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REVIEWS

Review

Toward Infinitely Recyclable Plastics Derived from Renewable Cyclic Esters

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Plastics, used in countless consumer products that our daily lives depend on, have become indispensable materials essential for modern life and the global economy. At the same time, currently unsustainable practices in the production and disposal of plastics continue to deplete our finite natural resources and create severe worldwide environmental consequences. In the search for feasible solutions to these issues, significant recent advances have been made in developing chemically recyclable plastics, which allow for recovery of the building-block chemicals via depolymerization, for repolymerization to virgin-quality plastics, or for creative repurposing into value-added materials. Among such recyclable plastics, polyesters derived from renewable cyclic esters possess real potential to meet these challenges. Hence, this review highlights the plastics derived from common four-, five-, six-, seven-, and eight-membered cyclic esters by covering synthetic strategies, material properties, and, particularly, chemical recyclability. Such studies have culminated a recent discovery of infinitely recyclable plastics with properties of common plastics.

INTRODUCTION

Since the commercial development of plastics in the 1930s and 1940s, they are now the most widely used man-made substances—ranging from food packaging, clothing, medical supplies, and construction materials to space exploration—thanks to their versatility in material properties, such as resistance to corrosion, light weight, high strength, transparency, low toxicity, and durability. The production of plastics is continuously increasing each year; specifically, plastics production has increased 20-fold since the 1960s, having reached 335 million tons in 2016, and is expected to rack up to over 1.12 billion tons in 2050.[1] By then, the plastics sector will account for ~20% of total oil consumption and 15% of the global annual carbon budget, considering the fact that over 90% of plastics produced currently are derived from finite fossil feedstocks.[1] Moreover, durability, one of plastic's greatest assets, also resulted in the tremendous growth of disposed plastics (and other types of polymers) waste, which has brought about severe environmental consequences.[2–5] A significant portion of the plastics produced enters and accumulates in marine ecosystems and may persist for hundreds of years,[6–9] causing the entanglement of wildlife.[10–12] If no changes are made, by 2050 the ocean is expected to contain more plastics than fish (by weight).[1]

Tackling these existing plastic waste problems requires efforts and greater cooperation by all the key players, from plastics producers to recyclers, retailers, and consumers.[13] At present, recycling and reuse is a direct way to reduce greenhouse gas emissions and fossil fuel use as well as minimize landfill deposition. Current recycling processes rely mainly on primary recycling (termed closed-loop recycling, reprocessing an uncontaminated, single plastic to give a product used for the same purpose as the original plastic) and secondary (mechanical) recycling (often called

The Bigger Picture

The development of biorenewable and chemically recyclable plastics holds real potential to not only preserve natural resources but also solve the end-of-life issue of plastic waste. However, materializing such potential and ultimately establishing a circular plastics economy requires that three challenges be met: energy cost, depolymerization selectivity, and depolymerizability and performance tradeoffs. Recent advances made in this field, especially the discovery of infinitely recyclable plastics, have yielded feasible solutions and design principles. Future directions will focus on designing monomer and polymer structures that deliver properties and performances for tailored application needs while maintaining complete recyclability and catalyst structures and integrated processes with high (de) polymerization activity, selectivity, and efficiency, ultimately solving the severe worldwide environmental problems created by non-recyclable plastics production and disposal.

"downcycling," affording lower-in-value materials with different uses from the original material).[14] However, the recovery rate of plastic waste for recycling is rather low, only 9.5% in the United States in 2014,[15] indicating that there is much room for improvement and highlighting the potential of the plastic recycling industry to contribute significantly to the global economy.[16] Even with current practices of recycling, it is estimated that about 95% of plastic materials value ($80–$120 billion) annually is lost to the economy after a single use.[1] Moreover, both primary and secondary recycling involve sorting, grounding, washing, and extruding, which cause varying degrees of polymer degradation, resulting in the limited number of reprocessing cycles of polymers. Ultimately, most polymers are landfilled or incinerated, which causes environmental pollution again.

Exploring feasible strategies for more sustainable future plastics production and disposal, the development of biodegradable polymers provides part of the solution, but no building-block chemicals are typically recovered, and degraded materials could create new or unintended environmental consequences, especially in the oceans. Industrial mechanical recycling always suffers from a significant quality loss (thus downcycling). It is argued that the development of biorenewable and chemically recyclable polymers offers a feasible solution to preserve our finite natural resources and solve the end-of-life issue of plastic waste. The chemically recyclable polymers are capable of being returned to the corresponding monomers in a depolymerization process for repolymerization to virgin-quality polymers or being converted to higher-value or value-added materials in an upcycling or repurposing process.[17] Thus, this depolymerization and/or upcycling process, or chemical recycling process, can also reduce the demand for finite raw materials and minimize the negative impact on the environment.[18–20] This seemingly ideal strategy has motivated the research on the exploration of chemically recyclable polymers and also the mild processes for the catalytic conversion of the recyclable polymers to monomers or new polymers, namely chemolysis (by depolymerizing or decomposing the polymer in the presence of a chemical catalyst, typically needing relatively low temperature or even ambient temperature). However, the reasons that limit the chemical recycling approach are mainly the high energy costs, especially in the case of thermolysis (by heating the polymer to its decomposition temperature in the absence of oxygen, typically requiring relatively high temperature), the often poor selectivity involved in chemical recycling processes and circular monomer-polymer-monomer cycles, as well as tradeoffs between polymers' depolymerizability and properties.[21,22] Therefore, to advance plastic recycling practices, improving chemical recycling selectivity and efficiency through monomer and polymer design and catalyst development, minimizing the need for sorting through compatibilizer design, and expanding recycling beyond thermoplastics represent some of the key ongoing and future research directions.

Several recent reviews have focused on sustainable polymers from renewable resources, but not the degradability and/or recyclability of such renewable polymers.[23–32] Noteworthy here is that polymers derived from biorenewable resources, commonly referred to as renewable polymers, bio-based polymers, or even sustainable polymers in the literature, are not necessarily sustainable or degradable, whereas degradable polymers are not necessarily recyclable. For example, 100% bio-based polythene (bio-PE) and bio-based polyethylene terephthalate (bio-PET) are not biodegradable.[33] Some reviews have summarized recent progress in chemical recycling of plastics, including the upcycling process and depolymerization process, such as commercial plastics (e.g., PET, PE, isotactic polypropylene [*i*PP], polyvinyl chloride [PVC], polystyrene [PS], and polycarbonate [PC]), as well as novel

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polymers developed recently (such as poly(1,4-dioxan-2-one), poly(*o*-phthalaldehyde), and polyesters based on γ-butyrolactone [γ-BL] or α-methylene-γ-butyrolactone [MBL], and CO_2-based polycarbonates).[16–18,20,34] This review will highlight the plastics derived from the ring-opening polymerization (ROP) of the most common four-, five-, six-, seven-, and eight-membered renewable cyclic esters, covering their synthetic strategies, materials properties, and chemical recyclability. The highlighted research results will show that the polymers based on the five-membered lactones belong to a special class of plastics possessing complete, repeatable (in principle, "infinite") chemical recyclability.

FOUR- AND EIGHT-MEMBERED CYCLIC ESTERS

β-Butyrolactone

Poly(3-hydroxybutyrate) (P3HB) is the most common, and thus most extensively studied, member of poly(hydroxyalkanoate)s (PHAs) that are naturally produced by bacteria, algae, and other living microorganisms from biorenewable resources such as carbohydrates and fats, and are accumulated intracellularly and function as carbon and energy store reserves.[35] PHAs are a unique class of commercially implemented bio-based biodegradable and/or biocompatible polyesters, which can be used in biomedical, pharmaceutical, and packaging applications because of their biodegradability.[36] Natural PHAs are isotactic polymers containing a chiral site in each repeating molecular unit, and their properties span a wide range depending on the length of the side aliphatic chain on β-carbon. For example, PHAs with a short side chain are very stiff and brittle, whereas they become more flexible by increasing the length of the side chain. Among these natural PHAs, the bacterial poly[(*R*)-3-hydroxybutyrate], P[(*R*)-3HB], is a perfectly stereoregular, pure isotactic crystalline thermoplastic material;[37,38] it exhibits thermal and mechanical properties comparable with those of high-performance isotactic polypropylene (*it*-PP) and is thus considered as an attractive biodegradable alternative to petroleum-based polyolefins, especially *it*-PP. However, owing to the complexity of extraction processes, high production costs, the challenges in processing, and limited production volumes by microorganisms, the PHAs market is still poorly developed and renders them impractical in many commodity thermoplastics applications.

To provide a more economical alternative to the bacteria-based production of PHAs, the chemical synthesis of PHAs via ROP of cyclic esters, a process typically catalyzed by a metal-based or organic catalyst, has been developed and has attracted much attention. In principle, the chemical synthesis route could produce PHAs with different structures or stereoregularities, thus tailored materials properties, by judiciously designing different monomer and catalyst structures. In this context, an efficient synthetic route to P3HB through the metal-catalyzed ROP of β-butyrolactone (β-BL) has been developed,[39–43] where the relief of ring strain of this highly strained four-membered lactone is the driving force for the polymerization. A still largely unmet challenge in the area of ROP of β-BL is the development of stereoselective ROP of the cost-effective racemic monomer, *rac*-β-BL, rather than the much more expensive enantiopure (*R*)-β-BL, for the production of isotactic P3HB. Extensive research has been devoted to the development of suitable catalysts that can render the stereoselective ROP of *rac*-β-BL since the 1960s, but only a few of the catalyst systems allow the control over the polymerization in terms of the stereomicrostructure and molecular weight of the synthetic P3HB. To date, syndiotactic P3HB materials from being modestly syndiotactic ($P_r \sim 0.70$)[44,45] to highly syndiotactic (P_r up to 0.95)[46–48] have been achieved through the ROP of *rac*-β-BL using alkyltinoxides and discrete yttrium complexes supported by tetradentate, dianionic

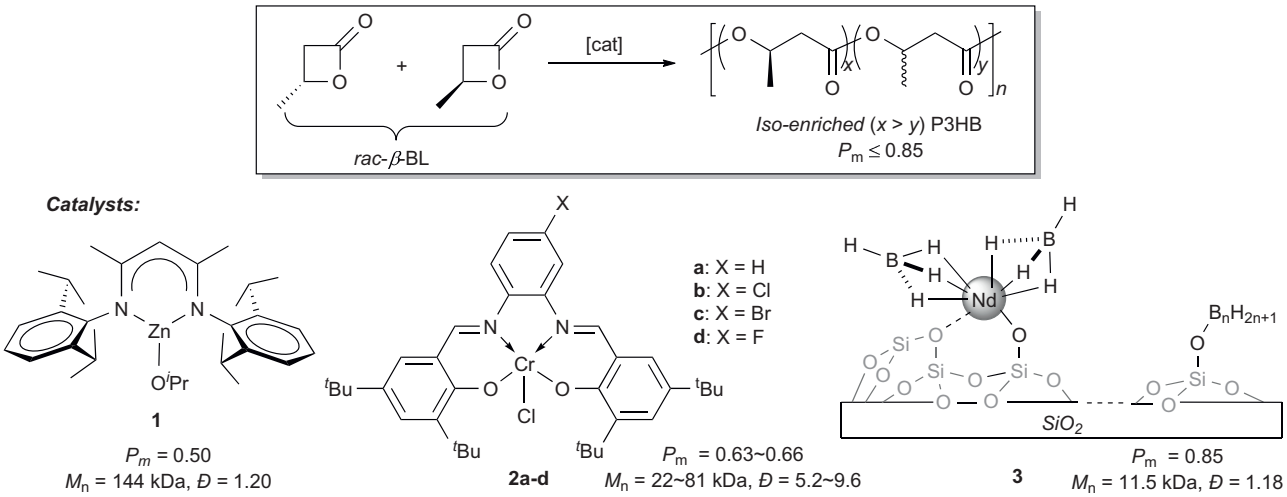


Figure 1. Chemical Synthesis Route via the ROP of *rac*-β-BL to Iso-enriched P3HB and Structures of Selected Metal Catalysts

alkoxy-amino-bis(phenolate) [O^-,*N*,*O*,O^-] ligands, respectively. However, only isotactic-enriched P3HB materials with isotacticity $P_m \leq 0.85$ have been obtained from the ROP of *rac*-β-BL (Figure 1).

Isotactic P3HB by ROP of rac-β-BL

Marchessault and coworkers reported the ROP of *rac*-β-BL with an oligomeric alumoxane catalyst obtained by the reaction of $AlEt_3$ with H_2O, whose stereoregularity can be adjusted by the $AlEt_3/H_2O$ mole ratios.[49] The P3HB with the highest isotacticity of P_m = 0.78 was obtained, which was separated into a soluble, low-molecular-weight fraction and an insoluble, high-molecular-weight fraction (M_n = 21.4 kg/mol, dispersity [Đ] = 5.6, P_m = 0.85). Later, Schue and coworkers used a similar method for the ROP of *rac*-β-BL by isobutylaluminum (Al^iBu_3) or tetraisobutylaluminoxane (TIBAO) with water and obtained P3HB with P_m up to 0.79.[50] Wu and Lenz also utilized the catalyst-monomer adducts obtained from the reaction between 2 molar equiv of β-BL and either methylalumoxane (MAO) or isobutylalumoxane (IBAO) to initiate the ROP of *rac*-β-BL.[51] Both MAO-BL and IBAO-BL adducts were found to be much more active than either MAO or IBAO alone, but yielding crude P3HB with a low P_m value of only 0.65. After solvent fractionation, the P_m of the insoluble P3HB increased to >0.78. The chiral initiator, obtained from the *in situ* reaction of $ZnEt_2$ with (*R*)(−)-3,3-dimethyl-1,2-butanediol by Spassky, was found to preferentially incorporate (*R*)-β-BL with a low stereoselectivity ratio r_R of 1.6, yielding a mixture of P3HB products that were fractionated in methanol into soluble atactic and insoluble (~25%) isotactic ($P_m \sim 0.80$) fractions.[52] Overall, the above methods need extraction using suitable solvents to remove the atactic polymer, and additionally the activities are very low.

Coates and coworkers reported that a discrete β-diiminate zinc alkoxide initiator (**1**; Figure 1) promoted a controlled ROP of *rac*-β-BL with high polymerization rates to produce P3HB with high molecular weight, but the resulting P3HB is an atactic, amorphous material.[53] Rieger and coworkers examined the ROP of *rac*-β-BL by achiral chromium(III) salophen complexes **2a–2d** in bulk condition at 100°C and obtained isoenriched P3HB with P_m = 0.63–0.66, medium molecular weight (M_n = 22–81 kg/mol), high dispersity (Đ = 5.2–9.6), and modest melting-transition temperature (T_m = 116, 142°C).[54] Gauvin and colleagues grafted neodymium borohydrides ($Nd(BH_4)_3(THF)_3$) onto silica to afford catalytic materials containing well-identified

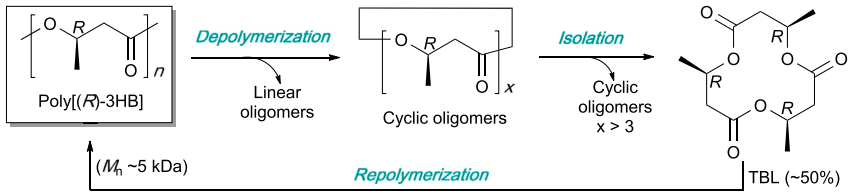


Figure 2. Chemical Recycling of P3HB via Depolymerization of Poly[(R)-3HB] to Cyclic Oligomers and Polymerization of the Cyclic Trimer to Low-Molecular-Weight Oligomers

bis(borohydride) surface species SiO_2-Nd (**3**), which polymerized *rac*-β-BL into P3HB with P_m up to 0.85, M_n = 11.5 kg/mol, and $Đ$ = 1.18.[55] This supported catalyst system exhibits the highest stereoselectivity for isoselective polymerization of *rac*-β-BL to date.

Overall, the current chemical synthesis of P3HB has so far been strictly limited to the ROP of the cyclic monomer of 3-hydroxybutyric acid (3HB), namely β-BL, which has not yet produced P3HB with high molecular weight and high isotacticity in a controlled manner.

Chemical Recycling of P3HB via a Cyclic Trimer

The ring-closing depolymerization of naturally produced poly[(*R*)-3HB] was developed to recover the cyclic trimer of 3HB, namely triolide of 3HB (TBL; Figure 2) with a yield of ~50%, by the Seebach[56] and Höcker[57] groups. Höcker and coworkers further investigated the catalyzed depolymerization of poly[(*R*)-3HB] in the melt and in solution.[57] In the melt, the catalyzed depolymerization yielded linear oligomers with ω-crotonate end groups and crotonic acid (CA) via an ester pyrolysis mechanism at 200°C–320°C independent of the catalyst used, while in solution cyclic oligomers (TBL as the main oligomer) were obtained via backbiting reactions in the presence of dibutyltin dimethoxide or *p*-toluenesulfonic acid as the catalyst. The TBL obtained by ring-closing depolymerization of P3HB can be polymerized in the melt with dibutyltin dimethoxide as initiator, resulting in poly[(*R*)-3HB] of low molecular weight (M_n = ~5 kg/mol, $Đ$ = 1.3–1.7).[57,58] However, both the TBL yield from the depolymerization of poly[(*R*)-3HB] and the M_n of the resulting poly[(*R*)-3HB] from the repolymerization of TBL in this P3HB chemical recycling scheme are too low to be practically useful.

