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Recyclable and (Bio)degradable Polyesters in a Circular Plastics Economy

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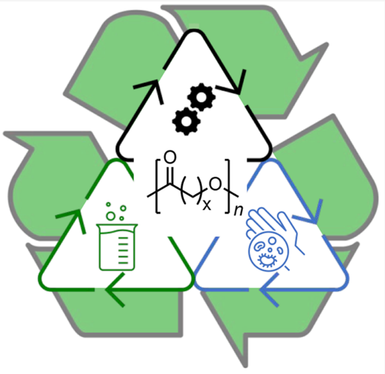
ABSTRACT: Polyesters carrying polar main-chain ester linkages exhibit distinct material properties for diverse applications and thus play an important role in today's plastics economy. It is anticipated that they will play an even greater role in tomorrow's circular plastics economy that focuses on sustainability, thanks to the abundant availability of their biosourced building blocks and the presence of the main-chain ester bonds that can be chemically or biologically cleaved on demand by multiple methods and thus bring about more desired end-of-life plastic waste management options. Because of this potential and promise, there have been intense research activities directed at addressing recycling, upcycling or biodegradation of existing legacy polyesters, designing their biorenewable alternatives, and redesigning future polyesters with intrinsic chemical recyclability and tailored performance that can rival today's commodity plastics that are either petroleum based and/or hard to recycle. This review captures these exciting recent developments and outlines future challenges and opportunities. Case studies on the legacy polyesters, poly(lactic acid), poly(3-hydroxyalkanoate)s, poly(ethylene terephthalate), poly(butylene succinate), and poly(butylene-adipate terephthalate), are presented, and emerging chemically recyclable polyesters are comprehensively reviewed.



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1. INTRODUCTION

Polyesters[1−7] are broadly defined by polymers bearing ester [−C(═O)−O−] linkages on their main-chain backbone. They are further classified into two major categories: aliphatic and aromatic or aliphatic/aromatic (semiaromatic) polyesters, which have backbone carbon linkages containing alkyl and aryl or both alkyl/aryl moieties, respectively. Aromatic polyesters,[3,8−12] such as poly(ethylene terephthalate) (PET) widely used in packaging (e.g., water or soda bottles) and textile (e.g., fiber fabrics) industries, tend to exhibit superior performance in thermal properties, including temperatures of decomposition (T_d), melting transition (T_m), and glass transition (T_g), and in mechanical properties, including Young's or elastic modulus (E), ultimate tensile strength at break (σ_B), and fracture strain or elongation at break (ε_B), to their aliphatic counterparts, especially in the packaging and textile industries. On the other hand, aliphatic polyesters,[12−22] such as "green" plastics polylactide or poly(lactic acid) (PLA) and poly(3-hydroxyalkanoate)s (PHAs), possess intrinsically better chemical degradability, biodegradability, and biocompatibility. Overall, since ester bonds can be cleaved chemically by base- or acid-catalyzed hydrolysis and transesterification or biologically by enzymes, polyesters exhibit several desirable end-of-life (EoL) options, other than mechanical recycling, for postconsumer polymer waste management, including chemical and biological recycling or upcycling, as well as composting. These desirable properties place polyesters in a unique position to effectively address the global plastics problem,[23−26] which is a trifecta concerning not just the environment, commonly known as the plastics pollution crisis resulting from an alarmingly low waste plastics recycling rate of only 9% and about 85% of plastic packaging worldwide ending up in landfills and oceans,[27−31] but also energy and climate, because the global production of plastics is predicted to consume about 20% of oil and contribute to about 15% of the carbon budget by 2050.[24,26,32]

Polyesters play an important role in today's plastics economy and have found use in many different applications.[33−36] However, as the world is transitioning from a traditional linear materials economy to a future circular materials economy toward sustainability,[20,37−42] polyesters will play an even greater role in tomorrow's plastics economy. This predicted trend is based on polyesters' abundant availability of their biosourced building blocks and the presence of the main-chain ester bonds that can be chemically or biologically cleaved on demand by multiple methods and thus bring about more desired EoL plastic waste management options.[43,44] Note here that chemical recycling consists of both open-loop recycling by deconstruction to chemicals, intermediates, or molecules that can be reutilized or repurposed for useful chemicals or materials and closed-loop recycling by depolymerization to building-block monomers (i.e., chemical recycling to monomer).[37,38,40,42]

In this review, we aim to capture recent exciting developments in technologically important legacy and emerging polyesters aiming to achieve materials circularity toward sustainability. In legacy polyesters, the research activities have been focused on addressing chemical recycling or upcycling, enhancing biodegradation of aromatic polyesters, toughening semicrystalline aliphatic polyesters, and identifying biorenewable alternatives. In emerging polyesters, major efforts have been directed at designing new, biobased, intrinsically circular polyesters[45] that exhibit not only chemical circularity but also performance properties that can rival or even exceed those of incumbent polyesters that are either petroleum based and/or harder to recycle. Although polyesters have been reviewed in the past,[1−22] this article takes a much needed new approach by focusing on efforts to establish materials circularity for polyesters (or circular polyesters) by various chemical, mechanical, and biological means. For the highlighted five most important commercial legacy polyesters, PLA, PHA, PET, poly(butylene succinate) (PBS), and poly(butylene-adipate terephthalate) (PBAT), synthetic routes are first briefly overviewed and summarized but are not discussed in detail as many prior reviews[21,46−49] have already covered their syntheses, followed by their chemical, mechanical, and biological recycling processes (Figure 1).

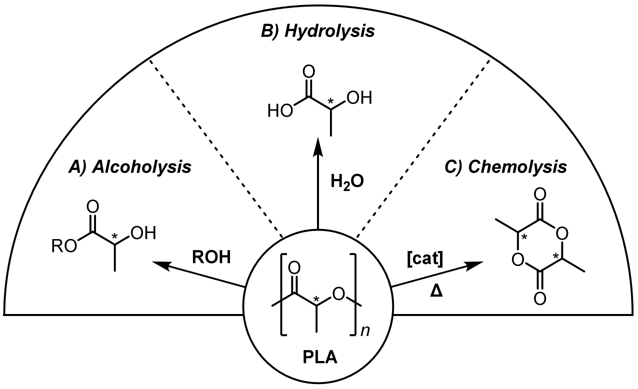
The general comparisons of these three main plastics recycling processes in terms of relative advantages and disadvantages are summarized in Table 1. For emerging polyesters designed to exhibit closed-loop chemical recyclability, their synthetic methods are classified into two major mechanisms: chain-growth ring-opening polymerization (ROP) and step-growth polycondensation (SGP). Enzymatic polymerization and copolymerization, where applicable, are also discussed. Mixed polyesters or polyesters in mixed waste plastics are ubiquitous in real-world waste plastics streams. Recycling of such mixtures presents the most daunting challenge, and its recent progress is categorized into four approaches: mechanical recycling, separation by dissolution/precipitation, biological funneling, and closed-loop recycling and upcycling. Lastly, we summarize emerging trends of research on polyesters and present our perspective on the need to further develop sustainable polyesters in a circular plastics economy, with the four most urgent issues to address outlined, and propose promising or potential solutions in the context of solving the current plastics problem.

2. LEGACY POLYESTERS

2.1. Polylactide or Poly(lactic acid) (PLA)

Polylactide or poly(lactic acid), more commonly known as PLA, is the most well-known commercially implemented aliphatic polyester and has found use in many industries including medical devices, 3D-printing filaments, single-use products, and agricultural applications.[47,48,50−52] PLA is bioderived from biorenewable sources such as corn or sugar beets and industrially compostable, making it a more sustainable polyester. PLA has been shown to be chemically recyclable through alcoholysis, hydrolysis, and chemolysis (Scheme 1). This section will discuss the synthesis as well as chemical, mechanical, and biological recycling methods and processes of this legacy polyester.

Scheme 1. Overview of the Chemical Recycling Pathways of PLA via (A) Alcoholysis, (B) Hydrolysis, and (C) Chemolysis



2.1.1. Synthetic Routes. PLA with high molecular mass (number-average molar mass (M_n) > 100 kDa) can be synthesized through the ROP of lactide (LA), the cyclic dimer of lactic acid, which is prepared through the catalyzed depolymerization of low molar mass PLA by the SGP of lactic acid derived from biological fermentation of certain carbohydrates (Scheme 2).[47,48,51−53] Owing to the pendant methyl groups on the PLA chain, the PLA material can exist in multiple forms based on its stereomicrostructure, the organization of the stereogenic centers with the pendant methyl groups attached. The most common form of PLA is enantiomerically pure PLLA synthesized from the corresponding enantiomerically pure (*S*,*S*)-L-LA or (*S*)-L-lactic acid or through the stereospecific polymerization of racemic LA (*rac*-LA) without transesterification (Scheme 2A). PDLA can also be synthesized from (*R*,*R*)-D-LA or (*R*)-D-lactic acid. Both PLLA and PDLA are defined as isotactic (*it*) and have a high T_m of up to 180 °C and an above room temperature T_g of ∼65 °C, making them glassy materials. Mechanically, PLLA is a stiff and strong material with a high modulus of $E \approx 3.0$ GPa and an ultimate strength of ∼50 MPa, but it is very brittle with ε_B only about 1−8% (Scheme 2B).[54] A 1:1 mixture of enantiomeric PLA chains, PLLA and PDLA, has also been shown to stereocomplex to form a strong stereocomplex with a higher T_m up to 230 °C (Scheme 2C).[55−57]

Other forms of PLA materials can be synthesized from *meso*-LA including syndiotactic (*st*)[54] and heterotactic (*ht*)[58] PLA (Scheme 2A). When *rac*-LA is polymerized without high to perfect stereocontrol, iso-rich (*ir*) PLA is produced; similarly, when *meso*-LA is polymerized without high to perfect stereocontrol, syndio-rich (*sr*) PLA results (Scheme 2A). Stereoblock PLA comprising L- and D-LA blocks has also been synthesized (Scheme 2A).[54] Mixtures of *rac*- and *meso*-LA can also be polymerized to form atactic (*at*)-PLA and other in-between stereomicrostructures. Other than stereoregular *it*-PLA and *st*-PLA, which are semicrystalline materials, these other forms of PLA are amorphous materials and thus less useful.

Other routes to PLA include biological fermentation and (solution and melt) polycondensation. The biological synthesis of PLA is not as robust as the ROP methods, but there are literature examples, mostly focusing on the bacterial fermentation to produce L-lactic acid, which is then used to synthesize PLA, rather than the direct biological synthesis of PLA (Scheme 2E). The majority (90%) of lactic acid is produced through bacterial fermentation due to its economic feasibility.[59] Several reviews and articles have well covered the PLA biosynthesis.[59−63] The most straightforward synthesis of PLA is through the direct polycondensation of lactic acid, which proceeds through a SGP mechanism (Scheme 2B and 2D).[64−67] The SGP method leads to PLA materials with low molar mass but high dispersity ($Đ > 2.0$), and the reactions are carried out in harsh conditions (∼180 °C or higher, >24 h). Industrial methods for the synthesis of PLLA rely on the SGP of (*S*)-L-lactic acid, where it is first condensed to low molar mass oligomers ≤ 5.0 kg mol^{-1} in a prepolymerization step. Either the prepolymer is further polymerized through a second-stage SGP process at higher temperatures to high molar mass PLLA or preferably the oligomers are depolymerized to L-LA (conditions: 10 mmHg, 0.05 wt % of Sn(II) catalyst, 225−250 °C) which can subsequently be polymerized through a ROP mechanism to high molar mass PLLA (Scheme 2B).[68] The advantage of the latter approach is that the resulting L-LA can be polymerized by the ROP via the rapid chain-growth polymerization mechanism to achieve low to

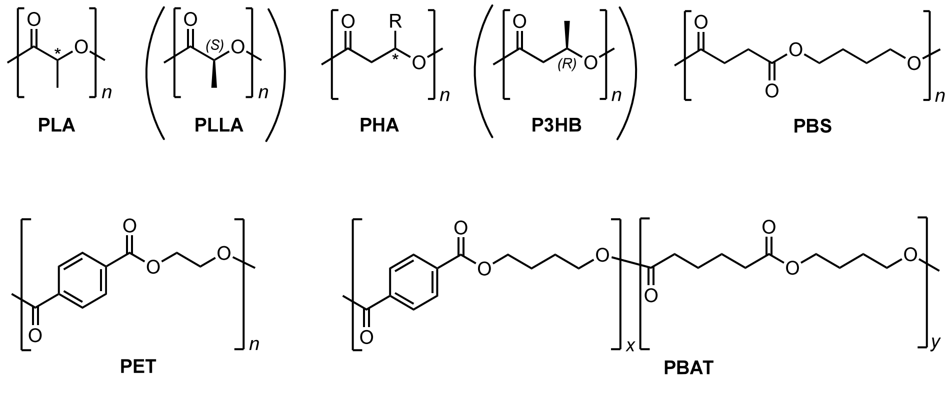


Figure 1. Legacy polyesters discussed in this review.

Table 1. General Comparisons of Plastics Recycling Methods Discussed in This Review

recycling method	description	advantages	disadvantages
chemical (closed loop)	selective depolymerization into constituent monomers via thermolysis or chemolysis-catalyzed thermodepolymerization	closed-loop monomer—polymer—monomer circular process	potentially high-energy inputs for (de)polymerization processes, especially for uncatalyzed processes
		virgin-quality materials are reproduced	polymers that can be readily recycled in a closed-loop manner often exhibit (de)polymerizability/performance trade-offs
		short path to establish a circular plastics economy	
		fast kinetics and short time scales (seconds to hours)	
chemical (open loop)	breaking down polymers into small molecules or intermediates through various deconstruction processes	access to higher value building blocks or materials from waste plastics which can be used in many industries (polymers, pharmaceuticals, fine chemicals, energy, etc.)	value-added materials typically are not more recyclable and do not exhibit (direct) circularity
			selectivity to single molecules or materials is typically not high, requiring further separation and/or purification
mechanical	reuse of postconsumer plastics products through various mechanical reprocessing methods	shortest path to establish a circular (polymer-to-polymer) economy	material quality and value is typically reduced upon recycling—"downcycling"
		short time scale of recycling on the order of minutes to hours	quality of the reprocessed products is highly sensitive to the purity of the collected polymers
		low environmental impacts and polymer reproduction costs	virgin-quality polymer is often added to the recycling process to maintain usable properties
biological	leveraging microbial or enzymatic processes to degrade polymers into monomers or small molecules	low energy inputs required under biological conditions (low temperature and pressure)	monomer recovery is typically low, and material inputs are high
		more environmentally benign processes	enzymes can struggle to degrade crystalline regions of polymers
			full biodegradation cycle (to CO_2 + H_2O + biomass) can be very long (years)

high molar mass PLLA in a controlled fashion, but an issue is the partial epimerization during depolymerization to generate a small amount of D-LA and *meso*-LA, which necessities further purification to obtain the pure L-LA when desired. Melt polycondensation of PLA oligomers and the implementation of solution polycondensation reactions using high-boiling solvents represent the recent advances in the polycondensation process of synthesizing PLA.[64,69−75]

The most active area of research in the synthesis of PLA is the ROP of LA. Advancements have been made in metal-based,[46,76−80] organic,[81−93] and enzymatic[62,94,95] catalysis for the efficient synthesis of both PLLA and other stereoisomers. The most noteworthy catalyst, which is used for the industrial ROP of LA, is tin(II) octoate, $Sn(Oct)_2$, thanks to its high activity, efficiency, and stability. Since the first report of the polycondensation to PLA in 1845 by Pelouze[96] and the first report of the ROP of LA in 1932 by Carothers,[97] subsequent intensive research has led to the commercial success of PLA. NatureWorks is the largest producer of PLLA, producing up to 75 000 t (MT) of PLLA a year, for packaging, textiles, diapers, and even engineering applications in cars, etc.[50,52,98]

PLA is marketed as a biobased polymer that can be industrially composted, which is the degradation of PLA into CO_2 and H_2O in a managed environment (e.g., at controlled temperature and humidity). Although this is an effective EoL option for PLA, the (complete or incomplete) degradation products are typically not collected and then used to remake PLA. Recycling of PLA is a better option and has been performed in three categories including chemical, either back to LA or lactic acid (closed-loop recycling) or to other useful chemicals (open-loop recycling), mechanical, and biological recycling.

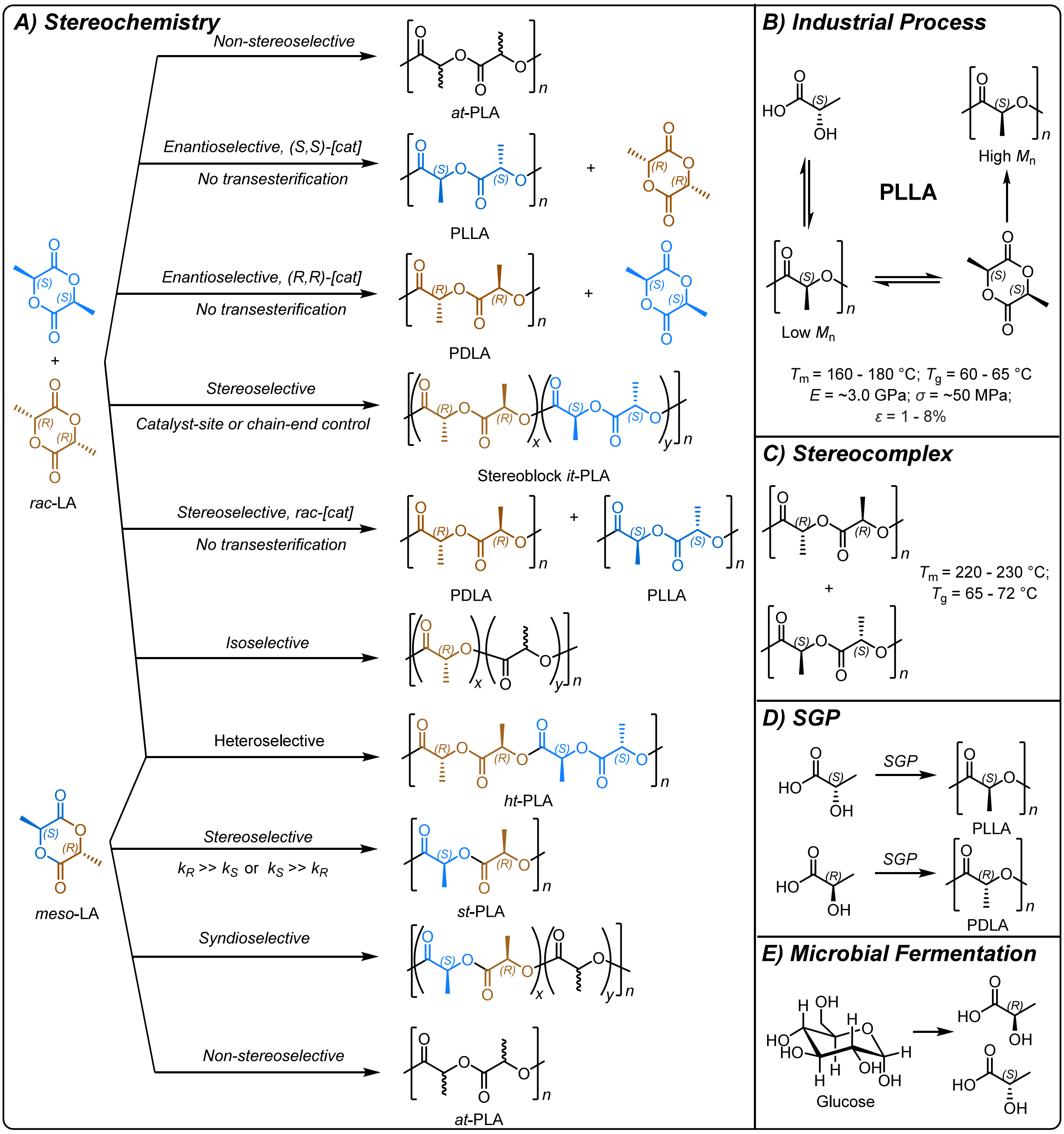
2.1.2. Chemical Recycling.

Chemical recycling, involving solvolysis or chemolysis depolymerization processes, effectively breaks down polymer chains into their constituent monomers or transforms the resulting intermediates into other valuable chemicals or materials. A notable advantage of closed-loop chemical recycling over other recycling strategies lies in its ability to indefinitely repolymerize the recovered monomers, regenerating polymers with virgin quality, which allows for the production of polymers in a closed-loop manner and paves the way toward a circular polymer economy. Discussed here are the three chemical recycling methods of PLA: hydrolysis, alcoholysis, and chemolysis.[99] Chemical recycling can occur in either closed- or open-loop processes whose products can either be repolymerized to PLA or used in other chemical transformations.

2.1.2.1. Hydrolysis.

Catalyzed or uncatalyzed hydrolysis of PLLA to L-lactic acid provides an efficient process for facile chemical recycling of PLLA (Scheme 3), which needs no further separation of enantiomers after hydrolysis as the L-lactic acid can be directly polymerized via SGP to PLLA or dimerized to L-LA that can be repolymerized to high molar mass PLLA via ROP.[100] Hydrolysis performed at a high temperature (250 °C) required no catalyst and a short reaction time (20 min), which produced lactic acid with a 90% yield with 90% selectivity toward L-lactic acid (81% L-lactic acid yield).[101] At temperatures above ∼250 °C, racemization of L-lactic acid occurs, leading to mixtures of D- and L-lactic acids, which hinders the synthesis of PLLA in quantitative isotacticity (with negligible stereoerrors). The NaOH-mediated hydrolysis of PLLA provided pure L-lactic acid with yields greater than 90% in 20 min at 180 °C.[102] Adding either an acid or a base catalyst has also been shown to greatly reduce the temperature needed (<100 °C) to depolymerize PLA. These methods are

Scheme 2. Overview of the Synthetic Methods Toward Various Types of PLA Materials[a]

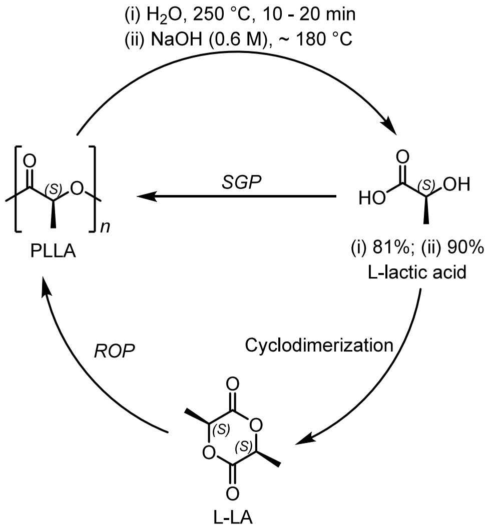


[a](A) ROP of *rac*-LA and *meso*-LA to the corresponding PLAs, (B) industrial approach toward the synthesis of PLLA, (C) physical properties of stereocomplexed PLA, (D) step-growth polymerization of L-lactic acid and D-lactic acid toward PLLA and PDLA, and (E) synthesis of lactic acid from fermentable carbohydrates such as glucose.

performed through either bulk or surface erosion of PLA due to its poor solubility in water.[103,104] The acid-mediated depolymerization is a chain end scission process leading directly to lactic acid. The base-mediated depolymerization is a random chain scission process leading first to lactide which is then hydrolyzed to lactic acid. Several reviews outline the specific processes for the hydrolysis of PLA.[99,100,105,106] Other forms of PLA have also been investigated for their hydrolysis. Once PLA is hydrolyzed to lactic acid, it can be transformed into many useful chemicals including propylene glycol, acrylic acid, alkyl lactate, and pyruvic acid or dimerized to lactide which can be repolymerized back to PLA. Lactic acid can also be repolymerized back to PLA via SGP, providing two methods for the closed-loop recycling of PLA through hydrolysis.

2.1.2.2. Alcoholysis. In a manner similar to hydrolysis, PLA can be depolymerized through catalyzed alcoholysis with various alcohols including methanol (MeOH), ethanol (EtOH), and butanol (BuOH), forming the corresponding methyl, ethyl, and butyl lactate (Scheme 4). These lactates can then be transformed into L-LA and subsequently PLA via ROP. Many metal-based and organic catalysts have been implemented in this process, including metal salts, alkali halide salts, ionic liquids, discrete metal complexes, and various organic

Scheme 3. Closed-Loop Chemical Recycling of PLLA via Hydrolysis of PLLA to L-Lactic Acid, Which Can Be Either Repolymerized to PLLA via SGP or Cyclodimerized to L-LA for Its Subsequent ROP to High Molar Mass PLLA



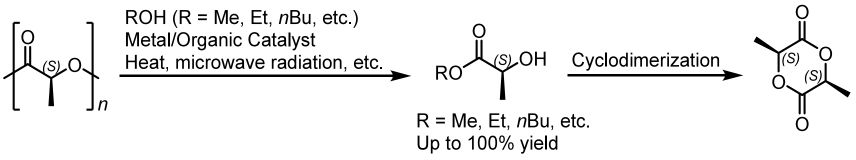
catalysts.[99,107] For example, Zn(II) and Mg(II) complexes with catalen ligands were found to be active for the methanolysis of PLA in THF under mild conditions (80 °C), leading to methyl lactate in 64% yield after 8 h.[108] Using microwave irradiation increased the rate of alcoholysis of PLLA with EtOH and BuOH.[109] Postconsumer PLA was depolymerized through a catalyzed transesterification mechanism to ethyl lactate using a zinc catalyst.[110] Zinc salts were also used to both polymerize and depolymerize PLA with zinc(II) acetate being highly active for the depolymerization of PLA to methyl lactate under microwave heating.[111]

2.1.2.3. Chemolysis. Uncatalyzed thermolysis of PLLA requires a high temperature and also causes racemization of stereocenters, but catalyzed thermolysis, or chemolysis, of PLLA (especially low molar mass PLLA) leads selectively to L-LA at medium to high temperatures. For example, depolymerization at 230−245 °C in the presence of Sn(Oct)$_2$ proceeded through intramolecular transesterification, leading to depolymerization yields of up to 89% and selectivity to L-LA of up to 98%.[112] Depolymerization studies at temperatures above and below 330 °C revealed that above 330 °C, cis-elimination reactions and intramolecular transesterification occur, while below 330 °C, intermolecular transesterification and unzipping depolymerization occur to yield low molar mass PLLA and L-LA.[113] It has also been shown that *meso*-LA can be obtained from PLLA through thermolysis.[114] In a closed system at temperatures of 250−290 °C, low depolymerization yields (<20%) were observed, likely due to the repolymerization of LA once it was formed.[115] Residual polymerization catalyst is necessary for these processes to occur, and the effect of tin-based catalyst Sn(Oct)$_2$ as the most prevalent polymerization catalyst for PLA was studied.[116] Using specific tin-based catalysts, tin(II) oxalate and tin(II) acetate, the degradation temperature of PLA can be drastically lowered.[117] Zeolites in appropriate solvents can also be used for the direct formation of L-LA, which reduces the energy input for this process.[118] Most recently, Williams, Buchard, and co-workers reported a highly efficient method of depolymerizing commercially relevant solid-state PLLA films to L-LA in high yields and selectivity. Pairing Sn(Oct)$_2$ with glycerolethoxylate (GEO) yielded a highly active (92% yield at 0.01 mol % of catalyst loading; turnover frequency (TOF) = 2800 h^{-1}) and selective (>99% selectivity to L-LA) depolymerization catalyst which operates at mild conditions (neat, 160 °C, 5 mbar or N$_2$ flow) (Scheme 5).[119]

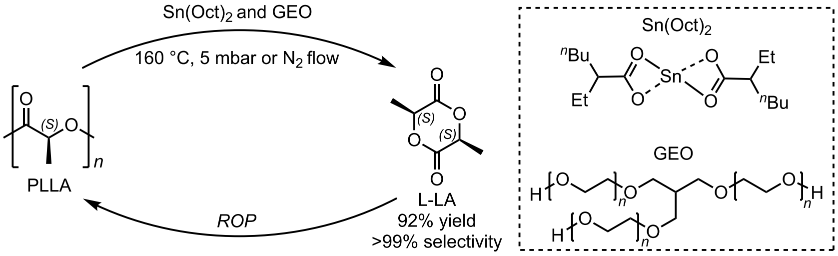
The ceiling temperature (T_c) of the monomer or polymer, expressed as $T_c = \Delta H_p^o / \{\Delta S_p^o + R \ln[M]_{eq}\}$,[120] is defined as the temperature at which $[M]_{eq} = [M]_0$ (i.e., no polymerization occurring), namely, the highest temperature the monomer can polymerize or the lowest temperature the polymer starts to depolymerize back to monomer. Hence, it serves as a measure of polymerizability or depolymerizability and determines the relative stability of monomer vs polymer states at different working temperature (T) regimes. In this context, PLA has a high T_c (>600 °C in bulk), which is why high temperatures are necessary for their depolymerization. In solution, lowering the concentration decreases T_c, shifting the equilibrium more to the monomer side and thus favoring the depolymerization. It is important to point out that T_c is affected by not only ΔH_p^o, ΔS_p^o, and $[M]_0$ (concentration) but also the solvent properties (which is not apparent from the T_c equation). For example, solvents were found to strongly affect the T_c of the depolymerization of PLLA using Sn(Oct)$_2$; utilizing such solvent effects on T_c, the Sn(Oct)$_2$-catalyzed depolymerization of PLLA in dimethyl formamide or γ-valerolactone led directly to L-LA (98−99% selectivity) within 1−4 h with >95% conversion at 140 °C.[121]

The above-discussed methods, which are used to produce L-lactic acid and alkyl lactates, can also be employed in the synthesis of other products and feedstocks.[99,104] For example, reduction of lactic acid leads to propylene glycol, which has uses in medicines, cosmetics, and food production, leading to open-loop recycling of PLA. It can also be dehydrated to acrylic acid, a useful monomer used to produce poly(vinyl alcohol) and acrylics.[122] Pyruvic acid can also be produced through the oxidation of lactic acid. Derivatives of the before mentioned chemicals can be synthesized from alkyl lactates. Recently, PLA was upcycled to methyl methacrylate (MMA), a monomer used in the synthesis of poly(methyl methacrylate) and its copolymers, which are used in paints, adhesives, and coatings. Here, PLA was valorized to methyl propionate at 220 °C using an α-MoC catalyst in MeOH and then transformed into MMA using a Cs−La/silica base−acid bifunctional catalyst in formaldehyde at 380 °C.[123] Even though there are

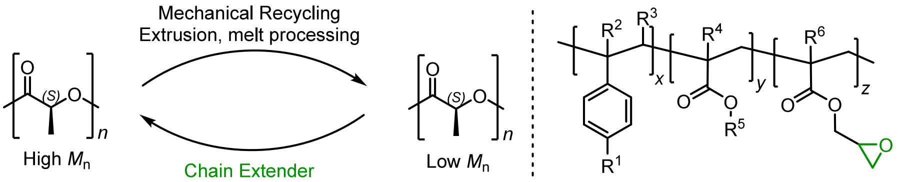
Scheme 4. Alcoholysis of PLLA to Alkyl Lactate, Followed by Cyclodimerization to L-LA



Scheme 5. Catalyzed Thermal Depolymerization of PLLA to L-LA for Repolymerization via ROP to High Molar Mass PLLA



Scheme 6. Addition of Chain Extender (Epoxide Highlighted in Green Is the Reactive Center) To Mechanically Degraded PLLA Can Yield Higher Molar Mass PLLA



more important closed-loop recycling pathways of PLA, these open-loop recycling methods show that PLA has many valuable EoL options.

2.1.3. Mechanical Recycling. Mechanical recycling provides the shortest closed loop for polymer-to-polymer recycling and is recognized as a more environmentally friendly process that requires relatively low investment and is straightforward to implement, making it a popular choice for the recycling of polymers.[124,125] The mechanical recycling process comprises several steps, including waste collection, separation, sorting, cleaning, drying, and grinding. However, it is important to acknowledge that products resulting from mechanical recycling often exhibit properties inferior to those of the original materials. Currently, PLA is not mechanically recycled on scale, as the major problem associated with mechanical recycling of PLA is loss of molar mass during the process due to considerable chain scission.[105] This loss of molar mass typically effects the physical properties of PLA, leading to materials of lower value. One such notable physical property change that has been observed is its thermal properties under mechanical recycling conditions. It has been shown that increased crystallization led to more opaque materials due to the faster crystallization kinetics of lower molar mass PLA after recycling cycles.[126,127]

The mechanical properties of PLA have also been shown to be reduced after multiple reprocessing cycles.[128−130] A solution to this problem is the addition of chain extenders to PLA during recycling (Scheme 6).[105,131−135] These chain extenders work by reacting with the (hydroxy) end groups of PLA and combining multiple chains together to increase the molar mass of the material. Bifunctional extenders lead to linear PLA with increased molar mass, while higher order extenders lead to branched or cross-linked PLA, again with increased molar mass. This increase in molar mass leads to PLA with physical properties more resembling those of the virgin PLA.

Mechanical recycling is a useful closed-loop recycling method of PLA. Because of inevitable degradation of PLA during the process and lack of infrastructure, mechanical recycling of PLA has not been widely implemented, but it will be necessary to help solve the plastics crisis.

2.1.4. Biological Recycling. Biological recycling leverages microbial or enzymatic processes for the degradation of biodegradable plastics. Given the advances made in protein engineering and the scaling up of protein production, there is burgeoning interest in enzyme-driven, bespoke plastics depolymerization. This recycling strategy holds several distinct advantages[136,137] as it operates under mild temperatures and pressures, thus demanding less energy than its mechanical and chemical counterparts. Moreover, it offers the opportunity to reclaim the original monomers, which can be either repolymerized into a new plastic material with virgin quality or transformed into other valuable compounds.

Biological recycling has been applied to PLA.[138] An enzyme was used to degrade PLLA to optically active L-lactic acid. Relatively low temperatures (40 °C) and short depolymerization times (8 h) were employed to depolymerize 2000 mg/L of PLA using 20 mg/L of enzyme to 600 mg/L of L-lactic acid, which could then be repolymerized to PLLA, demonstrating a closed-loop biological recycling route.[139] Other biological pathways have been reviewed well elsewhere.[140]

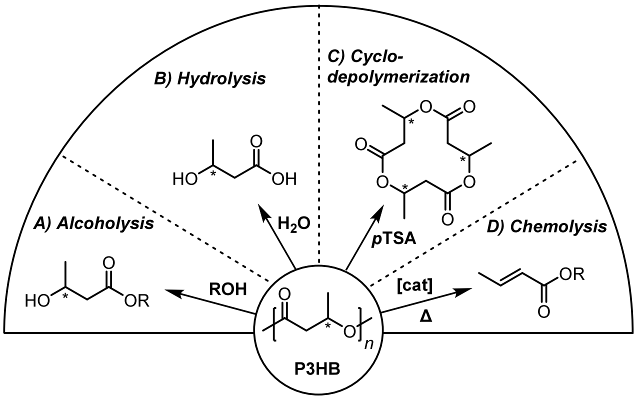
Enzymatic recycling pathway can be categorized into proteases, lipases, or cutinases. Degradation of PLA using Actonomycetes, which are categorized as proteases, has been shown to be effective for biological recycling at moderate temperatures (≤ 70 °C) and neutral to basic conditions.[139,141−143] Actonomycetes are the majority of the microbes used to degrade PLA, but bacteria[144] and fungi[145] have also been shown to be effective.

Biology offers a powerful handle for recycling bioplastics, especially PLA. There have been no large-scale biological processes implemented for recycling PLA due to current high costs and undesirable yields, as compared to other recycling methods. Continued research to overcome the cost and yield issues of biological recycling routes may lead to more efficient processes to recover L-lactic acid or L-LA monomer for repolymerization to PLLA.

2.2. Poly(3-hydroxyalkanoate)s (PHAs)

PHAs are a class of biobased and biodegradable polyesters that have been studied intensively for the last century.[49,146−151] There are over 150 unique PHAs with various side-chain compositions. The most attractive property of PHAs is their ability to biodegrade in unmanaged conditions.[152−155] Unlike PLA, which needs to be industrially composted due to its higher T_g (∼65 °C), PHAs have a lower T_g (typically below 0 °C), which allows for enough amorphous regions for the material to biodegrade in unmanaged conditions. PHAs have been commercialized for use as packaging materials, straws, cosmetics, plasticizers, and medical uses.[156] The methyl-substituted PHA, poly(3-hydroxybutyrate) (P3HB), is the most common and important member of the large PHA family, which will be used as a representative example to demonstrate the EoL options for PHAs, including alcoholysis, hydrolysis, cyclodepolymerization, and chemolysis (Scheme 7). This discussion will also include the mechanical and biological recycling of P3HB and other redesigned PHAs for closed-loop chemical recycling.

Scheme 7. Overview of the Chemical Recycling Pathways of P3HB via (A) Alcoholysis, (B) Hydrolysis, (C) Cyclodepolymerization, and (D) Chemolysis



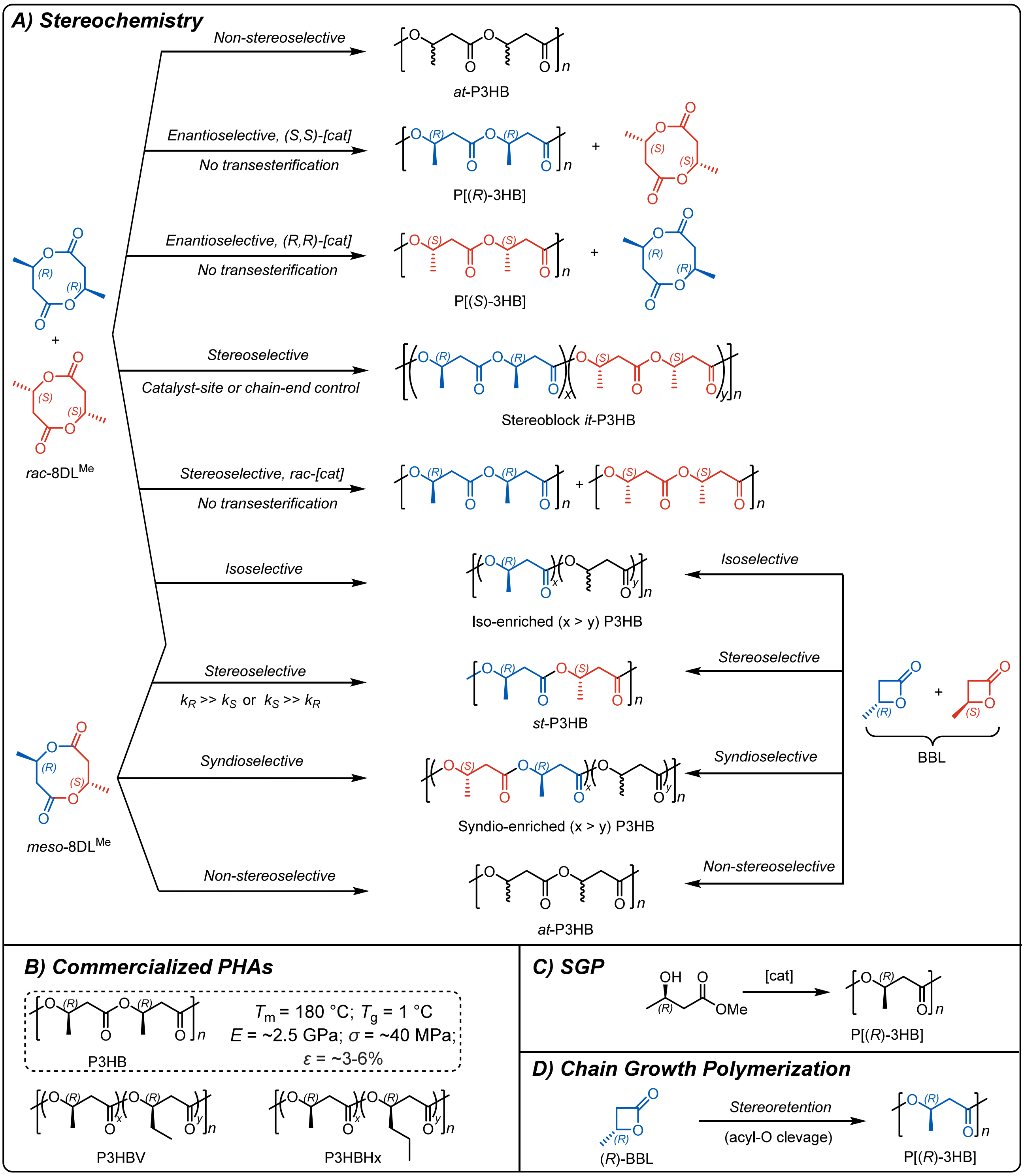
2.2.1. Synthetic and Biological Routes. PHAs are synthesized biologically, through fermentation, or synthetically, typically through the ROP of lactones and cyclic diesters (Scheme 8). In addition to P3HB, other common and commercially implemented short-chain-length PHAs include poly(3-hydroxyvalerate) (P3HV), poly(3-hydroxy-*co*-3-hydroxyvalerate) (P3HBV), and poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (P3HBHx), Scheme 8B. Biologically produced PHAs, including those with medium-chain-length and long-chain-length substituents, are made exclusively with an absolute (*R*) configuration on the PHA backbond, making it a stereoperfect isotactic PHA, *sp*-PHA, defined by $P_m > 0.99$ and $[mm] > 99\%$ (P_m = the probability of meso linkages between two consecutive monomer units, and $[mm]$ = the percent meso triads). This perfect stereochemistry gives *sp*-P3HB a high degree of crystallinity, excellent barrier properties, and high tensile strength, but it has the downside of being highly brittle.[21] To solve this brittleness problem, more flexible, longer chain alkyl substituents have been introduced in PHA homopolymers or copolymers, both biologically and synthetically, to reduce the material's crystallinity and increase the ductility, but this causes the material to decrease the elastic modulus and tensile strength. Synthetically, engineering the P3HB stereomicrostructures has led to ductile ($\varepsilon_B > 400\%$) and tough ($U_T = 96$ MJ m^{-3}) materials that also exhibit good barrier properties and excellent optical clarity.[157]

Using biorenewable feedstocks, such as fatty acids, PHAs have been biologically produced and commercialized, and many reviews outline these processes.[7,158−167] Synthetic PHAs are typically synthesized through the ROP of lactones and cyclic diesters, specifically four-membered *β*-substituted *β*-lactones and symmetric or unsymmetric eight-membered diolides (Scheme 8).[21] The copolymerization of epoxides and CO has also been thoroughly studied to produce a wide variety of PHAs.[21,168] Through the ROP of the eight-membered *rac*-dimethyl diolide (*rac*-8DL^{Me}), biomimetic *sp*-P3HB (i.e., $P_m > 0.99$, $[mm] > 99\%$) has been synthesized.[169] In contrast, the highest level of isotacticity achieved through the ROP of racemic *β*-butyrolactone (*rac*-BBL) was recently achieved and reported at $P_m = 0.95$.[170] In 2023, Reiger and co-workers developed a method to produce *ir*-P3HB (P_m up to 0.89) through an in situ generated catalyst system which yielded high molar mass materials with impressive mechanical properties.[171] High levels of syndiotacticity ($P_r > 0.99$) have been achieved through the ROP of *rac*-BBL and through the ROP of the eight-membered *meso*-dimethyl diolide (*meso*-8DL^{Me}; $P_r = 0.92$).[170,172,173] Notably, Zhu and co-workers developed spiro-salen catalysts for the stereoselective polymerization of *rac*-BBL, achieving the synthesis of stereoperfect *st*-P3HB.[170] Stereosequenced P3HB has also been synthesized through the ROP of diastereomeric (rac/meso) mixtures of 8DL^{Me}.[172] PHA copolymers have been synthesized through the ROP of *rac*-BBL derivatives or *rac*-8DL^{R} derivatives, leading to PHAs with lower crystallinity but higher ductility.[174,175] Unsymmetric 8DL$^{R1\text{-}R2}$ monomers have been used to afford alternating isotactic PHAs, and benzyl-substituted PHAs have also been prepared through a benzyl-substituted 8DL.[176,177] Additional structural diversifications of PHAs have extended to PHAs with a fused five-membered ring, *gem*-dimethyl groups at the *α* position, and dimethyl groups at the *α* and β positions.[178−180] Most recently, Beckham, Chen, and co-workers developed elastomeric PHA vitrimers through combined biosynthesis of medium-chain-length PHAs containing pendent terminal alkenes with chemical postfunctionalization via the pendent double bonds. The resulting dynamically cross-linked PHAs exhibit not only characteristic properties of a vitrimer, such as creep resistance and thermal reprocessability, but also chemical recyclability and biodegradability.[181]

2.2.2. Chemical Recycling. The recycling of biodegradable plastics represents a practical strategy to meet escalating industrial demand while simultaneously promoting a sustainable bioeconomy, reducing consumption of nonrenewable resources, and mitigating the high costs of production. Through the implementation of postconsumption recycling strategies, such as biological, mechanical, and chemical recycling, the lifespan of biodegradable plastics can be extended, and additional value can be derived before they are ultimately processed in biodegradable product facilities.[105,126,182] However, it is crucial to recognize that each recycling process has its own set of limitations and may not be universally applicable (Table 1). Selection of the appropriate recycling process should therefore be made based on the specific requirements of the final product and its intended applications.[183]

Although PHAs have been studied intensively for decades, there have been limited examples of their chemical recycling. Most examples are open-loop chemical recycling methods where the polymers are transformed into other feedstocks or

Scheme 8. Overview of the Synthetic Methods To Produce PHAs[a]

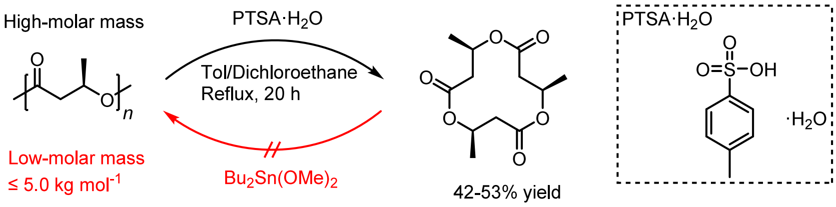


[a](A) Chemocatalytic route to P3HB from either eight-membered dimethyl diolides (both *rac*-8DL^{Me} and *meso*-8DL^{Me}) or racemic four-membered *ß*-butyrolactone (*rac*-BBL). (B) Representative structures of commercialized PHAs. P3HB = poly(3-hydroxybutyrate), P3HBV = poly(3-hydroxy-*co*-3-hydroxyvalerate), P3HBHx = poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate). (C) Stereoretentive SGP. (D) Stereoretentive chain-growth ROP of (*R*)-BBL.

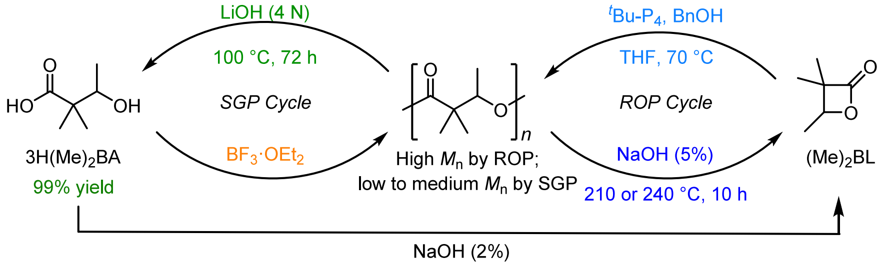
materials (often referred as "upcycling"). However, there are four examples of the closed-loop chemical recycling of PHAs: one for P3HB and three for redesigned PHAs. This section will first discuss the closed-loop chemical recycling processes and then the open-loop chemical recycling processes of PHAs.

2.2.2.1. Closed-Loop Recycling. P3HB can be depolymerized to a cyclic triolide, (*R*,*R*,*R*)-4,8,12-trimethyl-1,5,9-trioxacyclododeca-2,6,10-trione (TBL), using *p*-toluenesulfonic acid (PTSA) or dibutyltin dimethoxide in refluxing toluene/dichloroethane (4/1) for 20 h (Scheme 9).[184] TBL

Scheme 9. Scheme Showing the Potentially Closed-Loop Recycling of P3HB through TBL, Although the Repolymerization Failed To Produce Useful P3HB with Sufficiently High Molar Mass



Scheme 10. Dual- (SGP and ROP) Closed-Loop Chemical Recycling Scheme for P3H(Me)$_2$B

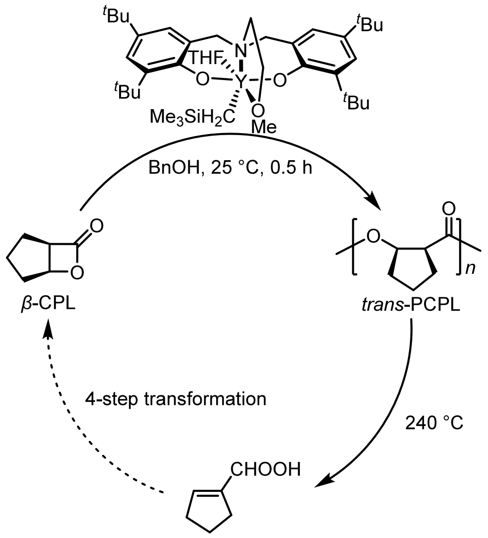


was then repolymerized to low molar mass (<5 kg mol^{-1}) P3HB using Bu$_2$Sn(OMe)$_2$.[184−186] This phenomenon is believed to be due to TBL's low ring strain, high thermodynamic stability, and thus low polymerizability. This method is technically a closed-loop method for recycling P3HB, but since only low molar mass P3HB was reproduced, this method is not considered a feasible route for closed-loop recycling of P3HB.

