JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JACS

Article

Polyethylene Materials with Tunable Degradability by Incorporating In-Chain Mechanophores

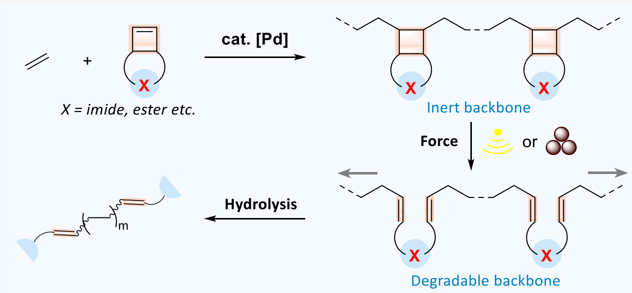
Xiaohui Zhang,[#] Yajun Zhao,[#] Meng Chen, Minghang Ji, Ye Sha, Kyoko Nozaki,* and Shan Tang*

Cite This: J. Am. Chem. Soc. 2024, 146, 24024−24032

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

Downloaded via ECOLE POLYTECHNIC FED LAUSANNE on October 23, 2024 at 12:01:53 (UTC).
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.



ABSTRACT: Polyolefins are recognized as fundamental plastic materials that are manufactured in the largest quantities among all synthetic polymers. The chemical inertness of the saturated hydrocarbon chains is crucial for storing and using polyolefin plastics, but poses significant environmental challenges related to plastic pollution. Here, we report a versatile approach to creating polyethylene materials with tunable degradability by incorporating in-chain mechanophores. Through palladium-catalyzed coordination/insertion copolymerization of ethylene with cyclobutene-fused comonomers, several cyclobutane-fused mechanophores were successfully incorporated with varied insertion ratios (0.35−26 mol %). The resulting polyethylene materials with in-chain mechanophores exhibit both high thermal stability and remarkable acid resistance. Upon mechanochemical activation by ultrasonication or ball-milling, degradable functional units (imide and ester groups) are introduced into the main polymer chain. The synergy of mechanochemical activation and acid hydrolysis facilitates the efficient degradation of high molecular weight polyethylene materials into telechelic oligomers.

■ INTRODUCTION

Due to their outstanding mechanical properties, low cost, easy processability and high chemical resistance, polyolefins are the most extensively produced synthetic polymers, finding widespread applications in modern society.[1] However, the majority of polyolefins are derived from inert hydrocarbons, resulting in their hydrophobic and nonpolar nature. Additionally, inadequate handling of polyolefin waste has led to significant environmental pollution, primarily due to the chemically inert nature of saturated hydrocarbon chains.[2] Incorporation of polar functional groups into polyolefins such as high-density polyethylene (HDPE) would enhance their surface properties, including adhesion, dyeability, printability, and miscibility, thus expanding the application of these materials.[3,4] The most direct approach to producing polar-functionalized polyethylene materials involves the copolymerization of ethylene with polar monomers, utilizing coordination/insertion or radical mechanisms (Scheme 1a).[5−7] In most cases, the polar groups were incorporated as pendent functional groups, without significant changing of the inert hydrocarbon backbone. Despite the considerable motivations, only a few methods were capable of incorporating polar functional groups into the polyethylene backbone to reduce their environmental persistence.

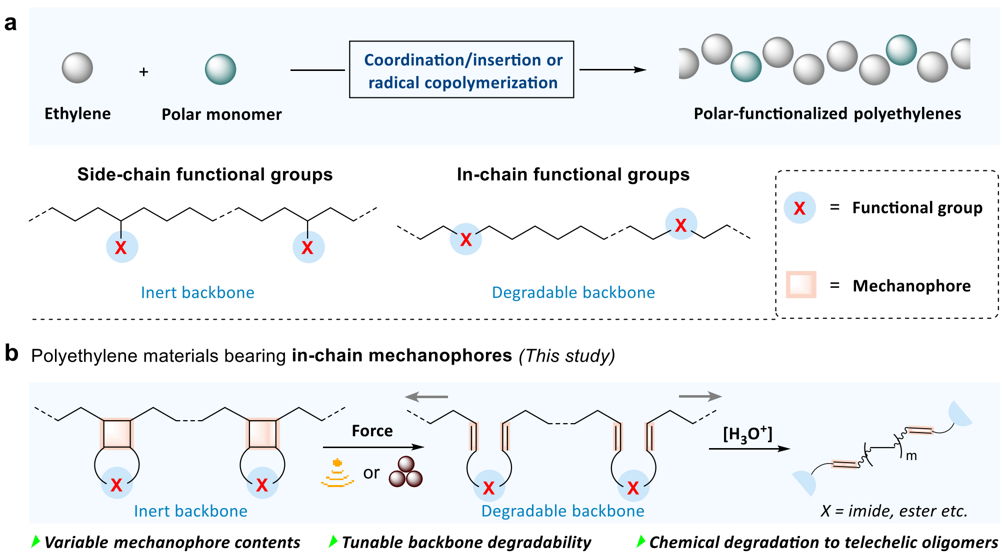
Introducing chemically reactive functional groups into the polyethylene backbone, while preserving high molecular weights and desirable material properties, poses a significant challenge. Since the 1950s, copolymerization of CO and ethylene has been known to produce polyketones through either radical or coordination/insertion copolymerization.[8−10] However, polyethylene copolymers with high carbonyl content generally suffer from poor processability due to their insolubility in common solvents and high melting temperatures. Therefore, attentions have been shifted to producing high molecular weight polyethylene materials with a low carbonyl content to achieve both excellent mechanical properties and good photodegradability.[11,12] Despite the insertion of ketone units, Zeng et al. reported the incorporation of degradable ester units into the main backbone of polyethylenes, albeit with low polymer molecular weights, using radical copolymerization.[13] As for the incorporation of oxidative degradable unsaturated carbon−carbon bonds, copolymerization of ethylene with butadiene has been reported to afford polyethylenes with in-chain vinylene units.[14,15] More recently, Coates and coworkers demonstrated the incorporation of unsaturated vinylene units using a cascade catalytic copolymerization/retro-Diels−Alder reaction approach, enabling the recycling of polyethylene materials through cross-metathesis.[16] While incorporating degradable functionalities into the polyethylene backbone is essential for reducing