Eight-Membered Cyclic Diolides

To address the above unmet challenge facing the chemical synthesis of isotactic P3HB, we recently developed a new route to P3HB via the ROP of a cyclic dimer of 3HB, namely eight-membered cyclic diolide (DL; Figure 3), and accomplished the synthesis of perfectly isotactic P3HB.[59] The design of this new strategy was inspired by the ingenious utilization of a cyclic dimer of L-lactic acid, namely L-lactide, which rendered the commercial production of high-molecular-weight, highly isotactic polylactide (PLA) as discussed below. Unlike β-BL, known to be carcinogenic (alkylating DNA), DL is benign and can be readily derived from biosourced dimethyl succinate.[60] Moreover, the significantly increased sterics present in DL relative to β-BL may bring about a higher degree of stereochemical control in the catalyzed ROP of DL, thereby potentially generating highly stereoregular P3HB materials.

Perfectly Isotactic P3HB by ROP of rac-DL

The ROP of *rac*-DL by $La[N(SiMe_3)_2]_3$ (**4**), discrete yttrium amido complexes **5** (**a**, R = ^{t}Bu; **b**, R = CMe_2Ph), and alkyl complex **6** supported by the tetradentate

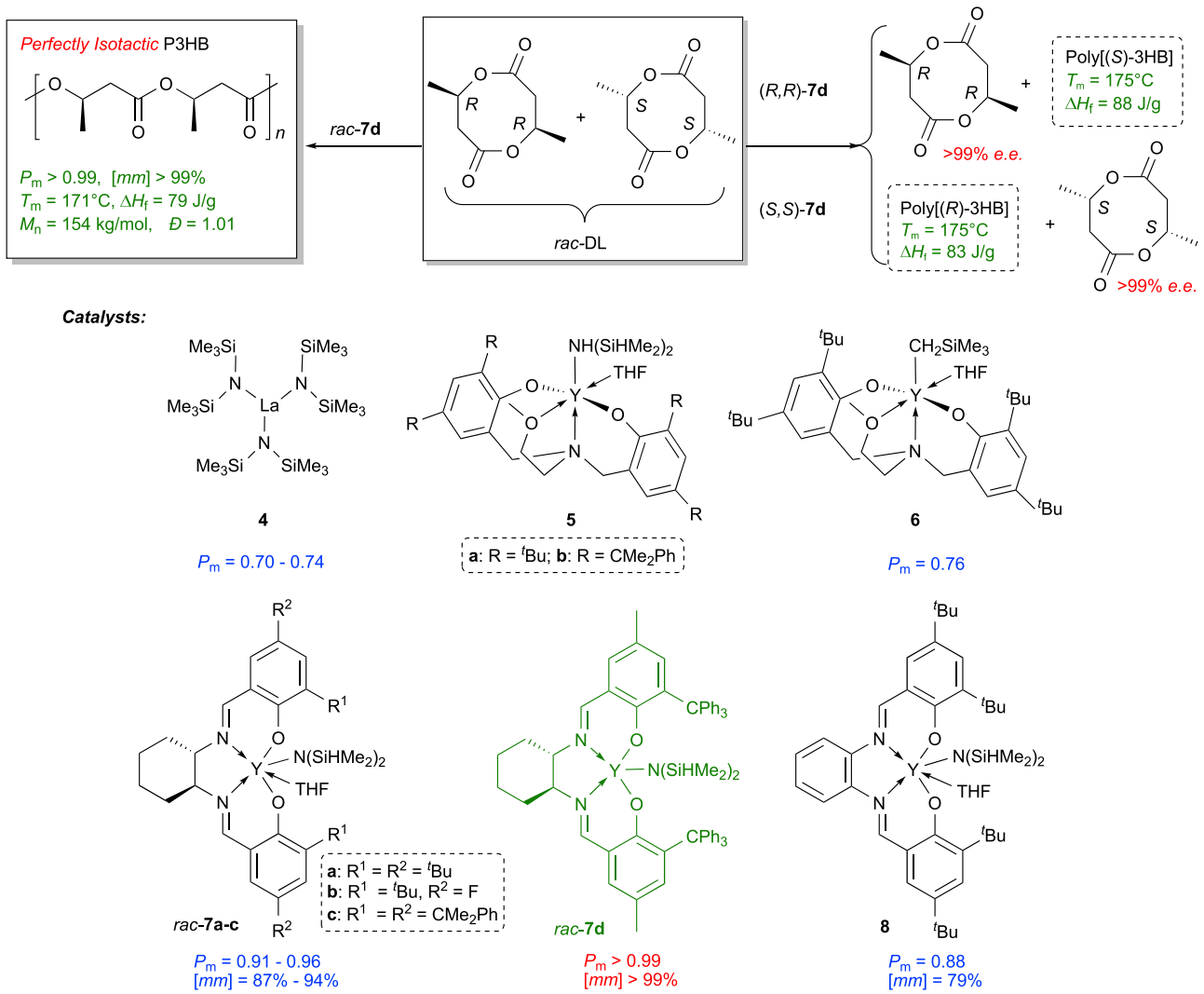


Figure 3. Chemical Synthesis Route via the ROP of *rac*-DL to Perfectly Isotactic P3HB and the Structures of Catalysts Employed for the Polymerization

[O^-,*N*,*O*,O^-] ligand in combination with benzoyl alcohol (BnOH) as an initiator, which have been shown to be effective for the ring-opening (co)polymerization of γ-BL,[61,62] MBL,[63] and/or the syndiospecific ROP of *rac*-β-BL,[46–48,64] exhibited moderate to low activities, producing isobiased amorphous P3HB. Considering the steric hindrance of *rac*-DL with the eight-membered-ring framework and the low activity and isoselectivity of also sterically encumbered catalysts **4**–**6** screened, the sterically more open yttrium racemic salen complexes *rac*-**7a**–**7d** were reasoned to be superior catalysts. Indeed, all the complexes **7a**–**7d** in the presence of BnOH can convert *rac*-DL completely into highly isotactic P3HB (P_m > 0.91) within minutes in a controlled manner; in particular, *rac*-**7d** produced perfectly isotactic P3HB with P_m > 0.99 and [*mm*] > 99% (*mm* is isotactic triad made up of two adjacent *meso* diads). These results further emphasize the critical effects of the ligand sterics on the polymerization stereoselectivity. Furthermore, the M_n of the resulting P3HB by *rac*-**7d** reached a practically useful range, up to 154 kg/mol with a low dispersity index of $Đ$ = 1.01 (versus a typical $Đ$ value of ~2.0 for bacterial P3HB); this semi-crystalline material also exhibits a high T_m of 171°C. The salph-based complex **8**

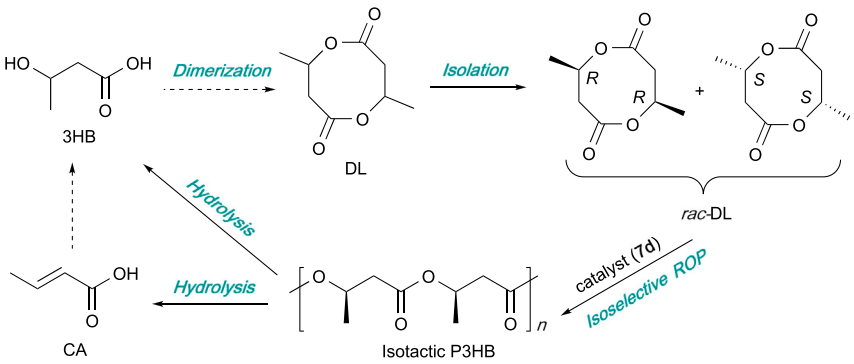


Figure 4. Proposed Chemical Recycling of P3HB via Dimerization of 3HB to Cyclic Dimer DL, Followed by Isoselective ROP of *rac*-DL to Isotactic P3HB and Hydrolysis of P3HB Back to 3HB

was also used to probe the effects of the geometry of the backbone diimine linker, which afforded P3HB with a considerably lower isotacticity than salcy-based analog complex **7a**.

With an enantiomeric catalyst (*R*,*R*)-**7d** or (*S*,*S*)-**7d**, kinetic resolution polymerizations of *rac*-DL automatically stops at 50% conversion and yields enantiopure (*R*,*R*)-DL or (*S*,*S*)-DL with >99% enantiomeric excess (ee) and the corresponding poly[(*S*)-3HB] or poly[(*R*)-3HB] with high T_m (175°C) and crystallinity, which is essentially identical to that of the commercial natural poly[(*R*)-3HB]. Up until now, this is the only report to have successfully obtained poly[(*S*)-3HB], poly[(*R*)-3HB], or perfectly isotactic P3HB through a chemical synthesis method, which should represent a paradigm shift in the chemical synthesis of P3HB and open up a plethora of opportunities for discovering new catalysts, materials, and processes in the ROP of *rac*-DL and other diastereomers of 3HB cyclic dimers or trimers.

Chemical Recycling of P3HB via a Cyclic Dimer

A proposed new route for chemical recycling of P3HB is shown in Figure 4, in which isolation and isoselective ROP of *rac*-DL can be realized by our recently reported approach[59] as described above. For abiotic hydrolysis of poly[(*R*)-3HB], Yu and coworkers investigated the hydrolysis process in acid and base media by monitoring the formation of two monomeric hydrolytic products, 3HB and CA.[65] Both 3HB and CA were detected as the major hydrolytic products from alkaline hydrolysis, but poly[(*R*)-3HB] was tolerant to hydrolysis under moderate acid conditions. However, poly[(*R*)-3HB] was completely decomposed into the two monomeric products with 2% of 3HB and 90% of CA in concentrated acid solutions, during which dehydration of 3HB to CA occurred. Accumulation of two monomeric products, 3HB and CA, was in agreement with the mass loss of P3HB films, indicating a sequential degradation from the ends of P3HB polymers and oligomers. The mass ratio of CA/3HB increased with temperature because of the different activity energy. Moreover, crotonate was formed neither via 3HB dehydration after hydrolysis nor via the dehydration of 3-hydroxyl groups before hydrolysis, but most likely via a transient structure of six-membered ring involving two neighboring 3HB units. Therefore, more effort should be devoted to preparing DL in high yields via dimerization of 3HB, and at the same time more selective hydrolysis of P3HB to 3HB should be developed. Once these two fronts have been accomplished, this proposed new route would become a preferred method for chemical recycling of P3HB.

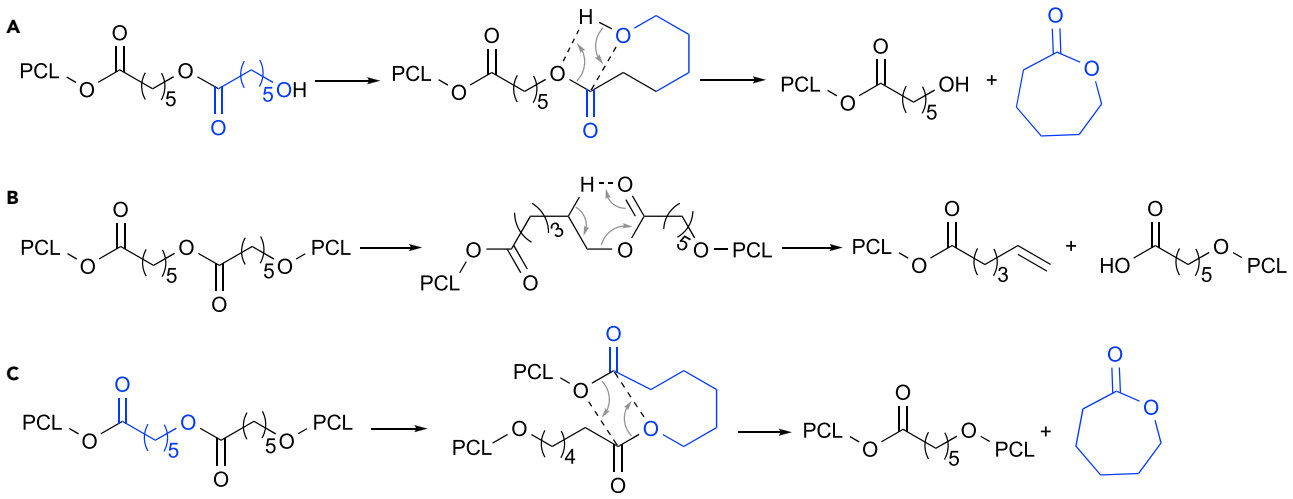


Figure 5. Proposed Mechanisms for Thermal Degradation of PCL

(A) Unzipping depolymerization process.

(B) Random chain scission via *cis*-elimination reaction.

(C) Intramolecular transesterification of PCL.

SEVEN-MEMBERED CYCLIC ESTERS

ε-Caprolactone

ε-Caprolactone (ε-CL) is considered as a fossil-based monomer, produced industrially by Baeyer-Villliger oxidation of cyclohexanone; alternatively, it can also be prepared from sugar-derived 5-hydroxymethylfurfural (HMF).[66] Furthermore, the corresponding semicrystalline polycaprolactone (PCL) from ROP of ε-CL with a low glass-transition temperature (T_g) of about −60°C and T_m of about 60°C is an important class of biodegradable and biocompatible polymer that can be easily degraded by aerobic and anaerobic microorganisms. PCL displays the rare property of being miscible with many other polymers, for example, poly(vinyl chloride), poly(styrene-acrylonitrile), poly(acrylonitrile butadiene styrene), poly(bisphenol-A) and other polycarbonates, nitrocellulose, and cellulose butyrate; PCL is also mechanically compatible with other polymers such as polyethylene, polypropylene, natural rubber, poly(vinyl acetate), and poly(ethylene-propylene) rubber.[67] Therefore, different catalytic systems (enzymatic, organic, and metal catalyst systems) and a large number of catalysts, spanning virtually the entire periodic table, have been developed in the ROP of ε-CL.[64,67–74]

The thermal degradation of PCL has been investigated by several groups, which is important for processing, application, and recycling of polymers, although there is no consistency in the mechanism.[75–82] Generally two mechanisms have been proposed: unzipping depolymerization process of PCL that proceeds by backbiting reaction from the hydroxyl end group onto the ester function of the last monomeric unit to give ε-CL (Figure 5A), and random chain scission via *cis*-elimination reaction to result in 6-hydroxyhexanoic acid and 5-hexenoic acid as the α- and ω-chain end, respectively (Figure 5B). Dubois and coworkers believed that PCL decomposes by a two-step mechanism in bulk pyrolysis.[76] The first process (starting at lower temperature of ca. 300°C) implies a statistical rupture of the polyester chains via ester pyrolysis reaction, wherein 5-hexenoic acid is one of the products, obtained by two *cis*-elimination reactions occurring with neighboring ester functions. The second step (at ca. 430°C) leads to the formation of ε-CL as a result of an unzipping depolymerization process. Yamashita and coworkers proposed a single-step mechanism in

which PCL degrades by pure unzipping of monomer to produce ε-CL almost exclusively in isothermal degradation experiments at 280°C.[77] Another mechanism that has been suggested by Madras and coworkers is that PCL degrades by both random chain scission and unzipping of monomer simultaneously on non-isothermal heating, and by unzipping of monomer from the hydroxyl end of the chain end during isothermal heating at 320°C or 340°C.[78]

Madras and coworkers also investigated thermal degradation of PCL in solution, which degrades through random chain scission and shows lower degradation temperatures (170°C–245°C) compared with bulk pyrolytic degradation.[79] These authors also studied the degradation of PCL in subcritical and supercritical toluene, ethylbenzene, *o*-xylene, or benzene from 250°C to 375°C at 50 bar.[82] PCL degrades by random chain scission in subcritical conditions (250°C–300°C) and by chain-end scission (325°C–375°C) to give ε-CL in supercritical conditions in toluene. The effects of chain-end structure and residual metal compounds on thermal degradation of PCL were investigated by Abe et al.[80] From both the isothermal and non-isothermal experiments, the thermal degradation of PCL samples containing high amounts of residual zinc compounds from synthesis process revealed the selective unzipping depolymerization step below 300°C producing ε-CL exclusively. In contrast, the thermal degradation of metal-free PCL samples occurred at temperatures above 300°C regardless of the chain-end structure, giving rise to the formation of cyclic monomer and oligomers of ε-CL. In addition, 5-hexenoic acid units were detected in the residual polymer samples as main ω-chain end. These results suggest that the dominant reaction of thermal degradation for PCL at a temperature above 300°C is a combination of the random chain scission via a *cis*-elimination reaction (Figure 5B) and the cyclic rupture via intramolecular transesterification of PCL chains (Figure 5C). The same authors also explored the effect of different metal chlorides (such as NaCl, $CaCl_2$, $ZnCl_2$, $SnCl_2$, and $AlCl_3$) on the thermal degradation of PCL.[81] Zn, Sn, and Al chlorides induced the thermal degradation of PCL at a lower temperature range by catalyzing the selective unzipping depolymerization from ω-hydroxyl chain end, while the presence of Na and Ca chlorides hardly induced any shift of degradation temperature. Overall, these investigations showed that, compared with simple thermolysis, metal-catalyzed degradation (or chemolysis) proceeds at a lower temperature in a more selective (unzipping) depolymerization fashion to yield ε-CL, thus demonstrating the chemical recyclability of PCL using the chemolysis approach.