With *gem*-dimethyl substitution to the parent P3HB structure, a chemically circular PHA, poly(3-hydroxy-2,2-dimethylbutyrate) [P3H(Me)$_2$B], was recently developed.[180] High molar mass (M_n up to 554 kg mol^{-1}) P3H(Me)$_2$B was synthesized by the ROP of *α*,*α*-dimethyl-ß-butyrolactone [(Me)$_2$BL] using organic superbase ^{t}Bu-P$_4$ catalyst with loading as low as 50 ppm. P3H(Me)$_2$B with low to medium molar mass can be obtained via the SGP of the hydroxy acid, 3-hydroxy-2,2-dimethylbutyric [3H(Me)$_2$HA], using BF$_3$·OEt$_2$ catalyst. Thanks to the Thorpe−Ingold *gem*-disubstitution effect, P3H(Me)$_2$B can be depolymerized to the lactone monomer (Me)$_2$BL under mild conditions (5 wt % of NaOH, 210−240 °C, 10 h), which can then be repolymerized infinitely to a high molar mass material. P3H(Me)$_2$B can also be hydrolyzed to 3H(Me)$_2$HA using LiOH as the catalyst, which can then be repolymerized through SGP or transformed back into (Me)$_2$BL with 2 wt % of NaOH (Scheme 10). Overall, high molar mass (M_n = 554 kg mol^{-1}), high T_m (243 °C for (*R*)-P3H(Me)$_2$B, 204 °C for *ir*-P3H(Me)$_2$B, and 176 °C for *at*-P3H(Me)$_2$B), tough (ε_b = 228 ± 24.6%, σ = 31.6 ± 1.8 MPa), and intrinsically crystalline PHA materials were created, and their closed-loop recycling was also demonstrated.[180]

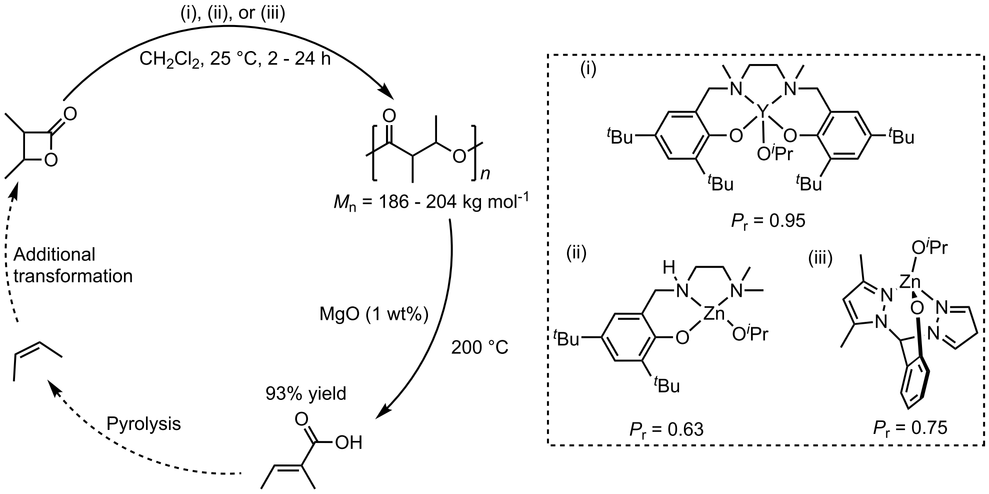
Another closed-loop recyclable PHA has been achieved by substituting the *α* and ß positions of BBL with a five-membered ring, leading to *cis*-6-oxabicyclo[3.2.0]-heptan-7-one (*β*-CPL), which was polymerized to poly(*β*-CPL) (PCPL).[179] PCPL can be generated through either an acyl or an alkyl propagation cycle, leading to either *cis*- or *trans*-PCPL, respectively, with the *cis*-PCPL being semicrystalline having T_m ≈ 185 °C and high M_n up to 101 kg mol^{-1}. *cis*-PCPL is thermally robust ($T_{d,5\%}$ ≈ 268 °C), while *trans*-PCPL is less so ($T_{d,5\%}$ ≈ 213 °C) and an amorphous material with T_g ≈ 15 °C. PCPL can be deconstructed thermally to the corresponding *α*,*β*-unsaturated carboxylic acid, which can be transformed back into *β*-CPL, although requiring four steps (Scheme 11). The rate of thermolysis at 240 °C varied between the *cis*- and the *trans*-PCPL; whereas after 6 h *trans*-PCPL led to 94% isolated yield, *cis*-PCPL led to 88% yield even after 12 h.

Scheme 11. Closing the Loop in the Recycling of PCPL



Monomethylated P3HB, poly(3-hydroxy-2-methylbutyrate) (PHMB), has been synthesized by the ROP of 3-hydroxy-2-methylbutyrate (HMB)[178] (Scheme 12). Previously, biosynthesis with tiglic acid as the carbon source lead to trans, isotactic (2*R*,3*R*)-PHMB with impressive thermal (T_m = 197 °C) and mechanical (*E* = 583 ± 64, σ = 37 ± 2 MPa, ε_b = 520 ± 117%) properties.[187] On the other hand, chemical synthesis of PHMB can utilize *cis*- or *trans*-HMB or both together at various ratios to control the tacticity of the resulting PHMB. In particular, HMB was polymerized to PHMB with high molar mass (M_n = 186−204 kg mol^{-1}) with varying levels of

Scheme 12. Synthesis and Recycling Scheme of PHMB

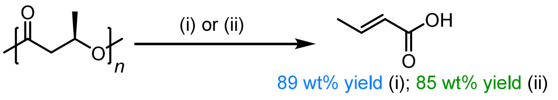


syndiotacticity (P_r = 0.63−0.95) depending on the catalyst used as well as various levels of *cis*-HMB content (70−90%), which gave high melting temperatures (T_m > 130 °C) and toughness values ($U_T \approx$ 96−177 MJ m^{-3}).[178] PHMD was shown to be deconstructed to tiglic acid in high yield (93%) under relatively mild conditions (1% MgO, 200 °C). Tiglic acid can then be pyrolyzed to 2-butene, a feedstock used in making HMB, or used as a feedstock in the biosynthesis of PHMB.[187]

2.2.2.2. Open-Loop Recycling. Open-loop chemical recycling methods for P3HB rely on the deconstruction of P3HB through thermolysis, hydrolysis, methanolysis, or other catalyzed processes to valuable feedstocks that can then be used in other processes or transformations. The most common deconstruction products of P3HB are crotonic acid (CA), methyl crotonate (MC), 3-hydroxybutyric acid (3HB), methyl 3-hydroxybutyrate (M3HB), and ethyl 3-hydroxybutyrate (E3HB), depending on the corresponding process or catalyst used. Here, we first present the methods used to degrade P3HB, followed by the open-loop chemical recycling methods using these degradation products.

Thermally, there are several methods to deconstruct P3HB. Without a catalyst, high temperatures (310 °C) are needed to produce CA in a moderate yield of 63%.[188] Implementing the high-boiling solvent cyclohexane into the thermal degradation process yielded CA at 89 wt % and in 91% purity (Scheme 13).[189] The mechanism of the thermal depolymerization of P3HB has been studied, which revealed that random chain scission, or *cis*-elimination, is the most prevalent pathway.[190−192] Another mechanism has been proposed through an E1cB pathway utilizing carboxylate end groups.[193] Well-defined P3HB and P3HBV oligomers with an unsaturated end group have also been shown to form at temperatures from 170 to 200 °C, which can be upcycled and used as macromonomers to create block copolymers.[194] Using thermolysis (200 °C) and vapor fractionation, P3HBV was shown to produce CA and *trans*-2-pentenoic acid in high yield.[195,196] The mechanism of P3HBV degradation has been suggested to be similar to that for P3HB.[197] The degradation of P3HB and other polyesters was examined in the presence of metal compounds.[198] In the presence of methanol and at 200 °C and 18 bar of pressure, P3HB was fully deconstructed into MC and CA with 70% selectivity for these crotonates.[199] With addition of a catalyst, MgO or $Mg(OH)_2$, the degradation temperature of P3HB was lowered by 40−50 °C, and using $Mg(OH)_2$ led to nearly exclusive formation of *trans*-CA (>97%) but only achieving 85 wt % yield.[200] Recoverable ionic liquids have also been used in the thermal deconstruction of P3HB to CA.[201]

Scheme 13. High-Yielding Deconstruction of P3HB to CA



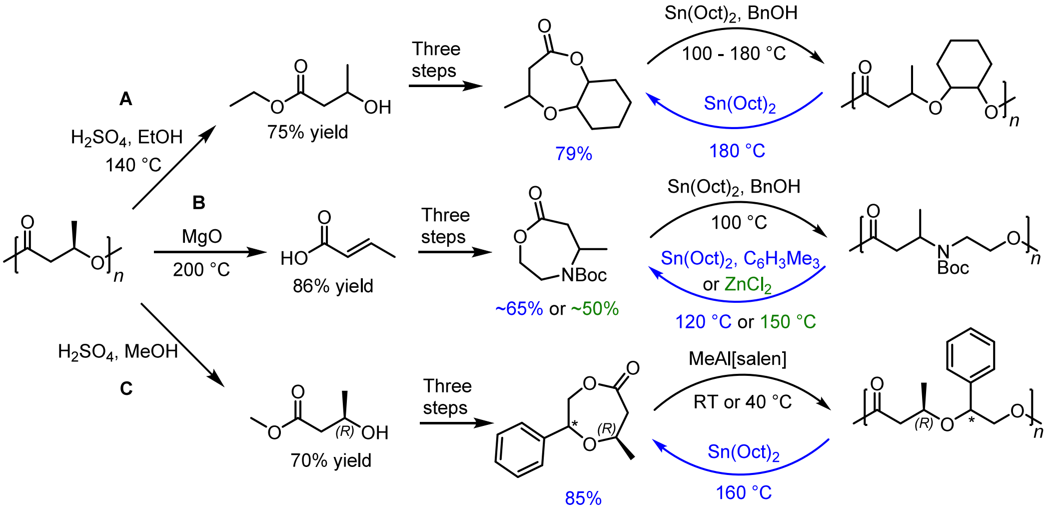
(i) 1) 210 °C, 5 h, cyclohexane, 2) Vaccum distillation (60 °C)
(ii) $Mg(OH)_2$, 240 °C

There are also several methods for the hydrolysis and methanolysis of P3HB. Under acidic and basic conditions, P3HB has been shown to be hydrolyzed to 3HB, often contaminated with various amounts of CA. Mild basic hydrolysis (0.1−0.4 M NaOH, 70 °C) led to a mixture of CA and 3HB, while mild acidic conditions (0.1−0.4 M H_2SO_4) did not lead to degradation. Hydrolysis of P3HB with concentrated H_2SO_4 led to CA exclusively.[202] Using acid catalysts, H_2SO_4 or PTSA monohydrate, (*R*)-P3HB was degraded to either (*R*)-3HB or (*R*)-M3HB.[203] At elevated pressure, M3HB and E3HB were produced using the appropriate alcohol (MeOH or EtOH) and catalyst PTSA at 151 °C.[204] Acidic functionalized ionic liquids were also employed in the methanolysis of P3HB.[205,206]

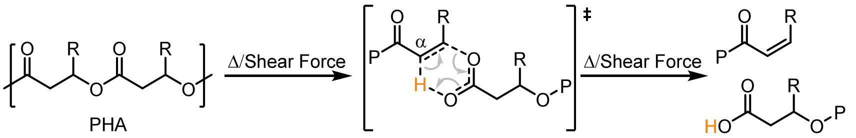
Other catalyzed P3HB deconstruction processes include the use of lanthanum(III) and ruthenium(II) catalysts. For example, a ruthenium(II) PNN pincer complex transformed P3HB to butyric acid in 88% yield after exposure to the catalyst in anisole/THF at 160 °C under 54.4 atm of H_2.[207] Interestingly, it was found that, unlike PLA, hydrosilylation of P3HB using Brookhart's iridium(III) catalyst did not proceed.[208] On the other hand, a low loading (1 mol %) of $La[N(SiMe_3)_2]_3$ promoted P3HB transformation to the borylated HA in high yield (95%) with HBPin for 3 h at 100 °C in C_6D_6.[209]

The resulting CA and the corresponding ester can be converted back to P3HB through microbial fermentation and have been used in many industries including resin modification, surface coatings, plasticizers, and perfumery

Scheme 14. (A) Transformation of P3HB to an Ether-Ester Monomer Which Then Is Polymerized to a Poly(ether ester), a Closed-Loop Recyclable Polymer; (B) Conversion of P3HB to an *N*-Heterocyclic Lactone Which Is Then Polymerized to Poly(amine-*alt*-ester), a Closed-Loop Recyclable Polymer; (C) Degradation of P3HB to a Phenyl-Substituted Enantiopure *O*-Heterocyclic Lactone Which Then Is Polymerized to a Poly(ether ester), Also a Closed-Loop Recyclable Polymer



Scheme 15. Pathway of PHA Degradation during Melt Processing or Mechanical Recycling



and as feedstocks for other transformations.[210,211] For example, the E3HB obtained from deconstruction of P3HB in concentrated H_2SO_4 with ethanol at 140 °C (75% yield after 5 h) was then transformed to bicyclic ether-ester monomers through a three-step synthesis, which was then polymerized into poly(ether ester)s using $Sn(Oct)_2$ and BnOH at 100−180 °C.[212] These polymers, with M_n up to 30.7 kg mol^{-1}, were shown to be chemically recyclable using $Sn(Oct)_2$ at 180 °C for 10 min, yielding 79% of repolymerizable monomer (Scheme 14A). In another approach, the *trans*-CA obtained in 86% yield through depolymerization using MgO at 200 °C for 10 min served as a building block for a boc-protected *N*-heterocyclic lactone through a three-step synthesis. This lactone monomer was then polymerized to poly(amine-*alt*-ester)s using $Sn(Oct)_2$ and BnOH in toluene at 100 °C, which were shown to be depolymerized back to monomer in ∼65% yield or ∼50% yield when using either $Sn(Oct)_2$ in trimethylbenzene ($C_6H_3Me_3$) at 120 °C or $ZnCl_2$ at 150 °C under reduced pressure (Scheme 14B).[213] Similarly, (*R*)-M3HB obtained from the depolymerization of (*R*)-P3HB with H_2SO_4 was used to produce phenyl-substituted enantiopure *O*-heterocyclic lactone monomers. These monomers can be polymerized with aluminum salen catalysts at room temperature (RT) to semicrystalline or amorphous poly(ether-ester)s depending on the stereochemistry of the monomer used. These poly(ether-ester)s can be depolymerized using $Sn(Oct)_2$ at 160 °C, achieving 85% depolymerization to monomer after 9 h (Scheme 14C).[214] As a β-substituted acrylic monomer, MC can be readily polymerized to high molar mass polymer, showing that P3HB can be recycled to useful polyacrylates.[215] Most recently, Li and co-workers upcycled P3HB to enantiopure ester-ether monomers and subsequently generated chemically recyclable, crystalline, stereoregular polyesters through a living polymerization.[216] Overall, these examples and their associated methods show P3HB can be successfully recycled in an open-loop fashion to new monomers which can then enter into closed-loop recycling.

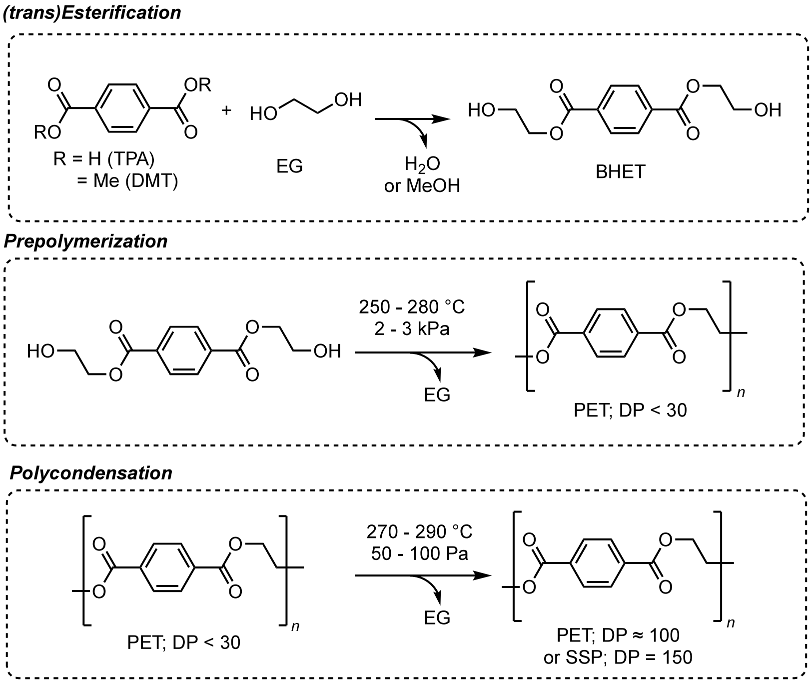
Here, we have discussed both open- and closed-loop chemical recycling pathways of PHAs. Overall, there are many more methods for the open-loop chemical recycling of PHAs as the depolymerization products of PHAs are difficult to directly repolymerize back to PHAs. The successful closed-loop recycling pathways, even though they are currently limited, show promise for the implementation of P3HB as a chemically recyclable polymer.

2.2.3. Mechanical Recycling.

Studies of extrusion of P3HB revealed a significant drop in molar mass at a temperature immediately above the T_m with several extrusion cycles.[105,217] P3HV was found to be more robust when subjected to cycles of extrusion, but molar mass loss and mechanical property degradation was still found.[217] Melt processing of P3HBV and P3HB showed that the thermal and mechanical properties of P3HBV held up for four cycles but showed a slight decrease in properties after the fifth cycle, while the molar mass of P3HB decreased after the third cycle.[218] When P3HB is extruded, its chemical composition does not change; as such, with addition of virgin P3HB or blending it with other polymers, mechanically recycled P3HB can be made into useful materials again even after a large decrease in mechanical properties after three extrusion cycles.[219]

As we can see from the limited reports of the mechanical recycling of PHAs, especially P3HB, it is a challenging process and has not yet been implemented globally at scale. The facile cis-elimination triggered by the α-hydrogens in PHAs renders them thermally and mechanically unstable (Scheme 15), which

Scheme 16. Industrial Synthesis of PET from EG and TPA or DMT



makes traditional mechanical recycling of PHAs difficult. P3HB's high T_m (∼175 °C) and relatively low degradation temperature (∼250 °C), due to the cis-elimination process, lead to a small processing and reprocessing window. This degradation can be shown through the large drop in viscosity when *sp*-P3HB is subjected to a shear force ($r = 1\ s^{-1}$) in the melt.[180]

The melt processability of PHAs can be improved by lowering the T_m and thus increasing the processing window through either copolymerization or introduction of stereodefects. As seen in P3HBV and P3HV, the incorporation of longer alkyl chain units makes them more melt processable and thus more mechanically recyclable as a result of the reduction in T_m. This T_m reduction can also be achieved in P3HB through stereomicrostructural engineering, allowing for a wider processing window. For example, syndio-rich (*sr*) P3HB (P_r = 0.55−0.75) obtained from *rac*-BBL showed high melt strength with potential to withstand mechanical recycling.[220] The synergistic coupling of moderate tacticity, which leads to lowered crystallinity and T_m, with high molar mass is critical for enhancing the melt processability of P3HB, which has been demonstrated by a more recent study on *sr*-P3HB prepared from *meso*-8DL^{Me}.[157,169,171] This method of reduction of P3HB's T_m has also been shown for *ir*-P3HB, and these *ir*-P3HBs may also be more easily mechanically recycled at lower temperatures.

Alternatively, PHAs can be redesigned to be devoid of α-hydrogens, leading to a more thermally stable and mechanically recyclable PHAs. By removing the cis-elimination-triggering α-hydrogens, P3H(Me)$_2$B solves the problems that traditional PHAs have in terms of mechanical recycling. P3H(Me)$_2$B was shown to be stable in the melt under shear, showing its potential for facile mechanical recycling.[180]

2.2.4. Biological Recycling.

One of the most attractive features of PHAs is that they can degrade in both soil and water under unmanaged conditions, facilitated by microorganisms secreting PHA depolymerase enzymes. This back-up biodegradation is important if PHAs are leaked into the environment. However, through this biodegradation in environment the carbon sources and materials values of PHAs are essentially lost. Ideally, PHAs would be mechanically recycled until they are no longer useful due to degradation and then either chemically or biologically recycled back to monomers or useful feedstocks.

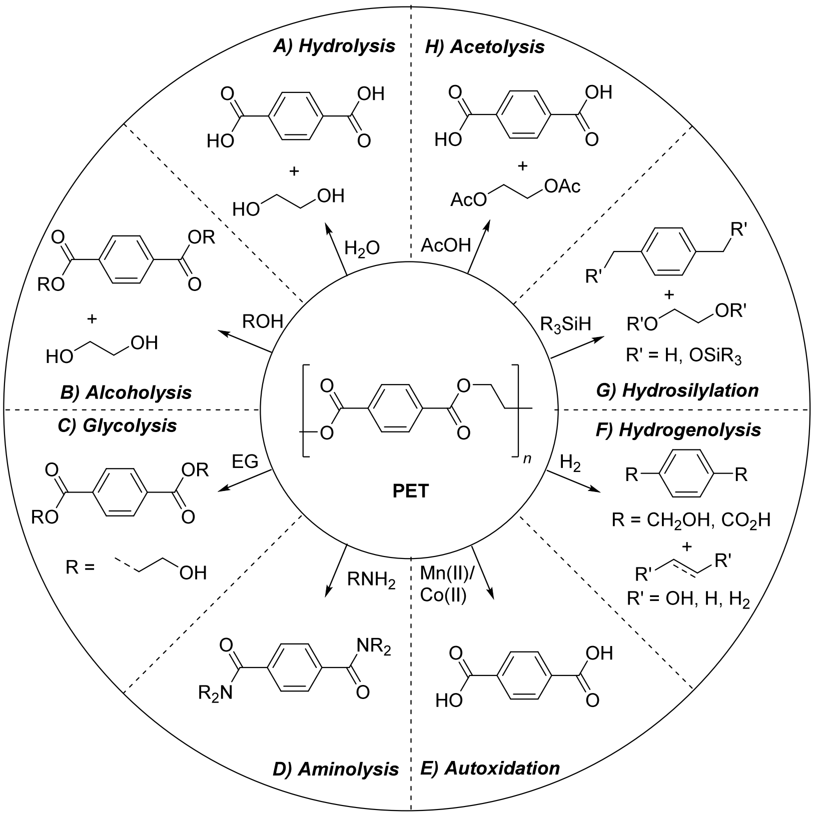
Anaerobic digestion of PHAs can produce biogas or syngas, which is a mixture of gases mainly composed of CH_4 and CO_2 and/or volatile fatty acids (VFAs).[221] Biogas is a useful fuel to produce electricity or as a cooking fuel, a case where PHAs are upcycled into energy sources. VFAs can also be used to biologically synthesize PHAs, creating a closed-loop biological recycling pathway for PHAs. Anaerobic degradation of a mixture of plastics including P3HB and of P3HB alone was studied and led to good degradation of P3HB in all cases.[222,223] Predegrading P3HB using a thermal alkaline method before digestion brought about a more efficient degradation and a higher CH_4 yield.[223] VFAs were also produced through similar pathways.[224] Other than use in the production of PHAs, VFAs can also be used as biofuels and feedstocks. Coupling the biological depolymerization of PHAs to VFAs with subsequent fermentation can close the biological recycling pathway of PHAs.[225−227]

2.3. Poly(ethylene terephthalate) (PET)

2.3.1. Synthetic Routes.

Poly(ethylene terephthalate) (PET) is the largest commercial market share polyester with current estimates stating that 24.2 Mt (i.e., 6.2% of the total plastics market) were synthesized in 2021 alone.[228] Common trade names for PET include Dacron, Terylene, and Mylar. PET displays excellent tensile (E = 3.3 GPa, σ_B = 50 MPa, ε_B = 175%) and barrier properties (PO_2 = 14.0 cc m^{-2} day^{-1}, $WVTR$ = 3.1 g m^{-2} day^{-1}) as well as good thermal properties and melt processability (T_g = 74 °C, T_m = 246 °C), which make it highly attractive to a broad range of applications including packaging and textiles.[229] The structure of PET

Scheme 17. Approaches to the Chemical Recycling of PET



consists of alternating repeating units of terephthalic acid (TPA) and ethylene glycol (EG) (Scheme 16); both monomers are typically sourced from fossil fuels, although bioderived routes to both monomers and, indeed, PET itself (termed *bio*-PET) are known.[230,231]

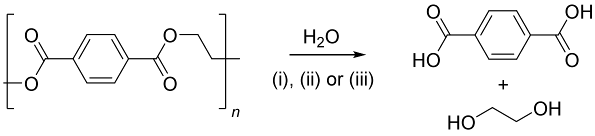
PET is industrially synthesized through SGP, either directly from the constituent monomers TPA and EG or via the intermediate compound dimethyl terephthalate (DMT) (Scheme 16). The commercial synthesis of PET progresses through several stages.[10,232] First, esterification between TPA and EG (or transesterification between DMT and EG) yields bis(2-hydroxyethyl) terephthalate (BHET) alongside some PET oligomers (degree of polymerization (DP) < 4) with concomitant water or methanol release (for TPA and DMT, respectively). Esterification with TPA over transesterification from DMT is considered preferable as no catalyst is required and the process shows higher rates.[10,231] The BHET/oligomers subsequently undergo prepolymerization to form low molar mass PET with a DP of around 30 with the concomitant release and removal of EG. Following this, melt polycondensation is used to generate higher molar mass PET (DP $\approx$ 100), which is appropriate for fiber or sheet applications.[232] For packaging applications, a higher molar mass is required, and so subsequent solid-state polymerization (SSP) can be performed, yielding PET with a DP of around 150.[233] These processes require both high temperatures (200−300 °C) and low pressures (i.e., applied vacuum) to remove the small-molecule side products (e.g., water, methanol, EG) and hence drive the polymerization to completion. Catalysts are applied to aid both the transesterification and the polycondensation procedures.[10,234] A wide range of metal (e.g., groups 1 and 2 metals, lead, zinc, aluminum) salts can be applied as transesterification catalysts; acetates of zinc, manganese, calcium, and sodium have been used commercially. During polycondensation, catalysts of antimony trioxide or triacetate are often applied.

2.3.2. Chemical Recycling. The chemical recycling of PET typically involves the breaking (-lysis) of the ester linkage within the monomer unit to directly furnish monomers that can be applied in PET synthesis (e.g., EG, TPA, DMT, BHET). Hydrolysis, alcoholysis, and glycolysis are all well-known and extensively studied techniques. Alongside these “traditional” techniques, recent years have seen innovative approaches to PET deconstruction and recycling that go beyond traditional transesterification methodologies. An overview of the various processes applied to PET recycling is provided in Scheme 17, and each process will be discussed in greater detail in the following sections. The reader is directed to a selection of excellent reviews for further details.[231,235−239]

The alternative to chemical recycling is mechanical recycling of PET, which is theoretically more desirable owing to the lower energy input required to yield usable recycled PET (*r*PET) (see section 2.3.3). However, practical difficulties mean that in many cases *r*PET is *down*cycled rather than being truly “closed loop”. The advantage of chemical recycling lies in the resynthesized polymer having identical properties to virgin PET (*v*PET), enabling repeat application to the highest grade applications. This is particularly advantageous when dealing with heavily contaminated waste PET unsuitable for mechanical recycling. Disadvantages lie in the energy costs associated with the recycling processes (depolymerization and repolymerization) and the requirement for purification of the reobtained monomers.[240] The chemical recycling of PET has been practiced by industry since the 1950s, around the same time as commercial PET introduction, whereby PET scrap from commercial processes could be recycled to enable recovery of the monomers and subsequent reapplication to the synthesis of *v*PET.[235]

2.3.2.1. Traditional Approaches. Hydrolysis of PET involves the breaking of the ester linkages using water. Acidic, alkaline, and neutral hydrolyses are all reported (Scheme 18). One advantage of this methodology is that many modern PET syntheses apply TPA, which is directly generated via hydrolysis.

Scheme 18. Hydrolysis of PET through Industrial Methods[a]



[a]Typical conditions vary significantly with applied system. (i) Alkaline conditions: T = 150−250 °C, P = 0.1−2 MPa, 2−20 wt % of MOH (M = K, Na), t = 1−5 h. (ii) Acidic conditions: T = RT − 100 °C, >87 wt % of H_2SO_4, t = ca. 5 min. (iii) Neutral conditions: T = 200−300 °C, P = 1−4 MPa, t = 2−6 h.

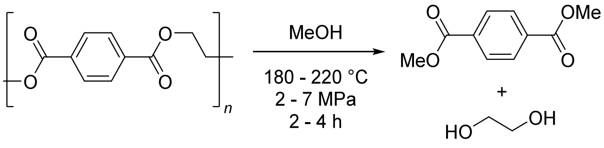
Alkaline hydrolysis typically applies an aqueous solution of sodium or potassium hydroxide (2−20 wt %) at temperatures of 210−250 °C and 1.4−2 MPa pressure,[235,241] yielding EG and the corresponding dicarboxylate salt of TPA. Typical reaction times are 3−5 h.[235] By utilizing higher concentrations of sodium hydroxide (i.e., >30 wt %), lower temperatures (80−150 °C), pressures (0.1−1 MPa), and reaction times (1−2 h) can be applied.[242,243] Alternative basic solutions of sodium alkoxide salts in their corresponding alcohol have also been applied (e.g. sodium methoxide in methanol, ethoxide in ethanol, etc.).[244] Recovery of TPA from the salt is typically performed via protonation using sulfuric acid, while EG can be recovered via vacuum distillation;[235] typical yields of TPA are >95%.[242,243,245] One advantage of this methodology is that it can tolerate highly contaminated postconsumer PET (POSTC−PET), and the recovered TPA exhibits high purity.[236] The mechanism for aqueous alkaline hydrolysis is proposed to follow a "shrinking-core" model and shows rate dependences on the concentration of hydroxide ions and the surface area of the PET flakes.[246−249] Application of phase transfer catalysts (e.g., trioctyl methylammonium bromide; TOMAB) has been shown to significantly improve the rate of hydrolysis and allow for lower temperatures to be applied: after 5 h at 80 °C, 5 wt % of NaOH, and 1 mol % of TOMAB, a 90% TPA yield was reported in comparison to a 7% TPA yield when no catalyst was applied.[250] It has also been reported that addition of ether cosolvents (such as dioxane and THF) can accelerate the reaction.[251] Utilizing a dioxane cosolvent (10 vol %) in methanol, >96% PET depolymerization (97% TPA yield) could be obtained in 40 min at 60 °C, whereas the same extent of depolymerization required 7 h without dioxane.

Acidic hydrolysis of PET typically utilizes concentrated sulfuric acid (>87 wt %) at temperatures between RT and 100 °C and ambient pressures, yielding EG and TPA.[235,236] Typical reaction times are around 5 min.[235,252] Nitric and phosphoric acids have also been applied.[239] Isolation of TPA requires initial neutralization of the reaction mixture with sodium hydroxide, forming the disodium TPA salt. Subsequent reacidification of the solution leads to TPA formation and precipitation with yields > 95%.[252] EG is isolated via solvent extraction from the remaining solution or "salting out".[235] Despite the less demanding operating conditions, the highly corrosive nature of concentrated acids is a significant drawback of this approach.[235,236] To combat the corrosive nature of concentrated H_2SO_4, application of dilute sulfuric acid (<10 M) has been investigated but required higher temperatures (150 °C) and longer reaction times (5 h) for full PET depolymerization.[253] Modified shrinking core models are proposed to operate for acidic hydrolysis with slight differences depending on the acid applied.[249,254,255] Karayannidis and Achilias proposed a model whereby at low acid concentrations the reaction rate is controlled by the rate of acid diffusion through a PET film, whereas at high acid concentrations, the rate is controlled by the depolymerization reaction (i.e., acidic ester hydrolysis) itself.[249] Very recently, Yang et al. described the application of PTSA to PET hydrolysis, reporting full depolymerization within 90 min at 150 °C, giving TPA in 96% yield.[256] Unlike mineral acids such as H_2SO_4, the PTSA could be relatively easily recovered by crystallization following neutralization and isolation of the TPA.

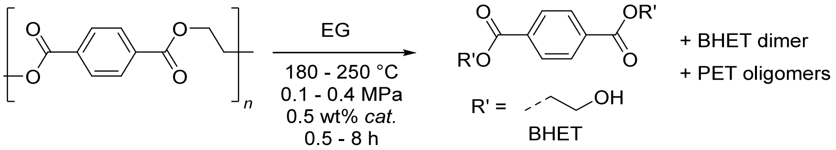
Neutral hydrolysis applies water at high temperatures (200−300 °C) and pressures (1−4 MPa) to depolymerize PET.[235,236] Reaction times of under 2 h are considered optimal with extended reaction times (>6 h) leading to an increase in formation of color-producing compounds.[257,258] The reaction proceeds significantly faster above the T_m (246 °C) of PET as its crystallinity significantly hinders chain mobility and permeability to water, which in turn significantly decreases the rate of hydrolysis.[241] TPA is isolated from the postdepolymerization mixture by filtration in yields of >95%,[257] and EG can be recovered by extraction or distillation.[235,241] In comparison to acidic or alkaline hydrolysis, no inorganic salts are generated and no corrosive reagents are used, and so neutral hydrolysis can be considered preferable from an environmental perspective.[231,235] However, the generated TPA typically carries impurities present in the PET feedstock and hence requires further purification before application.[235,249] The kinetics of hydrolytic melt depolymerization has been studied.[259−261] Kao et al. proposed an autocatalytic model where generated carboxylic acid (i.e., TPA) can catalyze the ongoing hydrolysis with a half-order dependence on its concentration, implying proton catalysis of the process.[261] Transesterification catalysts, including zinc[259] and alkali metal[262] salts, can accelerate the process.[235]

Alcoholysis of PET involves transesterification of the ester linkages in the presence of excess alcohols, rendering the corresponding diester of TPA, and EG. The most commonly employed process is methanolysis, which is commercially mature and yields DMT and EG (Scheme 19).[235] Alongside DMT, several other byproducts including BHET and 2-hydroxyethyl methyl terephthalate (MHET) can result, which complicates product separation and purification and hence increases costs associated with the process.[231,238] The obtained

Scheme 19. Solution-Phase Methanolysis of PET under Typically Applied Industrial Conditions



Scheme 20. Glycolysis of PET under Typically Reported Industrial Conditions[a]



[a] A range of catalysts have been reported for the process (vide infra).

DMT can be purified via distillation and/or crystallization;[249,263] however, since many modern processes utilize TPA over DMT, further conversion of the obtained DMT to TPA may be required.[231]

Typical conditions required for solution-phase methanolysis are 180−220 °C and 2−7 MPa of pressure, giving DMT yields of 80−90%,[264−267] with MHET being the major side product.[267] Typical time scales for the reaction are 2−4 h.[265−267] Various transesterification catalysts including metal (e.g., Zn, Mn, Pb, Mg) acetate and dioxide salts, particularly $Zn(OAc)_2$,[267] can be but are not always applied;[263] $Zn(OAc)_2/Pb(OAc)_2$[268] (4 mol %) and $Al(O^iPr)_3$ (10 mol %)[269] catalysts have been explicitly reported in the open literature. Microwave-assisted methanolysis has also been reported, which gave >95% yields of both TPA and EG in 20 min at 160 °C when used in tandem with a $Zn(OAc)_2$ (1 mol %) catalyst.[270]

Vapor-phase methanolysis whereby gaseous superheated methanol (230−270 °C; 0.1−1.5 MPa) is used for PET depolymerization is also applied.[263,271−273] More contaminated POSTC−PET waste can be applied than in liquid-phase methanolysis as the gaseous methanol acts as a carrier gas for the evolved DMT and EG, providing effective separation from a range of impurities.[271,274] DMT yields of up to 95% were achieved through this methodology.[272] The application of supercritical methanol (T > 250 °C, >8 MPa pressure), applied without a catalyst, has also been developed[263,275,276] and can yield high rates of reaction and good DMT yields. A 92% yield of DMT was obtained within 30 min at 330 °C, 9.8 MPa pressure.[275]

Various other alcohols, such as ethanol and butanol, have been applied to equivalent alcoholysis processes.[239] Application of supercritical ethanol, forming diethyl terephthalate (DET), can avoid the application of toxic methanol and was first reported by de Castro et al. in 2006.[277] A maximum of 98.5% DET recovery was reported under optimized conditions (255 °C, 11.5 MPa, 60:1 ethanol:water v:v). More recently, investigations of subcritical ethanolysis (4 MPa, 200−225 °C) have revealed that TPA can be evolved directly from the process.[278]

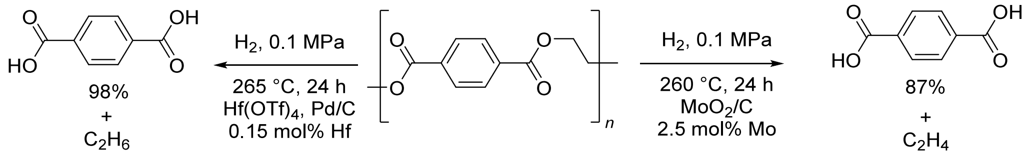
Glycolysis (Scheme 20) refers to the process of degrading PET utilizing EG or, occasionally, other diols such as propylene glycol or diethylene glycol[237] to yield the corresponding diester of TPA (if EG is used, BHET results). The process utilizing EG is commercially mature, and the resultant BHET can be applied directly to PET synthesis.[235] PET oligomers and dimers are also formed as byproducts. Uncatalyzed glycolysis is a slow process so, to improve the efficiency, several approaches have been reported including metal-catalyzed glycolysis, solvent- and microwave-assisted glycolysis, and application of supercritical EG.[238]

Typical conditions for metal-catalyzed glycolysis are 180−250 °C, 0.1−0.4 MPa pressure, and 0.5 wt % of catalyst and reaction times of 0.5−8 h.[236] A wide range of catalysts for glycolysis is reported,[237,279,280] including homogeneous (i.e., soluble in EG) divalent acetates of Zn, Pb, Mn, and Co[281,282] and organocatalysts.[283−285] The application of light, earth-abundant metal salts (e.g., Na_2CO_3, $NaHCO_3$, Na_2SO_4, and K_2SO_4) as catalysts has also been explored.[286−288] Typical yields of BHET with such catalysts are around 70−80%. Application of homogeneous catalysts can complicate product separation, and so application of heterogeneous catalysts is desirable. Several zeolites, spinels, and nanomaterials have recently been reported as effective heterogeneous catalysts.[238] Aside from easier catalyst separation, improved yields of BHET have been reported. Imran et al. reported on the application of several metal and mixed-metal oxide spinels as heterogeneous catalysts with the most effective being $ZnMn_2O_4$, which yielded 92% BHET (260 °C, 0.5 MPa, 60 min).[289] Park et al. utilized a Mn_3O_4−graphene oxide (GO) composite material to deliver 96% BHET (300 °C, 1.1 MPa, 80 min); Mn_3O_4 alone resulted in an 83% yield under the same conditions.[290]

Aside from catalyst selection, several other techniques have been investigated to either improve the BHET yield of, or provide access to milder operating conditions for, glycolysis. Application of supercritical EG enables the reaction to be performed without a catalyst at the cost of higher pressures (15.4 MPa) and temperatures (450 °C).[291] The process enables yields of up to 90% of BHET. Microwave irradiation has also been applied to PET glycolysis.[292] Utilizing a zinc acetate catalyst (0.5 wt %), Pingale and Shukla demonstrated that a 66% BHET yield was obtained within 35 min using a microwave-assisted process, while 63% BHET was obtained in 8 h using conventional heating methods. Solvent-assisted glycolysis applies EG in tandem with a solvent. Application of a biphasic system of EG and xylene was reported by Güçlü et al., which resulted in relatively high BHET yields of 80% (220 °C, 1 wt % of $Zn(OAc)_2$).[293] More recently, homogeneous cosolvents have been investigated.[294,295] Liu et al. reported that by adding dimethyl sulfoxide as a cosolvent to EG, an 82% BHET yield was obtained within 1 min (190 °C, 4 wt % of $Zn(OAc)_2$), while Le et al. demonstrated that an 86% BHET yield was obtained using an EG/anisole solvent system (153 °C, 4 mol % of NaOAc or KOAc, 2 h).

Ionic liquids (ILs) have recently emerged as a class of catalyst for transesterification depolymerization of PET. While the application of ILs can aid in catalyst separation and hence reusability, drawbacks come from their relative cost and, if metal-containing ILs are applied, potential metal-ion leaching. The first reports of their application came from Li and coworkers in 2009, who described both the catalyzed glycolysis and the degradation of PET using 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]).[296,297] Since then, reports of IL-catalyzed processes have also emerged for hydrolysis[298] and alcoholysis,[299,300] but the majority of the field has focused on IL-catalyzed glycolysis.[280] Both metal-containing and metal-free ILs have been reported for glycolysis of PET; typical conditions require temperatures of 170−195 °C, IL loadings of

Scheme 21. Hydrogenolysis of PET to TPA and Ethane or TPA and Ethene, Reported by Marks and Co-Workers[304,305]



5−20%, and reaction times of 1−5 h. Yields of BHET are typically 60−80%, although a recent report described an IL-coated $SiO_2@Fe_3O_4$ nanoparticle catalyst system that afforded BHET in quantitative yield.[301]

2.3.2.2. Emerging Approaches. Aside from the methods discussed above, which aim to directly regenerate one or both of the constituent feedstock chemicals applied in PET synthesis via transesterification/hydrolysis methodologies, several other approaches have been reported that can regenerate either the monomers directly or alternative value-added chemicals (Scheme 17). It should be noted that where the small molecules generated are not monomers in PET synthesis, the recycling should be considered open-loop, rather than closed-loop, recycling.

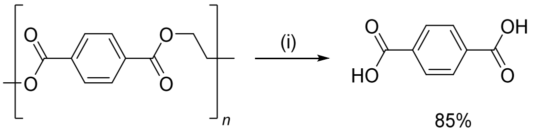
Hydrogenolysis of PET to diols or TPA by applying late-transition-metal catalysts has been investigated (Scheme 17). Milstein-type Ru(II) complexes supported by PNN ligands were applied (∼5 MPa H_2, 160 °C, 1 mol % of catalyst, 48 h, anisole/THF) to the hydrogenolytic depolymerization of PET, yielding 1,4-benzenedimethanol (BDM) and EG in quantitative yield.[207] Fuentes et al. described the application of an aryl phosphine diamine Ru(II) complex, yielding the same products in 73% yield (5 MPa, 110 °C, 2 mol % of catalyst, 48 h, anisole/THF).[302] Triphos-based Ru catalysts have also been applied and gave quantitative yields of TPA and EG under similar conditions (10 MPa H_2, 140 °C, 0.2−1 mol % of catalyst, 16 h, 1,4-dioxane) when applied to PET from a range of sources (e.g., water bottles, fibers).[303] In all cases, the BDM generated by the reactive depolymerization would require reoxidation to TPA for closed-loop recycling.

In 2020, Marks and co-workers reported the hydrogenolysis of PET to TPA and ethene using a Mo−dioxo catalyst grafted on activated carbon (MoO_2/C) and H_2 (0.1 MPa H_2, 260 °C, 24 h, 2.5 mol % of Mo loading), giving TPA in a 87% yield (Scheme 21).[304] Subsequently, in 2022, the same group applied a tandem catalytic system of $Hf(Otf)_4$ and Pd/C with H_2 (0.1 MPa H_2, 265 °C, 24 h, 0.15 mol % of Hf loading) to yield TPA in 98% yield alongside ethane (Scheme 21).[305] Of particular significance is that these hydrogenolytic routes regenerate TPA, rather than the reduced small molecules generated by other hydrogenolysis methods.

Reductive hydrosilylation and hydroborylation of PET are alternative methods that have been explored (Scheme 17). In 2015, Feghali and Cantat described the application of $B(C_6F_5)_3$ in combination with various silanes to depolymerize PET to silylated EG and BDM (4.3 equiv of Et_3SiH, RT, 3 h, 2 mol % of catalyst, CH_2Cl_2) in 82% and 91% yields, respectively.[306] When higher equivalents (>6 equiv) of silanes were applied, *p*-xylene and ethane were evolved instead. Subsequently, the Brookhart catalyst was applied to this process: applying 1 mol % of catalyst with 6 equiv of Et_3SiH (70 °C, 72 h, chlorobenzene) resulted in a 63% yield of silylated BDM and a 48% yield of silylated EG.[208] Recently, Fernandes reported the application of $Zn(OAc)_2{\cdot}2H_2O$ to hydrosilylation of PET, yielding *p*-xylene and EG.[307] Using 10 mol % of Zn and 10 equiv of $PhSiH_3$ (160 °C, 96 h, chlorobenzene), a 65% yield of *p*-xylene and a 43% yield of EG were reported. A dioxomolybdenum catalyst ($MoO_2Cl_2(H_2O)_2$) has also been reported for the same process.[308] Using Ph_3SiH (6 equiv), a 65% yield of *p*-xylene was obtained (160 °C, 96 h, 5 mol % of catalyst, chlorobenzene). In 2022, Kobylarski et al. reported the reductive hydroborylation of PET using catalytic $La[N(SiMe_3)_2]_3$ (1 mol %) and HBPin (4.4 equiv) (C_6D_6, 100 °C, 24 h).[309] Borylated BDM and EG were obtained in good yields of 71% and 75%, respectively.

Autoxidation of PET involves the aerobic oxidation in acetic acid using metal catalysts and bromide or *N*-hydroxyphthalimide cocatalysts. This process was first described by Partenheimer in 2003, where a $Co(OAc)_2/Mn(OAc)_2/NaBr/Zr(OAc)_4$ catalyst system (1:1:2:0.07, 3 mol % of Co, 190 °C, 7 MPa air, 8% water/acetic acid (v/v), 0.5−2 h) was utilized to produce TPA in ca. 55% yield.[310] More recently, in 2022, Sullivan et al. described the application of a combinatorial autoxidation/biological transformation approach to recycle mixed plastic wastes, including PET (Scheme 22).[311]

Scheme 22. Autoxidation of PET to TPA Reported by Sullivan et al.[311,a]



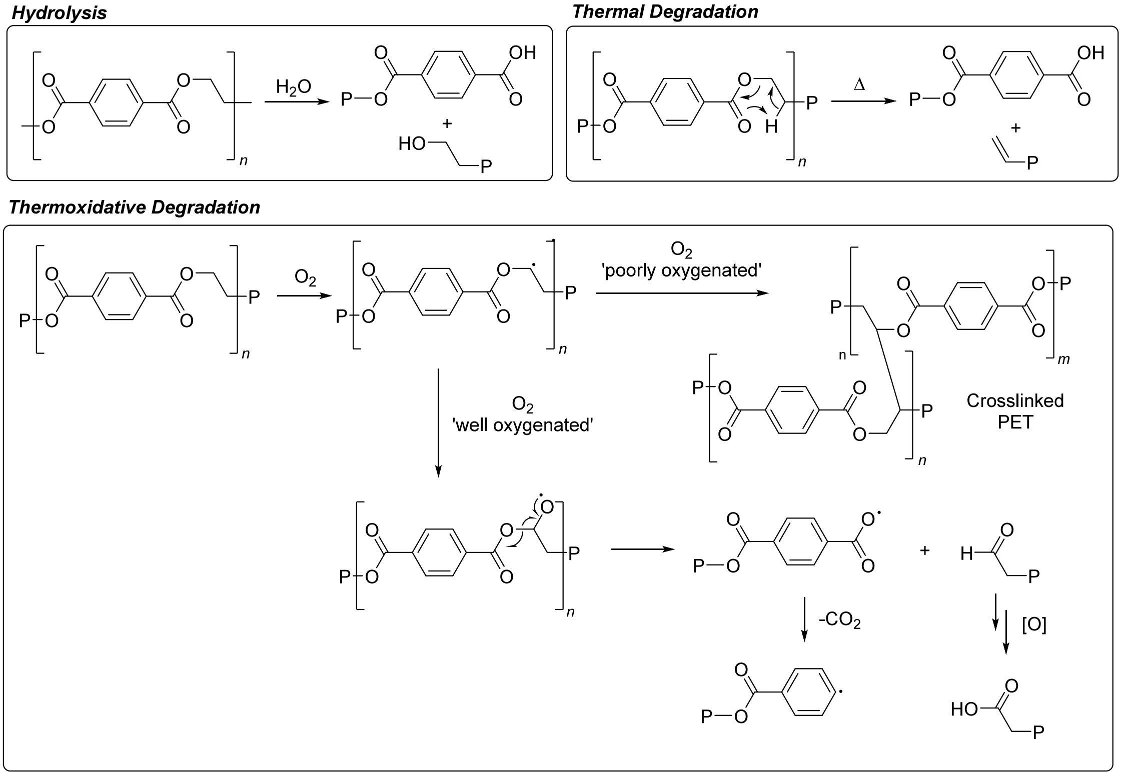
[a]Conditions: (i) $Co(OAc)_2/Mn(OAc)_2$ (9.7, 9.5 wt %), 11.3 wt % of NHPI, 6.7 wt % of $Zr(acac)_4$, acetic acid, 1% (v/v) water, 0.8 MPa O_2, 7.2 MPa N_2, 210 °C, 5.5 h.

Initial autoxidation of PET was performed using a $Mn(OAc)_2/Co(OAc)_2/N$-hydroxyphthalimide catalyst system in the presence of oxygen, which yielded TPA in 85% yield (based on theoretical TPA recovery). When applied to a mixed-plastic stream of PET, high-density polyethylene (HDPE), and polystyrene (PS), a 79% yield of TPA was obtained. Subsequently, the mixed oxygenated intermediates (including TPA and benzoic and α,ω-carboxylic acids from PS and HDPE, respectively) were converted to either β-ketoadipate or PHAs using strains of the bacterium *Pseudomonas putida* (see section 5.3 for further details).

Acetolysis (i.e., acidolysis with acetic acid) of PET was very recently described by Peng et al. (Scheme 17).[312] Using glacial acetic acid, PET bottle flakes were completely depolymerized in 2 h at 280 °C, giving TPA in 96% yield and very high purity. This technique utilizes the low solubility of TPA in acetic acid combined with the high solubility of various impurities (e.g., dyes) to both drive the reaction to completion and provide access to high-purity TPA.

Aminolysis/Ammonolysis. Two further chemical recycling techniques that have seen some academic interest are the

Scheme 23. Proposed PET Degradation Routes during Mechanical Recycling



aminolysis of PET using amines or ammonolysis with ammonia to yield terephthalamides (Scheme 17).[238,239,313] By their nature, these processes cannot furnish closed-loop recycling, but the amides produced could have further applications in the coatings industry, although these processes have yet to be commercialized.[238] A broad range of amines have been applied including alkyl and aryl amines and diamines and ethanolamine; specific reaction conditions depend on the amine chosen.[313] Typically, temperatures of 20−200 °C and ambient pressures are applied. The application of homogeneous catalysts, such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)[314] or sodium acetate,[315] and/or microwave irradiation[316,317] can assist the reaction.

2.3.3. Mechanical Recycling. The mechanical recycling of PET is a commonly applied commercial recycling methodology. Postconsumer PET (POSTC−PET) recycling involves separation of PET from the bulk plastic waste stream followed by washing, drying, flaking, and then melt processing the resulting PET flakes.[232] It is essential to remove contaminants (including other plastics and water) that can result in degradation of PET by a range of processes (vide infra).[125] Resultant PET flakes are reprocessed via melt extrusion, yielding *r*PET.[232] Despite significant purification efforts, *r*PET typically shows significant molar mass loss and a resultant decrease in a range of materials properties; several studies demonstrate that multiple rounds of mechanical recycling exacerbate the effect.[125,318,319] Accordingly, *r*PET is often applied to fiber applications;[231,320] true closed-loop "bottle-to-bottle" mechanical recycling of PET is more challenging, although this application is growing.[233]

PET undergoes significant degradation through a variety of mechanisms during mechanical recycling (Scheme 23).[125] Thermal degradation via C−H transfer leads to chain scission at the ester bonds, yielding carboxylic acid and vinyl end-capped polymers.[125] Radical decomposition mechanisms also operate in the presence of oxygen (i.e., thermal oxidation) and can lead to both chain scission and cross-linking.[321−323] This process can be catalyzed by both transesterification catalysts (such as those applied during PET synthesis) and the carboxylic end groups of PET itself, the latter of which renders the process somewhat autocatalytic.[324] Plastic contaminants within PET waste can also lead to decomposition during recycling. Poly(vinyl chloride) (PVC) in quantities as little as 100 ppm can be particularly harmful since its decomposition yields HCl, which catalyzes existing degradation mechanisms.[325] Further harmful acidic impurities that can arise from other plastic contaminants include acetic acid (produced from poly(vinyl alcohol) contamination) and lactic acid, from PLA hydrolysis.[125] The presence of PLA also complicates the melt processing of *r*PET due to its lower T_m.[326] The presence of residual amounts of water (>50 ppm) during reprocessing is also detrimental, as it leads to hydrolytic scission of the ester linkage.[232]

To overcome the degradation of PET during mechanical recycling, several techniques have been employed. Recycling under vacuum conditions can result in the removal of small-molecule volatiles (such as acids or water) that promote the various degradation mechanisms.[232] An additional method to suppress degradation side reactions is through the use of additives.[125,232] Examples include organic phosphates that decompose hydroperoxide radicals or metal-based compounds such as lead phthalate which typically act to suppress the impact of PVC contaminants.[232] Alongside methods that aim to suppress *r*PET degradation during melt extrusion, several techniques exist to restore the molar mass of *r*PET. Application of SSP at temperatures above the T_g but below the T_m of PET (i.e., 200−240 °C) enables coupling of PET chain ends, resulting in partial restoration of molar mass, although the process is disfavored industrially.[327] Chemical cross-linkers can also be applied to perform the same function.[125,327] This process is typically affected by reactive extrusion of PET in the presence of the chemical cross-linker. Many types of chain extenders are reported, including epoxides, anhydrides, lactams, and isocyanates, that can lead to both linear coupling of PET chains as well as branched structures.[327] Despite these developments, the application of chain extenders may render the *r*PET unsuitable for food-grade packaging due to potential leaching of any unreacted small molecules.[125]

For bottle-to-bottle recycling, extra cleaning processes are required in order to remove any contaminants that could leach from the obtained *r*PET and to prevent loss of molar mass during recycling.[233] If the intended application of *r*PET is food packaging, impurities can only be present at a parts per billion scale.[233] One approach to overcome this issue is to apply a thin layer of *v*PET around *r*PET (termed "multilayer packaging") to act as a protectant against any such contamination.[328] However, cross contamination between the two different grades of PET may occur during processing, which also carries significant manufacturing costs.[233] An alternate route to bottle-to-bottle recycling applies "superclean" recycling technologies, which allows for removal of contaminants within the solid *r*PET flakes and hence matching the purity of *v*PET.[233] A range of processes, including application of SSP as a decontamination process or direct decontamination of *r*PET flakes, are applied.

