

Performance-Guided Design of Chemically Recyclable Polymeric Materials: A Case Study on Thermoplastic Elastomers

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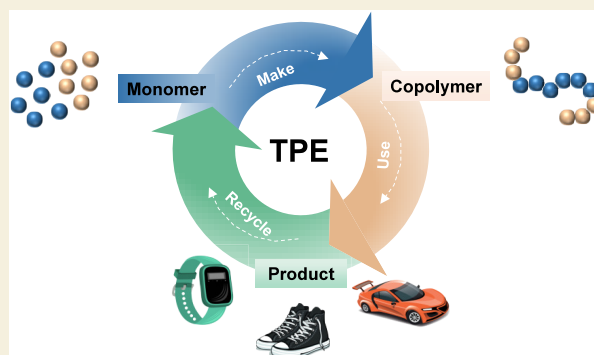
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ABSTRACT: Thermoplastic polymer materials include both plastics and elastomers. Elastomers stand out as a crucial class of materials because of their wide-ranging applications. Polymers that can depolymerize back to their original monomers present a hopeful avenue to tackle the problems associated with polymer sustainability. In recent years, a great deal of research has been centered on the chemical recycling of monomers of polymers, and there are numerous reviews on this topic. Nevertheless, these reviews typically classify materials according to polymerization methods or polymer types, seldom taking into account the functional classification of the products. This method of categorization creates difficulties for those interested in material application scenarios, as they find it hard to obtain relevant information. Hence, this perspective takes a function-oriented approach, offering solutions for recyclable thermoplastic elastomers (TPEs) by classifying them into polyurethanes, copolyesters, and polyolefins with specific sequence control (e.g., homo, random, alternating, triblock, pseudotriblock, and multiblock). We offer an overview of the synthesis methods of various polymers and the properties of the constructed TPEs, making comparisons with those of conventional TPEs. Special attention is given to the depolymerization process, including the necessary conditions and recovery efficiency of the constituent monomers. Finally, we put forward future directions for the chemical recycling of TPEs, highlighting the critical issue of "monomer reuse and performance degradation over successive recycling cycles" that has been overlooked. This perspective seeks to promote more in-depth, cross-disciplinary research involving both academic and industrial partners to develop next-generation TPEs with improved sustainability.

KEYWORDS: thermoplastic elastomer, depolymerization, closed-loop recycling, sustainable polymer, polyurethane, copolyester, polyolefin



1. INTRODUCTION

Thermoplastic polymers comprise plastics and elastomers. A thermoplastic elastomer is a noncross-linked rubber that combines the high elasticity of rubber with the reprocessability of thermoplastic materials. It has a wide range of applications in fields such as automotive, building and construction, electrical and electronics, medical, consumer goods, and others.¹ The TPE market witnessed significant growth over the recent years and will continue to grow up to 5.55 million tonnes by 2026.^{2,3}

The extensive production and consumption of thermoplastic elastomers have led to a significant portion of TPE waste being either landfilled or subjected to thermal treatment. Currently, only 25% of global TPE waste is being recycled, with mechanical recycling accounting for nearly all of this recovered material across all conventional TPE types,⁴ driven by advancements in sorting and reprocessing technologies, reducing overall waste, and supporting a circular economy. The slow progress in TPE recycling technology has become a

serious concern, directly leading to significant accumulation, disposal issues, and exacerbated environmental challenges. TPEs can withstand multiple mechanical recycling cycles, but irreversible thermal/mechanical degradation during each cycle progressively degrades material properties, ultimately compromising end-product quality and preventing extensive recycling while maintaining performance.^{5,6} Alternative recycling strategies that preserve the material properties are necessary. Among them, chemical recycling therefore offers an effective depolymerization strategy for monomer recovery.^{7,8} This approach enables a circular economy by ensuring infinite

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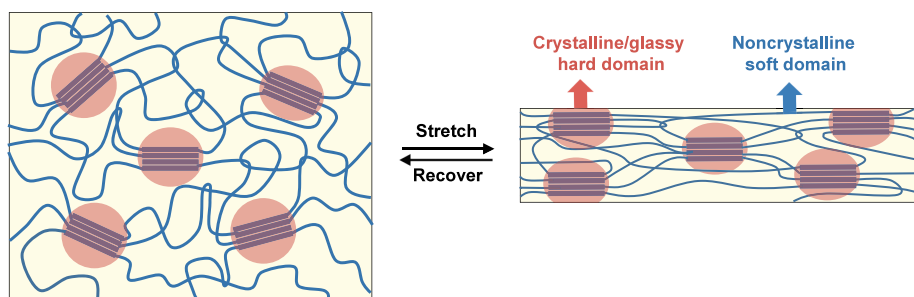


Figure 1. Schematic illustration of the TPE's structure.

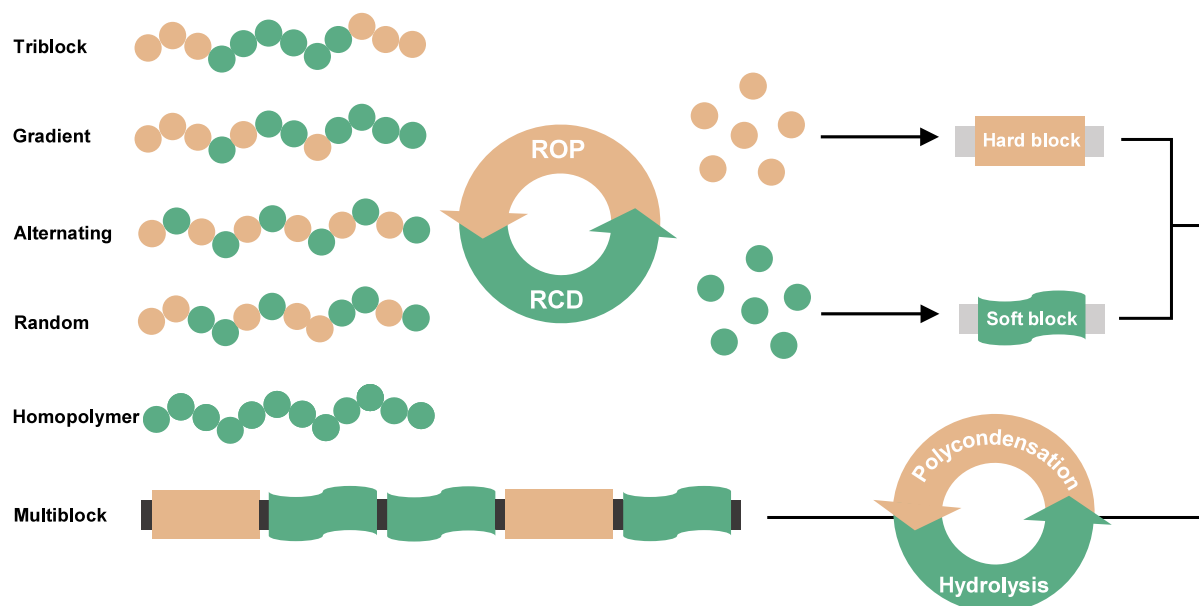


Figure 2. Synthesis and depolymerization strategies used in the TPEs. ROP: ring-opening polymerization. RCD: ring-closing depolymerization.

material recyclability without quality degradation, thereby creating a closed-loop lifecycle.^{9–11}

In recent years, a great deal of research has been centered on the chemical recycling of polymers, and there are numerous reviews on this topic. Nevertheless, these reviews typically classify materials according to polymerization methods,^{12,13} depolymerization methods,^{14,15} polymer types,^{16–22} or monomer structures,^{23–25} seldom taking into account the functional classification of the products. This way of categorization creates difficulties for those interested in material application scenarios, as they find it hard to obtain relevant information. To the best of our knowledge, there has been no review focused on the depolymerization recycling of TPE materials. The absence of effective guidance poses a challenge for industries seeking potential solutions for chemically circular TPEs. Therefore, this perspective aims to provide a function-oriented overview of the design strategies, depolymerization methods, and performance evaluation of TPEs. Finally, we put forward future directions for the chemical recycling of TPEs. Degradable TPEs but nonrecyclable to polymerizable monomers will not be included in this perspective. This perspective seeks to offer new perspectives and directions for the potential replacement of conventional TPEs with chemically recyclable TPEs.

2. DESIGN PRINCIPLE

The characteristic of thermoplastic elastomers lies in the presence of soft and hard segments in their phase-separated domains (Figure 1). Among them, the soft segments with low glass transition temperature (T_g) endow the material with high-elasticity characteristics, while the hard segments that form solid crystallites or glassy regions act as “physical cross-linking points” that restrict the viscous flow of the soft segment chains. The formation of microphase-separated structures imparts elastic and tough properties to TPEs. From a microscopic perspective, this microphase separation is governed by the chemical architecture of the polymer chains, necessitating that TPEs are typically composed of multiple chemically distinct segments. This stands in stark contrast to conventional plastics, which are predominantly single-component materials synthesized via homopolymerization. In contrast, the fabrication of TPEs generally requires multi-component copolymerization, underscoring the inherent synthetic complexity of these materials. Specifically, copolymerization can be achieved through step-growth or chain-growth polymerization. Step-growth polymerization involves the precise stoichiometric control of difunctional monomers, such as the A_2/B_2 type. Chain-growth copolymerization, on the other hand, can be realized through “one-pot” copolymerization or stepwise copolymerization. In “one-pot” copolymerization, the sequence distribution of monomers along the polymer

