.) influencing performances in traditional polymerizations were

varied in the studies of self-switchable polymerizations. Among the successful examples in Figure 4, zinc-based catalysts (β-diiminate complexes **1**,[62] **2**,[70] and a dinuclear complex **5**[69]) typically show very high activity. From mixtures of cyclohexene oxide (CHO) and other cyclic monomers, the reactions could be proceeded under 50−60 °C. However, propylene oxide (PO) is not as compatible as CHO in these polymerization systems. Catalysts under Salen-type framework (complexes **3**, **4**, **6**−**10**) were also widely studied. In these cases, cocatalysts like bis(triphenylphosphine)iminium chloride (PPNCl) were usually needed. Meanwhile, aluminum complexes (**3**,[48] **4**,[61] and **9**[60]) showed well-controlled features in polymerization and were amenable to a wide scope of monomers. For complex **9**, higher activity was further achieved aided by metallic cooperativity. Additionally, Cr (**6**,[68] **10**[76]), Co (**7**[67]), and Mn (**8**[72]) complexes also showed good selectivity from monomer mixtures. However, contamination by heavy metals is one of the biggest concerns, especially for the case using Cr and Co species. Recently, simple metal salt (catalyst **11**)[77] and organocatalysts[59] for self-switchable polymerization are becoming hot research fields. Similarly, the organocatalysts with multiple catalytic capabilities were selected: For example, *tert*-butyliminotris-(dimethylamino)phosphorene ($^{t}BuP_1$) and 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) are strong bases that could efficiently mediate the homopolymerization of cyclic esters;[78] On the other hand, they also showed activity on the alternating copolymerization of epoxides and cyclic anhydrides.[79] Therefore, these strong bases became potential catalysts for self-switchable polymerizations to produce polyester block copolymers. Moreover, recent development of triethyl borane (TEB) as a novel class of organocatalysts by Gnanou, Feng and co-workers[80] further expanded the scope of metal-free catalysts, and numerous following works have utilized TEB in self-switchable systems.[81,82] One of the biggest advantages of metal-free catalysts including $^{t}BuP_1$ and TEB is that the polymer product is free from additional purification steps and do not exhibit coloration. However, very careful storage of catalysts is needed because of their sensitivity to air and moisture.