Received: June 1, 2024
Revised: August 8, 2024
Accepted: August 9, 2024
Published: August 17, 2024

© 2024 American Chemical Society

https://doi.org/10.1021/jacs.4c07445
J. Am. Chem. Soc. 2024, 146, 24024−24032

Scheme 1. Catalytic Copolymerization to Produce Polar-Functionalized Polyethylene Materials



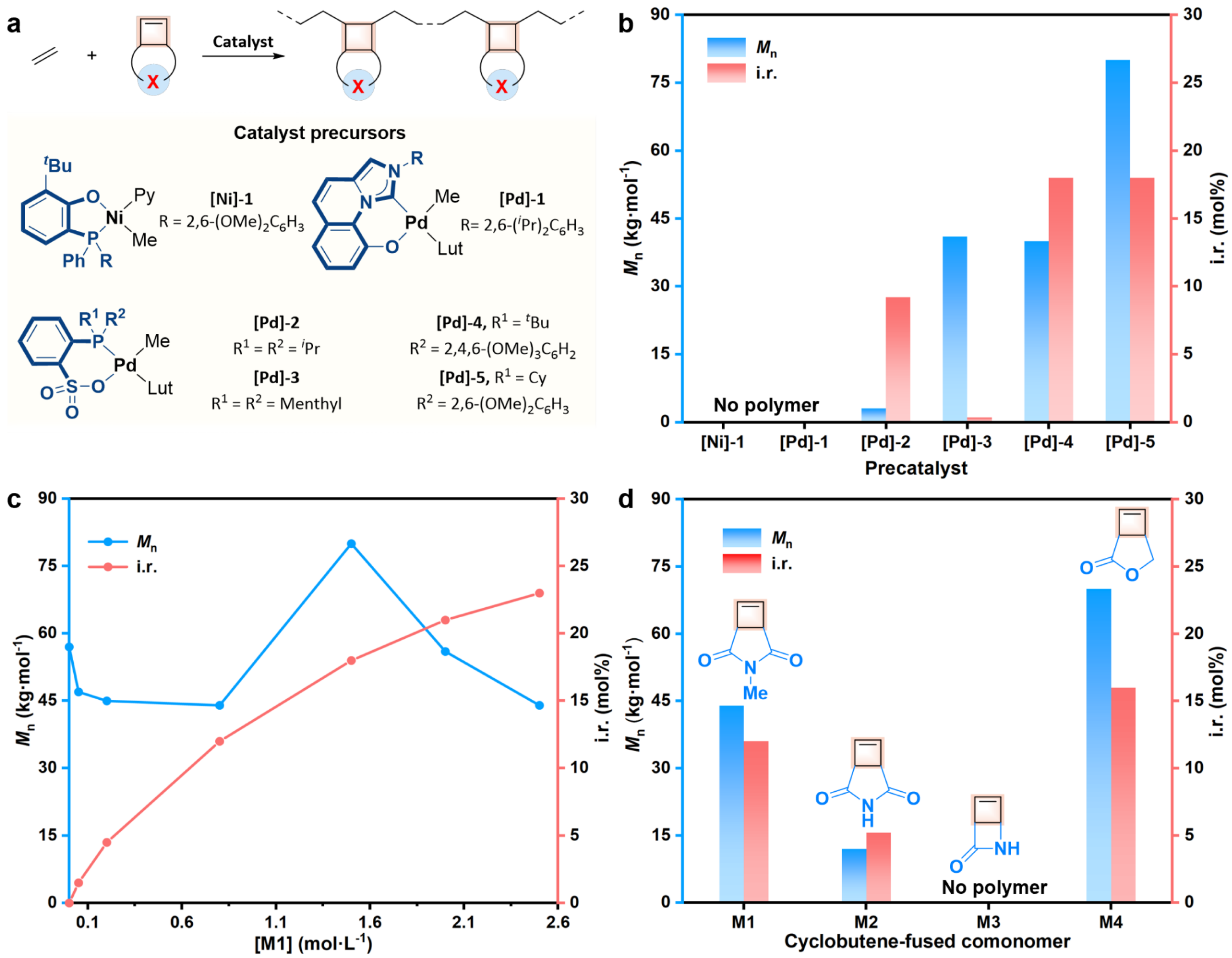


Figure 1. Catalytic copolymerization of ethylene with cyclobutene-fused comonomers (see Table S1 for the detailed polymerization results). (a) Studied catalyst precursors for the synthesis of polyethylene material bearing in-chain mechanophores. (b) The effect of different metal catalysts on the molecular weight (M_n) and **M1** incorporation ratio (i.r.). (c) The effect of initial concentration of **M1** on M_n and i.r. of copolymers using complex **[Pd]-5** as the catalyst. (d) The effect of cyclobutene-fused comonomers on the M_n and i.r. of mechanophores.