2.3.4. Biological Recycling.

While chemical recycling can enable the recovery of either monomers or value-added products from PET, it can incur significant costs given the relatively harsh conditions often applied combined with monomer recovery and purification. One potential solution to this issue is the application of enzymes, which operate at much lower temperatures and ambient pressures. The ester linkages in PET render it susceptible to enzymatic attack by polyester hydrolases, yielding TPA and EG as the main products, typically via the formation of the intermediates MHET and BHET.[329] In 2005, Müller and co-workers reported the first application of enzymatic degradation of commercial PET, where they described a hydrolase (cutinase) from the actinomycete *Thermobifida fusca* that was capable of degrading 40−50% of a PET film over 3 weeks at 55 °C.[330] Since then, many other enzymes have been reported for this process, and there are several excellent reviews that provide detailed accounts.[329,331−333] Herein, we aim to provide an overview of this field and highlight some of the key recent developments. It should be noted that another "biological" approach to processing PET waste is microbial degradation, but this does not typically result in isolation of the constituent monomers (TPA and EG), which are instead metabolized.[334]

Cutinases, named for their ability to degrade cutin within plants, are an important class of enzymes for PET hydrolysis. Indeed, while a range of lipases and cutinases[331] has been reported for surface modification/degradation of PET, it is only a smaller subsection of cutinase enzymes that have been reported for successful degradation of bulk PET (vide supra). A catalytic triad of serine, aspartic acid, and histidine is shared across these enzymes.[335] The activity of specific cutinases toward PET hydrolysis is, on the basis of a range of crystallographic and modeling studies, thought to be related to their open active site that facilitates polymer chain binding. In comparison, many lipases have "lid" structures around their active site which may inhibit polymer chain binding.[329] The presence of hydrophobic regions near the active site has also been proposed to aid PET binding and hence the degradation rate.[336] Accordingly, engineering of enzymes to increase their surface hydrophobicity has been shown to increase their activity.[337,338]

Several considerations are essential for effective enzymatic recycling of PET. First, since the enzymatic degradation of PET is significantly enhanced as the temperature approaches that of the T_g of PET (which, in water, is reduced to around 65 °C due to water diffusion within the polymer[331]), enzymes must be suitably thermally stable at such temperatures. As a result, enzymes from thermophilic bacteria and fungi are often targeted.[331,339] Enhancing the thermal stability of wild-type cutinases has proven essential for improving enzymatic activities. This can be achieved through several means. Enzyme engineering to introduce structural modifications such as additional disulfide bridges or alterations to the secondary structure can lead to increases in the thermal stability.[340,341] The presence of divalent calcium or magnesium ions can also enhance enzyme thermostability and activity.[332,342] Accordingly, enzyme engineering to introduce additional binding sites for these divalent metal ions can enhance the thermal stability provided that these ions are present in the reaction medium.[340,343] Other techniques to improve the thermal stability include the use of phosphate buffers, enzyme immobilization, and glycosylation.[333]

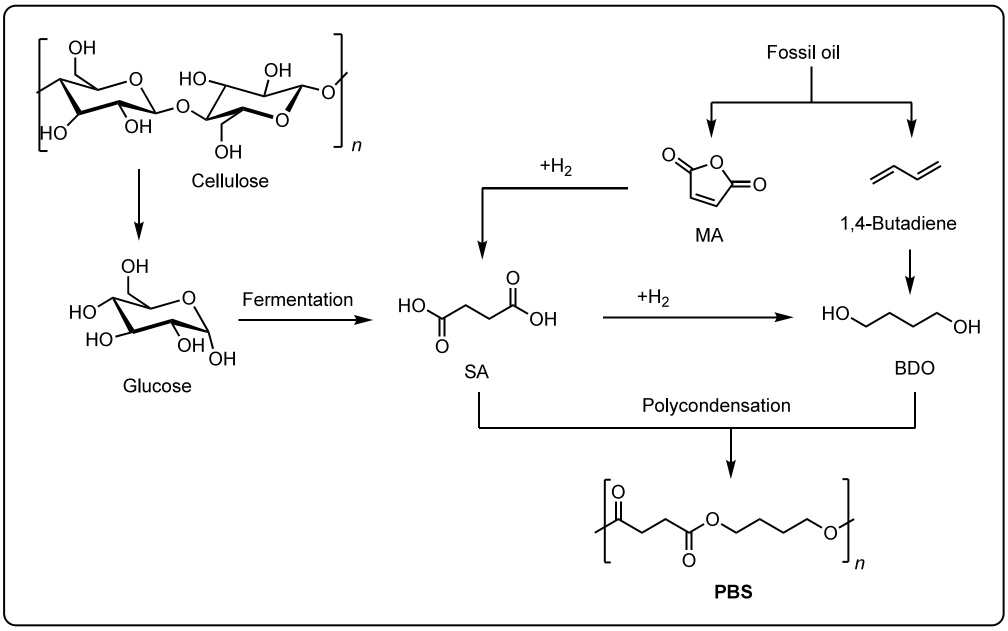
A second consideration is that enzymes often struggle to degrade crystalline regions of PET, and so recycling is often confined to amorphous samples or those with low crystallinity.[331] Mechanical or chemical pretreatment of PET can be applied to render it suitable for enzymatic recycling, although this drives up associated costs.[332,339] A further consideration is that enzymatic hydrolysis of PET may be inhibited by the products of the reaction, namely, MHET and BHET.[344−346] Application of dual-enzyme systems[346,347] and/or ultrafiltration reactor systems[348] can prevent buildup of these inhibitory substances and hence aid the enzymatic hydrolysis rate.

Recent research has resulted in significant breakthroughs in the ability of enzymatic hydrolysis to overcome these potential issues. In 2016, Yoshida and co-workers reported a novel bacterium capable of converting PET to EG and TPA (via MHET), although these products were subsequently metabolized by the bacterium.[349] This study, however, did identify the novel enzyme within the bacterium responsible for its PET-degrading ability, named IsPETase, which the authors noted to share structural similarities with the cutinase enzyme reported by Müller in 2005.[330]

In 2018, Austin et al. reported a detailed study on the structure of IsPETase as well as demonstrating an improved activity by modification of two amino acid residues to render it closer to typical cutinase enzymes.[350] Importantly, the modified enzyme also showed an enhanced ability to degrade crystalline PET (15% crystallinity); degradation with wild-type IsPETase resulted in a 1.5% absolute reduction in crystallinity compared to a 4.1% absolute reduction when applying the modified IsPETase.

In 2020, another ground-breaking study reported protein engineering on an LC-cutinase (LCC) to improve the thermal stability and increase the activity. The most effective variants demonstrated 85% degradation of a PET film in 15 h at 70 °C, compared to the previously reported wild-type LCC which obtained 53% degradation in 20 h at the same temperature.[351]

Scheme 24. Outline of the Synthesis of PBS from Biobased and Petrochemical Feedstocks



A very recent study applied directed evolution to a thermostabilized variant of IsPETase to yield a highly effective novel enzyme, named HotPETase, that contained 21 mutations from the original wild-type IsPETase.[352] It showed exceptional activity for the degradation of crystalline PET, even outperforming the engineered LCC from 2020; 31% of a crystalline PET (29.8% crystallinity) sample could be degraded within 5 h at 60 °C, although degradation of the amorphous region was still preferred.

Another study from 2022 detailed the machine learning-led development of an engineered PETase, named FAST-PETase, which contained 5 mutations from wild-type IsPETase.[353] This enzyme showed good activities for PET hydrolysis between 30 and 50 °C, outperforming several previously reported active variants including LCC and several engineered variants of IsPETase. It was also able to degrade a range of POSTC−PET.

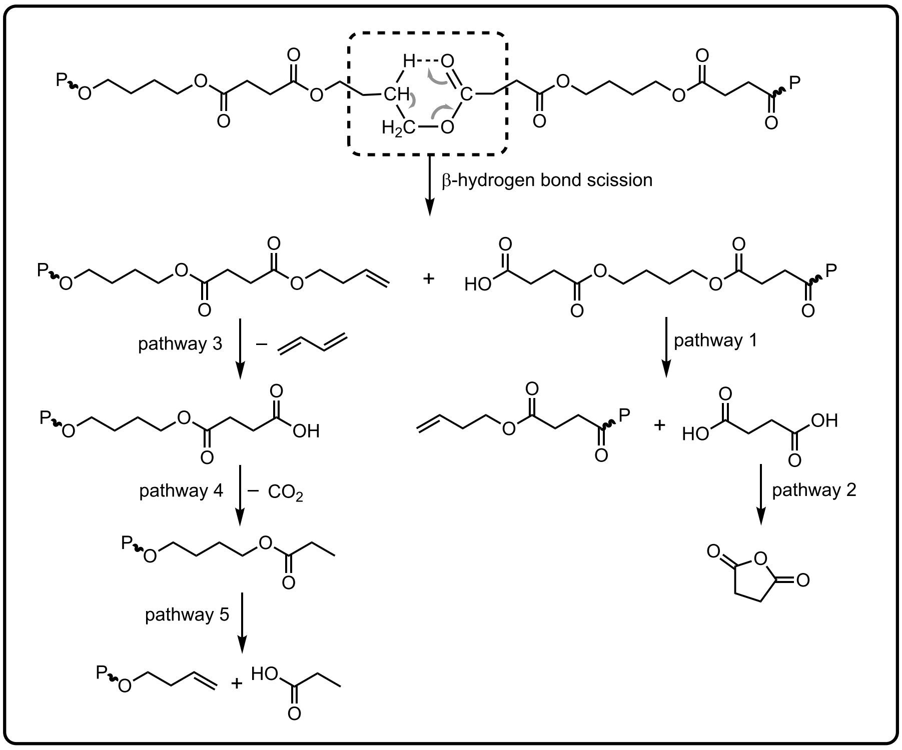
2.4. Poly(butylene succinate) (PBS) and Poly(butylene adipate-*co*-terephthalate) (PBAT)

2.4.1. Synthetic Routes. PBS is a biodegradable aliphatic polyester, synthesized through the polycondensation of succinic acid (SA) and 1,4-butanediol (BDO). Both of these A2 and B2 monomers can be derived from biobased or fossil-based sources, as depicted in Scheme 24.[354−356] PBS has gained considerable attention in the scientific and industrial communities due to its compliance with the ISO EN13432 standard for biodegradability.[154] In addition to its biodegradability, PBS boasts a remarkable combination of thermal and chemical resistance and melt processability, making it versatile and well suited for a wide array of applications including mulch films, packaging films, compostable bags, and foam products and various biomedical applications such as wound dressings, bioabsorbable surgical sutures, drug delivery systems, and implants.[357−360] As a sustainable alternative to nondegradable petrochemical-based plastics, PBS provides similar properties to widely used materials such as low-density polyethylene (LDPE), HDPE, and polypropylene (PP), which are typically utilized in short shelf-life products like packaging and mulch films.[361,362] However, the extensive utilization of PBS across various applications is hindered by several drawbacks, such as excessive softness, low viscosity, and inadequate gas-barrier properties. To overcome these limitations and fully exploit the potential of PBS, modifications can be implemented via the integration of other polymers through blending techniques or by introducing fillers into the PBS matrix. These strategies allow for the customization of PBS properties to better meet the specific demands of various applications, thereby enhancing its mechanical strength, viscosity, and gas-barrier performance.[105,355,356]

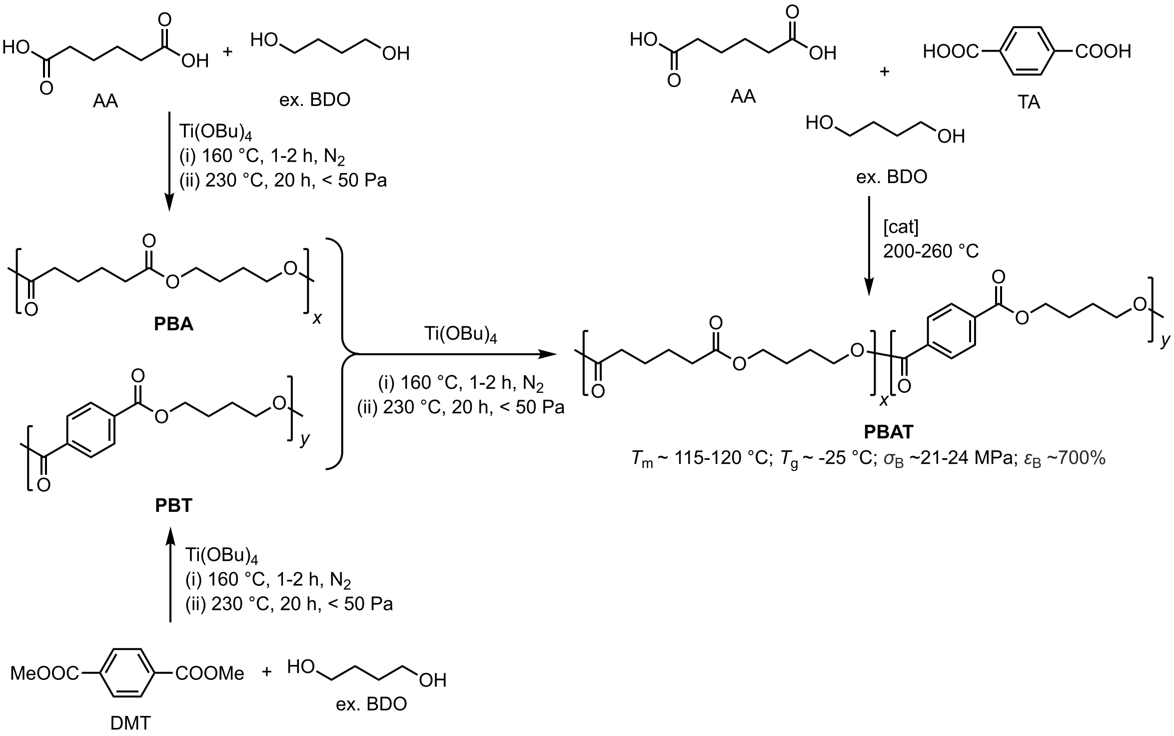
The synthesis of PBS typically follows a two-step procedure: (1) oligomer formation through the esterification of SA with BDO or via transesterification of dimethyl succinate and BDO; (2) polycondensation of these oligomers, along with the removal of excess BDO, leads to the production of high molar mass PBS. Stoichiometric quantities of SA (or dimethyl succinate) and BDO are typically applied; occasionally, a slight excess of BDO, typically no more than 15%, might be utilized. First, transesterification is carried out at temperatures between 160 and 190 °C under an N_2 atmosphere, which also ensures that the succinic acid fully melts. Any water or methanol generated during this phase is distilled off. Afterward, the temperature is elevated to a range of 220−240 °C under vacuum conditions, with the reaction sustained for a specific duration. Various catalysts have been explored to enhance the efficiency of the PBS synthesis. Jacquel et al. undertook an investigation on a variety of six organometallic catalysts, including $Ti(OBu)_4$, $Zr(OBu)_4$, $Sn(Oct)_2$, $Sb(OBu)_3$, $Hf(OBu)_4$, and $Bi(ODec)_3$, to evaluate their effectiveness. Their research illustrated that $Ti(OBu)_4$ was the most efficient, with the subsequent order of effectiveness being Zr > Sn > Sb > Hf > Bi.[363,364]

The thermal properties of PBS are largely influenced by its molar mass and thermal history. Typically, PBS exhibits high crystallinity, with a T_m around 115 °C, characterized by two endothermal peaks within the range of 90−120 °C and a T_g which varies between −40 and −10 °C depending on the manufacturing process, processing conditions, and synthesis methodology.[365] The crystallization temperature of PBS is

Scheme 25. Proposed Mechanism of the Thermal Degradation of PBS

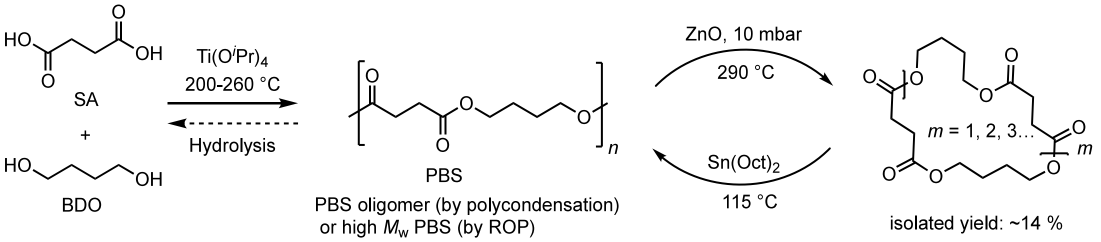


Scheme 26. Outline of the Synthesis of PBAT through Polycondensation



dependent on the cooling rate, usually ranging from 70 to 82 °C. PBS is notably recognized for its exceptional thermal resistance, featuring a heat deflection temperature (HDT) that surpasses 90 °C.[354,356] Additionally, the tensile properties of PBS are commonly characterized by σ_B ranging from 20 to 60 MPa, complemented by an E of ~300 MPa and elongation reaching up to 560%.[361] The thermal degradation of PBS typically occurs in a singular step, initiating at ~300 °C and completing around 430 °C under a nitrogen atmosphere. The degradation mechanism of PBS can be described as follows (Scheme 25): initially, a β-hydrogen-bond scission takes place, where the β-hydrogen migrates to an adjacent carbonyl group, leading to the cleavage of $-O-CH_2-$ bonds. This process results in the formation of two chains with alkenyl or

Scheme 27. Chemical Recycling of PBS through an Oligomerization−Cyclization−ROP Route



carboxylic acid end groups, giving rise to various subsequent degradation pathways. In pathway 1, a β-hydrogen-bond scission leads to the formation of an alkenyl-terminated chain and succinic acid. The succinic acid further transforms into succinic anhydride through the release of H_2O (pathway 2). Pathway 3 involves the generation of carboxylic acid-terminated chains and 1,4-butadiene. Following this, two main pathways can occur: either the decomposition of the carboxylic acid end of the chains, leading to the formation of succinic anhydride, through pathways 1 and 2, or the elimination of CO_2 resulting in acetate via pathway 4, further resulting in the formation of an acid (pathway 5).[366,367]

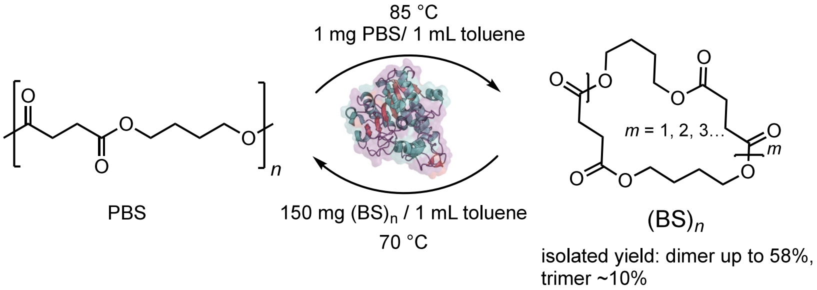
PBAT is an aliphatic−aromatic copolyester that presents enormous potential as a biodegradable material possessing excellent mechanical properties (Scheme 26). These properties are comparable to those of LDPE, making PBAT a suitable material for a broad range of applications, such as mulch films, food packaging, cutlery, and medical devices similar to LDPE.[154,368−370] The synthesis of PBAT consists of two main steps. First, an esterification reaction takes place between adipic acid (AA) and TPA with an excess of BDO in the presence of a catalyst, conducted at temperatures of 200−220 °C. During this step, distillation is employed to remove the major byproduct, water, thus facilitating a faster reaction. Second, in the polycondensation step, the PBAT oligomer produced in the initial stage undergoes further reaction at temperatures of 250−260 °C under a high vacuum to remove the excess BDO, yielding high molar mass PBAT. PBAT can also be synthesized from the transesterification of PBA and PBT catalyzed by Ti(OBu)$_4$. Specifically, AA and BDO, in the desired mole ratio, were introduced into a stainless steel reactor under a N_2 atmosphere. The temperature was raised to 160 °C with continuous stirring, and water produced during the reaction was distilled off. After 1−2 h, Ti(OBu)$_4$ was added under a N_2 atmosphere. The temperature was subsequently increased to 230 °C and maintained for 4 h under vacuum. DMT, BDO, and Ti(OBu)$_4$, following the predetermined mole ratio, were then introduced. The mixture was kept at 180 °C for 2 h and subsequently elevated to 230 °C over a 4 h period under vacuum. The reaction was continued for an additional 20 h under high vacuum (<50 Pa) (Scheme 26).[371] The commonly employed catalysts for PBAT preparation include organometallic compounds such as titanium oxides, alkoxides, and acetates, as well as compounds of tin, antimony, and iron.[372]

Moreover, the synthetic process of PBAT allows for the adjustment of the monomer composition and molar mass of the polymer, enabling customization of its mechanical properties to meet the requirements of specific applications.[370] The aliphatic fraction of PBAT enables biodegradation in favorable environments through the action of natural enzymes, while the aromatic component imparts robust mechanical properties, preserving the polymer's integrity and inhibiting degradation.[105,373,374] A molar ratio of AA:TPA = 50:50 has been identified as suitable for composting degradation and offering optimized mechanical properties for packaging film applications.[375] Specifically, PBAT exhibits remarkable flexibility and σ_B, ranging from 21 to 24 MPa, surpassing many other biodegradable polyesters. Additionally, it also demonstrates exceptional ε_B, ~700% for 50 mol % of TPA content.[376] Slight increases in the TPA monomer content result in a higher tensile strength, albeit at the expense of reduced ε_B. In addition, PBAT displays a T_m of around 115−120 °C and a crystallization temperature of 55−60 °C, as well as a low T_g of from −23 to −25 °C. It exhibits an initial degradation temperature of 350 °C, indicating a broad processing temperature range above the T_m and below the T_d.[372]

2.4.2. Chemical Recycling. The chemical recycling of diacid/diol-type polyesters typically involves hydrolysis, a process that converts the polyester back into its constituent A2 diacid and B2 diol components using an alkaline catalyst at elevated temperatures. However, these processes demand energy-intensive neutralization and purification steps. While specific studies focusing on the chemical recycling of PBS through hydrolysis or solvolysis have not been extensively undertaken, its feasibility can be anticipated due to the polyester's intrinsic nature. In 2001, a study by Cho et al. investigated the hydrolysis of PBS using 1 M NaOH at 25 °C over several days, particularly examining the impact of the crystalline morphology on the hydrolytic degradation behavior.[377] Their results revealed a consistent reduction in polymer weight over time with a weight loss of up to 8% during the experimental period. They also found that a higher degree of crystallinity inhibited the hydrolysis process, as hydrolysis primarily occurred within the amorphous regions of the PBS polymer.

An alternative chemical recycling route is the conversion of PBS into cyclic butylene succinate oligomers, $c(\text{BS})_n$, which can subsequently undergo ROP to regenerate PBS with high molar mass (Scheme 27). Interestingly, these $c(\text{BS})_n$ are typically found as byproducts in equilibrium with linear chains during the traditional two-step melt polycondensation process used for PBS synthesis. The high temperatures and low-vacuum conditions applied during polymerization cause a substantial amount of these cyclic byproducts to volatilize and be collected in the condensation vessel. Labruyere et al. harnessed this phenomenon to produce $c(\text{BS})_n$ via pyrolysis of oligomeric PBS in a glass oven at 290 °C under a 10 mbar vacuum with 1 wt % of ZnO catalyst. The bulb-to-bulb distillation enabled the production of the cyclic dimer $c(\text{BS})_2$ with a yield of 12.1%. Subsequently, PBS with a high weight-average molar mass (M_w = 65.0 kg mol^{-1}) was successfully produced via ROP, catalyzed by Sn(Oct)$_2$ in bulk at 115 °C.[378] Enzymes have been demonstrated to be a more efficient

Scheme 28. Biological Recycling of PBS via Cyclic Oligomers Using Lipase CA



catalyst for the generation of $c(\mathrm{BS})_n$ and will be discussed in the biological recycling section.

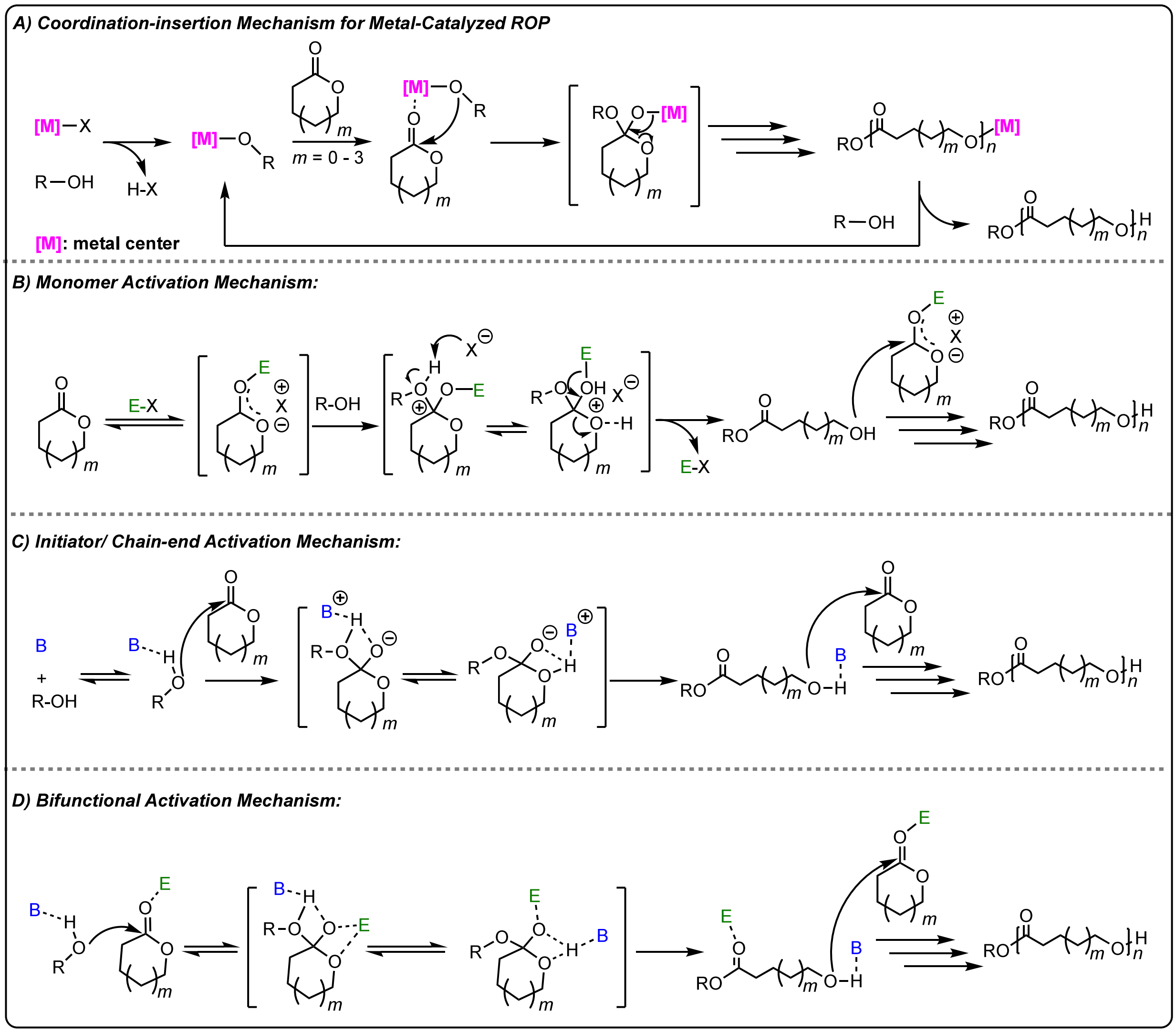
2.4.3. Mechanical Recycling. Despite the potential for the mechanical recycling of biodegradable plastics, such as PBS and PBAT, at a small scale, it has yet to be implemented on an industrial scale.[105] The potential for industrial mechanical recycling of PBS was explored by Fauster et al. using repeated polymer processing (extrusion) for up to seven cycles to examine changes in the polymer's mechanical performance. Their findings suggested that PBS was unsuitable for mechanical recycling, as reprocessing resulted in molecular degradation, translating into a significant drop in molar mass and viscosity. Moreover, the structural degradation of PBS caused a decrease in tensile strength and strain at break by up to 24% and 34%, respectively. However, there was a slight increase in the Young's modulus, and the number of reprocessing cycles did not noticeably affect the thermal parameters such as T_g and T_m.[379] In contrast, a study by Kanemura et al. reported an unexpected behavior in PBS during repeated processing. After the initial cycle, there was a decrease in the viscosity, molar mass, and mechanical strength of PBS due to chemical degradation caused by hydrolysis. However, in the subsequent reprocessing cycles, they observed an unexpected increase in the mechanical strength and molar mass of PBS, suggesting that the polymer underwent resynthesis (via chain-end coupling) to a higher molar mass during the reprocessing process. This increase in molar mass was mainly attributed to the autocatalytic action of PBS molecules during reprocessing via esterification, a mechanism offering a "cure" for the chemical degradation not seen in PLA, another common biodegradable plastic.[380]

Limited research has been conducted on the mechanical recycling of PBAT, primarily due to its low thermomechanical resistance.[105] The thermal degradation mechanism of PBAT mainly involves ester linkage hydrolysis, oxidative chain scission, and β-C−H transfer. These processes can lead to a significant decrease in M_w and viscosity when PBAT is subjected to high temperatures and shear rates, such as during the extrusion process, which can contribute to thermal degradation.[105] To mitigate this undesired degradation, Chaves et al. proposed the use of antioxidant stabilizers, such as Irganox 1010 (primary antioxidant) and Irgafos 168 (secondary antioxidant), during processing. Their results demonstrated that the inclusion of antioxidants effectively maintained the molar mass and viscosity of PBAT during the reprocessing with a torque rheometer operated at 60 rpm and processing temperatures of 180 and 200 °C, highlighting the influence of oxygen in the degradation process.[381] Exploring other strategies, Scaffaro et al. investigated the effect of incorporating organoclay into PBAT subjected to UV radiation. The resulting material exhibited enhanced polymer cross-linking and the formation of porous structures. While this approach offers the possibility of fabricating high-value materials from Bioplastic waste, it also compromises the biodegradability of PBAT-based polymers.[382] Further, Mantia et al. conducted a study on the reprocessing of PLA/PBAT blends through five consecutive extrusion cycles using a single-screw extruder under dry and wet conditions.[383] Interestingly, they found that the sample processed under dry conditions exhibited less degradation compared to those processed under wet conditions, a disparity attributed to additional hydrolysis instigated by the presence of water in addition to thermomechanical degradation. Importantly, despite undergoing five extrusion cycles, the PLA/PBAT blend did not show a significant decrease in the mechanical performance, suggesting the potential for additional reprocessing cycles without compromising the mechanical properties of the blend.[383]

2.4.4. Biological Recycling. Enzymatic depolymerization of PBS into cyclic BS oligomers followed by their repolymerization via ROP to regenerate PBS with high molar mass presents a more sustainable pathway for PBS recycling (Scheme 28). In this regard, Matsumura and co-workers conducted a comprehensive investigation into the synthesis of $c(\mathrm{BS})_n$, a precursor for regenerating high molar mass PBS via ROP, through using the enzymatic depolymerization of PBS.[384−386] Specifically, they used immobilized lipase *Candida antarctica* (CA) to catalyze the depolymerization of PBS in toluene (1 mg of PBS in 1 mL of toluene) at 85 °C for 24 h, resulting in the formation of $c(\mathrm{BS})_n$ with precise stoichiometry of the monomer units, predominantly composed of dimers and trimers. Notably, these cyclic oligomers, $c(\mathrm{BS})_n$, can undergo ROP under relatively concentrated conditions (150 mg/mL in toluene) to form high molar mass PBS using the same lipase as the catalyst. This innovative method illustrates the immense potential for regenerating high molar mass PBS and propels the advancement of sustainable chemical recycling in the realm of polymer materials.[384]

In addition, Matsumura and co-workers discovered that in a dilute toluene solution, the interaction between dimethyl succinate and BDO, catalyzed by lipase CA (100 wt %), at 90 °C for 48 h, predominantly yielded a cyclic oligomer in nearly quantitative yield. The isolated yield of $c(\mathrm{BS})_2$ was 58%.[385] This isolated $c(\mathrm{BS})_2$ displayed excellent polymerizability when subjected to bulk ROP using lipase CA (40 wt %) at 120 °C for 24 h. This ROP resulted in the formation of PBS with a notably high M_w of 172 kg mol^{-1} and a $Đ$ of 1.9, an accomplishment not attainable with conventional polymerization techniques. Following this, bulk ROP of the molecularly pure cyclic BS oligomer, specifically $c(\mathrm{BS})_2$ and

Scheme 29. Outline of the Four Mechanistic Pathways for the ROP of Cyclic Esters



$c(BS)_3$, was performed to investigate the kinetics using lipase CA (40 wt %) at 120 °C. It was observed that both $c(BS)_2$ and $c(BS)_3$ underwent rapid polymerization within a few hours, with the PBS obtained from $c(BS)_2$ consistently exhibiting a higher M_w than that of the polymer derived from $c(BS)_3$. Nevertheless, the PBS derived from $c(BS)_3$ still displayed a high M_w of 128 kg mol^{-1} and a $Đ$ of 1.8.[386]

Given that PBAT is an aliphatic−aromatic copolyester composed of BDO/AA and BDO/TA units, the aliphatic ester segments within PBAT render its ester bonds susceptible to enzymatic cleavage in microbiologically active environments like soil and compost. Degradation occurs with the assistance of enzymes such as esterases and cutinases, leading to release of the original monomers: BDO, AA, and TPA.[387,388] Postenzymatic degradation, the released compounds are mineralized by microorganisms, eventually yielding biomass, H_2O, and CO_2 under aerobic conditions.[389,390] Biodegradation of PBAT has been observed with individual microbes as well as aerobic or anaerobic microbial consortia.[391,392] Although natural degradation is slow, industrial composting facilities can break down PBAT within 60 days or even faster.[8,369,393]

2.4.5. Other PET Copolymers. Alongside PBAT, a large range of other copolymers of PET are known with a diverse range of potential applications.[394] Despite this, the chemical recycling of such materials is rarely reported. In 2023, Cochran and co-workers described the synthesis of PET copolymers with diethyl 2,5-hydroxyterephthalate (DHTE, <20 mol %), which yielded a polyester with similar material properties to PET.[395] The incorporation of the DHTE comonomer rendered the polyester significantly more labile with respect to hydrolysis. For example, using 0−1 wt % of $ZnCl_2$ for 8 h at 170 °C, 70% degradation was obtained with the main products being TPA, DHTE, and dimeric products. Under equivalent conditions, PET showed 16% hydrolysis. The authors further noted that $Zn(OAc)_2$ used in the polyester synthesis likely played a significant role in catalyzing the hydrolysis, explaining why significant hydrolysis was obtained even when no $ZnCl_2$ catalyst was applied.

In the same year, Shaver and co-workers described the glycolysis of glycol-modified PET (PET-G, a copolymer of TPA, EG, and 1,4-cyclohexanedimethanol, CHDM).[396] Utilizing the organocatalyst DBU, yields of up to 93% BHET were obtained (6 wt % of DBU, 140 °C, 20 min). Importantly, the PET-G was able to be resynthesized directly from the depolymerization mixture. The copolymer of TPA and CHDM, poly(1,4-cyclohexylenedimethylene terephthalate)

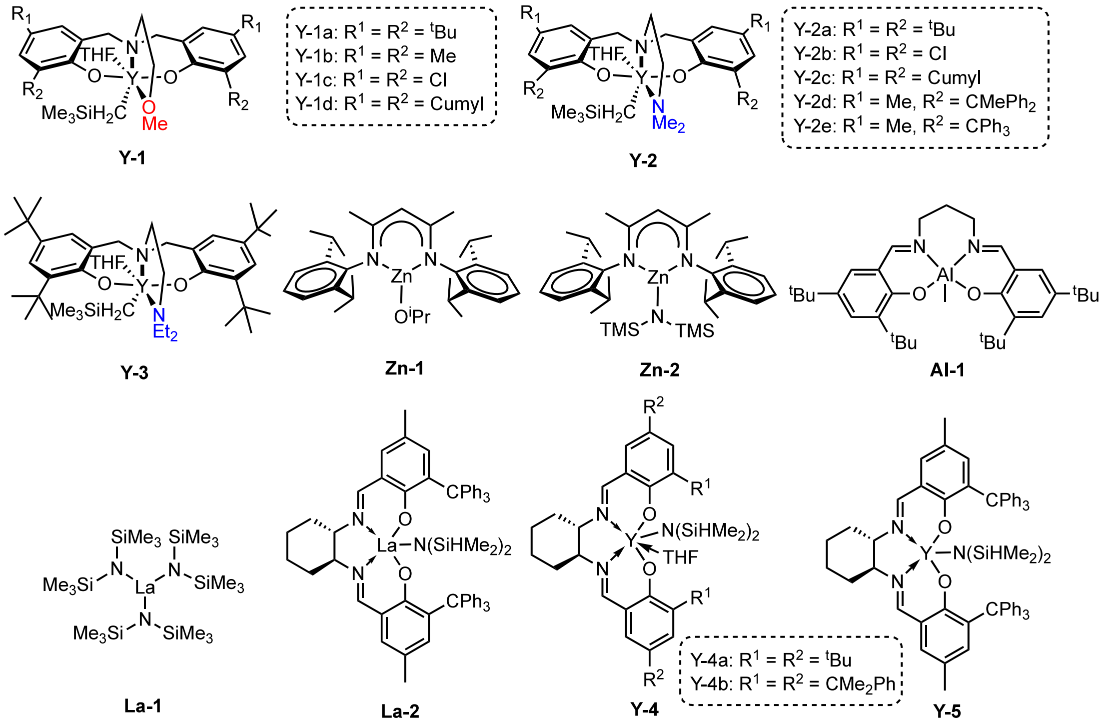


Figure 2. Representative discrete metal complexes employed for achieving high polymerization activity, efficiency, and stereoselectivity.

(PCT), has also been reported for glycolysis.[397] The use of the CHDM monomer results in poor glycolysis efficiency due to increased steric hindrance to transesterification. The application of a combined $Zn(OAc)_2$/NaOEt (0.12 mol %) catalyst system provided a rate enhancement over the typically applied $Zn(OAc)_2$, circumventing the typical rate issues present for PCT. An 82% yield of bis(2-(2-hydroxyethoxy)ethyl) terephthalate was obtained at 170 °C in 6 h.

3. EMERGING ALIPHATIC POLYESTERS

Alongside the intense efforts toward recycling and upcycling of legacy polyesters, researchers are also concurrently delving into design principles at a molecular level to construct chemically recyclable polyesters, which, within the scope of this review, we refer to as emerging polyesters, including aliphatic and aromatic polyesters.[20,37,38,41,45,398−400] In this section, we have categorized emerging aliphatic polyesters according to their polymerization mechanism and the characteristics of the catalyst used; it is hence divided into three principal classes of polymerization: Chain-Growth Ring-Opening Polymerization, Step-Growth Polycondensation, and Enzymatic Polymerization.

3.1. Chain-Growth Ring-Opening Polymerization

The ROP of cyclic esters is an efficient method for synthesizing aliphatic polyesters, which can be accomplished through four major mechanistic pathways (Scheme 29). It is typically a chain-growth polymerization process that is initiated through the ring opening of a cyclic monomer with an initiator to generate a reactive center. Further cyclic monomers can then be added to this reactive center, leading to the formation of a longer polymer chain.[401] Distinct from SGP, ROP offers several advantages, including milder reaction conditions (low temperatures, ambient pressure), faster kinetics, higher yield, and 100% atom economy, as well as precise control over polymer molar mass, dispersity, end-group fidelity, regio- and stereoregularity, and architecture.[402,403] Although most cyclic esters do not occur naturally, certain bioderived platform chemicals can be utilized for their synthesis.[14,16] As such, ROP is a highly efficient and environmentally friendly route for the synthesis of aliphatic polyesters.

Given the potential for both nucleophiles and electrophiles to initiate the polymerization of lactone monomers, a broad range of initiator/catalyst systems, including metal complexes, organic compounds, and enzymes, have been specifically designed for the ROP of cyclic esters. The nature of the reactive center in this polymerization process is dictated by the initiating species, which can be anionic, cationic, or covalent, leading to more specific variants of the ROP mechanism (Scheme 29).[86,404] Among the early classes of catalysts shown to efficiently initiate the anionic polymerization of lactones were alkali and earth-alkaline alkoxides, such as butyllithium and potassium methoxide. Specifically, the alkoxide anion engages in nucleophilic addition to the carbonyl carbon of the cyclic ester, releasing an alkoxide end group that propagates the reaction.[405] However, due to the strong nucleophilic and/or basic characteristics of the anionic initiator or chain ends, side reactions such as transesterification and epimerization are commonly observed.[406] Strong acids, including Brønsted and Lewis acids, can facilitate the polymerization of cyclic esters via a cationic pathway.[406] Synthesizing high molar mass polyester is challenging with these catalysts due to the strong tendency for intramolecular transesterification (cyclization) and proton transfer reactions of the cationic propagating species.[407,408] The most commonly used catalysts for ROP are transition- and post-transition-metal complexes, which mediate the ROP through a "coordination−insertion" mechanism (Scheme 29A).[406,409] Given that the monomer and alkoxide chain end are both covalently attached to the metal center, the catalyst can exercise exquisite control over the polymerization rate and selectivity. Simple metal alkoxides and carboxylates, such as commercial $Sn(Oct)_2$, are cost-effective and convenient

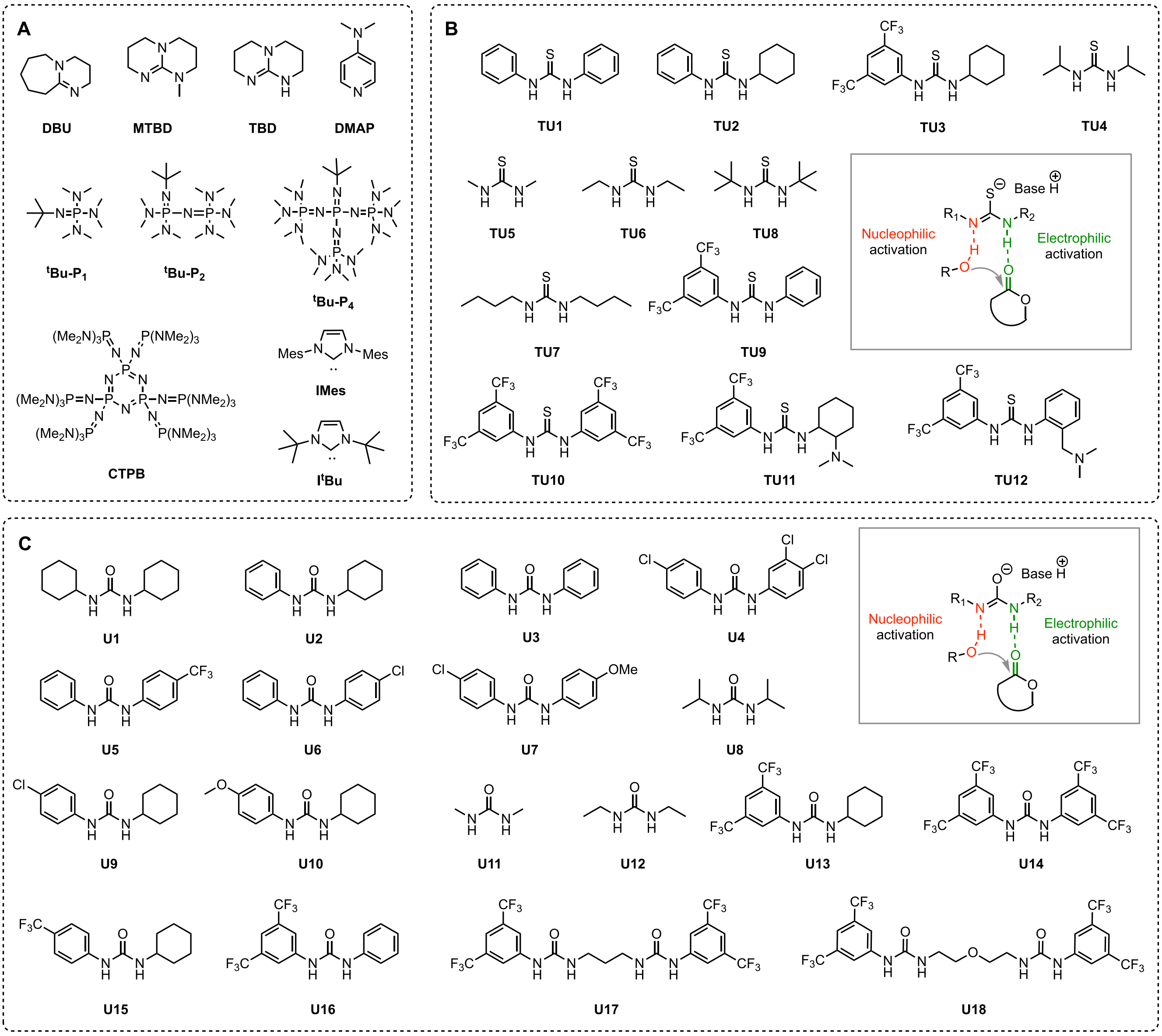
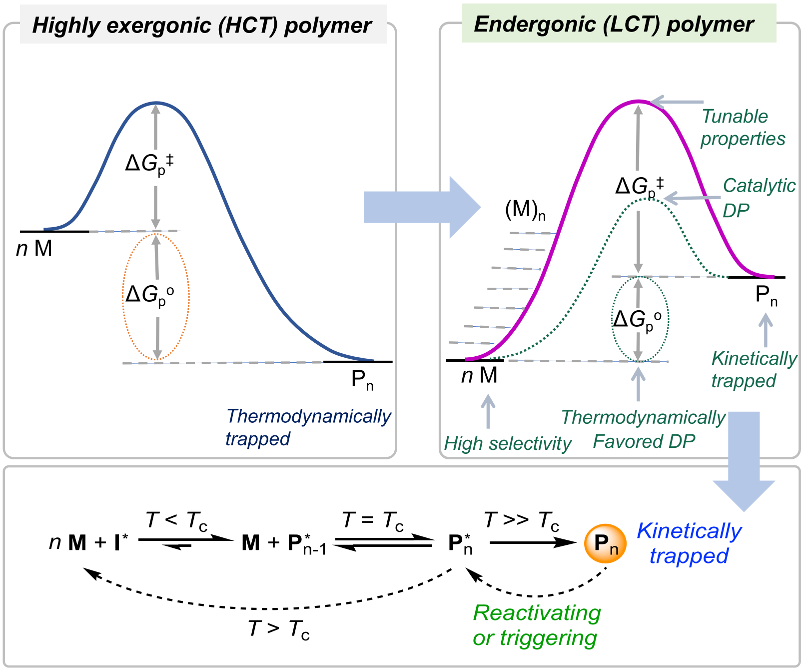


Figure 3. Representative (A) organic-(super)base catalysts, (B) thiourea-base catalysts, and (C) urea-base catalysts.

catalysts for ROP, earning them widespread use in industry.[403] Nonetheless, for applications requiring selectivity, particularly stereoselectivity, well-defined single-site metal catalysts supported by ancillary ligands typically are more effective.[402,410,411] The ancillary ligand has been demonstrated to be a critical component in ROP catalysis as it can be used to meticulously adjust the electronic, steric, and symmetry attributes of the metal center, thereby manipulating the reactivity and selectivity of the polymerization. Several representative discrete metal complexes, commonly used for achieving high polymerization activity, efficiency, and stereoselectivity, are summarized in Figure 2.

Ever since the pioneering work by Hedrick in 2001,[412] the employment of organic catalysts (Figure 3) in ROP has seen considerable advancements. In many instances, these catalysts now present a potent alternative to and sometimes even outperform traditional metal-based catalysts. Renowned for their cost effectiveness, widespread availability, ease of removal from polymers, low toxicity, and versatile catalytic mechanisms, organic catalysts lay the foundation for a more environmentally friendly and adaptable polyester synthesis pathway, particularly suitable for biomedical and microelectronic applications.[85,86,413] Depending on the specific catalyst used, organocatalyzed ROP can operate through various mechanisms (Scheme 29).[85] For instance, organic acids such as sulfonic or phosphoric acid can catalyze the polymerization process through the electrophilic activation of monomers. On the other hand, organic bases such as *N*-heterocyclic carbenes (NHCs)[414] and amidines[415,416] can activate the monomer through nucleophilic activation or the alcohol initiator or chain ends through hydrogen-bonding interactions.[83] Furthermore, catalytic systems that combine both hydrogen-bond donor and acceptor moieties, such as thiourea/amine catalysts, can simultaneously activate the monomer and the alcohol initiator/chain end,[83] demonstrating exceptional selectivity for chain propagation over transesterification and producing polyesters with a narrow dispersity. However, such catalytic systems that promote a neutral, "cooperative" mechanism typically suffer from slow kinetics.

Scheme 30. Schematic Design Strategies by Reverting Thermodynamically Trapped Polymers to Kinetically Trapped Ones[a]



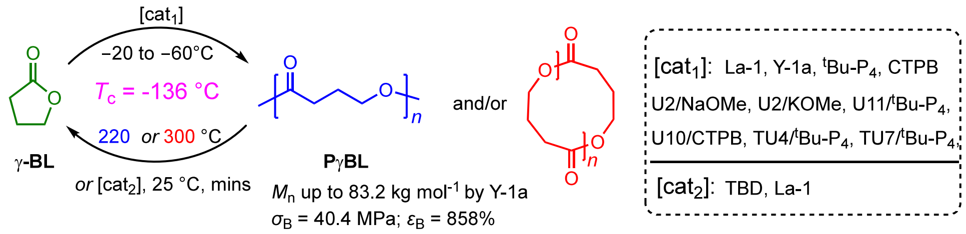
[a]Modified from ref 45. Copyright 2021 Elsevier.

Building off of the seminar work by Waymouth and co-workers, the use of (thio)urea anion catalysts in the ROP of cyclic esters, which demonstrated both high reactivity and selectivity, has broadened their application in the synthesis of emerging aliphatic and aromatic polyesters.[417,418] These ionic catalysts, prepared through a simple deprotonation process of neutral ureas or thioureas using strong bases like KOMe, NaOMe, or ^{t}Bu-P$_4$, provide the flexibility to modulate the polymerization rate across several orders of magnitude by adjusting the urea or thiourea substituents. According to density functional theory (DFT) calculations, these catalysts operate via a bifunctional mechanism similar to that of TBD, where (thio)imidiates act as a proton shuttle, acquiring the proton from the initiator/chain end, stabilizing the tetrahedral intermediate through double H bonds, and subsequently returning the proton to the chain end after ring opening.[417] The operational simplicity coupled with the high activity, selectivity, and versatility of these urea or thiourea anions highlight the potential of these catalysts for the more sustainable synthesis of metal-free polyesters. The representative ureas or thioureas are summarized in Figure 3B and 3C.

