

RECYCLABLE POLYMERS



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Chemically Recyclable Polymers: A Circular Economy Approach to Sustainability

This Critical Review article highlights selected major progresses, and technical and environmental benefits made in the field of chemically recyclable polymers through repurposing and depolymerization processes, which not only solves the end-of-life issue of polymers, but also provides a direct approach to circular materials' economy.

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Chemically recyclable polymers: a circular economy approach to sustainability

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The current practices in the generation and disposal of synthetic polymers are largely unsustainable. As part of the solution, the development of biodegradable polymers, which constitute a class of "green polymers" according to green chemistry principles, has been intensively pursued in the past two decades. However, the degradation of such polymers in Earth's landfills typically leads to no recovery of the materials' value, and their degradation in the Oceans could create new or unintended environmental consequences. Industrial mechanical recycling always suffers from a significant quality loss. The proposed more sustainable solution is to develop chemically recyclable polymers that not only solve the end-of-life issue of polymers, but also provide a direct approach to establish a circular materials economy. Accordingly, this critical review article captures some selected highlights of the emerging area of recyclable "green polymers" by focusing on the major progress made and the technical and environmental benefits obtained in the development of re-purposing and depolymerization processes for chemical recycling of polymers at the end of their useful life.

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1. Introduction

Synthetic polymeric materials are designed to meet the very different needs of end consumer products and are essential to modern life and the global economy. Their production has



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increased from 15 million tonnes in the sixties to 311 million tonnes in 2014 and is expected to triple by 2050.¹ However, current paradigms for the generation and disposal of polymers are unsustainable.² At present, synthetic polymers are predominantly based on petroleum resources, which are being rapidly depleted by our increasing energy demand.³ Thus, there is an imminent challenge to gradually replace petroleum-based polymers with those derived from renewable resources.^{4–10} Moreover, the vast majority of synthetic polymers are designed for performance and durability, not for degradability and recyclability, which has resulted in the tremendous growth of disposed polymer wastes over the past few decades.^{11,12} Three major conventional methods exist currently to deal with polymer wastes, including burying them in landfills, incinerating them to recover the embedded energy, and mechanical recycling. However, landfilling always suffers from nondegradability or the extremely slow degradation rate of most polymer wastes, to say nothing of the recovery of the materials' value, while incineration usually generates unsafe exhaust gas and has low energy recovery efficiency. Hence, both landfilling and incineration bring about severe environmental pollution or disasters and recover no, or minimal, value of the material. Mechanical recycling has been considered as a temporary solution, which involves sorting, washing and drying postconsumer polymer products before melt processing to produce a new polymer material.¹³ However, residual catalysts, moisture, and other contaminants present in the polymer waste lead to significant deterioration of properties during the secondary melt processing, and mechanical recycling of colored polymer products creates additional challenges. As a consequence, the large majority of these polymer wastes ultimately find their way to landfills or to incineration.

One strategy developed in the past two decades to address polymer sustainability issues is the use of biodegradable polymers, for example, poly(lactide) (PLA), poly(butylensuccinate), poly(3-hydroxybutyrate), and so on, with wide applications, especially in the short term, products such as packaging, foils, and utility in agriculture.^{14,15} Biodegradable polymers are mainly derived from biorenewable sources (*e.g.* starch and cellulose) and can be enzymatically or hydrolytically degraded into CO₂, water, CH₄, humic matter and other natural substances, leading to an environmentally closed circular ecosystem. To date, significant advances have been achieved in the synthesis of biodegradable polymers *via* organometallic, organic and enzymatic catalysis, producing a large body of publications and reviews on this important topic.^{16–24} Although biodegradable polymers constitute a class of “green polymers”, the degradation of this type of polymer to CO₂, water *etc.* is economically inefficient, as none of the material's value is typically recovered, and these biodegradable polymer products often end up in landfills after use. Moreover, some widely utilized biodegradable polymers, such as PLA, have turned out to be degraded primarily by hydrolysis, not microbial attack, resulting in a slow degradation rate.^{14,25,26} As a consequence, the large-scale consumption of disposable biodegradable

polymer products also causes an excess of wastes and associated environmental problems.

To reduce the demand for finite raw materials, minimize the negative impact on the environment, and also address the end-of-life issue of synthetic polymers, the logical and ideal solution is to develop a circular economy approach to sustainable polymers that can be easily recycled.²⁷ This recycling strategy is the so-called *chemical recycling* method, involving either a depolymerization process in which polymer wastes are depolymerized under controlled conditions back to their starting feedstocks that are purified and then subsequently repolymerized to yield virgin-quality polymeric materials, or a repurposing process in which polymer wastes are converted to building blocks for new value-added polymeric materials (Fig. 1). Recently, significant advances have been made in developing both repurposing and depolymerization processes for chemical recycling of polymer wastes. However, compared with biodegradable polymers, the study of *chemically recyclable polymers* is an emerging research area, and a critical review of the status of this important field from the green chemistry perspective is much needed, which is the objective of this article. Accordingly, this critical review highlights selected major progress made and the technical and environmental benefits obtained in the field of chemical recycling of polymeric materials. The first part of the review covers the recent progress in the repurposing process of a few important engineering plastics [*e.g.* polycarbonate (PC) and poly(ethylene terephthalate) (PET)] and commodity polyolefins [*e.g.* polyethylene (PE) and isotactic polypropylene (iPP)], while the second part focuses on the depolymerization process of commercially available polymeric materials including poly(L-lactide) (PLLA) and nylon 6, as well as novel polymers developed recently, including high-performance thermosets, poly(*o*-phthalaldehyde),

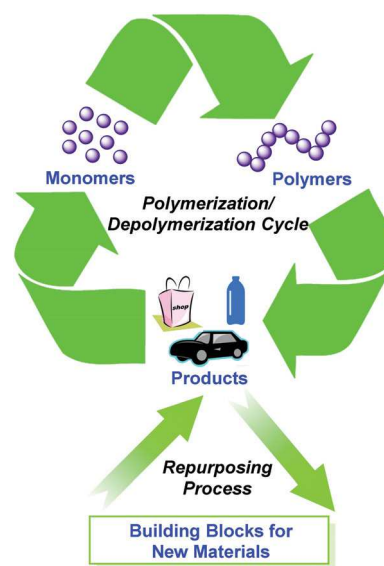


Fig. 1 Chemical recycling of polymer wastes by depolymerization and repurposing processes.

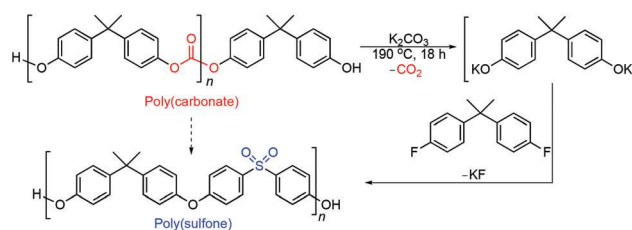
poly[2-(2-hydroxyethoxybenzoate)], PC by CO₂/epoxide copolymerization, and renewable and recyclable polymers (e.g. polyurethanes, elastomers, and polyesters). Examples of industrial mechanical recycling, which always suffers from a significant quality loss (*i.e.*, downcycling), are not covered in this review.

2. Repurposing processes

2.1. Repurposing of engineering plastics into new value-added materials

Engineering plastics exhibit excellent mechanical and/or thermal properties, and the global market for such polymeric materials was valued at \$57.2 billion in 2014 and is expected to reach \$91.8 billion by 2020 at a compound annual growth rate of 8.2%.²⁸ PC and PET are the two most important representative engineering plastics with high production volumes globally. However, PC materials are not typically recycled through conventional mechanical recycling, because they do not have a unique resin identification code, therefore tons of PC wastes often end up in landfills after use.²⁹ Despite the fact that mechanical recycling of PET represents one of the most successful and widespread examples of polymer recycling, the presence of contaminants and residual moisture induces cleavages of polymer chains during the mechanical recycling (melt processing), leading to a significant reduction in polymer molecular weight and consequently in melt viscosity and strength, and these decreases are more pronounced when the recycled resin is soiled.^{30,31} For example, the virgin quality of PET is ductile with >200% of elongation at break, but mechanically recycled PET bottles are brittle with <10% of elongation at break.²⁸ As a result, the overall utility and widespread application of these approaches are limited, and many of the PET materials ultimately find their way to landfills and contribute several billion pounds of wastes to landfills every year.