ε-Caprolactam

Although ε-caprolactam (ε-CLM) is not a cyclic ester, it is intimately related to its immediate precursor, ε-CL. The ROP of ε-CLM is an important commercial route to produce poly(ε-caprolactam), commercially known as nylon-6, which is the most produced and commercially available polyamide; it exhibits high strength, good fatigue resistance, moderate water absorption, and good resistance to most common solvents and weak acids.[83] The wide production of nylon-6 makes the development of chemical recycling necessary. In this context, Kamimura and Yamamoto explored an effective depolymerization pathway in ionic liquids to chemically recycle nylon-6 back to its monomer ε-CLM in good yields (Figure 6).[84] The authors found that no depolymerization took place from 6-nylon by simply heating in glycolic solvents, while treating nylon-6 in an ionic liquid afforded ε-CLM in yields of 77%–86% at 300°C in the presence of DMAP (*N*,*N*-dimethylaminopyridine) as a catalyst. The temperature affected the depolymerization significantly: in PP13-TFSI (Figure 6), 300°C is the optimum temperature, achieving the ε-CLM yield of 86%, and a much lower yield of 7% was obtained at 270°C, whereas some decomposition of the ionic liquid

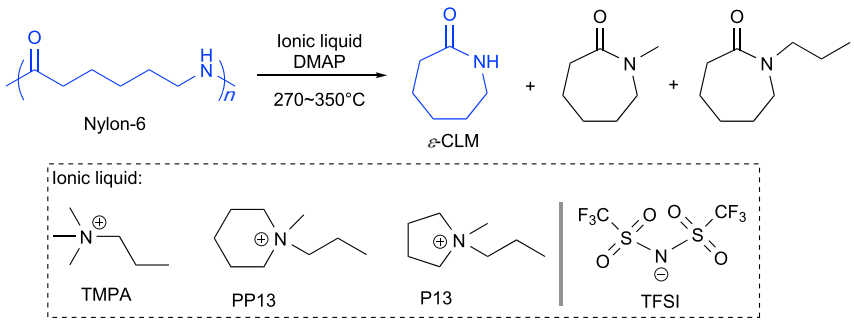


Figure 6. Depolymerization of Nylon-6 in Ionic Liquid to Recover ε-CLM

took place when treated at 330°C or higher. Moreover, by-products *N*-methyl and *N*-propyl lactams were also produced at 330°C or higher. The ionic liquid can be used repeatedly at least five times without significant decomposition. It should be noted that the recovered monomer was collected by direct distillation of the reaction mixture without a need for any special high-pressure apparatus.

2,3-Dihydro-5H-1,4-benzodioxepin-5-one

MacDonald and Shaver reported the ROP of 2,3-dihydro-5H-1,4-benzodioxepin-5-one (2,3-DHB) with aluminum salen catalyst **9**/BnOH or organocatalyst triazabicyclodecene (TBD), affording the corresponding polyester (P2HEB) that contained both aromatic and aliphatic linkages in the polymer backbone (Figure 7).[85] Higher conversions were observed at lower temperatures and/or higher initial monomer concentration, prompting an investigation into reversible polymerization and depolymerization of P2HEB, the most interesting feature of this polymerization system. A one-pot reaction was performed with an initial monomer concentration of 4.1 M to achieve monomer (2,3-DHB) conversion of 82% after 6 hr at 60°C; addition of toluene gave an apparent [2,3-DHB] concentration of 0.2 M, resulting in a depolymerization to give a mixture with 2,3-DHB/P2HEB = 94:6. Reconcentration of the reaction *in vacuo* to give an apparent $[2,3\text{-DHB}]_0$ of 4.1 M resulted in 84% monomer conversion to form P2HEB again after heating at 60°C for 6 hr. Importantly, no degradation products were produced, providing a clean and selective route to recycle the polymer back to monomer.

SIX-MEMBERED CYCLIC ESTERS

Lactide

Lactide (LA) is the cyclic dimer of lactic acid, obtained from renewable resources, such as corn starch, cassava roots, or sugarcane. Polylactide, or poly(lactic acid) (PLA), is a biodegradable and biocompatible thermoplastic aliphatic polyester with rigidity and clarity similar to those of PS and PET.[86] PLA can be prepared by direct polycondensation of lactic acid in the presence of a catalyst at reduced pressure, but usually producing low-molecular-weight, brittle, glassy PLA, as a result of the formation of water as the by-product that is difficult to be removed completely from the highly viscous reaction mixture. However, high-molecular-weight PLA can be obtained by the reaction of hydroxyl or carboxyl end groups of low-molecular-weight PLA with chain-coupling agents, bi-/multi-functional hydroxyl compounds (such as 2-butene-1,4-diol, glycerol, and 1,4-butanediol), or carboxylic acids (such as maleic, succinic, adipic, and itaconic acid).[87] Additionally, a one-step azeotropic condensation polymerization of lactic acid can also yield high-molecular-weight polymer, by which approach water is removed azeotropically whereas organic solvent is dried and recycled back in the reaction, and thus lactic acid is polycondensed

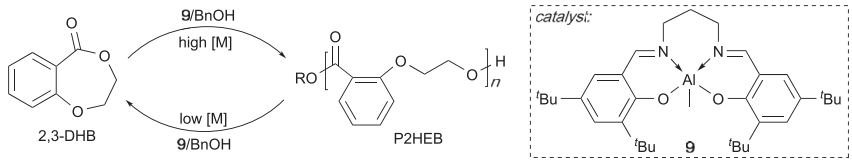


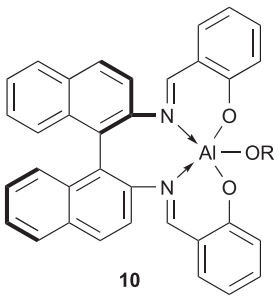
Figure 7. Polymerization-Depolymerization Cycle Realized by Adjusting Initial 2.3-DHB Concentration in the Presence of Salen-Supported Aluminum Complex

directly into a polymer with a high molar mass.[88–90] Solid-state polymerization is another process to prepare high-molecular-weight PLA, which is carried out by heating a semicrystalline, solid polymer with relatively low molecular weight at temperatures above T_g yet below T_m with simultaneous removal of by-products from the surface of the material either under reduced pressure or with a carrier, such as blowing inert gas.[91,92] This polymerization method also shows potential application in upcycling of PLA with low molecular weight, through which the resulting high-molecular-weight PLA can be reused.

Crystalline PLA by Stereoselective ROP of rac-LA

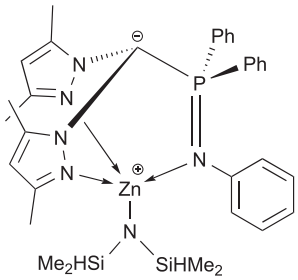
Thanks to the development of ROP of LA that proceeds through a chain-growth polymerization mechanism, high-molecular-weight PLA can be produced in a short time period and more controlled manner, which is usually employed for preparing PLA materials with a high degree of stereoregularity.[93] LA possesses two stereogenic centers, thus existing in three stereoisomers, (*S*,*S*)-lactide (L-LA), (*R*,*R*)-lactide (D-LA), and *meso*-lactide (*meso*-LA). Currently, crystalline isotactic PLA (*it*-PLA) is produced by either ROP of L-LA to isotactic poly(L-lactide) (PLLA) or the stereoselective ROP of *rac*-LA. Noteworthy here is that stereocomplexed PLA (*sc*-PLA) can be formed by an equal mixture of PLLA and poly(D-lactide) (PDLA), possessing a considerably higher T_m of ~230°C than *it*-PLA (typically ~170°C–180°C).[94] An alternative route to form *sc*-PLA or stereoblock PLA is the ROP of *rac*-LA with an isoselective catalyst. Whereas the ROP of *meso*-LA can only produce atactic, amorphous heterotactic, or syndiotactic PLA (*st*-PLA), the T_m of crystalline *st*-PLA is only ~150°C,[95] which is about 20°C–30°C lower than that of *it*-PLA.

Although much effort has been made on the ROP of *rac*-LA to prepare stereocomplex or stereoblock PLA using an isoselective catalyst, there are remarkably few isoselective metal catalysts to produce PLA with isoselectivity $P_m \geq 0.85$, above which the T_m of the resulting PLA will be higher than that of PLLA (170°C–180°C). Some selected metal catalysts with high isoselectivity are listed in Figure 8. Spassky first reported a one-step synthesis of gradient PDLA-PLLA with T_m = 187°C from the ROP of *rac*-LA using aluminum complex (*R*)-**10** (R = Me).[96] Baker, Smith, Coates, and their coworkers then found that *rac*-**10** (R = ^{i}Pr) can initiate the polymerization of *rac*-LA more efficiently than (*R*)-**10** at 70°C, giving a multiblock stereocopolymer PLA [(PLLA-*b*-PDLA)$_n$] material with T_m = 179°C–191°C.[97,98] Achiral heteroscorpionate zwitterionic zinc complex **11**,[99] chiral zinc amido-oxazolinate complex **12**,[100] and Zr(IV) 2,2′-bipyrrolidine-salan derived complex **13**[101] can produce isotactically enriched PLA with P_m = 0.85–0.91 at room temperature. Potassium complexes **14** and **15** with 18-crown-6 as an auxiliary ligand can catalyze the ROP of *rac*-LA to yield PLA with a P_m of 0.86–0.88 at a low temperature of −60°C to −70°C.[102,103] Long and Williams reported phosphasalen lutetium ethoxide initiator **16**, which shows a P_m value of 0.82 at 25°C, moving to 0.89 at −16°C.[104] Yttrium catalyst **17**, stabilized by an achiral bis(phenolate) ether ligand, can induce highly isoselective polymerization (P_m = 0.90) of *rac*-LA to give stereoblock isotactic PLA with a T_m of 186°C;[105]



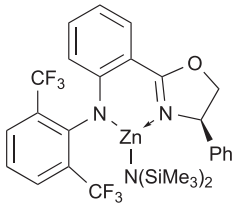
10

T_m = 179 ~ 191°C



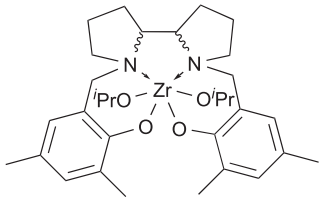
11

P_m = 0.85, T = 30°C
M_n = 96.6 kDa, $Đ$ = 1.49



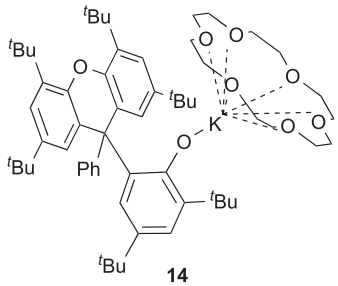
12

P_m = 0.91, T = 23°C
M_n = 52.2 kDa, $Đ$ = 1.32



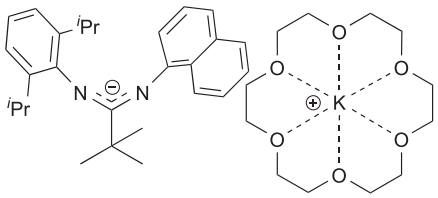
13

P_m = 0.86, T = 20°C
M_n = 16.5 kDa, $Đ$ = 1.05



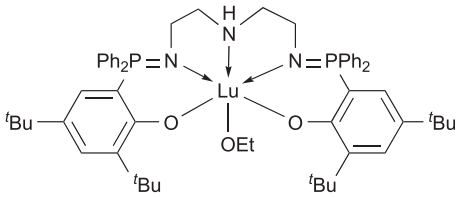
14

P_m = 0.86, T = -60°C
M_n = 6.1 kDa, $Đ$ = 1.06



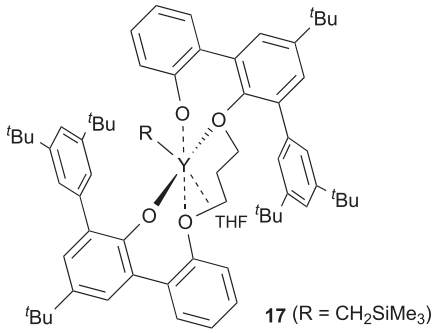
15

P_m = 0.88, T = -70°C
M_n = 117.7 kDa, $Đ$ = 1.14



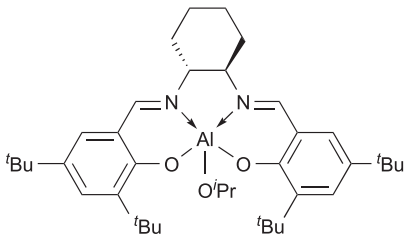
16

P_m = 0.89, T = -16°C
M_n = 46.6 kDa, $Đ$ = 1.01



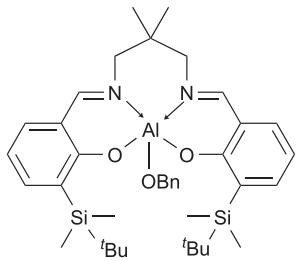
17 (R = CH_2SiMe_3)

P_m = 0.90, T = -15°C
M_n = 24.1 kDa, $Đ$ = 1.27



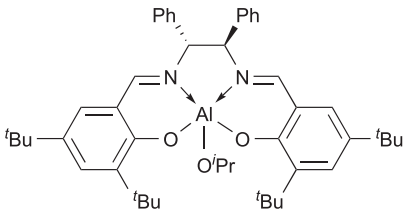
18

P_m = 0.93, T = 70°C
M_n = 7.7 kDa, $Đ$ = 1.06



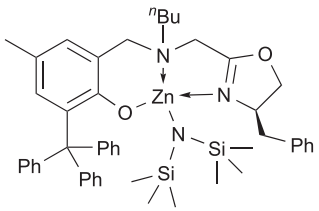
19

P_m = 0.98, T = 70°C
M_n = 43.9 kDa, $Đ$ = 1.09



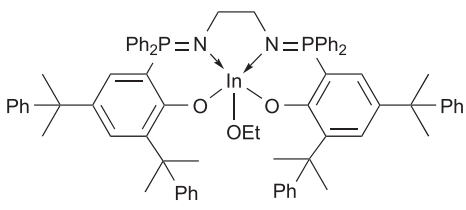
20

P_m = 0.90, T = 90°C
M_n = 5.3 kDa, $Đ$ = 1.05



21

P_m = 0.93, T = -40°C
M_n = 20.5 kDa, $Đ$ = 1.07



22

P_m = 0.92, T = -15°C
M_n = 69.2 kDa, $Đ$ = 1.14

Figure 8. Selected Isoselective Metal Catalysts for the ROP of *rac*-LA to Crystalline PLA

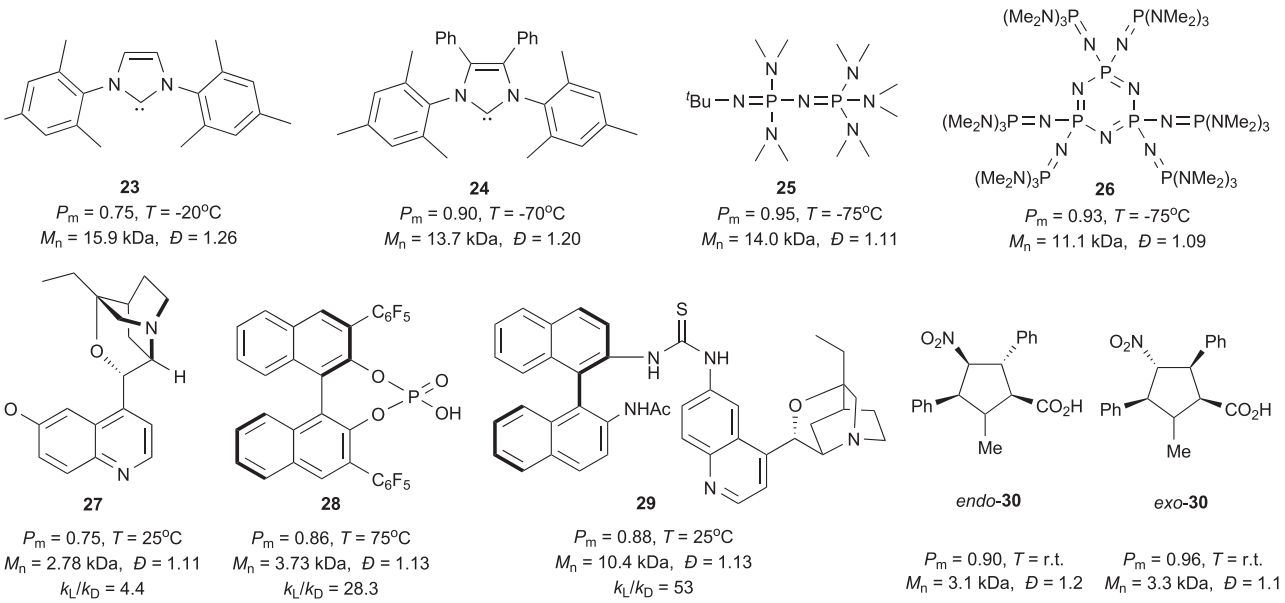


Figure 9. Selected Organocatalysts for the Stereoselective ROP of *rac*-LA

kinetic studies revealed that chain-end chirality differentiates an enantiomer with the same chiral sense from one that has the opposite chiral sense, and the monomer with the same chiral sense preferentially enters the reaction site for the propagation reaction. To date, salen-based aluminum complexes **18**–**20** exhibit the best isoselectivity at higher temperature of 70°C or 90°C.[106–108] Especially complex **19** reported by Nomura et al. shows a P_m of 0.98, and the T_m of the resulting stereoblock PLA up to 210°C was also observed;[107] the exceptional stereoselectivity of this achiral complex can be attributed to the two highly steric demanding substituents, $SiMe_2{}^tBu$ installed at the 3-positions of the salicylidene moieties, which enhances the chiral chain-end-chiral monomer stereodifferentiation in this chain-end control mechanism. Recently, Ma and coworkers reported a highly isoselective and active ROP of *rac*-LA with P_m up to 0.93 by zinc complex **21** bearing an oxazolinyl/benzoxazolyl-based aminophenolate ligand via a chain-end control mechanism, regardless of the existence of a chiral group within the ligand framework.[109] Indium phosphasalen catalyst **22** designed by Williams and coworkers shows very good performance on the ROP of *rac*-LA, yielding polymers with a strong isotactic bias (P_m = 0.87 at 25°C; P_m = 0.92 at −15°C) in a low loading of catalyst (0.2 mol %).[110]