3.1.1. Lactones. The feasibility of ROP of a cyclic monomer is influenced by its ring size and substitution pattern, as the thermodynamic driving force for polymerization can vary accordingly.[120,419] As such, only a limited set of cyclic esters can be polymerized under practical ROP conditions. For small-sized (i.e., 5- and 6-membered) and certain medium-sized (i.e., 7–11-membered) rings, the process of ring opening is largely driven by enthalpy, as it leads to the release of ring strain, which originates from deviations from nondistorted bond angle values, bond stretching and/or compression, repulsion between eclipsed hydrogen atoms, and nonbonding interactions between substituents associated with ring size (angular strain) and geometry (conformational and trans-annular strain).[120] Specifically, 4-, 6-, and 7-membered rings are favorable for ROP, attributable to their high ring strain. However, 5-membered lactones such as the parent γ-butyrolactone (γ-BL) exhibit a much less favorable enthalpy for polymerization, rendering them commonly considered as nonpolymerizable.[420] On the other hand, for cyclic esters featuring larger ring sizes, the enthalpy change (ΔH_p) associated with ring opening is minimal. As a result, the polymerization process is predominantly driven by entropy (ΔS_p), benefiting from the increase in conformational freedom when monomer is transformed to polymer.[421,422] The entropy-driven ROP of several macrolactones (MLs, those with a ring size > 12) has been successfully practiced to produce long-chain polyesters that exhibit similar structures to those obtained from the polycondensation of fatty acids yet with higher and more predictable molar mass.[423−425]

Consequently, when tackling the chemical recycling of polyesters derived from the ROP of lactones, it is necessary to implement specific strategies that are customized for lactones with different ring sizes and substitutions.[45] Central to this process is a comprehensive understanding and deliberate consideration of both the *thermodynamics*, specifically the relative energy levels of monomer versus polymer states under the given conditions, and *kinetics*, namely, the energy barrier that influences the rate, energy input, and selectivity of forward and reverse reactions within the de/polymerization system (Scheme 30).[45,120,419] Specifically, the relative thermodynamic stability of monomer versus polymer states can be modulated by the structure of the monomer (and consequently the polymer), which exerts a significant influence on the thermodynamics. However, systematic investigations of structural effects are often lacking, especially on the change in the entropy of polymerization and the interplay between the changes in the entropy and enthalpy of polymerization, making it still challenging to draw generalized conclusions. In addition, reaction conditions such as temperature, concentration, pressure, and state can also be strategically employed to fine tune the relative thermodynamic stability of monomer versus

Scheme 31. ROP of γ-BL into Chemically Recyclable PγBL with High Molar Mass and Topology Control



polymer states. From a kinetic standpoint, the energy barrier is typically reliant on the specific catalyst used. The use of a highly effective catalyst can substantially diminish the energy barrier, thus speeding up the polymerization process and allowing the system to reach equilibrium within a practical time frame.[404]

The feasibility of a polymerization process can be determined by evaluating the change in Gibbs free energy (ΔG) during the reaction. If ΔG_p is <0, the reaction is energetically favored. Conversely, if ΔG_p is >0, the reaction is energetically disfavored. Mathematically, ΔG_p can be expressed as the sum of the standard Gibbs free energy of polymerization (ΔG_p^o) and a term related to the instantaneous monomer concentration to the concentration of growing polymer chains, polymerization temperature (T), and the molar gas constant (R): $\Delta G_p = \Delta G_p^o + RT\ln\{[P^*_n]/[P^*_{n-1}][M]\}$. On the basis of Flory's assumption that the reactivity of an active center on a sufficiently long macromolecular chain is independent of the degree of polymerization, an additional approximation emerges: $\Delta G_p = \Delta G_p^o + RT\ln\{1/[M]\}$. Further considering that $\Delta G_p^o = \Delta H_p^o - T\Delta S_p^o$, ΔG_p can be related to the standard polymerization enthalpy (ΔH_p^o) and entropy (ΔS_p^o) and expressed as $\Delta G_p = \Delta H_p^o - T\{\Delta S_p^o + R\ln[M]\}$.[120] Theoretically, ΔH_p^o and ΔS_p^o are intrinsically determined by the structure of the monomer and, by extension, the polymer. Given these thermodynamic considerations, for any particular monomer−polymer equilibrium, the manipulation of the polymerization temperature (T) and initial monomer concentration ($[M]_0$) can be exploited to influence the equilibrium favorably in either direction as needed. However, the assumption that ring strain and polymerization entropy are independent of the concentration and solvent is not completely accurate. In practical scenarios, interactions with the surrounding solvent can differ depending on the monomer, and these interactions are subject to factors such as solvent polarity and concentration.[121,419] In addition, approaches that continuously disrupt this "monomer−polymer" equilibrium, such as the precipitation or crystallization of the formed polymer or the constant removal of the resultant monomer (e.g., through distillation, sublimation, etc.) during depolymerization, can allow de/polymerization reactions to deviate from the thermodynamic limitations, potentially leading to complete depolymerization.[45]

Specifically, as previously mentioned, a prerequisite for polymerization to occur is that $\Delta G_p < 0$. Depending on the changes in ΔH_p^o and ΔS_p^o values, there are four distinct scenarios that encapsulate the diverse polymerization behaviors. For monomers characterized by $\Delta H_p^o < 0$ and $\Delta S_p^o > 0$, spontaneous polymerization can occur at any temperature. In contrast, those monomers marked by $\Delta H_p^o > 0$ and $\Delta S_p^o < 0$ are inherently incapable of polymerization. When $\Delta H_p^o > 0$ and $\Delta S_p^o > 0$, there exists a critical temperature, also known as the floor temperature (T_f), which is the minimal temperature at which polymerization can take place, indicative of an entropy-driven process. Such a scenario is frequently observed for MLs. However, for the most prevalent cases of polymerization, such as ROP of small- to medium-sized rings, where $\Delta H_p^o < 0$ (attributable to the release of ring strain) and $\Delta S_p^o < 0$ (due to the loss of translational freedom resulting from the covalent linkage of monomer molecules), T_c controls the temperature at which polymerization can occur. Above the T_c, the entropic penalty will override the favorable (negative) enthalpy of polymerization, resulting in depolymerization ($\Delta G_p > 0$), while the opposite is true for polymerization.[120]

A low T_c is an important criterion for polymers to be efficiently recycled back to their constituent monomers. Chen and co-workers have previously referred to these chemically recyclable polymers with a low T_c (typically, $T_c < 200$ °C in bulk) as intrinsically circular polymers (ICPs).[45] Unlike prevalent commodity plastics of today, which are thermodynamically trapped, ICPs are kinetically trapped, with the monomer state being more thermodynamically stable than the polymer state. However, once the active polymerization is quenched and the catalyst is deactivated or removed, the resulting inert, metastable polymer chain no longer participates in the monomer−polymer equilibrium, endowing the polymer with stability even at temperatures far exceeding its T_c. Reactivating the trapped state to return it to the equilibrium state (P_n^*) for selective depolymerization to monomer when $T > T_c$ could necessitate a substantial energy input to overcome the kinetic barrier. However, using efficient catalysts, a low-energy pathway is enabled, thereby minimizing energy input while maximizing selectivity for depolymerization. In a broader sense, the performance characteristics of chemically recyclable polyesters can be adjusted by modulating the intrinsic or catalytic kinetic barrier, whereas the relative thermodynamic stability between monomer and polymer states, as determined by their respective T_c or T_f values, can be influenced via the structural design of the monomer. Therefore, both the monomer design and the catalyst innovation are essential components in the successful development of chemically recyclable polyesters, possessing not just complete chemical recyclability but also practically useful and adjustable properties.[45]

3.1.1.1. Five-Membered Lactones. **Parent Five-Membered Lactone.** The simplest five-membered lactone is γ-butyrolactone (γ-BL), a biobased, highly stable lactone with negligible ring strain; thus, it was traditionally considered to be nonpolymerizable.[420] Synthesis of γ-BL oligomers was reported in the 1960s via ROP of γ-BL under ultrahigh pressure (e.g., 20 000 atm)[426,427] or under lipase-catalyzed conditions,[428] but these techniques demand extreme conditions and only yield a mixture of oligomers ($M_n < 5.0$ kg mol^{-1}). The synthesis of high molar mass poly(γ-butyrolactone) (PγBL), which is structurally equivalent to microbial poly(4-hydroxybutyrate) (P4HB),[429] remained a challenge until 2016.[430] The interest in the synthetic route to P4HB via this ROP stems from the fact that γ-BL is readily sourced from biomass-based succinic acid.[431]

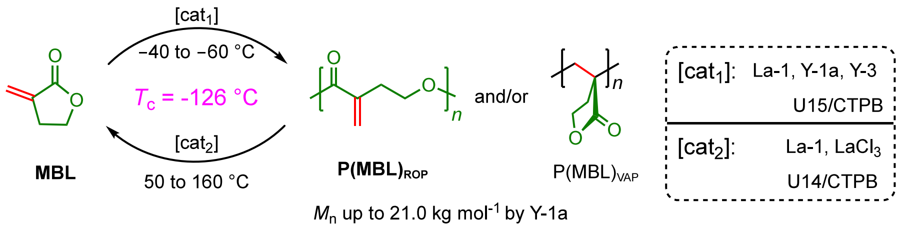
In 2016, Chen and co-workers successfully demonstrated that the ROP of γ-BL, which is catalyzed by Ln complexes (Y-1a, La-1) through a coordination−insertion mechanism, proceeded efficiently to high conversions (up to 90%) at a low temperature of −40 °C under ambient pressure, affording PγBL with M_n up to 30.2 kg mol^{-1} and controlled linear and/or cyclic topologies (Scheme 31).[430] The enthalpy change (ΔH_p^o) of this ROP was determined to be very small, −5.4 kJ mol^{-1}, while the entropic change (ΔS_p^o) was largely negative, −39.6 J mol^{-1} K^{-1}, thus corresponding to an extremely low T_c of −136 °C at $[\gamma\text{-BL}]_0 = 1.0$ M or ca. −9 °C at $[\gamma\text{-BL}]_0 = 10$ M.[430] According to the formula $\Delta G_p = \Delta H_p - T\Delta S_p$, it can be inferred that ΔG_p is positive (no polymerization) under standard conditions, as the negative ΔH_p is insufficient to offset the entropy penalty, $T\Delta S_p$. Therefore, to overcome the mentioned thermodynamics limitations, three key factors are crucial for achieving the successful ROP of γ-BL. First, the thermodynamic conditions must be satisfied by reducing the entropic penalty associated with this ROP, which can be done by conducting the polymerization at a temperature sufficiently low, specifically below the T_c of polymerization for a given monomer concentration [M]. Second, the use of efficient, kinetically fast catalysts is crucial. Such catalysts can achieve high conversion in a reasonable time frame, an essential factor as ROP must be performed at low temperatures due to thermodynamic constraints. Lastly, adjusting the reaction conditions such as the concentration, solvent, and temperature ensures that [M] exceeds the equilibrium concentration $[M]_{eq}$ and the resulting polymer crystallizes or precipitates from the solution during polymerization, which serves to continually disrupt the equilibrium between propagation and depropagation, effectively driving the reaction toward propagation and resulting in high monomer conversions.[20,430]

Various organic catalysts were also investigated for their effectiveness in the ROP of γ-BL. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was found to be ineffective, while TBD was active for this ROP, albeit achieving only a low monomer conversion of <33% and yielding oligomers with M_n < 6.9 kg mol^{-1}.[430] On the other hand, organic phosphazene superbase ^{t}Bu-P$_4$ in combination with an alcohol such as benzyl alcohol (BnOH) was shown to be highly effective in the ROP of γ-BL, affording linear PγBL with high monomer conversions (up to 90%) and M_n up to 26.7 kg mol^{-1}.[432] To enhance reaction control by suppressing side reactions induced by superbase catalysts, a cyclic trimeric phosphazene base (CTPB) possessing relatively lower basicity was employed.[433] The less basic nature of CTPB precluded the deprotonation of γ-BL during polymerization, which is a common occurrence when using stronger bases such as ^{t}Bu-P$_4$. The bulky [CTPB-H$^+$] ions stabilize the chain propagation center and effectively mitigate the occurrence of backbiting reactions. Notably, a nearly quantitative conversion (98%) was achieved within 4 h at −60 °C, leading to the formation of pure linear PγBL with a M_n of 17.6 kg mol^{-1} and a $Đ$ of 1.27.[433]

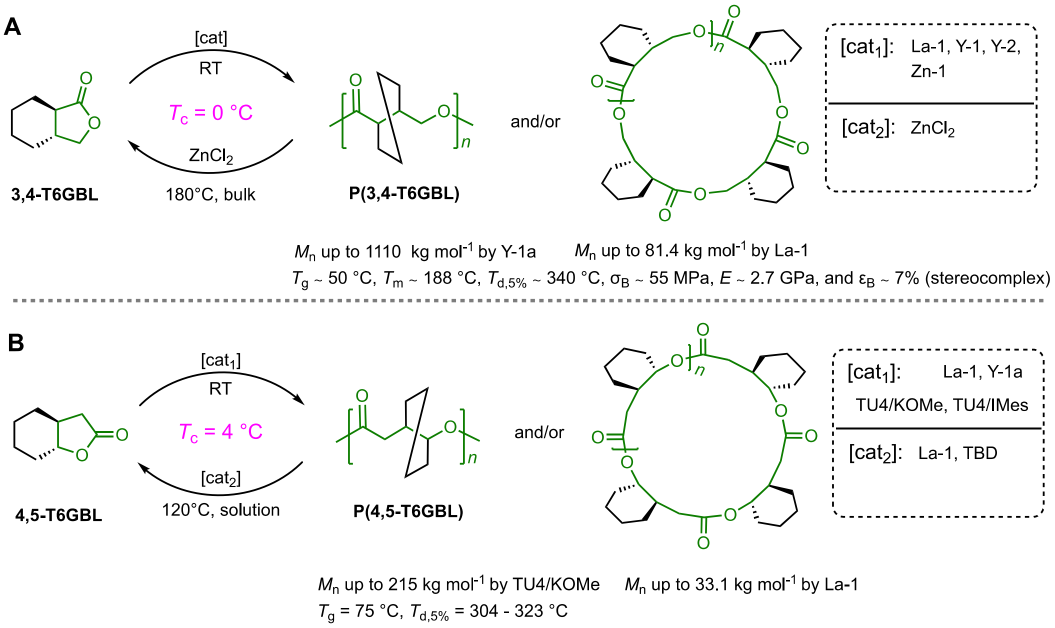
Contrasted with the utilization of a singular catalyst, binary catalysis—achieving bifunctional activation of both the monomer and the initiator/chain end—exhibits augmented activity and selectivity during the ROP of cyclic esters.[417,418] A series of catalyst systems comprising thiourea (TU)/urea (U) and a base was examined for their potential to polymerize γ-BL with the acidity of (thio)urea being adjusted by its substituents (as illustrated in Figure 3). When the polymerization was solely catalyzed by NaOMe, it was observed to yield a low monomer conversion and produce PγBL with a low molar mass. Notably, the ROP facilitated by U2/NaOMe achieved high monomer conversion (up to 86%) at −40 °C, yielding a high molar mass PγBL (M_n up to 68.2 kg mol^{-1}).[434] Even at a relatively higher reaction temperature (−20 °C), the ROP by U2/NaOMe achieved monomer conversion of 70% within 2 h. Similarly, compared to CTPB alone, the ROP catalyzed by the U10/CTPB binary system attained a superior monomer conversion at an augmented feed ratio ([γ-BL]/[I] = 1000/1), affording PγBL with M_n up to 80.4 kg mol^{-1}.[435] The TU3/^{t}Bu-P$_4$ binary catalyst demonstrated superior activity and selectivity with an apparent rate 39 times higher than that of ^{t}Bu-P$_4$ alone, affording PγBL with M_n up to 64.3 kg mol^{-1}.[436] Lewis pair polymerization (LPP) has also been shown to be effective for this ROP. An *N*-heterocyclic olefin (NHO)/LiCl system was used for the ROP of γ-BL for selectively preparing linear or cyclic polymers through different NHO/LiCl catalysts with varied nucleophilicity and steric hindrance.[437] Lastly, a high M_n (83.2 kg mol^{-1}) of linear PγBL was achieved by Chen and co-workers by using a metal-based catalyst (Y-1a) and adjusting the monomer to catalyst ratio ([γ-BL]/[Y-1a] = 500/1) and reaction scale (17.2 g).[438]

The thermal and mechanical performance of the resultant PγBL is determined not solely by its molar mass but also by its topology. For instance, PγBL with M_n = 35.0 kg mol^{-1} (determined by size-exclusion chromatography (SEC) in THF relative to PS standards at 40 °C) showed good mechanical properties, as evidenced by the σ_B of 40.4 ± 1.6 MPa and ε_B of 858 ± 79%. In contrast, PγBL with M_n = 18.3 kg mol^{-1} is a weak and brittle material, with its σ_B and ε_B reaching just 14.2 ± 0.4 MPa and 6.3 ± 0.1%, respectively.[435] A similar trend concerning the effect of molar mass on the mechanical properties was concurrently exemplified in the work of Zhang and co-workers, where the M_n and $Đ$ were determined by SEC in DMF relative to poly(methyl methacrylate) (PMMA) standards at 60 °C.[436] In terms of the thermal stability, the linear PγBL displayed a relatively low $T_{d,5\%}$ of 202 °C, whereas the cyclic PγBL exhibited a significantly higher $T_{d,5\%}$ of 326 °C,[430] which is consistent with the hypothesis that cyclic polymers without chain ends generally exhibit superior thermal stability as compared to their linear counterparts. In relation to this observation, although both linear and cyclic PγBL demonstrated full recyclability, their recycling strategies varied due to the notably different thermal stability properties of linear and cyclic PγBL. More specifically, PγBL was selectively and quantitatively depolymerized back to the initial monomer γ-BL through thermolysis by simply heating bulk materials at 260 (for the linear PγBL) or 300 °C (for the cyclic PγBL) for 1 h. Additionally, depolymerization of PγBL occurred rapidly at RT via chemolysis with either an organic catalyst (2 mol % of TBD; k_{obs} = 0.10 min^{-1}) or a metal catalyst (2 mol % of La-1, k_{obs} = 0.84 min^{-1}). Despite the complete recyclability of PγBL, the low polymerizability of γ-BL, which necessitates demanding polymerization conditions, coupled with its inadequate thermal properties—marked by a low T_g from −52 to −42 °C, a low T_m from 52 to 63 °C, and a low $T_{d,5\%}$ of ∼200 °C (for the linear PγBL)—limits its broad applications.[430]

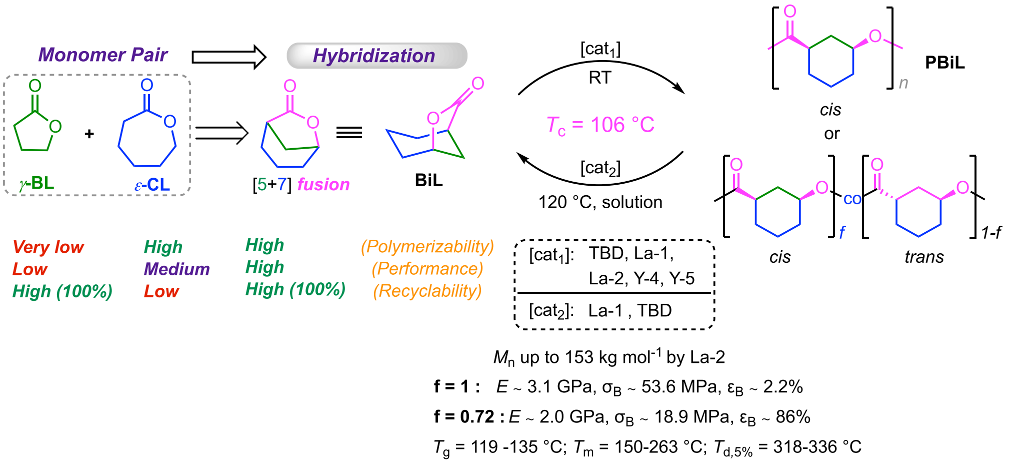
Scheme 32. Chemoselective ROP of MBL into Chemically Recyclable P(MBL)$_{ROP}$



Scheme 33. ROP of *trans*-Cyclohexyl Ring-Fused *γ*-BL (A) 3,4-T6GBL and (B) 4,5-T6GBL into High Molar Mass Linear and Cyclic Polymers with Full Chemical Circularity



***γ*-Butyrolactone Derivatives.** Given the above-described limitations within the P*γ*BL synthesis and properties, there is significant interest in the pursuit of high-performance iCPs by monomer redesign.[400] In this context, *α*-methylene-*γ*-butyrolactone (MBL) is a naturally occurring compound found in tulips and the simplest member of the sesquiterpene lactone family.[439,440] However, the concurrent existence of a highly reactive exocyclic C═C bond and a remarkably stable five-membered *γ*-BL has posed a long-standing challenge in favoring chemoselective ROP over vinyl-addition polymerization (VAP). Regardless of the polymerization method employed—be it radical, anionic, or coordination polymerization—these two competing processes typically favor VAP. Chen and co-workers successfully tackled this challenge by exploring the chemoselective polymerization of MBL through adjustment of the catalyst system, the reaction temperature, and the catalyst to initiator ratio. Their research elucidated that although the VAP pathway is thermodynamically favored, the ROP pathway holds a kinetic advantage, allowing for preferential selection of the latter pathway through judicious control of the reaction conditions. Specifically, despite the inherent thermodynamic challenges associated with the ROP pathway, as evidenced by $\Delta H_p^\circ = -5.9$ kJ mol^{-1} and $\Delta S_p^\circ = -40.1$ J mol^{-1} K^{-1}, corresponding to a low $T_c = -126$ °C, at standard conditions obtained in dichloromethane (DCM),[441] the chemoselective ROP of MBL was successfully achieved by utilizing a low polymerization temperature at −60 °C and a high initial monomer concentration of 5 M, with the catalysis of La-1, Y-1a, or Y-3, ultimately yielding linear P(MBL)$_{ROP}$ with $M_n = 21.0$ kg mol^{-1} and $Đ = 1.42$ (Scheme 32).[441] Notably, the resulting P(MBL)$_{ROP}$ with the reactive side-chain C═C bond in each repeating unit can be readily postfunctionalized into cross-linked or thiolated materials.[441] First, photocuring through UV irradiation (350 nm), initiated by photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA), resulted in a cross-linked, transparent film, P(MBL)$_{ROP}$-*hν*. Second, the polymer was also efficiently postfunctionalized through the thiol−ene click reaction, leading to a fully thiolated polyester, P(MBL)$_{ROP}$-SR. Importantly, P(MBL)$_{ROP}$ exhibited full chemical recyclability, as demonstrated by its capability to be depolymerized back to its original monomer, MBL, in quantitative yield. The depolymerization was accomplished by heating a "wet" dimethyl sulfoxide (DMSO) solution (0.2 M containing 3.5 mM water) at 100−130 °C for 1 h or 60 °C for 24 h (with 1 mol % of La-1).[441] Moreover, Li and co-workers demonstrated that a binary catalyst system, which combines CTPB and U15, operated effectively in facilitating the organocatalyzed chemoselective ROP of MBL, resulting in the production of a metal-free, chemically recyclable P(MBL)$_{ROP}$ with $M_n = 6.7$ kg mol^{-1} and $Đ = 1.34$.[442] Similar to the P(MBL)$_{ROP}$ generated using La-1, Y-1a, or Y-3 metal-based catalysts, the P(MBL)$_{ROP}$ obtained through organocatalytic ROP also demonstrated full recyclability, reverting back to its original monomer, MBL, Scheme 34. Hybridization of the LCT γ-BL with the HCT ε-CL To Create a Hybrid Monomer Structure, BiL, which Possesses the Structural Motifs of Both the LCT and the HCT Lactones and Leads to the Corresponding Circular Polyester with Synergistically Enhanced Performance and Recyclability

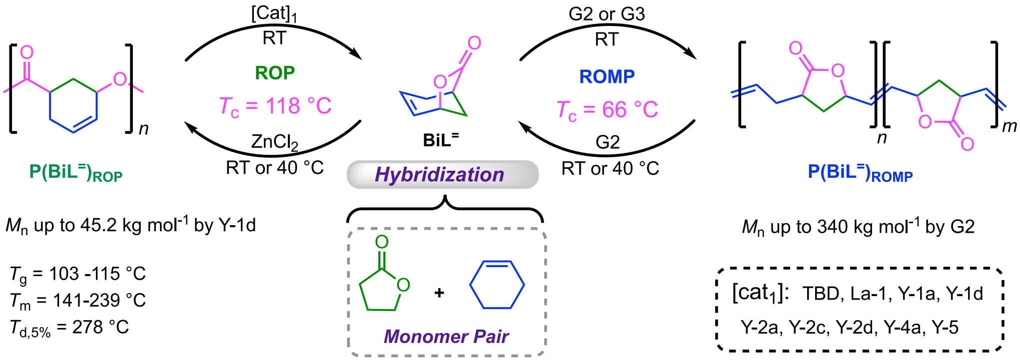


when heated to 50 °C (0.5 M $P(MBL)_{ROP}$ in THF, 48 h, 1 mol % of CTPB/U14 (1:3)). Notably, the use of U14, which features more electron-withdrawing substituents, inhibited the VAP process of the regenerated MBL during the depolymerization.

Despite this notable achievement in the chemoselective ROP of MBL, the process still necessitates relatively low polymerization temperatures, typically ranging from −50 to −78 °C. Furthermore, the resulting $P(MBL)_{ROP}$ polymers exhibit relatively low T_g values, typically in the range from −46 to −35 °C, and low T_m values of 39−44 °C. To overcome these challenges, Chen and co-workers devised a strategy involving the introduction of a fused *trans*-cyclohexyl ring at the α and β positions of γ-BL, affording a redesigned monomer termed 3,4-T6GBL. This modification significantly increases the ring strain of the γ-BL core of the monomer, thereby altering the thermodynamic parameters of its polymerization, as evidenced by $\Delta H_p^\circ = -20$ kJ mol^{-1} and $\Delta S_p^\circ = -72$ J mol^{-1} K^{-1}, corresponding to a substantially higher T_c of 0 °C at 1.0 M in toluene versus −136 °C for ROP of γ-BL.[430,443] As a result, the monomer's polymerizability is greatly enhanced at ambient temperature, resulting in the production of high molar mass polymers with much enhanced thermal stability and crystallinity, while retaining full chemical recyclability.[443] Specifically, utilizing La-1, Y-1a, and Zn-1 as catalysts, the ROP of 3,4-T6GBL was effectively carried out at RT to produce both linear P(3,4-T6GBL) with ultrahigh molar mass (M_n = 1110 kg mol^{-1}, $Đ$ = 1.09) and cyclic P(3,4-T6GBL) (M_n = 81.4 kg mol^{-1}, $Đ$ = 1.41), respectively (Scheme 33A). The presence of the PγBL backbone endowed P(3,4-T6GBL) with complete chemical recyclability, as demonstrated through consecutive polymer−monomer−polymer cycles catalyzed by 2 mol % of $ZnCl_2$ at 180 °C under vacuum (0.01 Torr) in 3−5 h. Furthermore, the fusion of an additional *trans*-cyclohexyl ring not only increased the polymerizability but also improved the material's performance. In particular, the linear P(3,4-T6GBL) exhibited a significantly higher $T_{d,5\%}$ of 316 °C and T_{max} = 394 °C, as compared to that of linear PγBL ($T_{d,5\%}$ = 201 °C and T_{max} = 218 °C). Notably, the crystalline stereocomplexed polymer derived from a physical blend of enantiomers, *sc*-P(3,4-T6GBL), exhibited further enhanced thermal ($T_g \approx 50$ °C, $T_m \approx 188$ °C, $T_{d,5\%} \approx 340$ °C), mechanical ($\sigma_B \approx 55$ MPa, $E \approx 2.7$ GPa, and $\varepsilon_B \approx 7\%$), and rheological (0.21 s relaxation time at 215 °C) properties.[443] Subsequently, a series of chiral yttrium complexes with *N,O*-tetradentate ligands was developed for the synthesis of *sc*-P(3,4-T6GBL) in situ, which not only circumvented the use of expensive enantiopure monomers but also actualized the closed-loop circularity between the stereocomplexed P(3,4-T6GBL) and racemic 3,4-T6GBL.[444] Furthermore, toward the aim of producing high-performance chemically recyclable packaging materials, PγBL-*co*-P(3,4-T6GBL) was synthesized via the copolymerization of 3,4-T6GBL and γ-BL catalyzed by Y-1a at 25 °C. This copolymer displayed full chemical recyclability with the catalysis of 2 mol % of $ZnCl_2$ in toluene (23 mg/0.6 mL) at 120 °C and superior mechanical and transport properties compared to those of most promising biobased plastics.[445]

Similar to 3,4-T6GBL, another constitutional isomer, 4,5-*trans*-cyclohexyl ring-fused γ-BL (4,5-T6GBL), also serves as a γ-BL derivative monomer with balanced thermodynamic parameters: $\Delta H_p^\circ = -18$ kJ mol^{-1} and $\Delta S_p^\circ = -65$ J mol^{-1} K^{-1}, corresponding to a moderate T_c = 4 °C, at standard conditions (Scheme 33B).[446] Although the fusion of a *trans*-cyclohexyl ring at the β and γ positions of the γ-BL ring increases the steric hindrance of the active center (ester bond), resulting in lower reactivity compared to 3,4-T6GBL, 4,5-T6GBL still exhibited good polymerization activity at RT with La-1 or Y-1a, affording P(4,5-T6GBL) with M_n up to 89 kg mol^{-1} and a T_g of 72−75 °C, as well as high thermal stability ($T_{d,5\%}$ = 304−323 °C). Heating P(4,5-T6GBL) at 230 °C resulted in full depolymerization of the resulting P(4,5-T6GBL), leading to 89% monomer recovery and 11% cis isomer, an undesired side product. The undesired isomerization can be prevented by solution depolymerization in toluene at 120 °C with quantitative monomer recovery yield when catalyzed by La-1. (Thio)urea/base pairs were also applied to the synthesis of P(4,5-T6GBL) with a high M_n up to 215 kg mol^{-1}.[447] The quantitative and selective organocatalyzed depolymerization of P(4,5-T6GBL) was achieved at 120 °C with catalyst La-1 in toluene (56 mg/mL) or TBD under dilute conditions in toluene (10.9 mg/mL), establishing "monomer−polymer−monomer" closed-loop circularity.[446,447]

Scheme 35. LCT/LCT Hybrid of the Lactone and Cyclic Olefin Pair for Constructing Circular Polyester or Poly(cyclic olefin) with Synergistically Enhanced (De)polymerization and Performance Properties

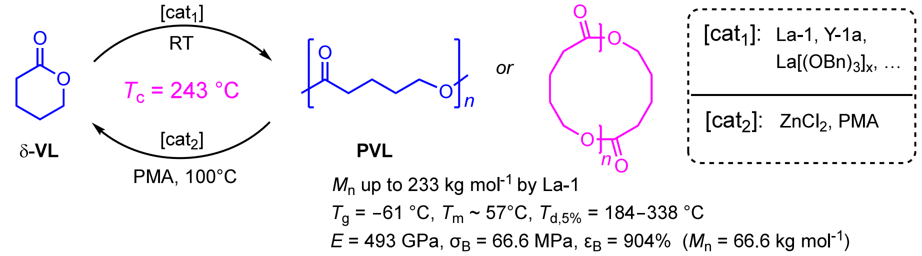


Chen and co-workers introduced a hybrid monomer design strategy that reconciles typically conflicting properties of polymerizability, recyclability, and material performance (Scheme 34).[448] This strategy synergistically couples a high ceiling temperature (HCT) substructure, known for boosting polymerizability and performance properties, with a low ceiling temperature (LCT) substructure, prized for enhancing depolymerizability and recyclability, within a single monomer structure. The structural hybridization between HCT ε-caprolactone (ε-CL) and LCT γ-BL afforded a [3.2.1]bicyclic lactone (BiL), which exhibited both high polymerizability and depolymerizability, as evidenced by balanced thermodynamic parameters (ΔH_p° = −21.1 kJ mol^{-1}, ΔS_p° = −55.8 J mol^{-1} K^{-1}, T_c = 106 °C) at standard conditions in toluene.[448] Intriguingly, when compared to its structural analogue 3,4-T6GBL, the ring strain of both BiL and 3,4-T6GBL contributed equally to their respective thermodynamic polymerizability as indicated by the similar ΔH_p° of −21.1 versus −20 kJ mol^{-1}, respectively. However, their T_c diverge significantly, with 106 °C for BiL and 0 °C for 3,4-T6GBL at 1.0 M, which can be attributed to a significant difference in the entropic factor, ΔS_p° of −55.8 vs −72 J mol^{-1} for the ROP of BiL and 3,4-T6GBL, respectively.[443,448] The decreased entropic penalty for the polymerization of BiL is a consequence of the confined atom-bridged monomer structure which acquires more conformational (rotational and vibrational) freedom (ΔS_c) following ring opening. This gain in conformational entropy partially offsets the loss of translational freedom (ΔS_t), resulting in a substantial decrease in the total entropic penalty (less negative ΔS_p° term) compared to that of the structural analogue 3,4-T6GBL. This example highlights the importance of entropy considerations in monomer design for circular polymers.

In addition, the bridged bicyclic framework of the hybrid monomer confines the monomer structure to the cis configuration, further enhancing the chemical recyclability and depolymerization selectivity. The thermal and mechanical properties of the resulting PBiL can be effectively tailored using salen-based yttrium (Y-4, Y-5) or lanthanum (La-1, La-2) catalysts, facilitating the synthesis of PBiL with various degrees of isotacticity (P_m up to 87%) and a high M_n of up to 153 kg mol^{-1}. Remarkably, PBiL exhibited high T_g and T_m up to 135 and 263 °C, respectively, each being about 200 °C higher than those of its parent homopolymers, PγBL and poly(ε-caprolactone) (PCL), or their copolymers. The all-*cis*-PBiL material can be best characterized as a hard, strong, and brittle glass, as evident by its high E of 3.1 GPa, which is approximately 10 times greater than that of its parent homopolymers. On the other hand, PBiL with 18% trans repeat units, obtained by the ROP with TBD, behaves like a traditional plastic material, as characterized by a slightly lower E of 2.0 GPa and an elevated ductility with ε_B up to 86%. The PBiL exhibits superior thermal stability with a $T_{d,5\%}$ of 318−336 °C, notably at least 116 °C higher than that of PγBL,[430] yet still preserving high chemical recyclability with near-quantitative monomer recovery (>95%) under the catalysis of La-1 or TBD at 120 °C in toluene. These findings underscored the effectiveness of the HCT/LCT hybrid monomer strategy in designing circular polymers with radically altered or substantially enhanced properties.

Building upon the success of the HCT/LCT hybrid monomer design, an LCT/LCT hybrid monomer design was proposed to accomplish the orthogonal (de)polymerization of a bifunctional monomer, bringing about "one monomer−two polymers−one monomer" closed-loop circularity (Scheme 35).[449] Specifically, γ-BL is an LCT monomer for ROP, while cyclohexene is considered a "nonpolymerizable" LCT monomer for ring-opening metathesis polymerization (ROMP). By combining these two different monomer classes, an LCT/LCT hybrid, bifunctional monomer, 6-oxabicyclo[3.2.1]oct-3-en-7-one (BiL$^=$), was synthesized. This bifunctional lactone/olefin hybrid is capable of undergoing orthogonal polymerization between ROP and ROMP, depending on the catalyst employed, thereby giving rise to two distinct classes of polymeric materials from this single monomer, BiL$^=$: polyester P(BiL$^=$)$_{ROP}$ via ROP and lactone-functionalized poly(cyclic olefin) P(BiL$^=$)$_{ROMP}$ via ROMP. Within the ROP manifold, characterized by thermodynamic parameters of ΔH_p° = −34.7 kJ mol^{-1}, ΔS_p° = −88.7 J mol^{-1} K^{-1}, and hence T_c = 118 °C at standard conditions, both organic and Y-based catalysts can efficiently mediate the polymerization via the ester bond while leaving the C═C bond intact. Notably, besides the topological control between cyclic and linear architectures, the microstructure of the resulting P(BiL$^=$)$_{ROP}$ can also be tuned from being atactic to highly syndiotactic or isotactic, corresponding to amorphous or semicrystalline polyesters with a T_m up to 239 °C. Notably, the inherent functional groups in the polymers P(BiL$^=$)$_{ROP}$ and P(BiL$^=$)$_{ROMP}$, specifically the C═C bond and the lactone ring, respectively, allow for their respective postfunctionalization.[449] Utilizing the thiol−ene click reaction, 1-octadecanethiol was successfully grafted onto both the linear and the cyclic P(BiL$^=$)$_{ROP}$, yielding the corresponding brush polyesters. This modification enabled the direct observation of their topologies via high-resolution transmission electron micros-

Scheme 36. Closing the Chemical Loop of the High Molar Mass, Strong, Ductile, and Tough PVL by Employing Highly Efficient Depolymerization Catalyst



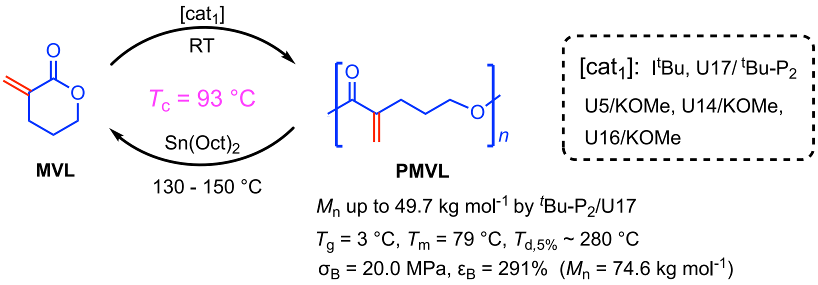
copy. On the other hand, the γ-BL ring in the $\mathrm{P(BiL^{=})_{ROMP}}$ was selectively hydrolyzed by NaOH, converting the polymer into a carboxylate ionomer. The resulting polyester $\mathrm{P(BiL^{=})_{ROP}}$ can be fully converted back into its constituent monomer $\mathrm{BiL^{=}}$ by employing a catalytic amount of $ZnCl_2$ at RT in DCM (20 mg mL^{-1}). An investigation into the effects of $ZnCl_2$ loading and particle size confirmed that the depolymerization of $\mathrm{P(BiL^{=})_{ROP}}$, catalyzed by $ZnCl_2$, operates as a surface-catalytic process. Additionally, the low activation energy barrier for depolymerization is likely associated with interactions between $ZnCl_2$ and the alkene/carbonyl groups present in $\mathrm{P(BiL^{=})_{ROP}}$, which alters the conformation of the polyester, thus reducing the energy barrier for ring-closing depolymerization.

3.1.1.2. Six-Membered Lactones. **Parent Six-Membered Lactone.** The simplest six-membered lactone is δ-valerolactone. (δ-VL), which is biomass derived and produced through the dehydrogenation of 1,5-pentanediol obtained from the hydrogenolysis of furfuryl alcohol.[450,451] Relative to γ-BL, δ-VL exhibits much higher polymerizability, thanks to the presence of an additional CH_2 group that increases the ring strain. δ-VL has been successfully polymerized by various catalyst systems through cationic,[452−454] anionic,[418,455] zwitterionic,[456,457] and coordination[458,459] mechanisms to the corresponding poly(δ-valerolactone) (PVL). The enhanced polymerizability of δ-VL is evidenced by its notably increased T_c of 298 °C at 1.0 M, as measured in a CH_2Cl_2/toluene (70:30 v/v) mixture, and its associated thermodynamic parameters: $\Delta H_p^\circ = -8.4$ kJ mol^{-1} and $\Delta S_p^\circ = -14.7$ J mol^{-1} K^{-1}.[460] Despite its chemical simplicity, abundant availability, and hydrolytic or biodegradable properties, PVL did not receive much attention as a sustainable plastic because of often-reported inadequate mechanical performance (due to the low molar mass of the PVL materials tested) and poor chemical recyclability impeded by its high T_c.

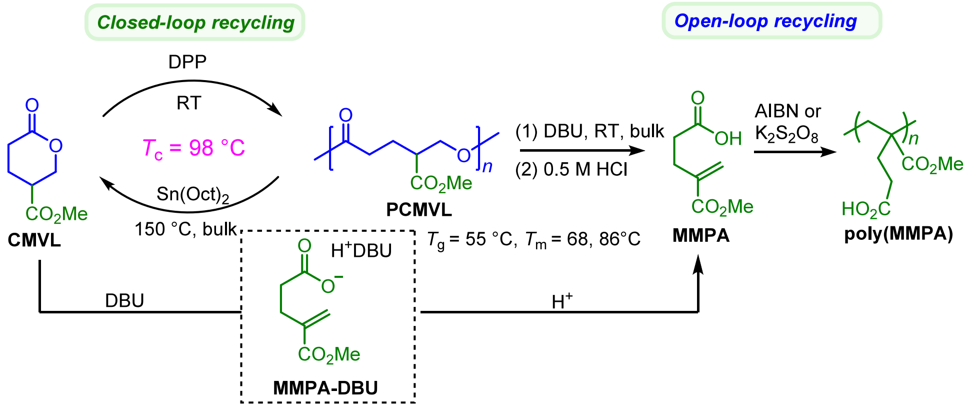
Recently, Chen, Xu, and co-workers took the solvent effect into consideration and re-evaluated the thermodynamic parameters of δ-VL polymerization in toluene, revealing that in this solvent δ-VL has a lower than previously reported T_c of 243 °C at 1.0 M along with thermodynamic values of ΔH_p° = −15.9 kJ mol^{-1} and ΔS_p° = −30.8 J mol^{-1} K^{-1}.[461] Despite this, the still relatively high T_c of δ-VL poses a challenge when it comes to the thermal depolymerization of PVL. Specifically, after 8 h at a temperature of 250 °C, the depolymerization of PVL resulted in only partial conversion to δ-VL (<50%) with about 11% of PVL remaining unreacted and nearly 40% being transformed into an insoluble cross-linked residue.[462] To address the issues, strategies were implemented involving the introduction of alkyl groups to the δ-VL ring at varied positions, yielding monoalkyl-substituted δ-VL monomers (vide infra). Despite the improved depolymerizability of the corresponding polyesters produced from those monosubstituted δ-VL monomers, the poor recyclability of PVL still needs to be solved.

To address the challenge in chemical recycling of the high molar mass PVL, a variety of catalysts were explored with the intention of enhancing the recycling efficiency and lowering the depolymerization temperature. It was discovered that, despite the thermodynamics of PVL rendering depolymerization unfavorable, the dynamic equilibrium of the "δ-VL−PVL" system can be tilted by continuously removing the produced monomer under vacuum conditions, thereby circumventing thermodynamic limitations.[461] In addition, effective catalysts significantly lower the energy barrier for depolymerization, enabling efficient depolymerization within an operable time frame and effectively circumventing potential side reactions during the process (Scheme 36).[461] Specifically, the depolymerization of PVL (M_n = 12.5 kg mol^{-1}) using 2.0 mol % of $ZnCl_2$ at 150 °C under reduced pressure (0.07 Torr) led to the recovery of δ-VL in near-quantitative purity and with an isolated yield of 99%. However, for high molar mass PVL (M_n = 70.9 kg mol^{-1}), the required depolymerization temperature was increased to 221 °C and the yield decreased to 92%. Raising the depolymerization temperature also enhanced the volatility of 5-hydroxypentanoic acid, which subsequently led to the repolymerization of the recovered δ-VL. It was further found that while common organic catalysts like diphenyl phosphate (DPP) and camphorsulfonic acid (CSA) were efficient in catalyzing the depolymerization of PVL, they tended to sublimate during the process, leading to contamination of the recycled δ-VL. To further minimize energy consumption and prevent organic acid sublimation during the recycling process, phosphomolybdic acid (PMA), a commercial solid inorganic polyacid, was employed. Remarkably, the depolymerization of 10.0 g of PVL (M_n = 70.9 kg mol^{-1}) was successfully achieved at a relatively low temperature of 100 °C in just 3.5 h, resulting in the recovery of 9.84 g of pure δ-VL monomer (98% yield). Notably, PMA exhibited excellent reusability, maintaining a recovery yield of 96.3% even after five successive cycles of reuse.[461] In this work, the significant impact of molar mass on the mechanical properties of PVL was also emphasized. The critical entanglement molecular weight (M_c) was determined to be approximately 26 kg mol^{-1} using oscillatory shear rheology. This clarified the brittle nature of previously studied PVL samples with low absolute molar mass values of M_n = 12.8−16.0 kg mol^{-1}, which had strain at break values of around 3−6%.[462] When reaching the appropriate molar mass range of M_n > 65 kg mol^{-1}, PVL exhibited excellent mechanical performance, including a high σ_B of around 66.6 MPa, a ε_B of approximately 904%, and toughness of about 308 MJ m^{-3}, outperforming that of most

Scheme 37. Chemoselective ROP of MVL into Chemically Recyclable, Vinyl-Functionalized Polyester $P(MVL)_{ROP}$



Scheme 38. ROP of CMVL and Divergent Chemical Recycling of PCMVL to CMVL (Closed-Loop Recycling) or Enoate MMPA and Its Polymerization to Poly(MMPA) (Open-Loop Recycling)

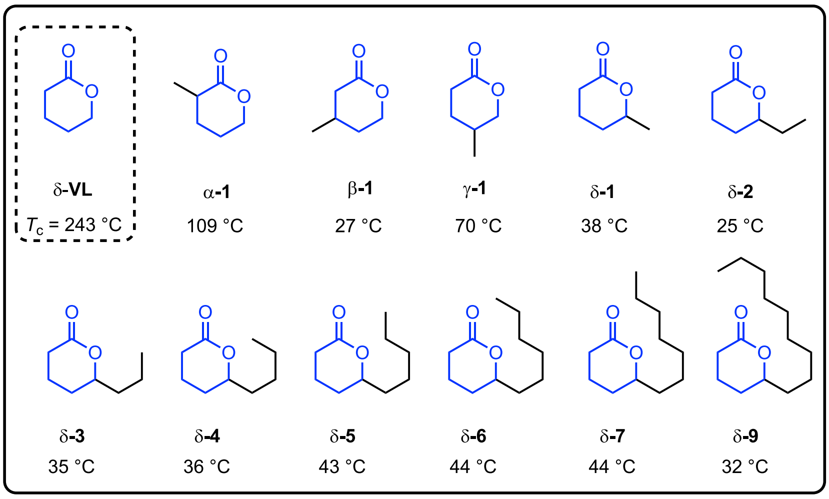


commodity polyolefins. Moreover, as the molar mass of PVL increases, the $T_{d,5\%}$ values of resulting PVL steadily rise from 184 to 338 °C, underscoring the critical role of high molar mass in optimizing material performance.

δ-Valerolactone Derivatives. *α*-Methylene-*δ*-valerolactone (MVL) is a bifunctional monomer, composed of a six-membered *δ*-VL ring and a highly reactive exocyclic C═C bond, offering potential in the synthesis of functionalized polyesters. As a structural analogue of MBL, MVL also displays divergent polymerization pathways: the exocyclic C═C bond can undergo VAP to yield polyacrylic, whereas the ROP of the six-membered lactone results in a vinyl-functionalized polyester. Notably, the thermally initiated free radical polymerization of MVL highlights the potential for mild depolymerization conditions, as evidenced by a relatively low T_c of 83 °C at 1.0 M, based on measured thermodynamic parameters of $\Delta H_p^o = -38.8$ kJ mol^{-1} and $\Delta S_p^o = -108.8$ J mol^{-1} K^{-1} in DMF.[463] On the other hand, the chemoselective ROP of MVL has been successfully achieved using *N*-heterocyclic carbene catalysts by Xu and co-workers[464] and strong base/urea binary catalysts by Li and co-workers[465] (Scheme 37). In comparison to the ROP of MBL, the substitution of the more stable *γ*-BL with the more strained *δ*-VL leads to a boost in polymerizability for the ROP of MVL, as supported by more favorable thermodynamic parameters ($\Delta H_p^o = -16.5$ kJ mol^{-1}, $\Delta S_p^o = -46.1$ J mol^{-1} K^{-1}, $T_c = 93$ °C at 1.0 M in THF).[465] Importantly, contrary to the amorphous nature of $P(MBL)_{ROP}$, $P(MVL)_{ROP}$ is a semicrystalline polymer with a T_m of 79 °C and a degree of crystallinity of 52%, an ∼24 °C increase from that of PVL ($T_m \approx 55$ °C). Similarly, the pendant exocyclic C═C bond present in the synthesized polymer $P(MVL)_{ROP}$ lends itself to straightforward postfunctionalization via the thiol−ene click reaction.[465] In a representative example, benzyl mercaptan was used as the thiol component to react with $P(MVL)_{ROP}$ in the presence of DMPA as a photocatalyst. This enhanced crystallization characteristic of $P(MVL)_{ROP}$ can be attributed to both the presence of the additional CH_2 linkage in the repeating unit and the existence of an exocyclic C═C bond. $P(MVL)_{ROP}$ with $M_n = 74.6$ kg mol^{-1} exhibited excellent mechanical properties, including a σ_B of 20.0 MPa and a ε_B of 291%, making it comparable to several commodity plastics.[465] Notably, $Sn(Oct)_2$ was identified to be an efficient catalyst for the bulk depolymerization of $P(MVL)_{ROP}$ under reduced pressure at temperatures between 130 and 150 °C, affording pure MVL with recovery yields up to 96% in 2−6 h.[464,465]

In 2018, Hoye and co-workers reported the synthesis of *γ*-monosubstituted PVL from a renewable monomer, 4-carbomethoxyvalerolactone (CMVL) sourced from malic acid (Scheme 38).[466] The ROP of CMVL catalyzed by DPP proceeded effectively in bulk at RT, resulting in a monomer conversion exceeding 98% and achieving M_n values of up to 71 kg mol^{-1}. The resultant PCMVL exhibited a semicrystalline nature, featuring a T_g of −18 °C and two T_m values at 68 and 86 °C. Notably, the semicrystalline PCMVL showed a tacticity-independent character, as this polymer was expected to be atactic due to the use of racemic CMVL and the nearly nonstereoselective catalyst DPP.[467] The thermodynamic parameters of CMVL polymerization in chloroform were determined to be $\Delta H_p^o = -15.2$ kJ mol^{-1} and $\Delta S_p^o = -41$ J mol^{-1}, corresponding to a moderate T_c of 98 °C at 1.0 M. However, when DBU was used as a catalyst to polymerize CMVL at low mol % levels, it showed no polymerization activity due to an undesired retro-oxa-Michael addition (i.e., elimination) side reaction, leading to the production of 5-methoxy-4-methylene-5-oxopentanoic acid (MMPA)-DBU. Acidification of this intermediate resulted in the formation of

Scheme 39. Structure of Monosubstituted δ-VL for Enhanced Chemical Recycling of Valerolactone-Based Aliphatic Polyesters[a]



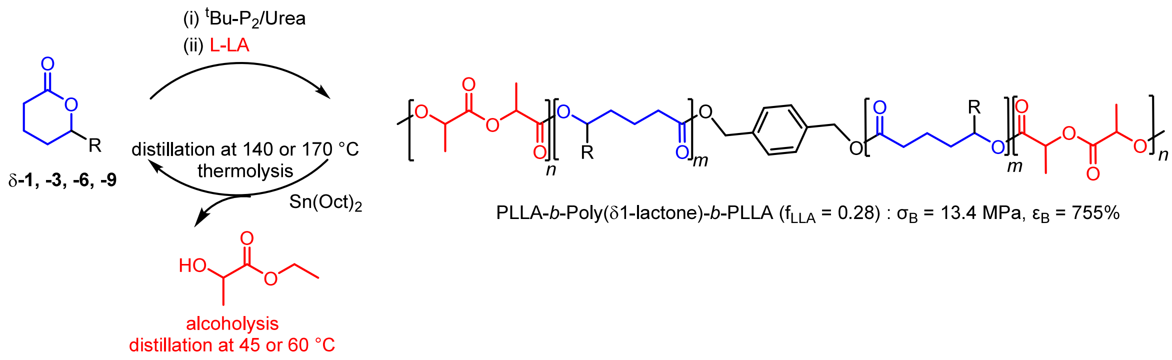
[a] T_c values reported at $[M]_0$ = 1.0 M.

