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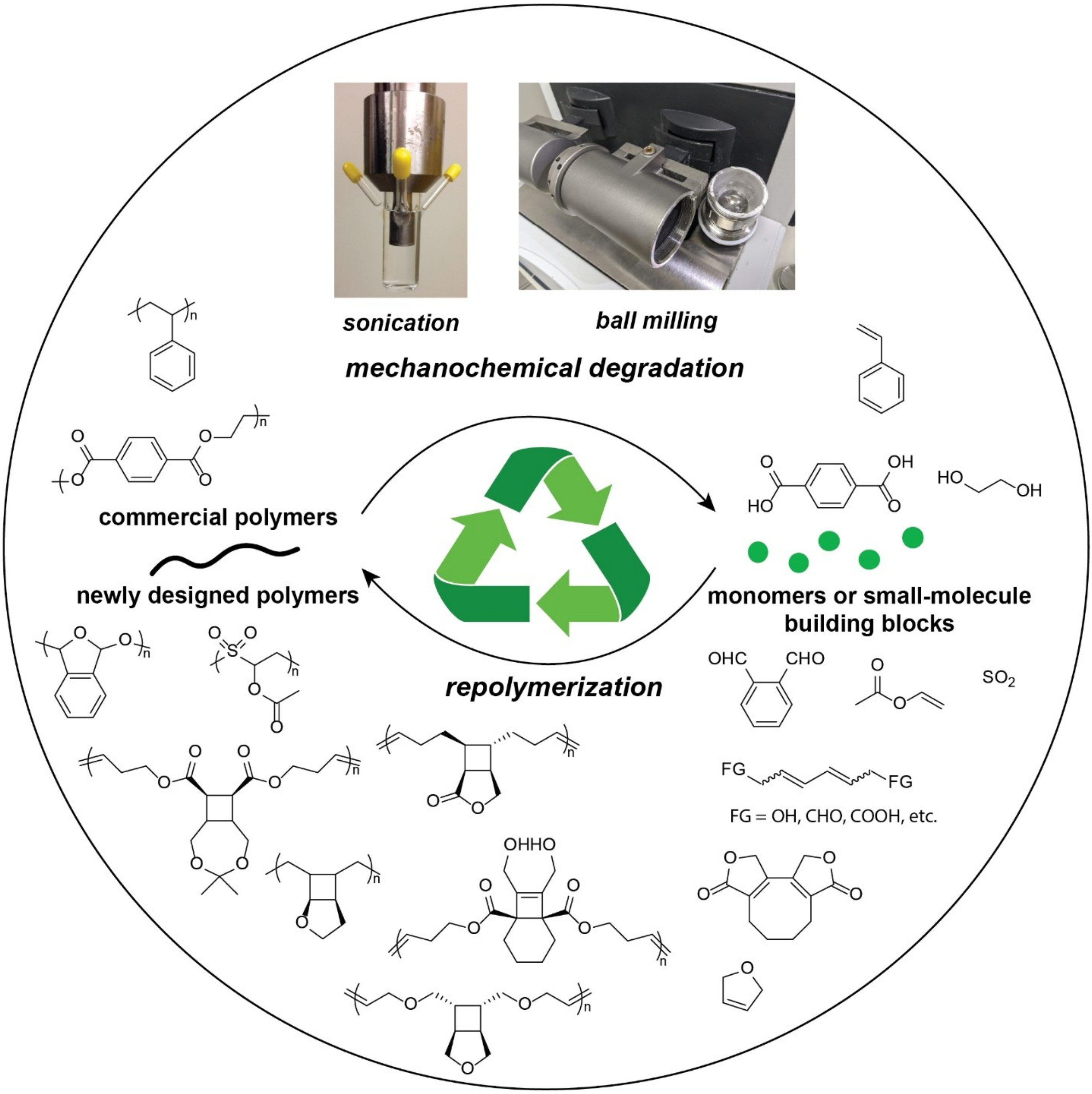
Renewable Polymers

# Mechanochemical Degradation and Recycling of Synthetic Polymers

*Junfeng Zhou*[+], *Tze-Gang Hsu*[+], *and Junpeng Wang**



**Abstract:** The accumulation of plastic waste, due to lack of recycling, has led to serious environmental pollution. Although mechanical recycling can alleviate this issue, it inevitably reduces the molecular weight and weakens the mechanical properties of materials and is not suitable for mixed materials. Chemical recycling, on the other hand, breaks the polymer into monomers or small-molecule constituents, allowing for the preparation of materials of quality comparable to that of the virgin polymers and can be applied to mixed materials. Mechanochemical degradation and recycling leverages the advantages of mechanical techniques, such as scalability and efficient energy use, to achieve chemical recycling. We summarize recent progress in mechanochemical degradation and recycling of synthetic polymers, including both commercial polymers and those designed for more efficient mechanochemical degradation. We also point out the limitations of mechanochemical degradation and present our perspectives on how the challenges can be mitigated for a circular polymer economy.

## 1. Introduction

Polymeric materials have become essential in our daily life owing to their light weight, low cost, and high durability. The rising demand for polymers has led to a continuous increase in the annual polymer manufacturing. It was reported that 359 million metric tons plastics were produced in 2018,[1] compared to 2 million metric tons in 1950.[2] However, the excellent chemical and physical stability of polymers also make them highly durable. Due to the lack of efficient recycling of disposed plastics, the massive accumulation of polymer materials has become a serious environmental burden. Since polymers are mainly produced from finite fossil fuels, the current linear polymer economy is causing global resource crisis. In order to curb plastic pollution and to address the unsustainable use of the resource,[3] it is an urgent matter to identify effective methods to recycle polymers.

Plastic recycling that enables material recovering can be generally categorized into mechanical recycling and chemical recycling.[4] Mechanical recycling is limited by the cost associated with sorting as well as the inevitable degradation and inconsistency in mechanical properties.[5] Chemical recycling involves deconstructing polymers into monomers or building blocks that can be repolymerized into polymers of quality comparable to that of the pristine polymers or be reused to make other useful materials. Chemical recycling has been demonstrated as a promising recycling process to achieve close-loop economy, and a series of depolymerizable systems have been developed.[6]

While mechanical recycling exhibits several drawbacks compared to chemical recycling, it needs to be noted that chemical change, i.e., bond breakage, also occurs during mechanical treatment of polymers.[7] The developments in polymer mechanochemistry, especially the incorporation of force-responsive moieties, namely mechanophores, have shown the potential of utilizing destructive mechanical forces to achieve constructive chemical transformations.[8] The promise in polymer mechanochemistry motivates us to think mechanochemical degradation and recycling as a unique route of plastic recycling. In fact, there have been some examples of using mechanochemistry to achieve degradation and recycling of polymers, including both commercial polymers and those specifically designed for more efficient degradation. In this Minireview, we summarize representative cases in both aspects. We also discuss current limitations of mechanochemical degradation/recycling and propose strategies to overcome these challenges. It is worth noting that although techniques for mechanochemistry are similar to that of mechanical recycling process, mechanochemical degradation/recycling focuses on leveraging mechanochemical reactions to recover the high-value monomers or building blocks and reuse materials. In other words, mechanochemical degradation/recycling is a unique type of chemical recycling by using mechanical techniques. Mechanical recycling and chemical recycling that have been summarized in other excellent reviews[5,6,9] are not covered in this Minireview. Well-developed dehalogenation of pollutants and recycling of rubber waste from scrap tires through mechanochemistry[10] are also excluded from this Minireview.