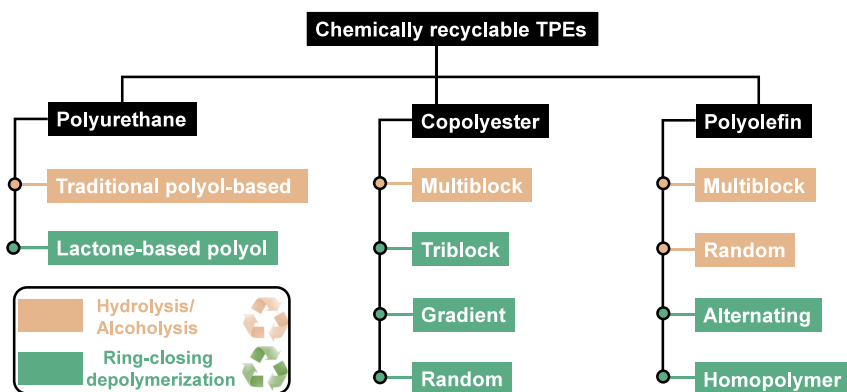


Figure 3. Types of chemically recyclable TPEs and the depolymerization strategy.

chain should be elaborately controlled to achieve the desired elastomeric functionality, necessitating precise regulation of the reactivity ratio (r_1/r_2). In terms of stepwise chain-growth polymerization, exemplified by triblock copolymers, living polymerization characteristics are required to ensure high fidelity of end groups, thereby facilitating the subsequent growth of additional blocks. The depolymerization strategy of TPEs presents complexities similar to those encountered during synthesis. The multicomponent repeating units within the polymer backbone may require different methods for depolymerization, followed by the separation and recovery of two or more monomer types, necessitating multistep depolymerization and purification processes. These monomer components are then purified and reused for the synthesis of second-generation TPEs, illustrating the complexity of the recycling process. In contrast, plastics based on homopolymers typically require only a single step for depolymerization and purification. In summary, the processes of polymerization and depolymerization for TPEs, aimed at achieving closed-loop recycling, are significantly more challenging than those for plastics. Consequently, research on the chemical recycling of TPEs is considerably less extensive than that on plastics.

Chemical recycling of TPEs to monomers can be categorized into two scenarios (Figure 2). For TPEs prepared via polycondensation, the process typically involves selectively cleaving the labile bonds in the main chain through hydrolysis or alcoholysis to yield difunctional monomers. On the other hand, for polymers obtained through chain polymerization, ring-closing depolymerization (RCD) is governed by the thermodynamic equilibrium between the monomer and polymer. The temperature at which the entropy loss offsets the enthalpy gain is defined as the ceiling temperature (T_c) of a polymerization system. Polymerization is favored when the temperature is below the T_c value, whereas depolymerization is favored when the temperature exceeds the T_c value. The efficiency of depolymerization is directly regulated by the relative value of the system temperature to T_c , providing a thermodynamic basis for designing controlled depolymerization processes.

3. POLYMER TYPES

Given the diversity of TPE types and their varied applications, this perspective categorizes the reported recyclable TPEs into several types (Figure 3), including polyurethanes, copolyesters, and polyolefins, along with their structural characteristics in relation to recycling potential. Table 1 then provides concrete examples detailing representative polymer structures, molec-

ular weight parameters, and recovered monomer structures. Building on this foundation, Table S1 (Supporting Information) offers a comprehensive comparative analysis evaluating these TPE systems across multiple dimensions: polymer structural features, key material properties, processing requirements, and depolymerization efficiency (including yield data).

3.1. Polyurethane

Thermoplastic polyurethane is a major class of TPEs, synthesized via the polycondensation of diisocyanates with diols or polyols. While various chemical recycling methods for polyurethanes have been developed—including hydrolysis, acidolysis, glycolysis, aminolysis, ammonolysis, and phosphorolysis—glycolysis currently stands as the most widely adopted approach due to its mild reaction conditions and the high reproducibility of recycled polyols.²⁶ A key challenge in polyurethane chemical recycling is the difficulty in recovering isocyanates; instead, the primary depolymerization products are recycled polyols, which can replace virgin polyols in the production of new polyurethane. Notably, polyurethane elastomers and conventional polyurethane plastics share the same chemical composition, differing only in the soft segment content. Consequently, the chemical recycling strategies for polyurethane-based TPEs are identical to those for polyurethane plastics.²⁷ Given the extensive coverage of polyurethane chemical recycling in existing reviews,^{17,28} this topic will not be discussed further here. Despite limited industrial-scale implementation, several European companies are now commercializing glycolysis-based recycling technologies for their waste streams, signaling progress toward broader adoption.²⁶

From a sustainability standpoint, the recovered polyols from polyurethanes still face challenges, including their non-degradable nature, excessive solvent use, tedious purification processes, and low efficiency.²⁹ However, if the polyols are derived from the ring-opening polymerization (ROP) of lactones, then depolymerization to recover small lactone monomers can be highly efficient through thermolysis followed by simple vacuum distillation. While both conventional polyurethane-based TPEs (via glycolysis) and lactone-derived systems typically require similar depolymerization temperatures (~ 200 °C), the latter offers distinct advantages in that lactone-based systems directly yield distillable monomers, whereas polyurethane systems necessitate complex separation and purification steps to recover polyols. This streamlined process grants lactone-derived TPEs superior economic viability. For instance, the Hillmyer group reported the

Table 1. Summary of the Polymer Structure, Molecular Weight, and Recycled Products for Representative Chemically Recyclable TPEs

Polymer type	Polymer structure	Sequence structure	M_n (kDa)	Chemically recycled products	Ref.
Entry 1 Polyurethane		Alternating	102.2		30
Entry 2 Polyurethane		Alternating	123.6		31
Entry 3 Polyurethane		Alternating	113.5		29
Entry 4 Copolyester		Triblock	121.7		33
Entry 5 Copolyester		Triblock	107.7		34
Entry 6 Copolyester		Triblock	144		35
Entry 7 Copolyester		Triblock	102.5		36
Entry 8 Copolyester		Triblock	80.3		37
Entry 9 Copolyester		Triblock	81		38
Entry 10 Copolyester		Gradient	121		39
Entry 11 Copolyester		Random	383		44
Entry 12 Copolyester		Random	84	Cyclic oligomers (DP = 2–8)	45
Entry 13 Copolyester		Multiblock	50.2		46
Entry 14 Polyolefin		Multiblock	31.8		61
Entry 15 Polyolefin		Multiblock	29.5		60
Entry 16 Polyolefin		Random	67.9		59
Entry 17 Polyolefin		Multiblock	40.4		62
Entry 18 Polyolefin		Homopolymer	158.3		70
Entry 19 Polyolefin		Alternating	1750		75

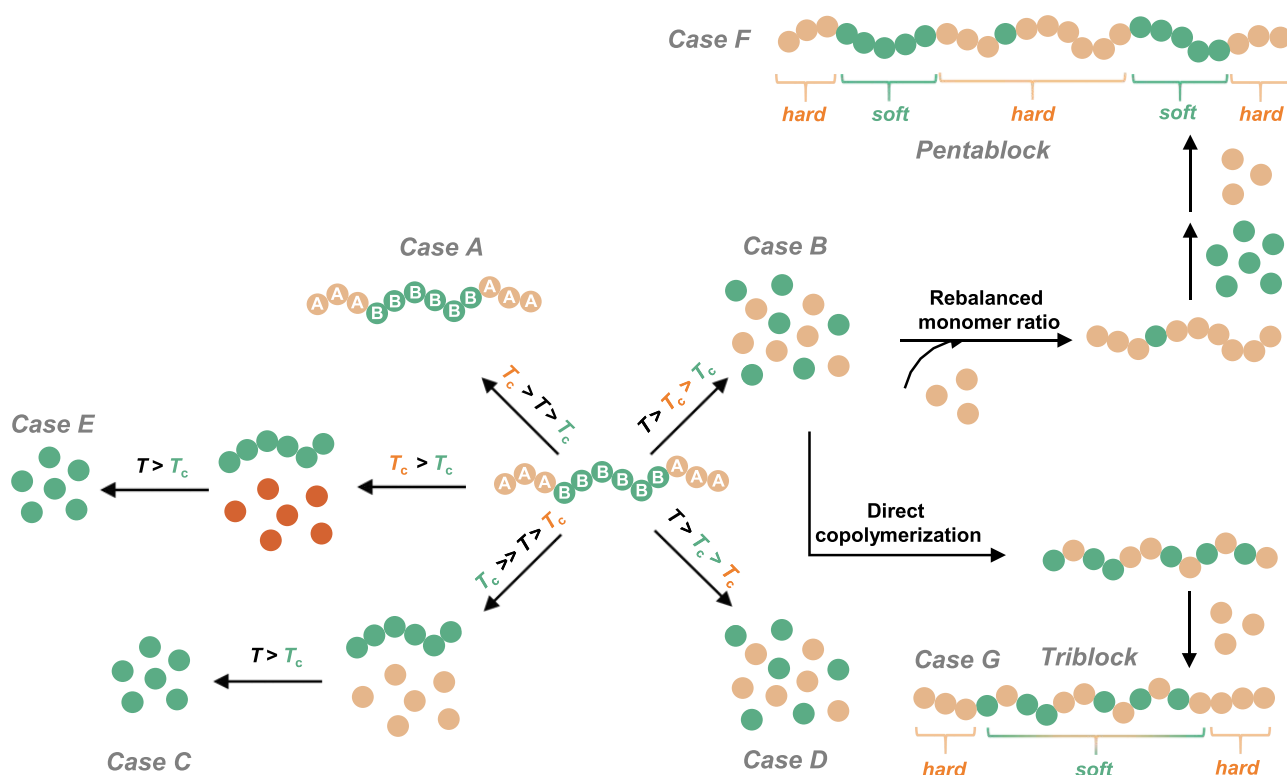


Figure 4. Depolymerization pathways in triblock copolymers: recycling scenario dependence on T_c of monomers A (khaki solid circle) and B (green solid circle). Case A: No depolymerization occurs when $T_{c,A} > T > T_{c,B}$. Case B: Nonselective depolymerization occurs when $T > T_{c,A} > T_{c,B}$. Case C: Selective depolymerization occurs when $T_{c,B} > T > T_{c,A}$. Case D: Nonselective depolymerization occurs when $T > T_{c,B} > T_{c,A}$. Case E: Selective depolymerization occurs when $T_{c,A} > T_{c,B}$. Case F: Pentablock copolymers were obtained from unseparated depolymerization products. Case G: Triblock copolymers were obtained from unseparated depolymerization products.