MMPA with a 95% yield, requiring no further purification beyond liquid−liquid partitioning. Accordingly, it was reported that PCMVL could be chemically recycled through an elimination process in the presence of DBU by cleaving the polyester in a retro-oxa-Michael fashion, yielding an 88% conversion to a methacrylate derivative, MMPA, thus creating "open-loop" circularity for PCMVL. Additionally, "closed-loop" recycling of PCMVL was also established by using $Sn(Oct)_2$ at 150 °C under reduced pressure (~0.05 Torr), which facilitated a backbiting depolymerization process from the hydroxy terminus, resulting in the formation of CMVL with a yield of 87%.

In 2016, Hillmyer and co-workers conducted a comprehensive investigation into the effects of *n*-alkyl substituents on the thermodynamics and kinetics of polymerization of monosubstituted δ-VL monomers (Scheme 39), establishing guiding design principles based on critical structure−property relationships for the resulting aliphatic polyesters.[19] First, the polymerization rate under bulk, RT conditions was found to be highly dependent on the substituent position, while the influence of the alkyl length (ranging from $-CH_3$ to $-(CH_2)_8CH_3$) exhibited a more modest effect. Second, the enthalpy and entropy of polymerization were significantly affected by the substituent position but showed limited sensitivity again to *n*-alkyl length. Third, the physical properties of the resulting aliphatic polyesters were found to be more influenced by the substituent length rather than the substituent position. Fourth, the polymer entanglement molar mass and solubility parameter could be systematically adjusted by varying the substituent length. Among the methyl-substituted lactones, β-1 and α-1 showed similar polymerization rates to the unsubstituted parent δ-VL under identical conditions, while δ-1 exhibited the slowest polymerization rate, with an observed rate constant approximately 1 order of magnitude smaller than that of δ-VL. The entanglement molar mass of representative poly(*n*-alkyl-δ-valerolactones) was estimated from the plateau modulus of high molar mass (~100 kg mol^{-1}) polymers. While poly(α1-lactone) showed a significantly higher entanglement molar mass (M_e) of 7.7 kg mol^{-1} compared to PCL (3.0 kg mol^{-1}), the other poly(methyl valerolactones) exhibited relatively lower values, 4.3, 2.2, and 3.4 kg mol^{-1} for poly(β1-lactone), poly(γ1-lactone), and poly(δ1-lactone), respectively.[19] When the substituent position was fixed, the entanglement molar mass of the polymer increased with the substituent length. For instance, poly(δ5-lactone) had an entanglement molar mass of 13.5 kg mol^{-1}, which was approximately four times larger than that of poly(δ1-lactone).

δ-Caprolactone (δ-1) is a naturally occurring δ-methyl-substituted six-membered lactone found in fruits, and it can also be derived from biobased 5-hydroxymethylfurfural.[468,469] It exhibited lower polymerizability compared to its unsubstituted δ-VL, mainly due to its less nucleophilic secondary alkoxide propagating chain end.[470,471] Leveraging the findings of Waymouth and co-workers that (thio)urea anions can activate cyclic lactones and propagating alkoxide species simultaneously,[417,418] Li and co-workers successfully implemented a rapid and controlled ROP of δ-1 using alkoxide base/urea binary catalysts (U18/^{t}Bu-P_2), leading to poly(δ1-lactone) with M_n up to 100 kg mol^{-1}.[472] The resultant poly(δ1-lactone) is an amorphous material with a T_g of −39 °C and a high $T_{d,5\%}$ of 330 °C. The thermodynamic parameters ΔH_p° and ΔS_p° for the δ-1 polymerization were determined to be −12.8 kJ mol^{-1} and −40.6 J mol^{-1} K^{-1} in THF, respectively, which are consistent with those obtained by Hillmyer and co-workers and correspond to a low T_c of 42 °C at $[M]_0$ = 1.0 mol L^{-1}, suggesting facile recyclability of the resultant poly(δ1-lactone).[19] As anticipated, the synthesized Pδ1 demonstrated excellent chemical recyclability, being able to revert to its original monomer in nearly quantitative yield (~99%) when simply heated in the presence of 0.5 wt % of $Sn(Oct)_2$ (130 °C, distillation under reduced pressure, 2 h). Furthermore, considering the soft nature of poly(δ1-lactone), well-defined triblock copolymers (tri-BCPs) composed of PLLA-*b*-poly(δ1-lactone)-*b*-PLLA can be synthesized through a sequential ROP of δ-1 and L-LA, exhibiting thermoplastic elastomer behavior with a tensile strength of 13.4 MPa and ε_B of 755%. More importantly, the chemical recycling of PLLA-*b*-poly(δ1-lactone)-*b*-PLLA tri-BCPs was achieved through a process of ethanolysis, followed by sequential distillation under

Scheme 40. Chemically Recyclable Triblock Copolyesters Based on a Sequential Depolymerization Process



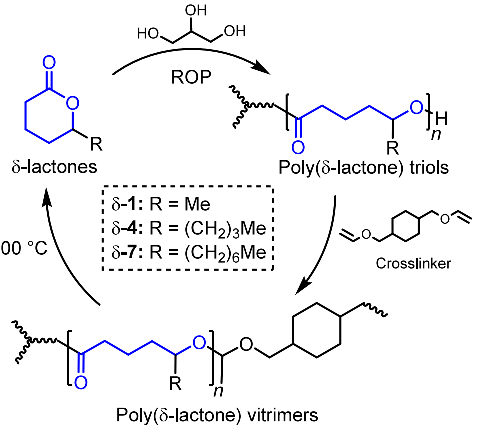
reduced pressure at 45 and 140 °C, respectively, resulting in the recovery of pure ethyl lactate and δ-1 with respective yields of 92% and 95% (Scheme 40).

Following this study, the same research group successfully achieved the synthesis of a telechelic poly(δ1-lactone) diol with ^{t}Bu-P$_2$/U3 binary catalyst,[473] which was subsequently utilized in the preparation of thermoplastic polyurethane elastomers (TPUs) via a one-pot process involving the cascade ROP of δ-1 and SGP of poly(δ1-lactone) diol precursors with diisocyanate under solvent-free conditions. The resulting PUs exhibited thermoplastic elastomeric behavior with excellent elastic recovery, tensile strength, and elongation and low residual strain. Furthermore, the TPUs were successfully chemically recycled by employing cascade urethane dissociation followed by depolymerization of the poly(δ1-lactone) diols using 2 wt % of Sn(Oct)$_2$ as a catalyst. Clean δ-1 monomer was recovered in an almost quantitative yield (~99%) through distillation at 180 °C under reduced pressure (~200 Pa) within 2 h.

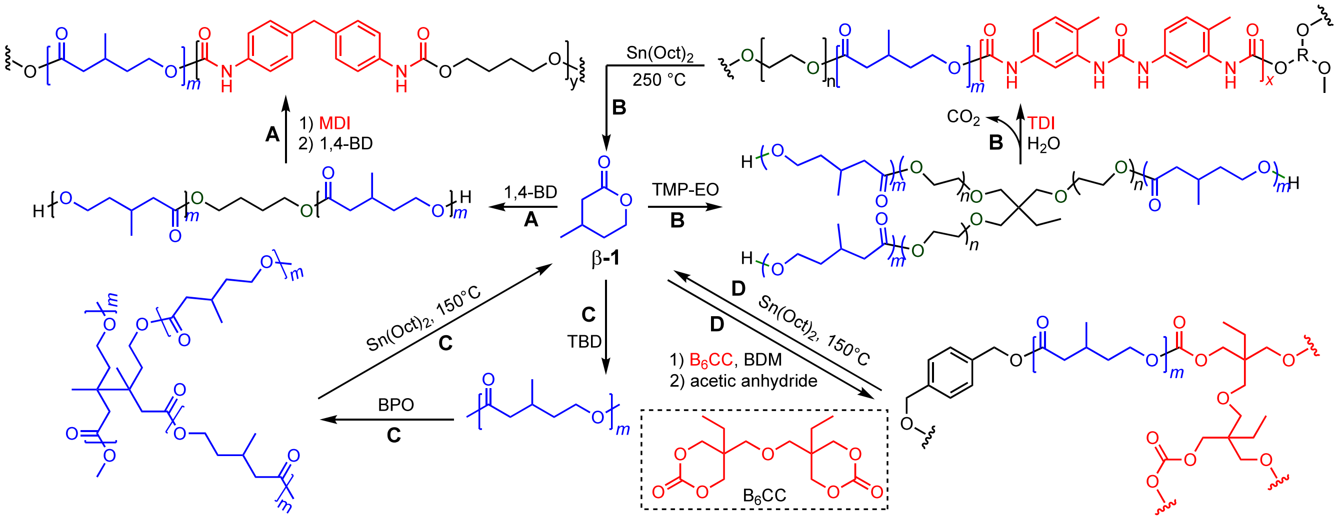
Recently, Li et al. demonstrated the fast and controlled ROP of δ-lactones (specifically δ-3, δ-6, and δ-9) to create closed-loop recyclable polyesters using a binary catalyst composed of an organophosphate base (^{t}Bu-P$_2$) and urea (U15 or U18).[474] The binary ^{t}Bu-P$_2$/U15 catalyst outperformed the previously reported DPP in the ROP of δ-3, exhibiting a TOF of 486 h^{-1}, compared to a TOF of ~1 h^{-1},[19] with 81% monomer conversion in 10 min. The resulting polyesters can be recycled back to their constituent monomers at yields greater than 96% by heating them in bulk at 170 °C in the presence of 0.5 wt % of Sn(Oct)$_2$ catalyst. The recovered pure monomers can be repolymerized to produce poly(δ-lactone)s with almost identical molar mass and dispersity after drying with CaH$_2$. Additionally, well-defined tri-BCPs comprising poly(alkyl-δ-lactone)s as a soft middle block and PLLA as a hard end block were successfully synthesized via a one-pot, sequential ROP of alkyl-δ-lactones and L-LA (Scheme 40). These tri-BCPs can be used as pressure-sensitive adhesives without needing tackifiers or other additives, exhibiting peel adhesion strength comparable to commercial PSA scotch tapes. Furthermore, the tri-BCPs can be chemically recycled to recover ethyl lactate and alkyl-δ-lactones using a two-step process. First, the copolymers undergo ethanolysis at 100 °C for 6 h in the presence of Sn(Oct)$_2$ as a catalyst, resulting in ethyl lactate that can be readily separated by distillation at 60 °C under reduced pressure (~1600 Pa) in over 95% yield. Throughout this process, the middle block of the tri-BCPs remains stable. Subsequently, an almost quantitative recycling of clean alkyl-δ-lactones (~93% yield) can be achieved by further distilling the remaining mixtures at 170 °C under reduced pressure (~200 Pa).

In 2023, Qi and co-workers reported a polyester-based vitrimer capable of both reprocessability and chemical recycling, achieved through a simple and scalable one-pot two-step synthesis from biobased δ-lactones with three distinct alkyl substituents (δ-lactone: δ-1, δ-4, δ-7) (Schemes 39 and 41).[475] DPP was employed for the controlled ROP of δ-lactones and was also found to effectively catalyze the click reaction between vinyl ethers and alcohols. As a result, the synthesized poly(δ-lactone) triols, initiated from glycerol, can be directly used for cross-linking without requiring any additional post-treatment steps. By utilizing a vinyl ether cross-linker with dynamic acetal linkages, the amorphous poly(δ-lactone) triols were transformed into elastomeric poly(δ-lactone) vitrimers, denoted as v-δ1, v-δ4, and v-δ7 with low T_g values of −31, −36, and −51 °C, respectively. The $T_{d,5\%}$ (10 °C min^{-1}) values of v-δ1, v-δ4, and v-δ7 were determined to be 196, 181, and 176 °C, respectively. Each poly(δ-lactone) vitrimer was efficiently recovered back to its constituent monomers with yields of 85−90% within 1 h through thermolysis at 200 °C under reduced pressure.[475] Upon heating to 200 °C, the acetal cross-linkages of the poly(δ-lactone) vitrimers underwent decomposition, producing 1,4-cyclohexanedimethanol and acetaldehyde, which then evaporated. This resulted in the formation of hydroxyl-capped aliphatic polyesters, poly(δ-lactone) triols, which were subsequently depolymerized back to monomer.

Scheme 41. Chemically Recyclable Vitrimers with Reprocessability and Monomer Recovery Based on Three Monosubstituted δ-Valerolactone



Scheme 42. Synthetic Routes and Chemical Recycling Processes of β-1-Based TPU and Flexible Foam as Well as Cross-Linked Elastomers[a]



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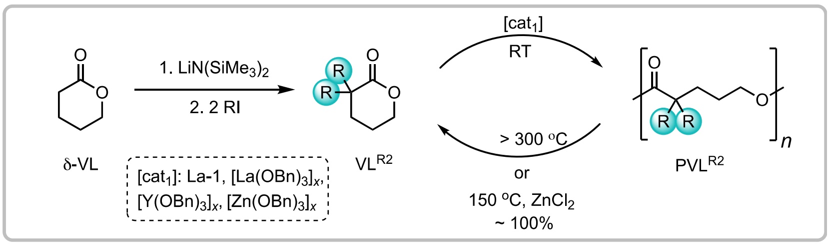
Scheme 43. Circular Polyethylene-Like Polyester Platform Based on α,α-Disubstituted Valerolactones with Enhanced Thermal and Mechanical Properties and Full Chemical Recyclability

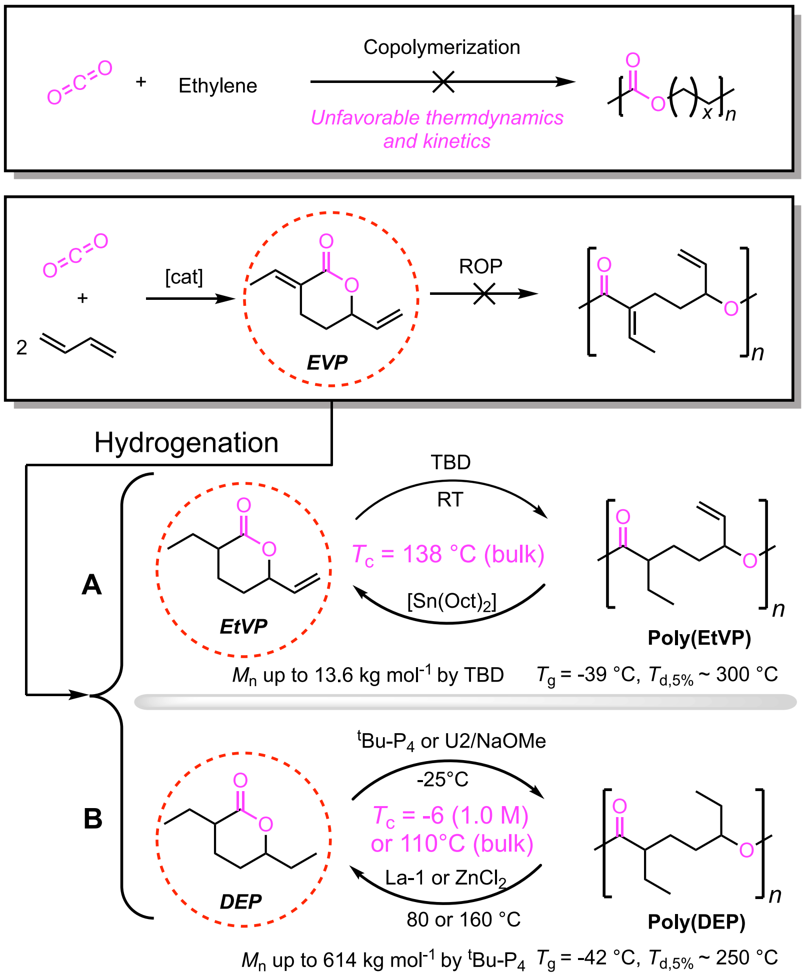


Monomer VL^{R2}	ΔH_p^o (kJ mol^{-1})	ΔS_p^o (J mol^{-1} K^{-1})	T_c (°C)	T_g (°C)	T_m (°C)	$T_{d,5\%}$ (°C)
δ-VL	-15.9	-30.8	243	-55	57	184-338
VL^{Me2}	-17.3	-44.6	115	-40	75	264
VL^{Et2}	-27.9	-79.6	78	18	140	241
VL^{Pr2}	-23.9	-70.2	67	-18	123	281
VL^{Bu2}	-19.4	-53.9	88	-28	77	291
VL^{Pen2}	-17.2	-46.5	100	-33	68	295
VL^{Hex2}	-23.9	-65.6	92	-41	80	322

Relocating the pendant methyl group from the δ position to the β position yielded a new six-membered lactone β-methyl-δ-valerolactone (β-1). Although β-1 is not a natural metabolite, Zhang and co-workers have successfully developed a "semi-synthetic" route for large-scale production of β-1 from glucose involving the dehydration of fermented mevalonate to anhydromevalonolactone followed by reduction to β-1.[476] The thermodynamic parameters associated with β-1 polymerization were determined to be $\Delta H_p^o = -13.8$ kJ mol^{-1} and $\Delta S_p^o = -46$ J mol^{-1} K^{-1} in neat polymerization, corresponding to a T_c of 227 °C, indicating potential recyclability under suitable conditions.[477] A rubbery hydroxyl telechelic poly(β1-lactone) with a low T_g of −51 °C can be readily synthesized from the neat polymerization of β-1 by employing a diol initiator and using TBD or DPP as the catalyst at RT. The linear poly(β1-lactone) diols were employed in a one-pot, two-step sequential procedure to synthesize TPUs (Scheme 42A). Similarly, poly(β1-lactone) triol can be obtained when trimethylolpropane ethoxylate (TMP-EO) was employed as the initiator, which can be further transformed into a cross-linked flexible polyurethane (PU) foam by reacting it with toluene diisocyanate and using water as the sole blowing agent (Scheme 42B). Importantly, the PU foam can be effectively recycled back to its constituent monomer, β-1, with high purity (>95%) and yield (up to 97%) by applying Sn(Oct)$_2$ at 250 °C through urethane dissociation followed by depolymerization of the resulting hydroxy-terminated poly(β1-lactone). This approach circumvents numerous technical difficulties that traditionally impede the practical chemical recycling of PUs, such as the low purity of the recovered polyol.

Hillmyer and co-workers also synthesized renewable and recyclable cross-linked elastomers with β-1 as a building block via two different methodologies: (1) cross-linking of a linear poly(β1-lactone) homopolymer with benzoyl peroxide as a free-radical generator (Scheme 42C), and (2) tandem copolymerization and cross-linking of β-1 with a bis(six-

Scheme 44. Strategies To Enable Circular Polyesters from CO_2 and Olefin



membered cyclic carbonate) (Scheme 42D).[478] The resulting cross-linked elastomers demonstrated exceptional mechanical properties with tensile strength reaching 12 MPa and elongation exceeding 2000%. Furthermore, the incorporation of fumed silica as a filler further enhanced the elastomers' performance, resulting in a remarkable 57% increase in Young's modulus and an 83% increase in tensile strength, while maintaining elongation at break. Importantly, both the peroxide-cross-linked and the cyclic carbonate-cross-linked poly(β1-lactone) materials exhibited the ability to undergo depolymerization in the presence of Sn(Oct)$_2$ and pentaerythritol ethoxylate (a high-boiling tetraol) at 150 °C under vacuum, facilitating the recovery of the monomer with high purity (93%) and yield (91%), thus demonstrating the chemical recyclability of these cross-linked polyesters.

Although the introduction of alkyl groups to the δ-VL ring can improve the chemical recyclability, the resulting polyesters typically are amorphous materials with inferior mechanical properties compared to the parent polymer PVL. To address this, Chen, Xu, and co-workers devised a synergistic approach that harnessed the *gem*-α,α-disubstitution of δ-VL to produce *gem*-dialkyl-substituted valerolactones (VL^{R2}) (Scheme 43).[462] These gem-disubstituted valerolactones enable the development of polymers that not only address the challenges of poor chemical recyclability but also overcome the limitations of low T_m and mechanical performance associated with the parent PVL. As an example, VL^{Me2} exhibits a lower T_c of 115 °C (at $[M]_0$ = 1.0 M in toluene) compared to the parent δ-VL (T_c = 243 °C in the same solvent),[461] with $\Delta H_p^o = -17.3$ kJ mol^{-1} and $\Delta S_p^o = -44.6$ J mol^{-1}. By varying the α,α-disubstituents on the δ-VL ring to ethyl (Et) and *n*-propyl (^{n}Pr), the T_c values decrease further to 78 and 67 °C ($[M]_0$ = 1.0 M), respectively, due to a more significant entropy loss during polymerization. However, increasing the alkyl chain length to *n*-butyl (^{n}Bu), *n*-pentyl (^{n}Pen), and *n*-hexyl (^{n}Hex) resulted in an increase in T_c to 88, 100, and 92 °C ($[M]_0$ = 1.0 M), respectively. The large decrease in T_c upon disubstitution is mainly ascribed to the larger entropic loss during polymerization, which overrides the more negative enthalpic change caused by the ring substitution (Scheme 43). The *gem*-dialkyl-substituted valerolactones exhibited controlled polymerization mediated by an $[La(OBn)_3]_x$ catalyst, yielding semicrystalline polyesters with M_n values up to 333 kg mol^{-1}. These PVL^{R2} polyesters can be selectively depolymerized under mild conditions (150 °C with a catalyst such as ZnCl$_2$ or >300 °C without a catalyst) to fully recover the monomers (VL^{R2}) in a pure state, demonstrating their full chemical recyclability. Additionally, PVL^{R2} showed good to excellent thermal stability ($T_{d,5\%}$ up to 330 °C). Alkyl chain length was found to greatly influence the crystallinity of the resulting polyester with PVL^{Et2} and PVL^{Pr2} displaying the highest T_m values of 140 and 123 °C, respectively, comparable to HDPE and LDPE. In terms of the mechanical properties, PVL^{Pr2} exhibited remarkable strength ($\sigma_B = 44 \pm 2.6$ MPa), ductility ($\varepsilon_B = 209 \pm 13\%$), and toughness ($U_T$ = 57.2 MJ

m^{-3}), showing a pronounced strain-hardening phenomenon after the yield point (σ_y = 20.7 ± 0.3 MPa). These properties surpass LDPE and rival or even surpass HDPE (σ_B = 21.4 ± 0.5 MPa) in multiple aspects.[462]

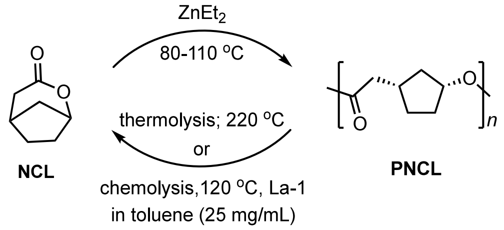
Although the majority of chemically recyclable polyesters discussed thus far could potentially be produced from biomass, the conversion process from biomass into these polymers can be intricate and inefficient. This typically involves multistep chemical or biological transformations that can be time consuming and resource intensive and result in relatively low yields.[14,16] Therefore, the potential to create recyclable or degradable polyesters through the direct copolymerization of CO_2 and olefins should be recognized for its appeal and promise. Given the abundance and low cost of CO_2, this notion presents a compelling direction for the future of sustainable polymer synthesis. However, the practical implementation of this strategy has been challenging due to the unfavorable kinetics and thermodynamics involved.[479,480] In response to these challenges, six-membered lactone 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one (EVP) has emerged as a versatile intermediary in CO_2/olefin copolymerization (Scheme 44).[481−483] Obtained through the efficient palladium-catalyzed coupling of CO_2 and butadiene, EVP contributes a high CO_2 content (28.9% by weight) to the resulting polymer. Moreover, EVP provides multiple polymerization sites, including an *α*,*β*-unsaturated ester and a pendant C═C double bond for radical polymerization and coordinate polymerization and ROP via the six-membered lactone. While direct polymerization of EVP via radical and coordinate polymerization has been achieved, the resulting polymer possesses an all-carbon main-chain structure, which limits its degradability and recyclability. On the other hand, ROP of EVP holds great promise for the production of degradable and recyclable polyesters. However, challenges still persist in the ROP process, primarily due to ester conjugation.

To overcome the reactivity and selectivity issues of the EVP monomer, Lin and co-workers performed a hydrogenation process prior to the polymerization, resulting in the fully hydrogenated disubstituted six-membered lactone, 3,6-diethyltetrahydro-2*H*-pyran-2-one (DEP) (Scheme 44).[484] ^{t}Bu-P_4 exhibited high catalytic activity for the ROP of DEP at −25 °C, affording ultrahigh molar mass cyclic polymers with M_n = 543−614 kg mol^{-1} and $Đ$ = 1.35−1.45 in the absence of an initiator. The resulting polyester is an amorphous material with a low T_g of −30 °C. These high molar mass cyclic poly(DEP) showed enhanced pressure-sensitive adhesive properties comparable to commercial tapes with peel strength = 1.5−3.8 N m^{-1}. The thermodynamic parameters of DEP polymerization were determined as ΔH_p^o = −13.1 kJ mol^{-1} and ΔS_p^o = −49.1 J mol^{-1}, resulting in a T_c of −6 °C in THF at $[DEP]_0$ = 1.0 mol L^{-1}. Importantly, the high molar mass cyclic poly(DEP) polymers can be chemically recycled back to DEP with quantitative recovery through depolymerization using either $ZnCl_2$ (0.5 M in 1,2-dichlorobenzene, 160 °C, 12 h) or La-1 (0.1 M in toluene, 80 °C, 12 h).

At about the same time, Tonks and co-workers reported on the ROP of semihydrogenated 3-ethyl-6-vinyltetrahydro-2*H*-pyran-2-one (EtVP), where the conjugated C═C double bond was selectively hydrogenated (Scheme 44). The polymerization was conducted under neat conditions using the bifunctional base TBD as a catalyst in the presence of phenylpropanol (PPA) initiator.[485] The resulting polymer exhibited a medium molar mass (M_n = 13.6 kg mol^{-1}, $Đ$ = 1.32) and a low T_g of −39 °C. The thermodynamic parameters of EtVP polymerization in bulk were determined as ΔH_p = −9.45 kJ mol^{-1} and ΔS_p = −23.0 J mol^{-1} with a T_c of 138 °C in bulk. Subsequently, chemical recycling of poly(EtVP) to recover EtVP was explored. Specifically, distillation with 3% $Sn(Oct)_2$ as a catalyst at 165 °C resulted in the recovery of EtVP at 84% yield within 2 h, leaving behind 16% residue. Furthermore, poly(EtVP) exhibited biodegradability in wastewater, according to the OECD-301B protocol,[486] with 67.4% of the theoretical CO_2 removed within a 60-day period. The authors also investigated the ROP of DEP using TBD as a catalyst, which showed lower reactivity compared to ^{t}Bu-P_4 catalyst, with only 46% conversion in 3 days. A NaOMe/1-cyclohexyl-3-phenylurea (U2) catalyst system polymerized DEP to high conversion (70%) but yielded polyesters with low molar mass (M_n = 9.7 kg mol^{-1}, $Đ$ = 1.27). The thermodynamic parameters of DEP polymerization in bulk were determined as ΔH_p = −11.8 kJ mol^{-1} and ΔS_p = −30.7 J mol^{-1} K^{-1}, corresponding to a calculated T_c of 110 °C.

The hybrid monomer design strategy put forth by Chen and co-workers can be further expanded into an HCT/HCT hybrid monomer system to enhance the thermal properties and chemical recyclability. For example, Rieger and co-workers devised a bicyclic lactone structure that combines features of HCT *δ*-VL (T_c = 298 °C at $[M]_0$ = 1.0 M) and HCT *ε*-CL (T_c = 1305 °C at $[M]_0$ = 1.0 M).[487] This hybrid monomer, abbreviated as NCL, derivable from readily available norcamphor through a one-step Baeyer−Villiger oxidation, was efficiently polymerized in bulk with $ZnEt_2$ at 110 °C into a high molar mass polymer, PNCL, with M_n up to 164 kg mol^{-1} (Scheme 45). The incorporation of the cyclopentane ring into the polymer main chain enhanced its rigidity, resulting in a 50 °C increase in T_g compared to the individual parent polymers. Notably, the resultant polymer achieved complete and selective depolymerization by thermolysis at 220 °C in bulk within 4 h. The chemolysis catalyzed by La-1 under dilute conditions at 120 °C (25 mg/mL PNCL in toluene) can also recover the monomer in 43% conversion after 3 h.

Scheme 45. Polymerization of HCT/HCT Hybrid Monomer NCL and Chemical Recycling of PNCL



Further modifying the *δ*-VL with a ketone functional group at the *γ* position, Hoye et al. reported a recyclable and degradable poly(4-ketovalerolactone) (PKVL) derived from levulinic acid.[488] However, due to its limited solubility, the formed PKVL exhibited a low M_n of <5.5 kg mol^{-1}. The DSC analysis of the 3.3 kg mol^{-1} sample showed it to be semicrystalline, displaying a T_g of 7 °C and two T_m values at 132 and 148 °C. The T_c of monomer KVL was measured to be 118 °C at $[KVL]_0$ = 1.0 mol L^{-1} in $CHCl_3$/HFIP = 9:1 mixed solvent, and the corresponding polyester PKVL can be chemically recycled through hydrolytic degradation to 5-

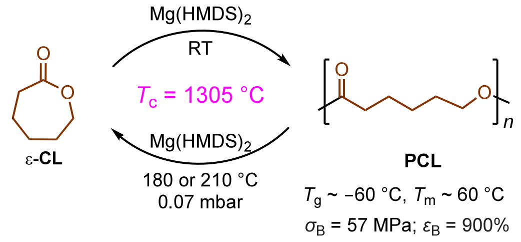
hydroxylevulinic acid, the ring-opened hydrolysis product of KVL.

In addition to the side-group modification, incorporation of heteroatoms such as N, S, and O is also an effective strategy to affect the (de)polymerization behaviors and material properties of polyesters. In 2014, Waymouth and co-workers demonstrated the oxidative lactonization of diethanolamines to *N*-acyl-substituted morpholin-2-ones and their subsequent organocatalytic ROP, providing a general strategy to functionalized poly(aminoesters).[489] Both experimental and theoretical studies have shown that the ease of polymerizing morpholin-2-ones is highly dependent on the substituents attached to the endocyclic N atom. The substitution of the N atom with an S atom was also explored by Du and Li.[490] Monomer 1,4-oxathian-2-one (OX) was synthesized by a one-pot, two-step method and measured to exhibit a T_c of 170 °C at $[OX]_0 = 1.0$ mol L^{-1} in DCM. The resultant polymer, poly(OX), was identified as a semicrystalline polyester with a T_g of −40 °C and T_m ranging from 40 to 60 °C.

Monomer 1,4-dioxan-2-one (PDO) is a well-studied heterocyclic six-membered lactone with an O atom installed at the *β* position.[491] A variety of catalysts have been employed to facilitate its ROP, including organometallic compounds such as $Sn(Oct)_2$,[492] $AlEt_3$,[493] $Al(O^iPr)_3$,[494] $La(O^iPr)_3$,[495] organotitanium complexes,[496] and Novozym 435.[497] The resultant polymer, poly(1,4-dioxan-2-one) (PPDO), is a semicrystalline aliphatic polyester renowned for its biomedical applications as a material for sutures, bone repair devices, and drug delivery systems thanks to its favorable mechanical properties coupled with its biodegradability, biocompatibility, and bioabsorbability.[491] The thermodynamic parameters for the PDO polymerization were determined by Tokiwa and co-workers to be $\Delta H_p = -14.1$ kJ mol^{-1} and $\Delta S_p = -26.1$ J mol^{-1}, corresponding to a T_c of 265 °C in bulk.[498] The isothermal degradation of PPDO under a nitrogen atmosphere at 230 °C and a reduced pressure of 7.6 mmHg resulted in a high PDO recovery yield of 99.3 wt % in just 3.5 h.[499] The homologue of PDO, 3-methyl-1,4-dioxan-2-one (MDO), has also been explored. Hillmyer and Tolman reported the ROP of MDO using $Y[N(TMS)_2]_3$, and they determined the thermodynamic parameters of the MDO polymerization to be $\Delta H_p^\circ = -12.1$ kJ mol^{-1} and $\Delta S_p^\circ = -42$ J mol^{-1}, corresponding to a low T_c of 15 °C at $[MDO]_0 = 1.0$ mol L^{-1} in toluene.[500] The resulting polymer, PMDO, displayed a low T_g of −24 °C. Leveraging the alternating structure of lactyl and ethylene glycolyl repeating units, the low molar mass PMDO was shown to act as an effective and degradable plasticizer to enhance the toughness of PLA.[500] Li and co-workers employed a synergistic DBU/U15 binary organic catalyst system for the ROP of MDO,[501] achieving PMDO with M_n up to 8.0 kg mol^{-1} and a monomer conversion rate of 84% in 7 h. Notably, the synthesized PMDO can be quantitatively recycled back to the pristine MDO by heating a toluene solution (60 mg/mL) of PMDO with 10 mol % of DBU catalyst at 140 °C for 6 h.

3.1.1.3. Seven- and Eight-Membered Lactones. **Parent Seven-Membered Lactone.** *ε*-CL, the parent seven-membered lactone, is predominantly produced industrially through the Baeyer−Villiger oxidation of cyclohexanone, thus being considered as a fossil fuel-based monomer. Alternatively, *ε*-CL can also be obtained from 5-hydroxymethylfurfural (HMF), which is derived from sugars.[502] The resultant polymer, poly(*ε*-caprolactone) (PCL), via ROP of *ε*-CL, is a commercially significant biodegradable polyester with a low $T_g \approx -60$ °C and $T_m \approx 60$ °C, which has been widely used in packaging, medicine, and other fields.[503,504] However, despite its widespread utility, the chemical recycling of PCL is challenging due to the significantly high ring strain of *ε*-CL. The thermodynamic parameters of *ε*-CL polymerization were determined to be $\Delta H_p^\circ = -21.8$ kJ mol^{-1} and $\Delta S_p^\circ = -16.7$ J mol^{-1} in toluene, corresponding to a high T_c of 1305 °C at $[M]_0 = 1.0$ mol L^{-1} (Scheme 46).[505]

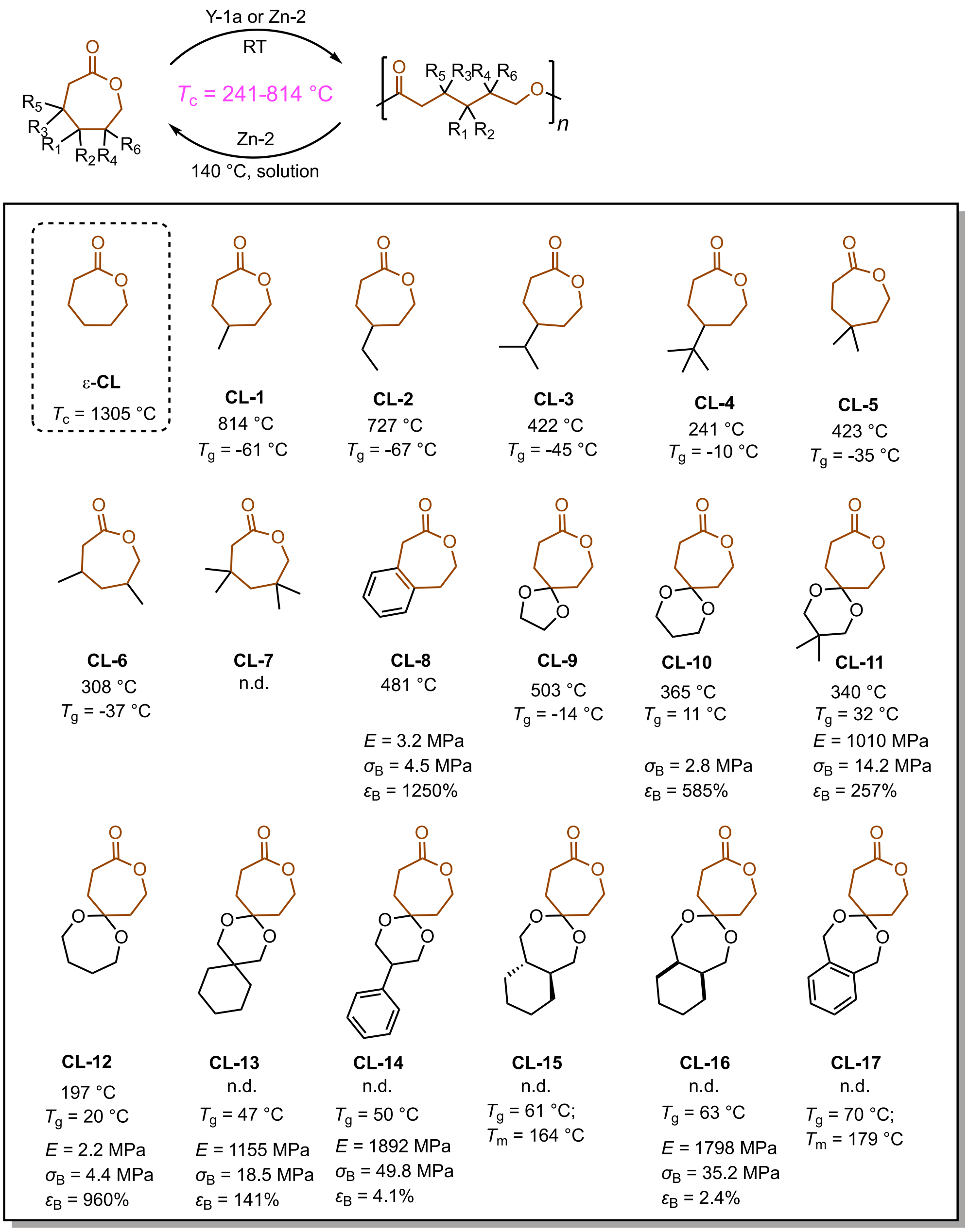
Scheme 46. Chemical Recycling of High Ring Strain Seven-Membered *ε*-CL[505,512]



Intensive research over recent decades has strived to understand the thermal degradation of PCL, driven by its significant implications for polymer processing, application, and recycling. However, the high temperatures required for depolymerization and the complex degradation mechanisms involved make effective conversion a substantial challenge. The thermolysis of PCL typically results in the formation of a wide range of degradation products, such as oligomers, CO_2, H_2O, *ε*-CL, and 5-hexenoic acid, among others. The main mechanism for PCL degradation is believed to be an unzipping process, facilitated by a backbiting reaction from the hydroxyl end group onto the ester function of the previous repeat unit, resulting in the generation of *ε*-CL. Additionally, random chain scission through cis-elimination reactions can also occur, leading to the formation of 6-hydroxyhexanoic acid and 5-hexenoic acid as the *α*- and *ω*-chain ends, respectively. For instance, Dubois and co-workers investigated the thermal degradation of PCL through TGA coupled with mass spectrometry (MS) and Fourier transform infrared spectrometry (FT-IR) for evolved gas analysis and proposed a two-step mechanism in bulk pyrolysis, where the initial process (starting at a lower temperature of ∼300 °C) involves statistical rupture of the polyester chains via ester pyrolysis reactions, resulting in the formation of 5-hexenoic acid through cis-elimination reactions with neighboring ester functions. The second step occurs at higher temperatures (∼430 °C) and involves the unzipping depolymerization of PCL, leading to the production of *ε*-CL.[506] Aoyagi et al., on the other hand, suggested a single-step mechanism in which PCL degrades exclusively through pure unzipping of monomers, resulting in the formation of *ε*-CL in isothermal degradation experiments at 250 °C.[191] Madras et al. proposed a mechanism involving both random chain scission and unzipping of monomers occurring simultaneously during nonisothermal heating, while isothermal heating at 320 or 340 °C primarily leads to unzipping of monomers from the hydroxyl end of the chain.[507] Madras and co-workers also investigated the thermal degradation of PCL in solution, revealing a random chain scission mechanism with a lower activation energy compared to bulk pyrolytic degradation.[508]

Abe et al. conducted a comprehensive investigation into the effects of chain-end structure and residual metal compounds

Scheme 47. Chemical Recycling of Polyesters Derived from Substituted ε-CL Monomers and Their Structures



on the thermal degradation of PCL.[509] Through both isothermal and nonisothermal experiments, they found that PCL samples containing high levels of residual zinc compounds from the synthesis process exhibited selective unzipping depolymerization below 300 °C, leading exclusively to the production of ε-CL. In contrast, metal-free PCL samples underwent thermal degradation at temperatures above 300 °C, regardless of the chain-end structure, leading to the formation of cyclic monomers and oligomers of ε-CL. Analysis of residual polymer samples also revealed the presence of 5-hexenoic acid units as the main ω-chain end. These findings suggest that the dominant reaction during the thermal degradation of PCL above 300 °C involves a combination of random chain scission via a cis-elimination reaction and cyclic rupture through intramolecular transesterification of PCL chains. The authors further explored the impact of different metal chlorides (such as NaCl, $CaCl_2$, $ZnCl_2$, $SnCl_2$, and $AlCl_3$) on the thermal degradation of PCL.[510] They observed that Zn, Sn, and Al chlorides catalyzed the selective unzipping depolymerization of PCL at lower temperature ranges, initiating from the ω-hydroxyl chain end. On the other hand, the presence of Na and Ca chlorides did not significantly affect the degradation temperature. Overall, these studies highlight the complexity of the PCL degradation process and the diverse mechanisms involved, which depend on various factors such as temperature, heating conditions, and chain structures.

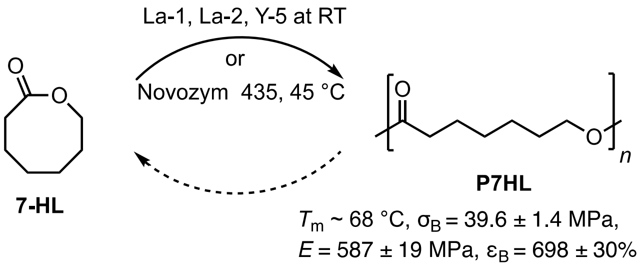
While pyrolysis of PCL to obtain ε-CL presents challenges, addition of catalysts has demonstrated a significant reduction in the required depolymerization temperature, enabling more efficient conversion to monomer. Hocker and co-workers employed $Bu_2Sn(OMe)_2$ as a catalyst to accomplish the catalyzed and selective depolymerization of PCL to ε-CL at 260 °C and 0.01 mbar, yielding ε-CL with 86% yield and 95% selectivity.[511] In 2022, Wang and co-workers presented a direct bulk depolymerization approach for PCL at a milder depolymerization temperature of 180 °C and under vacuum conditions of 0.07 mbar utilizing magnesium bis[bis(trimethylsilyl)amide] [Mg(HMDS)$_2$] (0.5 mol %) as a catalyst to facilitate the unzipping depolymerization process.[505] This method resulted in ε-CL with a yield of 88–92%. In addition, efficient and controllable depolymerizations of PCL commodities were also achieved at 210 °C under vacuum conditions (0.07 mbar), leading to the production of ε-CL with high yield (up to 98%), selectivity, and purity.[505]

Recently, Byers and co-workers introduced an effective and versatile catalyst system comprising ZnCl$_2$ and an additive amount of poly(ethylene glycol) (PEG) for the ring-closing depolymerization of polyesters and polycarbonates with high $T_c > 200$ °C, leading to complete recovery of their constituent monomers.[513] Reactive distillation, which prevents the polymer/monomer equilibrium from being established by removing the formed monomer, was performed under a vacuum of 0.1 Torr at 160 °C, employing 10 wt % of ZnCl$_2$ and 100 wt % of PEG600 as the catalyst, resulting in the full depolymerization of PCL and the quantitative recovery of ε-CL within 20 h. Control reactions conducted without ZnCl$_2$ or PEG600 exhibited no mass loss and no recovery of ε-CL. Furthermore, when the temperature was lowered to 140 °C, complete recovery of the monomer was still achievable by extending the reaction time to 66 h. Mechanistic investigations suggested a random chain scission mechanism with the optimal catalyst structure consisting of 1 equiv of ZnCl$_2$ per ethylene glycol repeat unit in the PEG polymer. These findings exemplified the ability to achieve depolymerization reactions at temperatures below the T_c of the polymer by employing suitable catalysts under nonequilibrium conditions.

ε-Caprolactone Derivatives. Recently, Zhu and co-workers conducted monomer redesign based on ε-CL to allow for milder recycling conditions of PCL, specifically by manipulating the T_c.[514] A comprehensive investigation of various substitution effects, such as the size and position of the substituent, was carried out, thereby establishing structure–property relationships within the ε-CL monomer system. Specifically, the introduction of bulky substituents to ε-CL was found to promote the depolymerization pathway and decrease the T_c values from 1305 to 241 °C.[505,514] Moreover, the location of the substituent was found to significantly influence the thermodynamics of polymerization. Detailed insights into the effects of substitutions on CL derivatives (CL-1–8) and their impacts on polymerization thermodynamics are summarized in Scheme 47, offering guidance for future monomer design with predictable T_c values. Solution depolymerization experiments were conducted by mixing the polymer solution (20 mM in toluene, based on the moles of repeat units in polymers) with 2 mol % of Zn-2 catalyst at 140 °C for 1 h, achieving 69–99% conversions, which confirmed the strong correlation between depolymerizabililty and T_c.

η-Heptalactone. The parent eight-membered lactone, η-heptalactone or 7-heptanolactone (7-HL), which can be obtained from a seven-membered ketone via Baeyer–Villiger oxidation, has not been investigated as extensively as its homologues, such as ε-CL. In 2006, E. W. Meijer and co-workers reported lipase-catalyzed ROP of 7-HL, yielding semicrystalline poly(7-hydroxyheptanoate) (P7HL) with a T_m of 65 °C. The M_n of P7HL obtained by lipase-catalyzed ROP reached only up to 23.6 kg mol^{-1} with broad dispersity ($Đ$ = 2.8).[515] In 2022, Tang and Chen et al. reported a metal-catalyzed coordination–insertion polymerization strategy to produce P7HL with M_n up 100 kg mol^{-1} and a T_m of 68 °C (Scheme 48). Moreover, to increase the T_m of P7HL-based polyesters, thus widening its application scenarios, the stereoselective copolymerization of 7-HL with *rac*-8DL^{Me} was investigated, which produced copolymers of P7HL and P3HB with T_m up to 164 °C.[516] In 2023, De Rosa and co-workers determined the single-crystal structure of P7HP by analysis of the X-ray powder diffraction profiles and of the electron diffraction patterns of single crystals and calculations of the lattice energy, which indicated that the P7HL chains in a trans planar conformation are packed in an orthorhombic unit cell with axes a = 7.37 Å, b = 5.05 Å, and c = 10.07 Å, corresponding to the space group symmetry $P2_1$.[517] However, the closed-loop recycling of P7HL has not yet been achieved.

Scheme 48. Preparation of High-Performance Aliphatic Polyester from Eight-Membered 7-HL



7-HL

P7HL

T_m ~ 68 °C, σ_B = 39.6 ± 1.4 MPa,
E = 587 ± 19 MPa, ε_B = 698 ± 30%

3.1.1.4. Large-Ring Lactones. The ROP of strained cyclic esters, particularly small (4 and 6 atoms) and medium (between 7 and 11 atoms) lactones, is well understood and is primarily thermodynamically driven by a negative change in enthalpy due to the release of angular and transannular strains.[120] In contrast, macrolactones (MLs, consisting of 12 or more atoms) exhibit little to no ring strain, suggesting that their change in ΔH_p is virtually zero. Guided by the Gibbs free energy equation, $\Delta G_p = \Delta H_p - T\Delta S_p$, it becomes clear that the ROP process of MLs is largely dictated by entropic changes, i.e., $\Delta G_p = -T\Delta S_p$.[120,421,422] Two types of entropy are of significance: conformational and translational entropy. The former, inherently associated with the conversion of MLs into polymers, increases significantly and is essentially independent of concentration. Meanwhile, translational entropy invariably decreases during ROP due to the uniaxial alignment and covalent linking of discrete monomers into a polymer chain. Both MLs and the subsequent polymers exhibit maximum translational entropy at high dilution. However, the translational entropy loss during ROP of MLs is less pronounced than that in the polymerization of small lactones. Thus, the increase in conformational entropy compensates for this decrease in translational entropy, ultimately leading to a positive change in total entropy.[45,400] Additionally, the entropic term ($T\Delta S_p$) in the Gibbs free energy equation can be enhanced by raising the reaction temperature. Therefore, the polymerization of MLs typically necessitates higher reaction temperatures compared to small- and medium-sized lactones to be energetically favorable ($\Delta G_p < 0$).

In 2002, Kobayashi et al. conducted a comprehensive investigation into the polymerization kinetics of lactones with different ring sizes, namely, 6-, 7-, 9-, 12-, 13-, 16-, and 17-membered lactones.[518] This investigation was executed using a zinc 2-ethylhexanoate/butanol catalyst–initiator system at 100

°C in bulk polymerization. The study revealed first-order polymerization kinetics for all of the monomers. The relative rates of polymerization were calculated to be 2500:330:21:0.9:1.0:0.9:1.0 for 6-, 7-, 9-, 12-, 13-, 16-, and 17-membered lactones, respectively. These findings are also consistent with thermodynamic expectations, which indicate that the ROP of small- and medium-sized lactones is associated with an unfavorable negative change in entropy and is driven by a negative change in enthalpy during the release of angular and transannular strains ($\Delta H_p < 0$, $\Delta S_p < 0$ and $|\Delta H_p| > -T\Delta S_p$), an effect that diminishes with increasing ring size. Therefore, it is not surprising that early attempts to polymerize MLs using conventional, nonenzymatic catalysts resulted in less efficiency, producing polymers with relatively low molar mass and/or poor control over the polymerization process.[519−521] The enzymatic-catalyzed polymerization is an inverse scenario and will be discussed in the section 3.3.

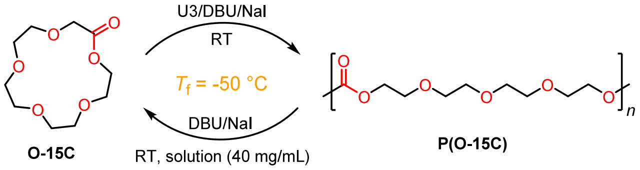
Despite inherent challenges, the polyesters produced from the ROP of MLs have continued to draw considerable interest due to their potential to mimic the properties of both LDPE and HDPE, dependent on the molar mass, coupled with the additional advantage of potential biodegradability.[522−524] Specifically, ω-pentadecalactone (PDL), which is readily available from the root of *Angelica archangelica* L,[525] has been extensively studied as a ML for the synthesis of aliphatic polyesters and copolyesters. As with many other MLs, the ROP of PDL is governed by entropy due to its negligible ring strain, and a diverse range of catalysts, including organic,[425,526−528] organometallic,[423,424,529−532] and enzymatic catalysts,[515,518,533,534] have been successfully employed for this purpose.[524] However, there are only limited recycling cases that have been demonstrated the efficient recycling of MLs through nonenzymatic processes. Therefore, the discussion about the recycling of PMLs will primarily be covered in section 3.3.