## 2. Techniques

Before diving into the progress on mechanochemical degradation and recycling, we first briefly summarize the techniques used below. In fact, these techniques have been discussed extensively in previous reviews, although not necessarily for the purpose of degrading polymers.[11] Mechanochemical techniques can be generally categorized into bulk methods and solution-phase methods. Ultrasonication is the most extensively used technique for polymer solution. During sonication, elongational flow fields are generated by cavitation, which includes the nucleation, growth, and collapse of microbubbles.[12] A velocity gradient is then formed in the direction of a collapsing bubble; the polymer segments that are closer to the bubble have a higher velocity than those farther from the bubble, and the polymer is thus stretched and elongated. The midchain of

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the polymer is typically where the highest force is located and where chain scission occurs.[12] Mechanical force can be applied in bulk materials through techniques such as extension,[13] compression,[14] swelling,[15] and ball milling.[10a] Among these, ball milling is a convenient and powerful technique to apply force to polymers; during the milling process, the collision and shear forces between balls or between balls and vessel walls are transmitted to the polymer chains, which can induce chemical transformation.[16] In this Minireview, most demonstrations of polymer mechanochemical degradation/recycling were achieved using ultrasonication or ball milling, largely because of their readily availability, simple operation, and the appreciable experimental scale for convenient spectroscopic characterization.

## 3. Commercial Polymers

The documentation on breakage of polymer chains under mechanical force can be traced back to 1930s.[17] However, for decades, mechanochemical degradation has been limited to random scission in polymers.[7,18] Recently, mechanochemical degradation/recycling beyond simple chain scission has been demonstrated with some commercial polymers, including both thermoplastics (linear polymers) and thermosets (chemically crosslinked polymer networks).

### 3.1. Thermoplastics

Polyolefins, including polyethylene and polypropylene, account for over 60 % of the thermoplastics produced worldwide.[19] Polyolefins have been used in a broad range of applications, including food packaging, bottles, construction materials, and automotives. Since polyolefins only contain highly stable C–C and C–H bonds, their chemical recycling is challenging; therefore, polyolefins are typically recycled through mechanical recycling.

Polystyrene is another important type of thermoplastic and has been widely used for packaging, construction, and electronics. However, due to its inert nature, chemical recycling of polystyrene typically requires high energy.[20] Recently, Balema and Luzinov reported the mechanochemical depolymerization of polystyrene to styrene monomer through ball milling.[21] After milling with media made of hardened steel or tungsten carbide in air, the molecular weight of polystyrene dropped from 88 kDa to 7–8 kDa, and 7 wt % styrene monomer was detected, as characterized by $^1$H NMR and GC-MS. When the ball milling was conducted under argon, despite a similar extent of reduction in the molecular weight, no monomer was obtained, suggesting the participation of oxygen in the depolymerization process. The ball-milled polystyrene was further characterized by electron paramagnetic resonance spectroscopy, which showed that both carbon-centered radical and oxygen-centered radical were present. In addition, when the milling media was switched to silicon nitride, almost no monomer was detected under otherwise identical conditions, indicating that the transition metal is essential for depolymerization. Based on these observations, the authors proposed the following depolymerization mechanism (Figure 1): During ball milling, polystyrene mechanochemically generated carbon-centered radicals, which then reacted with the ambient oxygen to form peroxide radicals. The peroxide reacted with the transition metal, which presumably served as a catalyst

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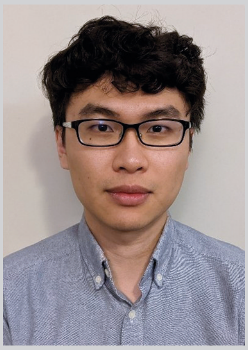

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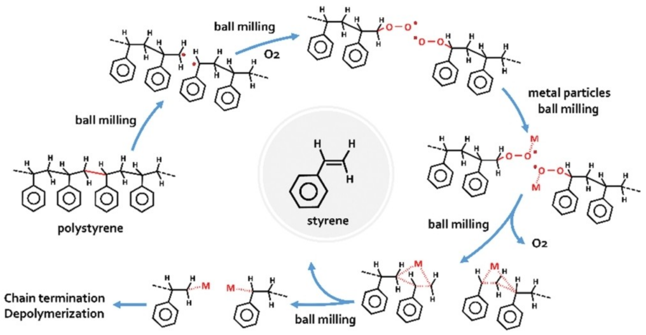
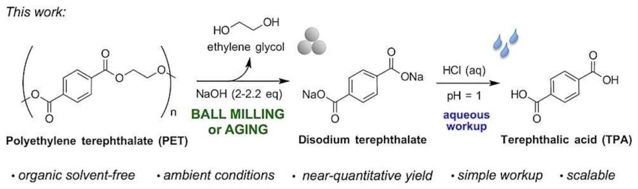


*Figure 1.* Proposed mechanism of the mechanochemical depolymerization of PS under ambient condition. Adapted with permission from Ref. [21]. Copyright 2021, RSC.

for depolymerization. While the mechanism still requires further investigation, and the depolymerization yield is low, this work shows the promise of depolymerizing polystyrene in an economic and scalable fashion. More recently, Jung et al. studied the ball milling of poly($\alpha$-methyl styrene) and demonstrated up to 64 % depolymerization within minutes of grinding. Compared to polystyrene, the more efficient depolymerization of poly($\alpha$-methyl styrene) could be due to a higher reactivity and more favorable thermodynamics enabled by the additional $\alpha$-methyl group.[22]

As the most abundant polyester, polyethylene terephthalate (PET) has been widely used to make bottles, films, and fibers, and its annual production has reached 70 million tons.[23] Compared to the inert hydrocarbon backbone of PS, the backbone of PET contains ester groups, which can be hydrolyzed (or more generally solvolyzed) to recover the monomer terephthalic acid (or its derivatives) and ethylene glycol. Despite the significant developments achieved in the chemical recycling of PET, it is still challenging to quantitatively recycle monomers from PET waste under ambient conditions. For example, due to the high ratio of aromatic groups in PET, the solvolysis of PET typically requires high temperature[24] or strong base.[25] Enzymatic depolymerization allows for the feedstocks to be recovered under mild conditions, but it is only effective for amorphous or low-crystallinity PET.[26] Recently, Štrukil demonstrated near-quantitative conversion of PET into terephthalic acid in the presence of alkaline under ambient conditions by applying ball milling (Scheme 1 ).[27] Importantly, crystallinity of the polymer—which limits the efficiency of enzymatic depolymerization—was found not to significantly affect the yield of mechanochemical depolymerization. In addition, the ball milling assisted degradation can be conveniently scaled up and can be applied to mixed plastics, which further adds practical values to the mechanochemical alkaline hydrolysis of PET.



*Scheme 1.* Efficient PET hydrolysis by mechanochemical milling and vapor-assisted aging. Adapted with permission from Ref. [27]. Copyright 2021, Wiley.

It has been demonstrated that MOFs can be synthesized under solvent-free conditions through extrusion or ball milling.[28] Since terephthalic acid can form MOFs with metal salts, mechanochemical degradation of PET (forming terephthalic acid) and the subsequent formation MOFs can potentially be conducted in a one-pot fashion. Recently, He et al. demonstrated the synthesis of MOFs through ball milling, using PET and metal salts as the starting materials.[29]

### *3.2. Thermosets*

Thermosets are covalently crosslinked polymer networks and are more difficult to recycle due to their permanent shapes—after curing, they cannot be mechanically recycled or thermally reshaped to new products. As a result, most thermosets are unrecycled or downcycled for low-value applications. Mechanochemistry offers an opportunity to address this challenge. To date, a smart strategy was demonstrated in epoxy resin (ER).