◼ CONTROL OVER CYCLIC ESTERS

Among the monomers used for synthesizing degradable polymers, cyclic esters exhibit relatively modest reactivity and
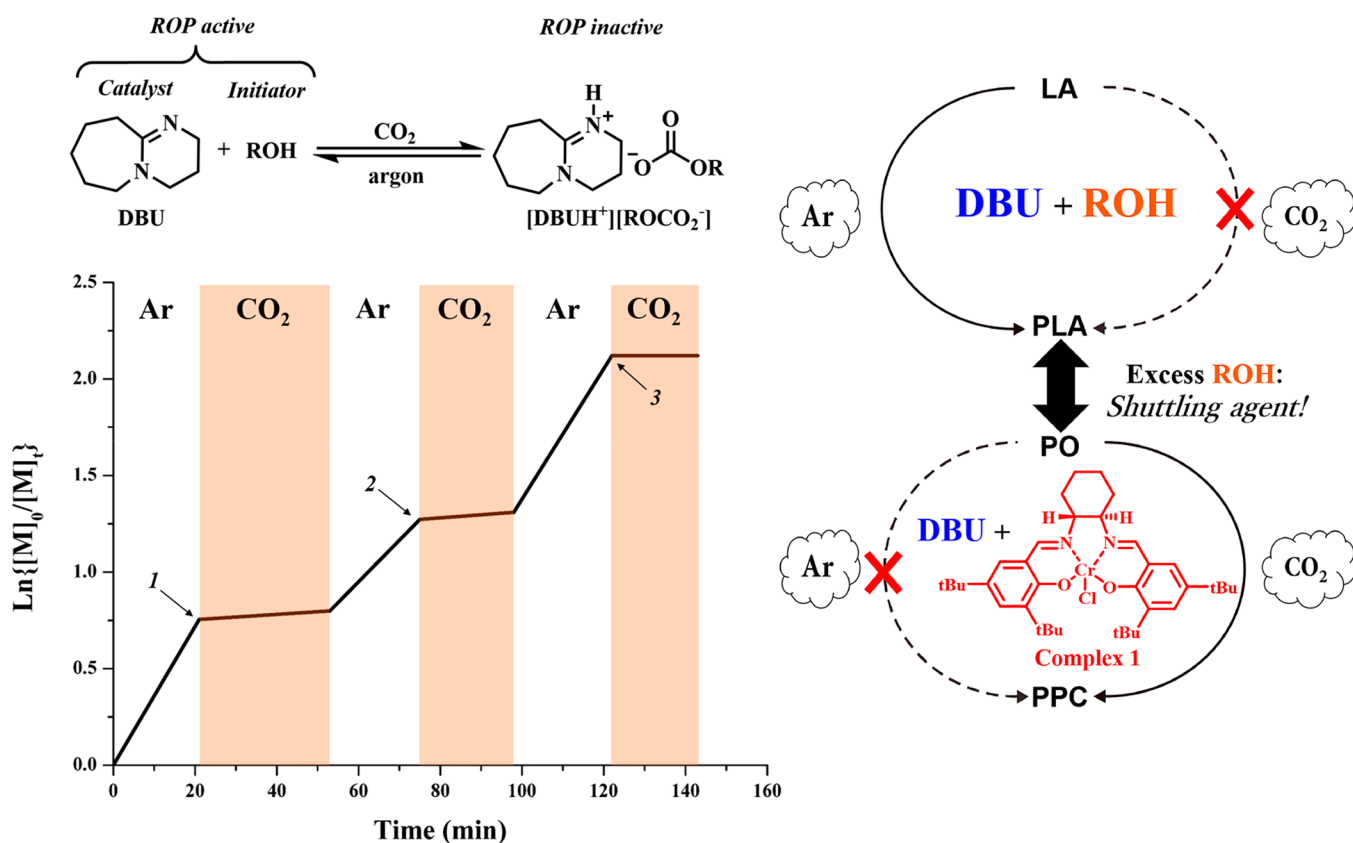
Figure 6. Reversible binding of CO_2 among DBU and alcohols and CO_2-controlled ROP of LA using DBU and ^iPrOH (left). Binary catalytic system with opposite gas-responsive features used in self-switchable polymerizations from LA, PO, and CO_2 (right). Reproduced with permission from ref 87. Copyright 2018 American Chemical Society.
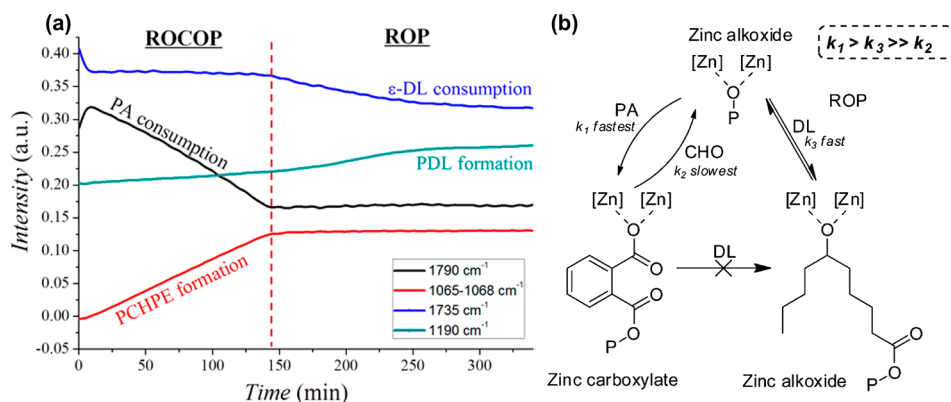
Figure 7. (a) Sequential consumption of PA and ε-DL monitored by in situ IR spectroscopy. (b) Related self-switchable polymerization mechanism with zinc species. Reproduced with permission from ref 89. Copyright 2015 American Chemical Society.

are suitable to be controlled by other comonomers. In early works controlling cyclic esters' polymerization, CO_2 (or heteroallenes) was extensively used as a switching monomer. In 2014, Williams et al. pioneered in the self-switchable polymerization from CO_2, ε-CL, and CHO with a dizinc catalyst (Figure 5).[83] The used dizinc catalyst proceeded the polymerization of ε-CL with a zinc alkoxide chain end. Taking advantage of the rapid insertion of CO_2 into the zinc alkoxide end group, the authors transformed this active species into inactive zinc carbonate. In this way, the original ε-CL polymerization was paused and switched into the copolymerization of CO_2/CHO, producing polycaprolactone-poly-(cyclohexene carbonate) (PCL–PCHC) copolymers. Impor-