https://doi.org/10.1021/jacs.4c07445
J. Am. Chem. Soc. 2024, 146, 24024−24032

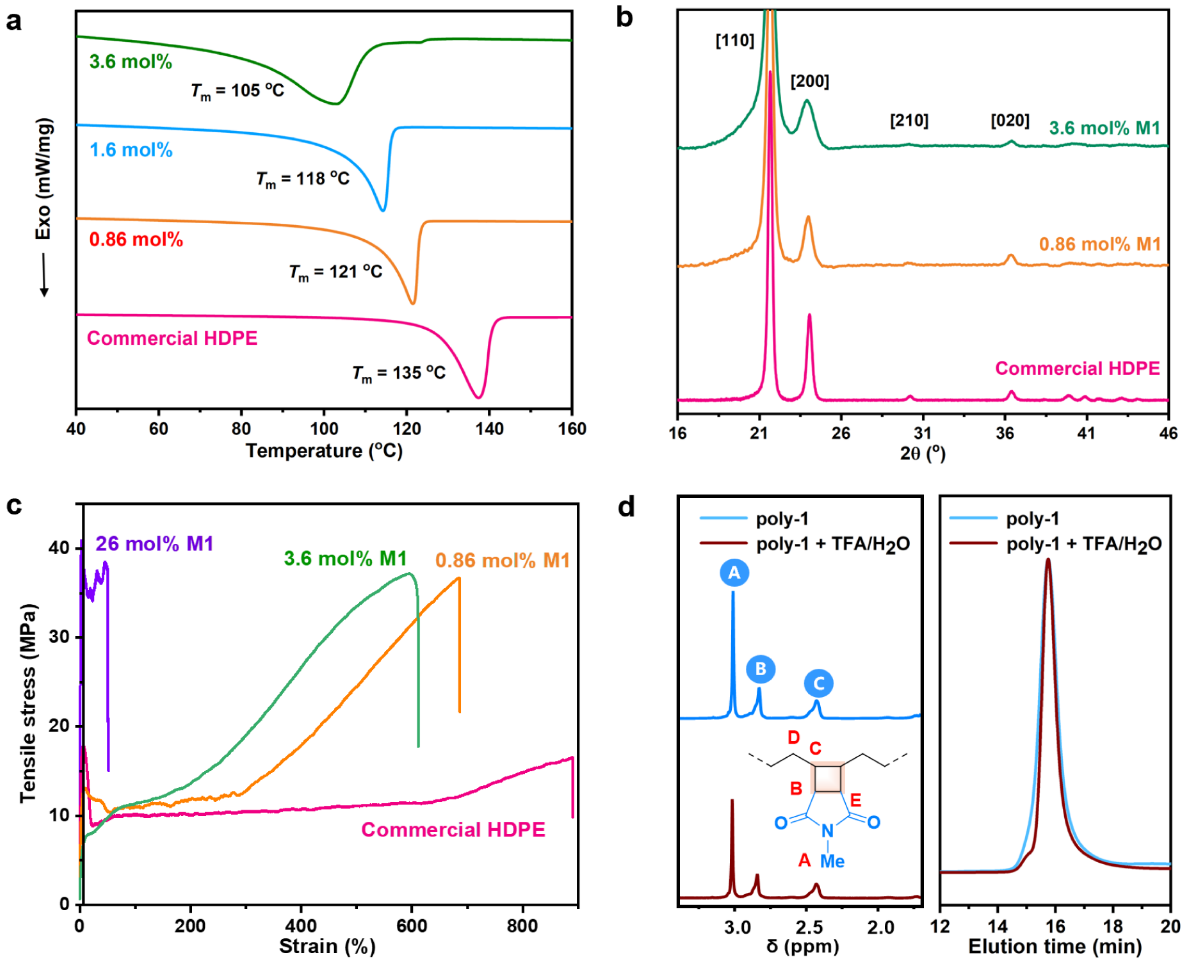


Figure 2. Properties and stability of the polyethylene materials bearing in-chain mechanophores. (a) DSC traces; (b) WAXS diffractograms; and (c) stress−strain curves of the polyethylene materials with varied **M1** incorporation ratios and commercial HDPE (see Supporting Information for detailed data). (d) ^{1}H NMR spectra and SEC traces of **poly-1** (18 mol % **M1**) before and after treating with TFA/H_2O.

environmental persistence, it also results in decreased stability and properties of polyethylene plastics under storage and/or in service.

Mechanophores, units responsive to mechanical force, have been shown to enable site-selective polymer chain scission or functional group transformation upon mechanochemical activation.[17,18] Specifically, cyclobutane-fused mechanophores have been demonstrated to undergo force-induced ring-opening reactions, leading to the formation of unsaturated linear polymers.[19−23] This offers an opportunity to tailor the backbone functionality of polymers via mechanochemical activation.[24] The concept of mechanically gated degradable polymers was elegantly introduced by Craig et al.[25] and Wang et al.[26] by installing cyclobutane-fused mechanophores into an unsaturated polymer chain. Notably, functional groups such as acetal,[25] ester,[26] and enol ether[27] positioned at the fused ring of mechanophores can be incorporated into the polymer backbone after ultrasonication treatment. However, application of this concept has been primarily limited to unsaturated linear polymers obtained from ring-opening metathesis polymerization (ROMP) of specially designed tricyclic monomers. Only recently have mechanophores been directly incorporated into saturated polymer chains via radical copolymerization to regulate the degradability of commodity vinyl polymers.[28,29] Until now, rare copolymerization protocols are available to insert mechanophores into the most widely used polyethylene materials.

Herein, we present the first preparation of polar-functionalized polyethylene materials bearing in-chain mechanophores via catalytic copolymerization of ethylene with cyclobutene-fused polar monomers (Scheme 1b). Different from the direct incorporation of degradable functionalities on the polyethylene backbone, fully saturated hydrocarbon chains may be maintained to ensure the backbone stability of polyethylene materials under storage and/or in service, and degradable functional units will be introduced into the main polymer chain upon mechanochemical activation by ultrasonication or ball-milling. Notably, subsequent hydrolysis of the unrevealed cleavable functional groups enables the degradation of high molecular weight polyethylene materials to telechelic oligomers. While molecular weight affects nonspecific mechanical degradation, the incorporation ratio of mechanophores is critical for controlled degradation via hydrolysis. Overall, the combination of mechanochemical activation and acid hydrolysis facilitated the efficient degradation of polyethylene materials bearing in-chain mechanophores.

RESULTS AND DISCUSSION

Catalytic Copolymerization. Photochemical [2 + 2] cycloaddition of succinimides with acetylene or 1,2-dichloroethylene was reported to produce cyclobutene-fused succinimides with high efficiency.[30,31] However, little was known regarding its reactivity in polymerization reactions. We were inspired by the fact that cyclic imide groups exhibit relatively stable behavior, whereas acyclic imides demonstrate significantly higher activity in hydrolysis, leading to the cleavage of C−N bonds.[32] Therefore, we anticipated the incorporation of cyclobutane-fused succinimide mechanophores to tune the backbone stability and degradability of polymers upon mechanochemical activation. Taking advantage of the reactivity of the highly strained cyclobutene rings, *N*-methyl cyclobutene-fused succinimide (**M1**) was first tested as a comonomer with ethylene to synthesize polyethylene materials bearing cyclobutane-fused succinimide units (Figure 1a). Nickel phosphine-phenolic,[33] and palladium carbene-phenolic complexes,[34] both employed in the copolymerization of ethylene with polar monomers, exhibited low polymerization activity in the presence of **M1** (Figure 1b, [**Ni**]-**1** and [**Pd**]-**1**).