ER is widely used as the matrix of high-performance composites owing to its excellent thermal stability, mechanical properties, and adhesion.[30] However, due to the high stability, the mechanically ground epoxy powder shows poor interfacial strength, resulting in inferior mechanical strength of the final composites. Solid-state shear milling (S3M) process was reported as a new method for mechanochemical recycling of ER at ambient temperature by Wang and coworkers.[30] Unlike traditional mechanical recycling, this process can break the crosslinked structure of ER through mechanochemical reaction and regenerate free hydroxy or amine group on the surface of ER powder. Mixing recycled ER powder with bifunctional epoxides and curing agents rebuilds new epoxy networks (Figure 2). The recovered resins exhibit comparable thermal properties and enhanced mechanical properties compared with the virgin ER. This work shows a potentially high-value recycling of waste ER through mechanochemical recycling.

Recently, Manas-Zloczower and co-workers, reported an approach of converting permanent crosslinked networks into dynamic covalent networks, i.e., vitrimerization.[31] The anhydride-cured ER was vitrimerized into an epoxy vitrimer via a planetary ball milling in the presence of catalytic amount of zinc acetate (Figure 3). After mechanochemical vitrimerization, the Young's modulus increased, and stress relaxation was observed, indicating the successful formation of vitrimer network. In addition, increasing the loading of zinc acetate was found to increase crosslink density and make the network material more rigid. The epoxy vitrimer showed similar mechanical properties after reprocessing and could be reprocessed for several cycles without adding additional catalyst.

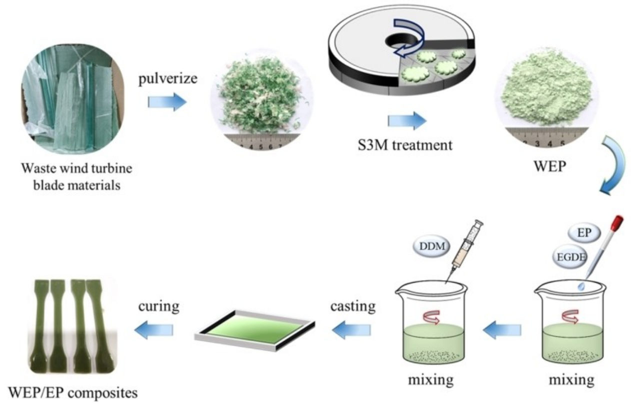


*Figure 2.* Mechanochemical recycling of waste ER: preparation of the waste ER powder and ER composites. Adapted with permission from Ref. [30]. Copyright 2021, ACS.

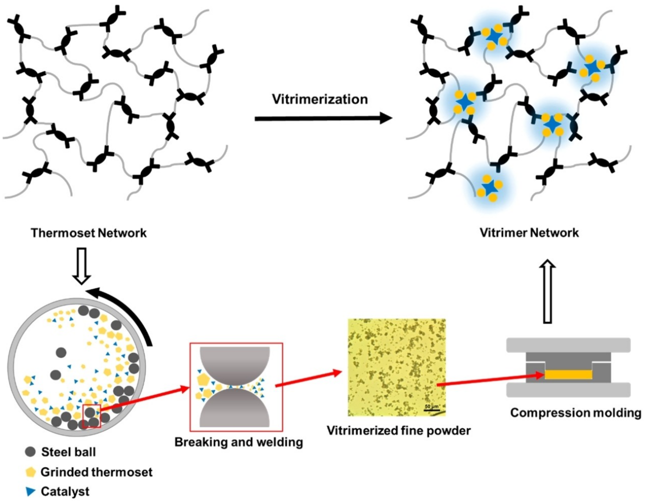


*Figure 3.* Mechanochemical activation of waste ER and the preparation of waste ER powder and ER composites. Adapted with permission from Ref. [31]. Copyright 2020, ACS.

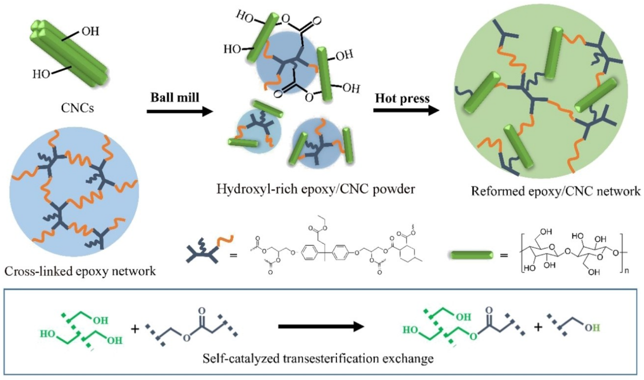


*Figure 4.* Mechanochemical reprocessing of ER to CNC nanocomposites via self-catalyzed transesterification. Adapted with permission from Ref. [32]. Copyright 2021, ACS.

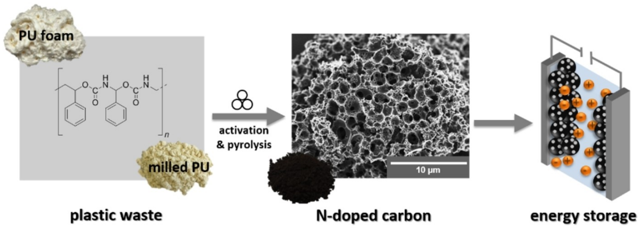


*Figure 5.* Upcycling of PU foam through high-energy ball milling to form nitrogen-doped porous carbon as an electrode material for supercapacitors. Adapted from Ref. [33] (open access). Copyright 2019, Beilstein Institute for the Advancement of Chemical Sciences.

More recently, the same group demonstrated the recycling of biobased diglycidyl ether of alkyl diphenolate ER into high-performance nanocomposites with cellulose nanocrystals (CNCs) through catalyst-free solid-state mixing (Figure 4).[32] CNCs not only serve as nanofillers to endow the nanocomposites excellent thermal and mechanical properties, but also provide abundant hydroxy groups to enable the mechanochemical vitrimerization through self-catalyzed transesterification. The ball milling of biobased ER with biobased fillers adds additional values of sustainability.

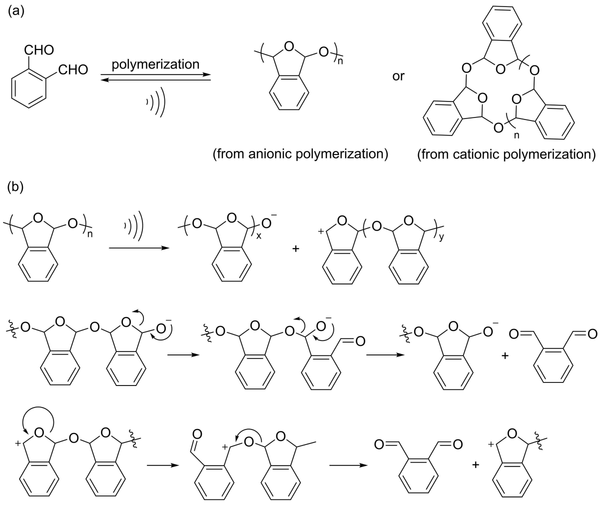
Polyurethane (PU), on its backbone, contains urethane linkages, which can be viewed as an ideal nitrogenous carbon precursor for the preparation of nitrogen-doped porous carbon materials. Recently, a case of upcycling polyurethane (PU) into supercapacitor electrodes was reported by the Borchardt group.[33] Ball milling and heating of waste PU foam enabled the formation of porous nitrogen-doped carbon material (Figure 5). When additional urea was milled with waste PU, the rate capability of the supercapacitor can be enhanced. This strategy of turning waste PU into energy materials through mechanochemical treatment provides an alternative solution for the recycling of plastic waste.

## 4. Newly Designed Polymers

As discussed above, except PET, most commercial polymers lack efficient mechanochemical degradation. To enhance mechanochemical degradation, new polymers have been creatively designed, which can be generally categorized into two types: low-ceiling-temperature ($T_c$) polymers and mechanically gated degradable polymers. We will discuss these cases in detail below.