tantly, the polymerization of ε-CL could be restarted upon replace of CO_2 atmosphere with N_2. Further, the same group synthesized ABA-block polymers showing enhanced properties through self-switchable polymerization of ε-decalactone (ε-DL), CHO, and CO_2 with catalyst **5**.[84] In 2017, Rieger and co-workers reported the self-switchable polymerization of CO_2, β-butyrolactone (BBL), and epoxides with a Lewis acid BDI^{CF_3}-Zn-N(SiMe$_3$)$_2$ catalyst **2**.[85] To avoid statistical composition, a high CO_2 pressure (40 bar) was necessary for the exclusive copolymerization of epoxides/CO_2. Similarly, complete release of CO_2 could restart the ROP of BBL. The system was amenable to CHO, cyclopentene oxide (CPO), and limonene oxide (LO).[86] Subsequently, Chen et al. revisited the reversible
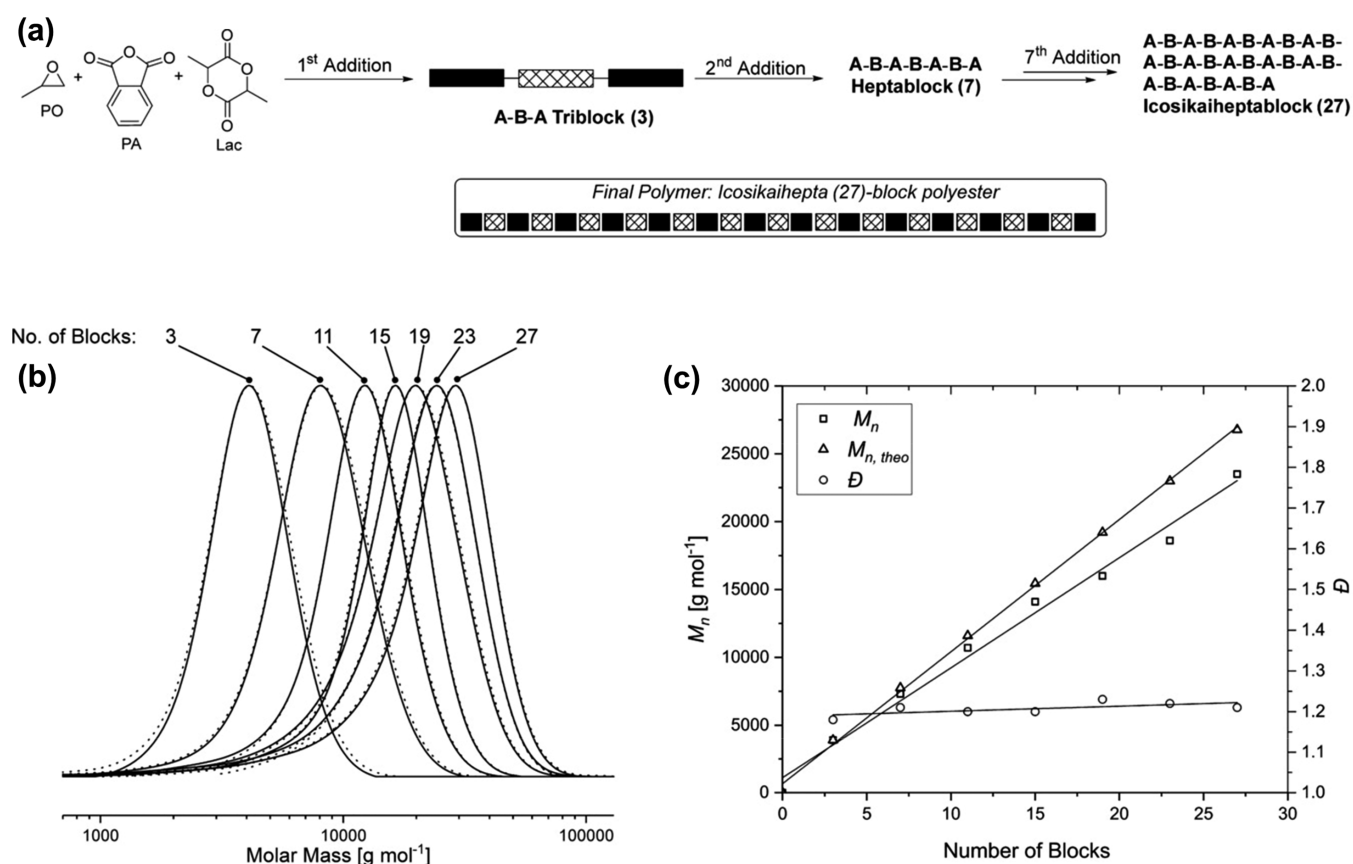
Figure 8. Self-switchable polymerization of LA, PA and PO to synthesize multiblock copolymers by multiple monomer addition: (a) Concept, (b) GPC traces, and (c) evolving of molecular weight and Đ. Reproduced with permission from ref 60. Copyright 2018 Wiley-VCH.

binding of CO_2 by amidine/alcohol system and applied it to the self-switchable polymerization of CO_2, LA, and PO.[87] CO_2 was found to insert into DBU and the alcohol chain end to stop the homopolymerization of LA (Figure 6). In conjugation with another Jacobsen-type Cr^{III} catalyst **6** that showed complementary activity for CO_2/PO copolymerization, the system of DBU/alcohol could produce diblock copolymers starting with either PPC or PLA block. Similar to CO_2, the ROCOP of carbonyl sulfide (COS) with epoxides has been proven to be an efficient and controlled way to synthesize polythiocarbonates.[88] In a similar self-switchable manner, Zhang reported the synthesis of polyester−polythiocarbonate block copolymers starting from lactones, epoxides, and COS mixtures.[81] Under bicomponent catalysts of triazabicyclodecene (TBD) and TEB, the polymerization of δ-valerolactone (δ-VL), ε-CL, or LA could be regulated by COS. However, the repolymerization of remaining lactones after COS treatment did not occur due to the difficulty in completely removing COS.