2.1.1. One-step conversion of PCs into poly(aryl ether sulfone)s. Recently, García *et al.* reported the repurposing of PC waste into value-added poly(aryl ether sulfone) (PSU) materials, which also are a type of high-performance engineering thermoplastic, commonly used for reverse osmosis and water purification membranes, as well as high-temperature applications.³² The authors took advantage of the inherent decomposability of PC under alkaline conditions to generate bisphenolate, with loss of CO₂ as the byproduct. In the presence of a carbonate salt, the formed bisphenolate then subsequently participated in the polycondensation reaction with bis(aryl fluoride) at 190 °C for 18 h (Scheme 1), negating the need for isolation or purification of intermediates, thus demonstrating a one-step conversion of PC into PSU. Although the conversion of the bisphenoxide to PSU is quantitative, the molecular weight of the resulting PSU is relatively low, with a number-average molecular weight (M_n) ≤ 11 kg mol⁻¹. Worth noting here also is that this one-pot strategy was applied to transform a compact disk as the PC source into PSU, as shown in Fig. 2, in which the conversion was equally efficient and the



Scheme 1 Synthetic route of poly(aryl ether sulfone)s via repurposing of PC.

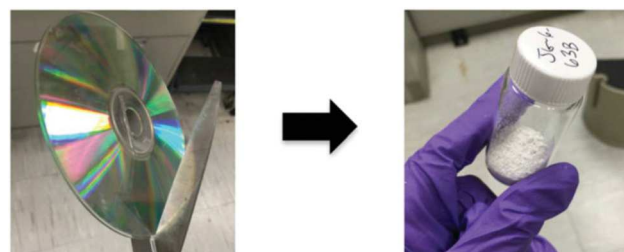
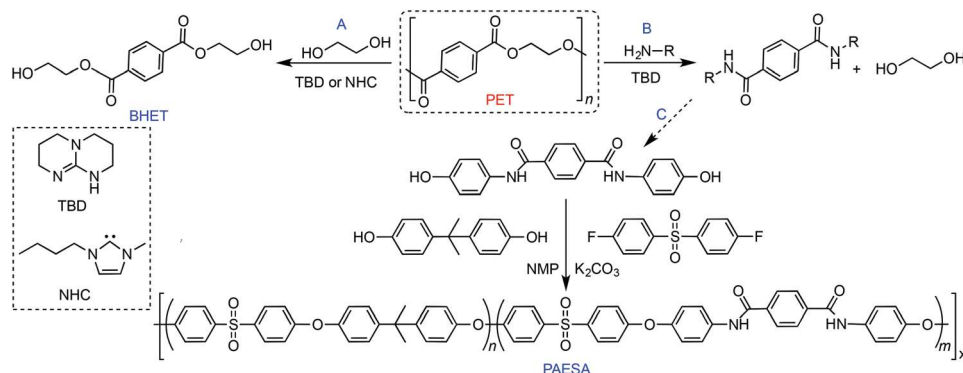


Fig. 2 Repurposing a compact disk as the PC source for the synthesis of PSU. Compact disk (left) and PSU powder (right) are shown before and after the repurposing process.³²

produced PSU exhibited a M_n of 11 kg mol⁻¹ and dispersity ($\bar{D}$) of 1.73 (for the purified PC pellets: M_n = 6.8 kg mol⁻¹, $\bar{D}$ = 2.79). Computational investigation performed with density functional theory (DFT) indicated that the carbonate salt played two important catalytic roles in this reaction: it decomposed the PC by nucleophilic attack and promoted the subsequent reaction of the bisphenolate formed *in situ* with the aryl fluoride.

2.1.2. Aminolysis and glycolysis of PET. In 2010, Hedrick and coworkers reported the repurposing process of PET waste (*i.e.*, postconsumer PET beverage bottles) by glycolysis in the presence of an excess amount of ethylene glycol using an organic catalyst, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), to produce bis(2-hydroxyethyl) terephthalate (BHET) (Scheme 2A), which is a promising monomer for subsequent condensation polymerization.³³ After glycolysis at 190 °C for 3.5 h, a BHET monomer was obtained as the major product, accompanied by a small amount of impurities such as the linear dimer of BHET terephthalic esters and additives (e.g. isophthalic acid, diethylene glycol, and cyclohexane dimethanol), which can be purified by recrystallization with 78% isolated yield. The catalytic efficiency of TBD was comparable to that of other metal acetate/alkoxide catalysts. Moreover, the chemical recycling of colored PET bottles was also feasible *via* this strategy, though the glycolysis rate was slower than that in the case of clear PET bottles as many pigments contained acidic components which inhibited the TBD catalyst. A computational study showed that both TBD and ethylene glycol activated PET through hydrogen bond formation/activation to facilitate this reaction. The excess of unreacted ethylene glycol and TBD catalyst can be recycled for more than 5 cycles.



Scheme 2 Repurposing of PET by organocatalysts: (A) glycolysis, (B) aminolysis, (C) synthesis of poly(aryl ether sulfone amide).

In their subsequent work, the organic catalyst for the glycolysis of PET was also extended to N-heterocyclic carbene (NHC) catalysis, where the reaction mixture was refluxed in anhydrous tetrahydrofuran to give BHET under relatively mild reaction conditions and a shortened reaction time of only 1 h.³⁴

Besides glycolysis, Hedrick *et al.* also established an effective aminolysis of PET waste by organocatalysis with TBD, producing a diverse set of crystalline terephthalamides that possess potential as additives, modifiers, and building blocks for high performance materials with desirable thermal and mechanical properties derived from the hydrogen bonding and rigidity of the structure (Scheme 2B).³⁵ As aminolysis is more thermodynamically favorable than alcoholysis, the reactions of the aminolysis work were carried out under relatively mild reaction conditions with typical temperatures of 110–120 °C for 1–2 h, providing terephthalamides in moderate to good yields. Computational and experimental studies concluded that the bifunctionality of TBD played a crucial role in the aminolysis, which differentiated TBD from other organic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and piperidine.

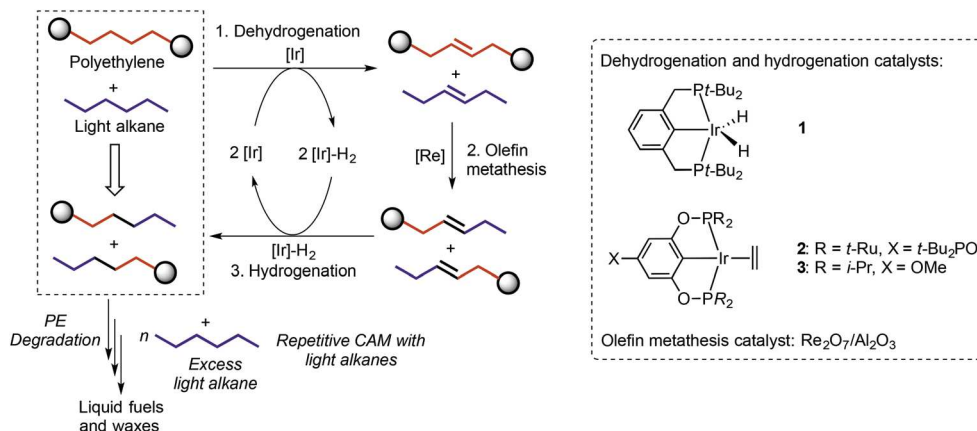
In their recent work, the obtained terephthalamide monomer was subjected to nucleophilic aromatic substitution (S_NAr) polymerizations, creating novel thermoplastic poly(aryl ether sulfone-amide)s (PAESAs, Scheme 2C) with 10–30 mol% incorporation of terephthalamide (M_n : 44.6–71.5 kg mol⁻¹, D : ~2).³⁶ Due to the existence of hydrogen bonding, the resulting PAESA samples exhibited good thermal properties with a maximum T_g of 215 °C. Moreover, a maximum modulus of ~3 GPa, yield strengths of 40–60 MPa and ductility of 6–11% can be observed, indicating that the resulting polymer was a hard, rather than a flexible, polymer material, consistent with the rigidity of the structure.