### 4.1. Low-ceiling-temperature polymers

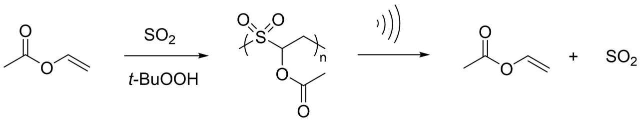
Poly(*o*-phthalaldehyde) (PPA) has a $T_c$ of $-36\,^{\circ}C$ and can depolymerize under acidic conditions or at an elevated temperature. In 2014, Moore and co-workers demonstrated the mechanically triggered depolymerization of PPA to its monomer *o*-phthalaldehyde (Scheme 2a).[34] The mechanochemically triggered depolymerization was observed in both linear and cyclic PPA, which can be synthesized from



***Scheme 2.*** a) Preparation of linear and cyclic PPA and mechanochemically recycling to monomer. b) Proposed mechanism for heterolytic unzipping of PPA.

cationic and anionic polymerization, respectively (Scheme 2a). While PPA is also sensitive to acid and heat, the control experiment using low molecular weight PPA ($M_w = 4.3$ kDa) showed no degradation, which confirmed the mechanical nature of the depolymerization. Unlike a typical force-induced chain scission event that forms two radical species,[35] the mechanochemical chain scission in PPA was found to be heterolytic: forming hemiacetalate and oxocarbenium chain ends. When PPA was sonicated in the presence a trapping agent (*tert*-butyldimethylsilyl chloride or 2-methylindole electrophilic to trap the hemiacetalate or oxocarbenium chain ends, respectively), a decrease in the rate of polymer degradation was observed. This observation suggests that both hemiacetalate and oxocarbenium chain ends can initiate depolymerization (Scheme 2b). The mechanism of heterolytic bond scission and depolymerization was also supported by ab initio steered molecular dynamics simulation, which showed that charge separation persisted until both C–O bonds were broken, i.e., an *o*-phthalaldehyde was formed. No change in the rate of polymer degradation was observed when the polymer was sonicated with a radical trap TEMPO, further ruling out the radical mechanism. In addition, the authors also demonstrated the repolymerization of the degradants by conducting anionic polymerization at a low temperature, and a PPA with useful thermal and mechanical properties was prepared, demonstrating a potential circular polymer economy.

Another example of mechanochemical degradation of low-$T_c$ polymers was reported by Goodwin in 2015.[36] In the study, an alternating copolymer, poly(vinyl acetate-*alt*-sulfur dioxide) (PVAS) was prepared from copolymerization of sulfur dioxide and vinyl acetate, using *t*-butylhydroperoxide (TBHP) radical initiator. When the polymer was subjected to ultrasonication, depolymerization to monomers was observed (Scheme 3). The metastable nature ($T_c \approx -20\,°C$) of PVAS was ascribed to the labile C–S bonds, which is perfectly distributed on the backbone of PVAS. In addition, the entropic gain by generation of a highly volatile sulfur dioxide small molecule also drives the equilibrium towards depolymerization. As a result, PVAS showed continuous decrease in polymer molecular weight after sonication.



***Scheme 3.*** Polymerization of PVAS from vinyl acetate and sulfur dioxide and its mechanochemical depolymerization to monomers.

## *4.2. Mechanically Gated Degradable Polymers*

The concept of mechanical gating was first demonstrated by Craig and co-workers in 2016.[37] In their demonstration, a molecular architecture containing two mechanophores was designed; the mechanophore that is directly coupled to force serves as a molecular gate—only after the gating mechanophore is activated will the second mechanophore experience force (Figure 6). The molecular design features a dual mechanophore 5,5-dichlorotricyclo(7.2.0.0)undecane that comprises cyclobutane and *cis*-*gem*-dichlorocyclopropane (*g*DCC), and cyclobutane serves as the molecular gate. Since cyclobutane is more mechanically inert than *cis*-*g*DCC, the reactivity of cyclobutane dictates that of gated *cis*-*g*DCC: the gated *cis*-gDCC was found to require a force of >0.8 nN higher than an ungated *cis*-gDCC does, for the reactivity of the electrocyclic ring opening to be accelerated to 10 $s^{-1}$. The sequential reactions—the force opens the molecular gate and then activates the gated mechanophore—endow a programed control on the reactivity of a mechanophore. It was soon realized that the design of mechanical gating can be extended to other types of reactions, such as photochemistry.[38]

The generality of the mechanical gating and the motivation to control the degradation of polymers inspired the concept of mechanically gated degradation (Figure 7), which was simultaneously reported by the Craig group and

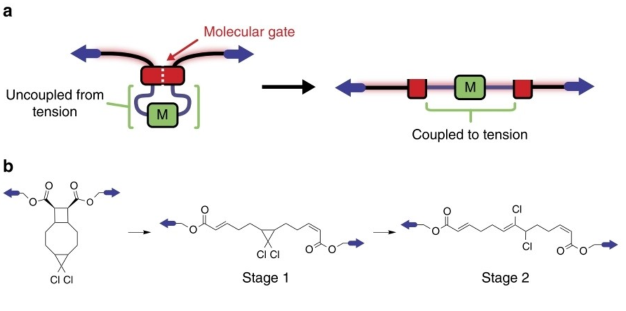


***Figure 6.*** Mechanical gating design. a) A red molecular gate locks green mechanophore substrate. b) Molecular design in which cyclobutane functions as the gate, and *cis*-gDCC serves as the model mechanophore. Adapted from Ref. [37] (open access). Copyright 2016, Nature Portfolio.

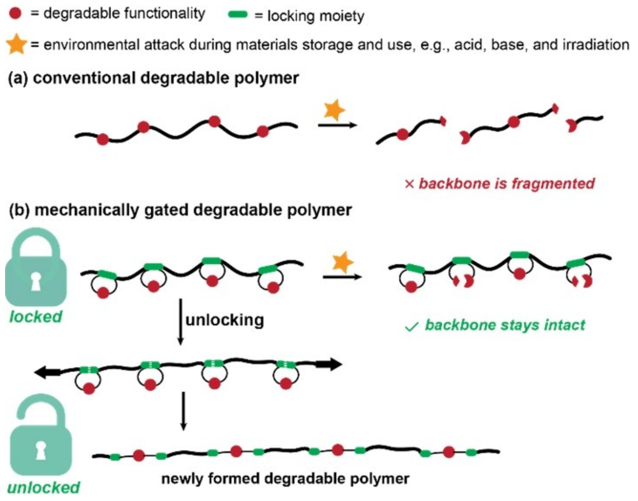


*Figure 7.* Schematic comparison between a conventional degradable polymer and a mechanically gated degradable polymer. a) The cleavable groups on a conventional degradable polymer can be attacked, causing polymer fragmentation. b) In a mechanically gated degradable polymer, the locking moiety keeps the polymer backbone intact under conditions that break the cleavable groups; when the polymer needs to be degraded, the locking moiety can be unlocked, forming a new degradable polymer.

our group in 2020.[39] The degradation of polymers is typically enabled by stimuli-responsive cleavable groups such as esters, acetals, and silyl ethers, which are embedded on the polymer backbone. While these functional groups enable degradation, they can also be triggered to degrade under ambient conditions, causing fragmentation of polymer backbone and deleteriation of mechanical properties (Figure 7a). In a mechanically gated degradable polymer, locking moieties are introduced on the polymer backbone and the degradable functional groups are brought to the side-chain (Figure 7b); the locking moiety keeps the polymer backbone intact under conditions where the degradable functional group is cleaved (Figure 7b). When degradation is needed, the locking moiety can be mechanically unlocked to bring the degradable functional groups to the polymer backbone, forming a readily degradable polymer. Compared to a conventional degradable polymer, the two-step degradation mechanism substantially increases the stability of polymers while still allowing the polymer to undergo on-demand degradation.