synthesis of telechelic poly(β -methyl- δ -valerolactone) diol oligomers via ROP, which served as well-defined soft segments ($T_g = -60$ °C) for polyurethane TPEs (Table 1, entry 1).³⁰ After purification, these oligomers were polycondensed with diphenylmethane diisocyanate to yield tough TPEs ($\sigma_b = 37$ MPa, $\epsilon_b = 1000\%$). Depolymerization at 220–250 °C for 10 h in the presence of $\text{Sn}(\text{Oct})_2$ catalyst recovered β -methyl- δ -valerolactone monomer in >95% yield.³⁰ Nevertheless, the biobased polyol required purification prior to polycondensation, and milder, more efficient depolymerization conditions remain to be explored. In a similar approach, the Li group employed renewable, degradable hydroxy-telechelic poly(δ -caprolactone) (P δ CL) as soft segments ($T_g = -40$ °C) to replace petroleum-derived polyols.³¹ This system enabled a one-pot, solvent-free cascade step-growth polymerization with diisocyanate, producing TPEs with 96% elastic recovery, $\sigma_b \approx 10$ MPa, and $\epsilon_b \approx 1000\%$. Remarkably, these polyurethanes could be chemically recycled to recover δ CL via thermolysis under milder conditions (180 °C, 2 h, $\text{Sn}(\text{Oct})_2$), achieving ~99% yield after distillation (Table 1, entry 2). Likewise, γ -butyrolactone was used to generate soft oligomer precursors ($T_g = -50$ °C) via ROP. Polycondensation with diphenylmethane diisocyanate yielded TPEs with superior mechanical properties ($\sigma_b = 31.8$ MPa, $\epsilon_b = 1254\%$), which could also be quantitatively depolymerized to recover γ -butyrolactone (Table 1, entry 3).²⁹ The recovered lactones can be repolymerized into their original polyols, establishing a closed-loop recycling system.

3.2. Copolyesters

3.2.1. Triblock Copolyesters. ABA-type triblock copolymers, composed of rigid terminal blocks A (either semicrystalline thermoplastics with T_m above ambient conditions or amorphous thermoplastics with T_g exceeding room temperature and a central elastomeric block B (a soft, flexible amorphous polymer exhibiting T_g below room temperature), demonstrate significant promise as recyclable TPEs. These materials are particularly attractive due to their inherent biodegradability and the feasibility of their synthesis via efficient ROP of cyclic esters or lactones.³² The thermodynamics of RCD in such triblock TPEs is primarily governed by the T_c of the constituent comonomers relative to each other and to the processing temperature. This relationship can be systematically classified into four distinct scenarios (Figure 4, cases A–D).

When $T_{c,A} > T_{c,B}$, repeating unit A functions as an end-capping agent, inhibiting the unzipping of block B via RCD even at operating temperatures above $T_{c,B}$ (Figure 4, case A). To circumvent this limitation, alternative depolymerization strategies can be employed. For instance, the Shen group synthesized a triblock TPE comprising poly(L-lactide) (PLLA) end blocks and a poly(δ -caprolactone) (P δ CL, $T_{c,B} = 42$ °C, 1.0 M) midblock.³³ Direct heating of this TPE in $\text{Sn}(\text{Oct})_2$ proves insufficient to recover pristine δ CL monomers (Table 1, entry 4).³³ Instead, the terminal blocks were selectively depolymerized via ethanol alcoholysis, yielding ethyl lactate (92% recovery by distillation at 45 °C under reduced pressure). The remaining P δ CL midblock subsequently underwent RCD at 140 °C under a vacuum, quantitatively

recovering δ -caprolactone (95% yield, case E). This approach can be generalized to other polymer systems. For example, in polyester-*b*-polyether-*b*-polyester TPEs (e.g., PLLA-*b*-polyTHF-*b*-PLLA, developed by the Matson group, Table 1, entry 5), sequential depolymerization can be achieved: (1) FeCl_3 -catalyzed cleavage of the polyTHF midblock releases THF (78% recovery by distillation), followed by (2) ZnCl_2 /PEG-catalyzed reactive distillation of the residual PLLA to recover lactide (80% yield).³⁴ When the operating temperature exceeds $T_{c,A}$, the entire copolyester may undergo RCD, producing a mixture of monomers A and B in a nonselective manner (Figure 4, case B). The selection of an appropriate separation method primarily depends on the isolation yield and efficiency. From an industrial perspective, energy consumption must also be carefully considered. On a laboratory scale, chromatographic separation is often feasible, achieving satisfactory yields of both monomers. However, this approach requires substantial solvent usage, leading to an increased cost for solvent recovery, making it less practical for large-scale applications. In contrast, distillation offers a more industrially viable solution. Despite its higher thermal energy requirements, distillation provides superior process efficiency and scalability, making it the preferred method for commercial implementation. The feasibility of this approach (Figure 4, case B) depends critically on the separation efficiency of the resulting monomers. If A and B exhibit sufficiently distinct volatilities or chemical properties, they can be effectively isolated and purified via straightforward techniques, such as fractional distillation. A representative example is the PLLA-*b*-polyTHF-*b*-PLLA TPE system developed by the Matson group.³⁴ During reactive distillation, this system enables the sequential recovery of both monomer types. This demonstrates how thermodynamic parameters and separation methodologies jointly govern the practical recyclability of triblock TPEs.

When the separation of monomers A and B incurs prohibitive energy costs, an alternative strategy is to directly repurpose the depolymerized mixture for synthesizing next-generation TPEs without purification, as demonstrated by the Xu group in their work on fully biobased triblock TPEs derived from δ -valerolactone (δVL) and its α -methyl-substituted ($\alpha^{\text{Me}}\text{VL}$) derivative (Table 1, entry 6).³⁵ ZnCl_2 -catalyzed RCD at 100 °C for 2 h yielded a quantitative (99%) monomer mixture of δVL and $\alpha^{\text{Me}}\text{VL}$, which could either be separated via column chromatography (δVL : 89% yield; $\alpha^{\text{Me}}\text{VL}$: 83% yield) at the expense of monomer loss and added energy expenditure or directly reused by supplementing with additional δVL to adjust the monomer ratio (δVL -dominant). This adjusted mixture was polymerized via 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)-catalyzed ROP in toluene at 25 °C to form a telechelic macroinitiator, followed by sequential addition of $\alpha^{\text{Me}}\text{VL}$ and δVL to synthesize a pentablock copolymer TPE (Figure 4, case F) with mechanical properties comparable to the parent TPE ($\sigma_b = 15$ MPa, $\epsilon_b = 1000\%$).³⁵ Similarly, the Shen and Li group modified the midblock chemistry by replacing poly $\alpha^{\text{Me}}\text{VL}$ with poly $\beta^{\text{Me}}\text{VL}$ (while retaining poly δVL end blocks), achieving a triblock TPE with exceptional mechanical performance ($\sigma_b = 48.2$ MPa, $\epsilon_b = 2007\%$) but reduced heat resistance ($T_m = 32\text{--}45$ °C, Table 1, entry 7).³⁶ Complete bulk depolymerization using $\text{Sn}(\text{Oct})_2$ at 130 °C under vacuum yielded a mixture of $\beta^{\text{Me}}\text{VL}$ and δVL , which was directly repolymerized via a one-pot, two-step ROP: first synthesizing a random copolymer soft block ($T_g = -57.8$ °C) from the $\beta^{\text{Me}}\text{VL}/\delta\text{VL}$ mixture, followed by δVL addition to

form triblock copolymers (case G), thereby circumventing comonomer separation entirely.³⁶

When $T_{c,A} < T_{c,B}$, this approach also enables sequential depolymerization, where the end blocks (A) undergo RCD under mild conditions while the midblock (B) remains intact (Figure 4, case C). The resulting monomer A can be separated, and the conditions can then be adjusted to depolymerize block B to monomer B. A notable example is the poly(2,2-diethyltrimethylene carbonate)-*b*-poly(ϵ -decalactone)-*b*-poly(2,2-diethyltrimethylene carbonate) triblock copolymer TPE developed by the Odelius group (Table 1, entry 8).³⁷ The terminal blocks selectively depolymerize in the presence of TBD at 110 °C for 1 h with 87% conversion, while the midblock can be isolated by precipitation in cold methanol, albeit with minor chain scission due to partial transesterification.³⁷ Similarly, the Williams group designed fully renewable poly(limonene carbonate)-*b*-poly(ϵ -decalactone)-*b*-poly(limonene carbonate) ABA triblock TPEs (Table 1, entry 9), where the high- T_g polycarbonate (A) and low- T_g polyester (B) blocks exhibit distinct depolymerization behaviors.³⁸ These materials, though mechanically soft ($\sigma_b = 0.32\text{--}1.1$ MPa, $\epsilon_b = 2563\text{--}3962\%$), allow quantitative recovery of limonene oxide via dizinc β -diiminate complex-catalyzed RCD in toluene at 80 °C for 6 h, leaving the poly(ϵ -decalactone) midblock intact for subsequent acid hydrolysis.³⁸ It should be noted that while Case D (Figure 4) is theoretically plausible, such a system has not yet been experimentally observed.