2.2. Repurposing of commodity polyolefins into equal- or higher value materials

Polyolefins, chiefly PE and iPP, account for nearly two-thirds of the world's plastics, totaling about \$200 billion in annual sales worldwide.³⁷ However, the inherent chemical inertness of such

polyolefins renders their degradation by low energy processes a challenging task, due to the fact that all atoms of PE and iPP are connected by strong single C–C and C–H bonds.³⁸ On the other hand, because of the high costs associated with sorting PE or iPP from one another, the immiscible PE and iPP materials tended to become recycled together into a lower-value, brittle material by melt processing (downcycling).^{39,40} Currently, polyolefins constitute more than 60% of the total plastic content of municipal solid waste.³⁸

2.2.1. Degradation of PE into liquid fuels and waxes. Recently, Huang and Guan *et al.* reported a repurposing process of various types of PE materials into liquid fuels (diesel) and waxes under relatively mild conditions.⁴¹ The strategy was based on a tandem catalytic cross alkane metathesis (CAM) process,^{42–45} which involved a class of highly efficient alkane dehydrogenation catalysts, molecular pincer-type iridium complexes **1–3**, to dehydrogenate the PE and the added light alkane, and then the resulting unsaturated PE and light alkene underwent rhenium-catalyzed cross metathesis to form two new olefins, which were subsequently hydrogenated by the iridium catalyst (Ir-H₂) to produce saturated alkanes (Scheme 3). With the use of low-value, short alkanes (*e.g.* petroleum ethers) as the cross metathesis partners, various PE materials with molecular weight (MW) ranging from thousands to millions can be converted into useful oils as the major products and low-MW waxes as the minor products, upon heating the reaction mixture at 150 °C for 3 days. The distribution of the degradation products can be controlled by the reaction time and Ir catalyst structure, producing liquid fuels in weight percentages of 56%, 98%, and 95% by catalysts **1**, **2**, and **3**, respectively. Moreover, this method showed good selectivity for linear alkanes without the formation of aromatic compounds or alkenes. The tandem catalytic system was compatible with various polyolefin additives, such as polyphenol- and phosphite-based stabilizers and zinc stearate, which allowed full degradation of waste PE bottles, films, and bags into valuable oils and waxes (Fig. 3). The supported Ir and Re catalysts, both on γ -Al₂O₃, were recycled for the alkane dehydrogenation and olefin metathesis reaction, respectively, but with reduced



Scheme 3 Degradation of PE through CAM with light alkanes (e.g., *n*-hexane): proposed PE degradation pathway through the catalytic CAM process and structures of the dehydrogenation and olefin metathesis catalysts used in this study. Modified from ref. 41 with permission from AAAS.

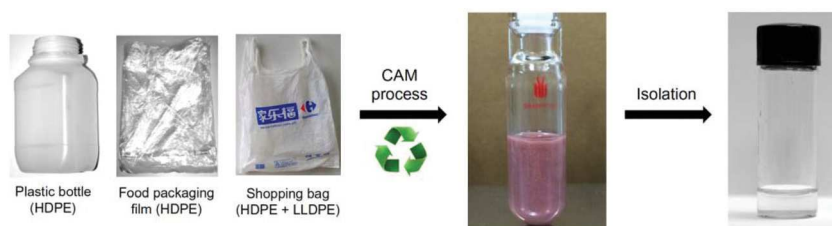


Fig. 3 Degradation of postconsumer PE plastic bottle (HDPE), food packaging film (HDPE), and grocery shopping bag (a blend of HDPE and LLDPE) into oils. Adapted from ref. 41 with permission from AAAS.

activity. The recyclability of the tandem catalysts in the PE degradation reaction was not provided.

2.2.2 Recycling PE/iPP blends by adding PE-iPP block copolymers. Very recently, Bates and Coates *et al.* developed a novel strategy of using PE-iPP tetrablock copolymers as additives or compatibilizers for effectively recycling mixed PE and iPP materials into equal or possibly higher value materials with lower sorting cost. The preparation of high-MW iPP and PE diblock and tetrablock copolymers ($M_n = 55\text{--}306\text{ kg mol}^{-1}$, $D = 1.29\text{--}1.38$) utilized a pyridylamidohafnium precatalyst and activator $B(C_6F_5)_3$ (Fig. 4).⁴⁶ The living characteristics of both ethylene and propylene polymerizations enabled the precise control of the block length, in which the MW of the PE block was controlled by varying the reaction time under a constant ethylene feed, whereas the MW of the iPP block was tuned by the monomer/catalyst ratio and monomer conversion. The resulting semicrystalline block copolymers can weld common grades of commercial PE and iPP together, depending on the molecular weights and architectures of the block copolymers. Peel tests showed that melt-molded PE/iPP laminate displayed poor interfacial adhesion and peeled apart easily with peel strength ($S = \text{force/sample width}$) lower than 0.5 N mm^{-1} . Incorporation of short diblock copolymers (PP₂₄PE₃₁ and PP₇₃PE₅₀) slightly increased the peel strength to $S = 1$ or 3 N mm^{-1} , but the resulting laminate still peeled apart easily (Fig. 4C). Using a long diblock copolymer beyond a threshold

MW (PP₇₁PE₁₃₇) led to a change in the failure mechanism from adhesive failure to cohesive failure (Fig. 4B, $S > 6\text{ N mm}^{-1}$), as the polymer block can bridge the amorphous layers associated with iPP and PE, leading to cocrystallization along the film interfaces. In contrast, short diblock copolymers are less capable of reaching the homopolymers' crystalline lamellae, resulting in a lower adhesive strength. Behaving differently from diblock copolymers, incorporating tetrablock copolymers (PP₃₆PE₂₀PP₃₄PE₂₄) brought about a considerably enhanced adhesive strength, despite the fact that the blocks were below the threshold MW, thereby transforming brittle materials into mechanically tough blends, owing to the different mechanism as the tetrablock molecular architecture ensured that half of the iPP and PE blocks were flanked by thermodynamically incompatible counterparts (Fig. 4A).

3. Depolymerization processes

3.1. Chemical recycling of high-performance thermosets under controlled pH

Many microelectronic, aerospace, and automotive devices contain heat-resistant, chemically stable thermosets that are not amenable to reprocessing or recycling once cured, and thermally decompose upon heating to high temperature. Moreover, polymerization processes for thermosets generally

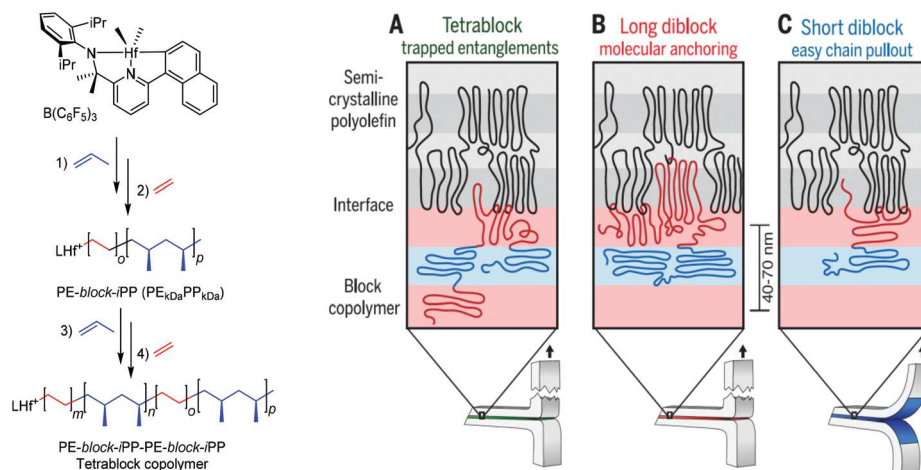
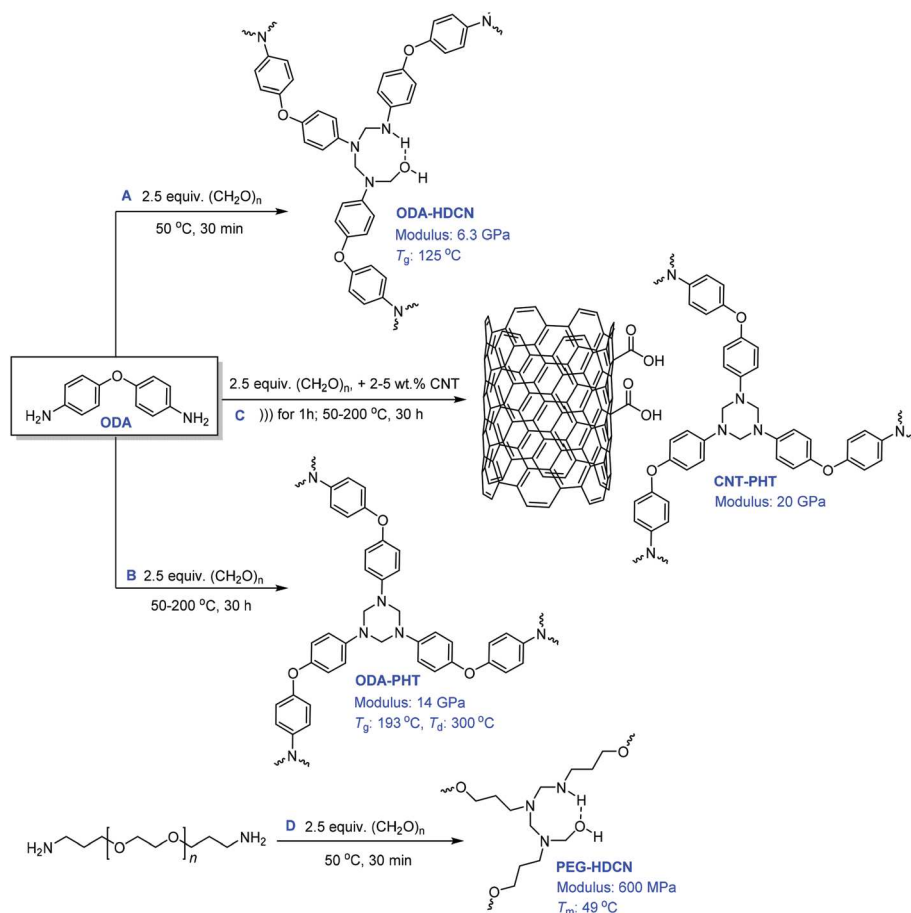