Both Craig's and our experimental designs utilized cyclobutane as the locking moiety because of its excellent stability under heat, acid, base, and UV irradiation.[40] In addition, a force of 2.2 nN is required for cycloreversion of cyclobutane to occur on the timescale of 100 ms,[37] higher than the reported mechanical strength of a C–Si bond and a C–S bond by 0.2 nN and 0.8 nN, respectively.[41] The mechanical stability of cyclobutane would allow the polymer to withstand the stress during the storage and use.

The demonstration by Craig and co-workers features a cyclobutane fused cyclic acetal (CCA) mechanophore. The CCA mechanophore was first placed in a macrocyclic olefin, which was and copolymerized with *cis-g*DCC-cyclooctene through entropy-driven ring-opening metathesis polymerization, resulting in a copolymer containing CCA and *cis-g*DCC on its backbone.[39a] The copolymer, upon ultrasonication for 240 min, showed up to ≈50 % of ring opening of cyclobutane accompanied by a reduction in molecular weight from 154 kDa to 28 kDa, and importantly, leading to a structural transformation to an acid degradable polymer containing multiple acetal groups on the main chain. Subsequent treatment with trifluoroacetic acid (TFA) led to a further (11-fold) decrease in molecular weight to 2.5 kDa, generating degradation products including furanone and several unsaturated diols (Figure 8, path B). On the other hand, if the polymer is first treated with TFA and then subjected to ultrasonication, the molecular weight of the resulting polymer is significantly higher (22 kDa) (Figure 8, path A). The less efficient degradation in path A can be attributed to the formation of scissile mechanophores: upon hydrolysis of the acetal, the fused ring on cyclobutane is broken, and the nonscissile CCA mechanophore was converted into to a scissile one. Each time a scissile mechanophore is broken, its constituent polymer would experience chain scission and stress relaxation, and the mechanochemical activation would cease. Chain scission will stop after several cycles, and the polymer will stay at a relatively high molecular weight, i.e., limiting molecular weight (typically $>10$ kDa);[12] thus, polymers with scissile mechanophores cannot be degraded efficiently through mechanically induced chain scission.

The gated degradation in our work was demonstrated with a cyclobutane-fused lactone (CBL) mechanophore.[39b] A cyclooctene monomer containing CBL was synthesized from photochemical [2+2] cycloaddition of cyclooctadiene

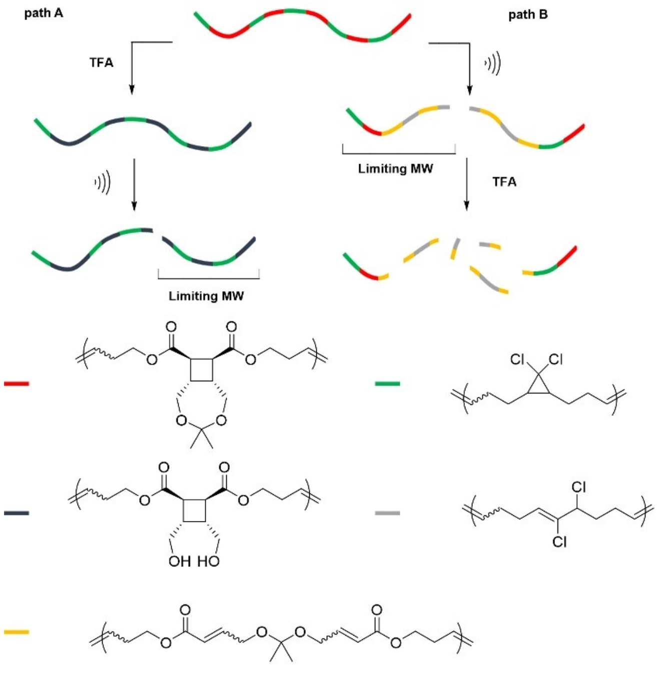
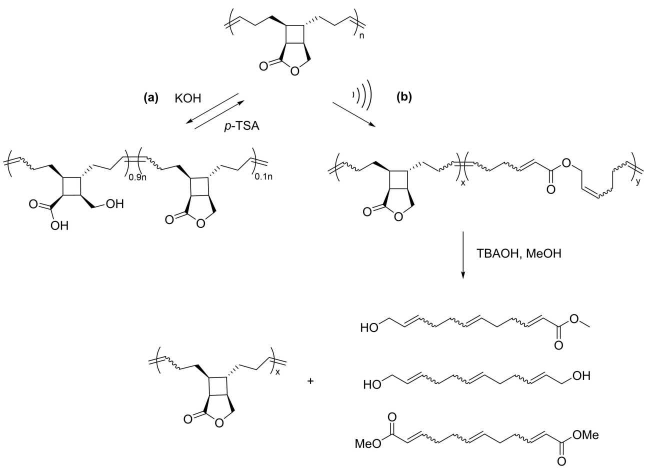


*Figure 8.* Two distinct degradation pathways caused by flipping the order in applying acid and mechanical force.

and maleic anhydride, and the monomer was subjected to ring-opening metathesis polymerization, yielding the polymer that comprises a CBL in each repeat unit (Scheme 4). As discussed above, hydrolysis of lactone prior to mechanochemical activation of cyclobutane can convert the non-scissile mechanophore into a scissile one and lead to inefficient degradation. In addition, the cleavage generates new functionality and induces changes in polymer properties (such as wettability and morphology). In case unintended hydrolysis occurs, it is desirable to restore the ester group in lactone. Indeed, we demonstrated that after the lactone was hydrolyzed under basic condition, it could be completely restored through acid-catalyzed lactonization (Scheme 4). Importantly, during the hydrolysis and lactonization, the molecular weight of the polymer remained the same, demonstrating excellent hydrolytic stability of the polymer backbone. Ultrasonication of a CBL polymer for 4 h led to a drop in molecular weight from 105 kDa to 35 kDa and 48 % ring opening of cyclobutane; the degradable ester group was therefore brought to the polymer backbone. Subsequent degradation of the sonicated polymer with 0.1 M tetrabutylammonium hydroxide in methanol resulted in small-molecule degradants including diester, diol, and hydroxy ester. The presence of different methanolysis products can be ascribed to the regioirregularity of repeat units. In addition to the small-molecule products, residual polymers with molecular weight below 16 kDa were also observed, which, as characterized by $^1$H NMR characterization, was assigned to be the unactivated part of the polymer during the sonication. The residual polymer showed a bimodal distribution on GPC traces (Figure 9a): the higher molecular weight peak (> 10 kDa) was ascribed to unactivated blocks near chain ends, and the lower molecular weight residual (1–3 kDa) was ascribed to the non-continuous activation zone between the fully activated and unactivated blocks (Figure 9b). The findings showed that detailed analysis of the mechanically activated degradation products can bring insights into understanding the force distribution during the sonication of polymer solution.



*Scheme 4.* a) Polylactone hydrolysis and restoration; b) Mechanical activation followed by degradation in basic condition.