3.2.2. Pseudotriblock Copolyesters. While triblock TPEs exhibit excellent phase separation and good mechanical properties, their synthesis typically requires complex stepwise chain extensions. A more attractive alternative is the one-pot copolymerization approach, which offers synthetic simplicity and reduced energy costs, achievable through pseudotriblock copolymer strategies. Recently, the Zhu Group developed a novel α -spiro-cyclohexyl-propiolactone (SHPL) monomer capable of forming a high-melting crystalline polymer ($T_m = 272$ °C).³⁹ The spiro-substitution not only enhances RCD efficiency (86% monomer recovery using NaOH at 265 °C) but also enables the one-pot synthesis of gradient copolymers when copolymerized with ϵ -caprolactone (ϵCL), yielding poly(ϵCL -grad-SHPL) with near-quantitative conversion (Table 1, entry 10). This gradient copolymer mimics a triblock architecture, featuring two crystalline hard blocks (PCL: $T_m = 46$ °C; polySHPL: $T_m = 266$ °C) and a chemically irregular middle block with a low T_g that imparts elastomeric behavior. Remarkably, this pseudotriblock TPE achieves unprecedented mechanical performance, including exceptional toughness (600 MJ/m³), high elastic recovery (>90%), and a record-breaking tensile strength ($\sigma_b = 59.8$ MPa) among chemically recyclable TPEs, while maintaining full depolymerizability.

3.2.3. Random Copolyesters. One-pot ring-opening copolymerization of mixed cyclic monomers (A and B) represents a conceptually elegant and operationally simple strategy for synthesizing copolymers without laborious stepwise monomer feeding. For random copolyesters to exhibit TPE properties, they must achieve a delicate balance of semicrystalline characteristics—low crystallinity, high T_m , and low T_g —despite their inherent chemical irregularity that typically inhibits crystallization. This can be addressed through two design principles: (1) incorporating long, flexible polyethylene-like or polyethylene glycol-like oligomer segments to enable efficient chain folding, or (2) introducing controlled

monomer sequences (e.g., “AAAA”/“BBBB” homosequences) to preserve crystallinity while maintaining statistical distribution.^{40,41} However, such structures inherently limit lamellar thickness, resulting in thin crystalline domains with depressed T_m .⁴² Intriguingly, these finely dispersed small crystals often outperform larger crystals at equivalent crystallinity in mechanical performance,⁴³ as demonstrated by the Tang group’s semicrystalline statistical copolyester poly[CL₄₈-stat-(4^{Ph}-BL)₅₂] ($T_g = 3\text{ }^\circ\text{C}$, $T_m = 74\text{ }^\circ\text{C}$, Table 1, entry 11).⁴⁴ Synthesized via coordinating solvent-assisted transesterification of 4-phenyl-2-oxabicyclo[2.1.1]hexan-3-one (4^{Ph}-BL) and ϵ CL, this system achieved good properties ($\sigma_b = 34.5\text{ MPa}$, $\epsilon_b = 812\%$, >99.3% elastic recovery) at $M_n = 383\text{ kDa}$. A slight variation in the monomer ratio of the resulting copolymer results in a large difference in T_g and T_m , making the adjustable composition range window for optimizing TPE properties rather small. Considering that these statistical copolyesters still show semicrystalline characteristics, it is expected that the low degree of randomness (28%) still leaves a certain extent of multiblock domains on the backbone. Y-(CH₂SiMe₃)₃(THF)₂ was demonstrated to catalyze efficient depolymerization (98% 4^{Ph}-BL, 94% ϵ CL recovery at 250 $^\circ\text{C}$ /1 h), and the feasibility of closed-loop recycling via repolymerization remains unexplored for this mixed-monomer system.

Yagihara and Matsumura developed an enzymatic route to synthesize semicrystalline polyester TPEs through lipase-catalyzed copolymerization of macrocyclic diol with succinate and alkylthiosuccinate monomers.⁴⁵ By strategically incorporating branched alkylthio groups as soft segments along the poly(alkylene succinate) backbone, they achieved tunable mechanical properties ($\sigma_b = 2.6\text{--}4.4\text{ MPa}$, $\epsilon_b = 10\text{--}338\%$, Table 1, entry 12) that correlated with the alkyl side chain incorporation ratio. This biocatalytic approach demonstrated enzyme recyclability: the copolymers underwent enzymatic degradation back to cyclic oligomers, which were subsequently repolymerized to regenerate polymers with molecular weights comparable to those of the original materials. The closed-loop system highlights the potential of enzyme-catalyzed processes for sustainable TPE production and recycling, although the relatively modest mechanical properties suggest opportunities for further optimization of the monomer design and polymerization conditions.

3.2.4. Multiblock Copolyesters. The strategic combination of “hard” and “soft” polymeric blocks also enables the rational design of TPEs. The Ren group developed a versatile synthetic approach for sulfur-rich polytrithiocarbonates through transesterification and polycondensation of dithiols with dimethyl trithiocarbonate, yielding heterotelechelic macromonomers.⁴⁶ This strategy creates a dual-component system where crystalline macromonomers with long methylene alkyl chains serve as hard blocks, while oxygen-embedded alkyl chain macromonomers function as soft segments. Random copolymerization of these components under alkali hydride catalysis (120 $^\circ\text{C}$ for 2 h) produces semicrystalline TPEs with tunable thermal properties ($T_g = -46\text{ }^\circ\text{C}$, $T_m = 38.1\text{--}78.7\text{ }^\circ\text{C}$, Table 1, entry 13) by adjusting feed ratios. The optimal composition achieved notable mechanical performance ($\sigma_b = 14.3\text{ MPa}$, $\epsilon_b = 320\%$). While TPE depolymerization remains unverified, the research team demonstrated quantitative chemical recycling (>96% yield) of homopolymeric polytrithiocarbonates via alkali hydroxide-catalyzed reverse transesterification in methyl mercaptan (50 $^\circ\text{C}$, 24 h), cleaving at the in-chain functional groups to regenerate pure dimethyl

trithiocarbonate and dithiols after recrystallization. This suggests potential TPE recyclability, though separation challenges may arise from mixed dithiol products.

3.3. Polyolefin

Polyolefin TPEs derive their unique properties from a semicrystalline architecture combining low crystallinity, high T_m crystalline domains, and low T_g amorphous segments.¹ This structural design creates an elastomeric network where the high- T_m crystallites serve as physical cross-links, while the low- T_g amorphous regions provide elasticity.⁴⁷ However, conventional polyolefins face significant depolymerization challenges due to their chemically inert carbon–carbon backbones.^{48,49} Recent advances demonstrate that strategic incorporation of labile functional groups (e.g., ester, acetal, amide, silyl ether, or thioester linkages) along the polymer backbone can enable controlled deconstruction while preserving the essential crystalline characteristics and mechanical performance.^{50–55} This approach maintains the beneficial polyolefin-like properties while introducing cleavable bonds that facilitate chemical recycling under mild conditions,^{18,56–58} offering a promising pathway toward sustainable polyolefin TPEs.

3.3.1. Multiblock Polyolefins. For polyolefin TPEs, ester groups represent the most commonly incorporated functional groups, with their controlled placement along the polyolefin backbone achieved through telechelic macromonomers instead of small monomers.¹⁸ The introduction of branches to an otherwise linear polyethylene backbone can enable the synthesis of TPE.⁵¹ The Miyake group pioneered this approach through pincer-catalyst-mediated dehydrogenative polymerization of hydroxyl-terminated oligomers (A_2 type), which not only eliminates the need for stoichiometric matching of coupling partners but also enables the production of diverse TPE materials by adjusting the feed ratio of building blocks.^{59–61} In their initial study, they synthesized a multiblock TPE via ruthenium-catalyzed dehydrogenative copolymerization of telechelic hydroxyl-capped polyethylene-like oligomers prepared by ring-opening metathesis polymerization (ROMP), where linear polyethylene oligomers (A_2 type, $M_n = 1.9\text{ kDa}$) served as crystalline hard blocks while hexyl-branched polyethylene oligomers (A_2 type, $M_n = 1.8\text{ kDa}$) with low T_g functioned as soft blocks, with elastic properties emerging when the hard block incorporation ratio was below 40%. The optimal composition containing 40% soft block exhibited 17% crystallinity (Table 1, entry 14), a T_g of $-50.6\text{ }^\circ\text{C}$ and T_m of $109\text{ }^\circ\text{C}$, delivering TPE mechanical properties ($\sigma_b = 12\text{ MPa}$, $\epsilon_b = 1030\%$), while also allowing quantitative depolymerization (>99% conversion) through hydrogenation at $150\text{--}160\text{ }^\circ\text{C}$ for 24–72 h, with 91.7% recovery of hard and soft macromonomers via selective solvent isolation.⁶¹ This methodology was subsequently extended to unsaturated polynorbornene oligomers with telechelic hydroxyl groups, where linear and branched A_2 -type polynorbornene macromonomers underwent dehydrogenative coupling to form TPEs that could be depolymerized at $120\text{ }^\circ\text{C}$ using Ru-MACHO catalyst (Table 1, entry 15).⁶⁰ Further advancing this platform, the Miyake group later developed plant oil-derived TPEs from linear and sulfur-hexyl-branched 1,18-octadecanediols (both A_2 type) using cost-effective manganese catalysts, where the linear C_{18} diol formed high- T_m crystalline domains, while the branched analog created amorphous soft domains.^{59–61} This elastomer shows low crystallinity (7.6%) and a T_m of $41\text{ }^\circ\text{C}$, endowing it