Fig. 4 Synthesis of PE/iPP tetrablock copolymers by a pyridylamidohafnium catalyst, and the peel strength of a commercial PE/iPP blend with or without various block copolymers. Adapted from ref. 46 with permission from AAAS.

require high temperature and a long reaction time.⁴⁷ In 2014, García *et al.* reported recyclable and strong thermosetting polymers by a one-pot, relatively low-temperature polycondensation between paraformaldehyde and a A_2 monomer containing two

$-\text{NH}_2$ units [*e.g.* 4,4'-oxydianiline (ODA)] at 50 °C for 30 min, after which a hemiaminal dynamic covalent network (ODA-HDCN, Scheme 4A) was formed; it was further cyclized at higher temperatures (50–200 °C, 3 h), producing poly(hexa-



Scheme 4 Tunable HDCN/PHT platforms: (A) ODA-HDCN dynamic covalent network, (B) ODA-PHT cross-linked polymer network, (C) CNT-PHT composite, and (D) PEG-HDCN.

hydrotriazine), a highly cross-linked polymer network (ODA-PHT, Scheme 4B).⁴⁸ Both the dynamic covalent network and cross-linked network materials showed distinctive mechanical properties and exhibited high Young's moduli (ODA-HDCN: 6.3 GPa, ODA-PHT: 14.0 GPa), which were comparable to, or even higher than, those of the conventional thermosets. When ODA-PHT was reinforced with surface-treated carbon nanotubes (CNT, Scheme 4C), the Young's modulus of the resulting composite (CNT-PHT) was further enhanced to 20 GPa.

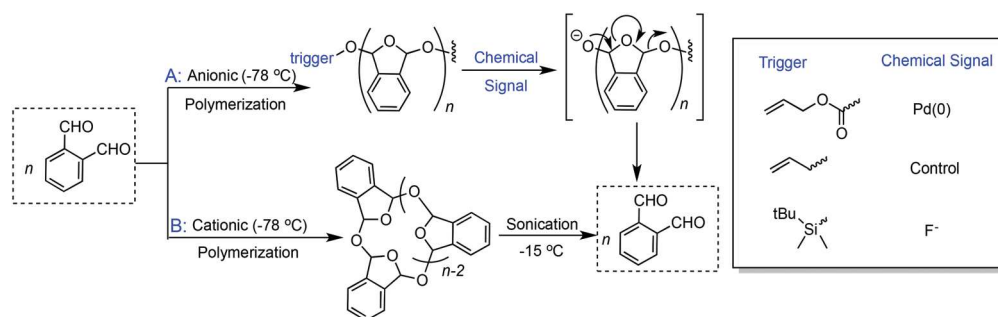
Both HDCNs and PHTs are chemically resistant and also insensitive to weak acids ($\text{pH} > 2$), but at low $\text{pH} \leq 2$ they can be depolymerized to recover the bisaniline monomers for reuse [e.g., using 0.5 M H_2SO_4 (10 mL, $\text{pH} = 0$), ODA-PHT (25.0 mg) was depolymerized in 24 h, while ODA-HDCN (27.3 mg) required 56 min], representing a novel and useful route for recycling and reprocessing of thermosets. Although thermoreversible, reprocessable thermosets have been reported previously, such as those cross-linked by physical interactions (e.g. hydrogen bonding or noncovalent interaction of metal with polymer), the problem is that such thermosets typically cannot withstand high temperatures, a property that is crucial for thermoset application. In comparison, thermosets developed in this work not only exhibit covalently cross-linked structures responsible for enhanced resistance to temperature, but also are uniquely recyclable. The synthetic platform can also be extended by using different diamine monomers, for example, diamine-terminated poly(ethylene glycol), which led to the formation of elastic organogels that exhibited self-healing properties (PEG-HDCN, Scheme 4D).

3.2. Chemically or mechanically triggered depolymerization of poly(*o*-phthalaldehyde)

Poly(*o*-phthalaldehyde) (PPA) has been shown to have a low ceiling temperature (T_c) of around -40°C ; without a kinetically stabilizing end cap, it rapidly depolymerizes back to a monomer at a temperature above -40°C .^{49–52} Adding a suitably functional group to the end of the polymer can prevent such cleavage and stabilize the polymer up to 180°C .⁵³ High-MW PPA can also enable polymer stability above its T_c even without end capping.⁵³ Seo and Phillips prepared three linear

PPAs by anionic polymerization at -78°C , each of which contained a different end-capping group, or a “trigger”, and was capable of responding to a different chemical signal and depolymerizing once the signal reacted with the trigger (Scheme 5A).⁵⁴ For example, PPA with an ester moiety chain end can be cleaved by palladium(0), PPA with a silane group can be cleaved by fluoride, while PPA with an alkene chain is stable under both conditions thus acting as a control (Scheme 5A). Each polymer was stable in solution at 25°C , but those bearing reactive end-groups rapidly depolymerized upon addition of their specific signals [palladium(0) or fluoride], enabling the recyclability of PPAs.

Recently, Moore *et al.* reported mechanically triggered depolymerization of cyclic PPA⁵⁵ synthesized *via* cationic polymerization at -78°C (Scheme 5B).⁵⁶ Utilizing sonication as the mechanical force, rapid unzipping to monomers can be observed in the case of PPA with M_w higher than 26 kg mol^{-1} . For example, PPA ($M_w = 458\text{ kg mol}^{-1}$) was sonicated in THF under argon at -40°C for 6 h, resulting in 60% depolymerization of the original polymer to its monomer as confirmed by GPC. However, no significant change was observed for PPA with M_w lower than 26 kg mol^{-1} , because mechanochemical bond scission has an inherent limiting MW, below which mechanochemical energy is not accumulated to a sufficient degree to break a covalent bond.^{57,58} Unlike the prevalence of radical intermediates in typical mechanochemical reactions, *ab initio* steered molecular dynamic calculations, coupled with end group trapping experiments, indicated the heterolytic-bond scission mechanism in the case of cyclic PPA, in which bond scission produced a linear zwitterionic chain containing oxocarbenium and hemiacetalate chain ends, both of which underwent head-to-tail depolymerization to yield a monomer. The resulting monomer can be subsequently repolymerized to PPA under suitable conditions, successfully completing a depolymerization–repolymerization cycle. For example, after adding *n*-BuLi as an initiator to the depolymerization mixture and repolymerizing at -78°C for 10 h, two peaks were observed in the GPC curves, one of which corresponded to the polymer remaining after sonication, while the other was a new, lower-MW peak formed by repolymerization. Owing to the dependence of mechanochemical bond scission on MW,



Scheme 5 Anionic and cationic polymerization methods used to synthesize linear and cyclic PPAs, and subsequent chemically or mechanically triggered depolymerization of PPAs.

the monomer recovery in this mechanically triggered depolymerization was not quantitative.