As demonstrated in the CBL system, unintended cleavage can be undone by intramolecular bond forming reactions; however, the restoration typically requires treatment such as heating and the addition of catalysts, which might not be suitable for certain applications. In this case, it would be desirable to replace the cleavable functional group with a moiety that is not cleavable but can become cleavable in response to mechanochemical activation. Xia and coworkers reasoned that under acidic conditions, alkyl ethers are stable, but enol ethers are susceptible to hydrolysis; they therefore designed a polymer that in each repeat unit, contains a cyclobutyl ether (Scheme 5),[42] which upon force-induced ring opening of cyclobutane, forms an enol ether. The polymer was intact under acidic (0.1 M HCl) and basic (0.1 M KOH) conditions, as characterized by GPC and $^1$H NMR. Sonication for 480 min brought the molecular weight of the polymer from 141 kDa down to 18 kDa, which was accompanied by 65 % of ring opening. The resulting polymer was subjected to an acidic condition with 10 mM TFA, resulting in a mixture of low-molecular weight polymer, dialdehyde, diol, and hydroxy aldehyde. Notably, the authors further demonstrated the activation of degradability in solid state by grinding a norbornene-cyclic ether copolymer in a mortar. After TFA treatment, lower molecular weight fractions were observed on GPC traces while no such response was found in TFA-treated unground sample.

In the mechanically gated degradable polymers discussed above, after mechanochemical activation, a second stimulus,

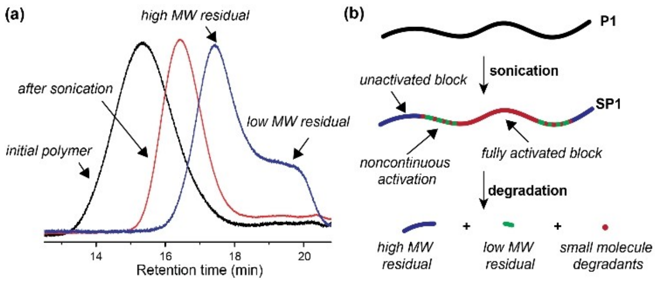
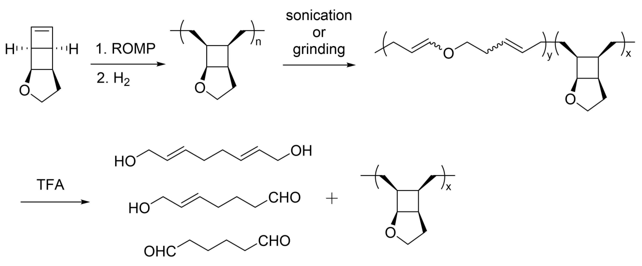


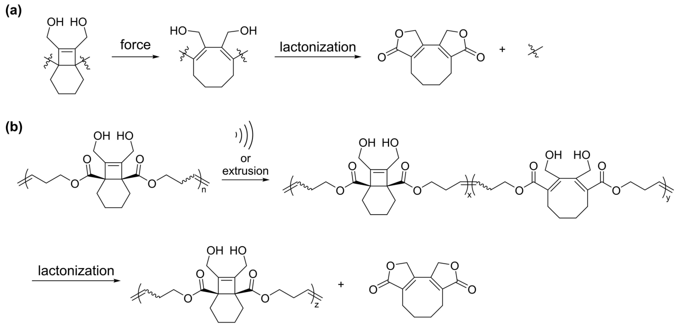
*Figure 9.* Molecular weight analysis of the polymer. a) GPC traces of the polymer before sonication (black), after sonication (red), and after degradation (blue). b) A schematic showing how different degradants are formed through the sequence of sonication and degradation.



*Scheme 5.* Synthesis and mechanochemical degradation of the cyclobutyl ether polymer; the polymer does not contain any degradable functional groups but generates an acid degradable enol ether group upon mechanochemical activation.

such as acid or base, needs to be introduced to degrade the polymers. In case where it is inconvenient to add the second stimulus, spontaneous degradation following mechanochemical activation is desired. Craig and co-workers designed a 7,8-dimethanol-functionalized [4.2.0]bicyclooctene (BCOE) mechanophore, which, upon force-induced electrocyclic ring opening of cyclobutene, can undergo lactonization spontaneously, breaking the backbone and releasing a bis-lactone product (Scheme 6a).[43] A polymer with the dimethanol-functionalized BCOE was prepared. Ultrasonication of the polymer solution for 60 min reduced the molecular weight from 120 kDa to 4.4 kDa. When the hydroxy groups were protected with tetrahydropyran, under identical sonication conditions, the molecular weight of the polymer only decreased to 51 kDa. In addition, the mechanically activated degradation was also demonstrated through extrusion of a blend of the BCOE polymer and commercial polycaprolactone at 65 °C, which showed decrease in molecular weight from 69 kDa to < 10 kDa.

As discussed in 4.1, while low-$T_c$ polymers can depolymerize under mild conditions, they typically suffer from poor stability. Recently, inspired by the mechanically gated degradation mechanism, we envisioned a new type of polymer: a high-$T_c$ polymer that can be converted into a low-$T_c$ polymer on demand. We designed and synthesized a polyether that comprises cyclobutane-fused tetrahydrofuran in each repeat unit, which upon mechanochemical activation, generates poly(2,5-dihydrofuran), a low-$T_c$ polymer that is challenging to directly synthesize from the monomer 2,5-dihydrofuran (Figure 10).[44] The mechanochemical activation was demonstrated with ultrasonication in solution as well as extrusion, compression, and ball milling in bulk. While limited activation (< 1 %) was observed when the polymer was extruded or compressed, up to 68 % and 17 % activation were detected for sonication and ball milling, respectively. The sonicated and ball-milled polymers contained significant fractions of poly(2,5-dihydrofuran), and when they were added to a DCM solution of Grubbs 2nd-generation catalyst, depolymerization that forms 2,5-dihydrofuran was observed.



*Scheme 6.* Mechanically activated latent degradation via lactonization. a) Design of the dimethanol-functionalized BCOE mechanophore: force-induced electrocyclic ring opening of cyclobutene unveils lactonization. b) Mechanically activated polymer degradation of the BCOE through sonication and extrusion. Note that the polymer used was a copolymer of BCOE and gDCC; for clarity, the gDCC part is omitted.

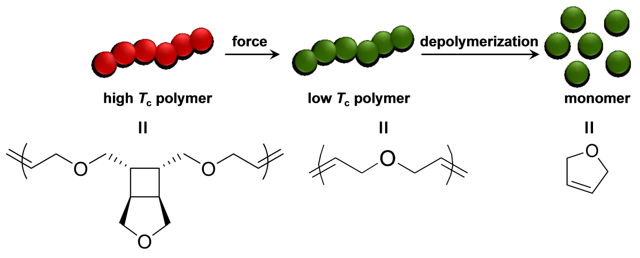


*Figure 10.* Mechanically converting a poly(cyclobutane-fused tetrahydrofuran) into poly(2,5-dihydrofuran) for depolymerization. Adapted from Ref. [44] (open access). Copyright 2023, Nature Portfolio.

## 5. Summary and Outlook

The challenges in plastics sustainability have motivated research innovations in two aspects: recycling current polymers and designing new polymers that can be more efficiently recycled. Mechanochemistry, as a promising, game-changing chemical innovation identified by IUPAC,[45] has been applied in both fronts. In this Minireview, we have summarized recent work on mechanochemical degradation and recycling of commercial polymers and newly designed polymers. It needs to be noted that despite the progress made thus far, there still exist many limitations in current developments. For example, except for PET, the demonstrated mechanochemical degradation of most commercial thermoplastics is inefficient. Vitrimerization of thermosets provides a pathway to recycle the materials, but the networks are thermosets only up to their topology freezing transition temperatures, which limits their applications. While the newly designed low-$T_c$ polymers show efficient degradation, due to their low thermal stability, their processing and storage need to be conducted under low temperatures. Mechanochemical conversion of PU into electrode provides a pathway of upcycling these materials, but the process involves heating and can lead to carbon loss to $CO_2$. Compared to most commercial polymers, mechanically gated degradable polymers show improved efficiency in degradation while maintaining stability; however, roadblocks such as the cost of monomers and the presence of mixed degradants need to be overcome before these polymers become real consideration for plastic applications. We discuss our perspective in terms of how the field will advance in the following three interconnected aspects: cost, scale, and efficiency.