In contrast, palladium phosphine-sulfonate complexes[35] demonstrated remarkable tolerance toward polar cyclic imide groups in the copolymerization of ethylene with **M1**. The substituents on the phosphorus atom played a pivotal role in the incorporation of cyclobutane-fused succinimide units and significantly influenced the molecular weights of the resulting polymers (Figure 1b, [**Pd**]-**2**−**5**). Among the palladium phosphine-sulfonate complexes, the one with two isopropyl groups on phosphorus atom ([**Pd**]-**2**) exhibited the highest activity. Nevertheless, it yielded **poly-1** with a low molecular weight and broad dispersity, potentially attributed to rapid chain transfer. The introduction of bulky menthyl substituents on phosphorus atom ([**Pd**]-**3**) was important for enhancing molecular weight but hindering the insertion of **M1** (0.35 mol %, M_n = 44 kg·mol^{-1}). Optimized complexes [**Pd**]-**4** and [**Pd**]-**5** were both able to achieve a high **M1** incorporation ratio (18 mol %), while complex [**Pd**]-**5** furnished copolymers with the highest molecular weight (M_n = 80 kg·mol^{-1}) and narrowest dispersity (M_w/M_n = 1.1).

The microstructures of the obtained polymers were elucidated in detail as follows. In the ^{1}H NMR spectrum of **poly-1**, resonances of the cyclobutane-fused succinimide groups were determined at 3.01 ppm (m, **A**), 2.83 ppm (m, **B**), and 2.43 ppm (m, **C**) (Figure 2d). In the ^{13}C{^{1}H} NMR spectrum (Figure S35), the resonance of the carbonyl carbon was observed around 179.5 ppm (m) while the sp^3-carbon of the *N*-methyl group was determined at 25.0 ppm (m). Moreover, the sp^3-carbons of the cyclobutane ring were found at 42.7 ppm (m) and 40.2 ppm (m). Two characteristic absorption bands at 1768 and 1693 cm^{-1}, corresponding to the C═O stretching of the cyclic imide group, were observed in the IR spectrum of **poly-1** (Figure S39). Intriguingly, the continuous insertion of **M1** was not observed. To substantiate this observation, attempts to produce homopolymers of **M1** were unsuccessful in the absence of ethylene. No polymer could be precipitated under high monomer concentration while only oligomers were precipitated under low concentration of **M1** (see Table S3).

Given the crucial role of high molecular weight in effective mechanochemical activation,[17,36] complex [**Pd**]-**5** was selected as the optimized catalyst for further investigation. The augmentation of **M1** feed ratio enhanced the mechanophore incorporation (Figure 1c). Notably, higher yields and molecular weights were observed when the ethylene pressure was maintained throughout the reaction process (see Table S2). Additionally, elevating the reaction temperature facilitated the insertion of **M1** (26 mol %) (see Table S1, entries 15 and 16). The mechanophore-functionalized polyethylene materials demonstrate high molecular weights and narrow dispersities, suggesting that the inclusion of **M1** does not trigger problematic chain transfer reactions. Rather, the presence of **M1** appears to suppress chain transfer and branching, possibly by obstructing coordination sites for β-hydride elimination (see Figure S66). Moreover, signals indicative of branching, such as methyl group chain ends, proved challenging to observe in the ^{1}H NMR spectra, indicating the highly linear architecture of the obtained polyethylene materials (see Figures S10, S12, S14, S16, S18, S20, S22, S24, S26, S28, S30, S32, S34, S40, and S42).

It is noteworthy that the current copolymerization protocol allows for the incorporation of other cyclobutane-fused mechanophores into polyethylene materials. A decreased polymerization activity was also observed in the case of unprotected cyclobutene-fused succinimide, producing a copolymer with both decreased molecular weight (M_n = 22 kg·mol^{-1}) and mechanophore incorporation ratio (6.4 mol %) (Figure 1d, **M2**). Possibly due to the poisoning coordination of amide group with [**Pd**]-**5**, no polymer was precipitated in the case of β-lactam-fused cyclobutene (Figure 1d, **M3**). A cyclobutene-fused lactone showed high activity in the copolymerization with ethylene. Compared to cyclobutene-fused succinimides, it achieved a much higher insertion ratio under the same comonomer concentration (Figure 1d, **M4**). In addition to the incorporation of mechanophores in the main chain, it is also possible to incorporate side-chain functional groups via terpolymerization of ethylene, cyclobutene-fused succinimides and commodity vinyl polymers. In the presence of methyl acrylate (**MA**), both **M1** and **MA** participated in the copolymerization with ethylene, affording a terpolymer with 17 mol % **M1** and 1.2 mol % **MA** (Scheme S1). The diffusion-ordered spectroscopy (DOSY) NMR of the obtained polymer exhibited that all the characteristic signals shared single one diffusion coefficient with a sharp peak (Figure S63).

Polymer Properties. The thermal properties of the resulting polyethylene materials were assessed through differential scanning calorimetry (DSC) and thermogravimetric (TGA) analyses. DSC analyses were conducted on the produced polyethylene materials with low **M1** incorporation ratios, revealing distinct endothermic peaks. As the **M1** incorporation ratio increased from 0.86 to 3.6 mol %, the melting points (T_m) showed a decrease from 121 to 105 °C (Figure 2a). No distinct melting points was observed, but glass transition temperatures were detected in copolymers with 12 mol% or more **M1** incorporation (see Figure S68). This phenomenon could be attributed to the influence of bulky cyclobutane units, which may have disrupted the crystalline region of the polyethylene. TGA curves for these polyethylene materials demonstrated high thermal decomposition temperatures (T_d > 419 °C), compatible to the commercially available HDPE (Figures S69 and S70). These findings suggest that the inclusion of cyclobutane-fused succinimide mechanophores, even at a high incorporation ratio, did not compromise the thermal stability of the polyethylene materials.