3.3. Thermal and chemical recycling of polyurethanes, cross-linked PC and polyester elastomers

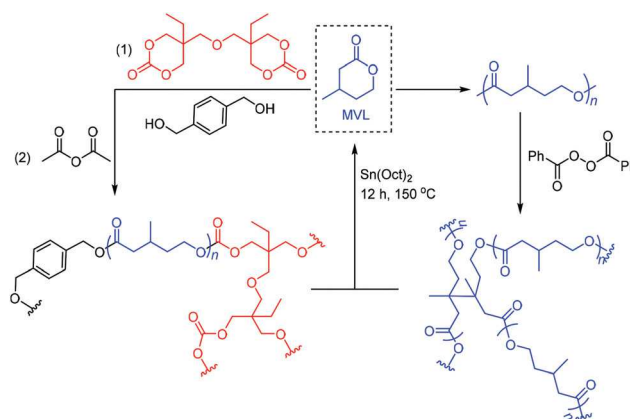
Recently, Hillmyer *et al.* developed an economical route to a biorenewable lactone monomer β -methyl- δ -valerolactone (MVL) through a total biosynthetic pathway from glucose, or an efficient semisynthetic approach with high yield from mevalonate that relied upon the fermentation of glucose.^{17,59} Based on the MVL platform, a series of thermoplastic polyurethanes (PUs) and cross-linked flexible PU foams were synthesized by employing hydroxyl telechelic poly(MVL) (PMVL) obtained by the ring-opening polymerization (ROP) of MVL as a replacement for petroleum-derived polyols (Scheme 6).⁶⁰ PUs, generally obtained by the condensation of polyols and multifunctional isocyanates, have achieved incredible commercial success due to their low cost and high versatility, and the properties of PUs can be optimized for applications ranging from soft and flexible foams for cushioning to hard and rigid materials for construction. However, the nondegradability of postconsumer PU products has caused a massive waste management problem that has not yet been solved. In their work, flexible foams were shown to be chemically recycled by exploiting the reversibility of the urethane bond and the thermodynamic tendency of PMVL to depolymerize to recover the MVL monomer (Scheme 6). Under pyrolysis conditions, the recycled monomer was isolated in high yield up to 97% with high purity ($\geq 95\%$ by ^1H NMR spectroscopy) after 10 h under optimized conditions. It was also possible to recycle PMVL foams by adding stannous octoate $[\text{Sn}(\text{Oct})_2]$ with an enhanced depolymerization rate (Scheme 6). Moreover, the authors used the recovered MVL from the depolymerization of PMVL foams to synthesize new PMVL polyols which were shown to be indistinguishable from an analogous sample prepared from virgin monomers using the same synthetic method.

Very recently, recyclable cross-linked PC and polyester elastomers based on biorenewable MVL with improved solvent resistance and thermal stability were also developed by Hillmyer *et al.* through two different methodologies, including tandem copolymerization/cross-linking with bis(six-membered

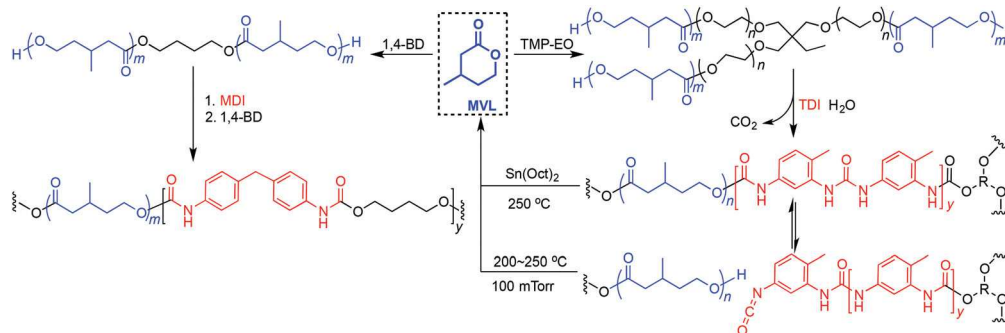
cyclic carbonate) as the cross-linker to the PC elastomer, and cross-linking of a linear PMVL in the presence of benzoyl peroxide as the free-radical generator to the polyester elastomer (Scheme 7).⁶¹ Tensile strength up to 12 MPa and elongation up to 2000% were observed for these elastomeric materials. By incorporating fumed silica, the Young's modulus and tensile strength were improved by 57% and 83%, respectively, without a significant loss in elasticity. Both elastomers were shown to depolymerize in the presence of $\text{Sn}(\text{Oct})_2$ and pentaerythritol ethoxylate at 150 °C overnight under vacuum, recovering the MVL monomer in up to 93% yield. Aqueous degradation studies indicated that these cross-linked elastomeric materials were capable of degradation under both acidic and basic conditions at 60 °C.

3.4. Thermal and chemical recycling of poly(L-lactide)

Poly(L-lactide) (PLLA), a commercially implemented, notable biodegradable polymer derived from biorenewable resources, such as corn and other agricultural products, has attracted considerable attention as a promising alternative to the petroleum-based commodity resins.^{62–65} However, disposal of large-scale postconsumer PLLA products in landfills causes loss of materials' value after a single use and also contributes



Scheme 7 Synthetic route and chemical recycling of cross-linked PC and polyester elastomers.



Scheme 6 Synthetic route to thermoplastic PU and flexible foam, and chemical recycling of flexible PU foam. TDI = toluene diisocyanate; MDI = 4,4'-methylene diphenyl diisocyanate; TMP-EO = trimethylolpropane ethoxylate; 1,4-BD = 1,4-butanediol.

to excess plastic wastes and other environmental problems as PLLA has a slow degradation rate under landfilling conditions.^{14,25,26} An ideal solution to the above issues is the chemical recycling of the postconsumer PLLA to recover L,L-lactide feedstock before it winds up in the landfill. In this context, Kopinke and coworkers examined the thermal decomposition of PLLA and found that it proceeded through random transesterification degradation with intramolecular transesterification as the dominant reaction pathway, giving rise to the formation of cyclic oligomers and lactide with considerable racemization (Scheme 8A).⁶⁶ In addition, acrylic acid from *cis*-elimination, as well as carbon dioxide, carbon monoxide, and acetaldehyde from fragmentation reactions, was also detected. The existence of *meso*-lactide, formed by racemization which was proposed to proceed through an ester-semiacetal tautomerization occurring in a lactate unit in the chain under higher temperature, would significantly diminish some of the useful properties, such as crystallizability and crystallinity, after the reproduction of PLLA.

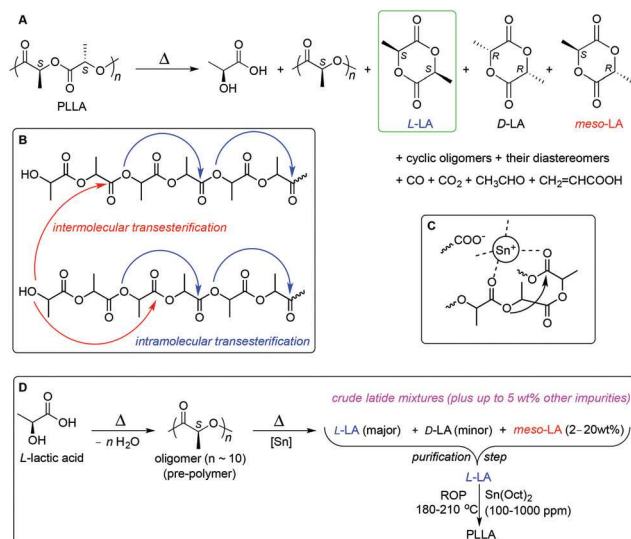
PLA samples contaminated with residual Sn from the polymerization process using Sn(Oct)₂ as a catalyst can decrease the degradation temperature. Nishida *et al.* prepared PLLA samples with different Sn content varying from 20 to 607 ppm to clarify the effect of the residual Sn on PLLA pyrolysis.⁶⁷ The pyrolysis of PLLA Sn-607 (Sn content: 607 ppm) in the temperature range of 40–400 °C produced lactide (including *meso*-lactide, L,L-lactide and D,D-lactide) predominately, plus cyclic oligomers (0.90%), with *meso*-lactide/(L,L-lactide + D,D-lactide) = 11.4/88.6. In contrast, the pyrolysis of PLLA Sn-20 (Sn content: 20 ppm) was accompanied by the production of much more cyclic oligomers (20.5%), with *meso*-lactide/(L,L-lactide + D,D-lactide) = 36.8/63.2. The kinetic analysis of the