### 5.1. Cost

Cost is a typical issue for new materials. Theoretically, the multiple-time recycling and reuse of the materials can reduce the cost for each use. Techno-economic analysis will be required to navigate the pathway for material preparation with competitive economic value. The cost in materials for the mechanically gated degradable polymers can be reduced by copolymerizing the new monomers with commercial monomers so that only a small fraction of the new monomers is used—a strategy that has been applied to other types of degradable polymers.[46] In addition, commericial polymers can be converted into mechanically gated degradable polymers through post-polymerization functionalization, which is expected to be more cost-effective than starting from scratch.

### 5.2. Scale

To apply mechanochemical degradation and recycling on industrial scales, the feasibility of scaling up needs to be tested to establish the degradation profiles at varied scales. Ball mill and extrusion involve no or little solvent use and have been applied in industry for other applications. The preliminary degradation study by ball milling suggests the feasibility of using ball milling for the mechanochemical degradation and recycling of polymers. Sonication in dilute solution has shown efficient polymer degradation, but it is not scalable, as the use of solvent causes envrionmental concerns and the removal of solvents requires intense energy. Extrusion is scalable,[47] but it bings about limited extent of degradation in polymers. The technqiue of ultrasonic-assisted extrusion[48] combines the high mechanical energy of sonication and the scalability of extrusion and can potentially be used for mechanochemical degradation and recycling of polymers on industrial scales. In addition, Torkelson and co-workers have developed a mechanical process, namely solid-state shear pulverization (SSSP), which is conducted in a modified twin-screw extruder with additional cooling zones to process the polymer in the solid state.[49] Compared to a regular extrusion process, the high shear and compression forces generated during SSSP can lead to more efficient degradation and recycling of polymers.

### 5.3. Efficiency

Compared to mechanical recycling, chemical recycling is advantageous in that (1) monomers or molecular building blocks can be recycled so that the quality of material is retained during the recycling and (2) it is suitable for recycling of mixed materials, such as polymer composites and multilayer packaging materials, but this is only true when the recycling reaches a high efficiency. As a chemical recycling method, mechanochemical recycling needs to reach a high efficiency in order to play to its strengths. Since force is typically not evenly distributed on a polymer chain in mechanical processes, it is difficult to efficiently degrade a polymer only using force. In fact, the efficient degradation of PET is enabled by mechanical energy and base. To increase the efficiency of degradation, it is important to couple mechanical force with other stimuli, such as acid, base, and catalysts. It is also fundamentally interesting to study how force and other stimuli can work together to facilitate the degradation reactions. The experimental work will also stimulate and be guided by theoretical effort on reaction potential energy surface coupled to force and other stimuli. In addition, the efficient mechanochemical degradation of low-$T_c$ polymers suggests that with rational design, a mechanically induced bond breakage can be amplified to induce the breakage of the entire polymer chain. We expect that systems with amplified mechanochemical degradation and improved stability will be designed to further enhance the efficiency responses.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Degradation · Mechanochemistry · Polymer · Recycling · Sustainability

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[1] Plastics—The Facts 2019, PlasticsEurope, **2019**.

[2] R. Geyer, J. R. Jambeck, K. L. Law, *Sci. Adv.* **2017**, *3*, e1700782.

[3] a) C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y. Chen, F. A. Leibfarth, H. Sardon, *Nature* **2022**, *603*, 803–814; b) D. E. Fagnani, J. L. Tami, G. Copley, M. N. Clemons, Y. D. Y. L. Getzler, A. J. McNeil, *ACS Macro Lett.* **2021**, *10*, 41–53; c) J. M. Millican, S. Agarwal, *Macromolecules* **2021**, *54*, 4455–4469.

[4] J. Hopewell, R. Dvorak, E. Kosior, *Philos. Trans. R. Soc. London Ser. B* **2009**, *364*, 2115–2126.

[5] a) J. Payne, M. D. Jones, *ChemSusChem* **2021**, *14*, 4041–4070; b) Z. O. G. Schyns, M. P. Shaver, *Macromol. Rapid Commun.* **2021**, *42*, 2000415.

[6] a) M. Hong, E. Y. X. Chen, *Green Chem.* **2017**, *19*, 3692–3706; b) G. W. Coates, Y. D. Y. L. Getzler, *Nat. Rev. Mater.* **2020**, *5*, 501–516; c) B. A. Abel, R. L. Snyder, G. W. Coates, *Science* **2021**, *373*, 783–789; d) C. Shi, L. T. Reilly, V. S. Phani Kumar, M. W. Coile, S. R. Nicholson, L. J. Broadbelt, G. T. Beckham, E. Y. X. Chen, *Chem* **2021**, *7*, 2896–2912; e) H. Chen, K. Wan, Y. Zhang, Y. Wang, *ChemSusChem* **2021**, *14*, 4123–4136; f) G. Xu, Q. Wang, *Green Chem.* **2022**, *24*, 2321–2346.

[7] H. Hinsken, S. Moss, J.-R. Pauquet, H. Zweifel, *Polym. Degrad. Stab.* **1991**, *34*, 279–293.

[8] a) N. Willis-Fox, E. Rognin, T. A. Aljohani, R. Daly, *Chem* **2018**, *4*, 2499–2537; b) M. A. Ghanem, A. Basu, R. Behrou, N. Boechler, A. J. Boydston, S. L. Craig, Y. Lin, B. E. Lynde, A. Nelson, H. Shen, D. W. Storti, *Nat. Rev. Mater.* **2021**, *6*, 84–98.

[9] a) K. Ragaert, L. Delva, K. Van Geem, *Waste Manage.* **2017**, *69*, 24–58; b) I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes, B. M. Weckhuysen, *Angew. Chem. Int. Ed.* **2020**, *59*, 15402–15423; c) Y. Miao, A. von Jouanne, A. Yokochi, *Polymer* **2021**, *13*, 449.

[10] a) M. Baláž, *Environmental Mechanochemistry Recycling Waste into Materials Using High-Energy Ball Milling*, Springer, Cham, **2021**; b) X. Guo, D. Xiang, G. Duan, P. Mou, *Waste Manage.* **2010**, *30*, 4–10; c) G. Cagnetta, K. Zhang, Q. Zhang, J. Huang, G. Yu, *Waste Manage.* **2018**, *75*, 181–186.

[11] a) P. A. May, J. S. Moore, *Chem. Soc. Rev.* **2013**, *42*, 7497–7506; b) J. G. Hernández, C. Bolm, *J. Org. Chem.* **2017**, *82*, 4007–4019; c) J. L. Howard, Q. Cao, D. L. Browne, *Chem. Sci.* **2018**, *9*, 3080–3094; d) M. J. Muñoz-Batista, D. Rodriguez-Padron, A. R. Puente-Santiago, R. Luque, *ACS Sustainable Chem. Eng.* **2018**, *6*, 9530–9544; e) R. F. Martínez, G. Cravotto, P. Cintas, *J. Org. Chem.* **2021**, *86*, 13833–13856; f) B. A. Versaw, T. Zeng, X. Hu, M. J. Robb, *J. Am. Chem. Soc.* **2021**, *143*, 21461–21473.

[12] M. M. Caruso, D. A. Davis, Q. Shen, S. A. Odom, N. R. Sottos, S. R. White, J. S. Moore, *Chem. Rev.* **2009**, *109*, 5755–5798.

[13] a) B. A. Versaw, M. E. McFadden, C. C. Husic, M. J. Robb, *Chem. Sci.* **2020**, *11*, 4525–4530; b) H. Qian, N. S. Purwanto, D. G. Ivanoff, A. J. Halmes, N. R. Sottos, J. S. Moore, *Chem* **2021**, *7*, 1080–1091.