The emerging organopolymerization of LA offers a metal-free alternative synthesis of PLA products without any residual metal contaminates, but there are even fewer organocatalysts reported for stereoselective or kinetic resolution ROP of *rac*-LA (Figure 9). Tolman and coworkers reported the stereoselective organopolymerization of *rac*-LA achieved at −20°C in dichloromethane by *N*-heterocyclic carbene (NHC) **23**, resulting in the formation of isotactic-enriched PLA with P_m = 0.75.[111] Hedrick and coworkers then demonstrated that sterically encumbered NHC **24** produced PLA with higher isotacticity of P_m = 0.90 (versus 0.83 by NHC **23**) at −70°C;[112] they attributed the isoselectivity to the bulky phenyl groups at the back of **24** that can presumably influence the steric hindrance around the catalytic site and thus enhance the stereoselectivity. Phosphazene superbase P_2-*t*-Bu (**25**) was found by Wade and coworkers to exhibit excellent stereocontrol (P_m = 0.95) for the ROP of *rac*-LA at −75°C, thanks to its high basicity and steric hindrance.[113] Very recently, Li and

coworkers reported that cyclic trimeric phosphazene base **26** catalyzes stereoselective ROP of *rac*-LA to produce isotactic stereoblock PLA with P_m up to 0.93 at −75°C via a chain-end control mechanism.[114] The kinetic studies reveal a faster rate for the ROP of L-LA as compared with *rac*-LA under the same conditions. We utilized cinchona alkaloids as organocatalysts for the ROP of LA and reported the first successful kinetic resolution polymerization of *rac*-LA by an organocatalyst (**27**).[115] The ROP of *rac*-LA by **27**/alcohol affords crystalline isotactic-rich, stereogradient PLA (P_m = 0.75) that exhibits multiple T_ms as a result of a partial kinetic resolution polymerization that preferentially polymerizes L-LA and kinetically resolves D-LA (k_L/k_D = 4.4). Chiral phosphoric acid **28** was shown to exhibit a high enantioselectivity for the ROP of *rac*-LA at much higher temperature of 75°C.[116] During this polymerization, D-LA is preferentially polymerized via kinetic resolution with the maximum selectivity factor k_L/k_D of 28.3; this high k_L/k_D value can be attributed to selective dual activation of the monomer and chain end by the bifunctional chiral phosphoric acid catalyst. Subsequently, we designed and synthesized highly enantioselective bifunctional chiral organic catalyst **29**, which incorporates three key elements (β-isocupreidine core, thiourea functionality, and chiral BINAM) into a single organic catalyst molecule.[117] In the presence of catalyst **29**, *rac*-LA is kinetically polymerized into PLLA with P_m = 0.88 at 25°C (P_m = 0.94 at −75°C); when the polymerization was stopped at 50.6% monomer conversion, L-LA was selectively polymerized with a high stereoselectivity k_L/k_D of 53, and optically resolved D-LA had a high ee of 91%. The densely substituted amino acids, *endo*-**30** and *exo*-**30**, developed by Cossío and coworkers, combined with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as the co-catalyst, show the ability to produce isotactic-enriched PLA with a P_m > 0.90 at room temperature; *exo*-**30** preferentially polymerized L-LA, whereas *endo*-**30** preferred D-LA as the substrate.[118] Hence, by switching from the *endo* to the *exo* configuration in unnatural densely substituted proline **30**, the chirality of the catalyst is transferred efficiently to the polymer, thus obtaining a different stereochemical outcome.

Overall, the metal-based catalysts are still dominant and have more examples for effecting stereoselective ROP of *rac*-LA relative to organocatalysts. Furthermore, most organocatalysts need much lower temperatures to achieve high isoselectivity and produce PLA with lower molecular weights. Therefore, more effort is needed to realize the organocatalyzed stereoselective ROP of *rac*-LA with the ability to produce crystalline PLA materials with practically useful molecular weights under ambient or higher temperatures and, preferably, solvent-free conditions.

Chemical Recycling of PLA

In efforts to achieve a circular life cycle of PLA materials, chemical recycling of post-consumer PLLA has been studied. Kopinke and coworkers found that the dominant reaction pathway of thermal decomposition of PLLA is intramolecular transesterification, giving rise to the formation of cyclic oligomers and LA with considerable racemization.[119] In addition, during the process a *cis*-elimination reaction produces acrylic acid and acyclic oligomers, whereas radical and concerted non-radical reactions give CO_2, CO, and CH_3CHO. On the other hand, PLA samples contaminated with residual Sn from the polymerization process using stannous 2-ethylhexanoate ($Sn(Oct)_2$) as a catalyst showed a more selective depolymerization to produce LA. To clarify the effects of the residual Sn species on PLLA pyrolysis, Nishida et al. investigated the pyrolysis of the PLLA samples with different Sn contents ranging from 20 to 607 ppm.[120] The pyrolysis of PLLA with Sn-607 (Sn content: 607 ppm) in the temperature range of 40°C–400°C selectively produced an LA diasteromeric mixture (*meso*-LA/[L-LA + D-LA] = 11.4/88.6) with only 0.9% cyclic oligomers. In contrast,

the pyrolysis of PLLA with Sn-20 afforded an LA diasteromeric mixture (*meso*-LA/[L-LA + D-LA] = 36.8/63.2), accompanied by cyclic oligomers up to 20.5%. The authors also examined the pyrolysis of PLLA samples with different chain-end structures and found that as-polymerized PLLA-ap (containing 1,006 ppm of Sn in the form of PLLA-O-Sn) and precipitated-with-methanol PLLA-pr (containing 689 ppm of Sn in the form of a salt, HO-PLLA-$COO^{-}Sn^{2+}X^{-}$) produced L-LA selectively with only a small amount of *meso*-LA (<1.3% and <1.9%, respectively), whereas the purified PLLA-H (containing only 23 ppm of Sn) led to a large amount of *meso*-LA (8%–15%) and cyclic oligomers (3%–64%) as a result of random degradation.[121] Thermal degradation of *sc*-PLA followed the same trend, whereby the sample contained ≥266 ppm Sn, affording predominantly L-LA/D-LA (>90%) via unzipping depolymerization while the purified sample with <10 ppm of Sn yielded a large amount of *meso*-LA (~20%) and cyclic oligomers (32%) via random degradation.[122] Overall, these studies consistently showed that the presence of a sufficient amount of the residual metal catalyst (Sn species) renders the thermal degradation of PLLA and *sc*-PLA to proceed via a more selective unzipping depolymerization pathway, thus producing predominantly L-LA/D-LA with diminished *meso*-LA and cyclic oligomer formation.

The pyrolysis of PLLA was shown to be influenced by the different kinds of end structures, specifically, the carboxyl and calcium ion end capped types (PLLA-H and PLLA-Ca).[123] About 95% of the PLLA-Ca pyrolysis products were lactides, which is higher than that of PLLA-H (68%). However, in the case of PLLA-Ca racemization took place, producing *meso*-LA dominantly at temperatures lower than 250°C (specifically, >75% at lower than 220°C), and also forming *meso*-LA <50% at temperatures higher than 320°C.[124] Interestingly, only a small amount of *meso*-LA (2.1%) was detected at the temperatures in the range of 250°C–320°C, because unzipping depolymerization proceeded as the main reaction in this temperature range. Nishida's group also found that metal oxides such as CaO and MgO not only lower the degradation temperature but also completely suppress the production of oligomers other than lactides (98%).[125] However, CaO caused LA racemization (10%–20%) at the temperature lower than 250°C, whereas with MgO racemization was avoided at temperatures under 220°C (*meso*-LA <3% even at 270°C). This observation can be ascribed to the fact that the pyrolysis of PLLA/MgO composite occurred smoothly via unzipping depolymerization, resulting in selective L-LA recovery at temperatures lower than 270°C. Moreover, the depolymerization process was also affected by MgO particles with primary particles of different dimensions, surface areas, and chemical structures and species.[126]

The current industrial crystalline isotactic PLLA is produced by the ROP of L-LA, which is furnished via $Sn(Oct)_2$-catalyzed depolymerization of a low-molecular-weight condensation prepolymer of L-lactic acid (Figure 10).[127,128] During the depolymerization process, 2–20 wt % *meso*-LA plus up to 5 wt % other (non-LA) impurities can be also obtained besides L-LA as the major product. Noda and Okuyama utilized a series of less toxic Al, Ti, Zn, and Zr compounds as intramolecular transesterification catalysts for the thermal depolymerization reaction of PLLA oligomers.[129] The activity of the intramolecular transesterification compared with that of $Sn(Oct)_2$ was found to follow the order of Sn > Zn > Zr > Ti > Al. The aluminum and titanium compounds did not yield the desired results; both *meso*-LA and D-LA as the by-products were observed. Although the activity of the zinc and zirconium compounds was lower than that of conventional $Sn(Oct)_2$, they can be used as economical catalysts to produce L-LA without toxic residue. However, as described above, the PLLA depolymerization processes are often accompanied by formation of LA diastereomers including a considerable amount of *meso*-LA resulting from epimerization, seriously

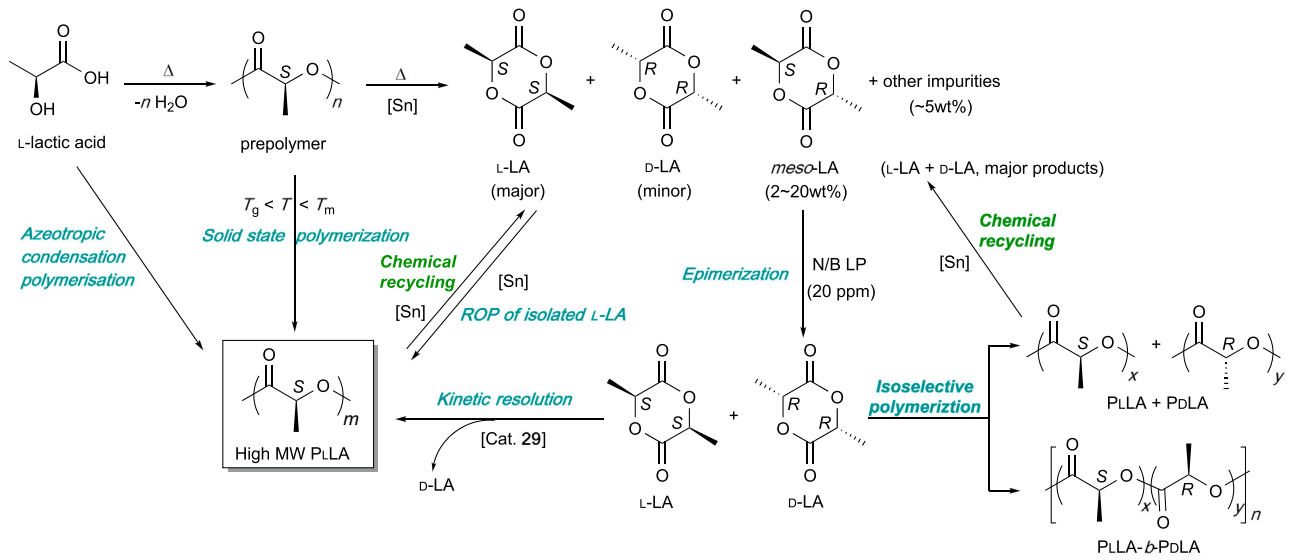


Figure 10. Current Strategies for Production of High-Molecular-Weight PLLA, Conversion of Waste By-product *meso*-LA into *rac*-LA and Subsequent Stereoselective Polymerization, and Chemical Recycling of PLA Materials

affecting the economy of the manufacture of PLLA. The optical purity of the LA monomer also significantly affects the materials properties of PLLA, and any incorporation of *meso*-LA into the PLLA product will significantly deteriorate the properties of the PLLA materials. The *meso*-LA formation is also a significant issue in the industrial process for L-LA monomer production. In terms of this issue, efforts have been made on the isomerization *meso*-LA to *rac*-LA, which can be used to produce stereocomplex or stereoblock PLA through an isoselective polymerization process or PLLA via a kinetic resolution polymerization process.[117]

Shuklov et al. employed organic and inorganic bases, such as DBU, 1,4-diazabicyclo[2.2.2]octane (DABCO), imidazole, K_3PO_4, K_2CO_3, and NaOH, to initiate the epimerization of stereoisomeric lactides.[130] A diasteromeric LA mixture containing L-LA + D-LA (up to 65 mol %) and *meso*-LA (35 mol %) was obtained in the presence of DBU (DBU/LA = 1:1) in toluene at room temperature for 16 hr. Benson and Schroeder also investigated epimerization of *meso*-DL, affording a diastereomeric mixture containing 36% L-LA + 36% D-LA + 28% *meso*-LA, plus 0.5 wt % linear oligomers by the best-performing sodium ethylhexanoate (0.05%) in bulk at 160°C for 15 hr.[131] We found that the Lewis pair (LP) DABCO/$B(C_6F_5)_3$ (20 ppm) catalyzes rapid and quantitative epimerization of *meso*-LA to *rac*-LA in toluene at room temperature after several minutes.[117] This rapid and quantitative conversion of *meso*-LA to *rac*-LA is attributed to the following: (1) the highly effective LP catalyst system enables the rapid epimerization of *meso*-LA into *rac*-LA at room temperature, avoiding LA oligomerization at the same time; and (2) precipitation or crystallization of *rac*-LA from the reaction mixture (*rac*-LA is insoluble in toluene) continuously shifts the equilibrium toward *rac*-LA. Significantly, this quantitative *meso*-LA into *rac*-LA conversion can also be performed in bulk at 70°C (i.e., solvent-free conditions), under which temperature *meso*-LA melts to a liquid while *rac*-LA crystallizes to a solid. Moreover, this epimerization method also works similarly, irrespective of the initial *meso*-LA/*rac*-LA ratio in feed, which means that any mixed stereoisomers of LA can be used to produce pure *rac*-LA quantitatively and rapidly. Worth noting here also is that the epimerization (by DABCO/$B(C_6F_5)_3$) and

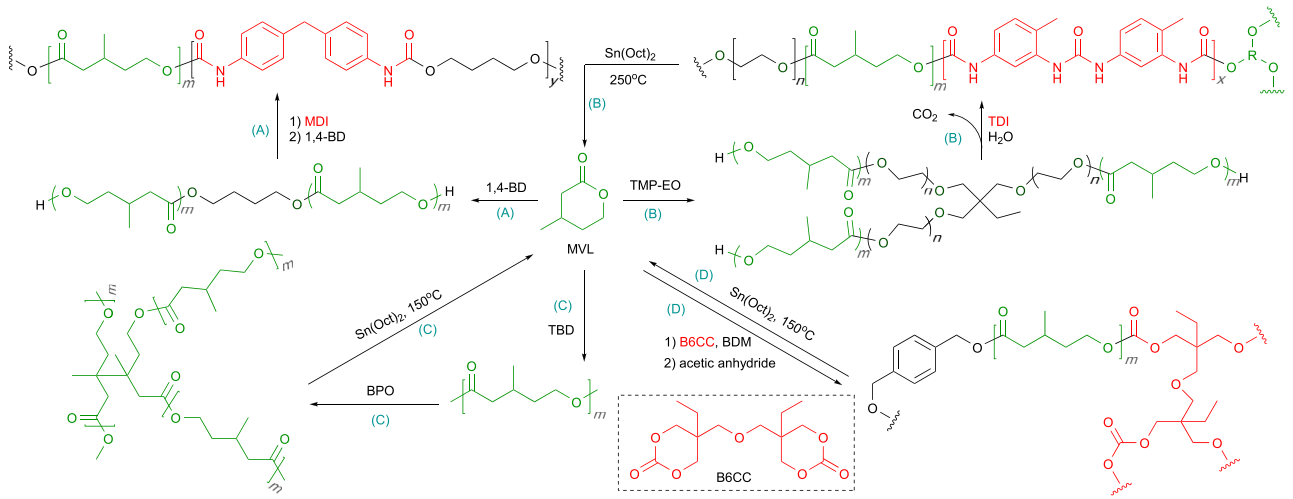


Figure 11. Synthetic Route and Chemical Recycling of MVL-Based Thermoplastic PU and Flexible Foam as well as Crosslinked Elastomers

(A) Synthetic route of thermoplastic PU. MDI, 4,4′-methylene diphenyl diisocyanate; 1,4-BD, 1,4-butanediol.