dynamic pyrolysis data indicated that the pyrolysis started through random transesterification degradation and then shifted to Sn-catalyzed unzipping degradation with increasing Sn content (Scheme 8B). Nishida and coworkers found that the calcium salt end capped PLLA (PLLA-Ca) exhibited a temperature-dependent degradation.⁶⁸ At temperatures lower than 250 °C, *meso*-lactide was predominantly formed (>75%, especially at temperatures lower than 220 °C), while at temperatures higher than 320 °C it was one of the components (*meso*-lactide < 50%). At temperatures in the range of 250–320 °C, the unzipping depolymerization mechanism dominated, resulting in more selective L,L-lactide formation with a small amount of *meso*-lactide (2.1%). Moreover, less toxic and more easily available alkali earth metal oxides, including calcium oxide (CaO) and magnesium oxide (MgO), were blended with PLLA to prepare the PLLA/metal oxide composites (5 wt%) and investigated to ascertain the effect of such metal oxides on the thermal decomposition.⁶⁹ Both metal oxides markedly lowered the degradation temperature, but CaO caused some racemization of lactide, especially at temperatures lower than 250 °C, while the pyrolysis of the PLLA/MgO composite occurred smoothly, resulting in more selective L,L-lactide formation with unzipping depolymerization. Furthermore, the effect of different chain end structures, including as-polymerized PLLA-ap, precipitated-with-methanol PLLA-pr, and PLLA-H purified by a liquid–liquid extraction method with 1 M HCl, on the pyrolysis of PLLA was also investigated by Nishida *et al.*⁷⁰ Both pyrolysis of PLLA-ap and PLLA-pr produced L,L-lactide selectively while a large amount of diastereoisomers and cyclic oligomers was formed by random degradation of PLLA-H.

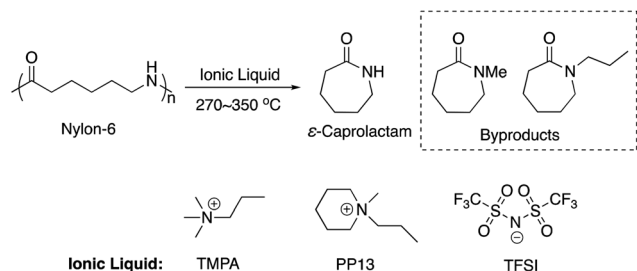
It is important to note here that the commercial production of L-LA monomer relies on the catalyzed degradation of a low MW PLLA pre-polymer prepared by a continuous condensation reaction of aqueous L-lactic acid (Scheme 8C).⁷¹ This pre-polymer is then depolymerized into a mixture of lactide stereoisomers, the depolymerization process of which is catalyzed using a Sn catalyst to enhance both the rate and selectivity of the intramolecular cyclization reaction. The molten crude lactide stereoisomer mixture, consisting of 2–30 wt% *meso*-LA plus up to 5 wt% other (non-lactide) impurities, is then purified by vacuum distillation, and the resulting pure L-LA is polymerized by ROP with Sn(Oct)₂/ROH to high MW PLLA. In short, racemization of L-LA represents a major problem with the feedstock recycling of PLLA,^{72,73} even in the catalyzed depolymerization of the low MW pre-polymer.

3.5. Thermal and chemical recycling of nylon-6

The depolymerization of nylon-6 in ionic liquids to recycle ε-caprolactam monomers was examined by Kamimura *et al.* (Scheme 9).⁷⁴ It was found that the ionic liquids favored the depolymerization, achieving a monomer recovery yield of 43–55% after heating nylon-6 chips at 300 °C for 5–6 h and collecting the monomers by distillation from the reaction mixture. In contrast, no depolymerization of nylon-6 took place by heating it in glycolic solvents such as ethylene



Scheme 8 A mixture of products formed by typical thermal decomposition of PLLA (A), proposed random transesterification degradation (B), Sn-catalyzed unzipping (more selective) degradation (C), and commercial route to L-LA monomer and high MW PLLA (D).



Scheme 9 Depolymerization of nylon-6 into its constituent monomer ϵ -caprolactam in the presence of an ionic liquid.

glycol and triethylene glycol. Quaternary ammonium salts (Scheme 9), such as *N*-methyl-*N*-propylpiperidinium (PP13) and *N,N,N*-trimethyl-*N*-propylammonium (TMAP) with bis(trifluoromethanesulfonyl)imide (TFSI) as the counter anion, were found to be the most effective ionic liquids for this depolymerization. Adding *N,N*-dimethylaminopyridine as the catalyst enhanced the efficiency of depolymerization and the monomer yield was further increased to 86%. It was also found that the optimum temperature for more efficient and selective depolymerization was 300 °C. The temperature below or above 300 °C led to much lower yields of the desired monomer product (270 °C: 7%; 330 °C: 55%; 350 °C: 6%). Moreover, byproducts such as *N*-methyl and *N*-propyl lactams (Scheme 9) formed at a temperature of 330 °C or higher due to the decomposition of the ionic liquid. After the depolymerization, ionic liquids can be recycled and reused five times without the loss of depolymerization efficiency.

3.6. Complete thermal or chemical recyclability of poly(γ -butyrolactone)

γ -Butyrolactone (γ -BL) is a key downstream chemical of succinic acid, a top ranked biomass-derived chemical best suited to substitute petroleum-derived chemicals.^{75,76} The ROP of γ -BL would provide a convenient and inexpensive pathway to poly(γ -butyrolactone) (P γ BL) which is a structural equivalent of poly(4-hydroxybutyrate) (P4HB) produced *via* a bacterial fermentation process and shown to exhibit more desired properties (for example, a faster degradation rate and better mechanical properties) relative to other commonly used aliphatic polyesters.^{77,78} However, because of the negligible strain energy of its five-membered ring,^{79,80} ring-opening polymerization of γ -BL has been a challenge, and it is commonly referred to as being 'non-polymerizable'.^{81–85} The ROP of γ -BL can be realized under ultrahigh pressure (e.g. 20 000 atm, 160 °C), but producing only oligomers with low yield ($\leq 20\%$) and low MW (< 3.5 kg mol^{−1} or > 5.0 kg mol^{−1} with acid catalysts).^{86–88} Recently, Hong and Chen achieved, for the first time, an efficient chemical synthesis of relatively high MW P γ BL *via* the ROP of γ -BL with high conversion under ambient pressure.⁸⁹ The three strategies employed in this work are critical for success. The first is to meet the thermodynamic conditions for this ROP *via* reducing the entropic penalty of the ROP by performing the polymerization at a low-enough temperature

(i.e., below the T_c of polymerization, for a given monomer concentration $[M]$). The second is to control the reaction conditions (concentration and solvent) so that $[M]$ becomes greater than the equilibrium $[M]_{eq}$ and the formed polymer crystallizes or precipitates from the solution during the polymerization; such conditions allow continuous perturbation of the propagation/depolymerization equilibrium and shifting it towards propagation. The third is to modulate the kinetic conditions by employing powerful ROP catalysts so that high monomer conversions can be achieved under the low temperature reaction conditions and within a practically feasible time period. By adopting the above three strategies, the ROP of γ -BL carried out at -40 °C with powerful metal catalysts such as $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ in combination with a suitable alcohol initiator, and discrete Y catalysts (Fig. 5) successfully produced P γ BL with relatively high MW of M_n up to 30 kg mol^{−1} and high conversion of up to 90%. Intriguingly, varying the alcohol initiator structure and the ratio of γ -BL/La/alcohol provided a synthetic control over the P γ BL topology: linear *vs.* cyclic structure. Significantly, the thermal decomposition study of the purified P γ BL (upon removal of the catalyst residue) showed that P γ BL can quantitatively depolymerize back into γ -BL monomers without any by-products, by simply heating the bulk material at 220 °C (for the linear polymer) or 300 °C (for the cyclic polymer) for 1 h under a nitrogen atmosphere, thereby demonstrating the completely thermal recyclability of P γ BL. The complete chemical recyclability of P γ BL has also been established. Thus, in the presence of an organic or metal catalyst (2.0 mol%), the depolymerization of P γ BL to the pure monomer occurred rapidly even at room temperature. For instance, the half-life ($t_{1/2}$) for TBD-catalyzed depolymerization was 6.9 min, while much faster depolymerization was observed in the $\text{La}[\text{N}(\text{SiMe}_3)_2]_3$ -catalyzed depolymerization, with a $t_{1/2}$ of only 0.82 min.⁸⁹