Wide angle X-ray scattering (WAXS) profiles of the resultant materials displayed four major diffraction peaks centered at 2θ = 21.7°, 24.1°, 30.2°, 36.4°, and other minor diffraction peaks of lower intensities at higher 2θ values, which are consistent with those of commercially available HDPE (Figure 2b).

https://doi.org/10.1021/jacs.4c07445
J. Am. Chem. Soc. 2024, 146, 24024−24032

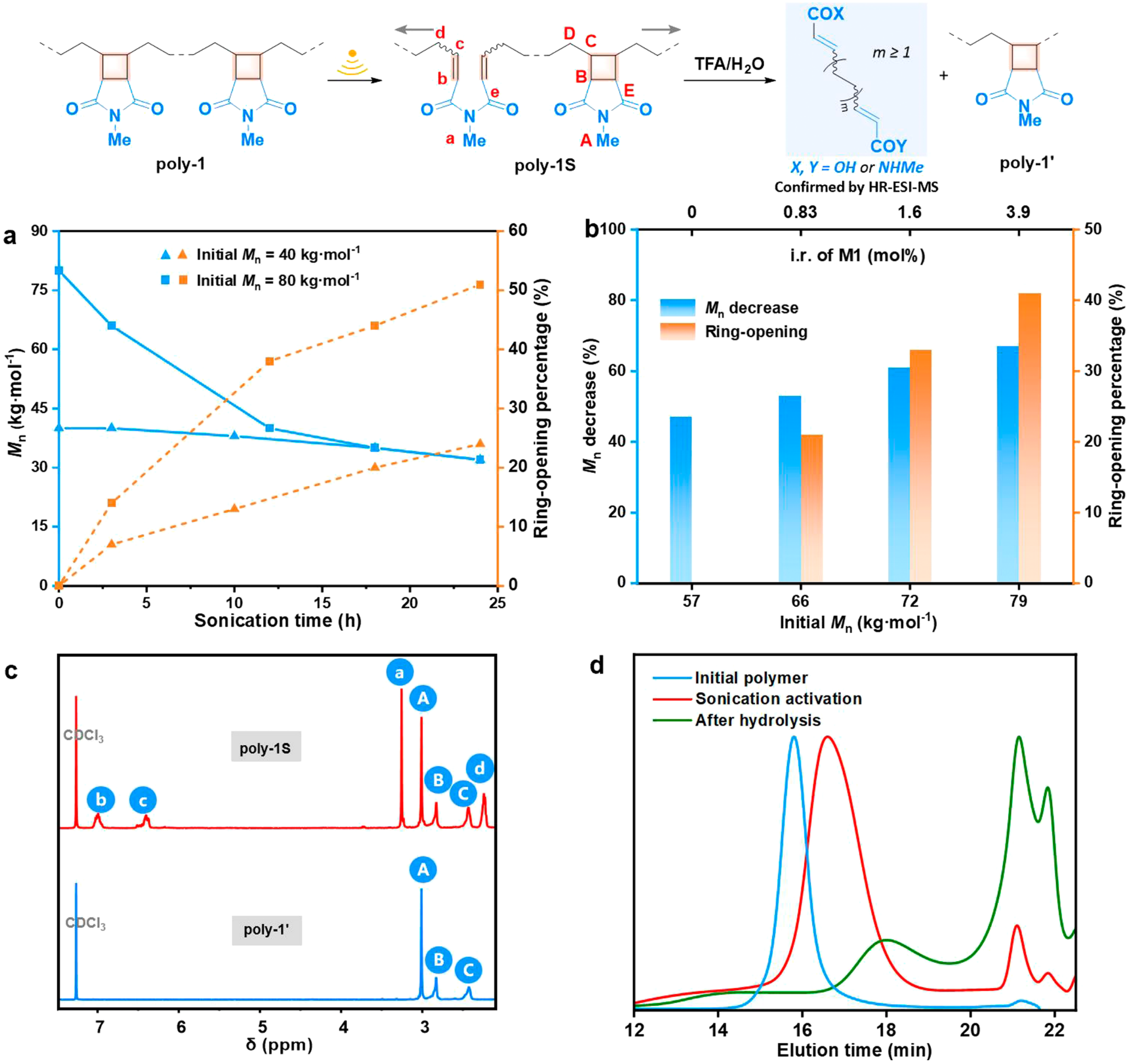


Figure 3. Ultrasonication activation and degradation. (a) Molecular weights (M_n) and ring-opening percentages of polyethylene materials with 18 mol % **M1** incorporation over ultrasonication time in THF (0 °C). (b) Ring-opening percentages of polyethylene materials with low mechanophore content in toluene (65−70 °C). (c) ^{1}H NMR spectra of **poly-1S** (24 h) and **poly-1'**. (d) Comparison of the SEC traces of **poly-1** (M_n = 80 kg·mol^{-1}, 18 mol % **M1** content, blue line), **poly-1S** (ultrasonication for 24 h, red line) and hydrolyzed **poly-1S** (green line).