(B) Synthetic route and chemical recycling of flexible PU foam. TMP-EO, trimethylolpropane ethoxylate; TDI, toluene diisocyanate.

(C) Synthetic route and chemical recycling of peroxide crosslinked PMVL. TBD, triazabicyclodecene; BPO, benzoyl peroxide.

(D) Synthetic route and chemical recycling of cyclic carbonate crosslinked PMVL. BDM, 1,4-benzenedimethanol.

enantioselective polymerization (by catalyst **20**) can be coupled into a one-pot process for transforming *meso*-LA directly into PLLA and D-LA.

Overall, a circular life cycle for PLLA (Figure 10) could be realized by optimizing the conditions for epimerization of *meso*-LA (the waste co-product in the L-LA production and PLA recycling) to *rac*-LA, enhancing stereoselectivity in the ROP of *rac*-LA, and improving selectivity in the chemical recycling of PLLA and *sc*-PLA.

β-Methyl-δ-valerolactone

Although β-methyl-δ-valerolactone (MVL) is not a natural metabolite, direct fermentation of glucose and a semisynthetic approach to MVL from glucose that relies upon dehydration of fermented mevalonate to anhydromevalonolactone and subsequent reduction to MVL were developed by Zhang and coworkers.[132] This bio-derived monomer possess a moderate ceiling temperature of 227°C for the polymerization of neat MVL, and thus can be readily converted from the neat state to a rubbery hydroxyl telechelic poly(β-methyl-δ-valerolactone) (PMVL) using diol initiator and TBD or diphenyl phosphate (DPP) as the catalyst at room temperature.[133] The resulting linear PMVL diols were employed to synthesize thermoplastic polyurethanes (TPUs) in a one-pot, two-step sequential procedure as outlined in Figure 11A. Trimethylolpropane ethoxylate (TMP-EO) was used to prepare a PMVL triol, which can be transformed to flexible polyurethane (PU) foam using toluene diisocyanate with water as the sole blowing agent (Figure 11B). Moreover, the PU foam can be readily recycled to recover MVL monomer in high purity (≥95% by ^{1}H NMR) and high yield (up to 97%) in the presence of $Sn(Oct)_2$ at 250°C via urethane dissociation, followed by depolymerization of the resulting hydroxy-terminated PMVL, as the major degradation pathway. A commercial PU foam added to a PMVL recycling experiment did not significantly diminish the yield or purity of MVL recovered after 10 hr. This recycling strategy bypasses many of the technical challenges that currently preclude the practical chemical recycling of PUs. Additionally, MVL recovered from the depolymerization of PMVL foam can also produce PMVL polyols, which are indistinguishable from

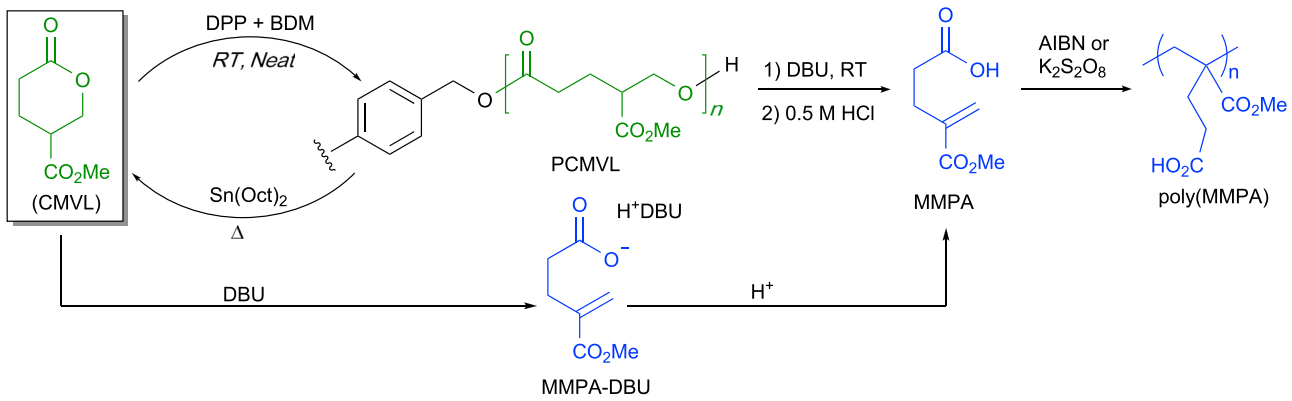


Figure 12. ROP of CMVL and Divergent Chemical Recycling of PCMVL to CMVL or Enoate MMPA and Its Polymerization to Poly(MMPA)

an analogous sample prepared from virgin monomer using the same synthetic method. Therefore, the renewable and degradable hydroxy telechelic PMVL can act as a replacement for petroleum-derived polyols in the synthesis of both TPUs and flexible foams, which rival petroleum-derived PUs in performance.

Hillmyer and coworkers also synthesized renewable and recyclable crosslinked elastomers based on MVL using two different methodologies: (1) crosslinking of a linear PMVL homopolymer with a free-radical generator (Figure 11C), benzoyl peroxide and (2) tandem co-polymerization and crosslinking of MVL with a bis(six-membered cyclic carbonate) (Figure 11D).[134] Tensile strengths up to 12 MPa and elongations up to 2,000% were observed for the resulting crosslinked elastomers based on MVL. Inclusion of a filler (fumed silica) can enhance the performance of the elastomers; the Young's modulus and tensile strength were improved by 57% and 83%, respectively, without sacrificing the elongation at break by incorporating up to 25 wt % fumed silica in peroxide crosslinked PMVL. Moreover, both of the peroxide and cyclic carbonate crosslinked PMVLs can be depolymerized in the presence of $Sn(Oct)_2$ and pentaerythritol ethoxylate (a high-boiling tetraol) at 150°C under vacuum, yielding monomer in high purity and yield (93% and 91%, respectively), demonstrating their chemical recyclability.

4-Carbomethoxyvalerolactone

Recently, Fahnhorst and Hoye reported a renewable monomer, 4-carbomethoxyvalerolactone (CMVL), synthesized from malic acid, known as a "top value-added chemical,"[135] as being a promising renewable and scalable feedstock.[136] The ROP of CMVL by DPP as the catalyst with 1,4-benzenedimethanol as the initiator proceeded smoothly in bulk at room temperature to high equilibrium monomer conversion (>98%) to give semicrystalline poly(4-carbomethoxyvalerolactone) (PCMVL) with M_n up to 71 kg/mol, T_g of −18°C, T_c of 32°C, and two T_ms at 68°C and 86°C. When DBU at low mol % levels was employed as the catalyst to polymerize CMVL, it showed no polymerization activity, as a result of the reaction of DBU with CMVL through retro-oxa-Michael addition (i.e., elimination) that forms the MMPA-DBU. Acidification of this intermediate leads to 5-methoxy-4-methylene-5-oxopentanoic acid (MMPA) in 95% yield without purification beyond liquid-liquid partitioning. PCMVL can be chemically recycled back to monomer CMVL in 87% yield with $Sn(Oct)_2$ at 150°C (ca. 0.05 Torr) via a backbiting depolymerization from the hydroxy terminus. This polymer can be also chemically recycled by an eliminative process in the presence of base (DBU) leading to a methacrylate derivative, MMPA, in 88% yield by cleaving the polyester in a retro-oxa-Michael fashion (Figure 12). The

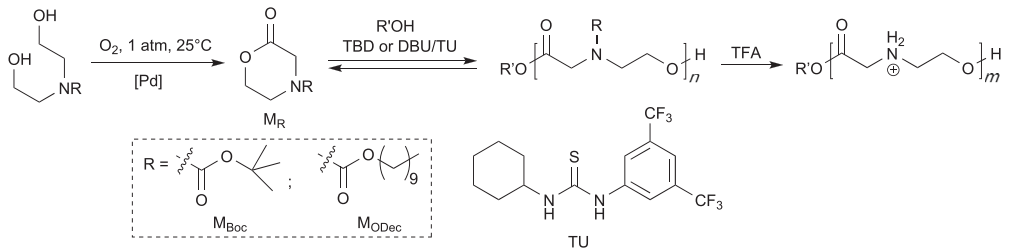


Figure 13. Synthesis and ROP of *N*-Acyl Morpholin-2-Ones and Deprotection of the Polymer Derived from M_{Boc} to Cationic Water-Soluble Poly(Aminoester)

obtained methacrylate-like monomer MMPA can be polymerized radically by azobis(isobutyronitrile) or potassium persulfate to a new polymethacrylate analog, poly(MMPA), with a T_g of 101°C. This represents a rare example of a polymer that has been shown to have two independent chemical recycling pathways by leading to two different classes of monomers.

N-Acyl Morpholin-2-ones

The ROP of *N*-acyl morpholin-2-ones reported by Blake and Waymouth provides a general strategy to prepare a family of functionalized poly(aminoesters).[137] The monomers can be obtained by the catalytic oxidative lactonization of diethanolamines with a cationic Pd complex $[(neocuproine)Pd(OAc)]_2(OTf)_2$ (Figure 13). The organocatalytic ROP of *N*-acyl morpholin-2-ones occurs readily in the presence of TBD or DBU/TU as the catalyst and 1-pyrenebutanol as the initiator to generate poly(aminoesters) with *N*-acylated amines in the polyester backbone. In the case of morpholinone M_{Boc}, no further monomer conversion was observed when the concentration of monomer approached 0.13 M in toluene at 25°C; depolymerization of the resulting polymer, poly(M_{Boc}), in the presence of TBD also resulted in a final monomer concentration of 0.13 M. Thermodynamic parameters for this equilibrium polymerization were determined to be ΔH_p = (−4.8 ± 0.3 kcal/mol) and ΔS°_p = −12.2 cal/(mol·K). The ceiling temperature was calculated to be 393 K (120°C) at $[M]_0$ = 1.0 M, indicating the conditions for achieving chemical recycling of poly(M_{Boc}).

FIVE-MEMBERED CYCLIC ESTERS

γ-Butyrolactone

γ-BL is a bio-derived industrial solvent and cleaning agent from succinic acid, a top-ranked biomass-derived chemical best suited to substitute petroleum-derived chemicals.[138] The polymer obtained from the ROP of γ-BL, poly(γ-butyrolactone) (PγBL), is a structural equivalent of microbial poly(4-hydroxybutyrate) (P4HB, also a key member of PHAs) through a bacterial fermentation process,[139] which has been shown to exhibit more desired properties as a biomaterial (e.g., faster degradation rates and better mechanical properties) relative to other commonly used aliphatic polyesters.[140] Because of the negligible strain energy of the five-membered lactone ring, γ-BL was often considered to be non-polymerizable.[141] Although the synthesis of oligomers of γ-BL has been achieved via ROP of γ-BL under ultra-high pressure (e.g., 20,000 atm)[142–145] or lipase-catalyzed conditions[146] since the 1960s, it required extreme conditions, and the resulting product was just a mixture of oligomers. We recently reported that the ROP of γ-BL by catalysts **4** and **6** proceeded smoothly to high conversions (up to 90%) at −40°C under ambient pressure, affording PγBL materials with relatively high molecular weights (M_n up to 30 kg/mol) and controlled linear and/or cyclic topologies by varying the alcohol initiator structure and the molar ration of [**4**]/[alcohol] (Figure 14).[61] The keys to

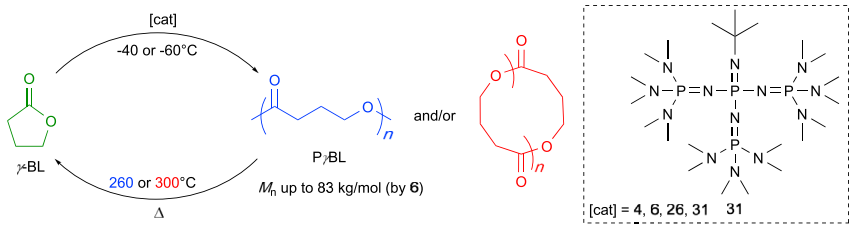


Figure 14. ROP of γ-BL into PγBL with Relatively High Molecular Weight and Complete Recyclability and Metal-Based and Organic Catalysts Used for the Polymerization

achieving the successful ROP of γ-BL are (1) to meet the thermodynamic conditions by reducing the entropic penalty of the ROP by performing the polymerization at a low-enough temperature (i.e., below the ceiling temperature of polymerization, for a given monomer concentration [M]); (2) to employ potent, kinetically fast catalysts that enable high conversion within a reasonable time period because the ROP must be performed at low temperatures because of thermodynamic limitations; and (3) to modulate reaction conditions (concentration, solvent, and temperature) such that [M] becomes greater than the equilibrium $[M]_{eq}$ and the formed polymer crystallizes or precipitates out of solution during the polymerization to perturb continuously the propagation and depropagation equilibrium and shift it toward propagation. Subsequently, we also utilized organic phosphazene superbase ^{t}Bu-P$_4$ (**31**), combined with an alcohol such as BnOH, to enable a more effective of ROP of γ-BL with high conversions, producing linear PγBL with M_n up to 26.7 kg/mol.[147] More recently, Li and coworkers employed cyclic trimeric phosphazene base **26** for the ROP of γ-BL and achieved high conversions (up to 98%) in the presence of alcohol at −60°C, producing linear PγBL with M_n up to 22.9 kg/mol.[148] Most recently, by using catalyst **6** and adjusting the monomer to catalyst ratio and reaction scale, we were able to prepare linear PγBL with M_n up to 83.2 kg/mol.[149]

Uniquely, PγBL materials, either linear or cyclic structure, can be recycled back into the monomer in quantitative selectivity and yield via thermolysis by simply heating the bulk material at 260°C (for linear polymer) or 300°C (for cyclic polymer) for 1 hr. Depolymerization of PγBL to the clean monomer can also occur rapidly by chemolysis in the presence of a simple organic or metal catalyst (such as TBD or complex **4**) even at room temperature.[61,147] These recyclability studies showed the full chemical recyclability of PγBL.

α-Methylene-γ-butyrolactone

As the simplest member of the sesquiterpene lactone family, natural Tulipalin A, or MBL, is found in tulips and can also be produced chemically from biomass feedstocks.[150,151] MBL contains both a highly reactive exocyclic C=C bond conjugated to an ester carbonyl and a highly stable five-membered γ-BL ring, which is typically polymerized via the vinyl-addition polymerization (VAP) pathway to produce $P(MBL)_{VAP}$ exclusively (Figure 15). Recently, we reversed this conventional chemoselectivity by turning on the ROP pathway while shutting down the VAP process with catalyst **4** (combined with 3 equiv ROH) or **6** at low temperature (−60°C).[63] The uncovering of this new ROP of MBL enabled the synthesis of a biorenewable and degradable unsaturated polyester, $P(MBL)_{ROP}$, with T_g in the range of −40.2°C to −34.9°C and M_n up to 21.0 kg/mol. A third reaction pathway has also been uncovered, which is crossover propagation between VAP and ROP processes, thus affording crosslinked polymer $P(MBL)_{CLP}$ having predominately VAP chains. The formation

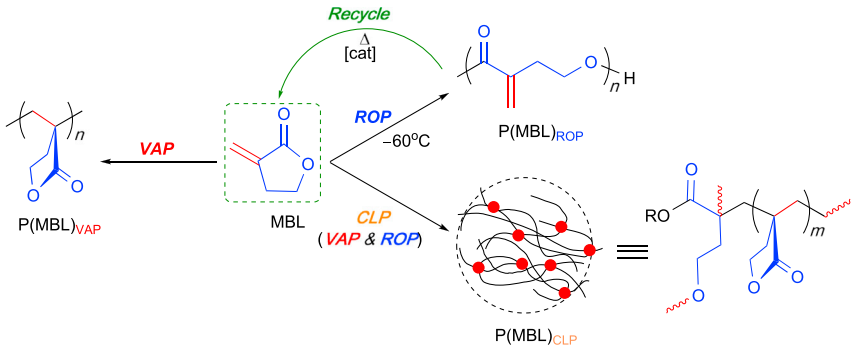


Figure 15. Polymerization Pathways of MBL (VAP, ROP, and CLP) and Chemical Recycling of $P(MBL)_{ROP}$

of the three types of polymers, $P(MBL)_{VAP}$, $P(MBL)_{CLP}$, and $P(MBL)_{ROP}$, can be readily controlled by adjusting the catalyst (**4**)/initiator (ROH) ratio of 1:0, 1:1, and 1:3, respectively, which is determined by the unique chemoselectivity of the La-X (X = OR, NR_2, R) group: the La-NR_2 group leads to the VAP process, whereas the La-OR group favors the ROP. $P(MBL)_{ROP}$ can be readily postfunctionalized via photocuring and the thiol-ene click reaction into crosslinked or thiolated materials. Significantly, $P(MBL)_{ROP}$ can be fully recycled back to its monomer MBL after heating its solution at $\geq$100°C for 1 hr in the presence of a simple catalyst (e.g., $LaCl_3$), thus establishing its complete chemical recyclability. It should be noted here that $P(MBL)_{ROP}$ cannot be recycled back to MBL cleanly via thermolysis by simply heating in bulk, which resulted in crosslinking of $P(MBL)_{ROP}$ via its side-chain C=C bonds.

trans-Ring-Fused γ-Butyrolactones

The monomers that generated the two completely recyclable polymers, PγBL and $P(MBL)_{ROP}$, have the common γ-BL core. We hypothesized that this core structure renders its complete chemical recyclability during the depolymerization process for both thermodynamic (formation of the most stable product—the monomer) and kinetic (via the low barrier five-membered transition state during unzipping of the monomer) reasons. To further test this hypothesis, we designed a monomer based on γ-BL with a *trans*-cyclohexyl ring fused at the α and β positions of γ-BL, namely 3,4-T6GBL.[22] In this monomer structure, the highly stable, five-membered γ-BL core is kept so that the complete chemical recyclability of the resulting polymer could be preserved (vide supra), while the *trans*-ring fusion should enhance the resulting polymer properties and increase ring strain of the monomer that could render this monomer polymerizable at room temperature. The latter point is also significant, as the synthesis of PγBL and $P(MBL)_{ROP}$ requires energy-intensive, industrially undesirable low-temperature conditions (typically at −40°C or below); in addition, PγBL exhibits limited thermostability and crystallinity with a low T_m of ~60°C, while $P(MBL)_{ROP}$ is a non-crystalline, amorphous material with a T_g of −40°C to −35°C.