The ROP of γ -BL was also successfully promoted by organic phosphazene superbase 'Bu-P₄ (Scheme 10).⁹⁰ It was found that 'Bu-P₄ itself directly initiated the ROP through deprotona-

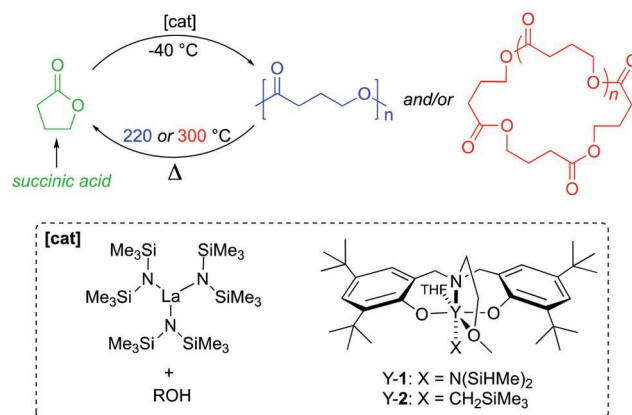
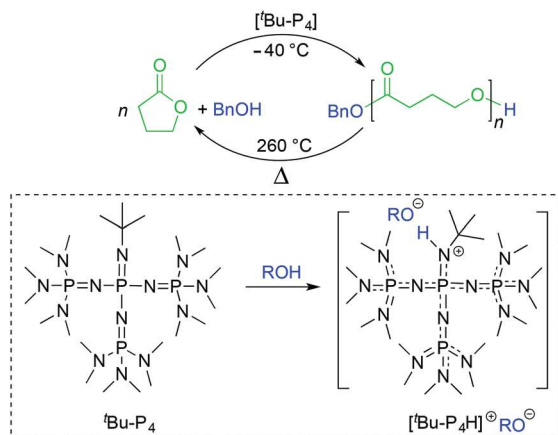


Fig. 5 ROP of 'non-strained' γ -BL into P γ BL with high MW and complete (thermal and chemical) recyclability, and the structures of catalysts used for the ROP.



Scheme 10 ROP of γ -BL by organic superbases $^t\text{Bu-P}_4$ and complete thermal or chemical recyclability of the resulting $\text{P}\gamma\text{BL}$, including the end groups.

tion of γ -BL to generate the reactive enolate species that produced $\text{P}\gamma\text{BL}$ with $M_n = 26.4\text{ kg mol}^{-1}$ at a conversion of 30.4%. Combining $^t\text{Bu-P}_4$ with a suitable alcohol (such as BnOH), which formed an ion pair weakly associated with H-bonding $[\text{Bu-P}_4\text{H}^+\cdots\text{OBn}^-]$ (Scheme 10), enabled a more effective ROP, thus converting 90% γ -BL in 4 h to produce $\text{P}\gamma\text{BL}$ with $M_n = 26.7\text{ kg mol}^{-1}$. In contrast, commonly used organic catalysts, such as TBD, known to be highly effective for the ROP of typical cyclic esters, failed to produce high MW $\text{P}\gamma\text{BL}$ ($M_n \leq 6.2\text{ kg mol}^{-1}$ and yield $\leq 33\%$). More importantly, upon treatment of the bulk material of the resulting $\text{P}\gamma\text{BL}$ at $260\text{ }^\circ\text{C}$ for 1 h, not only was the main chain completely recycled back to monomer γ -BL, but also the BnO/H end groups reformed back to the starting initiator BnOH . Overall, owing to its biorenewable resource, organocatalytic synthesis, and completely thermal or chemical recyclability, $\text{P}\gamma\text{BL}$ bears the hallmarks of a 'truly sustainable' polymer.

3.7. Chemically recyclable polyester based on α -methylene- γ -butyrolactone

Owing to its higher reactivity and ability to form an acrylic polymer with superior material properties relative to its linear analog methyl methacrylate (MMA), α -methylene- γ -butyrolactone (MBL) or tulipalin A (Fig. 6), found naturally in tulips^{91,92} or produced chemically from biomass feedstocks,⁹³ is being considered as a renewable alternative to the petroleum-based MMA.^{94,95} Considering the presence of a highly reactive exocyclic $\text{C}=\text{C}$ bond and a relatively non-strained stable five-membered lactone ring, not surprisingly MBL was reported previously to proceed exclusively through the vinyl-addition polymerization (VAP) pathway (Fig. 6),^{96–105} although the ROP of MBL can be realized in its copolymerization with a lactone having high ring strain energy such as ϵ -caprolactone (ϵ -CL).^{106,107} Recently, Chen *et al.* successfully suppressed the conventional VAP and enabled the ring opening homopolymerization of MBL by using La and Y-2 catalysts (Fig. 5),¹⁰⁸ producing exclusively unsaturated polyester $\text{P}(\text{MBL})_{\text{ROP}}$ with M_n up

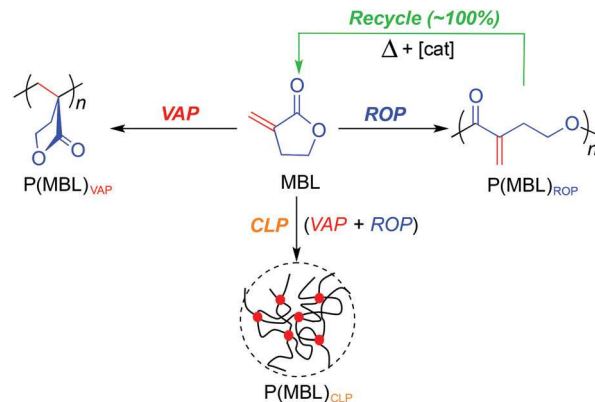
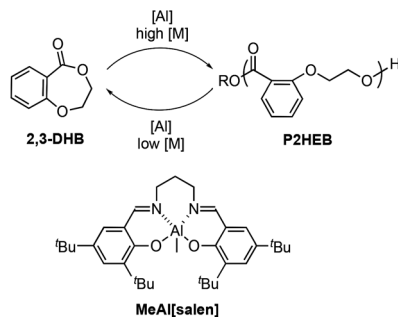


Fig. 6 Three reaction pathways revealed for MBL polymerization, where the ROP leads to the unsaturated polyester that is completely recyclable in the presence of a simple catalyst. Adapted with permission from ref. 108. Copyright 2016 The American Chemical Society.

to 21.0 kg mol^{-1} (Fig. 6). A third reaction pathway for the MBL polymerization—cross-linking polymerization was also realized by promoting crossover propagation between VAP and ROP processes, leading to the formation of cross-linked polymer $\text{P}(\text{MBL})_{\text{CLP}}$ (Fig. 6). The chemoselectivity of the MBL polymerization can be controlled by adjusting the reaction conditions such as the catalyst (La)/initiator (ROH) ratio and temperature; for example, the ROP of MBL was the exclusive reaction when carried out at $-60\text{ }^\circ\text{C}$ with a La/ROH ratio of 3 and $[\text{MBL}]_0$ of 5.0 M. Thermal decomposition of the resulting $\text{P}(\text{MBL})_{\text{ROP}}$ was investigated to examine the thermal recyclability. However, heating the bulk material at the high temperature resulted in the formation of insoluble polymer products rather than MBL monomers, due to thermally induced cross-linking via the $\text{C}=\text{C}$ double bonds in the unsaturated polyester. Moreover, chemical recycling of $\text{P}(\text{MBL})_{\text{ROP}}$ in the presence of a La catalyst at $25\text{ }^\circ\text{C}$ was also not feasible as the depolymerization initially produced some MBL monomers which were subsequently polymerized by the La catalyst into $\text{P}(\text{MBL})_{\text{VAP}}$, plus some insoluble cross-linked material. The complete chemical recyclability was finally realized by heating a solution of $\text{P}(\text{MBL})_{\text{ROP}}$ in DMSO in the presence of the La catalyst (or LaCl_3 , 1 mol%) and water (3.5 mM, added to inhibit the VAP polymerization) at $100\text{--}130\text{ }^\circ\text{C}$ for 1 h, or $60\text{ }^\circ\text{C}$ for 24 h, recovering the MBL monomers in quantitative yield.