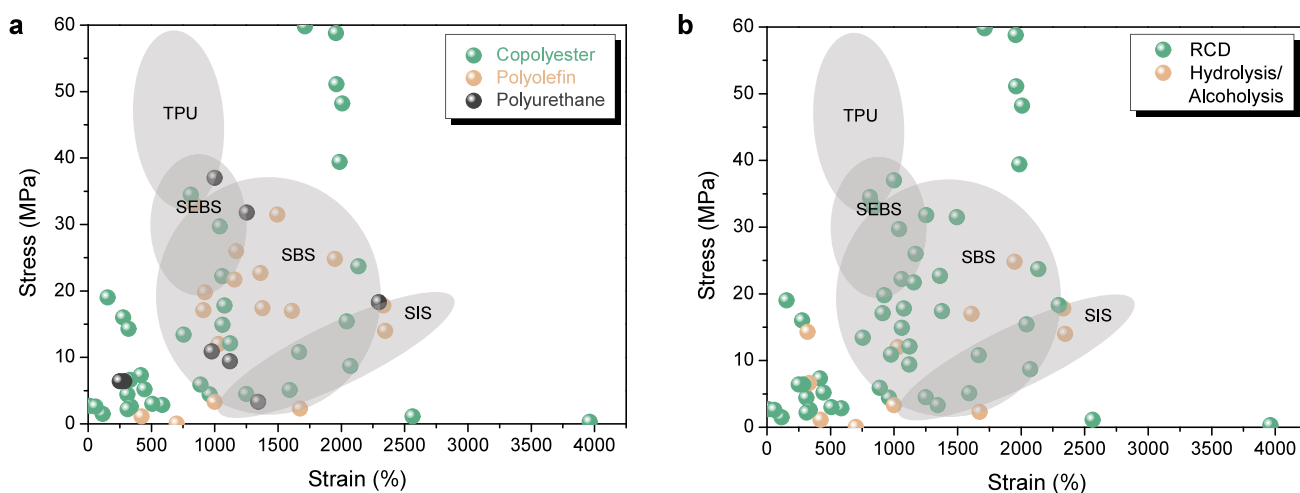


Figure 5. Comparative performance metrics: conventional vs chemically recyclable TPEs in tensile strength-elongation space. (a) Plotted by backbone chemistry. (b) Plotted by recycling strategy.

with good mechanical properties ($\sigma_b = 17$ MPa, $\epsilon_b = 1610\%$, Table 1, entry 16). These materials could be depolymerized back to monomers through hydrogenation at 140°C for 48 h and were separable with a monomer recovery of up to $>90\%$, with linear 1,18-octadecanediols recrystallized and filtered from the solution, and branched 1,18-octadecanediols remain in the filtrate for further purification.⁵⁹

Similar to $A_2 + A_2$ systems in polycondensation, AB heterotelechelic building blocks likewise circumvent the requirement for precise stoichiometric control, thereby enabling the modular Lego-like assembly of tailored polyolefin TPEs. The Gao and Tang group synthesized a series of well-defined AB-type heterotelechelic polyethylene-like macromonomers via coordination copolymerization of ethylene and α -octene.⁶² These macromonomers exhibit tunable crystallinity through systematic variation of the α -octene incorporation ratio. Subsequent homopolycondensation of these building blocks using a conventional $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst at 190°C under high vacuum for 24 h yields robust multiblock TPEs, with optimal mechanical properties (e.g., $\sigma_b = 17.83$ MPa, $\epsilon_b = 2333\%$, Table 1, entry 17) achieved at α -octene incorporation ratios between 8.9–14.8%. Alternatively, these macromonomers can be employed in the random copolymerization of soft-block macromonomers (high α -octene content) with hard-block macromonomers (low α -octene content) to produce multiblock copolymer TPEs. The resulting homopolymers undergo efficient closed-loop chemical recycling via methanolysis-mediated transesterification at 150°C for 24 h, with the macromonomers readily recovered through simple filtration. For copolymer systems, selective *n*-hexane extraction followed by filtration achieves an impressive 96% isolation yield of the constituent telechelic building blocks. Notably, after two consecutive depolymerization cycles, the regenerated TPEs retain thermal properties comparable to those of the first-generation materials, demonstrating the robustness of this approach.

3.3.2. Homopolymer-Based Polyolefins. Beyond polycondensation approaches, ROMP offers an alternative route to synthesize polyolefins, where the residual backbone unsaturation enables catalyst-mediated depolymerization.^{63–69} The Sha group designed a fully biomass-derived, strainless macrocyclic olefin (26-membered ring) from starch and castor oil precursors.⁷⁰ This judiciously engineered monomer undergoes

ROMP to yield unsaturated polyolefins ($M_n = 40\text{--}800$ kDa) with controlled crystallinity, forming a unique homopolymer TPE system containing self-assembled crystalline “hard” domains and amorphous “soft” regions. Through optimization of chain entanglement and crystallinity, exceptional mechanical properties ($\sigma_b = 31.5$ MPa, $\epsilon_b = 1495\%$, Table 1, entry 18) were achieved. The material exhibits efficient depolymerization via ruthenium-carbene-catalyzed ring-closing metathesis, leveraging the ring–chain equilibrium to recover pristine monomers or macrocyclic mixtures for direct repolymerization, all while maintaining original thermomechanical properties. This elegant single-component system eliminates the need for complex comonomer separation processes.⁷¹ This strategy leverages the integration of multicomponent functional motifs into a single monomer with a built-in sequence.^{72–74} Although the initial monomer synthesis may be intricate, it significantly simplifies the subsequent polymerization and depolymerization processes. Notably, this advantage becomes increasingly pronounced with repeated recycling iterations, effectively embodying a “one-time effort, long-term benefit” principle.

3.3.3. Alternating Polyolefins. Despite variability in cycle size, the key design consideration for depolymerization of cycloolefin is ensuring the low ring strain of the monomer. For instance, cyclohexene, a strain-free small ring, demonstrates a strong thermodynamic depolymerization driving force. The Xia group developed semicrystalline polycyclohexene TPEs via radical alternating copolymerization of butadiene/methacrylate, which completely depolymerizes at ambient temperature with Grubbs’ catalyst (Table 1, entry 19).⁷⁵ However, unlike the biomass-derived system, the inability to repolymerize the cyclohexene monomer back to the original TPE underscores the critical role of finely balanced polymerization-depolymerization thermodynamics in achieving truly closed-loop recyclability.

4. CONCLUSIONS AND OUTLOOK

With the increasing depletion of fossil resources and the environmental challenges posed by end-of-life polymer materials, there is an urgent need to develop novel synthesis-depolymerization methodologies to achieve closed-loop polymer recycling. This paradigm shift not only addresses the ecological impacts of waste incineration and environmental

leakage but also reduces fossil resource consumption in polymer production and mitigates carbon emissions throughout the material lifecycle. Such sustainable strategies are also crucial for resolving the sustainability dilemma of conventional TPEs, thereby reducing the carbon footprint. Here, we have offered mechanistic considerations for the design, synthesis, and depolymerization strategy of TPE libraries to enhance structure–property understanding and accelerate circular TPE design. Chemically recyclable TPEs primarily include polyurethanes, copolyesters, and polyolefins. Their chemical recycling pathways can be categorized into two distinct mechanisms: depolymerization into macromolecular monomers and small-molecule monomers. TPEs synthesized via step-growth polymerization typically undergo depolymerization through hydrolysis or alcoholysis to recover macromolecular building blocks. In contrast, TPEs produced through chain-growth polymerization generally exhibit thermal depolymerization at temperatures above their T_c , yielding small-molecule monomers. Table S1 summarizes the structural characteristics, material properties, and depolymerization performance of representative chemically recyclable polymers reported in the recent literature. The depolymerization conditions (temperature, duration, and catalyst types) in Table S1 provide valuable insights for potential industrial implementation of energy requirements for chemical recycling. Owing to significant advances in chemically recyclable TPEs, many sustainable TPEs now exhibit mechanical properties that are comparable to—or even surpass—those of conventional TPEs (Figure 5).⁷⁶ While the development of chemically recyclable TPEs holds great promise for environmental sustainability, several key challenges remain to be addressed in both research and industrial applications.

4.1. Design Concerns

From a design perspective, researchers often synthesize diverse plastics and elastomers following the development of new depolymerization methods. However, insufficient optimization of the copolymer composition frequently results in TPEs with subpar performance, failing to meet commercial standards. Future studies should prioritize refining monomer ratios within depolymerization-compatible polymer systems to enhance the TPE properties. Structurally, TPEs encompass a wide range of frameworks including polystyrene, polymethacrylate, polyolefin, polyurethane, polyester, and polycarbonate. While numerous depolymerizable homopolymers have been developed, their integration into TPE chemical recycling remains limited, with polyesters being the most extensively studied. For example, despite established depolymerization routes for polymethacrylate,^{77–79} no chemically recyclable polymethacrylate-based TPEs have been reported to date. Expanding the use of homopolymer depolymerization techniques to design TPEs with tailored compositions could unlock new performance optimizations. Currently reported chemically recyclable TPEs predominantly feature linear architectures. However, nonlinear variants including branched and star-shaped polymers could provide enhanced or unique material properties while retaining recyclability. These architectures represent highly promising targets for future research on chemically recyclable TPEs.

4.2. Sustainability Concerns

The growing emphasis on sustainability has expanded research frontiers beyond depolymerization methods, creating substantial opportunities for biobased TPE development.⁸⁰ Derived from renewable resources such as plant oils and

biomass, biobased TPEs already captured nearly 10% of the global TPE market in 2022—a share projected to grow substantially.⁴ This commercial success reflects their viability in meeting stringent regulatory demands and consumer preferences, particularly in automotive interiors and biodegradable packaging applications. While conventional methods (e.g., precipitation and filtration) can effectively recover macromolecular monomers, concerns persist regarding their environmental persistence and potential microplastic formation.⁸¹ Biobased diols emerge as a strategic solution for developing closed-loop polymer systems, offering two key advantages: (1) enabling chemical recycling for circular reprocessing and (2) providing inherent biodegradability as an environmental safeguard against plastic accumulation. This dual-functionality approach uniquely addresses both technical and ecological challenges in establishing a sustainable plastic economy.⁵⁹ The reusability of catalysts during polymer synthesis and depolymerization should also be considered to improve catalyst sustainability.