Indeed, 3,4-T6GBL can be effectively polymerized into high-molecular-weight polymers under ambient temperature and neat (solvent-free) conditions.[22] With complex **4**, in combination with 3 equiv of Ph_2CHCH_2OH as the initiator, the ROP exhibited high selectivity and activity to afford a linear polymer [*l*-P(3,4-T6GBL)] with M_n up to 67.9 kg/mol and $Đ$ = 1.01. On the other hand, with complex **4** alone (no alcohol), cyclic polymer *c*-P(3,4-T6GBL) with M_n = 73.0–85.5 kg/mol was obtained. Using

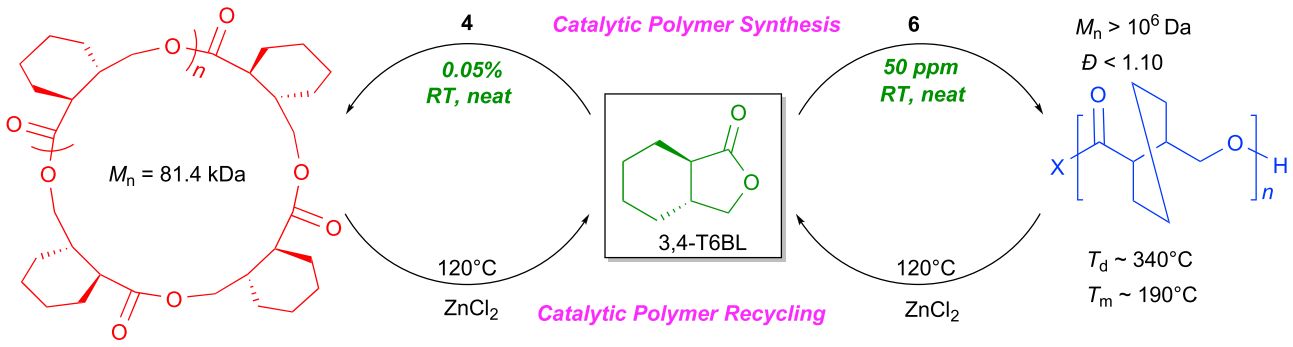


Figure 16. ROP of 3,4-T6GBL to High-Molecular-Weight Polymers with Linear or Cyclic Topology and Selective Chemical Recycling of the Resulting Linear and Cyclic Polymers

yttrium complex **6** as the catalyst with loading as low as 50 ppm, high-molecular-weight P(3,4-T6GBL) with M_n = 1.11 × 10^6 g/mol ($Đ$ = 1.09) was produced under neat and room-temperature conditions (Figure 16). Furthermore, complex **6** brought about "immortal" ROP of 3,4-T6GBL in the presence of ROH (Ph_2CHCH_2OH), producing well-defined *l*-P(3,4-T6GBL) materials with near ideal dispersity (1.01) in a catalytic fashion and thus affording up to 100 polymer chains per **6** molecule. Additionally, zinc complex **1** can also initiate the ROP of 3,4-T6GBL in a more controlled manner than complex **6** when used alone under similar conditions, in terms of its higher polymerization activity and lower polymer dispersity, obtaining P(3,4-T6GBL) with M_n up to 588 kg/mol ($Đ$ = 1.02).

Cyclic polymer *c*-P(3,4-T6GBL) exhibited a noticeably higher onset decomposition temperature (T_d = 337°C) than the linear polymer *l*-P(3,4-T6GBL) (316°C). Notably, The T_d of *l*-P(3,4-T6GBL) is >100°C higher than that of the linear PγBL. Interestingly, crystalline stereocomplexed materials (*sc*-P(3,4-T6GBL)) can be readily generated by blending 1:1 enantiomeric isotactic polymers derived from enantiomeric monomers, either linear enantiomer pair *l*-P[(*R*)-3,4-T6GBL] and *l*-P[(*S*)-3,4-T6GBL] or cyclic enantiomer pair *c*-P[(*R*)-3,4-T6GBL] and *c*-P[(*S*)-3,4-T6GBL]. The *sc*-P(3,4-T6GBL) showed a much higher T_m (188°C–200°C) and faster crystallization rate than each enantiomeric polymer (~127°C). Key thermal and mechanical properties of *sc*-P(3,4-T6GBL) compare well with those of typical crystalline PLLA materials.[152]

Importantly, behaving just like PγBL, linear or cyclic P(3,4-T6GBL) can be fully recycled back to monomer in quantitative yield via thermolysis by heating in a sealed tube at ≥300°C. The complete chemical recycling of P(3,4-T6GBL) can also be achieved via chemolysis at lower temperature (120°C) using a catalytic amount of a simple metal salt ($ZnCl_2$), thus significantly reducing the energy input in the recycling process. Employing this catalyzed chemical recycling process, three consecutive polymerization-depolymerization-repolymerization (or polymer-monomer-polymer) circular cycles on a multi-gram scale have been realized; during each cycle, the monomer was recovered in pure state and in quantitative yield from the depolymerization, which can be directly repolymerized without a decrease in the subsequent monomer conversion and polymer quality.[22]

When *trans*-fusing the cyclohexyl ring at the β,γ- (i.e., 4,5)-positions of the γ-BL ring, a constitutional isomer, 4,5-T6GBL, is created. This isomer was found to be polymerizable even at 40°C by typical anionic initiators; however, the resulting products were oligomers with M_n up to only 6.2 kg/mol, and "no polymer products were

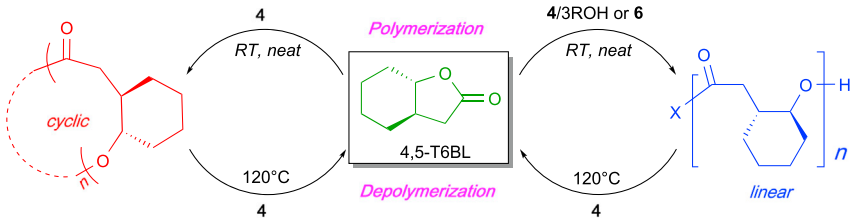


Figure 17. ROP of 4,5-T6GBL to Linear and Cyclic Polymers and Selective Chemical Recycling of the Resulting Polymers

obtained via cationic and coordination polymerization."[153] Most recently we found that, in fact, it can be readily polymerized by the coordination ROP with lanthanide catalysts such as **4** and **6** under ambient temperature and solvent-free conditions, producing the corresponding polymer P(4,5-T6GBL) with M_n up to 47 kg/mol, high thermal stability, and a controlled linear or cyclic topology (Figure 17).[154] This coordination polymerization is also living, enabling the synthesis of well-defined block copolymer with another lactone. Noteworthy also is that the positions of *trans*-fusion in the monomer structure significantly affect the polymer properties; for example, in contrast to the observed facile formation of a highly crystalline stereocomplex between enantiomeric polymers of P(3,4-T6GBL), mixing of enantiomeric polymers P[(+)-4,5-T6GBL] and P[(−)-4,5-T6GBL] did not form the corresponding stereocomplex. Attempts to recycle P(4,5-T6GBL) via thermolysis by heating the bulk material at 300°C for 1 hr under a nitrogen atmosphere resulted in regeneration of 4,5-T6GBL and its *cis* isomer (which is not polymerizable); lowering the depolymerization temperature to 230°C for longer time (40 hr) resulted in complete conversion of the polymer into the monomer (89%), but still contaminated with undesirable *cis* isomer (11%). To suppress the isomerization that occurs at high temperatures, the depolymerization was performed at lower temperatures in the presence of catalyst **4**. With this chemolysis strategy, both linear and cyclic polymers were selectively depolymerized back to 4,5-T6GBL quantitatively at 120°C for 24 hr, without formation of any undesirable products.

SUMMARY AND OUTLOOK

Chemically recyclable polymers are designed to allow for (ideally full) recovery of the building-block chemicals via depolymerization for repolymerization to virgin-quality polymers or creative repurposing to value-added materials, thus offering a feasible solution to the end-of-use issue of polymeric materials and also providing a closed-loop approach toward a circular materials economy. Centering on this theme, this review captures the highlights of the renewable plastics derived from the ROP of the most common four-, five-, six-, seven-, and eight-membered, bio-derived cyclic esters and examines their synthetic strategies, materials properties, and, particularly, chemical recyclability.

The ROP of either four-membered *rac*-β-BL or eight-membered *rac*-DL (a racemic cyclic dimer of 3HB) affords biodegradable P3HB, the most prominent member of the PHA family, but the tacticity of the resulting P3HB is significantly different. Whereas the isoselective ROP of *rac*-β-BL by various classes of chiral or achiral catalysts afforded isotactic P3HB with only modest isotacticity (up to 85%) and T_m values (~142°C), the stereoselective ROP of *rac*-DL produced P3HB with perfect isotacticity (>99%) and high T_m (175°C), which matched naturally produced bacterial P3HB. However, an efficient scheme for the chemical recycling of P3HB is currently lacking. Depolymerization of P3HB can lead to triolide of 3HB (TBL) but in low yield

of ~50%; in addition, repolymerization of TBL yielded only low-molecular-weight P3HB. Our proposed new strategy for the chemical recycling of P3HB, as outlined in Figure 4, could lead to a circular monomer-polymer-monomer cycle, provided that an efficient dimerization of 3HB to *rac*-DL and more selective hydrolysis of P3HB to 3HB can be realized.

The ROP of a seven-membered cyclic ester or amide, namely ε-CL or ε-CLM, leads to important polymer PCL or nylon-6, which also shows potential to recycle back to its monomer with good selectivity (up to 86% for nylon-6 in ionic liquid). Achieving higher depolymerization selectivity and lower costs for the chemical recycling process need to be considered for practical applications. A benzene-fused seven-membered lactone, 2,3-DHB, leads to polyester P2HEB containing both aromatic and aliphatic linkages in the polymer backbone, which can be recycled back to its monomer by diluting the polymerization in the presence of an aluminum catalyst.

For the polyesters from the six-membered cyclic ester, PLLA is a bio-based biodegradable polymer and has been produced on a commercial scale. The research on the depolymerization of PLA by pyrolysis to a mixture of L-LA, D-LA, *meso*-LA, cyclic oligomers and other side products provided insight into the limited recyclability of PLA, but the metal-catalyzed unzipping depolymerization under milder conditions typically gave high selectivity for regeneration of L-LA/D-LA. In addition, the catalyzed epimerization of stereoisomeric lactides can transform the *meso*-LA by-product from the L-LA production or the PLA chemical recycling to the higher-value monomer *rac*-LA. The *rac*-LA can be used to produce stereocomplex or stereoblock PLA through an isoselective polymerization process or PLLA via a kinetic resolution polymerization process. However, the molecular weights of the resulting PLA material from isoselective or kinetic resolution ROP of *rac*-LA by the current metal or organic catalysts need to be further enhanced to a practically useful range (>10^5 g/mol). The bio-derived lactone MVL has been utilized for the synthesis of thermoplastic PU as well as flexible foam and crosslinked elastomers in which the MVL portion is chemically recyclable. Another renewable six-membered lactone derivative, CMVL, forms the corresponding polymer that is chemically recyclable by two independent pathways to form two different classes of monomers. The ROP of *N*-acyl morpholin-2-ones provides a general strategy for preparing a family of functionalized poly(aminoester)s, which can also be chemically recycled back to its monomer.

Among the chemically recyclable polymers reviewed herein, the polymers based on five-membered γ-BL developed mainly by our group display a distinctly important feature: complete and, in principle, "infinite" chemical recyclability. Our earlier work in 2016 demonstrated that the relatively high-molecular-weight polymers derived from the ROP of previously considered "non-polymerizable" γ-BL and MBL can be quantitatively depolymerized back to their monomers under appropriate thermolysis and chemolysis conditions. However, these two first-generation recyclable polymer systems have two limitations: the synthesis of PγBL and $P(MBL)_{ROP}$ requires energy-intensive, industrially undesirable low-temperature conditions (typically −40°C to −60°C), and they exhibit limited thermostability and crystallinity (for PγBL) or non-crystallinity in the case of $P(MBL)_{ROP}$. The *trans*-ring fusion strategy yielded two γ-BL derivatives with the *trans*-fused cyclohexyl ring at the α,β, positions (3,4-T6GBL) and β,γ positions (4,5-T6GBL) of the γ-BL ring. Both *trans*-ring fused monomers can now be readily polymerized under ambient temperature and solvent-free conditions to high-molecular-weight polymers, especially 3,4-T6GBL that can lead to P(3,4-T6GBL) with ultra-high molecular weight as well as practically useful thermal, mechanical, and rheological properties of common plastics.

Importantly, both second-generation polymer systems not only render their monomers' room-temperature polymerizability and exhibit much enhanced materials properties, they also retain the complete chemical recyclability during depolymerization processes by thermolysis (for P(3,4-T6GBL)) at high temperatures (typically $\geq 300^{\circ}C$) or chemolysis in the presence of a simple catalyst under much milder conditions (typically at 120°C for both polymers).

Overall, these fully recyclable polymer examples based on the five-membered lactones further reinforced our hypothesis that, as long as the stable core γ-BL structure remains intact, the γ-BL ring can be substantially substituted to modulate the polymerizability of the derived monomers and the materials properties of the resulting polymers, while preserving the complete chemical recyclability of such polymers. However, to reach the ultimate goal of establishing a circular plastics economy, much more fundamental and applied studies are required, such as more efficient, cost-effective monomer and polymer design and synthesis, polymer property characterizations (including transport properties), and economic and life-cycle assessments. The cost of the building blocks or monomers for producing bio-derived polymers or bioplastics is generally a major concern for industry, and future efforts should be continuously devoted toward the development of more cost-effective biomass conversion processes so that the bioplastics would become more economically competitive compared with the petroleum-based plastics. However, this conventional economic model of "reduced raw materials costs for higher profit margins" is based on the linear, economically expedient, but environmentally unsustainable, economy model of resource utilization that follows the flow of "mine, make, use, and dispose." In the circular plastics economy model, the building blocks of the materials are recycled after end use for reuse again and again, in principle, infinitely for the polymers based on γ-BL and its derivatives described in this review; therefore, the costs associated with the initial bio-based building block are gradually diminished as the number of the recycle/reuse increases. In this context, the γ-BL ring could be described as a "gene" for chemical recyclability that should guide future monomer and polymer design based on renewable cyclic esters for achieving both tailored application needs of the plastics and "infinite" chemical recyclability.

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AUTHOR CONTRIBUTIONS

X.T. and E.Y.-X.C. conceived the topics and outline of the review. X.T. wrote the initial draft of the paper, and E.Y.-X.C. edited the draft. Both authors contributed to subsequent revisions and read and approved the final submission version of the manuscript. E.Y.-X.C. directed the project.

REFERENCES AND NOTES

1. Ellen MacArthur Foundation (2017). The new plastics economy: rethinking the future of plastics & catalysing action. https://www.ellenmacarthurfoundation.org/publications/the-new-plastics-economy-rethinking-the-future-of-plastics-catalysing-action.

2. GESAMP: Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (2016). Sources, fate and effects of microplastics in the marine environment: part two of a global assessment. http://www.gesamp.org/publications/microplastics-in-the-marine-environment-part-2.

3. Rochman, C.M., Browne, M.A., Halpern, B.S., Hentschel, B.T., Hoh, E., Karapanagioti, H.K., Rios-Mendoza, L.M., Takada, H., Teh, S., and Thompson, R.C. (2013). Classify plastic waste as hazardous. Nature *494*, 169–171.