Cyclic anhydrides are another common type of switching monomers to control the polymerization of cyclic esters. In 2015, Williams group reported the self-switchable polymerization of lactones, epoxides/anhydrides in one pot using the same dizinc catalyst (Figure 7).[89] Similarly, cyclic anhydrides inserted into the Zn-alkoxide bond significantly faster than lactones; and once anhydrides were fully consumed, lactones continued to be polymerized in the second phase. In combination with phthalic anhydride (PA) and the monomers of ε-DL, LA, δ-VL, and CHO, 4-vinyl-1-cyclohexene 1,2-epoxide (vCHO) could be utilized. ABA triblock copolymers with a viable structure were produced in one-pot with a diol (1,2-

cyclohexanediol) as a chain transfer agent. Then, the same group conducted the self-switchable polymerization of LA, PA and PO through multiple feedings of monomer mixtures to deliver multiblock copolymers of up to 27 blocks (Figure 8) with a powerful aluminum salphen catalyst **9**.[60] In 2018, Li et al. reported metal-free self-switchable polymerizations of epoxides, cyclic anhydrides and LA using a phosphazene organocatalyst $^tBuP_1$.[59] In this system, a wide scope of monomers could be used, including PO, n-butyl glycidyl ether (NBGE), styrene oxide (SO), allyl glycidyl ether (AGE), CHO as the epoxides and PA, norbornene anhydride (NA), diglycolide anhydride (DGA), succinic anhydride (SA) as the monomers of cyclic anhydride. By changing initiators, copolymers with various topologies including multiblock and six-arm star copolymers were obtained. In the meantime, Zhao separately realized the self-switchable polymerization of PA, epoxides (ethylene oxide (EO), 1,2-butylene oxide (BO), AGE, SO), and LA using $^tBuP_1$.[90,91] Thereafter, Chen et al. fulfilled the self-switchable polymerization of LA, epoxides, and anhydrides with a binary catalytic system composed of Salen-Al(III) (catalyst **3**) and PPNCl.[92] Notably, besides using epichlorohydrin (ECH), PO, CHO, and AGE as the epoxides, glycidyl propargyl ether (GPE) was used for the first time to install alkyne group onto the sequence-controlled polymer. And the polymer featuring both alkyne and vinyl groups could undergo independent functionalization through azide−alkyne cycloaddition and thiol−ene chemistry. Following this, efforts have been made to expand the scope of catalysts to bimetallic aluminum complexes **4**,[61] Lewis pairs,[93,94] and alkali metal carboxylates **11**.[77] Moreover, this switchable technique was also conjugated with RAFT polymer-
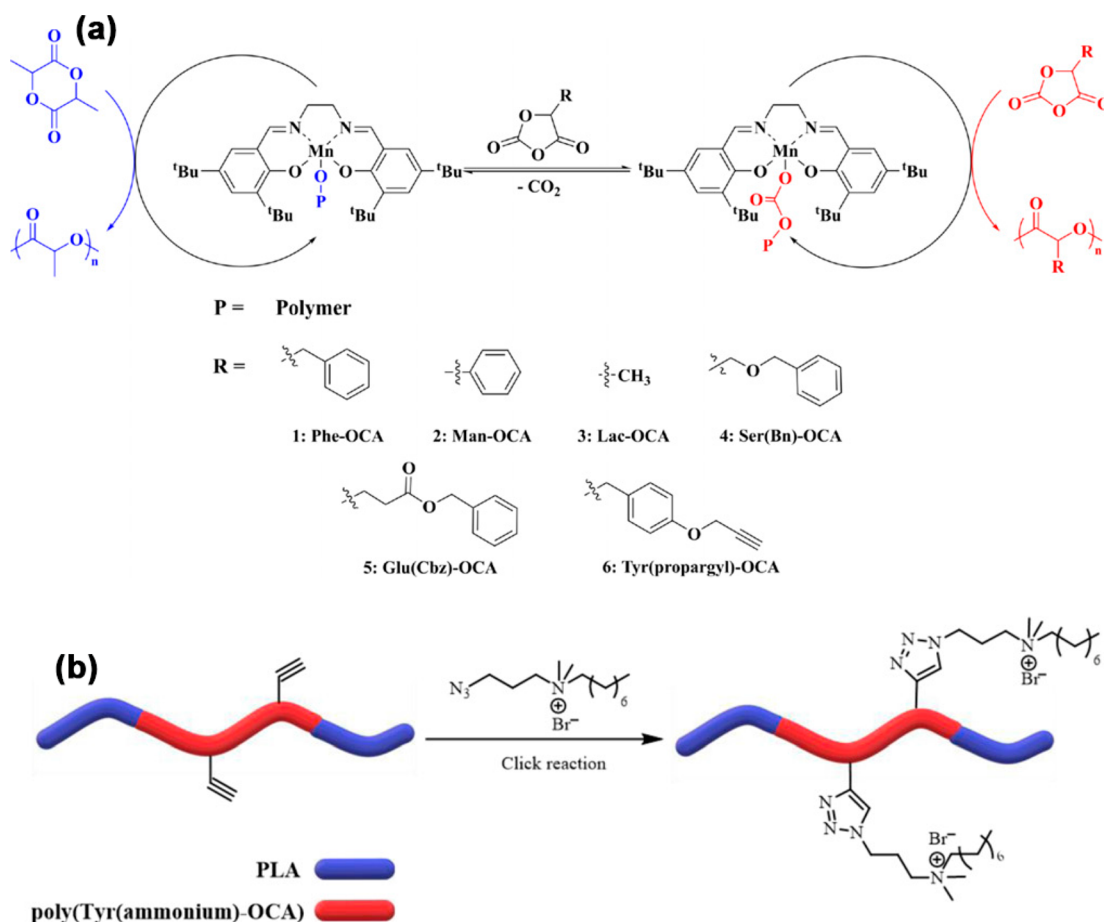
Figure 9. (a) Self-switchable polymerization of OCA and LA with a Mn complex. (b) Postfunctionalization of block copolymer. Reproduced with permission from ref 102. Copyright 2021 Wiley-VCH.
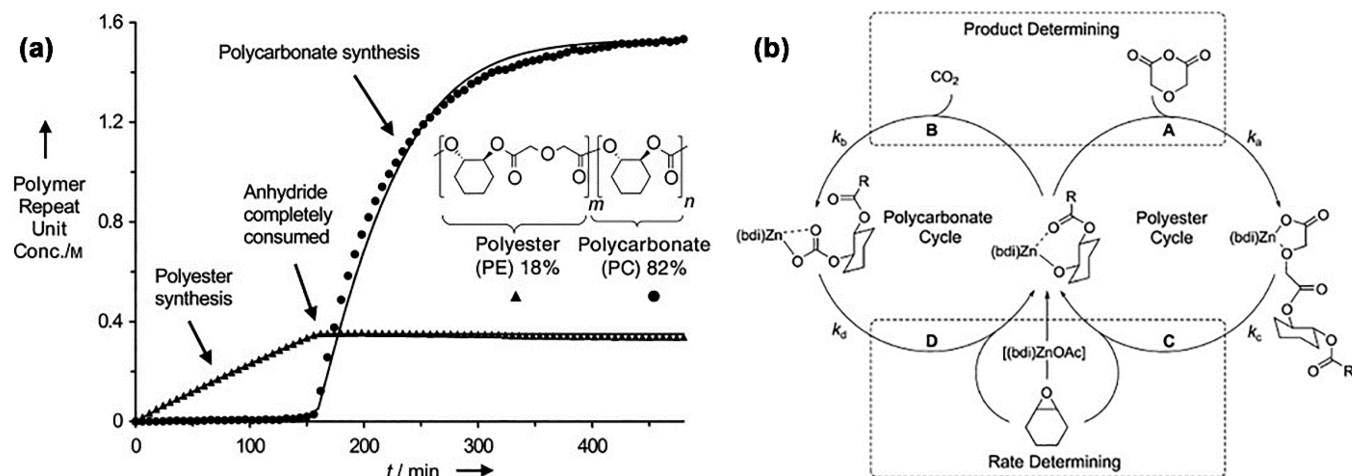
Figure 10. (a) Sequential reaction of DGA/CHO and CO_2/CHO monitored by in situ IR spectroscopy. (b) Related self-switchable polymerization mechanism. Reproduced with permission from ref 62. Copyright 2008 Wiley-VCH.