Amorphous halo of the prepared materials, determined by deconvolution of WAXS data, increased with higher incorporation ratio of **M1** (Figures S73−75), which is constituent with DSC analyses. Tensile testing for the polyethylene materials with varied incorporation ratios of mechanophores was then conducted (Figure 2c). With 0.86 mol% incorporation, the obtained materials showed high tensile strength, with σ_B = 34.1 ± 2.3 MPa, ε_B = 666 ± 24%, and E' = 5.53 ± 0.98 MPa (see Table S5), which is comparable to commercially available HDPE (σ_B = 17.9 ± 3.1 MPa, ε_B = 934 ± 85%, and E' = 11.7 ± 0.98 MPa) (see Table S4), revealing the admirable toughness and ductility. When the incorporation ratio reached 3.6 mol%, the materials still showed promising mechanical properties with σ_B = 33.7 ± 3.7 MPa at 515 ± 85% strain (see Table S6, E' = 2.43 ± 0.98 MPa). A significantly increased tensile strength (σ_B = 42.0 ± 4.1 MPa, and E' = 35.2 ± 9.6 MPa) and a significantly reduced elongation to failure (ε_B = 49.8 ± 0.20%) were observed for the polymer with a high M1 content (26 mol %) in the stress−strain experiment (see Table S7). Based on ^{1}H NMR analyses, there was no apparent cyclobutane ring-opening observed following processing and tensile strength tests (Figure S76). This observation further indicates the stability of the produced polyethylene materials during common melt processing and stretching.

To verify the chemical stability, **poly-1** (M_n = 80 kg·mol^{-1}, 18 mol% **M1**) was treated with trifluoroacetic acid and water (TFA/H_2O = 10/1) for 24 h. Based on the ^{1}H NMR and size exclusion chromatography (SEC) analysis, there was no observed changes in the chemical shifts of the *N*-methyl group or the cyclobutane ring, and there was no discernible alteration in the molecular weight of **poly-1** before and after acid treatment (Figure 2d). These results suggest that, in addition to the backbone's high acid resistance, the cyclic imide groups remained relatively stable during acid treatment.

Mechanochemical Activation and Degradation. It was demonstrated that polyethylene materials with in-chain mechanophores exhibit high thermal stability and acid resistance. Subsequent efforts focused on investigating the mechanochemical activation of **poly-1** through pulsed ultrasonication. Solution of **poly-1** in tetrahydrofuran (THF) with different initial molecular weights (M_n = 80 kg·mol^{-1} and M_n = 40 kg·mol^{-1}), but the same mechanophore content (18 mol %), was activated by pulsed ultrasonication at 0 °C (Figure 3a). Aliquots were taken at designated time intervals from the reaction solution for ^{1}H NMR and SEC analyses to monitor the mechanochemical activation process. The initial molecular weight of **poly-1** has a significant effect on the mechanochemical activation efficiency. As shown in Figure 3a (dashed lines), the cyclobutane ring-opening percentage of the high molecular weight **poly-1** increased more rapidly than that of the low molecular weight **poly-1**. After 24 h of ultrasonication, the cyclobutane ring-opening percentages for **poly-1S** reached 51% and 24%, respectively. The higher efficiency of cyclobutane ring-opening in high molecular weight **poly-1** can be attributed to a greater accessible force for the long polymer chains, reflecting the nature of mechanochemical activation.[37]

Concurrently with the cyclobutane ring-opening reaction, a noticeable reduction in polymer molecular weight caused by nonspecific homolytic chain scission was observed with increased ultrasonication time (Figure 3a, solid lines).[38] Despite different ring-opening percentages, both polymers with initial molecular weights of M_n = 80 kg·mol^{-1} and M_n = 40 kg·mol^{-1} reached an identical molecular weight of 35 kg·mol^{-1} after 18 h of ultrasonication. Since these activated polymers are approaching the limiting molecular weight (around 30 kg·mol^{-1})[17,36] via ultrasonication activation, both exhibited a slight molecular weight decrease to 32 kg·mol^{-1} after an additional 6 h of ultrasonication. Additionally, we have compared the ring opening efficiency for polymers with similar molecular weights but different mechanophore incorporation ratios. While they demonstrate similar molecular weight reduction rates, slightly lower cyclobutane ring-opening efficiency was observed for the polymer with a higher **M1** content (Figure S106).

Due to the poor solubility of polyethylene materials with low mechanophore contents in THF, their mechanochemical activation through pulsed ultrasonication was performed in toluene at 65−70 °C. According to the results in Figures 3a and S106, mechanochemical ring-opening efficiency was mainly affected by the initial molecular weight but not the mechanophore content. After 12 h of ultrasonication, reasonable cyclobutane ring-opening percentages (27−41%) were determined for polyethylene materials with 0.8−3.9 mol % **M1** incorporation (Figure 3b). Meanwhile, a certain degree of the molecular weight decrease facilitated by mechanochemical chain scission was observed for these polyethylene materials and HDPE. Notably, no further degradation was achievable for the regular HDPE upon hydrolysis (Figure S114).

In the ^{1}H NMR spectrum of the precipitated **poly-1S** (initial M_n = 80 kg·mol^{-1}, 24 h), characteristic resonances of conjugated cyclic imide groups were identified at 7.00 ppm (m, **b**), 6.40 ppm (m, **c**), and 3.26 ppm (d, **a**) (Figure 3c, red line). In the ^{13}C{^{1}H} NMR spectrum (see Figure S81), the resonance of the carbonyl carbon was observed around 168.7 ppm (m). Notably, the sp^2-carbons of the C═C double bonds appeared at 150.9 and 123.9 ppm. The IR spectrum of the activated polyethylene material revealed absorption bands at 1634 cm^{-1}, corresponding to the C═C stretching of the conjugated unsaturated imide group (see Figure S84). Despite the mechanochemical activation of polyethylene materials bearing cyclobutane-fused succinimide mechanophores, similar cyclobutane ring-opening and nonspecific chain scission enabled molecular weight decrease were observed in the case of polyethylene materials bearing cyclobutane-fused lactone mechanophores upon ultrasonication treatment (Figures S100 and S104).

Next, the degradability of the activated polymer was explored by treating with a TFA/H_2O (10:1) solution at room temperature for 24 h. Following the removal of all volatiles, the reaction mixture was analyzed via ^{1}H NMR and SEC. In contrast to **poly-1** and **poly-1S** (24 h), the SEC trace of hydrolyzed **poly-1S** (24 h) displayed a broad multimodal distribution (Figure 3d). The low molecular weight peaks, representing the main component, corresponded to the oligomers produced from hydrolysis. Meanwhile, the peak with high molecular weight (M_n = 12 kg·mol^{-1}) was identified as the unactivated fraction of the copolymer, likely situated at the ends of **poly-1S**. Only a very small amount of polymer was reprecipitated from the reaction mixture by methanol (**poly-1'**, 11% yield, 17 kg·mol^{-1}). In its ^{1}H NMR spectrum (Figure 3c, blue line), only signals corresponding to the unactivated cyclobutane-fused succinimide groups were observed.