4. Thompson, R.C., Moore, C.J., vom Saal, F.S., and Swan, S.H. (2009). Plastics, the environment and human health: current consensus and future trends. Philos. Trans. R Soc. Lond. B Biol. Sci. *364*, 2153–2166.

5. Barnes, D.K.A., Galgani, F., Thompson, R.C., and Barlaz, M. (2009). Accumulation and fragmentation of plastic debris in global environments. Philos. Trans. R Soc. Lond. B Biol. Sci. *364*, 1985–1998.

6. Worm, B., Lotze, H.K., Jubinville, I., Wilcox, C., and Jambeck, J. (2017). Plastic as a persistent marine pollutant. Annu. Rev. Environ. Resour. *42*, 1–26.

7. Derraik, J.G.B. (2002). The pollution of the marine environment by plastic debris: a review. Mar. Pollut. Bull. *44*, 842–852.

8. Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., and Russell, A.E. (2004). Lost at sea: where is all the plastic? Science *304*, 838.

9. Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., and Law, K.L. (2015). Plastic waste inputs from land into the ocean. Science *347*, 768–771.

10. Wilcox, C., Van Sebille, E., and Hardesty, B.D. (2015). Threat of plastic pollution to seabirds is global, pervasive, and increasing. Proc. Natl. Acad. Sci. U S A *112*, 11899–11904.

11. GESAMP: Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (2015). Sources, fate and effects of microplastics in the marine environment: a global assessment. http://ec.europa.eu/environment/marine/good-environmental-status/descriptor-10/pdf/GESAMP_microplastics%20full%20study.pdf.

12. Kaiser, J. (2010). The dirt on ocean garbage patches. Science *328*, 1506.

13. European Commission (2018). A European strategy for plastics in a circular economy. http://ec.europa.eu/environment/circular-economy/pdf/plastics-strategy-brochure.pdf.

14. Singh, N., Hui, D., Singh, R., Ahuja, I.P.S., Feo, L., and Fraternali, F. (2017). Recycling of plastic solid waste: a state of art review and future applications. Compos. B Eng. *115*, 409–422.

15. US Environmental Protection Agency. Facts and figures about materials, waste and recycling. https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/advancing-sustainable-materials-management.

16. Rahimi, A., and García, J.M. (2017). Chemical recycling of waste plastics for new materials production. Nat. Rev. Chem. *1*, 0046.

17. Nishida, H. (2011). Development of materials and technologies for control of polymer recycling. Polym. J. *43*, 435–447.

18. Hong, M., and Chen, E.Y.-X. (2017). Chemically recyclable polymers: a circular economy approach to sustainability. Green Chem. *19*, 3692–3706.

19. Sardon, H., and Dove, A.P. (2018). Plastics recycling with a difference. Science *360*, 380–381.

20. Fortman, D.J., Brutman, J.P., De Hoe, G.X., Snyder, R.L., Dichtel, W.R., and Hillmyer, M.A. (2018). Approaches to sustainable and continually recyclable cross-linked polymers. ACS Sustain. Chem. Eng. *6*, 11145–11159.

21. Garcia, J.M., and Robertson, M.L. (2017). The future of plastics recycling. Science *358*, 870–872.

22. Zhu, J.-B., Watson, E.M., Tang, J., and Chen, E.Y.-X. (2018). A synthetic polymer system with repeatable chemical recyclability. Science *360*, 398–403.

23. Gandini, A., and Lacerda, T.M. (2015). From monomers to polymers from renewable resources: recent advances. Prog. Polym. Sci. *48*, 1–39.

24. Isikgor, F.H., and Becer, C.R. (2015). Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. Polym. Chem. *6*, 4497–4559.

25. Delidovich, I., Hausoul, P.J.C., Deng, L., Pfützenreuter, R., Rose, M., and Palkovits, R. (2016). Alternative monomers based on lignocellulose and their use for polymer production. Chem. Rev. *116*, 1540–1599.

26. Galbis, J.A., García-Martín Mde, G., de Paz, M.V., and Galbis, E. (2016). Synthetic polymers from sugar-based monomers. Chem. Rev. *116*, 1600–1636.

27. Gandini, A., Lacerda, T.M., Carvalho, A.J.F., and Trovatti, E. (2016). Progress of polymers from renewable resources: furans, vegetable oils, and polysaccharides. Chem. Rev. *116*, 1637–1669.

28. Stempfle, F., Ortmann, P., and Mecking, S. (2016). Long-chain aliphatic polymers to bridge the gap between semicrystalline polyolefins and traditional polycondensates. Chem. Rev. *116*, 4597–4641.

29. Zhu, Y., Romain, C., and Williams, C.K. (2016). Sustainable polymers from renewable resources. Nature *540*, 354–362.

30. Gregory, G.L., López-Vidal, E.M., and Buchard, A. (2017). Polymers from sugars: cyclic monomer synthesis, ring-opening polymerisation, material properties and applications. Chem. Commun. (Camb.) *53*, 2198–2217.

31. Schneiderman, D.K., and Hillmyer, M.A. (2017). 50th Anniversary perspective: there is a great future in sustainable polymers. Macromolecules *50*, 3733–3749.

32. Zhang, X., Fevre, M., Jones, G.O., and Waymouth, R.M. (2018). Catalysis as an enabling science for sustainable polymers. Chem. Rev. *118*, 839–885.

33. Lambert, S., and Wagner, M. (2017). Environmental performance of bio-based and biodegradable plastics: the road ahead. Chem. Soc. Rev. *46*, 6855–6871.

34. Lu, X.-B., Liu, Y., and Zhou, H. (2018). Learning nature: recyclable monomers and polymers. Chem. Eur. J. *24*, 11255–11266.

35. Rehm, B.H.A. (2003). Polyester synthases: natural catalysts for plastics. Biochem. J. *376*, 15–33.

36. Philip, S., Keshavarz, T., and Roy, I. (2007). Polyhydroxyalkanoates: biodegradable polymers with a range of applications. J. Chem. Technol. Biotechnol. *82*, 233–247.

37. Anjum, A., Zuber, M., Zia, K.M., Noreen, A., Anjum, M.N., and Tabasum, S. (2016). Microbial production of polyhydroxyalkanoates (PHAs) and its copolymers: a review of recent advancements. Int. J. Biol. Macromol. *89*, 161–174.

38. Sudesh, K., Abe, H., and Doi, Y. (2000). Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters. Prog. Polym. Sci. *25*, 1503–1555.

39. Teranishi, K., Iida, M., Araki, T., Yamashita, S., and Tani, H. (1974). Stereospecific polymerization of β-alkyl-β-propiolactone. Macromolecules *7*, 421–427.

40. Inoue, S., Tomoi, Y., Tsuruta, T., and Furukawa, J. (1961). Organometallic-catalyzed polymerization of propiolactone. Makromol. Chem. *48*, 229–233.

41. Jedliński, Z., Kurcok, P., and Lenz, R.W. (1998). First facile synthesis of biomimetic poly-(R)-3-hydroxybutyrate via regioselective anionic polymerization of (S)-β-butyrolactone. Macromolecules *31*, 6718–6720.

42. Agostini, D.E., Lando, J.B., and Shelton, J.R. (1971). Synthesis and characterization of poly-β-hydroxybutyrate. I. Synthesis of crystalline DL-poly-β-hydroxybutyrate from DL-β-butyrolactone. J. Polym. Sci. A1 *9*, 2775–2787.

43. Iida, M., Araki, T., Teranishi, K., and Tani, H. (1977). Effect of substituents on stereospecific polymerization of β-alkyl- and β-chloroalkyl-β-propiolactones. Macromolecules *10*, 275–284.

44. Kemnitzer, J.E., McCarthy, S.P., and Gross, R.A. (1993). Syndiospecific ring-opening polymerization of.beta.-butyrolactone to form predominantly syndiotactic poly(.beta.-hydroxybutyrate) using tin(IV) catalysts. Macromolecules *26*, 6143–6150.

45. Kricheldorf, H.R., and Eggerstedt, S. (1997). Polylactones. 41. Polymerizations of β-d,l-butyrolactone with dialkyltinoxides as initiators. Macromolecules *30*, 5693–5697.

46. Amgoune, A., Thomas, C.M., Ilinca, S., Roisnel, T., and Carpentier, J.-F. (2006). Highly active, productive, and syndiospecific yttrium initiators for the polymerization of racemic β-butyrolactone. Angew. Chem. Int. Ed. *45*, 2782–2784.

47. Ajellal, N., Bouyahyi, M., Amgoune, A., Thomas, C.M., Bondon, A., Pillin, I., Grohens, Y., and Carpentier, J.-F. (2009). Syndiotactic-enriched poly(3-hydroxybutyrate)s via stereoselective ring-opening polymerization

of racemic β-butyrolactone with discrete yttrium catalysts. Macromolecules *42*, 987–993.

48. Bouyahyi, M., Ajellal, N., Kirillov, E., Thomas, C.M., and Carpentier, J.-F. (2011). Exploring electronic versus steric effects in stereoselective ring-opening polymerization of lactide and β-butyrolactone with amino-alkoxy-bis(phenolate)–yttrium complexes. Chem. Eur. J. *17*, 1872–1883.

49. Bloembergen, S., Holden, D.A., Bluhm, T.L., Hamer, G.K., and Marchessault, R.H. (1989). Stereoregularity in synthetic β-hydroxybutyrate and β-hydroxyvalerate homopolyesters. Macromolecules *22*, 1656–1663.

50. Jaimes, C., Arcana, M., Brethon, A., Mathieu, A., Schue, F., and Desimone, J.M. (1998). Structure and morphology of poly([R,S]-β-butyrolactone) synthesized from aluminoxane catalyst. Eur. Polym. J. *34*, 175–185.

51. Wu, B., and Lenz, R.W. (1998). Stereoregular polymerization of [R,S]-3-butyrolactone catalyzed by alumoxane-monomer adducts. Macromolecules *31*, 3473–3477.

52. Le Borgne, A., and Spassky, N. (1989). Stereoelective polymerization of β-butyrolactone. Polymer *30*, 2312–2319.

53. Rieth, L.R., Moore, D.R., Lobkovsky, E.B., and Coates, G.W. (2002). Single-site β-diiminate zinc catalysts for the ring-opening polymerization of β-butyrolactone and β-valerolactone to poly(3-hydroxyalkanoates). J. Am. Chem. Soc. *124*, 15239–15248.

54. Zintl, M., Molnar, F., Urban, T., Bernhart, V., Preishuber-Pflügl, P., and Rieger, B. (2008). Variably isotactic poly(hydroxybutyrate) from racemic β-butyrolactone: microstructure control by achiral chromium(III) salophen complexes. Angew. Chem. Int. Ed. *47*, 3458–3460.

55. Ajellal, N., Durieux, G., Delevoye, L., Tricot, G., Dujardin, C., Thomas, C.M., and Gauvin, R.M. (2010). Polymerization of racemic β-butyrolactone using supported catalysts: a simple access to isotactic polymers. Chem. Commun. (Camb.) *46*, 1032–1034.

56. Seebach, D., Müller, H.-M., Bürger, H.M., and Plattner, D.A. (1992). The triolide of (R)-3-hydroxybutyric acid—direct preparation from polyhydroxybutyrate and formation of a crown estercarbonyl complex with Na ions. Angew. Chem. Int. Ed. *31*, 434–435.

57. Melchiors, M., Keul, H., and Höcker, H. (1996). Depolymerization of poly[(R)-3-hydroxybutyrate] to cyclic oligomers and polymerization of the cyclic trimer: an example of thermodynamic recycling. Macromolecules *29*, 6442–6451.

58. Melchiors, M., Keul, H., and Höcker, H. (1994). Synthesis of highly isotactic poly[(R)-3-hydroxybutyrate] by ring-opening polymerization of (R,R,R)-4,8,12-trimethyl-1,5,9-trioxacyclododeca-2,6,10-trione. Macromol. Rapid Commun. *15*, 497–506.

59. Tang, X., and Chen, E.Y.-X. (2018). Chemical synthesis of perfectly isotactic and high melting bacterial poly(3-hydroxybutyrate) from bio-sourced racemic cyclic diolide. Nat. Commun. *9*, 2345.

60. Seebach, D., Hoffmann, T., Kühnle, F.N.M., Kinkel, J.N., and Schulte, M. (1995). Preparation, structure, and properties of all possible cyclic dimers (diolides) of 3-hydroxybutanoic acid. Helv. Chim. Acta *78*, 1525–1540.

61. Hong, M., and Chen, E.Y.-X. (2016). Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of γ-butyrolactone. Nat. Chem. *8*, 42–49.

62. Hong, M., Tang, X., Newell, B.S., and Chen, E.Y.-X. (2017). "Nonstrained" γ-butyrolactone-based copolyesters: copolymerization characteristics and composition-dependent (thermal, eutectic, cocrystallization, and degradation) properties. Macromolecules *50*, 8469–8479.

63. Tang, X., Hong, M., Falivene, L., Caporaso, L., Cavallo, L., and Chen, E.Y.-X. (2016). The quest for converting biorenewable bifunctional α-methylene-γ-butyrolactone into degradable and recyclable polyester: controlling vinyl-addition/ring-opening/cross-linking pathways. J. Am. Chem. Soc. *138*, 14326–14337.

64. Carpentier, J.-F. (2015). Rare-earth complexes supported by tripodal tetradentate bis(phenolate) ligands: a privileged class of catalysts for ring-opening polymerization of cyclic esters. Organometallics *34*, 4175–4189.

65. Yu, J., Plackett, D., and Chen, L.X.L. (2005). Kinetics and mechanism of the monomeric products from abiotic hydrolysis of poly[(R)-3-hydroxybutyrate] under acidic and alkaline conditions. Polym. Degrad. Stab. *89*, 289–299.

66. Buntara, T., Noel, S., Phua, P.H., Melián-Cabrera, I., de Vries, J.G., and Heeres, H.J. (2011). Caprolactam from renewable resources: catalytic conversion of 5-hydroxymethylfurfural into caprolactone. Angew. Chem. Int. Ed. *50*, 7083–7087.

67. Labet, M., and Thielemans, W. (2009). Synthesis of polycaprolactone: a review. Chem. Soc. Rev. *38*, 3484–3504.

68. Dagorne, S., Normand, M., Kirillov, E., and Carpentier, J.-F. (2013). Gallium and indium complexes for ring-opening polymerization of cyclic ethers, esters and carbonates. Coord. Chem. Rev. *257*, 1869–1886.

69. Sutar, A.K., Maharana, T., Dutta, S., Chen, C.-T., and Lin, C.-C. (2010). Ring-opening polymerization by lithium catalysts: an overview. Chem. Soc. Rev. *39*, 1724–1746.

70. Agarwal, S., Mast, C., Dehnicke, K., and Greiner, A. (2000). Rare earth metal initiated ring-opening polymerization of lactones. Macromol. Rapid Commun. *21*, 195–212.

71. Guillaume, S.M., Kirillov, E., Sarazin, Y., and Carpentier, J.-F. (2015). Beyond stereoselectivity, switchable catalysis: some of the last frontier challenges in ring-opening polymerization of cyclic esters. Chem. Eur. J. *21*, 7988–8003.

72. Piotrowska, U., and Sobczak, M. (2015). Enzymatic polymerization of cyclic monomers in ionic liquids as a prospective synthesis method for polyesters used in drug delivery systems. Molecules *20*, 1–23.

73. Fuoco, T., and Pappalardo, D. (2017). Aluminum alkyl complexes bearing salicylaldiminato ligands: versatile initiators in the ring-opening polymerization of cyclic esters. Catalysts *7*, 64.

74. Li, X., Chen, C., and Wu, J. (2018). Lewis pair catalysts in the polymerization of lactide and related cyclic esters. Molecules *23*, 189.

75. Abe, H. (2006). Thermal degradation of environmentally degradable poly(hydroxyalkanoic acid)s. Macromol. Biosci. *6*, 469–486.

76. Persenaire, O., Alexandre, M., Degée, P., and Dubois, P. (2001). Mechanisms and kinetics of thermal degradation of poly(ε-caprolactone). Biomacromolecules *2*, 288–294.

77. Aoyagi, Y., Yamashita, K., and Doi, Y. (2002). Thermal degradation of poly[(R)-3-hydroxybutyrate], poly[ε-caprolactone], and poly[(S)-lactide]. Polym. Degrad. Stab. *76*, 53–59.

78. Sivalingam, G., Karthik, R., and Madras, G. (2003). Kinetics of thermal degradation of poly(ε-caprolactone). J. Anal. Appl. Pyrolysis *70*, 631–647.

79. Sivalingam, G., and Madras, G. (2003). Thermal degradation of poly (ε-caprolactone). Polym. Degrad. Stab. *80*, 11–16.

80. Abe, H., Takahashi, N., Kim, K.J., Mochizuki, M., and Doi, Y. (2004). Effects of residual zinc compounds and chain-end structure on thermal degradation of poly(ε-caprolactone). Biomacromolecules *5*, 1480–1488.

81. Kim, K.J., Doi, Y., and Abe, H. (2008). Effect of metal compounds on thermal degradation behavior of aliphatic poly(hydroxyalkanoic acid)s. Polym. Degrad. Stab. *93*, 776–785.