4.3. Performance Concerns

From the perspective of the performance of chemically recyclable TPEs, current research primarily focuses on strength, elongation, and resilience. However, in practical applications, thermal resistance is also a crucial parameter. Although some reported chemically recyclable TPEs exhibit excellent mechanical properties, their limited thermal resistance restricts their application scenarios. To achieve practical utility, TPEs must possess hard segments with T_g or T_m substantially exceeding ambient conditions. When these thermal transitions surpass 150 °C, the materials exhibit promising characteristics for heat-resistant applications.⁸² Therefore, future research on chemically recyclable TPEs should systematically provide comprehensive thermal property parameters, including T_g , T_m , and T_d , to assess the material's thermal resistance and phase separation behavior. In some cases, the T_g of hard segments—particularly in polyurethane TPEs—cannot be reliably detected by differential scanning calorimetry (DSC). Therefore, complementary dynamic mechanical analysis (DMA) measurements are recommended for future studies to ensure the accurate characterization of thermal transitions. Furthermore, a systematic evaluation of thermal processability and environmental factors (e.g., moisture and humidity) is essential for the successful industrial implementation of chemically recyclable TPEs. The TPE industry urgently needs to establish standardized protocols and evaluation criteria for assessing both chemical recyclability and long-term performance retention under service conditions.

4.4. Depolymerization Concerns

From a depolymerization perspective, TPEs present unique challenges and opportunities compared to homopolymers due to their multicomponent architecture. The process can yield two or more distinct monomers through either (1) non-selective single-pot depolymerization using one catalyst or (2) sequential depolymerization employing a single catalyst with controlled conditions or multiple catalysts in staged reactions. Key considerations in process design include (1) potential interference between monomers/catalysts in single-pot systems that may compromise efficiency and (2) separation strategies that can be implemented either concurrently with depolymerization or as discrete steps. The inherent structural complexity of TPEs enables multiple thermodynamically favorable depolymerization pathways. Future investigations should

systematically evaluate these pathways through techno-economic analysis and life cycle assessment to identify optimal pathways that minimize both energy consumption and processing costs while maintaining high monomer recovery yields. The development of tailored catalytic systems remains crucial for establishing sustainable circular economies for TPEs.

4.5. Repolymerization Concerns

From the perspective of repolymerization using recovered monomers, the one-pot depolymerization and direct repolymerization of TPEs using recovered mixed monomers offers an energy-efficient recycling approach, yet faces a fundamental stoichiometric challenge: even with high monomer recovery rates (>90%), slight variations in individual monomer recovery (e.g., 97% vs 92%) disrupt the original copolymer stoichiometry, leading to performance degradation in subsequent generations due to imbalanced comonomer ratios—an effect amplified over multiple cycles. Current studies rarely exceed two generations, highlighting the need for precise monomer ratio adjustment before repolymerization. In contrast, homopolymer-based recycling avoids such issues.⁷¹

Additionally, for TPEs derived from macromolecular monomers, purification is often impractical due to structural similarities, and nonselective cleavage during service can deactivate monomers, impairing repolymerization efficiency and material performance in subsequent generations. Unlike plastics, elastomers may undergo significant main-chain degradation in use,^{83–87} introducing nonselective bond scissions that reduce end-group fidelity of macromonomers over multiple cycles.^{88,89} Since these compromised macromonomers cannot be removed during recycling, performance declines accumulate with each iteration—highlighting the need to evaluate postservice recyclability to identify degradation mechanisms of TPE materials. We recommend conducting systematic tests, for instance, subjecting the elastomer to tensile failure, followed by an evaluation of its depolymerization—repolymerization efficiency. This cyclic process should be repeated for a minimum of 5–10 iterations to establish statistically significant circularity performance data. Such assessments should guide the structural optimization in future TPE designs. In contrast, small-molecule monomer recovery relies on purification, which impacts the monomer yield but not the properties of regenerated materials.

4.6. Concluding Remarks

Currently, poly(ethylene terephthalate) (PET) constitutes the predominant plastic species chemically recycled in industrial settings, accounting for over 60% of the total volume. While PET dominates the current recycling infrastructure, emerging materials like TPEs have been still limited to bench-scale demonstrations, remaining at the proof-of-concept stage without industrial-scale validation. As with all recyclable polymers, significant obstacles for recyclable TPEs persist, including recycling and depolymerization selectivity as well as trade-offs between recyclability and performance attributes such as mechanical strength and thermal stability. The inherent complexity of TPEs, stemming from their multicomponent nature, further exacerbates these challenges, particularly due to the high energy demands associated with both polymer synthesis/depolymerization processes and comonomer recovery/purification systems. Future research should prioritize the development of simplified, efficient, and low-energy methods for these processes. Addressing these challenges will necessitate

substantial research encompassing the design of innovative monomer and polymer architectures and the development of more environmentally sustainable processes for TPE synthesis and recycling. When the energy consumption of chemical recycling processes decreases to a level that is economically favorable compared to virgin material production, it is reasonable to anticipate that chemically recyclable TPEs will increasingly displace conventional TPEs in diverse applications through sustained technological innovations within defined industrial timelines.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acspolymersau.Sc00033>.

Summary of the polymer structure, molecular weight, material properties, and depolymerization protocol and yield for representative chemically recyclable TPEs (PDF)