3.8. Polymerization–depolymerization cycle for an aromatic polyester and CO_2 /epoxide copolymer or PC

Recently, Shaver *et al.* observed that the ROP of 2,3-dihydro-5H-1,4-benzodioxepin-5-one (2,3-DHB) with an aluminum catalyst ($\text{MeAl}[\text{salen}]$) to poly[2-(2-hydroxyethoxybenzoate)] (P2HEB), a polyester with an aromatic ring in the backbone, is thermally reversible, achieving higher monomer conversion at lower reaction temperature (room temperature) (Scheme 11).¹⁰⁹ This monomer–polymer equilibrium was utilized to establish a reversible polymerization–depolymerization cycle by simply adjusting the initial monomer concentration in



Scheme 11 Polymerization–depolymerization cycle modulated by adjusting the monomer concentration in the presence of a MeAl(salen) catalyst.

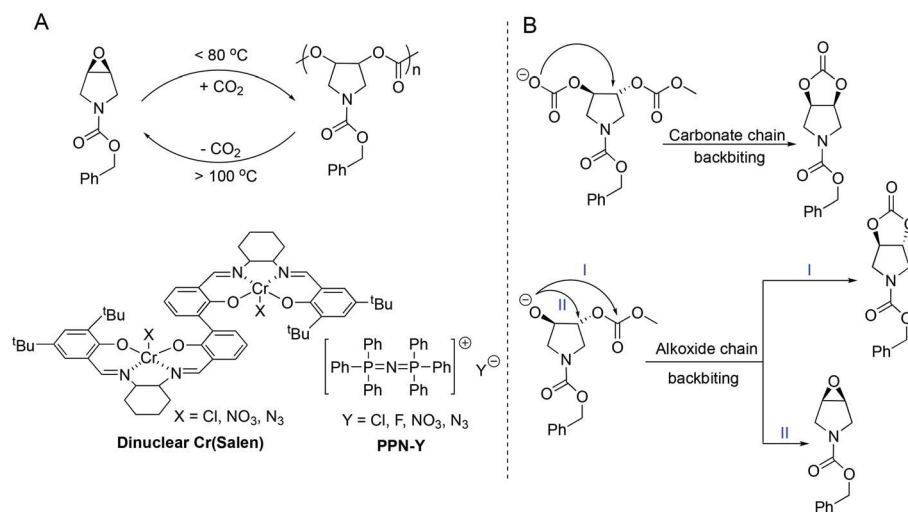
a one-pot reaction. For example, the ROP began with an initial monomer concentration of 4.1 M, producing P2HEB with a conversion of 82% after 6 h at 60 °C. Then, toluene was added to the mixture to reach an apparent $[2,3\text{-DHB}]_0$ of 0.2 M, which resulted in a depolymerization to form a monomer/polymer mixture in a 94/6 ratio. Subsequent re-concentration of the mixture under vacuum gave an apparent $[2,3\text{-DHB}]_0$ of 4.1 M, and then the polymerization restarted, achieving 84% conversion to P2HEB after heating the mixture at 60 °C for 6 h. During the depolymerization, the resulting monomer was found to be of high purity without the formation of any degradation products. Moreover, sequential addition of 2,3-DHB to growing poly(3-hydroxybutyrate) (P3HB) yielded a block copolymer, in which the P2HEB block was readily depolymerized (>90%) leaving chiefly the P3HB chains.

Very recently, Lu and coworkers reported the recyclable PC synthesized by selective copolymerization of CO_2 with 1-benzyl-oxycarbonyl-3,4-epoxy pyrrolidine (BEP) with a dinuclear salen–chromium complex in the presence of nucleophilic cocatalyst PPN-Y [PPN: bis(triphenylphosphine)iminium]

(Scheme 12A).¹¹⁰ By varying reaction temperature, a reversible copolymerization–depolymerization cycle was established in a one-pot fashion, where the BEP monomer was fully converted into PC at 60 °C while the complete and selective depolymerization of PC into BEP was observed when the temperature was raised to 100 °C. *In situ* FT-IR and ^1H NMR studies revealed that this copolymerization–depolymerization process can be recycled several times without any change in the epoxide monomer and copolymer structure. After removing the catalyst, the resulting PC was stable at 200 °C for 10 h. At a raised temperature of 260 °C, the depolymerization occurred and finished in 1 h under a nitrogen atmosphere, forming exclusively the epoxide monomer without any byproduct. The addition of Cr-salen catalyst/PPN-Cl was found to be beneficial for the depolymerization of PC, which can proceed at a relatively low temperature of 150 °C in solution or bulk. The comparison of free energy barriers determined by a computational study for three possible depolymerization products (Scheme 12B), including *trans*-cyclic carbonate (26.6 kcal mol^{−1}), *cis*-cyclic carbonate (14.5 kcal mol^{−1}), and the starting epoxide monomer (12.3 kcal mol^{−1}), further provided the basis for the observed selective depolymerization into the epoxide monomer.

4. Conclusions and outlook

The successful development of recyclable polymers can not only reduce the demand for finite raw materials and alleviate the negative impact of polymeric materials on the environment, but can also establish a circular economy approach to sustainability. To this end, remarkable success has been accomplished in both types of chemical recycling of polymer wastes: repurposing and depolymerization processes. This critical review highlighted three useful and practical strategies



Scheme 12 (A) Copolymerization–depolymerization cycle between PC and CO_2 /BEP monomer in the presence of a dinuclear salen–chromium complex and a PPN-Y cocatalyst; (B) possible depolymerization products.

for repurposing of polymer wastes: (1) decomposition of polymer wastes under controlled pH or in the presence of a reagent to converting them into building blocks for new value-added polymeric materials, such as one-step conversion of PCs into poly(aryl ether sulfone)s and aminolysis of PETs to poly(aryl ether sulfone-amide)s; (2) degradation of polymer wastes to high value oligomers, for example, breakdown of polyethylenes into liquid fuels and waxes; (3) recycling of the polymer mixture by adding a third component to weld the mixture together to equal or higher value materials, for example, recycling of commercial PE and iPP with compatibilizing iPP and PE block copolymers. Compared with the repurposing process, the depolymerization process features a depolymerization–repolymerization cycle and is an ideal and economically efficient way of recovering pure feedstock and remodeling the material with virgin polymer quality; this process emulates the recycling of biomaterials in biological systems comprising amino acids, carbohydrates and nucleic acids. This review highlighted the following useful depolymerization processes with different methodologies: (1) pH triggered chain scission leading to the decomposition of polymers, such as the depolymerization of cross-linked poly(hexahydrotriazine) thermoset under strongly acidic conditions to recover the bianiline monomer; (2) depolymerization of low T_c polymer under mechanical force, with the representative example being the mechanically triggered depolymerization of PPA; (3) thermal depolymerization of polymers to recover the thermodynamically stable monomers, such as thermally recyclable PU foams based on MVL and completely thermally recyclable P γ BL; (4) catalyst-promoted depolymerization, such as Sn(Oct)₂-catalyzed depolymerization of P ϵ LA, Sn(Oct)₂-catalyzed depolymerization of cross-linked elastomers based on MVL, DMAP-catalyzed depolymerization of nylon 6, and LaCl₃-catalyzed depolymerization of PMBL; and (5) recycling of feedstock by perturbing the polymerization–depolymerization equilibrium *via* changing the monomer concentration, in the case of the depolymerization of P2HEB, or *via* changing the reaction temperature, in the case of the depolymerization of the CO₂/BEP epoxide copolymer or PC (removal of CO₂ from the PC).

In our opinion, future research in the area of chemically recyclable polymers will be largely directed at addressing the following *four major challenges*: (1) the polymers that can be easily depolymerized often suffer from undesired thermal and mechanical properties for poor materials performance. Thus, more intensive research is needed to identify new recyclable polymer systems without compromising performance; (2) the complete recycling of feedstock in the depolymerization process is still rare. One such example is the complete recyclability of P γ BL *via* thermal or chemical depolymerization back to its constituent monomer γ -BL without formation of by-products, due to both *kinetically and thermodynamically* favored γ -BL formation during depolymerization while shutting down other decomposition pathways. Future research should aim to discover new monomer–polymer systems that exhibit the capacity for quantitative polymer reversal and isolation of pure monomers; (3) current processes for chemical

recycling usually encounter the problems of high cost and high energy consumption. Besides, the addition of solvents and catalysts during the recycling process also brings about the requirement for isolation and purification procedures. Therefore, future chemical recycling processes should minimize their associated costs by designing more efficient chemical processes; and (4) recyclable polymers, when derived from biorenewable resources and synthesized with “green” methods and procedures,¹¹¹ can be regarded as recyclable “green” polymers. Hence, future research in the synthesis of chemically recyclable polymers should also concern the use of their renewable resources and “green” polymerization methods or procedures, thus altogether providing a circular economy approach to sustainability.

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