The catalyst system developed by Byers and co-workers consisting of $ZnCl_2$/PEG-600 has been demonstrated to be effective for the recycling of PMLs.[513] Notably, the depolymerization of PPDL under conditions found to be optimal for the depolymerization of PCL (160 °C, 0.1 Torr, 10 wt % of $ZnCl_2$, 20 wt % of PEG-600) resulted in a high yield of 82% for the primary product, the cyclic dimer of PDL. Moreover, increasing the reactive distillation temperature to 210 °C led to near-quantitative depolymerization of the PPDL and boosted the yield of PDL to 92%. In addition to PPDL, the polymer obtained from the unsaturated ML, 6-hexadecenelactone (6HDL), can also be depolymerized at 210 °C, although the yield was lower, at 40%.

In 2023, Li and co-workers reported an efficient cyclodepolymerization method for the chemical recycling of poly(ethylene adipate) (PEA) into its cyclic oligomers as MLs, termed cyclic oligo(ethylene adipate)s (COEAs), achieving up to 99% yield.[535] This process is catalyzed by 3% dibutyltin oxide in toluene (25 g/L), conducted at 110 °C over 96 h. Their findings highlighted the superior performance of toluene over chlorobenzene or dichlorobenzene as a solvent. Significantly, the obtained MLs (COEAs) can be repolymerized back to PEA, achieving M_n of 22.2 kg mol^{-1} and $Đ$ of 1.82, thus establishing a chemically closed-loop recycling pathway for PEA.

Another example demonstrating the chemical recyclability of MLs was reported by Chen and co-workers in 2022 (Scheme 49).[536] In their study, they described the rapid and controlled ROP of 2-oxo-15-crown-5 (O-15C5) catalyzed by the DBU/U3/NaI system for the synthesis of well-defined PEG-like polyesters, specifically P(O-15C5). Through computational and mechanistic studies, they found that the Na^+ ions preferentially bind to the O-15C5 monomer over the resultant polymer. This selective interaction facilitates the initiation and propagation of ring opening while suppressing side transesterification reactions, thus enabling the controlled polymerization of O-15C5 at RT. The obtained values of $\Delta H_p^\circ = 13.8$ kJ mol^{-1} and $\Delta S_p^\circ = 61.9$ J mol^{-1} K^{-1} correspond to a floor temperature (T_f) of −50 °C, confirming that the ROP of O-15C5 is primarily entropy driven. Notably, it was also demonstrated that P(O-15C5) can be efficiently depolymerized back into O-15C5 under the influence of Na^+ and 5 wt % of DBU at RT in DCM solution (40 mg/1 mL), achieving >90% conversion to monomer within 2 h, as confirmed by ^{1}H NMR analysis.[536]

Scheme 49. Chemical Recycling of PEG-Like Polyester Derived from O-15C5, Regulated by T_f

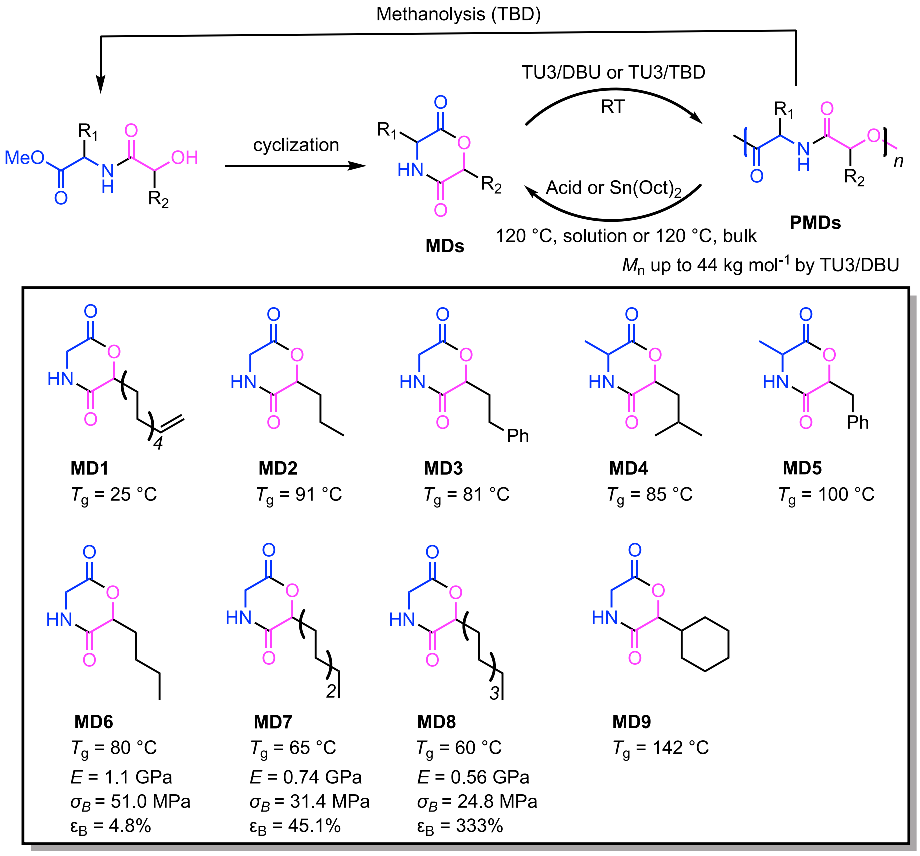


3.1.2. Heterocyclic Diesters.

Given the limitations of PLA in terms of depolymerization efficiency and selectivity (see section 2.1), which is susceptible to elimination reactions leading to the formation of acrylic acid and α-position epimerization, Li and co-workers developed chemically recyclable poly(ester-amide)s (Scheme 50).[537] These polymers are synthesized by the ROP of morpholino-2,5-dione derivatives (MDs), which are analogues of six-membered ring lactides where an amino acid replaces the lactic acid unit. Thiourea-based bifunctional catalytic systems, such as TU3/DBU and TU3/TBD, were employed to control the ROP of MDs and minimize side reactions caused by the amide bond, affording well-defined poly(ester-amide)s with M_n up to 44.0 kg mol^{-1}.[538,539] The resulting poly(ester-amide) materials exhibited excellent mechanical properties, with modulus up to 1.3 GPa, tensile strength up to 51.0 MPa, and elongation at break up to 333%, which could be further adjusted by tuning the side-chain substituents.[540] Efficient recovery of the constituent monomers was achieved through either solution depolymerization in toluene with quantitative conversion to monomer at 120 °C using Amberlyst 15 ion-exchange resin as the catalyst or bulk depolymerization under vacuum at 140 °C catalyzed by $Sn(Oct)_2$ to recover the monomer with high purity and in a high yield of 90−97%. Moreover, given the higher lability of ester bonds compared to the more robust amide bonds, methanolysis of poly(ester-amide)s catalyzed by TBD was conducted to selectively generate constituent monomer precursors at RT, which could be used for monomer regeneration through a cyclization reaction.[537] These depolymerization strategies allow effective recovery of the MD monomers, paving the way for the closed-loop chemical recycling of poly(ester-amide) materials.[537,540]

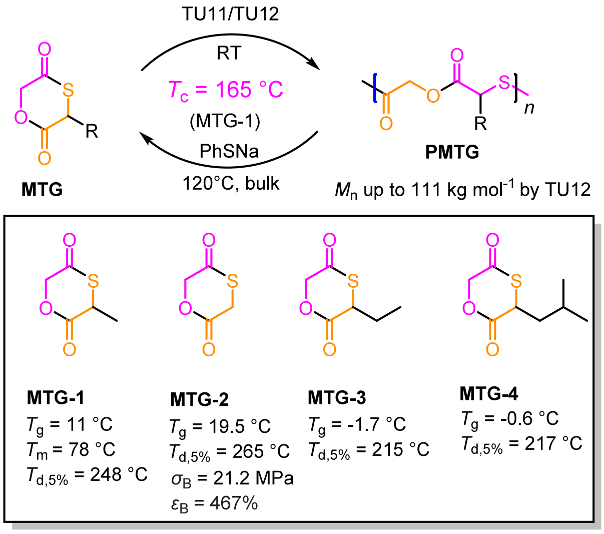
Tao and co-workers introduced an approach to transform "nonrecyclable" polyesters into chemically recyclable polymers using a single-atom oxygen-to-sulfur substitution strategy.[541] As illustrative examples, the authors synthesized four

Scheme 50. Dual Recycling Strategies of Poly(ester-amide)s Derived from the Controlled ROP of Morpholino-2,5-dione Derivatives



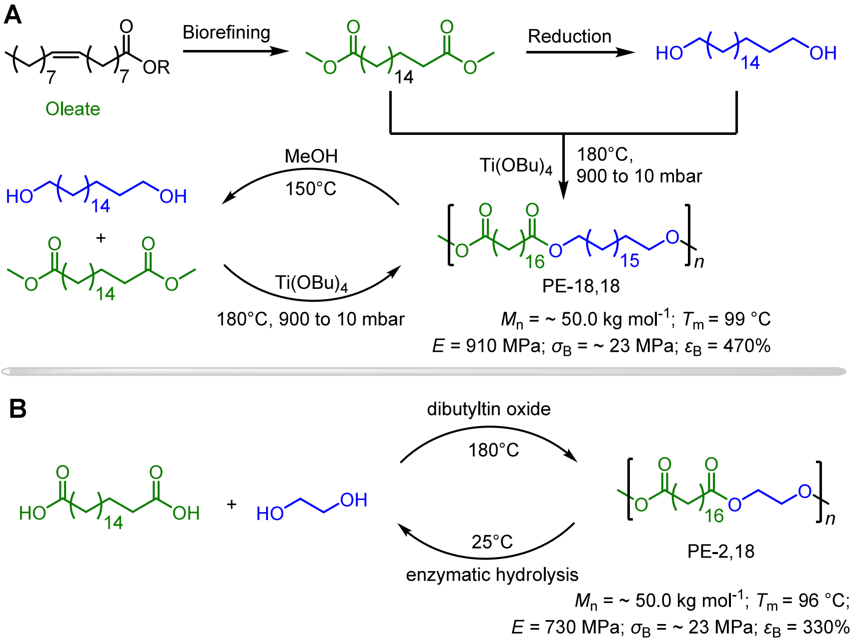
monothiodilactone monomers, namely, methyl monothioglycolide (MTG-1), monothioglycolide (MTG-2), ethyl monothioglycolide (MTG-3), and isobutyl monothioglycolide (MTG-4) (Scheme 51). The regioselective ROP of these monomers from the acyl−S bond site was achieved by monocomponent thiourea-amine-based catalysts (TU-11 and TU-12), resulting in well-defined polymers with M_n up to 121 kg mol^{-1} from MTG-1 and 131 kg mol^{-1} from MTG-2. Thermodynamic analysis revealed the standard-state parameters for MTG-1 polymerization, with ΔH_p° determined as −22.2 kJ mol^{-1} and ΔS_p° as −50.7 J mol^{-1} K^{-1}, corresponding to a T_c of 165 °C at $[M]_0$ = 1.0 M in DCM. Importantly, these PMTGs were proven to be chemically recyclable. Under vacuum conditions at 120 °C and employing PhSNa as the catalyst, monomer recovery was achieved at a yield of 95%. PMTG-1 is semicrystalline with a T_m of 78 °C observed during the initial heating scan. PMTG-2 with a high M_n of 131 kg mol^{-1} displayed enhanced mechanical properties compared to the parent polymer, PGA, including a σ_B of 21.2 MPa and an ε_B of 467%.

Scheme 51. Chemically Recyclable Poly(thioester-ester)s Derived from Monothiodilactones



Recently, Hadjichristidis and co-workers reported the living/controlled anionic ROP of glycolide (GL) using strong protic fluoroalcohols (FAs) as (co)solvents, a class of solvents traditionally considered incompatible with anionic polymerization.[542] NMR titration and computational studies revealed that the FAs play a dual role in the process by not only solubilizing the polymeric product but also serving as an activator for the simultaneous activation of the monomer and living chain end without participating in the initiation step. Accordingly, successful synthesis of well-defined poly(glycolic acid) (PGA) with M_n up to 55.4 kg mol^{-1} and $Đ$ < 1.15 was achieved at RT with optimized polymerization conditions (^{t}Bu-P$_2$/TU3 binary catalyst, in 37.5 v/v% hexafluoroisopropanol (HFAB)/toluene). The low-boiling-point FAs can be efficiently recovered through a simple distillation process and, after drying with 3 Å molecular sieves, can be readily reused for subsequent polymerization. PGA can also be

Scheme 52. Closed-Loop Recycling PE-Like Polyesters Derived from SGP of (A) Biobased Long-Chain Diacid and Diol or (B) EG for Better Biodegradation



chemically recycled through sublimation using a sublimation apparatus operating at 220 °C under reduced pressure (~10 mbar), resulting in crude GL with 90% purity. This recycled GL monomer, upon recrystallization from ethyl acetate to achieve >99% purity, was repolymerized to create new PGA.

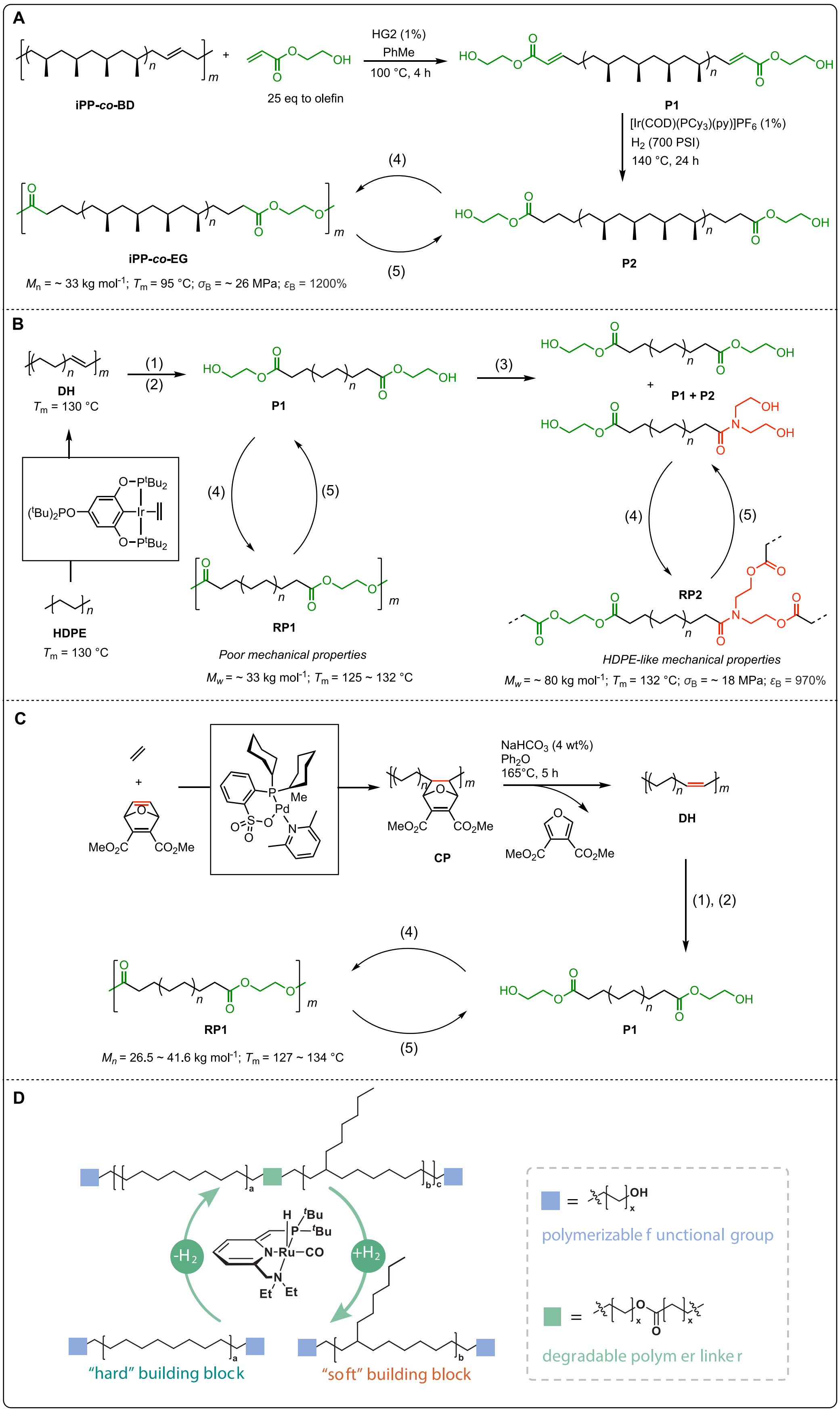
3.2. Step-Growth Polycondensation

Over the last half-century, polyolefins have solidified their position as the preferred materials for single-use applications owing to their versatile and adjustable material properties as well as the cost effectiveness and the abundance of their raw materials. Nevertheless, their exceptional strength and chemical stability contribute to their extended lifespan of several hundred years, leading to their massive accumulation in the environment. In addition, their inert nature also poses a challenge for chemical recycling, necessitating extremely high temperatures exceeding 600 °C and achieving a yield of ethylene of less than 10%.[543,544] For an ideal commodity material, it would be desirable to possess comparable properties while offering viable EoL options such as biodegradability or chemical recycling.[545] On the other hand, although SGP has been known since the discovery of synthetic polymers in the early 20th century,[546] it is still the most frequently used method for the synthesis of polyesters in industry (PET as a chief example among these), benefiting from the wide availability of diols, diacids (or diesters), or hydroxy acids. Unlike chain-growth polymerization, SGP is not restricted by the monomer's ring size and the substitution pattern of the monomers, rendering it particularly effective for the fabrication of polyesters featuring extended alkyl segments interspersed between each ester moiety. For instance, SGP of plant oil-derived diols and diacids with more than 20 methylene sequences affords polyesters possessing structural and thermal properties similar to those of PE, which are otherwise inaccessible through traditional chain-growth polymerization methods.[547−549] Moreover, this polymerization method allows easy modulation of material performance of the resulting polymers, such as T_g and T_m, by altering the structure of the constituent building blocks.[550,551] In addition, the inclusion of multifunctional monomers, like glycerol and citric acid, further bolsters the capacity for facile synthesis of biodegradable thermosets.[552]

In 2021, Mecking and co-workers made a significant advancement in the field of chemically recyclable "polyethylene-like" polyesters derived from plant oil feedstocks or microalgae oils (Scheme 52A).[553] Polyester-18,18 (PE-18,18) with M_w up to 80 kg mol^{-1} was synthesized via Ti(OBu)$_4$-catalyzed SGP using a stoichiometric ratio of the biorefinery-sourced C18 diester and diol. These polyesters were engineered with a low density of in-chain cleavable linkages (ester bonds) strategically incorporated as break points within the polyethylene chain without compromising the material performance of the polymer. This design enabled PE-18,18 to undergo efficient chemical recycling through methanolysis at 150 °C without the need for a catalyst at a polymer concentration of 40 g/L, yielding a well-controlled 1:1 mixture of C18 diester and C18 diol at near-quantitative yield. Notably, this mixture was directly repolymerized to high molar mass PE-18,18 using Ti(OBu)$_4$ catalyst. The mechanical strength, modulus of elasticity, and ductility of PE-18,18 rival those of commercial HDPE. Furthermore, the wide-angle X-ray scattering (WAXS) diffraction patterns of PE-18,18 are almost identical with those of HDPE, suggesting that the introduction of ester linkages does not impede or alter the inherent crystalline structure of PE and hence retains a high T_m of 99 °C and a degree of crystallinity of approximately 80%. Although the presence of breakable points resulted in a decrease in T_m compared to HDPE (~130 °C), owing to the energy penalty resulting from incorporation of the in-chain functional groups in crystalline lamellae, the still relatively high T_m and crystallization temperature of PE-18,18 ensured the ease of melt processing and stable work temperature for practical applications.

Mecking and co-workers also synthesized "PE-like" polyester using EG and 1,18-octadecanedicarboxylic acid, which

Scheme 53. Tandem Unsaturation/Cross Metathesis/Hydrogenation Strategies Enable Chemically Recyclable Polyolefins[a]



Scheme 53. continued

[a]Conditions: (1) 10 equiv of acrylate, 1 mol % of HG2, toluene, 100 °C; (2) 1 mol % of $RhCl(PPh_3)_3$, 48 atm H_2, toluene, 140 °C; (3) 10 equiv of $HN(CH_2CH_2OH)_2$, toluene, 120 °C; (4) 1 mol % of $Ti(OBu)_4$, vacuum, 180 °C; (5) 15 mol % of TBD, $HO(CH_2)_2OH$, Ph_2O, 200 °C.

possessed a T_m of 96 °C and tensile properties on par with HDPE (Scheme 52B).[554] Despite its inherent hydrophobic nature and crystallinity, polyester-2,18 underwent rapid and complete degradation by enzymes isolated in vitro. Under industrial composting conditions, the material underwent biodegradation with a mineralization rate (the speed at which a biodegradable polymer degrades into its basic mineral components, such as CO_2 and H_2O) exceeding 95% within a span of 2 months. A comparison study on polyester-18,18 indicated that the incorporation of the EG repeating unit significantly impacted the degradation rates, which could be attributed to the density of ester linkages in the amorphous phase. This innovative Trojan-horse strategy, involving the deliberate incorporation of breakable points for efficient recycling or degradation, has also been explored by introducing a low density of individual in-chain ketone groups in PE chains to enable the photodegradability of reconstructed PE.[555]

In 2022, Coates and co-workers developed a series of methodologies aimed at introducing controlled unsaturation into the backbone of polyolefins, specifically PP and PE, subsequently followed by sequential operations that involved cross-metathesis with 2-hydroxyethyl acrylate and hydrogenation to afford telechelic macromonomers that enable the establishment of chemically recyclable polyolefins based on "oligomer−polymer" closed-loop circularity (Scheme 53A).[556] Specifically, the copolymerization of propylene and butadiene catalyzed by a bridged bisphenylphenoxide−hafnium complex afforded PP with high isotacticity ([*mmmm*] = 0.88) and incorporated in-chain olefin double bonds via 1,4-insertion of butadiene in quantities ranging from 0.25 to 0.40 mol %. The isotactic propylene copolymer (iPP-*co*-BD) resulting from this process, characterized by main-chain unsaturation, was subsequently metathesis depolymerized to yield a telechelic macromonomer P1 using an olefin metathesis catalyst (HG2) and 2-hydroxyethyl acrylate. This was followed by olefin hydrogenation to produce the hydroxy-terminated telechelic macromonomer P2. The obtained telechelic macromonomer P2 (M_n = 10.5 kg mol^{-1}) was subjected to SGP using 1 mol % of $Ti(OBu)_4$ as the catalyst at 180 °C under vacuum for 16 h, facilitating the removal of the in situ generated EG and producing an ester-linked PP material (iPP-*co*-EG) with M_n up to 32.6 kg mol^{-1} and T_m up to 98 °C. The thermal and mechanical properties of this ester-linked PP material were found to be similar to those of LDPE. Critically, the ester-linked PP can be depolymerized back to the telechelic macromonomer P2 in the presence of EG and TBD. Upon heating at 190 °C for 24 h, the process resulted in a 93% conversion of ester linkages back to 2-hydroxyethyl-terminated chains P2, thereby accomplishing closed-loop chemical recycling of a PP-like material.

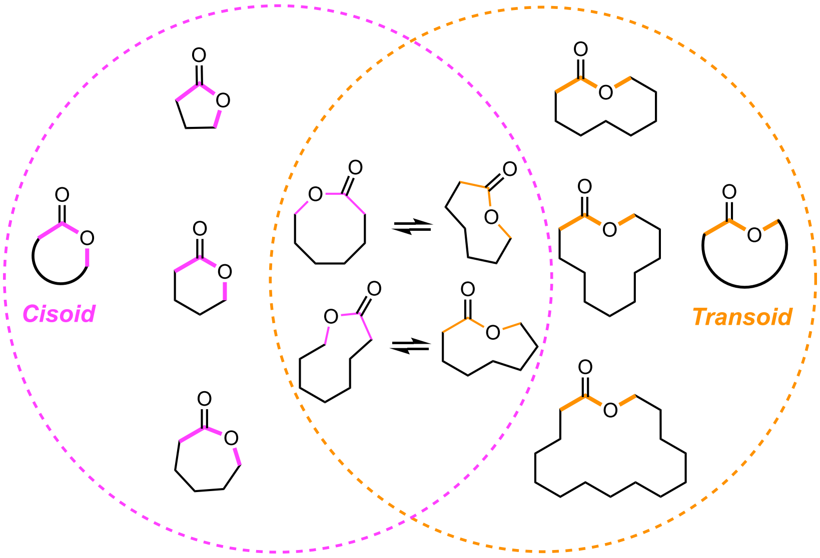
Coates and co-workers subsequently reported a tandem dehydrogenation/cross metathesis/hydrogenation process, effectively transforming postconsumer HDPE into ester-terminated telechelic macromonomers and thereby establishing a closed-loop circularity for chemically recyclable PE-like polyesters (Scheme 53B).[557] More specifically, the introduction of controlled unsaturation into the backbone of HDPE was facilitated by employing an Ir−POCOP pincer catalyst at 200 °C under vacuum conditions, which removed the generated hydrogen. Subsequent cross metathesis with an excess of 2-hydroxyethyl acrylate followed by hydrogenation yielded the telechelic macromonomer P1. Repolymerization of P1 via transesterification catalyzed by $Ti(OBu)_4$ led to the production of a linear polymer, RP1, which exhibited brittleness due to its relatively low molar mass (M_w = 33 kg mol^{-1}).

To enhance the M_w values and hence the mechanical properties of the chemically recyclable polyester, a trifunctional cross-linker was employed to introduce a controlled degree of branching in the repolymerized material. Accordingly, P1 was subjected to 10 equiv of diethanolamine, leading to a mixture of macromonomers ([P1 + P2]) with ∼8 mol % of amide incorporation relative to the total functionalities. Subsequently, these resultant macromonomers (P1 + P2) were polymerized via transesterification, yielding a branched polymer with a M_w of 80.3 kg mol^{-1} and a T_m of 132 °C, comparable to those of HDPE. This branched polymer exhibited comparable mechanical performance to the initial postconsumer waste HDPE with a yield strength of 18 MPa and a strain at break of 970%. To close the recycling loop, depolymerization of the branched polyester material was performed using TBD as a catalyst and excess EG. This process was able to regenerate the telechelic macromonomers with a conversion exceeding 95%, thereby demonstrating the potential for waste PE materials to be chemically recycled.

Recently, Coates and co-workers further introduced a "bottom-up" synthesis approach for the production of unsaturated HDPE by copolymerizing ethylene with dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-3,5-dicarboxylate using palladium phosphine−sulfonate catalysts (Scheme 53C).[558] A postpolymerization retro-Diels−Alder reaction was subsequently carried out to unveil the latent double bonds within the polymer backbone. The spacing of these double bonds in the resulting PE segments could be easily controlled by adjusting the concentration of the Diels−Alder comonomer during the polymerization process, allowing for the synthesis of unsaturated HDPE with block lengths of 1.2, 1.9, and 3.5 kg mol^{-1}, denoted as P1-a, P1-b, and P1-c, respectively. A similar protocol involving cross metathesis and hydrogenation was employed to generate telechelic ester-terminated PE macromonomers suitable for the production of ester-linked PE. Notably, when the methylene chain spacing between functional groups was extended, the material's thermal and mechanical properties closely resembled those of conventional PE. For example, RP-1-a, RP-1-b, and RP-1-c were observed to have T_m values of 127.4, 130.6, and 133.9 °C, respectively.

In 2023, Miyake and co-workers developed the synthesis of chemically recyclable polyolefin-like materials with a wide spectrum of mechanical properties (Scheme 53D).[559] More specifically, ester-linked multiblock olefin copolymers were constructed via ruthenium-catalyzed dehydrogenative SGP of (linear) hard and (branched) soft oligomeric telichelic diols, which were prepared via ruthenium-mediated ring-opening metathesis polymerization of cyclooctenes in the presence of a suitable chain-transfer reagent followed by hydrogenation. The resulting multiblock copolymers exhibited a diverse range of

Scheme 54. Cisoid and Transoid Conformations of Ester Bonds Where Colored Bonds Signify Conformationally Locked Bonds



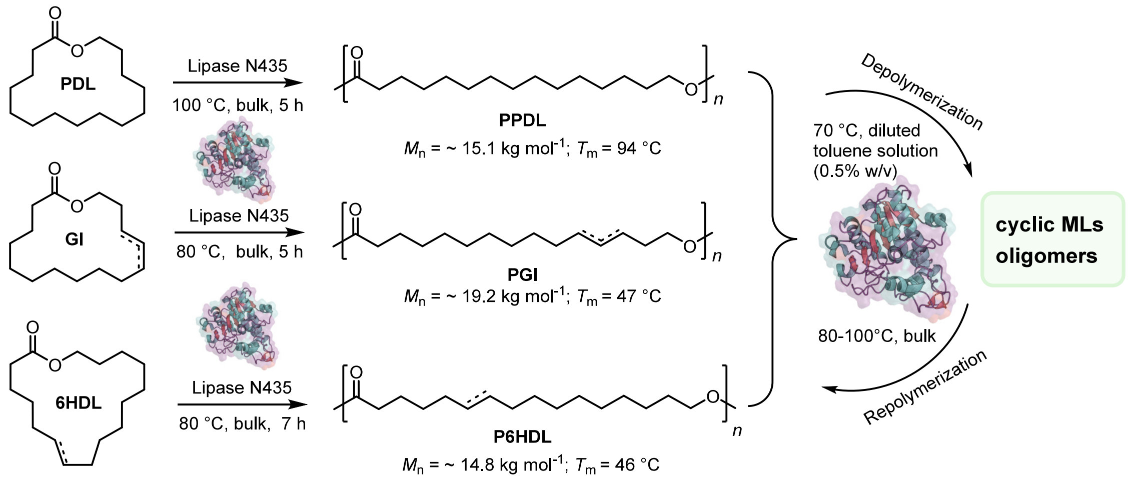
mechanical properties, ranging from elastomers to plastomers to thermoplastics. This variability was achieved by adjusting the ratio of hard and soft oligomeric building blocks, resulting in high T_m values ranging from 106 to 128 °C and low T_g values ranging from −47 to −60 °C. These materials also demonstrated excellent thermostability with $T_{d,5\%}$ values ranging from 405 to 421 °C, rendering them suitable for a multitude of applications. By increasing the proportion of hard components, the crystallinity of the polymers significantly increased, ranging from 0 to 68%. Moreover, both E and σ_B experienced substantial enhancements, with E values increasing from 580 kPa for PE0 (with 100% soft oligomeric building blocks) to 800 MPa for PE100 (with 100% hard oligomeric building blocks) and σ_B values increasing from 40.5 kPa for PE0 to 24.7 MPa for PE100. Remarkably, all multiblock polymers exhibited an average ε_B exceeding 700%. These materials also displayed tunable U_T within a range from 0.19 to 150 MJ m^{-3}. Another compelling feature of these materials is their recyclability as they can be efficiently deconstructed into their constituent hard and soft components. This hydrogenative deconstructive process was accomplished by treating the materials with a ruthenium catalyst under 40 bar of H_2 at 160 °C in toluene for 24 h, resulting in a ~92% isolated yield. This innovative approach established a closed-loop chemical recycling system, offering an environmentally responsible solution for managing these advanced ester-linked multiblock copolymer materials.

3.3. Enzymatic Polymerization

Polyester synthesis through ROP often involves the use of metal catalysts, which raises concerns about the potential harmful effects of metallic residues, especially for medical applications.[560,561] In response to these concerns, there is a growing interest in developing biodegradable and biocompatible polymers using more sustainable synthesis methods. Enzymatic ROP (eROP) has emerged as a promising "green" alternative to conventional polymerization catalysts for polyester synthesis due to its high selectivity, nontoxic nature, and capability for regio- and stereoselective reactions under mild conditions.[560−565] The selection of enzymes for polymerization processes is influenced by a multitude of factors including enzyme substrate specificity, optimal reaction conditions (such as temperature, pH, and solvent tolerance), enzyme stability and robustness, and reaction kinetics and efficiency as well as practical aspects like cost and availability. Each enzyme operates best under specific conditions, making this a key consideration. Enzymes are typically categorized into six groups, with three of these—oxidoreductases, transferases, and hydrolases—known to facilitate or induce polymerization in vitro. Hydrolases, particularly lipases, are notable for their ability to hydrolyze fatty acid esters at cellular water−lipid interfaces. In organic media, lipases can effectively catalyze ester bond formation, making them widely used in the in vitro synthesis of polyesters through polycondensation or ROP without requiring any cocatalyst. A standout enzyme in enzymatic ROP is *Candida antarctica* lipase B (CALB). Commercially available as Novozym 435, when adsorbed onto macroporous cross-linked beads of PMMA, CALB exhibits versatility with a wide range of substrates. Additionally, this immobilized enzyme is thermostable and maintains activity in various organic solvents. Although the recyclability of aliphatic polyesters produced through enzymatic polymerization has not been extensively explored, it is reasonable to anticipate comparable recyclability between these enzymatically produced polyesters and their chemically synthesized counterparts given their identical polymer structures. Therefore, this section will focus on the enzymatic polymerization of lactones, including 5-, 6-, and 7-membered lactones and their derivatives, as well as MLs that have been demonstrated to be chemically recyclable.

The ROP of lactones mediated by lipases follows an activated monomer mechanism. The active site of a lipase consists of a catalytic triad made up of serine, histidine, and aspartate, all of which are electronically stabilized.[566−568] The reactions catalyzed by lipases proceed through the formation of an intermediate compound known as an acyl−enzyme.[569] Uyama et al. elucidated the mechanism of lipase-catalyzed ROP. First, the lactone substrate binds to the lipase, which promotes ring opening and the formation of an active acyl−enzyme intermediate, also referred to as the enzyme-activated monomer (EM). The polymerization is then initiated by a

Scheme 55. Enzymatic Polymerization and Recycling Enable the Closed-Loop Circularity of MLs



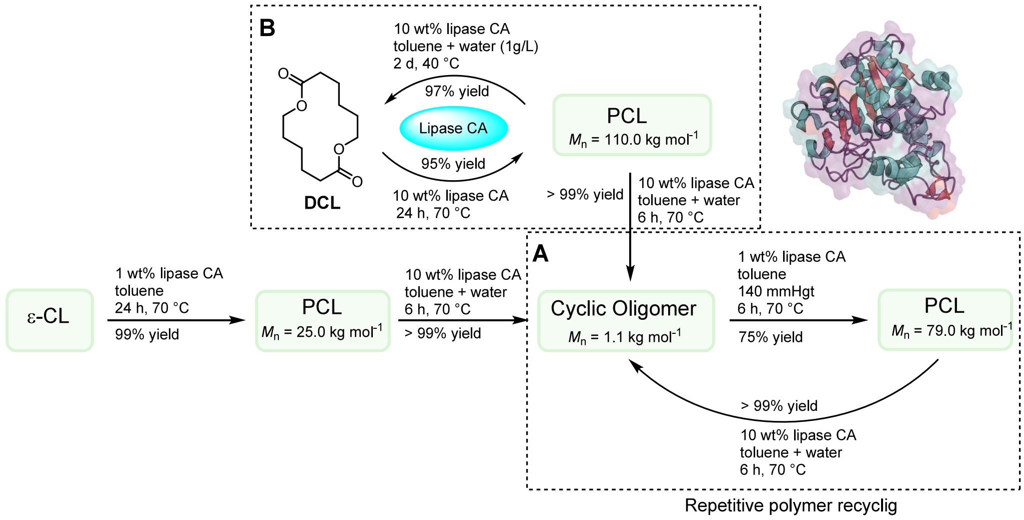
nucleophilic attack from water or alcohol on the acyl carbon of the EM. During the subsequent polymer chain propagation, the terminal hydroxyl group of the growing polymer chain performs a nucleophilic attack on the EM, which results in chain elongation by one unit. Taken together, the formation of the EM represents the rate-limiting step in lipase-catalyzed ROP, which typically follows Michaelis–Menten kinetics.[570]

Intriguingly, lipases exhibit higher polymerizability toward MLs compared to smaller lactones with small to medium ring sizes, which contrasts with anionic and metal-catalyzed ROP of lactones where the ring strain of lactones drives the reaction. Comparative studies conducted by Kobayashi et al. evaluated the ROP of unsubstituted lactones with ring sizes ranging from 6 to 17.[518,562,564,567] It was observed that the relative rates of polymerization dramatically decreased with increasing lactone ring size in metal catalysis. Conversely, lipase-catalyzed reactions exhibit increased reaction rates with larger lactone ring sizes, as reported by Namekawa et al., who employed lipase-catalyzed polymerization using *Pseudomonas fluorescens*/octanol in isopropyl ether at 60 °C, revealing relative orders of polymerization rate of 0.1:0.13:0.19:0.74:1.0 for 7-, 12-, 13-, 16-, and 17-membered lactones, respectively.[571] The superior polymerizability of MLs in lipase-catalyzed ROP, a phenomenon in contrast with nonenzymatic scenarios, can be attributed to the fact that the formation of the enzyme-activated monomer (the rate-limiting step) is promoted by the increased hydrophobicity of the monomer, which corresponds with the hydrophobic nature of the enzyme's active site.[515,518,572] Additionally, these variations are further linked to the lactone's ester bond conformation, which can be either the higher energy cisoid or the lower energy transoid conformation. The latter, which is associated with considerably faster eROP rates, is the exclusive conformation for 10-membered rings and larger, while 7-membered rings and smaller can only adopt the cisoid conformation, as shown in Scheme 54.[515,572,573]

In 2022, Ilarduya and co-workers demonstrated a full circularity based on three PMLs, namely, PPDL, polyglobalide (PGl), and poly(*ω*-6-hexadecenlactone) (P6HDL), facilitated by lipase-catalyzed (de)polymerization processes (Scheme 55). Specifically, the eROP of these three MLs was conducted in bulk at temperatures ranging from 80 to 100 °C under an inert atmosphere.[574] The resulting PMLs exhibited semicrystalline characteristics with T_m values of 94, 47, and 46 °C for PPDL, P6HDL, and PGl, respectively. Additionally, all three PMLs exhibited excellent thermal stability, remaining intact above 300 °C and undergoing a single-step thermal decomposition process with peak degradation rates observed between 359 and 387 °C. The depolymerization of these three PMLs was achieved in highly diluted (0.5% w/v) toluene solutions at 70 °C using an immobilized *Candida antarctica* lipase B (CALB) enzyme (N435), affording MLs with ~95% conversion.[574] The proposed mechanism for this depolymerization process involves the enzyme's active site binding to the polyester chain and facilitating progressive intramolecular transesterifications and alcoholysis reactions, resulting in the formation of macrocyclic oligoesters, primarily monomers and dimers, which follows a Michaelis–Menten kinetic model. This research provides a biosynthetic method for chemical recycling of these PE-like aliphatic polyesters, providing a path toward a circular plastic economy.

Lipases have also been successfully applied in the polymerization of small- to medium-sized lactones, albeit with less favorable kinetics. The first in vitro example of eROP was reported in 1993, demonstrating the catalytic activity of lipases in the ROP of medium-sized lactones, specifically *ε*-CL and *δ*-VL.[575−577] Industrial lipases derived from *Candida cylindracea* (lipase CC), *Burkholderia cepacia* (lipase BC), *Pseudomonas fluorescens* (lipase PF), and porcine pancreas (PPL) were employed in these studies. Notably, lipase PF efficiently catalyzed the bulk polymerization of *ε*-CL at 75 °C over 10 days, yielding PCL with M_n of 7.7 kg mol^{-1} and $Đ$ = 2.4, while *δ*-VL was polymerized at 60 °C, yielding PVL with M_n = 1.9 kg mol^{-1} and $Đ$ = 3.0. Since these initial reports, extensive research has been conducted on the eROP of lactones using lipases, exploring a broad range of lactone sizes. Various factors, such as enzyme source, concentration, temperature, organic solvent, and water content, have been examined to optimize the reaction parameters. While crude lipases like PPL and lipases CR, PC, and PF exhibit polymerization activity, they often required relatively high catalyst loadings (over 40 wt %) for effective polymer production.[560] Conversely, lipase CA displayed high catalytic activity for *ε*-CL polymerization with less than 1 wt % being sufficient to initiate the polymerization.[578,579] It was found that the polymer structure was influenced by the reaction conditions. Bulk polymerization resulted in linear polymers, while the use of organic solvents favored the formation of cyclic structures.[580] A noteworthy

Scheme 56. **Lipase-Catalyzed Recycling of PCL into Cyclic Oligomers (A) and Exclusive *ε*-CL Dimer (B) That Can Be Repolymerized**



achievement by Gross and co-workers was the production of the highest molar mass PCL to date with M_n up to 44.8 kg mol^{-1}, which was accomplished by performing eROP of *ε*-CL using Novozyme 435 as the catalyst in toluene at 70 °C, achieving 85% conversion within 4 h.[581]

Matsumura and co-workers reported the enzymatic degradation of PCL in the presence of water, which resulted in oily PCL oligomers with a M_n of 1.1 kg mol^{-1}. Interestingly, these PCL oligomers were capable of repolymerization under 70 °C in toluene with a 10 wt % of lipase CA catalyst, leading to the formation of PCL with a M_n up to 79.0 kg mol^{-1} (Scheme 56A).[582] In addition to this, the same research group found that the yield of dimeric *ε*-CL (DCL) increased with decreasing PCL concentration. At a concentration of 1 g/L PCL in toluene, PCL can be selectively transformed into the cyclic dimer of *ε*-CL, *c*(CL)$_2$, with a yield of 97% under optimized depolymerization conditions (e.g., 2.0 g of PCL, 4.0 g of water, 200 mg of lipase CA, and 1.0 L of toluene). Lipase CA also demonstrated effective polymerization of the cyclic dimer at 70 °C, resulting in PCL with a M_n of 18.0 kg mol^{-1}, further advancing the field of sustainable polymer recycling (Scheme 56B).[583]

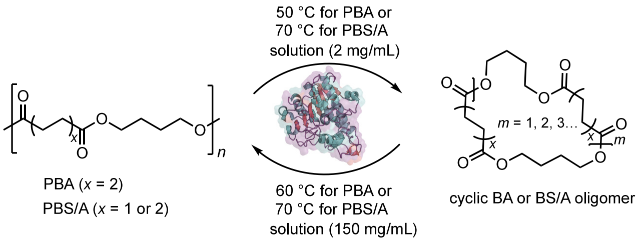
Similarly, through extensive exploration of *δ*-VL polymerization using various lipases from different sources and optimized polymerization conditions, Uyama and co-workers successfully synthesized PVL with a low M_n of 3.2 kg mol^{-1} in isooctane at 45 °C, achieving a high monomer conversion of 98%, utilizing lipase CC derived from *Candida cylindracea* as the catalyst.[584] Furthermore, Meijer and co-workers managed to produce higher molar mass PVL with a M_n of up to 19.0 kg mol^{-1} by conducting the polymerization in a "dry" conditions (to prevent water initiation) using lipase-N435 as the catalyst in toluene at 45 °C.[515]

Prior to the metal-catalyzed ROP of *γ*-BL under extremely low temperature and high monomer concentration,[430] *γ*-BL was subjected to polymerization using lipases, which resulted in the formation of oligomers with $M_n < 1.0$ kg mol^{-1}. Marchessault and co-workers reported the formation of oligomers from *γ*-BL with conversions ranging from 25% to 42% using porcine pancreatic lipase (PPL) or lipase PS30 (from *Pseudomonas cepacia*) as catalyst in *n*-hexane at 60 °C for 430 h.[428] Similarly, Shen and co-workers obtained P*γ*BL oligomers using lipase from *Pseudomonas* sp. as the catalyst in bulk at 45 °C for 20 days, albeit with a low conversion of 8%.[585]

The eROP of 2,5-morpholinediones was first reported in 1999 by Feng et al., who demonstrated the synthesis of polydepsipeptides from 2,5-morpholinediones bearing various alkyl substituents (methyl, isopropyl, *sec*-butyl) at the 3 or 6 position, employing different lipases as catalysts, including PPL, *Pseudomonas* species, *Pseudomonas cepacia*, and lipase N-435.[586−588] The ROP occurred at the ester bond selectively and achieved high conversions of up to 92% at temperatures of 100−130 °C. The resulting polymers had carboxylic acid and hydroxyl end groups and exhibited M_n up to 30 kg mol^{-1}. Increasing the water content in the reaction system was found to enhance the reaction rates and decrease the molar mass of the polymers. Steric effects also influenced the ring opening, particularly for monomers with a methyl substituent at the 6 position (lactic acid derivatives), which showed lower conversions. The polymerization of 2,5-morpholinediones with an isopropyl group at the 3 position (valine moiety) in different optical configurations resulted in materials with significantly lower optical rotations compared to those obtained via Sn(Oct)$_2$-catalyzed ROP.[587] Notably, racemization of 6(*S*)-methyl-2,5-morpholinedione was observed during PPL-catalyzed polymerization, underscoring the susceptibility of amino acids and lactic acid residues to racemization in the PPL-catalyzed ROP of 3- and/or 6-substituted 2,5-morpholinediones.[588]

In 2003, Matsumura and co-workers explored the lipase-catalyzed transformation of poly(butylene adipate) (PBA) and poly(butylene adipate-*co*-succinate) copolymers (PBS/A) into cyclic oligomers that can be repolymerized (Scheme 57).[384] In this work, PBA with a M_w of 22.0 kg mol^{-1} was almost quantitatively converted (98%) into the corresponding cyclic BA oligomers, primarily dimers, using lipase CA in a dilute toluene solution (2 mg of polymer/1 mL of toluene) containing 5 mol % of water at 50 °C. These cyclic BA oligomers were then repolymerized to generate high molar mass PBA with an M_w of 52.0 kg mol^{-1} in 86% yield when catalyzed by the same lipase CA under azeotropic dehydration

Scheme 57. Lipase-Catalyzed Recycling of PBA or PBS/A Copolymer into Cyclic BA or BS/A Oligomers That Can Be Repolymerized



conditions at 60 °C for 6 h. The authors also described the depolymerization of PBS/A with a M_w of 98.0 kg mol^{-1} and a succinate to adipate molar ratio of 4:1 using 100 wt % of lipase CA at 70 °C for 4 h. This process led to cyclic BS/A oligomers, primarily consisting of the cyclic BS/A dimer and trimer. The obtained cyclic (BS/A) oligomers were repolymerized by lipase CA in toluene under azeotropic dehydration conditions at 70 °C for 6 h, yielding PBS/A with an M_w of 43.0 kg mol^{-1} and $Đ$ of 1.5 in a yield of 62%. Notably, the molar ratio of succinate and adipate remained unchanged before and after repolymerization.

In 2008, Matsumura and co-workers expanded their prior research to further examine the lipase-catalyzed ROP of pure (i.e., solely dimers, trimers, or tetramers) cyclic oligomers.[386] Specifically, the isolated yields of the cyclic BA monomer, dimer, trimer, and tetramer were 6, 47, 17, and 5 wt %, respectively. ROP of each these cyclic BA oligomers was performed using lipase CA (20 wt %) in a concentrated toluene solution (300 mg mL^{-1}) at 60 °C for 24 h. Although cyclic BA dimers, trimers, and tetramers polymerized faster than the cyclic BA monomer, it was the monomer that resulted in the PBA with the highest M_w (173 kg mol^{-1}, $Đ = 1.6$), while the polymers obtained from the BA dimer and trimer had lower M_w of 63.8 and 55.1 kg mol^{-1}, respectively. This phenomenon was explained by the slower ring opening of the cyclic monomer, which resulted in a lower initiator concentration compared to that produced by the cyclic BA dimer and trimer.

These findings together with observations that cyclic BS oligomers, derived from the lipase-catalyzed depolymerization of PBS, can be subjected to lipase-catalyzed polymerization to generate high molar mass PBS (see section 2.4.4) indicate that the lipase-catalyzed depolymerization of polyesters in dilute organic solvent for the generation of repolymerizable cyclic oligomers presents a practical approach, applicable to different types of polyesters. Notably, diol/diacid-type polyesters can be transformed exclusively into cyclic oligomers with precise stoichiometry of the two monomer units, mitigating the challenges associated with traditional SGP scenarios where an exact stoichiometry of the diol and diacid is required.[589] Therefore, this biocatalytic approach represents a promising strategy for the establishment of closed-loop circularity in aliphatic polyester production and recycling, fostering greater sustainability in the polymer industry.

4. EMERGING AROMATIC AND AROMATIC−ALIPHATIC POLYESTERS

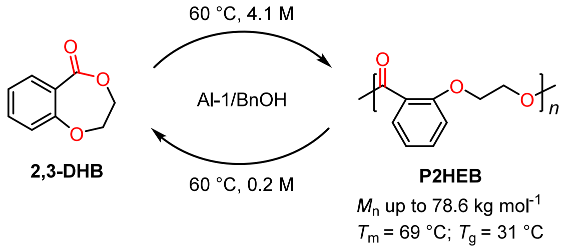
Aside from legacy semiaromatic polyesters (such as PET, PBT, and PBAT), a range of more recently developed (semi)-aromatic polyesters has also been reported to be chemically recyclable. Routes to these polyesters include chain-growth polymerization (ROP), SGP, and copolymerization. For the purposes of this review, we focus on those where the chemical recycling of such polyesters has been reported over those where such a process should in theory be possible but has yet to be explored in the open literature.

The incorporation of aromatic units into polymeric backbones has been strategically employed to enhance the thermal and mechanical properties of the resulting materials, capitalizing on the augmented rigidity offered by aromatic ring structures. Aromatic polyesters, exemplified by PET, are extensively utilized in various applications including fibers, resins, and films due to their favorable cost effectiveness, thermal stability, and mechanical properties. However, in contrast to aliphatic counterparts, the primary challenge lies in the degradation and chemical recyclability of aromatic polyesters, which has consequently contributed to the accumulation of plastic waste and raised significant environmental concerns. Therefore, strategies to achieve the recyclability of aromatic polyesters should be explored.