ization of vinyl monomers to bridge three types of polymerization cycles.[95] With a TEB/DBU catalytic system, a special trithiocarbonate compound with carboxylic group was selected as a versatile chain transfer agent. In this way, concurrent and self-switchable ROCOP/RAFT and ROP/RAFT from epoxides, cyclic anhydrides, LA, and vinyl monomers proceeded. This approach allowed for the synthesis of triblock quaterpolymers with a narrow distribution.

Very recently, OCAs emerged to be a novel type of monomer to control the polymerization of cyclic esters. OCAs are structurally equivalent to α-lactone with much higher reactivity, and their polymerization also produced polyester with equivalent CO_2 released.[96] Because they are readily available from α-hydroxyacids, OCAs have become a versatile platform for the synthesis of functionalized polyesters.[97,98] For example, man-OCA originates from renewable resources and could be
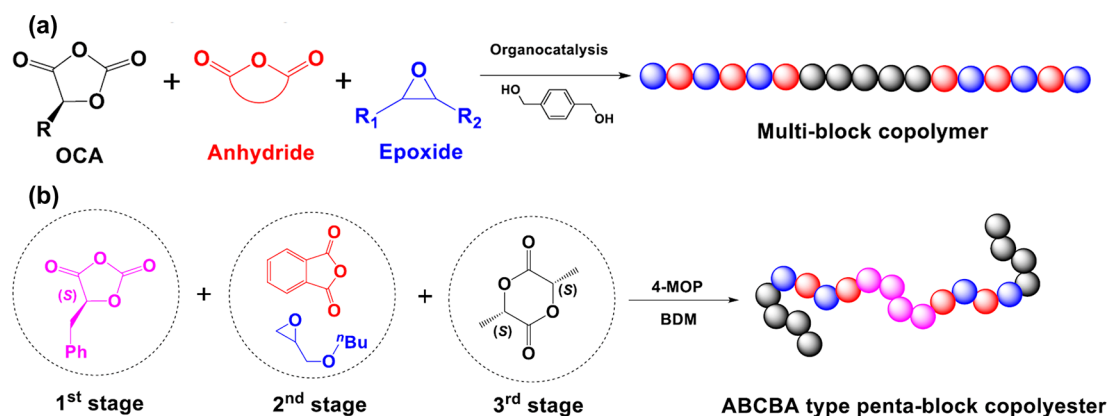
Figure 11. Self-switchable polymerization from monomer mixtures of (a) OCA/anhydride/epoxide and (b) Bnz-OCA/PA/NBGE/LA. Reproduced with permission from ref 111. Copyright 2021 American Chemical Society.