82. Joshi, P., and Madras, G. (2008). Degradation of polycaprolactone in supercritical fluids. Polym. Degrad. Stab. *93*, 1901–1908.

83. Kohan, M.I. (1995). Nylon Plastics Handbook (Hanser Publishers).

84. Kamimura, A., and Yamamoto, S. (2007). An efficient method to depolymerize polyamide plastics: a new use of ionic liquids. Org. Lett. *9*, 2533–2535.

85. MacDonald, J.P., and Shaver, M.P. (2016). An aromatic/aliphatic polyester prepared via ring-opening polymerisation and its remarkably selective and cyclable depolymerisation to monomer. Polym. Chem. *7*, 553–559.

86. Al-Itry, R., Lamnawar, K., and Maazouz, A. (2012). Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. Polym. Degrad. Stab. *97*, 1898–1914.

87. Gupta, A.P., and Kumar, V. (2007). New emerging trends in synthetic biodegradable polymers – polylactide: a critique. Eur. Polym. J. *43*, 4053–4074.

88. Enomoto, K., Ajioka, M., and Yamaguchi, A. (1994). Polyhydroxycarboxylic acid and preparation process thereof. US Patent

5310865, filed December 18, 1992, and granted May 10, 1994.

89. Kashima, T., Kameoka, T., Higuchi, C., Ajioka, M., and Yamaguchi, A. (1995). Aliphatic polyester and preparation process thereof. US Patent 5428126, filed January 5, 1995, and granted June 27, 1995.

90. Ichikawa, F., Kobayashi, M., Ohta, M., Yoshida, Y., Obuchi, S., and Itoh, H. (1995). Process for preparing polyhydroxycarboxylic acid. US Patent 5440008, filed May 19, 1994, and granted August 8, 1995.

91. Moon, S.I., Lee, C.W., Taniguchi, I., Miyamoto, M., and Kimura, Y. (2001). Melt/solid polycondensation of l-lactic acid: an alternative route to poly(l-lactic acid) with high molecular weight. Polymer *42*, 5059–5062.

92. Moon, S.-I., Taniguchi, I., Miyamoto, M., Kimura, Y., and Lee, C.-W. (2001). Synthesis and properties of high-molecular-weight poly(L-lactic acid) by melt/solid polycondensation under different reaction conditions. High Perform. Polym. *13*, S189–S196.

93. Stanford, M.J., and Dove, A.P. (2010). Stereocontrolled ring-opening polymerisation of lactide. Chem. Soc. Rev. *39*, 486–494.

94. Tsuji, H. (2005). Poly(lactide) stereocomplexes: formation, structure, properties, degradation, and applications. Macromol. Biosci. *5*, 569–597.

95. Ovitt, T.M., and Coates, G.W. (1999). Stereoselective ring-opening polymerization of meso-lactide: synthesis of syndiotactic poly(lactic acid). J. Am. Chem. Soc. *121*, 4072–4073.

96. Spassky, N., Wisniewski, M., Pluta, C., and Le Borgne, A. (1996). Highly stereoelective polymerization of rac-(D,L)-lactide with a chiral schiff's base/aluminium alkoxide initiator. Macromol. Chem. Phys. *197*, 2627–2637.

97. Radano, C.P., Baker, G.L., and Smith, M.R. (2000). Stereoselective polymerization of a racemic monomer with a racemic catalyst: direct preparation of the polylactic acid stereocomplex from racemic lactide. J. Am. Chem. Soc. *122*, 1552–1553.

98. Ovitt, T.M., and Coates, G.W. (2002). Stereochemistry of lactide polymerization with chiral catalysts: new opportunities for stereocontrol using polymer exchange mechanisms. J. Am. Chem. Soc. *124*, 1316–1326.

99. Mou, Z., Liu, B., Wang, M., Xie, H., Li, P., Li, L., Li, S., and Cui, D. (2014). Isoselective ring-opening polymerization of rac-lactide initiated by achiral heteroscorpionate zwitterionic zinc complexes. Chem. Commun. (Camb.) *50*, 11411–11414.

100. Abbina, S., and Du, G. (2014). Zinc-catalyzed highly isoselective ring opening polymerization of rac-lactide. ACS Macro Lett. *3*, 689–692.

101. Jones, M.D., Hancock, S.L., McKeown, P., Schafer, P.M., Buchard, A., Thomas, L.H., Mahon, M.F., and Lowe, J.P. (2014). Zirconium complexes of bipyrrolidine derived salan ligands for the isoselective polymerisation of rac-lactide. Chem. Commun. (Camb.) *50*, 15967–15970.

102. Zhang, J., Xiong, J., Sun, Y., Tang, N., and Wu, J. (2014). Highly iso-selective and active catalysts of sodium and potassium monophenoxides capped by a crown ether for the ring-opening polymerization of rac-lactide. Macromolecules *47*, 7789–7796.

103. Chen, C., Jiang, J., Mao, X., Cong, Y., Cui, Y., Pan, X., and Wu, J. (2018). Isoselective polymerization of rac-lactide catalyzed by ion-paired potassium amidinate complexes. Inorg. Chem. *57*, 3158–3168.

104. Bakewell, C., White, A.J.P., Long, N.J., and Williams, C.K. (2014). Metal-size influence in iso-selective lactide polymerization. Angew. Chem. Int. Ed. *53*, 9226–9230.

105. Xu, T.-Q., Yang, G.-W., Liu, C., and Lu, X.-B. (2017). Highly robust yttrium bis(phenolate) ether catalysts for excellent isoselective ring-opening polymerization of racemic lactide. Macromolecules *50*, 515–522.

106. Zhong, Z., Dijkstra, P.J., and Feijen, J. (2002). [(salen)Al]-mediated, controlled and stereoselective ring-opening polymerization of lactide in solution and without solvent: synthesis of highly isotactic polylactide stereocopolymers from racemic d,l-lactide. Angew. Chem. Int. Ed. *41*, 4510–4513.

107. Nomura, N., Ishii, R., Yamamoto, Y., and Kondo, T. (2007). Stereoselective ring-opening polymerization of a racemic lactide by using achiral salen- and homosalen-aluminum complexes. Chem. Eur. J. *13*, 4433–4451.

108. Maudoux, N., Roisnel, T., Dorcet, V., Carpentier, J.-F., and Sarazin, Y. (2014). Chiral (1,2)-diphenylethylene-salen complexes of triel metals: coordination patterns and mechanistic considerations in the isoselective ROP of lactide. Chem. Eur. J. *20*, 6131–6147.

109. Kan, C., Hu, J., Huang, Y., Wang, H., and Ma, H. (2017). Highly isoselective and active zinc catalysts for rac-lactide polymerization: effect of pendant groups of aminophenolate ligands. Macromolecules *50*, 7911–7919.

110. Myers, D., White, A.J.P., Forsyth, C.M., Bown, M., and Williams, C.K. (2017). Phosphasalen indium complexes showing high rates and isoselectivities in rac-lactide polymerizations. Angew. Chem. Int. Ed. *56*, 5277–5282.

111. Jensen, T.R., Breyfogle, L.E., Hillmyer, M.A., and Tolman, W.B. (2004). Stereoelective polymerization of d,l-lactide using N-heterocyclic carbene based compounds. Chem. Commun. (Camb.), 2504–2505.

112. Dove, A.P., Li, H., Pratt, R.C., Lohmeijer, B.G.G., Culkin, D.A., Waymouth, R.M., and Hedrick, J.L. (2006). Stereoselective polymerization of rac- and meso-lactide catalyzed by sterically encumbered N-heterocyclic carbenes. Chem. Commun. (Camb.), 2881–2883.

113. Zhang, L., Nederberg, F., Messman, J.M., Pratt, R.C., Hedrick, J.L., and Wade, C.G. (2007). Organocatalytic stereoselective ring-opening polymerization of lactide with dimeric phosphazene bases. J. Am. Chem. Soc. *129*, 12610–12611.

114. Liu, S., Li, H., Zhao, N., and Li, Z. (2018). Stereoselective ring-opening polymerization of rac-lactide using organocatalytic cyclic trimeric phosphazene base. ACS Macro Lett. *7*, 624–628.

115. Miyake, G.M., and Chen, E.Y.-X. (2011). Cinchona alkaloids as stereoselective organocatalysts for the partial kinetic resolution polymerization of rac-lactide. Macromolecules *44*, 4116–4124.

116. Makiguchi, K., Yamanaka, T., Kakuchi, T., Terada, M., and Satoh, T. (2014). Binaphthol-derived phosphoric acids as efficient chiral organocatalysts for the enantiomer-selective polymerization of rac-lactide. Chem. Commun. (Camb.) *50*, 2883–2885.

117. Zhu, J.-B., and Chen, E.Y.-X. (2015). From meso-lactide to isotactic polylactide: epimerization by B/N Lewis pairs and kinetic resolution by organic catalysts. J. Am. Chem. Soc. *137*, 12506–12509.

118. Sanchez-Sanchez, A., Rivilla, I., Agirre, M., Basterretxea, A., Etxeberria, A., Veloso, A., Sardon, H., Mecerreyes, D., and Cossío, F.P. (2017). Enantioselective ring-opening polymerization of rac-lactide dictated by densely substituted amino acids. J. Am. Chem. Soc. *139*, 4805–4814.

119. Kopinke, F.D., Remmler, M., Mackenzie, K., Möder, M., and Wachsen, O. (1996). Thermal decomposition of biodegradable polyesters—II. Poly(lactic acid). Polym. Degrad. Stab. *53*, 329–342.

120. Nishida, H., Mori, T., Hoshihara, S., Fan, Y., Shirai, Y., and Endo, T. (2003). Effect of tin on poly(l-lactic acid) pyrolysis. Polym. Degrad. Stab. *81*, 515–523.

121. Mori, T., Nishida, H., Shirai, Y., and Endo, T. (2004). Effects of chain end structures on pyrolysis of poly(l-lactic acid) containing tin atoms. Polym. Degrad. Stab. *84*, 243–251.

122. Fan, Y., Nishida, H., Shirai, Y., Tokiwa, Y., and Endo, T. (2004). Thermal degradation behaviour of poly(lactic acid) stereocomplex. Polym. Degrad. Stab. *86*, 197–208.

123. Fan, Y., Nishida, H., Hoshihara, S., Shirai, Y., Tokiwa, Y., and Endo, T. (2003). Pyrolysis kinetics of poly(l-lactide) with carboxyl and calcium salt end structures. Polym. Degrad. Stab. *79*, 547–562.

124. Fan, Y., Nishida, H., Shirai, Y., and Endo, T. (2003). Racemization on thermal degradation of poly(l-lactide) with calcium salt end structure. Polym. Degrad. Stab. *80*, 503–511.

125. Fan, Y., Nishida, H., Mori, T., Shirai, Y., and Endo, T. (2004). Thermal degradation of poly(l-lactide): effect of alkali earth metal oxides for selective l,l-lactide formation. Polymer *45*, 1197–1205.

126. Motoyama, T., Tsukegi, T., Shirai, Y., Nishida, H., and Endo, T. (2007). Effects of MgO catalyst on depolymerization of poly-l-lactic acid to l,l-lactide. Polym. Degrad. Stab. *92*, 1350–1358.

127. Lunt, J. (1998). Large-scale production, properties and commercial applications of polylactic acid polymers. Polym. Degrad. Stab. *59*, 145–152.

128. Drumright, R.E., Gruber, P.R., and Henton, D.E. (2000). Polylactic acid technology. Adv. Mater. *12*, 1841–1846.

129. Noda, M., and Okuyama, H. (1999). Thermal catalytic depolymerization of poly(l-lactic acid) oligomer into LL-lactide : effects of Al, Ti, Zn and Zr compounds as catalysts. Chem. Pharm. Bull. *47*, 467–471.

130. Shuklov, I.A., Jiao, H., Schulze, J., Tietz, W., Kühlein, K., and Börner, A. (2011). Studies on the epimerization of diastereomeric lactides. Tetrahedron Lett. *52*, 1027–1030.

131. Benson, R.D. and Schroeder, J.D. (2015). Recovery of lactic acid values from a meso-lactide stream. US Patent 9035076B2, filed September 27, 2013, and granted May 19, 2015.

132. Xiong, M., Schneiderman, D.K., Bates, F.S., Hillmyer, M.A., and Zhang, K. (2014). Scalable production of mechanically tunable block polymers from sugar. Proc. Natl. Acad. Sci. U S A *111*, 8357–8362.

133. Schneiderman, D.K., Vanderlaan, M.E., Mannion, A.M., Panthani, T.R., Batiste, D.C., Wang, J.Z., Bates, F.S., Macosko, C.W., and Hillmyer, M.A. (2016). Chemically recyclable biobased polyurethanes. ACS Macro Lett. *5*, 515–518.

134. Brutman, J.P., De Hoe, G.X., Schneiderman, D.K., Le, T.N., and Hillmyer, M.A. (2016). Renewable, degradable, and chemically recyclable cross-linked elastomers. Ind. Eng. Chem. Res. *55*, 11097–11106.

135. Werpy, T., and Petersen, G. (2004). Top Value Added Chemicals from Biomass Volume I: Results of Screening for Potential Candidates (US Department of Energy).

136. Fahnhorst, G.W., and Hoye, T.R. (2018). A carbomethoxylated polyvalerolactone from malic acid: synthesis and divergent chemical recycling. ACS Macro Lett. *7*, 143–147.

137. Blake, T.R., and Waymouth, R.M. (2014). Organocatalytic ring-opening polymerization of morpholinones: new strategies to functionalized polyesters. J. Am. Chem. Soc. *136*, 9252–9255.

138. Bozell, J.J., and Petersen, G.R. (2010). Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. Green Chem. *12*, 539–554.

139. Moore, T., Adhikari, R., and Gunatillake, P. (2005). Chemosynthesis of bioresorbable poly(γ-butyrolactone) by ring-opening polymerisation: a review. Biomaterials *26*, 3771–3782.

140. Martin, D.P., and Williams, S.F. (2003). Medical applications of poly-4-hydroxybutyrate: a strong flexible absorbable biomaterial. Biochem. Eng. J. *16*, 97–105.

141. Houk, K.N., Jabbari, A., Hall, H.K., and Alemán, C. (2008). Why δ-valerolactone polymerizes and γ-butyrolactone does not. J. Org. Chem. *73*, 2674–2678.

142. Oishi, A., Taguchi, Y., Fujita, K., Ikeda, Y., and Masuda, T. (2000). Production of poly-γ-butyrolactone. Japanese Patent JP2000281767A, filed March 31, 1999, and published October 10, 2000.

143. Oishi, A., Taguchi, Y., and Fujita, K. (2003). Production method of poly(γ-butyrolactone) using metal complex catalyst. Japanese Patent JP2003252968A, filed March 5, 2002, and published September 10, 2003.

144. Korte, F., and Glet, W. (1966). Hochdruckreaktionen. II. Die polymerisation von γ-butyrolacton und δ-valerolactam bei hohen drücken. J. Polym. Sci. B *4*, 685–689.

145. Yamashita, K., Yamamoto, K., and Kadokawa, J.-I. (2014). Acid-catalyzed ring-opening polymerization of γ-butyrolactone under high-pressure conditions. Chem. Lett. *43*, 213–215.

146. Nobes, G.A.R., Kazlauskas, R.J., and Marchessault, R.H. (1996). Lipase-catalyzed ring-opening polymerization of lactones: a novel route to poly(hydroxyalkanoate)s. Macromolecules *29*, 4829–4833.

147. Hong, M., and Chen, E.Y.-X. (2016). Towards truly sustainable polymers: a metal-free recyclable polyester from biorenewable non-strained γ-butyrolactone. Angew. Chem. Int. Ed. *55*, 4188–4193.

148. Zhao, N., Ren, C., Li, H., Li, Y., Liu, S., and Li, Z. (2017). Selective ring-opening polymerization of non-strained γ-butyrolactone catalyzed by a cyclic trimeric phosphazene base. Angew. Chem. Int. Ed. *56*, 12987–12990.

149. Tang, J., and Chen, E.Y.-X. (2018). Effects of chain ends on thermal and mechanical properties and recyclability of poly(γ-butyrolactone). J. Polym. Sci. A Polym. Chem. https://doi.org/10.1002/pola.29180.

150. Kitson, R.R.A., Millemaggi, A., and Taylor, R.J.K. (2009). The renaissance of α-methylene-γ-butyrolactones: new synthetic approaches. Angew. Chem. Int. Ed. *48*, 9426–9451.

151. Hoffmann, H.M.R., and Rabe, J. (1985). Synthesis and biological activity of α-methylene-γ-butyrolactones. Angew. Chem. Int. Ed. *24*, 94–110.

152. Engelberg, I., and Kohn, J. (1991). Physico-mechanical properties of degradable polymers used in medical applications: a comparative study. Biomaterials *12*, 292–304.

153. Haba, O., and Itabashi, H. (2014). Ring-opening polymerization of a five-membered lactone trans-fused to a cyclohexane ring. Polym. J. *46*, 89–93.

154. Zhu, J.-B., and Chen, E.Y.-X. (2018). Living coordination polymerization of a six-five bicyclic lactone to produce completely recyclable polyester. Angew. Chem. Int. Ed. *57*, 12558–12562.