[14] a) M. B. Larsen, A. J. Boydston, *J. Am. Chem. Soc.* **2013**, *135*, 8189–8192; b) Y. Lin, T. B. Kouznetsova, S. L. Craig, *J. Am. Chem. Soc.* **2020**, *142*, 99–103.

[15] a) C. K. Lee, C. E. Diesendruck, E. Lu, A. N. Pickett, P. A. May, J. S. Moore, P. V. Braun, *Macromolecules* **2014**, *47*, 2690–2694; b) K. Imato, A. Irie, T. Kosuge, T. Ohishi, M. Nishihara, A. Takahara, H. Otsuka, *Angew. Chem. Int. Ed.* **2015**, *54*, 6168–6172.

[16] G. I. Peterson, W. Ko, Y.-J. Hwang, T.-L. Choi, *Macromolecules* **2020**, *53*, 7795–7802.

[17] H. Staudinger, H. F. Bondy, *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 734–736.

[18] a) G. J. Price, P. F. Smith, *Polymer* **1993**, *34*, 4111–4117; b) Y. Li, J. Li, S. Guo, H. Li, *Ultrason. Sonochem.* **2005**, *12*, 183–189; c) Y. Liu, L. Xie, Y. Ma, K. Xue, W. Qiu, T. Shan, G. Gao, *Polym. Eng. Sci.* **2015**, *55*, 2566–2575.

[19] A. H. Westlie, E. Y. X. Chen, C. M. Holland, S. S. Stahl, M. Doyle, S. R. Trenor, K. M. Knauer, *Macromol. Rapid Commun.* **2022**, *43*, 2200492.

[20] T. Maharana, Y. S. Negi, B. Mohanty, *Polym.-Plast. Technol. Eng.* **2007**, *46*, 729–736.

[21] V. P. Balema, I. Z. Hlova, S. L. Carnahan, M. Seyedi, O. Dolotko, A. J. Rossini, I. Luzinov, *New J. Chem.* **2021**, *45*, 2935–2938.

[22] E. Jung, D. Yim, H. Kim, G. I. Peterson, T.-L. Choi, *J. Polym. Sci.* **2023**, *61*, 553–560.

[23] *PET Polymer Chemical Economics Handbook*, S&P Global Inc., Arlington, **2021**.

[24] M. Imran, D. H. Kim, W. A. Al-Masry, A. Mahmood, A. Hassan, S. Haider, S. M. Ramay, *Polym. Degrad. Stab.* **2013**, *98*, 904–915.

[25] S. Ügdüler, K. M. Van Geem, R. Denolf, M. Roosen, N. Mys, K. Ragaert, S. De Meester, *Green Chem.* **2020**, *22*, 5376–5394.

[26] V. Tournier, C. M. Topham, A. Gilles, B. David, C. Folgoas, E. Moya-Leclair, E. Kamionka, M. L. Desrousseaux, H. Texier, S. Gavalda, M. Cot, E. Guemard, M. Dalibey, J. Nomme, G. Cioci, S. Barbe, M. Chateau, I. Andre, S. Duquesne, A. Marty, *Nature* **2020**, *580*, 216–219.

[27] V. Štrukil, *ChemSusChem* **2021**, *14*, 330–338.

[28] a) P. J. Beldon, L. Fábián, R. S. Stein, A. Thirumurugan, A. K. Cheetham, T. Friščić, *Angew. Chem. Int. Ed.* **2010**, *49*, 9640–9643; b) D. Crawford, J. Casaban, R. Haydon, N. Giri, T. McNally, S. L. James, *Chem. Sci.* **2015**, *6*, 1645–1649.

[29] P. He, Z. Hu, Z. Dai, H. Bai, Z. Fan, R. Niu, J. Gong, Q. Zhao, T. Tang, *ChemSusChem* **2023**, *16*, e202201935.

[30] P. Kang, S. Yang, S. Bai, Q. Wang, *ACS Sustainable Chem. Eng.* **2021**, *9*, 11778–11789.

[31] L. Yue, H. Guo, A. Kennedy, A. Patel, X. Gong, T. Ju, T. Gray, I. Manas-Zloczower, *ACS Macro Lett.* **2020**, *9*, 836–842.

[32] L. Yue, K. Ke, M. Amirkhosravi, T. G. Gray, I. Manas-Zloczower, *ACS Appl. Bio Mater.* **2021**, *4*, 4176–4183.

[33] C. Schneidermann, P. Otto, D. Leistenschneider, S. Gratz, C. Essbach, L. Borchardt, *Beilstein J. Nanotechnol.* **2019**, *10*, 1618–1627.

[34] C. E. Diesendruck, G. I. Peterson, H. J. Kulik, J. A. Kaitz, B. D. Mar, P. A. May, S. R. White, T. J. Martinez, A. J. Boydston, J. S. Moore, *Nat. Chem.* **2014**, *6*, 623–628.

[35] M. K. Beyer, H. Clausen-Schaumann, *Chem. Rev.* **2005**, *105*, 2921–2948.

[36] K. Kumar, A. P. Goodwin, *ACS Macro Lett.* **2015**, *4*, 907–911.

[37] J. Wang, T. B. Kouznetsova, R. Boulatov, S. L. Craig, *Nat. Commun.* **2016**, *7*, 13433.

[38] X. Hu, M. McFadden, R. Barber, M. J. Robb, *J. Am. Chem. Soc.* **2018**, *140*, 14073–14077.

[39] a) Y. Lin, T. B. Kouznetsova, S. L. Craig, *J. Am. Chem. Soc.* **2020**, *142*, 2105–2109; b) T. G. Hsu, J. Zhou, H. W. Su, B. R. Schrage, C. J. Ziegler, J. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 2100–2104.

[40] a) C. T. Genaux, F. Kern, W. D. Walters, *J. Am. Chem. Soc.* **1953**, *75*, 6196–6199; b) H. N. C. Wong, K.-L. Lau, K.-F. Tam in *Small Ring Compounds in Organic Synthesis I* (Ed.: A. de Meijere), Springer Berlin Heidelberg, Berlin, **1986**, pp. 83–157.

[41] M. Grandbois, M. Beyer, M. Rief, H. Clausen-Schaumann, H. E. Gaub, *Science* **1999**, *283*, 1727–1730.

[42] J. Yang, Y. Xia, *Chem. Sci.* **2021**, *12*, 4389–4394.

[43] Y. Lin, T. B. Kouznetsova, C. C. Chang, S. L. Craig, *Nat. Commun.* **2020**, *11*, 4987.

[44] T.-G. Hsu, S. Liu, X. Guan, S. Yoon, J. Zhou, W.-Y. Chen, S. Gaire, J. Seylar, H. Chen, Z. Wang, J. Rivera, L. Wu, C. J. Ziegler, R. McKenzie, J. Wang, *Nat. Commun.* **2023**, *14*, 225.

[45] F. Gomollón-Bel, *Chemistry International* **2019**, *41*, 12–17.

[46] P. Shieh, W. Zhang, K. E. L. Husted, S. L. Kristufek, B. Xiong, D. J. Lundberg, J. Lem, D. Veysset, Y. Sun, K. A. Nelson, D. L. Plata, J. A. Johnson, *Nature* **2020**, *583*, 542–547.

[47] D. E. Crawford, J. Casaban, *Adv. Mater.* **2016**, *28*, 5747–5754.

[48] Y. Lou, X. Liu, J. He, M. Long, *Ultrasonics* **2018**, *83*, 194–202.

[49] N. Furgiuele, A. H. Lebovitz, K. Khait, J. M. Torkelson, *Macromolecules* **2000**, *33*, 225–228.

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