polymerized into poly(mandelic acid).[99,100] As a polyester with pendant phenyl groups, it shows comparable properties to polystyrene as well as excellent degradability.[101] In 2021, Chen and co-workers realized the first self-switchable polymerization of OCAs over LA using a Salen-Mn^{III}-Cl catalyst **8** (Figure 9).[102] From mixed monomers of LA and OCA, OCA would be converted exclusively at first. Because the Mn species were still occupied by the released CO_2 from ring-opening of OCA (as Salen-Mn^{III}-OCOOR), further coordination and ring-opening of LA were hampered. Through removal of CO_2, the repolymerization of LA could be proceeded. In this way, various triblock copolymers of poly(LA-*b*-OCA-*b*-LA) were synthesized. Postfunctionalization of copolymers from propargyl-containing OCA and LA with quaternary ammonium further enabled the polymer with antibacterial ability.

Collectively, CO_2/COS, cyclic anhydride, and OCA are all potentially efficient switching monomers to control the polymerization of cyclic esters. Meanwhile, one major difference among these cases is the way to restart the original polymerization of cyclic esters: For CO_2, simple gas exchange to remove CO_2 would restart the polymerization of cyclic esters. However, this becomes challenging for COS due to the difficulty to completely remove COS. On the contrary, cyclic anhydride needs to be fully consumed to switch back to the polymerization of cyclic esters. The process of OCA is more complicated: the OCA monomer also needs to be consumed, and at the same time, removal of produced CO_2 is usually necessary.

CONTROL OVER HETEROALLENES/CYCLIC ANHYDRIDES

The control of CO_2/epoxides polymerization by cyclic anhydrides has also attracted considerable attentions. In 2008, the Coates group first reported the proof of concept finding for self-switchable polymerization from epoxides, cyclic anhydrides, and CO_2 (Figure 10):[62] with a β-diiminate ZnOAc catalyst **1**, DGA was preferentially inserted into the active species followed by regeneration of zinc alkoxide with CHO. And only after consumption of DGA, the insertion of CO_2 became competitive again. It should be noted that the pressure of CO_2 was less than 27 atm to avoid its insertion during the polymerization of DGA. And the monomers were further expanded to SA and vinyl cyclohexene oxide. Following efforts realized the self-switchable polymerization of various monomers using mononuclear chromium **6**[103−105] and dinuclear chromium complexes **10**,[106] cobalt complexes **7**,[107] and a heterogeneous catalyst (Zn−

Co(III) double metal cyanide complex[108]). In these studies, a wide scope of cyclic anhydrides could be used, including SA, cyclopentane-1,2-dicarboxylic acid anhydride (CPA), cyclo-propane-1,2-dicarboxylic acid anhydride (CPrA), PA, maleic anhydride (MA) and NA. It is interesting to note that CO_2 was further discovered to efficiently reduce side reactions during self-switchable polymerizations: Duchateau et al. reported that the presence of CO_2 avoided the homopolymerization of CHO and facilitated the synthesis of poly(ester-*b*-carbonate) when using chromium catalysts **6** and 4-(*N,N*-dimethylamino)pyridine (DMAP) cocatalyst.[103] Liu, Wang, and Theato also found that CO_2 suppressed the configuration transformation of a NA monomer.[105] When using a salcyCrCl (catalyst **6**)/PPNCl binary catalytic system, the isomer configuration of NA monomer unit was retained as *cis*-2,3-(*exo,exo*). Recently, important contributions of metal-free TEB-assisted catalysis have been made separately by the groups of Xiao and Meng[109] and Gnanou and Feng[110] as well as Liu, Kang, and Li.[82] Relatively high loading of cyclic anhydrides and the use of THF as a solvent appeared to be key factors to avoid polyether and taper structures. The TEB/PPNCl Lewis pair as organocatalysts could mediate the self-switchable polymerization of cyclic anhydride/epoxide over CO_2/epoxide to produce polyester-*b*-polycarbonate diblock copolymers. The self-switchable mechanism was proposed to be a similar pre-rate-determining manner and verified by DFT calculations. And the system of TEB/PPNCl was amenable to CHO, PO, and BO monomers. The monomer of cyclic anhydrides was extended to SA and PA.