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Notes

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REFERENCES

- (1) Zanchin, G.; Leone, G. Polyolefin thermoplastic elastomers from polymerization catalysis: Advantages, pitfalls and future challenges. *Prog. Polym. Sci.* **2021**, *113*, No. 101342.
- (2) Smithers *The Future of Thermoplastic Elastomers To 2026*. 2024. <https://www.smithers.com/services/market-reports/materials/the-future-of-thermoplastic-elastomers-to-2024>.
- (3) Gao, C.; Poon, K. C.; Concilio, M.; Zinn, T.; Gregory, G. L.; Williams, C. K. High-Performance Recyclable Polyester Elastomers Through Transient Strain-Stiffening. *Adv. Mater.* **2025**, No. 2416674.
- (4) *Thermoplastic Elastomers (TPE) Market Size, Share, Growth, and Industry Analysis, By Types (TPU, TPO/TPV, Styrene-based TPE(SBCs). Applications(Building & construction, Automobile, Footwear, Other applications), Regional Insights and Forecast to 2033*. 2025. <https://www.globalgrowthinsights.com/market-reports/thermoplastic-elastomers-tpe-market-105376>.
- (5) Korley, L. T. J.; Epps, T. H., II; Helms, B. A.; Ryan, A. J. Toward polymer upcycling-adding value and tackling circularity. *Science* **2021**, *373* (6550), 66–69.
- (6) Jehanno, C.; Alty, J. W.; Roosen, M.; De Meester, S.; Dove, A. P.; Chen, E. Y. X.; Leibfarth, F. A.; Sardon, H. Critical advances and future opportunities in upcycling commodity polymers. *Nature* **2022**, *603* (7903), 803–814.
- (7) Hong, M.; Chen, E. Y. X. Completely recyclable biopolymers with linear and cyclic topologies via ring-opening polymerization of γ -butyrolactone. *Nat. Chem.* **2016**, *8* (1), 42–49.
- (8) Coates, G. W.; Getzler, Y. D. Y. L. Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mater.* **2020**, *5* (7), 501–516.
- (9) Shi, C.; Reilly, L. T.; Chen, E. Y. X. Hybrid Monomer Design Synergizing Property Trade-offs in Developing Polymers for Circularity and Performance. *Angew. Chem., Int. Ed.* **2023**, *62* (31), No. e202301850.
- (10) Hong, M.; Chen, E. Y. X. Future Directions for Sustainable Polymers. *Trends Chem.* **2019**, *1* (2), 148–151.
- (11) Sun, Y.; An, Z.; Gao, Y.; Hu, R.; Liu, Y.; Lu, H.; Lu, X.-B.; Pang, X.; Qin, A.; Shen, Y.; et al. New sustainable polymers with on-demand depolymerization property. *Sci. Chin. Chem.* **2024**, *67*, 2803–2841.
- (12) Jones, G. R.; Wang, H. S.; Parkatidis, K.; Whitfield, R.; Truong, N. P.; Anastasaki, A. Reversed Controlled Polymerization (RCP): Depolymerization from Well-Defined Polymers to Monomers. *J. Am. Chem. Soc.* **2023**, *145* (18), 9898–9915.
- (13) Plummer, C. M.; Li, L.; Chen, Y. Ring-Opening Polymerization for the Goal of Chemically Recyclable Polymers. *Macromolecules* **2023**, *56* (3), 731–750.
- (14) Sathe, D.; Yoon, S.; Wang, Z.; Chen, H.; Wang, J. Deconstruction of Polymers through Olefin Metathesis. *Chem. Rev.* **2024**, *124* (11), 7007–7044.
- (15) Ibrahim, T.; Ritacco, A.; Nalley, D.; Emon, O. F.; Liang, Y.; Sun, H. Chemical recycling of polyolefins via ring-closing metathesis depolymerization. *Chem. Commun.* **2024**, *60* (11), 1361–1371.
- (16) Shi, C.; Quinn, E. C.; Diment, W. T.; Chen, E. Y. X. Recyclable and (Bio)degradable Polyesters in a Circular Plastics Economy. *Chem. Rev.* **2024**, *124* (7), 4393–4478.
- (17) Rossignolo, G.; Malucelli, G.; Lorenzetti, A. Recycling of polyurethanes: where we are and where we are going. *Green Chem.* **2024**, *26* (3), 1132–1152.
- (18) Schwab, S. T.; Baur, M.; Nelson, T. F.; Mecking, S. Synthesis and Deconstruction of Polyethylene-type Materials. *Chem. Rev.* **2024**, *124* (5), 2327–2351.
- (19) Wu, P.; Hu, Q.; Ogunfowora, L.; Li, Z.; Marquardt, A.; Savoie, B.; Dou, L. Toward Sustainable Polydienes. *J. Am. Chem. Soc.* **2025**, *147* (4), 2960–2977.
- (20) Li, X.; Mahadas, N. A.; Zhang, M.; DePodesta, J.; Stefik, M.; Tang, C. Sustainable high-density polyethylene via chemical recycling: From modification to polymerization methods. *Polymer* **2024**, *295*, No. 126698.
- (21) Wang, X.-Y.; Gao, Y.; Tang, Y. Sustainable developments in polyolefin chemistry: Progress, challenges, and outlook. *Prog. Polym. Sci.* **2023**, *143*, No. 101713.
- (22) Li, X.-L.; Ma, K.; Xu, F.; Xu, T.-Q. Advances in the Synthesis of Chemically Recyclable Polymers. *Chem. - Asian J.* **2023**, *18* (3), No. e202201167.
- (23) Li, Z.; Shen, Y.; Li, Z. Ring-Opening Polymerization of Lactones to Prepare Closed-Loop Recyclable Polyesters. *Macromolecules* **2024**, *57* (5), 1919–1940.
- (24) Xu, G.; Wang, Q. Chemically recyclable polymer materials: polymerization and depolymerization cycles. *Green Chem.* **2022**, *24* (6), 2321–2346.
- (25) Yang, S.; Du, S.; Zhu, J.; Ma, S. Closed-loop recyclable polymers: from monomer and polymer design to the polymerization-depolymerization cycle. *Chem. Soc. Rev.* **2024**, *53* (19), 9609–9651.
- (26) Sahu, P.; Oh, J. S.; Isayev, A. I. Chapter 21 - Recycling and circular economy of thermoplastic elastomers. In *Advances in Thermoplastic Elastomers*, Singha, N. K.; Jana, S. C., Eds.; Elsevier: 2024; pp 529–561.
- (27) Huang, L.; Zhang, J.; Chen, S.; Wu, G.; Wang, Y. Recyclable and Degradable Poly(p-dioxanone)-based Copolymer with Enhanced Mechanical Properties by Microphase-separated Interface Crystallization. *Chin. J. Polym. Sci.* **2025**, 1–13.
- (28) Liu, B.; Westman, Z.; Richardson, K.; Lim, D.; Stottlemeyer, A. L.; Farmer, T.; Gillis, P.; Vlcek, V.; Christopher, P.; Abu-Omar, M. M. Opportunities in Closed-Loop Molecular Recycling of End-of-Life Polyurethane. *ACS Sustainable Chem. Eng.* **2023**, *11* (16), 6114–6128.
- (29) Yuan, L.; Zhou, W.; Shen, Y.; Li, Z. Chemically recyclable polyurethanes based on bio-renewable γ -butyrolactone: From thermoplastics to elastomers. *Polym. Degrad. Stab.* **2022**, *204*, No. 110116.
- (30) Schneiderman, D.; Vanderlaan, M.; Mannion, A.; Panthani, T.; Batiste, D.; Wang, J.; Bates, F.; Macosko, C.; Hillmyer, M. Chemically Recyclable Biobased Polyurethanes. *ACS Macro Lett.* **2016**, *5* (4), 515–518.
- (31) Yan, Q.; Li, C.; Yan, T.; Shen, Y.; Li, Z. Chemically Recyclable Thermoplastic Polyurethane Elastomers via a Cascade Ring-Opening and Step-Growth Polymerization Strategy from Bio-renewable δ -Caprolactone. *Macromolecules* **2022**, *55* (10), 3860–3868.
- (32) He, Y.; Li, Z.; Zhao, D.; Shen, Y.; Fu, W.; Li, Z. Ring-opening polymerization of representative carbocyclic and oxacyclic monomers: Versatile platform toward advanced functional polymers. *Prog. Polym. Sci.* **2025**, *160*, No. 101921.
- (33) Li, C.; Wang, L.; Yan, Q.; Liu, F.; Shen, Y.; Li, Z. Rapid and Controlled Polymerization of Bio-sourced delta-Caprolactone toward Fully Recyclable Polyesters and Thermoplastic Elastomers. *Angew. Chem., Int. Ed.* **2022**, *61* (16), No. e202201407.
- (34) Liu, J.; Bloch, S. E.; Volokhova, A. S.; Crater, E. R.; Gallin, C. F.; Moore, R. B.; Matson, J. B.; Byers, J. A. Using Redox-Switchable Polymerization Catalysis to Synthesize a Chemically Recyclable Thermoplastic Elastomer. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202317699.
- (35) Ma, K.; An, H.-Y.; Nam, J.; Reilly, L. T.; Zhang, Y.-L.; Chen, E. Y.-X.; Xu, T.-Q. Fully recyclable and tough thermoplastic elastomers from simple bio-sourced delta-valerolactones. *Nat. Commun.* **2024**, *15* (1), 7904.
- (36) Yu, X.; Wang, L.; Zhang, M.; Dong, X.; Shen, Y.; Li, Z. Tough and Closed-Loop Recyclable Thermoplastic Elastomers From Sequential Ring-Opening Copolymerization of Bio-Renewable β -Methyl- δ -Valerolactone and δ -Valerolactone. *Adv. Funct. Mater.* **2025**, *35*, No. 2422779.