Efforts were made to characterize the degraded main component. In the crude ^{1}H NMR spectrum of the oligomers in the filtrate (see Figure S112, green line), a clear resonance of carboxylic acid was observed at 12.08 ppm (bs). Additionally, multiple signals corresponding to the olefinic and amide protons were present in the range of 7.90−6.40 ppm. In the high-resolution electrospray ionization mass (HR-ESI-MS) spectra, a series of unsaturated telechelic diacids, acid-amides and diamides were identified in the molecular weight range of 170−420 g·mol^{-1} (see Tables S8 and S9, Figures S115 and S116). The elongational flow force is reported to reach its maximum near the midchain and diminishes to zero at the chain ends,[38] leading to a complete mechanophore activation block at the midchain, along with unactivated blocks at the chain ends. This feature explained the multimodal distribution of the hydrolyzed products (**poly-1'** and telechelic oligomers). Similarly, hydrolysis of ultrasonication activated polyethylene materials bearing in-chain cyclobutane-fused lactone mechanophores also produced products with a bimodal distribution (Figure S117).

Solid state activation of the obtained polymers is more appealing for practical applications as it avoids the use of solvents. Mechanophore activation under bulk conditions, especially for crystalline polymers, has traditionally been considered challenging.[24] Inspired by our observation of efficient ultrasonication activation of polyethylene materials with low mechanophore content (Figure 3b), we explored the possibility of bulk mechanical activation for these highly crystalline polymers. Notably, the polyethylene materials with both high and low incorporation ratios of **M1** were able to undergo cyclobutane ring-opening via ball-milling grinding.

https://doi.org/10.1021/jacs.4c07445
J. Am. Chem. Soc. 2024, 146, 24024−24032

After 2.0 h of ball-milling at a frequency of 50 Hz, the cyclobutane ring-opening percentage reached 18% for **poly-1** with 26 mol % **M1** incorporation (initial M_n = 40 kg·mol^{-1}) (Figure 4a, red line), and 17% for **poly-1** with 3.6 mol% **M1** incorporation (initial M_n = 66 kg·mol^{-1}) (Figure 4a, blue line). Similar to ultrasonication activation, nonspecific mechanical degradation to M_n = 6.9 kg·mol^{-1} was observed for the crystalline polyethylene material with 3.6 mol % **M1** incorporation (Figure 4b, red line). Upon acid treatment, the acyclic imide units undergo hydrolysis, leading to further degradation of the ball-milling activated polyethylene copolymer (Figure 4b, green line, M_n = 0.4 kg·mol^{-1}). The existence of crystalline polyethylene fragments and polymer segments with unactivated mechanophores likely accounts for the bimodal distribution after hydrolysis. Therefore, the developed polyethylenes bearing low content in-chain mechanophores might serve as more environmentally friendly alternative plastics compared to conventional polyolefins.

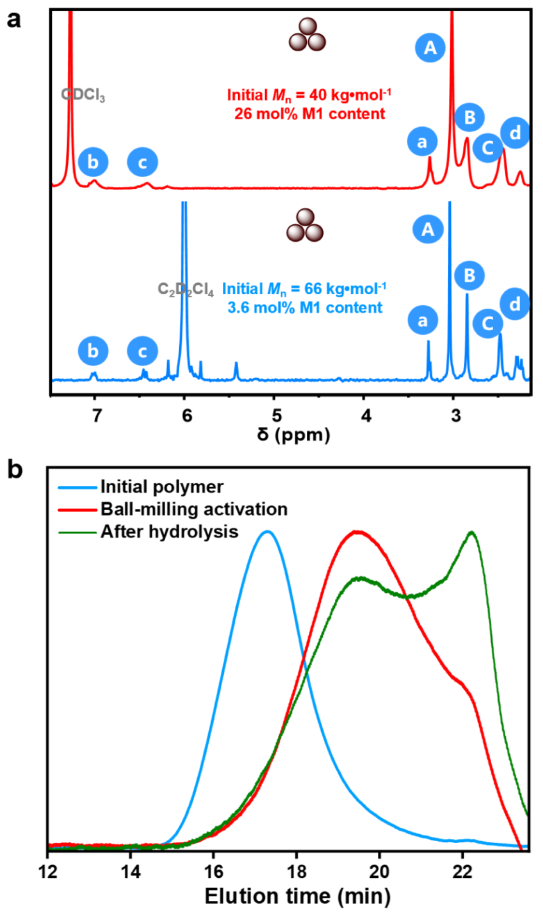


Figure 4. Ball-milling activation and degradation. (a) ^{1}H NMR spectra of the ball-milling activated polymers. (b) Comparison of the SEC traces of **poly-1** (initial M_n = 66 kg·mol^{-1}, 3.6 mol% **M1** content, blue line), **poly-1S** (ball-milling for 2 h, red line) and hydrolyzed **poly-1S** (green line).

CONCLUSION

In summary, we reported a versatile approach to the preparation of polar polyethylene materials with tunable degradability. Through palladium-catalyzed direct coordination/insertion copolymerization of ethylene with cyclobutene-fused comonomers, we successfully incorporated several cyclobutane-fused mechanophores at varied insertion ratios (0.35−26 mol %). The resulting polyethylene materials bearing in-chain mechanophores exhibit both high thermal stability and remarkable acid resistance. Moreover, the incorporated mechanophore units remain intact upon common melt processing and stretching. Degradable functional units (imide and ester groups) can be introduced into the main polymer chain upon mechanochemical activation by ultrasonication or ball-milling. Importantly, the combination of mechanochemical activation and acid hydrolysis enables the efficient degradation of high molecular weight polyethylene materials into telechelic oligomers. Overall, the polyethylene materials bearing in-chain mechanophores possess an ideal combination of desirable material properties and accessible degradability.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c07445.