Because of their high reactivity, the control over cyclic anhydrides is challenging. Recently, Wang, Li, and co-workers reported the self-switchable polymerization of anhydrides/epoxides by using OCAs.[111] Starting from monomer mixture of PA/NBGE/Phe-OCA with an organocatalyst 4-methoxypyridine (4-MOP) and an initiator 1,4-benzenedimethanol (BDM), the polymerization of OCA proceeded exclusively at first (Figure 11a), and the copolymerization of PA/NBGE started only after the consumption of OCA. Notably, the authors further realized multistage self-switchable polymerization with OCA, PA/epoxides, and LA monomers to prepare ABCBA-type pentablock copolymer (Figure 11b). This one-pot quadri-polymerization occurred in a strict order of OCA → PA/NBGE → LA.
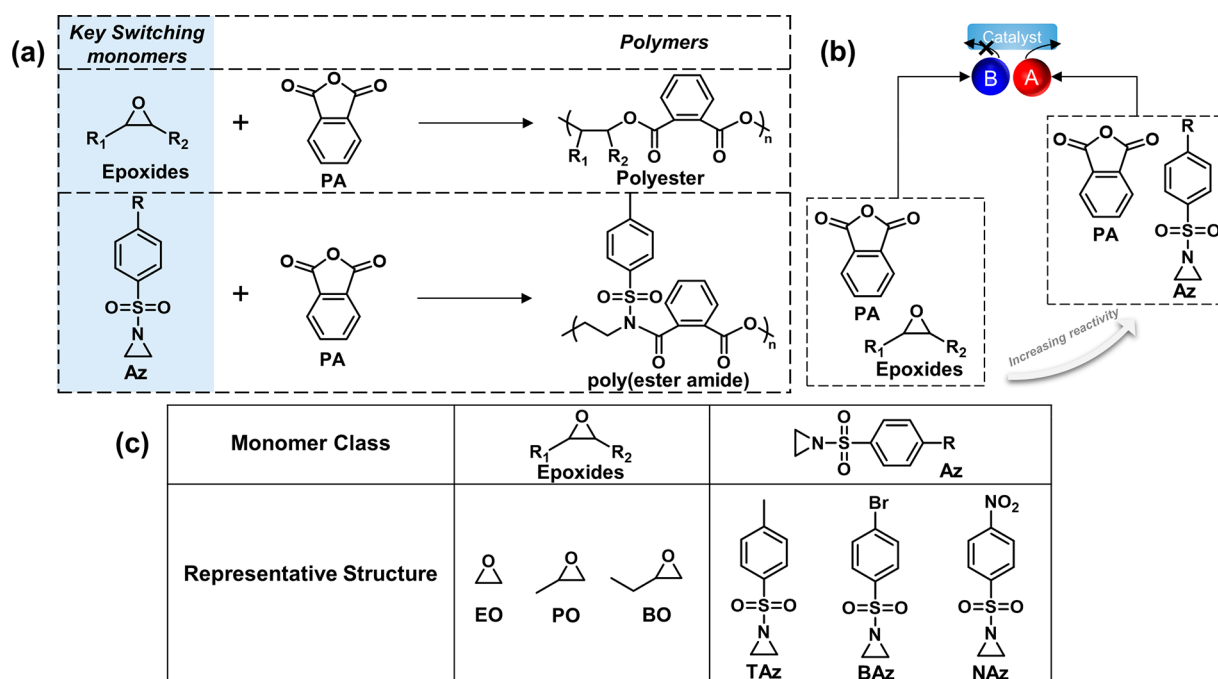
Figure 12. Self-switchable ring-opening copolymerizations of Az over epoxides. (a) Copolymerizations and key switching monomers. (b) Monomer pairs. (c) Examples of monomers.

CONTROL OVER EPOXIDES

As mentioned above, epoxides typically acted as comonomers that did not directly guide the self-switchable polymerization. Recently, Hadjichristidis et al. reported a breakthrough finding of N-sulfonyl aziridines (Az)'s control over the copolymerization of epoxides in couple with PA (Figure 12).[112] With the $^tBuP_1$ catalyst, perfect diblock copolymers were produced from a mixture of Az, PA, and epoxide monomers. The first-stage ROCOP of PA/Az proceeded very fast. After consumption of Az, the ROCOP of PA/PO continued to produce poly(ester amide-b-ester). A mechanism of self-switchable terpolymerization was proposed: The ring-opening of PA was fast throughout the polymerization. In the presence of TAz, the active species was transformed between $-COO^-/^tBuP_1-H^+$ and $-N(Ts)$-$H/^tBuP_1$, leaving PO unreacted. After the complete consumption of TAz, the $-COO^-/^tBuP_1-H^+$ continued to alternatively react with PO. The reaction system was well controlled and no side reactions occurred including trans-esterification and production of ether or amine linkages. The monomers were further expanded to EO, PO, BO, N-tosylaziridine (TAz), N-brosylaziridine (BAz), and N-(4-nitrobenzenesulfonyl) aziridine (NAz). This result validated the possibility of controlling the insertion of epoxides in self-switchable polymerizations and offered implications that epoxides may exert control over another type of weak monomer in the copolymerization with cyclic anhydrides.

CONCLUSIONS

As new catalysts and monomer types are continuously discovered, the field of self-switchable polymerization to synthesize degradable copolymers is seeing a rapid growth. In this Perspective, we have introduced its basic concept, corresponding versatile catalysts and various types of monomers. The order between different monomer types with distinct reactivity from current documents were highlighted, including cyclic esters < heteroallenes/epoxides < cyclic anhydrides/

epoxides < OCAs and cyclic anhydrides/epoxides < cyclic anhydrides/Az. And the general principles of monomer orders are to be verified and replenished upon upcoming works in the future. In addition, it is believed that distinct types of monomers would result in dramatic change of material properties. Studies on expanding applications of the sequence-controlled polymers will also be the next research focus.