- (37) Cederholm, L.; Olsén, P.; Hakkarainen, M.; Odelius, K. Design for Recycling: Polyester- and Polycarbonate-Based A-B-A Block Copolymers and Their Recyclability Back to Monomers. *Macromolecules* **2023**, *56* (10), 3641–3649.
- (38) Carrodegua, L. P.; Chen, T. T. D.; Gregory, G. L.; Sulley, G. S.; Williams, C. K. High elasticity, chemically recyclable, thermoplastics from bio-based monomers: carbon dioxide, limonene oxide and ϵ -decalactone. *Green Chem.* **2020**, *22* (23), 8298–8307.
- (39) Huang, H.; Xie, M.; Wang, S.; Huang, Y.; Luo, Y.; Yu, D.; Cai, Z.; Zhu, J. Ultratough Thermoplastic Elastomers Based on Chemically Recyclable Cycloalkyl-Substituted Polyhydroxyalkanoates. *J. Am. Chem. Soc.* **2025**, *147* (9), 7788–7798.
- (40) Xia, Y.; Shao, T.; Sun, Y.; Wang, J.; Gu, C.; Zhang, C.; Zhang, X. Precise placement of thioester bonds into sequence-controlled polymers containing ABAC-type units. *Nat. Commun.* **2025**, *16* (1), 1974.
- (41) Shi, J.; Zheng, T.; Wang, Z.; Wang, P.; Yang, H.; Guo, J.; Wang, D.; Guo, B.; Xu, J. Filler effects inspired high performance polyurethane elastomer design: segment arrangement control. *Mater. Horiz.* **2024**, *11* (19), 4747–4758.
- (42) Hu, W. The physics of polymer chain-folding. *Phys. Rep.* **2018**, *747*, 1–50.
- (43) Miao, X.; Han, R.; Tian, J.; Ma, Y.; Müller, A. J.; Li, Z. Building Ultrastrong, Tough and Biodegradable Thermoplastic Elastomers from Multiblock Copolyesters Via a ‘Reserve-Release’ Crystallization Strategy. *Angew. Chem., Int. Ed.* **2025**, *64* (5), No. e202417627.
- (44) Weng, C.; Li, X.; Tang, X. Solvent-Dependent Sequence-Controlled Copolymerization of Lactones: Tailoring Material Properties from Robust Plastics to Tough Elastomers. *Angew. Chem., Int. Ed.* **2025**, *64* (3), No. e202415388.
- (45) Yagihara, T.; Matsumura, S. Enzymatic Synthesis and Chemical Recycling of Novel Polyester-Type Thermoplastic Elastomers. *Polymers* **2012**, *4* (2), 1259–1277.
- (46) Zhao, J.-Z.; Yue, T.-J.; Ren, B.-H.; Lu, X.-B.; Ren, W.-M. Closed-loop recycling of sulfur-rich polymers with tunable properties spanning thermoplastics, elastomers, and vitrimers. *Nat. Commun.* **2024**, *15* (1), 3002.
- (47) De Rosa, C.; Auriemma, F. Structure and physical properties of syndiotactic polypropylene: A highly crystalline thermoplastic elastomer. *Prog. Polym. Sci.* **2006**, *31* (2), 145–237.
- (48) Yuan, L.; Tang, C. Reactive bonds for closed-loop chemical processing of polyethylene mimics. *Chem.* **2021**, *7* (4), 847–848.
- (49) Williams, C.; Gregory, G. Closing the loop on recycling bioplastics. *Nature* **2021**, *590* (7846), 391–392.
- (50) Johnson, A. M.; Johnson, J. A. Thermally Robust yet Deconstructable and Chemically Recyclable High-Density Polyethylene (HDPE)-Like Materials Based on Si-O Bonds. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202315085.
- (51) Si, G.; Chen, C. Cyclic–acyclic monomers metathesis polymerization for the synthesis of degradable thermosets, thermoplastics and elastomers. *Nat. Syn.* **2022**, *1* (12), 956–966.
- (52) Zhang, X.; Zhao, Y.; Chen, M.; Ji, M.; Sha, Y.; Nozaki, K.; Tang, S. Polyethylene Materials with Tunable Degradability by Incorporating In-Chain Mechanophores. *J. Am. Chem. Soc.* **2024**, *146* (34), 24024–24032.
- (53) Chen, P.; Kang, X.; Li, K.; Jian, Z. Tailored synthesis of circular polyolefins. *Nat. Sustain.* **2025**, *8*, 422–431.
- (54) Mahadas, N.; Suhail, A.; Sobczak, M.; Li, X.; Chen, K.; Song, K.; Dong, G.; Kuksenok, O.; Tang, C. High Molecular Weight Biobased Long-Chain Aliphatic Polyesters with Degradability: Insights into Mimicking Polyethylene. *Macromolecules* **2025**, *58* (8), 4070–4081.
- (55) Li, X.; Suhail, A.; Mahadas, N.; Zhang, M.; Hu, Z.; Stefik, M.; Kuksenok, O.; Tang, C. Modulating Polyethylene Mimics with Degradability via Synthesis and Modeling. *Macromolecules* **2025**, *58* (4), 2094–2105.
- (56) Jang, Y.; Nguyen, S.; Hillmyer, M. Chemically Recyclable Linear and Branched Polyethylenes Synthesized from Stoichiometrically Self-Balanced Telechelic Polyethylenes. *J. Am. Chem. Soc.* **2024**, *146* (7), 4771–4782.
- (57) Haessler, M.; Eck, M.; Rothauer, D.; Mecking, S. Closed-loop recycling of polyethylene-like materials. *Nature* **2021**, *590* (7846), 423–427.
- (58) Tang, S.; Seidel, F. W.; Nozaki, K. High Density Polyethylenes Bearing Isolated In-Chain Carbonyls*. *Angew. Chem., Int. Ed.* **2021**, *60* (51), 26506–26510.
- (59) Liu, X.; Hu, Z.; Rettner, E.; Harry, K.; Miscall, J.; Rorrer, N.; Miyake, G. Catalytic closed-loop recycling of polyethylene-like materials produced by acceptorless dehydrogenative polymerization of bio-derived diols. *Nat. Chem.* **2025**, *17* (4), 500–506.
- (60) Liu, K.; Battson, M. E.; Hu, Z.; Zhao, Y.; Rettner, E. M.; Miscall, J.; Rorrer, N. A.; Miyake, G. M. Upcycling polynorbornene derivatives into chemically recyclable multiblock linear and thermoset plastics. *Angew. Chem., Int. Ed.* **2025**, *64*, No. e202423111.
- (61) Zhao, Y.; Rettner, E. M.; Harry, K. L.; Hu, Z.; Miscall, J.; Rorrer, N. A.; Miyake, G. M. Chemically recyclable polyolefin-like multiblock polymers. *Science* **2023**, *382* (6668), 310–314.
- (62) Han, X.-W.; Zhang, X.; Zhou, Y.; Maimaitiming, A.; Sun, X.-L.; Gao, Y.; Li, P.; Zhu, B.; Chen, E. Y. X.; Kuang, X.; et al. Circular olefin copolymers made de novo from ethylene and α -olefins. *Nat. Commun.* **2024**, *15* (1), 1462.
- (63) Sathe, D.; Zhou, J.; Chen, H.; Su, H.-W.; Xie, W.; Hsu, T.-G.; Schrage, B. R.; Smith, T.; Ziegler, C. J.; Wang, J. Olefin metathesis-based chemically recyclable polymers enabled by fused-ring monomers. *Nat. Chem.* **2021**, *13* (8), 743.
- (64) Kamau, S. D.; Hodge, P.; Hall, A. J.; Dad, S.; Ben-Haida, A. Cyclo-depolymerization of olefin-containing polymers to give macrocyclic oligomers by metathesis and the entropically-driven ROMP of the olefin-containing macrocyclic esters. *Polymer* **2007**, *48* (23), 6808–6822.
- (65) Wu, L.; Kim, H.; Choi, T. Degradable Alternating Copolymers from Living Radical Copolymerization of Natural Levoglucosenone and Dienes. *J. Am. Chem. Soc.* **2025**, *147* (14), 11682–11687.
- (66) Ibrahim, T.; Kendzula, K.; Ritacco, A.; Monetti, M.; Sun, H. Functional Group Transformation Approach to Chemically Recyclable Polymers from Ultra-Low to Moderate Strain Monomers. *Macromolecules* **2025**, *58* (8), 3898–3905.
- (67) Chen, L.; Wang, Z.; Fang, E.; Guo, Y.; Liu, Z.; Song, W.; Li, H.; Xu, J.; Fan, Z.; Winnik, M.; Song, S. Recyclable Polypentenamers with Precise Crystallization and Versatile Functionalization. *Macromolecules* **2025**, *58* (2), 1048–1059.
- (68) Dreiling, R.; Huynh, K.; Fors, B. Degradable thermosets via orthogonal polymerizations of a single monomer. *Nature* **2025**, *638*, 120–125.
- (69) Hu, Y.; Ran, Q.; Wei, S.; Wang, C.; Wu, Z.; Xu, E.; Luo, Z.; Jia, P.; Sha, Y. Closed-loop recycling of lignin-based sustainable polymers with an all-hydrocarbon backbone. *Green Chem.* **2023**, *25* (15), 5858–5864.
- (70) Sha, Y.; Chen, X.; Sun, W.; Zhou, J.; He, Y.; Xu, E.; Luo, Z.; Zhou, Y.; Jia, P. Biorenewable and circular polyolefin thermoplastic elastomers. *Nat. Commun.* **2024**, *15* (1), 8480.
- (71) Quinn, E.; Knauer, K.; Beckham, G.; Chen, E. Mono-material product design with bio-based, circular, and biodegradable polymers. *One Earth* **2023**, *6* (6), 582–586.
- (72) Gutekunst, W. R.; Hawker, C. J. A General Approach to Sequence-Controlled Polymers Using Macrocyclic Ring Opening Metathesis Polymerization. *J. Am. Chem. Soc.* **2015**, *137* (25), 8038–8041.
- (73) Yu, Z.; Wang, M.; Chen, X.; Huang, S.; Yang, H. Ring-Opening Metathesis Polymerization of a Macrobicyclic Olefin Bearing a Sacrificial Silyloxy Bridge. *Angew. Chem., Int. Ed.* **2022**, *61* (2), No. e202112526.
- (74) Nowalk, J. A.; Fang, C.; Short, A. L.; Weiss, R. M.; Swisher, J. H.; Liu, P.; Meyer, T. Y. Sequence-Controlled Polymers Through Entropy-Driven Ring-Opening Metathesis Polymerization: Theory, Molecular Weight Control, and Monomer Design. *J. Am. Chem. Soc.* **2019**, *141* (14), 5741–5752.

- (75) Zheng, K.; Yang, J.; Luo, X.; Xia, Y. High Molecular Weight Semicrystalline Substituted Polycyclohexene From Alternating Copolymerization of Butadiene and Methacrylate and Its Ambient Depolymerization. *J. Am. Chem. Soc.* **2024**, *146* (36), 25321–25327.
- (76) Jeon, J. H.; Jung, J. H.; Choi, C. Toward a greener future: Exploring sustainable thermoplastic elastomers. *J. Polym. Sci.* **2024**, *62* (4), 662–678.
- (77) Wang, H. S.; Agrachev, M.; Kim, H.; Truong, N. P.; Choi, T.-L.; Jeschke, G.; Anastasaki, A. Visible light-triggered depolymerization of commercial polymethacrylates. *Science* **2025**, *387* (6736), 874–880.
- (78) De Luca Bossa, F.; Yilmaz, G.; Matyjaszewski, K. Fast Bulk Depolymerization of Polymethacrylates by ATRP. *ACS Macro Lett.* **2023**, *12*, 1173–1178.
- (79) Young, J. B.; Hughes, R. W.; Tamura, A. M.; Bailey, L. S.; Stewart, K. A.; Sumerlin, B. S. Bulk depolymerization of poly(methyl methacrylate) via chain-end initiation for catalyst-free reversion to monomer. *Chem.* **2023**, *9* (9), 2669–2682.
- (80) Rosenboom, J.-G.; Langer, R.; Traverso, G. Bioplastics for a circular economy. *Nat. Rev. Mater.* **2022**, *7* (2), 117–137.
- (81) Yang, T.; Xu, Y.; Liu, G.; Nowack, B. Oligomers are a major fraction of the submicrometre particles released during washing of polyester textiles. *Nat. Water* **2024**, *2* (2), 151–160.
- (82) Critchley, J.; Knight, G.; Wright, W. W. *Heat-resistant polymers: technologically useful materials*; Springer Science & Business Media: 2013.
- (83) Calvo-Correas, T.; Benitez, M.; Larraza, I.; Ugarte, L.; Peña-Rodríguez, C.; Eceiza, A. Advanced and traditional processing of thermoplastic polyurethane waste. *Polym. Degrad. Stab.* **2022**, *198*, No. 109880.
- (84) Smorawska, J.; Wloch, M.; Glowinska, E. Structure-Property Relationship and Multiple Processing Studies of Novel Bio-Based Thermoplastic Polyurethane Elastomers. *Materials* **2023**, *16* (18), 6246.
- (85) Jiun, Y.; Tze, C.; Moosa, U.; Tawawneh, M. Effects of Recycling Cycle on Used Thermoplastic Polymer and Thermoplastic Elastomer Polymer. *Polym. Polym. Compos.* **2016**, *24* (9), 735–739.
- (86) Plummer, K.; Vasquez, M.; Majewski, C.; Hopkinson, N. Study into the recyclability of a thermoplastic polyurethane powder for use in laser sintering. *Proceedings Of The Institution Of Mechanical Engineers Part B-Journal Of Engineering Manufacture.* **2012**, *226* (B7), 1127–1135.
- (87) Skrockiene, V.; Zukiene, K.; Jankauskaite, V.; Baltusnikas, A.; Petraitiene, S. Properties of mechanically recycled polycaprolactone-based thermoplastic polyurethane/polycaprolactone blends and their nanocomposites. *J. Elastom. Plast.* **2016**, *48* (3), 266–286.
- (88) Wang, Z. J.; Wang, S.; Jiang, J.; Hu, Y.; Nakajima, T.; Maeda, S.; Craig, S. L.; Gong, J. P. Effect of the Activation Force of Mechanophore on Its Activation Selectivity and Efficiency in Polymer Networks. *J. Am. Chem. Soc.* **2024**, *146* (19), 13336–13346.
- (89) Lloyd, E.; Vakil, J.; Yao, Y.; Sottos, N.; Craig, S. Covalent Mechanochemistry and Contemporary Polymer Network Chemistry: A Marriage in the Making. *J. Am. Chem. Soc.* **2023**, *145* (2), 751–768.