4.1. Chain-Growth Ring-Opening Polymerization

In 2016, Shaver and co-workers reported the first example of a ROP-derived polyester with an aromatic ring incorporated into the backbone.[590] They investigated the ROP of 2,3-dihydro-5*H*-1,4-benzodioxepin-5-one (2,3-DHB) using a salen-supported aluminum complex, Al-1 (Scheme 31), as a catalyst, yielding the corresponding aromatic−aliphatic polyester poly(2-(2-hydroxyethoxy) (P2HEB) with a M_n of up to 78.6 kg mol^{-1} (Scheme 58). Notably, this polyester contains both aromatic and aliphatic linkages within its polymer backbone, conferring several unique properties that differentiate it from conventional aliphatic polyesters, such as a relatively high T_g.[591] P2HEB is a semicrystalline material with a T_m of 69 °C and a T_g of 31 °C. The conversion of monomer (2,3-DHB) was found to be higher at lower temperatures and/or higher initial monomer concentrations. This observation, consistent with a typic LCT monomer, prompted an investigation into the reversible polymerization and depolymerization of P2HEB, both of which could be catalyzed by Al-1. To illustrate reversibility, a one-pot reaction with an initial monomer concentration of 4.1 M was set up. After 6 h at 60 °C, a monomer conversion of 82% was achieved. The addition of toluene led to an apparent concentration of 2,3-DHB of 0.2 M, causing depolymerization and a resulting mixture with a ratio of 2,3-DHB to P2HEB of 94:6. The reaction was then reconcentrated under vacuum to obtain an apparent concentration of 2,3-DHB of 4.1 M, resulting in 84% monomer conversion and the regeneration of P2HEB after heating at 60

Scheme 58. Polymerization−Depolymerization Equilibrium Achieved by Manipulating Initial 2,3-DHB Concentration in the Presence of salen-Supported Aluminum Complex



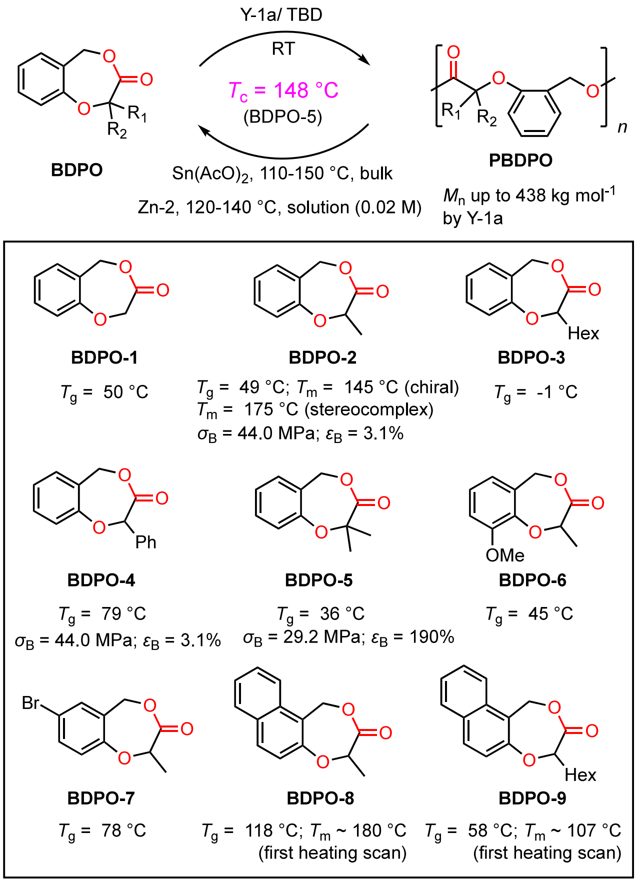
°C for 6 h. Importantly, no degradation products were generated, demonstrating a clean and selective pathway for recycling the semiaromatic polyester back to its monomer state.

In a study addressing the limited thermal stability of PDHB ($T_{d,5\%} \approx 180$ °C), Lizundia and co-workers investigated the effects of substituents at the meta position of the benzene ring on the polymerization and depolymerization kinetics.[592] Utilizing the Al-1 catalyst, they observed that electron-withdrawing groups accelerated the degradation rates and enabled selective depolymerization back to cyclic monomers in just 10 min at 110 °C. Notably, polymers P(R-DHB) with R = Me, OMe, F, and Br exhibited improved thermal stabilities with $T_{d,5\%}$ ranging between 230 and 260 °C. In 2023, Zhu and co-workers synthesized a series of semiaromatic monomers (DHB-R and DHN-R, R = Me and Et) from aromatic hydroxy acids and epoxides.[593] The ROP of these monomers produced high molar mass semiaromatic polyesters P(DHB-R) and P(DHN-R). These polymers showcased high thermal stability with $T_{d,5\%}$ between 335 and 350 °C. A switch from a benzene ring to a naphthalene ring in the polymer backbone significantly boosted the T_g from 49 to over 100 °C. The mechanical properties of these polymers varied, from P(DHB-Me) being strong but brittle with an σ_B of 33.69 ± 5.39 MPa, an E of 2.17 ± 0.36 GPa, and an ε_B of 10.91 ± 2.15% to P(DHB-Et) being highly ductile with an ε_B of 762.63 ± 94.40%. Notably, P(DHB-R) and P(DHN-R) can be effectively and selectively depolymerized back to the corresponding monomer when catalyzed by 5 mol % of Zn-2 at 120 °C for P(DHB-R) or 10 mol % of TBD at 140 °C for P(DHN-R) in dilute solution.

On the other hand, Zhu and co-workers reported the synthesis of a structural isomer of 2,3-DHB, specifically 5*H*-1,4-benzodioxepin-3(2*H*)-one (BDPO), in 2021.[594] This biobased seven-membered lactone incorporates both aromatic and aliphatic moieties, uniquely characterized by nonadjacent ester groups in relation to the aromatic moieties. This structural arrangement significantly amplifies the reactivity of the ester bond, thereby enhancing the polymerization activity. Notably, when the Y-1a catalyst was applied, the polymerization of BDPO-1 achieved a remarkably high TOF of up to 2.1×10^5 h^{-1}. Through substituting at the *α* position of BDPO-1, monomers BDPO-2−5 were derived. This adjustment not only resolved the issue of the poor solubility of PBDPO-1 but also diversified the material performance of BDPO-based semiaromatic polyesters. Importantly, these enhancements were achieved without significantly compromising the high polymerization activity, as evidenced by a high TOF of up to 5.9×10^4 h^{-1}. The resulting semiaromatic polyesters achieved high M_n of up to 438 kg mol^{-1} and demonstrated high thermostability with $T_{d,5\%}$ from 275 to 331 °C and tunable T_g values from −1 to 79 °C. The stereocomplex formation between complementary polymer enantiomers, specifically P(*R*)BDPO-2 and P(*S*)BDPO-2, which each displayed a T_m of 154 °C, demonstrated a notable enhancement in the crystallization rate and T_m, resulting in a highly crystalline material with a T_m of up to 175 °C. The geminal dimethyl-substituted monomer, BDPO-5, was chosen as an exemplary case for thermodynamic study. The thermodynamic parameters were determined as $\Delta H_p^\circ = -27.3$ kJ mol^{-1} and $\Delta S_p^\circ = -64.8$ J mol^{-1} K^{-1}, corresponding to a T_c of 148 °C at $[M]_0 = 1.0$ M in toluene. Both solution depolymerization, catalyzed by 2 mol % of Zn-2 at 120−140 °C in toluene (0.02 M), and bulk thermal depolymerization, catalyzed by $Sn(OAc)_2$ at 115−150 °C, of these resulting PBDPOs afforded their constituent monomers with recovery yields of 93−98%, demonstrating the effective chemical recyclability of these semiaromatic polyesters.

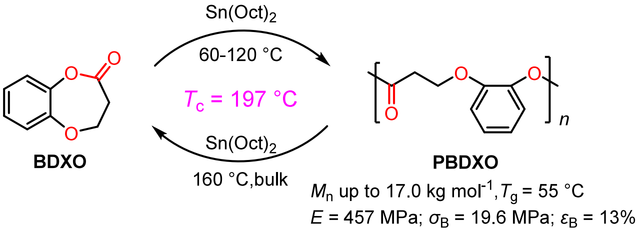
Subsequently, the same group targeted a series of BDPO-based monomers with differing benzene ring substitution, including the introduction of methoxy, bromo, and naphthalene groups, with the goal of tailoring the properties of the resultant semiaromatic polyesters (Scheme 59).[595] These monomers retained high polymerization activity with a TBD catalyst and led to high M_n (up to 297 kg mol^{-1}) semiaromatic polyesters. Introducing a bromo substituent to BDPO-2 led to the monomer BDPO-7, and the resultant polyester exhibited a slight improvement in T_g, increasing from 49 to 75 °C compared to the nonsubstituted PBDPO-2. Further engineering of the BDPO-2 with a naphthalene group, resulting in BDPO-8, significantly enhanced the T_g of the resulting polymer, reaching 118 °C. Interestingly, the copolymerization of BDPO-3 with BDPO-8 enabled control of the polyester mechanical properties, enabling a transition from brittleness to ductility. This demonstrates the remarkable versatility of these semiaromatic polyesters, capable of tailoring their mechanical properties to suit various applications. Bulk chemical recyclability of the produced PBDPO-6−9 was achieved by employing $Sn(OAc)_2$ as the catalyst at 110 °C in the presence of PEG, resulting in high yields ranging from 86% to 99%.

Scheme 59. Substitution Engineering of Both Aromatic and Aliphatic Segments To Enhance Both the Recyclability and the Material Performance



In 2023, Wang and co-workers reported a distinct structural isomer of 2,3-DHB taking a different approach by switching the ester bond of 2,3-DHB with the connecting position of the benzene ring (Scheme 60). This design led to a seven-membered aromatic lactone, 3,4-dihydro-2*H*-benzo[*b*][1,4]-dioxepin-2-one (BDXO), that could be obtained through a one-step Baeyer–Villiger oxidation.[596] The ROP of BDXO was successfully achieved in both bulk and solvent conditions, catalyzed by $Sn(Oct)_2$ at 80 °C, yielding well-defined PBDXO with M_n of up to 17.0 kg mol^{-1} and broad $Đ$ ranging from 1.4 to 2.1, likely attributed to the dynamic nature of the phenol ester bond. Thermodynamic analysis of the BDXO polymerization revealed a T_c of 197 °C at $[M]_0$ = 1.0 mol L^{-1} in toluene with $\Delta H_p^\circ = -14.5$ kJ mol^{-1} and $\Delta S_p^\circ = -30.9$ J mol^{-1} K^{-1}. The resulting PBDXO polymer exhibited moderate thermal properties with $T_{d,5\%}$ values ranging from 232 to 258 °C and T_g values between 40 and 55 °C, which were dependent on the polymer molar mass. In addition, PBDXO with M_n = 17.0 kg mol^{-1} exhibited a typical brittle fracture with ε_B = 13%, σ_B = 19.6 MPa, and E = 457 MPa. To evaluate its biocompatibility, a film of PBDXO was cocultured with NIH-3T3 mouse fibroblasts for several days. Observations of robust cell proliferation and growth indicated excellent cell viability, thereby confirming the high biocompatibility of the PBDXO film. Bulk thermal depolymerization of PBDXO to its constituent monomer BDXO was achieved at 160 °C using 2 wt % of $Sn(Oct)_2$ catalyst under reduced pressure. Utilizing a distillation apparatus, a recovery yield of over 92% and a purity of up to 96% were achieved. Moreover, the recycled BDXO monomer could be directly repolymerized to obtain PBDXO with the same quality as the virgin polymer, showcasing an effective and sustainable closed-loop cycle.

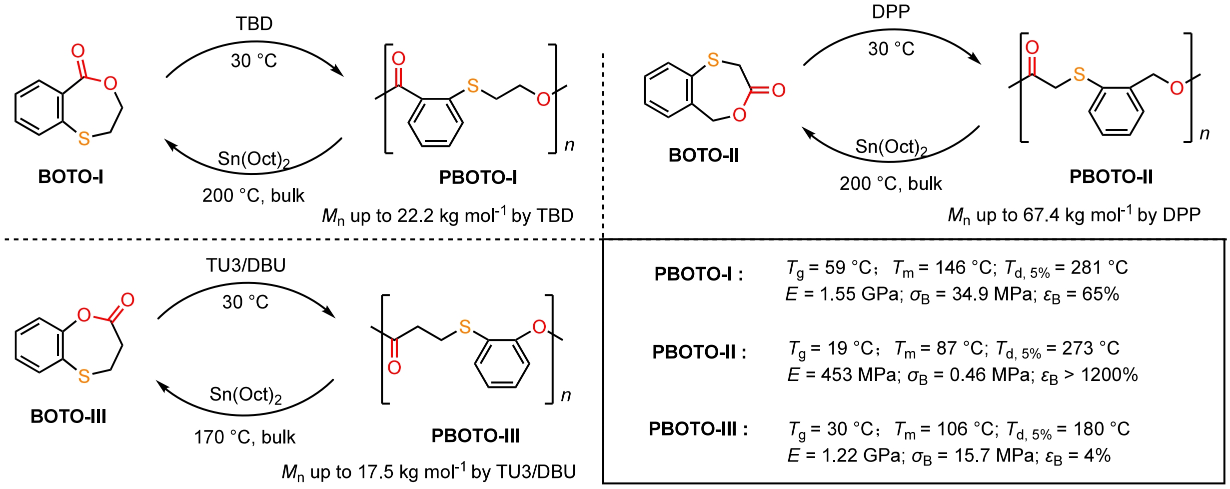
Scheme 60. Chemically Recyclable Semiaromatic Polyester with a Dynamic Phenol Ester Bond



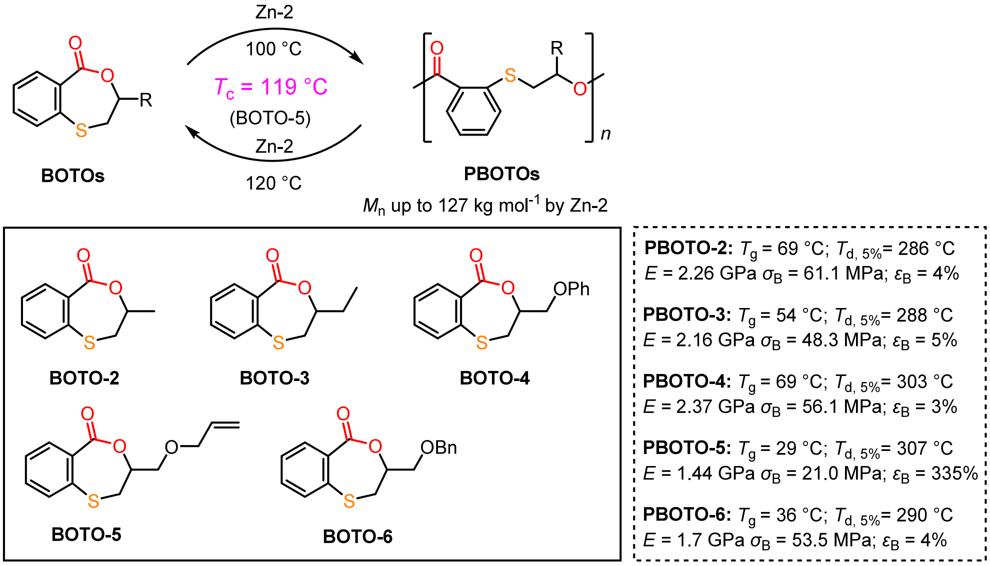
In 2021, Du, Li, and co-workers systematically investigated three constitutional isomers of benzothiacaprolactones (BOTO-I, BOTO-II, and BOTO-III) to elucidate the influence of structural isomerization on the polymerizability, depolymerizability, as well as thermal and mechanical properties, providing insights into the structure–performance relationship of chemically recyclable semiaromatic polyesters (Scheme 61).[597] Specifically, BOTO-I is a less strained monomer with an equilibrium monomer concentration, $[M]_e$, value of 0.15 M at 30 °C, and its TBD-catalyzed ROP led to the corresponding P(BOTO-I) with moderate molar mass of M_n up to 22 kg mol^{-1}. BOTO-II, however, is a highly strained monomer with a small $[M]_e$, and its ROP catalyzed by DPP achieved high conversion with good control. In the case of BOTO-III, a phenolic benzothiacaprolactone, its ROP catalyzed by TBD or DBU/TU is successful, albeit with relatively poor control due to severe transesterification associated with phenolic esters. Both P(BOTO-I) and P(BOTO-II) exhibited thermal stability up to 270 °C, whereas the thermal stability of P(BOTO-III) is comparatively lower. All three polymers are semicrystalline but with slow crystallization rates. Among them, P(BOTO-I) showed the highest T_m of 146 °C, a T_g of 59 °C, and the most favorable mechanical properties. The bulk thermal depolymerization of P(BOTO) materials, catalyzed by $Sn(Oct)_2$ at temperatures ranging from 170 to 200 °C through sublimation, proved to be a general and efficient method for the selective recycling of pure BOTO monomers, resulting in recovery yields of up to 95%.

Subsequently, Fan and co-workers synthesized a series of BOTO-I derivatives with varied substitutions through a facile one-pot synthesis from thiosalicylic acid and epoxides (Scheme 62).[598] The resulting BOTO2–5 were then polymerized in toluene at 100 °C using Zn-2 as the catalyst and *p*-tolylmethanol as the initiator, yielding semiaromatic polyester with M_n up to 127 kg mol^{-1}. Kinetics studies revealed similar polymerization activities of these monomers, suggesting the substitution on the ε position of the monomer has only a subtle impact on the polymerization activity. Further

Scheme 61. Influence of Structural Isomerization on the Chemically Recyclable Semiaromatic Polyesters through Comparing Three Constitutional Isomers of Benzothiacaprolactones, BOTO-I, BOTOII, and BOTO-III



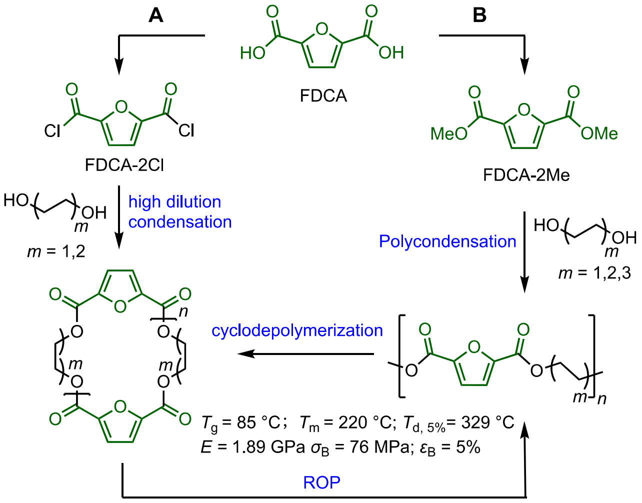
Scheme 62. Design of Chemically Recyclable Aromatic Polyesters with Diverse Functionalities Derived from Seven-Membered PBOTO Derivatives



investigation into the thermodynamic properties of BOTO-5 yielded $\Delta H_p^\circ = -18.9$ kJ mol^{-1} and $\Delta S_p^\circ = -48.1$ J mol^{-1} K^{-1}, corresponding to a T_c of 119 °C at $[M]_0 = 1.0$ M in toluene. The resulting polymers, PBOTOs, exhibited high thermal stability with $T_{d,5\%}$ ranging from 286 to 307 °C and T_g values varying from 29 to 69 °C, achieved by modifying the bulkiness and flexibility of the side chains. By adjusting factors such as stereocomplexation and side-chain flexibility, the physical and mechanical properties of the PBOTOs can be tuned, resulting in a range of high-performance properties, including enhanced thermal stability, crystallinity (T_m up to 209 °C), as well as polyolefin-like mechanical strength, ductility, and toughness, (e.g., σ_B = 21.0 MPa, ε_B = 335%). Depolymerization of PBOTOs was accomplished using Zn-2 (2 mol %) as the catalyst in toluene at 120 °C. Specifically, PBOTO-2 and PBOTO-3 were depolymerized with 98% and 89% conversions to monomer, respectively. The depolymerization of PBOTO-4 to PBOTO-6 required a higher Zn-2 loading of 4 mol % to achieve similar conversions of 89−97%. Postfunctionalization studies, including "click" reactions, oxidation reactions, cross-linking reactions, and deprotection reactions, were conducted to expand the scope of functionalized aromatic polyesters for value-added applications.

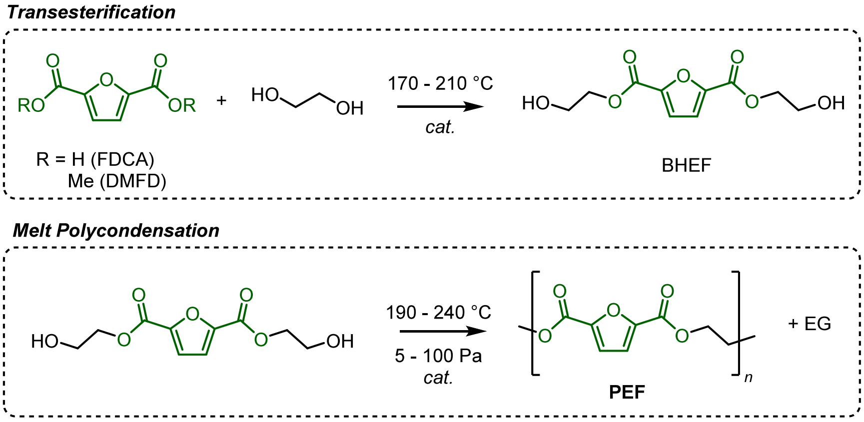
Furanic polyesters, chiefly poly(ethylene furanoate) (PEF) and poly(butylene furanoate) (PBF), derived from 2,5-furandicarboxylic acid (FDCA), are desirable materials due to their low permeability,[599] high-performance properties,[600,601] and compatibility with existing processing and recycling infrastructures (Scheme 63).[602] Additionally, their potential to be manufactured from renewable feedstocks positions them as promising more sustainable alternatives to traditional fossil-based semiaromatic polyesters such as PET and PBT. The production of furanic polyesters has typically relied on traditional SGP methods. However, this technique comes with significant drawbacks, including the need for byproduct removal, long reaction times, and the resulting polymers' relatively low molar mass. Obtaining high molar mass polymers is challenging without employing extreme reaction conditions, which, unfortunately, can intensify polymer discoloration. This constraint is especially problematic in the SGP of FDCA due to the inherently lower thermal stability of furanic compounds. The obstacles associated with traditional SGP techniques of FDCA underline the need for more efficient and sustainable methods in the production of these promising materials.

Scheme 63. Synthesis of PEF and PBF by ROP of Cyclic Oligo(alkylene 2,5-furandicarboxylate)s Prepared by Either Condensation in Solution (A) or Cyclodepolymerization (B)



ROP stands out as a promising alternative route to circumvent the inherent limitations of traditional SGP, providing a milder, byproduct-free, and controlled approach for producing these sought-after materials. However, for this strategy to be effective, it is crucial to develop a feasible synthesis method for the required cyclic precursors. In 2015, Morbidelli and co-workers developed the synthesis of PBF via ROP of a mixture of cyclic oligomers of butylene-2,5-furandicarboxylate, denoted as $c(BF)_n$ (Scheme 63). The resulting PBF had a low M_n in the range of 5.8−7.8 kg mol^{-1}. The $c(BF)_n$ was derived from 2,5-furandicarboxylic acid and 1,4-butanediol, although the yield was relatively low, between

Scheme 64. Outlined Synthesis of PEF via SGP



18% and 21%.[603] Almost concurrently, Muñoz-Guerra et al. synthesized higher molar mass PBF from either $c(\mathrm{BF})_n$ or isolated dimer, trimer, and tetramer species.[604] These individual species were isolated from the $c(\mathrm{BF})_n$ mixture using preparative high-performance liquid chromatography (HPLC). The polymerizations were carried out at 220 °C with $\mathrm{Sn(Oct)_2}$ serving as the catalyst. The resultant PBF, which was derived from the individual cyclic species and their mixtures, was obtained in comparable yields and with M_w ranging from 58 to 65 kg mol^{-1}, indicating that the size of the oligomer had minimal influence on the polymerization. Notably, by employing high-dilution condensation and thermal cyclodepolymerization methods, the isolated yield of $c(\mathrm{BF})_n$ was significantly improved to 60−67%. In a parallel development, these researchers prepared higher molar mass PEF with an M_w of 55 kg mol^{-1} from the ROP of cyclic ethylene 2,5-furandicarboxylate oligomers, $c(\mathrm{EF})_n$.

In 2018, Morbidelli and co-workers conducted a comprehensive study to optimize the production of $c(\mathrm{EF})_n$ through thermal cyclodepolymerization of PEF with $M_\mathrm{n} < 5$ kg mol^{-1} by exploring a variety of solvents including polar aprotic and aromatic solvents and ionic liquids (Scheme 63B). Among these, 2-methylnaphthalene was found to be the most effective solvent due to PEF's high solubility in it.[605] Specifically, $c(\mathrm{EF})_n$ oligomers were obtained by depolymerizing low molar mass linear PEF oligomers over a period of 6−8 h using high-boiling solvents such as 2-methylnaphthalene or 1,2-dichlorobenzene, achieving yields exceeding 95%, which were obtained as white powders through precipitation. The resulting $c(\mathrm{EF})_n$ was then subjected to ROP, yielding bottle-grade PEF.[606] Notably, while the T_m of the mixture of cyclic oligomers was approximately 370 °C, significantly above the degradation temperature of PEF (~329 °C), the authors exploited the self-plasticizing effect of the polymer itself, which melts at around 220 °C. The rapid polymerization was achieved by initiating the reaction in the presence of a high-boiling, inert liquid plasticizer (33 wt % of tetraglyme) at an optimized polymerization temperature of 280 °C, leading to the production of PEF with a relatively high molar mass ($M_\mathrm{n} > 30$ kg mol^{-1}), conversion exceeding 95%, and color-free PEF products. The ROP-derived PEF, similar to polycondensation-derived PEF, outperforms bottle-grade PET in both thermal and mechanical aspects. It has a higher T_g of 85 °C, offering better ambient thermal stability and additionally a lower T_m (220 °C), which decreases energy consumption during postprocessing. Mechanically, PEF shows a 50% increase in tensile strength (76 vs 50 MPa) and a 70% increase in Young's modulus (1894 vs 1102 MPa), making it more resilient in end-use applications.[606−608]

In 2019, Flores et al. reported the synthesis of cyclic hexamethylene 2,5-furandicarboxylate oligomers, denoted as $c(\mathrm{HF})_n$, which involved enzymatic cyclization of dimethyl 2,5-furandicarboxylate and 1,6-hexanediol diol, using toluene as the solvent and *Candida antarctica* lipase B (CALB) as the catalyst.[609] Following a reaction period of 7 days at 90 °C, the resultant cyclic fraction comprised a mixture of dimer to hexamer species, with the dimer species being dominant. Owing to the high flexibility of the hexamethylene segments, the produced cycles were less strained and could be polymerized via an entropy-driven process. The enzymatic ROP of $c(\mathrm{HF})_n$ was carried out at 100 °C in a high monomer concentration with CALB serving as the catalyst, yielding poly(hexamethylene 2,5-furandicarboxylate) (PHF) with a low M_n of 8.9 kg mol^{-1}. Notably, it was found that PHF could enzymatically degrade to yield the original cyclic oligomers, suggesting the potential for a new biosynthetic route for recycling such furane-based polyesters.

4.2. Step-Growth Polycondensation

The development of sustainable novel semiaromatic polyesters via SGP broadly focuses on application of two types of aromatic monomers: those derived from lignin, such as vanillic acid and ferulic acid, and those derived from carbohydrates, such as 5-hydroxymethylfurfural (HMF) and furfural.[6,610−613] The chemical recycling of emerging step-growth-derived polymers is generally underexplored and, given that many would be valid candidates for hydrolysis/methanolysis/glycolysis-type recycling, should be targeted by researchers in the search for more sustainable polyesters. In this section, we present an overview of recent developments in the chemical recycling of such polyesters.

4.2.1. Poly(ethylene furanoate) (PEF). PEF is a polyester featuring repeat units of FDCA and EG (Scheme 64). It has similarities to PET but displays superior tensile properties as well as improved $\mathrm{O_2}$ and $\mathrm{CO_2}$ barrier properties (see section 4.1).[602,614,615] This is proposed to be due to the increased difficulty in rotation of the furanyl ring in PEF compared to the phenyl ring in PET.[600] Both FDCA[612,616] and EG[615] can be derived from biomass, and the first syntheses of PEF were reported almost contemporaneously to PET,[617,618] but commercialization of the material was hindered by the lack of cost-effective synthesis for FDCA. Recently, this roadblock has been overcome by Avantium, seeking to bring PEF to market imminently.[616]

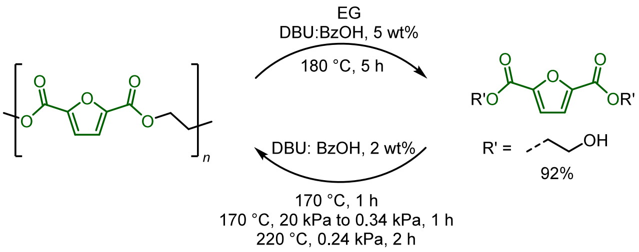
The synthesis of PEF is typically achieved via SGP of FDCA or the corresponding dimethyl ester (DMFD)[617] and EG (Scheme 64).[602,616,619,620] It is worth noting that routes to the synthesis of PEF via ROP are reported, but this methodology is not applied in the commercialized approach to PEF synthesis (vide supra).[604,606] The typical SGP methodology applies a two-step melt polymerization method.[621] First, FDCA or DMFD is combined with EG and heated to 170−210 °C, affecting transesterification to the diglycolic ester of FDCA (BHEF), with concomitant removal of water or methanol. Subsequently, melt polymerization is applied at temperatures from 190 to 240 °C and low vacuum (5−100 Pa) to yield PEF.[617,619,621−623] A range of catalysts can be applied, including tetrabutyl titanoate,[622,624] titanium(IV) isopropoxide,[617,625] tin(II) and alkyltin(IV) salts,[602,621,623] antimony oxide,[626,627] zinc acetate,[619] and aluminum acetylacetonate.[619] A subsequent solid-state polymerization can be applied to increase the molar mass as required.[616,617]

Like PET, PEF can be mechanically recycled and, owing to its similarity to the former, can even be recycled using the same current commercial systems;[616] it can be distinguished from PET using near-infrared sorting. Should some cross-contamination occur, it has been shown that PEF impurities within PET waste streams up to 2% result in no noticeable degradation in the *r*PET's properties nor does it result in hazing.[602] However, much like PET, PEF undergoes degradation (molar mass loss) during mechanical recycling via both hydrolysis and thermal chain scission.[616,623] It has also been demonstrated that the catalyst applied during PEF synthesis can accelerate the decomposition.[623] While application of SSP can regenerate some of the loss in molar mass,[616] the development of chemical recycling for PEF is still clearly appealing.

To this end, several approaches to chemically and enzymatically recycle PEF have been advanced. Methanolysis, glycolysis, and hydrolysis processes are all reported, although they are far less explored than the equivalent processes for PET. In a patent, Sipos et al. described the hydrolysis, glycolysis, and alcoholysis of PEF and related homologue polyesters.[628] Suitable catalysts for these processes are indicated to include metal alkoxides (e.g., sodium and potassium methoxides) and guanidines (e.g., TBD), and application of temperatures of 90−100 °C is specifically highlighted. Broad temperature (from RT to 350 °C) and pressure (0.5−200 bar) ranges are reported to be suitable depending on the choice of alcohol and desired reaction time.

There are a handful of reports in the open literature of catalyzed PEF recycling processes. In 2021, Gabirondo et al. reported the application of an organocatalyst system (DBU:benzoic acid = 1:1) to the glycolysis of PEF (M_n = 12.4 kg mol^{-1}, $Đ$ = 2.6), yielding BHEF (Scheme 65).[629] By applying conditions of 180 °C and 5 wt % of catalyst, 92% conversion to BHEF was obtained within 5 h, with minor side products consisting of oligomers of BHEF. The BHEF was subsequently applied to the synthesis of PEF using the same organocatalyst system; following melt polycondensation and subsequent SSP at 200 °C, PEF with M_n = 11.2 kg mol^{-1} and $Đ$ = 3.4 was obtained. In 2022, the application of a deep eutectic solvent (DES) of urea and $Zn(OAc)_2$ (4:1) to glycolysis was reported by Agostinho et al.[630] Utilizing similar conditions (180 °C, 2 wt % of DES as catalyst), 85% PEF degradation was reported within 1 h, with BHEF being the main product. Interestingly, taking the crude reaction mixture, with the DES catalyst still present, and applying vacuum allowed for resynthesis of PEF (with concomitant removal of EG) with a 69% yield (relative to PEF that had initially depolymerized) of *r*PEF. Improved yields of 91% *r*PEF were obtained through addition of a titanium(IV) butoxide polycondensation catalyst.

Scheme 65. Exemplar Glycolysis of PEF

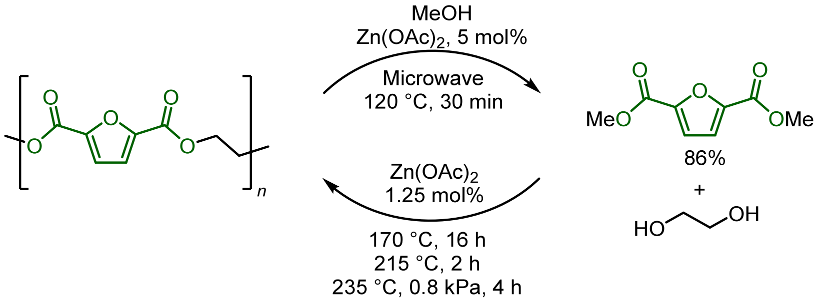


The microwave-assisted methanolysis of PEF (M_n = 3.9 kg mol^{-1}) with a range of ZnX_2 (X = Cl, Br, OTf, OAc, methacrylate) catalysts was reported by Alberti et al. in 2021 (Scheme 66).[631] Utilizing $Zn(OAc)_2$ (1 mol %) at 140 °C, a 51% yield of DMFD was obtained in 10 min or 66% when DMSO was used as a cosolvent. At 5 mol % loading and 120 °C, an 86% DMFD yield was obtained in 30 min. Utilizing these conditions, the authors also showed that DMFD could be effectively recovered from PEF even in the presence of other plastics, although if other polyesters such as PLA and PCL were present they were concomitantly methanolyzed. Further, they demonstrated that PEF could be readily resynthesized from the DMFD obtained through utilizing the same $Zn(OAc)_2$ catalyst. In the same year, Qu et al. reported on the application of ILs as catalysts for the methanolysis of PEF (M_n = 39−41 kg mol^{-1}, $Đ$ = 2.1).[632] A series of tetrabutyl phosphonium ($[P_{4444}]$)-containing ILs with a range of acetate anions was initially screened at a temperature of 130 °C, 5:1 w:w methanol:PEF, and 0.15 mol % of IL catalyst (relative to methanol), with the best activity being $[P_{4444}][OAc]$, giving 99% PEF depolymerization and in 75% DMFD yield in 130 min. A subsequent screen of cations revealed the most effective IL catalyst to be 1-butyl-3-methylimidazolium ([Bmim]) acetate, which achieved 99% PEF depolymerization and 78% DMFD yield in 30 min under the same conditions. This catalyst can be reused 6 times while maintaining its high activity.

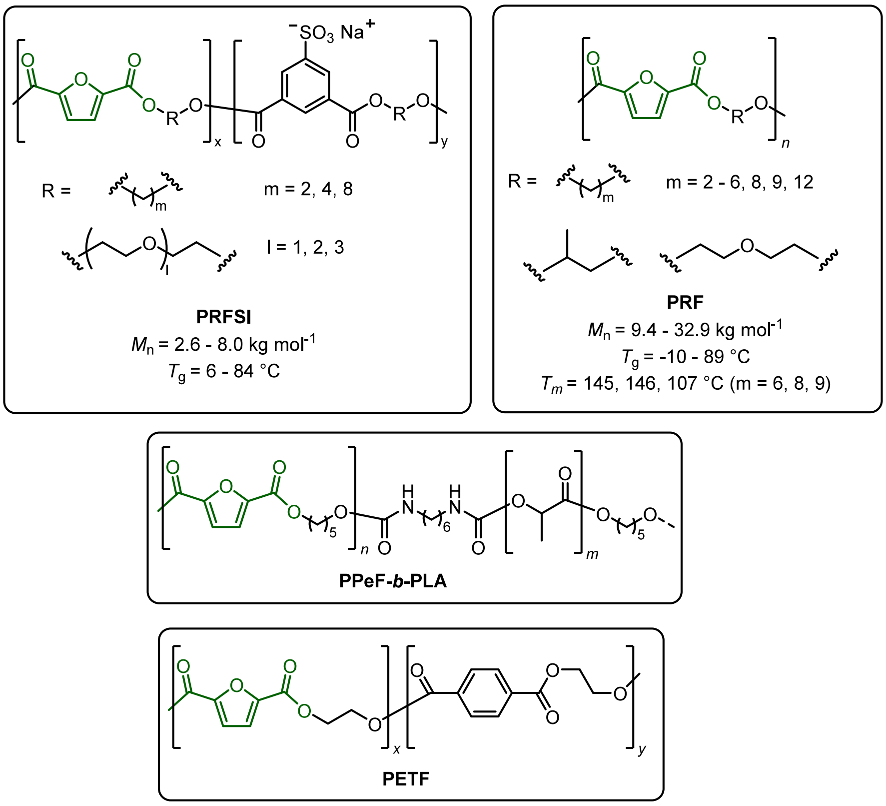
The enzymatic hydrolysis of PEF has also been investigated, with the first reports coming from Pellis et al. in 2016, where they described the application of *Thermobifida cellulosilytica* cutinase 1 (Thc_Cut1).[624] Three different molar mass values (M_n = 6, 10, and 40 kg mol^{-1}) of PEF were trialed, and the samples were incubated at 50 °C in 0.1 M potassium phosphate buffer at pH 7 for 72 h. The major release product was reported to be FDCA, although oligomers up to DP = 4 were also observed. The highest activity was obtained with the highest molar mass sample (M_n = 40 kg mol^{-1}), where 13 mM FDCA was released in 72 h, compared to 5.6 and 10.2 mM FDCA for the M_n = 6 and 10 kg mol^{-1} samples, respectively. The authors noted that all samples were amorphous; hence, differences in sample crystallinity could not explain the differences in enzymatic activity.

Subsequently, Weinberger et al. investigated the combined impacts of crystallinity, particle size, and molar mass on PEF

Scheme 66. Exemplar Methanolysis of PEF



Scheme 67. PEF Homologues and Copolymers Reported for Chemical Recycling



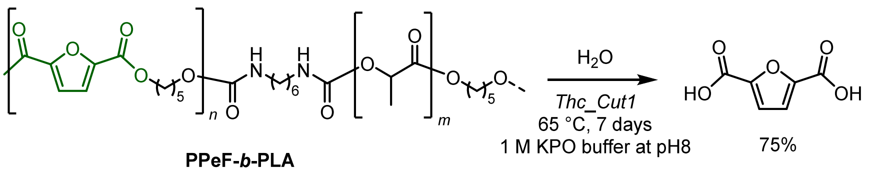
degradation using Thc_Cut1.[633] Two powdered samples of PEF (M_n = 55 kg mol^{-1}, $Đ$ = 1.9, crystallinity = 46%; M_n = 18 kg mol^{-1}, $Đ$ = 1.8, crystallinity < 1%) were prepared at two separate particle sizes each. Degradation studies indicated that enzymatic hydrolysis occurred faster for the low M_n, amorphous sample than for the high M_n, crystalline sample. For the low M_n samples, the particle size of PEF had a minimal impact on the rate, but for the high M_n samples, a significant rate enhancement was found when smaller PEF particles were used. They subsequently compared the activity of Thc_Cut1 with another cutinase from *Humicola insolens* (HiC) for the degradation of amorphous PEF films under a range of conditions. By applying the latter enzyme to PEF degradation, 100% PEF weight loss could be obtained within 72 h under optimized conditions (1 M potassium phosphate buffer at pH 8, 65 °C).

In 2018, Austin et al. investigated the application of both wild-type IsPETase and an IsPETase double mutant (see section 2.3 for further details) to PEF degradation, with both enzymes showing activity for the process and releasing FDCA at 30 °C in 50 mM potassium phosphate buffer at pH 7.2 over 96 h.[350] The authors also noted that DSC data indicated a reduction in the relative crystallinity of the PEF samples, indicating that both enzymes were capable of degrading crystalline regions with the polymer. In 2022, Kawai et al. described the application of an engineered cutinase, Cut190*SS, to the hydrolysis of PEF of two different molar masses (M_n = 27.9 kg mol^{-1}, $Đ$ = 2.7; M_n = 9.2 kg mol^{-1}, $Đ$ = 2.3) as part of a larger study on PET hydrolysis.[634] Applying the enzyme at 63 °C in 0.1 M HEPES−NaOH buffer at pH 9 for 72 h resulted in formation of FDCA and another secondary product, which the authors hypothesized to be HMF. In accordance with results reported by Pellis et al.,[624] they also noted faster hydrolysis for a higher M_n sample (27.9 kg mol^{-1}, 55.6 mM total products; 9.2 kg mol^{-1}, 44.4 mM total products).

4.2.2. PEF Homologues and Copolymers.

Alongside PEF, a large range of homologous polymers with interesting properties can be obtained by alteration of the diol monomer (Scheme 67).[608,614,617] This includes increasing the length of

Scheme 68. Enzymatic Recycling of PPeF-*b*-PLA Copolymers[a]



[a] Recovered FDCA was subsequently reused in the synthesis of PPeF.

the alkyl chain (e.g., $m = 2$ (EG), 3 (1,3-propanediol), 4 (1,4-butanediol), etc.) as well as introducing branching within the alkyl chain (e.g., propylene glycol). Other applied diols include isosorbides, 1,4-benzene dimethanol, and hydroquinone.[614] Such polyesters are again typically synthesized through melt polycondensations, although solution methods have also been investigated, particularly when diols with higher boiling points are utilized.[613,635] In this case, it is typically required that the acid dichloride of FDCA is used over DMFD or FDCA. Other PEF-related homologues include substitutional isomers of 2,5-FDCA, namely, 2,4-FDCA and 3,4-FDCA.[625] PEF copolymers can also be formed, often with the aim of increasing the biodegradability of PEF-type polyesters.[614,620]

The patent literature indicates that typical transesterification methods such as hydrolysis, alcoholysis, and glycolysis are all effective for FDCA-based polyesters including both homologues and copolymers.[628] In 2021, Joshi et al. described the alkaline hydrolysis of an oligomeric PET−PEF copolymer (PETF20, 20 mol % of FDCA; M_n = 1 kg mol^{-1}, Đ = 1.1; Scheme 67).[636] By applying conditions of 90 °C and 1.1 M NaOH for 72 h, they observed a >80% depolymerization of the copolymer and >80% combined diacid yield. In comparison, the depolymerization of pure PET applied under the same conditions yielded ca. 40% depolymerization and diacid yield. The authors proposed the rate enhancement could be due to the higher solubility of PETF20 over PET, which would enhance interactions between the polymers and the solvent molecules (i.e., water), or that the ester linkage within FDCA may be more susceptible to hydrolytic degradation compared to PET.

Enzymatic recycling, both in the context of biodegradation[620] and biological recycling, has also been studied. Here, we focus on work where the emphasis is specifically placed on the recyclable nature of the polyester and recovery and identification of the respective monomers rather than studies which solely highlight the biodegradability of an FDCA-derived polyester.

In 2017, Haernvall et al. investigated the enzymatic hydrolysis of a range of PEF-related polyesters with alkyl linkers of n = 2−6, 8, 9, and 12 as well as propylene glycol and diethylene glycol (PRF, Scheme 67; M_n = 9.4−32.9 kg mol^{-1}, Đ = 2.5−3.5).[637] These polyesters displayed a broad range of T_g values, which generally decreased with chain length (e.g., from 56 °C for PPF (m = 3) to −10 °C for PDF (m = 12)). Interestingly PHF, POF, and PDF (m = 6, 8, and 12, respectively) were semicrystalline with T_m values of 145, 146, and 107 °C, respectively, while the remaining polyesters were amorphous. The cutinase enzyme Thc_Cut1 was applied at 50 °C, 0.1 M potassium phosphate buffer at pH 7, and the hydrolyses were monitored over 72 h. All polyesters synthesized were successfully hydrolyzed by the Thc_Cut1 enzyme, and monomer products, over oligomers, were isolated. Poly(pentylene furandicarboxylate) (PPeF; M_n = 17.8 kg mol^{-1}, Đ = 3.1) and poly(nonylene furandicarboxylate) (PNF; M_n = 16.6 kg mol^{-1}, Đ = 3.0) were the most efficiently hydrolyzed polyesters out of all those derived from straight-chain aliphatic diols with 58% and 53% hydrolysis achieved in 72 h, respectively. The authors noted that these polyesters are both amorphous, compared to the other semicrystalline polyesters in the series, which bears comparison with much enzymatic work on PET that demonstrates preferential hydrolysis of amorphous regions (see section 2.3). It was also found that increased hydrolytic activities were obtained for branched propylene glycol (M_n = 14.1 kg mol^{-1}, Đ = 2.5) over linear 1,3-propanediol (M_n = 21.0 kg mol^{-1}, Đ = 2.8) derived polyesters (18% cf. 5% hydrolysis after 72 h). The diethylene glycol-derived polyester (M_n = 32.9 kg mol^{-1}, Đ = 2.7) showed particularly high susceptibility to hydrolysis (quantitative hydrolysis within 72 h).

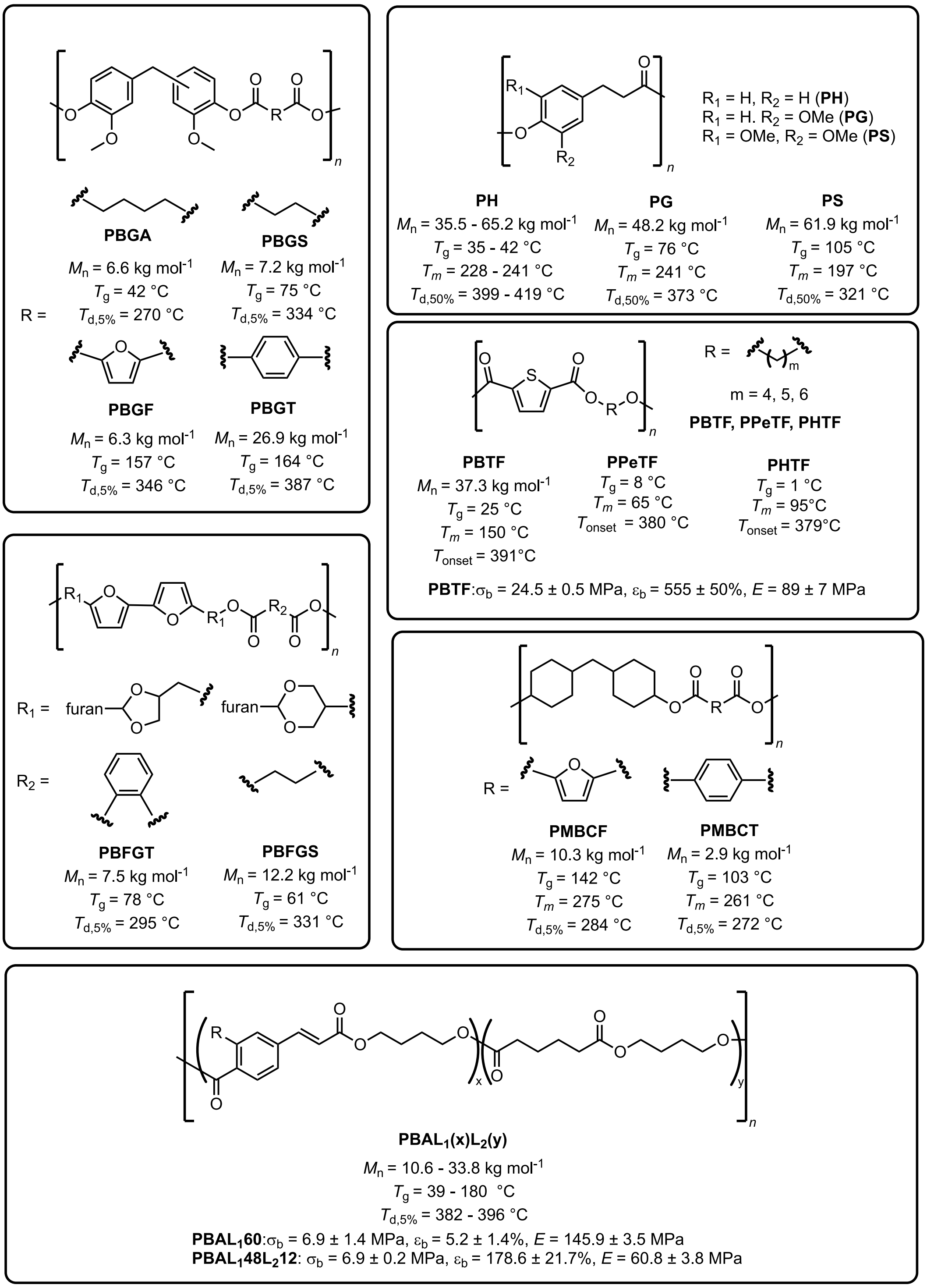
Later in 2017, the same group also reported on the enzymatic hydrolysis of a series of copolymers derived from PEF (and related homologues) and sodium 5-sulfoisophthalate (NaSIP) (PRFSI, Scheme 67; M_n = 2.6−8.0 kg mol^{-1}, Đ = 1.3−2.3).[638] The copolymers contained 30−40 mol % of NaSIP (70−60 mol % of FDCA) and showed T_g values from 6 °C (POFSI, m = 8) to 84 °C (PEFSI, m = 2). Utilizing the cutinase Thc_Cut1 at 50 °C and 0.1 M potassium phosphate buffer at pH 7, it was found that all polyesters synthesized in the study can be hydrolyzed, with FDCA release being observed in all cases. In comparison to their prior study, the authors found that faster hydrolysis occurred with short-chain alkyls (for both aliphatic- and ether-containing diols), with polyesters based on ether containing diols yielding faster hydrolysis than their respective counterpart based on aliphatic diols. It was also demonstrated that hydrolysis of the esters occurred fastest adjacent to FDCA, rather than NaSIP. Despite this, the inclusion of NaSIP units within the polyester provided an overall rate enhancement to hydrolysis rates when compared to the purely aliphatic-derived diol polyesters reported in the previous study.

In 2023, Siracusa et al. reported the enzymatic hydrolysis of the block copolymer PPeF-*b*-PLA (50:50) alongside a series of blends of the two polymers (Scheme 68).[639] Utilizing Thc_Cut1 at 65 °C and with 1 M potassium phosphate buffer at pH 8, 57% hydrolysis of the block copolymer was obtained within 7 days. The authors noted that hydrolysis preferentially occurred in the PPeF segments over the PLA segments. The FDCA was recovered in 75% yield from the hydrolysis solution and could be used to resynthesize PPeF. The *r*PPeF displayed similar M_n, dispersity, and mechanical and thermal properties to the *v*PPeF utilized in the study.

4.2.3. Lignin- and Other Biomass-Derived Polyesters.

In the search for greener alternatives to petrochemical-derived semiaromatic polymers such as PET, PBT, or PBAT, lignin represents a major source of aromatic-containing small molecules that could be utilized as potential monomers in

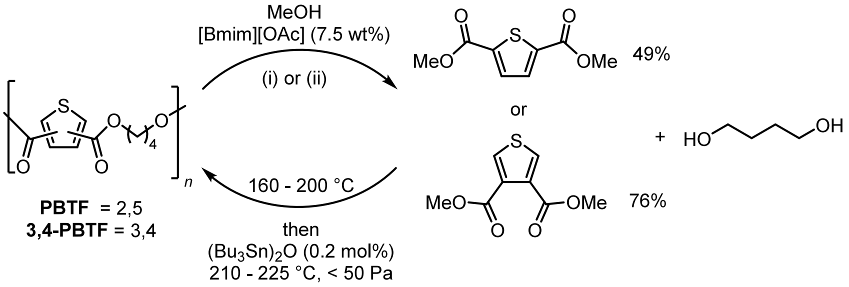
Scheme 69. Semiaromatic Polyesters Reported for Chemical Recycling



polyester synthesis.[610,611] The structure of lignin contains phenylpropane units; deconstruction of lignin can lead to a range of substituted phenols which can be subsequently transformed to diacids and/or diols for application in polyester synthesis.[611] A broad range of polyesters have hence been derived from such phenols, sometimes in combination with FDCA or TPA.[6,611] Alongside lignin-derived aromatics, other routes to aromatic compounds include the bioderived platform chemicals furfural and HMF which, alongside the previously discussed FDCA, can also lead to a range of other aromatic compounds.[612,613] Despite such materials being good candidates for chemical recycling, this is much less investigated by researchers; we discuss here those polyesters for which chemical recycling routes have been reported (Scheme 69).