PERSPECTIVE ON POSSIBLE MONOMERS

Besides the monomers mentioned above, many other types of monomers with similar polymerization mechanism still have not been explored for self-switchable polymerization. The expansion of monomer types is intriguing and crucial for building diverse sequence-controlled block copolymers with infinite functions in the future:

(1) Cyclic carbonates are another important type of cyclic monomers to produce polycarbonates. Because of their excellent biocompatibility and tunable degradation, polycarbonates have wide biomedical applications.[6] However, the self-switchable polymerization with cyclic carbonates is still underexplored, and preliminary results showed they had similar reactivity to cyclic esters.[77] Indeed, cyclic carbonates are the adducts of CO_2 and epoxides (oxetanes).[113] Considering epoxides are relatively dormant in self-switchable systems, in some cases cyclic carbonates may very possibly behave just like CO_2 in self-switchable polymerization. And the further competition between additional epoxides or CO_2 with cyclic carbonates is an interesting research topic.

(2) Isocyanates have been recently discovered to copolymerize with epoxides and deliver perfect polyurethanes.[114,115] Regarding the similar ROCOP mechanism, isocyanates are speculated to participate in the copolymerizations with above-mentioned monomers. Because isocyanates are a type of extremely reactive monomers, they may play a dominating role in the self-

switchable polymerizations. Explorations are required for the amenable cyclic monomers with isocyanates in the future.

(3) Carbon monoxide (CO) was reported to undergo alternating copolymerization with epoxides to produce polyesters.[116−119] Although there is no precedent of using CO in self-switchable polymerizations, the much higher nucleophilicity of CO over CO_2 may render this combination as an efficient switching agent.

(4) In recent years, there has been a surge of interests in developing sulfur-rich cyclic monomers, many of which realized efficient modulation between polymerization and depolymerization. To name a few, the monomers include thionolactones,[120,121] *S*-carboxyanhydride,[122] episulfides/thioanhydrides,[123] or isothiocyanates,[124] etc. However, how the O-to-S substitution affects the performance in self-switchable polymerization remains largely unknown and is worth studying. These sulfur-rich monomers are speculated to exhibit similar reactivity as pristine monomers.

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Notes

The authors declare no competing financial interest.

Biographies

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Xuan Pang is a professor at Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. He received his Ph.D. (2008) in polymer chemistry from Changchun Institute of Applied Chemistry, under the supervision of Prof. Xuesi Chen. From 2008 to 2010, he had been a postdoctoral associate at Cornell University, United States. His research focused on the design of intelligently catalytic system and controlled polymerization and application of biodegradable polymers, including polylactide, a CO_2-based copolymer, and polycaprolactone.

Xuesi Chen is an academician of the Chinese Academy of Sciences and the executive deputy director of CIAC Academic Committee. He received his Ph.D. degree at Waseda University, Japan, in 1997, and completed his postdoctoral fellowship at the University of Pennsylvania, United States, in 1999. He has been a full Professor at CIAC, CAS, since 1999. He has mainly engaged in the synthesis, characterization, and application of biodegradable polymer materials. He carries out research and development in the fields of green plastics industrialization, fracture internal fixation devices, tissue engineering scaffolds, gene/drug nanocarriers, and other medical materials.

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■ LIST OF ABBREVIATIONS

4-MOP	4-methoxypyridine
AGE	allyl glycidyl ether
Az	*N*-sulfonyl aziridine
BAz	*N*-brosylaziridine
BBL	*β*-butyrolactone
BDM	1,4-benzendimethanol
BO	1,2-butylene oxide
CHO	cyclohexene oxide
CO	carbon monoxide
COS	carbonyl sulfide
CPA	cyclopentane-1,2-dicarboxylic acid anhydride
CPO	cyclopentene oxide
CPrA	cyclopropane-1,2-dicarboxylic acid anhydride
DBU	1,8-diazabicyclo(5.4.0)undec-7-ene
DGA	diglycolide anhydride
DMAP	4-(*N,N*-dimethylamino)pyridine
ECH	epichlorohydrin
EO	ethylene oxide
GPE	glycidyl propargyl ether
LA	lactide
LO	limonene oxide
MA	maleic anhydride
NA	norbornene anhydride
NAz	*N*-(4-nitrobenzenesulfonyl)aziridine
NBGE	*n*-butyl glycidyl ether
OCA	*O*-carboxyanhydride
PA	phthalic anhydride
PCHC	poly(cyclohexene carbonate)
PLA	poly(lactic acid)
PO	propylene oxide
PPNCl	bis(triphenylphosphine)iminium chloride
ROCOP	ring-opening copolymerization
ROP	ring-opening polymerization
SA	succinic anhydride
SO	styrene oxide
TAz	*N*-tosylaziridine
TBD	triazabicyclodecene
*t*BuP$_1$	*tert*-butyliminotris(dimethylamino)phosphorene
TEB	triethyl borane
vCHO	4-vinyl-1-cyclohexene 1,2-epoxide
δ-VL	*δ*-valerolactone
ε-CL	*ε*-caprolactone
ε-DL	*ε*-decalactone

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