In 2018, Curia et al. reported the development of aromatic and semiaromatic polyesters derived from the lignin-derived diol bisguaiacol (BG).[640] BG was synthesized from condensation of vanillyl alcohol and guaiacol and is isolated as a mixture of substitution isomers (*p,p′*, 85%; *m,p′*, 15%; *o,p′*, 3%). They subsequently synthesized a range of polyesters from

Scheme 70. Chemical Recycling of PBTF and 3,4-PBTF by IL-Catalyzed Methanolysis[a]



[a]Conditions: (i) for PBTF, 130 °C, 5 h; (ii) for 3,4-PBTF, 110 °C. 1 h.

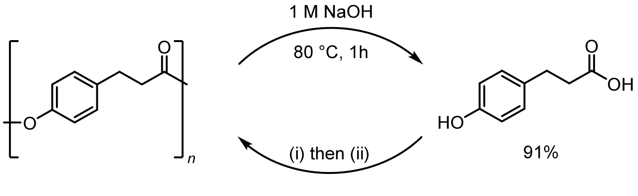
the condensation of BG with acid chlorides of FDCA (PBGF; M_n = 6.3 kg mol^{-1}, $Đ$ = 1.6), TPA (PBGT; M_n = 26.9 kg mol^{-1}, $Đ$ = 2.3), adipic acid (PBGA; M_n = 6.6 kg mol^{-1}, $Đ$ = 1.8), and succinic acid (PBGS; M_n = 7.2 kg mol^{-1}, $Đ$ = 2.2) (Scheme 69). All polyesters were amorphous and displayed T_g values from 42 (PBGA) to 164 °C (PBGT) and $T_{d,5\%}$ from 270 (PGBA) to 387 °C (BGPT). The enzymatic hydrolysis of each polyester was investigated using two cutinase enzymes Thc_Cut1 and Thc_Cut2 at 50 °C. The semiaromatic polyesters showed significantly greater extents of hydrolysis as judged by BG release using both enzymes (e.g., Thc_Cut1 ca. 0.7 mM BG for both PBGA and PBGS; 0.15 μM BG for both PBGF and PBGT). Thc_Cut2 showed enhanced activity over Thc_Cut1 for PBGA and PBGF but similar activities for PBGS and PBGT, which the authors correlated with the T_g of the polyesters.

In 2019, Gigli et al. described the enzymatic hydrolysis of poly(butylene 2,5-thiophenedicarboxylate) (PBTF; M_n = 37.3 kg mol^{-1}, $Đ$ = 1.6),[641] a novel bioderived PEF-like polyester, that had been reported by the same group a year prior (Scheme 69),[642] which shows useful thermal (T_g = 25 °C, T_m = 150 °C, T_{onset} = 391 °C) and mechanical (σ_b = 24.5 ± 0.5 MPa, ε_b = 555 ± 50%, E = 89 ± 7 MPa) properties. Applying enzymes and conditions that had previously yielded successful hydrolysis of PEF,[633] namely, Thc_Cut1 and HiC at 65 °C, 1 M potassium phosphate buffer at pH 8, they reported a ca. 18% weight loss of PBTF over 72 h with the monomer 2,5-thiophenedicarboxylate (TPCA) being isolated. Interestingly, in comparison to PEF, which was proposed to undergo exo (i.e., chain-end) degradation, PBTF was proposed to be hydrolyzed in an endo fashion (i.e., chain scission), which was supported by a slow initial build of TFDCA followed by more rapid evolution toward the end of the hydrolysis period (1.28 mM TFDCA at 48 h but 3.40 mM at 72 h). In subsequent work, Bertolini et al. described the enzymatic hydrolysis of a series of TFDCA-derived polyesters (PBTF, PPeTF, PHTF) with varied aliphatic chain lengths (Scheme 69).[643] These polyesters displayed lower thermal transitions than PBTF (T_g = 8 (PPeTF) and 1 °C (PHTF); T_m = 65 (PPeTF) and 95 °C (PHTF)) but maintained good thermal stability (T_{onset} = 380 (PpeTF) and 379 °C (PHTF)). Thc_Cut1 and Thc_Cut2 were trialed, utilizing the same conditions previously reported (temperature, buffer),[641] for the polyester series. PPeTF was found to be fastest hydrolyzed, showing 100% weight loss in 3 days, and PHTF was also significantly degraded, showing 80% weight loss after 4 days, with concomitant formation of TPCA alongside some oligomers observed. PBTF was notably slower, consistent with their prior report.

Very recently, Tian et al. reported the IL-catalyzed methanolysis of PBTF (M_n = 47.7 kg mol^{-1}, $Đ$ = 1.6) alongside that of the 3,4-TPCA-derived equivalent (3,4-PBTF; M_n = 44.3 kg mol^{-1}, $Đ$ = 1.4) (Scheme 70). Unlike semicrystalline PBTF, 3,4-PBTF is an amorphous polymer with a T_g of 17 °C, $T_{d,5\%}$ of 372 °C, and low tensile stress (σ_b = 0.8 ± 0.1 MPa) but high strain at break (ε_b = 1242 ± 41%).[644] Both polymers were subjected to methanolysis utilizing the IL (7.5 wt %), but lower temperatures and shorter reactions times could be obtained for 3,4-PBTF (PBTF, 130 °C, 5 h; 3,4-PBTF, 110 °C, 1 h). The corresponding TPCA (2,5 or 3,4) was obtained in 49% or 76% yield, respectively as the dimethyl ester derivative. Subsequent application of these dimethyl esters allowed for resynthesis of the polyesters, demonstrating full circularity.

In 2020, Schijndel et al. reported the synthesis of several semiaromatic polyesters (Scheme 69) from the self-condensation of three 4-hydroxy-dihydrocinnamic acids (named poly(p-hydroxycinnamyl, guaiacal, and syringyl lignin, PH (M_n = 35.5−65.2 kg mol^{-1}, $Đ$ = 1.2−1.3), PG (M_n = 48.2 kg mol^{-1}, $Đ$ = 1.2), and PS (M_n = 61.9 kg mol^{-1}, $Đ$ = 1.3), respectively).[645] The corresponding monomers were formed by hydrogenation of p-coumaric acid, ferulic acid, and sinapinic acid. Direct melt condensation of the 4-hydroxy-dihydrocinnamic acids gave low molar mass oligomers, and so to access improved molar mass polyesters, the monomers were initially acetylated on the phenol, yielding mixtures of the acetylated monomers as well as oligomers. This mixture was subsequently applied to base-catalyzed melt or solvent-assisted polycondensation to yield the desired polyesters. The new polyesters displayed thermal properties relatively similar to PET (PH: T_g = 35−42 °C, T_m = 228−241 °C, $T_{d,50\%}$ = 399−419 °C; PG: T_g = 76 °C, T_m = 243 °C, $T_{d,50\%}$ = 373 °C; PS: T_g = 105 °C, T_m = 197 °C, $T_{d50\%}$ = 321 °C). The authors described the subsequent alkaline hydrolysis of PH using a 1 M NaOH solution at 80 °C (Scheme 71). After 1 h, a 91% yield of the monomer,

Scheme 71. Chemical Recycling of PH[a]



[a]Conditions: (i) 1.5 equiv of acetic anhydride, 0.1 equiv of NaOAc, 1 h, 90 °C, (ii) 10 mol % of NaOH, 1 mol % of Zn(OAc)$_2$, 1,2-xylene, 144 °C, 3 h then 240 °C, <133 Pa.

dihydrocoumaric acid, was recorded. This monomer could subsequently be applied to the repolymerization of PH, and the closed-loop process was repeated 10 times to underscore the circularity of the process.

In 2021, Hayashi et al. reported the application of bicyclic furans derived from furfural to polyester synthesis.[646] Bifufural (BFF) was initially acetylated to bifurylidene bis(glycerol acetal) (BFG), which is isolated as a mixture of isomers (both 5- and 6-membered ring acetals as well as optical and stereoisomers of each). The BFG diol was polymerized with phthalic and succinic anhydride to yield PBFGP (M_n = 7.5 kg mol^{-1}, $Đ$ = 1.2) and PBFGS (M_n = 12.2 kg mol^{-1}, $Đ$ = 1.5), respectively, using a DMAP catalyst and DIC as a condensation reagent. PBFGS displayed a T_g of 61 °C and a $T_{d,5\%}$ of 331 °C, while PBFGP displayed a T_g of 78 °C and a $T_{d,5\%}$ of 295 °C. No T_m endotherms were observed, implying the acetal units prevent crystallization of the polymer chains. PBFGS was recycled utilizing glycerol with a $ZnCl_2$ (0.3 wt %) catalyst at 150 °C with quantitative recovery of BFG being achieved within 3 h. In an alternative approach, acidic hydrolysis with trifluoracetic acid yielded BFF in quantitative yield after 15 h at RT.

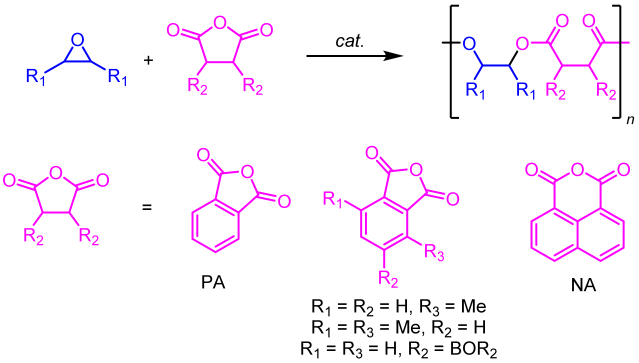
In 2023, Shi et al. described the synthesis of a series of poly(butylene adipate-*co*-lignin monomers) (PBAL, Scheme 69).[647] Using reductive catalytic fractionation of herbaceous plant biomass, ethyl *p*-coumarate and ethyl ferulate were isolated. These were subsequently functionalized into dicarboxylic esters (L_1 = coumaric acid-derived diester (R = H); L_2 = ferulic acid-derived diester (R = OMe)) and then copolymerized with adipic acid and butane diol to yield a family of aliphatic−aromatic copolyesters ($PBAL_1(x)L_2(y)$; M_n = 10.6−33.8 kg mol^{-1}, $Đ$ = 1.3−3.4). The thermal properties of the polyesters depended on the composition of the copolymer, with T_m values ranging from 180 (PBL_1) to 39 °C ($PBAL_1$20), T_g values from −43 ($PBAL_1$20) to 61 °C (PBL_1) and $T_{d,5\%}$ values between 382 and 396 °C. Study of the tensile properties revealed that PBL_1 behaved like hard plastics (e.g., $PBAL_1$60; σ_b = 6.9 ± 1.4 MPa, ε_b = 5.2 ± 1.4%, E = 145.9 ± 3.5 MPa), but incorporation of a fraction of L_2 yielded tougher and more ductile materials ($PBAL_1 48L_2 12$; σ = 6.9 ± 0.2 MPa, ε_b = 178.6 ± 21.7, E = 60.8 ± 3.8 MPa). The polyesters were chemically recycled using $Zn(OAc)_2$-catalyzed (10 wt % of catalyst) ethanolysis at 100 °C over 93 h. Under these conditions, combined recoveries (L_1/L_2 + adipic ester) of 30−40% were recorded. Higher incorporations of L_1 gave slightly lower acid monomer recovery rates (e.g., PBL_1 yielded 32% L_1 recovery over 90 h, $PBAL_1$20 yielded 41% L_1 + AA recovery in the same time period). By refluxing a PBAL sample in acidified (50 mM H_2SO_4) ethanol for 70 h, 90% recovery of L_1/L_2 was reported alongside 80% recovery of the adipate ester.

In 2023, Wu et al. described the synthesis of polyesters featuring the lignin-derived diol 4,4′-methylenebiscyclohexanol (MBC Scheme 69).[648] Semiaromatic polyesters based on MBC and FDCA (PMBCF; M_n = 10.3 kg mol^{-1}, $Đ$ = 1.8) or TPA (PMBCT; M_n = 2.9 kg mol^{-1}, $Đ$ = 2.9) were synthesized via melt polycondensation (conditions: 2.5 mmol of diol, 2.5 mmol of comonomer, 1 mol % of Ti(IV) butoxide, 190 °C, 1 h, and then 230 °C, 100 Pa, 1 h). These semiaromatic polyesters displayed high T_m and T_g values (PMBCF = 275 and 142 °C, respectively; PMBCT = 261 and 103 °C, respectively) and reasonable degradation temperatures ($T_{d,5\%}$ = 284 °C for PMBCF and 272 °C for PMBCT). Since MBC exists as an isomeric mixture, the authors showed that applying pure isomers of MBC could be used to modulate the T_g of PMBFC (101 °C for pure cis−cis MBC PE, 129 °C for trans−trans MBC, and 142 °C for a mixture of isomers). The novel polyesters were all shown to be recyclable via methanolysis (190 °C, 4 h, 0.1 MPa); 90% and 88% isolated yields of MBC were recorded for the methanolysis of PMBCT and PMBCF, respectively.

4.3. Copolymerization

The ring-opening copolymerization (ROCOP) of epoxides and aromatic anhydrides (e.g., phthalic anhydride (PA) and substituted derivatives,[649,650] naphthalic anhydride (NA)[651]) can yield semiaromatic polyesters (Scheme 72).[652,653] Typical syntheses include application of homogeneous catalysts/catalyst systems and temperatures between 60 and 140 °C.[654,655] The reactions can be performed either in organic solvents or utilizing the epoxide monomer as a solvent. The polyesters themselves are typically amorphous, high T_g,[649,651,656] brittle but strong materials.[657] Semicrystalline polyesters can be obtained if enantioselective catalysts are applied.[658,659] Amorphous semiaromatic polyesters have seen significant application as “hard blocks” within polyester block copolymers.[660] Recycling of these materials is complicated by the need for separation of the comonomers (that is, epoxide and anhydride) before repolymerization, and as such, no reports exist so far of a one-step chemical recycling protocol for these materials. In comparison, a handful of ROCOP-derived polycarbonates have been shown to be efficiently chemically recycled back to epoxides and CO_2 using homogeneous catalysts.[661−664]

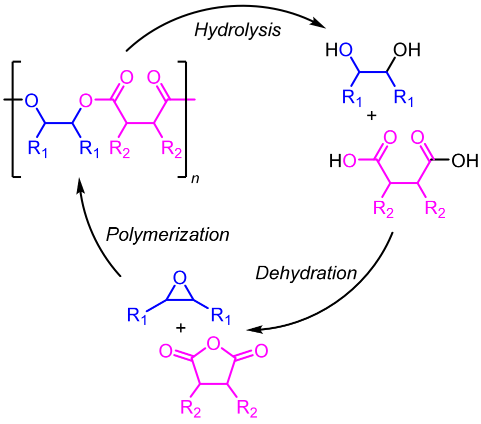
Scheme 72. Synthesis of Semiaromatic Polyesters via ROCOP[a]



[a]Typical aromatic anhydrides include phthalic anhydride (PA) and substituted derivatives and naphthalic anhydride (NA).

Several reports from Williams and co-workers describe the acidic and basic hydrolysis of semiaromatic ROCOP-derived polyesters, sometimes within block copolyester materials.[650,665−667] The hydrolysis of related semiaromatic ester-ethers has also been reported by the same group.[668] Diacids, diols, and oligomers, rather than the constituent epoxide/anhydride monomers, are typically isolated as the hydrolysis products, indicating that this particular approach is not true closed-loop recycling. However, a very recent report from Young et al. demonstrated that a closed-loop approach (e.g., Scheme 73) to recycling such materials can be achieved by first applying basic hydrolysis to poly(cyclohexene phthalate-*co*-napthalimide) (Nap-PA-CHO), yielding a diacid salt and diol,

Scheme 73. Closed-Loop Recycling of ROCOP-Derived Polyesters



and subsequent dehydration of these to yield the true starting materials of PA and cyclohexene oxide.[669] Depolymerization of the Nap-PA-CHO was performed in THF with a 40% w/v KOH solution added, which was heated to 90 °C for 72 h. The two major components of the mixture (cyclohexene diol and potassium phthalate) were isolated individually by solvent extraction. PA and cyclohexene oxide (CHO) were subsequently reformed by dehydration procedures (acetic acid reflux for 18 h for PA, PPh_3/diethyl azodicarboxylate at RT for 18 h for CHO). The authors further demonstrated that the recycled monomers were of sufficient purity to resynthesize poly(cyclohexene phthalate).

5. RECYCLING OF MIXED POLYESTERS

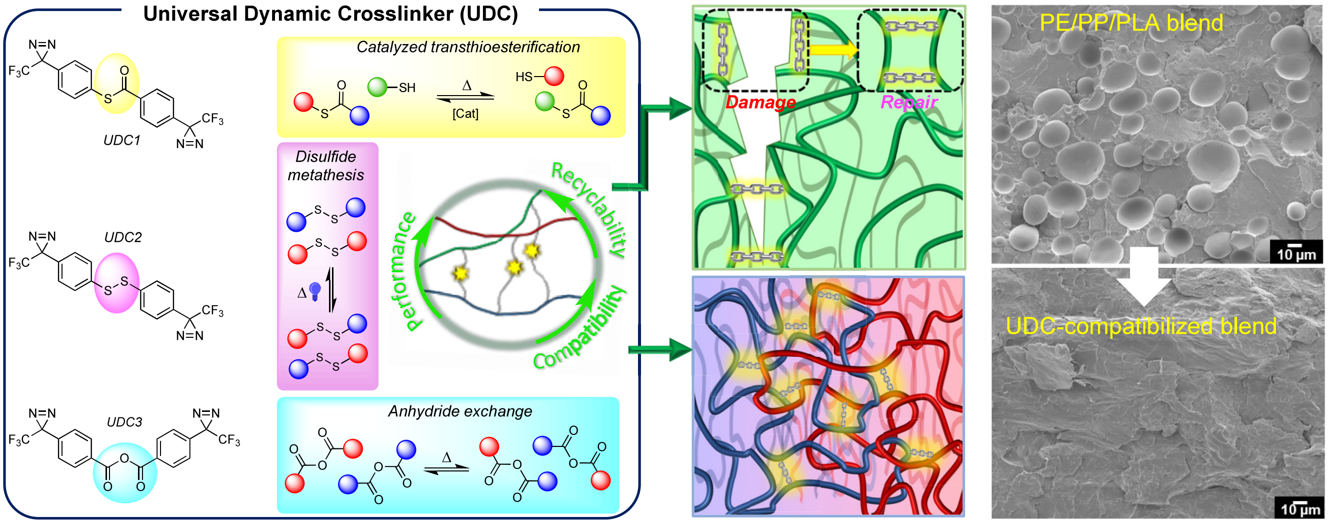
The preceding sections have primarily focused on the chemical recycling of homopolyesters or copolymers back to their constituent monomers for the resynthesis of virgin-quality polymers or the creation of other value-added products. In these scenarios, the materials involved are typically monocomponent, which facilitates their recycling. However, the situation becomes substantially more complicated when considering real-world applications. For instance, everyday plastic products, such as packaging materials, are often elaborately engineered, incorporating a variety of different plastics with distinct chemical structures to customize material properties to meet specific needs. When a plastic product requires unique performance characteristics that a single polymer cannot provide, a typical design strategy involves the integration of diverse polymers or the use of additives to achieve the desired product properties. Despite the indisputable benefits of these highly engineered plastic products, traditional mechanical recycling methods encounter significant hurdles when attempting to recycle these multimaterial products, mainly due to the formation of heterogeneous and immiscible blends.[670] While several initiatives have adopted traditional sorting techniques such as dense media separation, infrared spectroscopy, electrostatic separation, pneumatic separation, or induction sensor-based separation, only a few have attained the technological maturity necessary for industrial-scale implementation. Moreover, these techniques often fall short in efficiency when tasked with separating multilayered or blended polymers.[671]

Given these challenges, we have outlined below several emerging strategies that have been proposed to facilitate a more sustainable EoL option for mixed plastics: (1) compatibilization of immiscible blends during mechanical recycling, (2) plastic separation by dissolution/precipitation, (3) biological funneling, and (4) closed-loop recycling and upcycling.

5.1. Mechanical Recycling

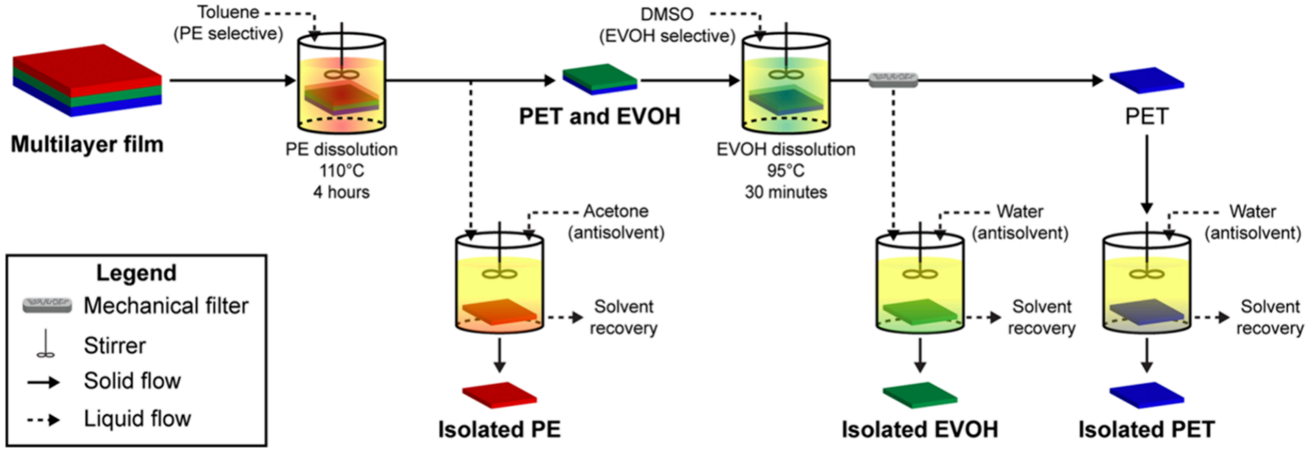
Mechanical recycling, despite being the most cost-effective, energy-efficient, and environmentally friendly option, often leads to polymer degradation and inferior material performance.[124,182] Moreover, the recycling of mixed plastics presents additional challenges. The heterogeneity of plastic waste along with the presence of low molar mass compounds (such as degradation products, additives, and contaminants) often results in poor mechanical performance of most polymer blends due to their thermodynamic immiscibility.[672] As a

Scheme 74. Design of UDCs and Their Molecular and Macromolecular Features for Compatibilizing Mixed Plastics of Even Polar Extremes via In Situ Formation of Value-Added Graft Multiblock Copolymers[675,a]



[a]Modified from ref 675. Copyright 2023 Springer Nature.

Scheme 75. Process Schematic for Deconstructing an Amcor Evolution Multilayer Film into Its Constituent Resins Using the STRAP Process[677,a]



[a]Reprinted from ref 677. Copyright 2020 AAAS.

result, there is a pressing need to develop suitable technologies to enhance the properties of these waste materials and make them suitable for new applications. To improve the properties of these immiscible polymer blends, additives can be used to enhance the miscibility of the polymers by lowering the interfacial tension and reducing stress transmission across the interface. This process, known as compatibilization, results in optimized interfacial tension, stabilization of dispersed droplets against coalescence (which leads to the preservation of morphology), and improved adhesion between solid-state phases, thereby facilitating stress transfer and enhancing the mechanical properties.[673] Traditional compatibilization strategies are implemented either chemically or physically by introducing small amounts of specific components. Incompatible blends may achieve compatibility or even miscibility by introducing functional groups that interact with one or both polymer components of the blend. Numerous intermolecular interactions, including hydrogen bonding, acid−base interactions, ion−ion, ion−dipole, donor−acceptor interactions, charge transfer complexation, and metal coordination, can be employed to increase the compatibility between polymer blend components.[124] A proactive alternative involves in situ generation of these copolymers during blend preparation, a method known as reactive compatibilization.[674]

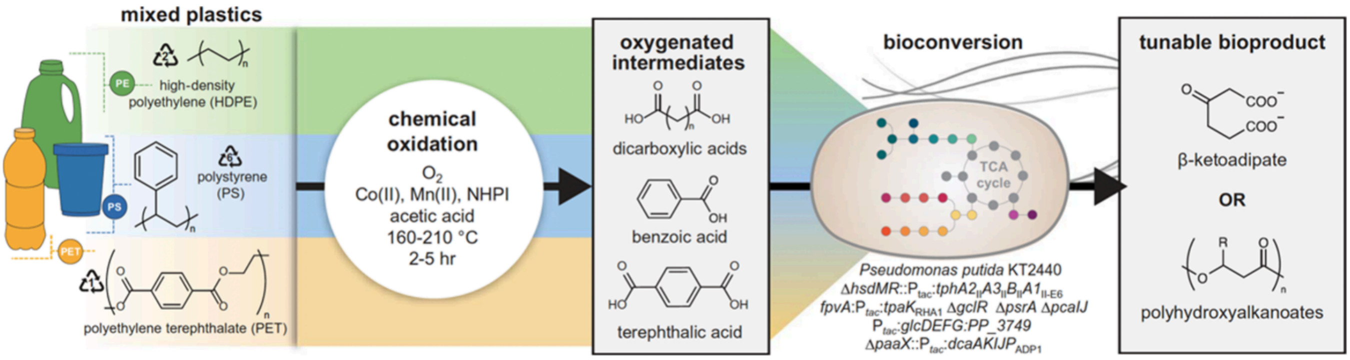
To surmount this obstacle, in 2023, Chen and co-workers developed a novel compatibilization strategy that incorporated universal dynamic cross-linkers (UDCs) into various binary, ternary, and postconsumer immiscible polymer mixtures in situ (Scheme 74).[675] These UDCs, featuring functional moieties such as thioester, disulfide, and anhydride, are designed to become exchangeable under stimulation. A combination of experimental and modeling studies demonstrated that these UDCs could rejuvenate mixed-plastics chains, specifically apolar polyolefins and polar polyesters (P3HB or PLLA), by facilitating their compatibility through the dynamic formation of graft multiblock copolymers. The resulting dynamic thermosets, generated in situ, showcase inherent reprocessability and displayed improved tensile strength and creep resistance compared to virgin plastics. The introduction of these UDCs effectively merges the dynamic nature of vitrimers with the universal cross-linking of polymer mixtures, providing a promising pathway toward achieving the elusive goal of compatibility and multiple usage cycles for mixed-plastics recycling. This UDC approach avoids polymer de/reconstruction, which can be energy intensive, thus preserving the endowed energy and materials value of the individual plastics via in situ formation of value-added graft multiblock copolymers.

5.2. Separation by Dissolution/Precipitation

Dissolution/precipitation methods present a promising strategy for recovering additive-free polymers from plastic waste, including pigments and potentially reusable additives like flame retardants. These techniques may involve a single solvent or the combination of a solvent and an antisolvent. In the latter scenario, the solvent selectively dissolves a specific polymer and the addition of an antisolvent precipitates out the polymer for recovery. Nondissolved materials, such as pigments, are separated from the polymer solution between the dissolution and the precipitation stages. Subsequently, the solvent and antisolvent mixture can be separated again for reuse. In 2018, Ni and co-workers highlighted an eco-friendly, potentially profitable method for plastics separation and recovery and solvent extraction, which yielded high-quality recovered plastics that were comparable to virgin materials from waste mass-produced plastics, such as PS, polycarbonate (PC), polyolefins, PET, poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS), and poly(vinyl chloride).[676]

Building upon these foundational techniques, researchers have been developing innovative approaches to address more complex challenges. For example, to tackle the challenge of recycling multilayered plastic packaging materials, Huber and co-workers introduced a strategy termed solvent-targeted recovery and precipitation (STRAP) to deconstruct multilayer films into their individual resins using a sequence of solvent washes guided by thermodynamic calculations of polymer solubility (Scheme 75).[677] The STRAP process was proven to be effective in separating three representative polymers—PE, poly(ethylene-*co*-vinyl alcohol) (EVOH), and PET—from commercially available multilayer films, providing near 100% material efficiency and yielding recyclable resins that are cost competitive with virgin materials. Specifically, the separation process involved selective dissolution of PE in toluene at 110 °C followed by EVOH in DMSO at 95 °C with the respective fractions recovered by cooling and the addition of antisolvent

Scheme 76. Outlined Flowchart for Upcycling of Mixed Plastic Waste through Tandem Chemical Oxidation and Bioconversion[311,a]



[a]Reprinted from ref 311. Copyright 2022 AAAS.

(e.g., acetone or water). The recovered PE and EVOH were then separated from toluene−acetone or DMSO−water mixtures by filtration, and the solvents were recovered via distillation for reuse, boosting the efficiency and sustainability of the process.

5.3. Biological Funneling

Another promising approach to address the challenge of recycling mixed plastics is to transform waste plastics or polymers into chemicals or materials of higher value—a process often called "upcycling". In 2020, Blank and co-workers introduced the EU Horizon 2020 project MIX-UP, "Mixed plastics biodegradation and upcycling using microbial communities".[678] The project sought to reshape the conventional linear plastic value chain into a sustainable, biodegradable-based model. The initiative used mixed plastics, including five of the most persistent fossil fuel-based plastics (PE, polyurethane (PUR), PP, PET, PS) and emerging bioplastics like PHA and PLA as feedstock for microbial transformations. The approach involved a series of controlled, systematic enzymatic and microbial degradations of mechanically pre-treated plastic waste followed by microbial conversion into polymers and value-added chemicals. This circular approach toward plastic life cycle management involves using engineered enzymes, such as cutinases, lipases, and carboxylesterases, to depolymerize unsorted, mixed plastic waste into monomeric components. These components along with any resulting metabolites and additives are then converted into central metabolites by dedicated microbial communities. These metabolites serve as the building blocks for the synthesis of novel polymers (e.g., hydroxy alkanoyl oxy-alkanoic acids (HAA), PHAs), biosurfactants, or chemocatalytic building blocks, facilitating the transition toward a low-carbon, circular bioeconomy.

In 2022, Beckham and co-workers introduced a process where metal-catalyzed autoxidation was used to depolymerize comingled polymers into a mixture of oxygenated small molecules. These molecules are advantageous substrates for subsequent biological conversion, thereby establishing a strategy for the selective transformation of mixed plastic waste into valuable chemical products (Scheme 76).[311] Specifically, this strategy was demonstrated using mixtures of HDPE, PS, and PET, which are among the most abundant components of postconsumer plastic waste. In the initial catalytic step, metal-promoted autoxidation, specifically using cobalt(II) acetate or manganese(II) acetate along with *N*-hydroxyphthalimide (NHPI), is carried out at 160−250 °C to oxidatively deconstruct mixed plastics into oxygenated intermediates. These intermediates, such as dicarboxylic acids, benzoic acid, and terephthalic acid, serve as advantageous substrates for subsequent bioconversion. In the subsequent biological step, two robust, engineered bacterial strains of *Pseudomonas putida* were used to convert the mixed oxygenates into the target product, the first to convert acetate, C4−C17 dicarboxylates, benzoate, and terephthalate into a PHA, a naturally occurring polyester with increasing industrial applications, and the second to use acetate and dicarboxylates for growth while converting benzoate and terephthalate into β-ketoadipate, a monomer for high-performance polymers.

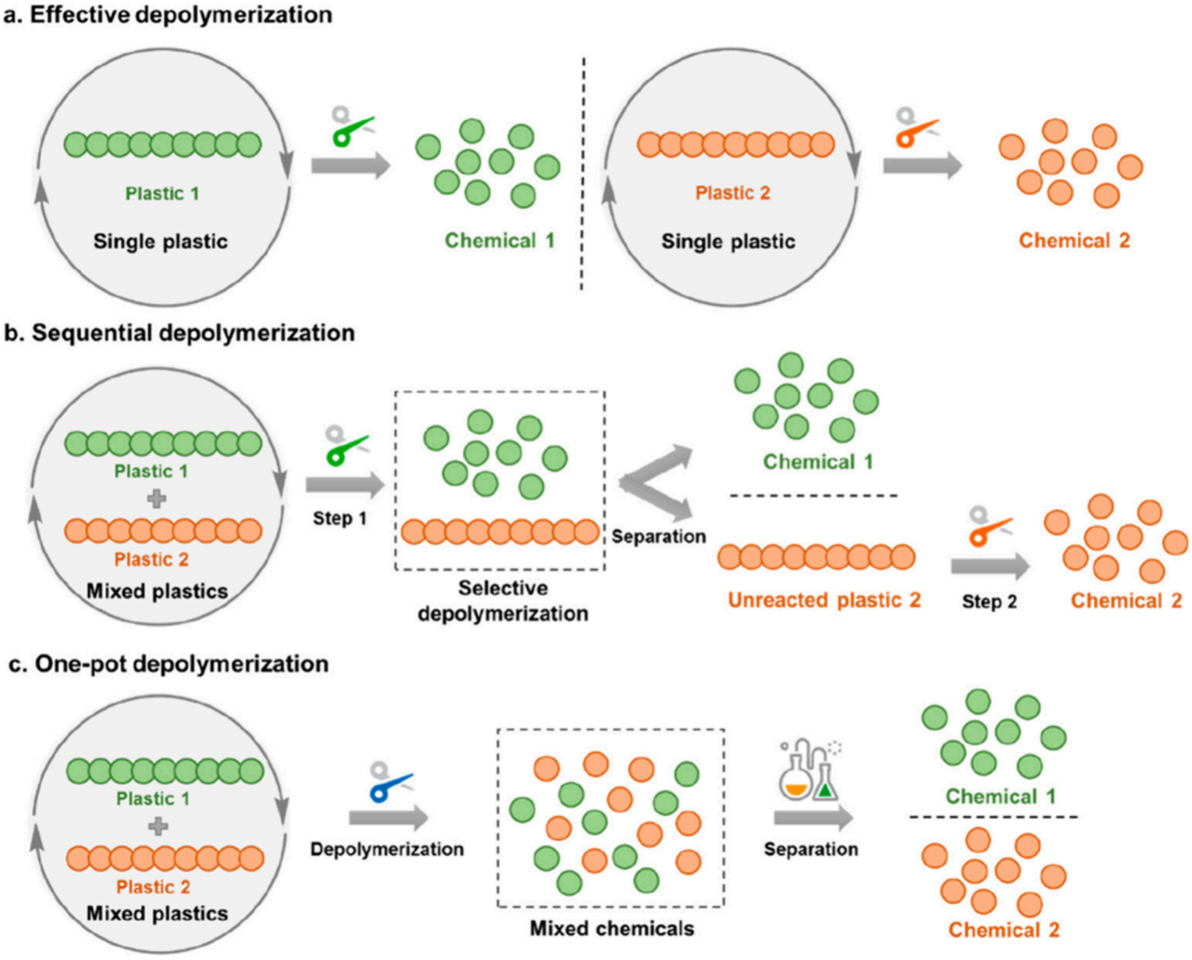
5.4. Closed-Loop Recycling and Upcycling

The fourth strategy to address mixed-plastic recycling involves selectively and sequentially depolymerizing polymers from mixed plastics based on their differing reactivities or using a one-pot depolymerization of mixed plastics followed by product separation leveraging their varied solubility or boiling points.

In 2011, Sánchez and Collinson demonstrated a selective recycling approach for mixed-plastic waste of PLA and PET.[679] They reported conversion of waste PLA into methyl lactate using $Zn(OAc)_2$ as a catalyst in a methanolysis process at reflux, achieving a 65% yield while leaving the PET untouched. The remaining PET was then isolated through filtration. In a subsequent step using EG as a solvent and $Zn(OAc)_2$ as a catalyst, they glycolyzed the PET under reflux conditions to yield BHET with a yield of 78%.

In 2019, Hong, Chen, and co-workers described the upcycling of PGA by upconversion to poly(glycolic acid-*co*-butyrolactone) (PGB) via catalyzed transesterification in γBL (γBL as solvent and reagent, TBD or $La[N(SiMe_3)_2]_3$ as catalyst, 160 °C, 1−6 h).[680] Incorporation of up to 20% γBL was achieved. Of particular significance, it was also demonstrated that a mixture of the two homopolymers (PGA and PBL) could also be *co*-transesterified under the same conditions to yield a PGB copolymer. The resulting PGB is sequence defined with isolated glycolic sequences, which are attributed to the much enhanced thermal stability (≥44 °C) over both homopolymers or copolymers without such sequences. This copolymer could be recycled through basic hydrolysis (1 M NaOH, RT, 2 h), which resulted in the formation of sodium glycolate and sodium γ-hydroxybutyrate,

Scheme 77. Sequential and "One-Pot" Depolymerization Strategies for Chemical Recycling of Commercial Plastics and Mixed Plastics[685,a]



[a]Reprinted from ref 685. Copyright 2022 American Chemical Society.

which could subsequently be converted back to GA and γBL in 98% and 94% yields, respectively.

In 2021, Sardon and co-workers demonstrated the chemical recycling of mixed plastics through the selective and sequential depolymerization of bis-bisphenol A-polycarbonate (BPA-PC) and PET using a protic ionic salt (TBD, methanesulfonic acid) catalyst.[681] This catalyst was previously showed to be efficient for the individual depolymerization of both PET and BPA-PC.[285,682,683] Computational investigations highlighted mechanistic similarities between the depolymerizations of PET and BPA-PC but considerable energetic differences. Leveraging these reactivity differences, they achieved the selective and sequential glycolysis of BPA-PC and PET. Initially, the depolymerization of BPA-PC was undertaken at 130 °C using 0.15 equiv of catalyst, yielding 95% of BPA after 10 h. At this point, the BHET yield from PET depolymerization was less than 2%. By increasing the temperature to 180 °C, PET was then depolymerized into BHET over 31 h in 88% yield. This selectivity was maintained with different alcohols, resulting in functionalized cyclic carbonates from BPA-PC. Hence, this process is not only a selective depolymerization approach but also an upcycling methodology. Ultimately, this strategy proved effective for various BPA-PC/PET mixtures, including commercial pellets, real plastic waste, and a formulated BPA-PC/PET blend material from an end user.

In 2022, Thielemans and co-workers investigated the depolymerization of BPA-PC and PET in separate and mixed streams.[684] It was shown that selective depolymerization of mixed PET and PC streams and the one-step separation of their constituent monomers can be achieved with remarkable energy efficiency through a cost-effective hydrolysis process involving KOH in methanol, specifically developed for PET hydrolysis. The activation energies required for the depolymerization of PC and PET pellets were found to be 68.6 and 131.4 kJ mol^{-1}, respectively. When subjected to microwave heating, randomly mixed streams were completely depolymerized within 2 min at 120 °C using 30 mL of depolymerization solution per gram of polymer. The separation of BPA and TPA was successfully demonstrated in a one-step process facilitated by solubility differences, achieving 98% and 97% purity with no secondary reactions detected.

In 2022, Wang and co-workers presented sequential and "one-pot" depolymerization strategies for chemical recycling of various mixed commercial plastics, including PLA, BPA-PC, PBS, PBAT, PCL, and PET (Scheme 77).[685] They utilized zinc bis[bis(trimethylsilyl)amide] (Zn(HMDS)$_2$), which has been previously used for methanolysis of a variety of polyesters such as PLA, P3HB, and PCL, as a versatile catalyst to achieve efficient and selective depolymerization under mild conditions.[686] In the sequential depolymerization approach, they were able to selectively depolymerize specific plastics from mixed batches by adjusting the depolymerization conditions. For instance, the depolymerization of 6 g of BPA-PC/PET mask at 70 °C exclusively degraded BPA-PC, yielding 2.6 g of BPA (97% yield) while leaving PET untouched. Subsequently, PET was depolymerized by raising the temperature to 110 °C, resulting in 2.4 g of DMT with an 80% yield. Similarly, the sequential depolymerization of 12 g of PLA/PBS straw was also successful, yielding 3.8 g of methyl lactate (MeLA) (61% yield) after RT PLA degradation, followed by the depolymerization of PBS at 100 °C to produce 10 g of dimethyl succinate (DS) (68% yield) and 10 g of BDO (74% yield). These processes clearly demonstrated the feasibility of leveraging reactivity differences to achieve selective sequential depolymerization of mixed plastics. On the other hand, the "one-pot" depolymerization approach simultaneously processed mixed plastics under the identical depolymerization conditions. The resulting products were then recycled separately by capitalizing on their distinct solubility and boiling points. For example, 6 g of BPA-PC/PET mask was depolymerized at 100 °C, resulting in 2.6 g of BPA (97% yield) and 2.7 g of DMT (90% yield). Likewise, the "one-pot" depolymerization of PLA/PBS and PLA/PBAT plastic mixtures at 100 °C effectively yielded MeLA, BDO, and DS products. Following appropriate postprocessing, the isolated yields of MeLA, BDO, and DS were 86%, 83%, and 100% respectively. These examples underscored that isolation of chemicals after "one-pot" depolymerization provided another efficient strategy for mixed plastic depolymerization.

In 2023, Xu and co-workers presented a facile and efficient one-pot method for transforming PET waste into constituent monomers from various plastic streams such as colored PET bottles, PET blending textiles (PET/cotton blending or PET/Spandex blending), and PET multilayer packaging film (PET/PE blending).[687] A mixed solvent of DCM and ethanol was employed to selectively hydrolyze PET into TPA and EG at RT in the presence of KOH. DCM plays a pivotal role in selectively degrading PET composites. As computational results revealed, DCM interacts with PET's ester groups and significantly lowers the energy barrier for PET degradation. Furthermore, DCM also increases the reactivity difference between PET and non-PET components, thus enabling selective degradation of PET and enhancing degradation efficiency through its pore-forming effects on PET. Additionally, the degradation solution exhibits excellent cycling performance and can be easily recovered via simple distillation. This approach, notable for its RT operation, high efficiency, and cost effectiveness, provides an interesting avenue for the industrial recycling of mixed PET materials.

An alternative approach to enabling closed-loop chemical recycling of mixed polyesters involves producing two or more distinct polymers, each with distinct material properties, through orthogonal polymerization of a single, bifunctional monomer. All resulting polymers can then be depolymerized back into their constituent monomer, thus establishing a "one monomer−two or more polymers−one monomer" closed-loop circularity. In this context, Chen and co-workers have recently developed a hybrid monomer design that combines parent monomer pairs with contrasting, mismatching, or matching properties into offspring monomers that not only unify the conflicting properties but also dramatically alter the properties of the resulting polymers, pushing beyond the limitations of either parent homopolymers or their copolymers (Scheme 38). Specifically, the olefin/lactone bifunctional hybrid monomer lead to polyester through ROP of the γ-BL manifold and poly(cyclic olefin) via ROMP of the cyclohexene manifold, respectively, thus establishing a unique orthogonal (de)-polymerization and a "one monomer−two polymers−one monomer" closed loop.[449] The resulting polyolefin and polyester from the ROMP and ROP processes are two different classes of polymers and thus exhibit significantly different thermal and mechanical properties, making them suitable for a range of applications. More importantly, the combination of the two classes of polymers as a polyolefin−polyester copolymer or as a physical blend still leads to a completely recyclable system that can be efficiently depolymerized back to the same single-hybrid monomer, thus closing the chemical recycling to monomer loop for homopolymers, copolymers, and blends. Likewise, MBL is also a bifunctional monomer capable of producing either a vinyl-functionalized polyester, $P(MBL)_{ROP}$, via the kinetically favored ROP pathway[441] or the acrylic polymer $P(MBL)_{VAP}$ via the thermodynamically favored vinyl-addition polymerization (VAP) pathway (Scheme 35).[688] Both $P(MBL)_{ROP}$ and $P(MBL)_{VAP}$ can be broken down back into the same monomer MBL via chemical recycling, but they exhibit markedly different performance properties, offering another example of a closed one monomer−two polymers−one monomer loop.

6. SUMMARY AND OUTLOOK

In this review, we have described the recent progress made in the design and development of circular aliphatic and aromatic polyesters with either direct closed-loop or indirect open-loop life cycles, or both, through chemical, mechanical, and biological recycling processes. Our discussions have been focused on the broader context of legacy and emerging polyesters. In the category of legacy polyesters, we have spotlighted commercial PLA, PHA, PET, PBS, and PBAT as representative examples to highlight the fundamental principles required for establishing sustainable EoL options, which includes synthetic routes and recycling processes. Specifically, chemical recycling is a process that breaks polymers down into their monomers for repolymerization or other feedstocks for value-added applications. This method regenerates polymers with virgin-quality material performance but often requires high energy input. Mechanical recycling, on the other hand, physically reprocesses polymers without the need for de/reconstruction. This process represents the shortest circular cycle and is thus more energy efficient, but material quality tends to degrade over multiple cycles, and issues of sorting and contamination in mixed plastics waste streams often arise. Biological recycling, which leverages cellular organisms or enzymes, breaks down polymers in an environmentally friendly manner, although it is typically slower and less effective with synthetic polymers, especially aromatic polyesters, unless specifically designed for biodegradation. For these legacy polyesters, some of recycling methods detailed in this review are commercially practiced. PLA is typically chemically recycled to either methyl lactate or lactide as mechanical recycling leads to lower quality material, while biological recycling has yet to be widely commercialized. PHA recycling is gaining increasing interest but not yet commercialized due to a smaller market share and lack of viable recycling route. Industrial chemical recycling of PET principally applies glycolysis or methanolysis. Mechanical recycling of PET is a common commercial practice, although it typically results in downgraded materials, unless bottle-to-bottle recycling technologies are applied.[233] Currently, there are no commercialized methods of recycling PBS or PBAT.

To the domain of emerging polyesters, we have underscored the importance of thermodynamics and kinetics in achieving intrinsic circularity for polyesters, which is especially true when enabled through ROP pathways. We have also discussed several examples of SGP of long-chain diols and diacids, which provides additional strategies for constructing polyethylene-like materials with closed-loop circularity. Furthermore, we drew attention to enzymatic de/polymerization, which exhibits high reactivity toward macrolactones and predisposition to convert polyesters regardless of their chemical composition into cyclic oligomers under lipase-catalyzed dilution conditions. This bridges the gap between conventional SGP and chain-growth ROP, facilitating the production of high molecular weight polyesters, typically unattainable through SGP. Finally, we reviewed four emerging strategies to address recycling of polyester mixtures or polyesters in mixed plastics through compatibilization of immiscible blends during mechanical recycling, separation by dissolution/precipitation, biological funneling, and closed-loop recycling and upcycling.

Despite the above reviewed significant progress that has already been made in the design and development of circular polyesters with closed-loop life cycles through chemical, mechanical, and biological recycling processes, several important issues still remain to be solved. Accordingly, we lay out below four emerging trends and associated critical challenges and thus opportunities to address in future research and development efforts toward truly sustainable, circular polyesters in a circular plastics economy.

6.1. Polyolefin-Like Circular Polyesters

An important emerging trend is to develop polymers with polyolefin-like performance properties and polyester-like EoL management options, that is, closed-loop polyesters with performance properties that are comparable to or even better than commodity polyolefins, particularly PE and PP. In the context of emerging aliphatic polyesters by SGP, we have discussed several examples of SGP of long-chain diols and diacids, which provides notable strategies for constructing PE-like materials with closed-loop circularity, as well as the upcycling PE and PP into closed-loop polyesters through tandem unsaturation/cross metathesis/hydrogenation strategies. Yet, several challenges persist. For instance, when compared to the readily available and inexpensive ethylene and propylene, the potential hurdles might include higher production costs, the scalability of sourcing the required building blocks, and necessary adjustments in polymer production and processing. Innovative strategies that can produce polyolefin-like polyesters de novo from abundantly available and inexpensive industrial feedstocks (e.g., ethylene and propylene), and existing industrial polymer production and process facilities will be most impactful and a potential game changer.

6.2. Circular Polyesters with Back-up Biodegradation

Polyesters, especially those aliphatic ones, are typically biodegradable, but few high-performance polyesters are chemically recyclable to monomer via fast, economical, chemical recycling. It is hence crucial to building circular plastic economies that effective EoL solutions for plastics are implemented, yet the dearth of economic incentives has led to insufficient recycling and material recovery. To better conserve and recapture the inherent value of these materials, we must advance our chemical, mechanical, and biological processes with catalyst innovation and material redesign. Biodegradable polyesters should not, in the first instance, be considered waste to be landfilled, and they should be recycled first to recover the materials value and energy still endowed in the EoL product. In addition, considering the scenario where the rate of biodegradation of waste plastics to eventually CO_2 and H_2O is faster than what nature can capture, there will be overall net CO_2 emission. However, having biodegradability as a "back-up" option is also important as plastic waste can leak into the environment and cause adverse environmental and health effects. Thus, such polymers would be reinforced by biodegradability if leaked to the environment. Polymers that are both chemically recyclable and environmentally biodegradable have the potential to be seamlessly integrated into these circular material economies of the future, providing optimal sustainable EoL solutions.

6.3. Recycling of Polyesters in Mixed Plastics Waste Streams

Postconsumer or EoL plastic products are predominately in mixed waste forms and incompatible, which presents the most daunting challenge to recycle all or most of the individual component. The recently reported universal dynamic cross-linking strategy can compatibilize seemingly any plastic mixtures into superior reprocessable thermosets in the form of multiblock graft copolymers, but a key barrier here is the cost of UDCs, considering millions of tons of plastic waste. Like many fundamental discoveries made in history, practical obstacles exist at the very beginning, but there is practical potential if more efficient and cost-effective UDCs could be developed. Another promising approach is the tandem chemical/chemical and chemical/biological processes, which takes advantage of the ability of fast, catalytic chemical processes to break plastic mixtures down to smaller chains or molecules that can be transformed or utilized for repurposing or biologically funneled into discrete molecules or polymers. This approach includes alcoholysis of mixed polyesters into diesters that can be further separated and then reutilized for reforming polymers or other products. The third approach is centered on monomaterial design for achieving closed-loop recycling of mixed-plastic materials. Polyesters that are based on the same monomers and can be stereomicrostructurally or architecturally engineered to single-monomer-sourced materials with on-demand properties suitable for different components of a product will significantly simplify mechanical, chemical, or other emerging recycling processes.

6.4. Scalable Monomer Resources and Depolymerization Systems

Sustainable polymers that are circular and economically viable can only derive from abundant and scalable resources, including building blocks derived from renewable plant-based sources or sequestered from EoL or waste materials. Plant biomass possesses an intrinsically negative carbon footprint, while full capture of monomers from waste plastics would enable a carbon-neutral plastics economy. Current depolymerization systems reported by academic research groups involve solution-based processes (using dilution to lower the T_c of the polymer to promote depolymerization to a monomer in larger extents), distillation (for liquid monomers), or sublimation (for solid monomers) using heat and vacuum to remove the reformed monomer from the equilibrium to achieve high to quantitative monomer yields that far exceed the thermodynamic limits of given temperatures. Solution-based processes would incur additional energy costs and environmental impacts due to the need for solvents and separation; while distillation or sublimation is more scalable, industrially energy cost must be minimized to be cost efficient. Using catalysis or redesigned polymers will render these processes more rapid and selective under milder conditions. Overall, it is thus critical to develop expedient, selective, energy-efficient, and cost-effective extractions and interconversions of those resources to monomers to polymers and then to monomers back, closing the circular loop.

In closing, polyesters have played and are still playing an important role in yesterday's and today's plastics economies thanks to their structure and function that render their unique materials properties and more desired EoL options as compared to today's commodity polymers. Polyesters will play an even greater role in tomorrow's circular plastics economy that focuses on sustainability, chiefly because they have great potential to be designed and developed into sustainable polymers that exhibit designer functions to perform, renewable resources to produce, and circular paths to regenerate. Therefore, there is a great future in recyclable and (bio)degradable polyesters.

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Notes

The authors declare no competing financial interest.

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