Experimental details, materials, methods, NMR spectra, SEC, TGA, DSC, WAXS, tensile strength, and HR-ESI-MS data (PDF)

AUTHOR INFORMATION

Corresponding Authors

Kyoko Nozaki − *Department of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, Tokyo 113-8656, Japan*; Email: nozaki@chembio.t.u-tokyo.ac.jp

Shan Tang − *Frontiers Science Center for Transformative Molecules, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Zhangjiang Institute for Advanced Study, Shanghai Jiao Tong University, Shanghai 200240, China*; orcid.org/0000-0001-5662-8401; Email: tang.shan@sjtu.edu.cn

Authors

Xiaohui Zhang − *Frontiers Science Center for Transformative Molecules, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Zhangjiang Institute for Advanced Study, Shanghai Jiao Tong University, Shanghai 200240, China*

Yajun Zhao − *Frontiers Science Center for Transformative Molecules, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Zhangjiang Institute for Advanced Study, Shanghai Jiao Tong University, Shanghai 200240, China*; orcid.org/0000-0001-8571-9994

Meng Chen − *Frontiers Science Center for Transformative Molecules, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Zhangjiang Institute for Advanced Study, Shanghai Jiao Tong University, Shanghai 200240, China*

Minghang Ji − *Frontiers Science Center for Transformative Molecules, Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Zhangjiang Institute for Advanced*

https://doi.org/10.1021/jacs.4c07445
J. Am. Chem. Soc. 2024, 146, 24024−24032

Study, Shanghai Jiao Tong University, Shanghai 200240, China

Ye Sha − Department of Chemistry and Material Science, College of Science, Nanjing Forestry University, Nanjing 210037, China; orcid.org/0000-0003-3338-1228

Complete contact information is available at:
https://pubs.acs.org/10.1021/jacs.4c07445

Author Contributions

[#]X.Z. and Y.Z. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Fundamental Research Funds for the Central Universities (24X010301678, 23X010301599), Shanghai Jiao Tong University 2030 Initiative (WH510363002/002), JST ERATO (Grant JPMJER2103), National Natural Science Foundation of China (22375099) and the China Postdoctoral Science Foundation (2022M722068). The authors thank Prof. Zhaoguo Zhang (SJTU) for the loan of lab space, and Prof. Xuzhou Yan (SJTU) for the technical help with tensile strength measurements.

■ REFERENCES

(1) Stürzel, M.; Mihan, S.; Mülhaupt, R. From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites. *Chem. Rev.* **2016**, *116*, 1398−1433.
(2) Jambeck, J. R.; Geyer, R.; Wilcox, C.; Siegler, T. R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K. L. Plastic Waste Inputs from Land into the Ocean. *Science* **2015**, *347*, 768−771.
(3) Franssen, N. M. G.; Reek, J. N. H.; de Bruin, B. Synthesis of Functional 'Polyolefins': State of the Art and Remaining Challenges. *Chem. Soc. Rev.* **2013**, *42*, 5809−5832.
(4) Keyes, A.; Basbug Alhan, H. E.; Ordonez, E.; Ha, U.; Beezer, D. B.; Dau, H.; Liu, Y.-S.; Tsogtgerel, E.; Jones, G. R.; Harth, E. Olefins and Vinyl Polar Monomers: Bridging the Gap for Next Generation Materials. *Angew. Chem., Int. Ed.* **2019**, *58*, 12370−12391.
(5) Nakamura, A.; Ito, S.; Nozaki, K. Coordination−Insertion Copolymerization of Fundamental Polar Monomers. *Chem. Rev.* **2009**, *109*, 5215−5244.
(6) Tan, C.; Chen, C. Emerging Palladium and Nickel Catalysts for Copolymerization of Olefins with Polar Monomers. *Angew. Chem., Int. Ed.* **2019**, *58*, 7192−7200.
(7) Kermagoret, A.; Debuigne, A.; Jérôme, C.; Detrembleur, C. Precision Design of Ethylene- and Polar-Monomer-Based Copolymers by Organometallic-Mediated Radical Polymerization. *Nat. Chem.* **2014**, *6*, 179−187.
(8) Brubaker, M. M.; Coffman, D. D.; Hoehn, H. H. Synthesis and Characterization of Ethylene/Carbon Monoxide Copolymers, a New Class of Polyketones. *J. Am. Chem. Soc.* **1952**, *74*, 1509−1515.
(9) Sommazzi, A.; Garbassi, F. Olefin-Carbon Monoxide Copolymers. *Prog. Polym. Sci.* **1997**, *22*, 1547−1605.
(10) Drent, E.; Budzelaar, P. H. M. Palladium-Catalyzed Alternating Copolymerization of Alkenes and Carbon Monoxide. *Chem. Rev.* **1996**, *96*, 663−682.
(11) Baur, M.; Lin, F.; Morgen, T. O.; Odenwald, L.; Mecking, S. Polyethylene Materials with in-Chain Ketones from Nonalternating Catalytic Copolymerization. *Science* **2021**, *374*, 604−607.
(12) Tang, S.; Seidel, F. W.; Nozaki, K. High Density Polyethylenes Bearing Isolated in-Chain Carbonyls. *Angew. Chem., Int. Ed.* **2021**, *60*, 26506−26510.
(13) Zeng, T.; You, W.; Chen, G.; Nie, X.; Zhang, Z.; Xia, L.; Hong, C.; Chen, C.; You, Y. Degradable PE-Based Copolymer with Controlled Ester Structure Incorporation by Cobalt-Mediated Radical Copolymerization under Mild Condition. *iScience* **2020**, *23*, 100904.
(14) Shiono, T.; Yoshino, O.; Ikeda, T. Synthesis and Oxidative Degradation of Poly(Ethene-ran-1,3-Butadiene). *Macromol. Rapid Commun.* **2000**, *21*, 1297−1301.
(15) Wu, C.; Liu, B.; Lin, F.; Wang, M.; Cui, D. Cis-1,4-Selective Copolymerization of Ethylene and Butadiene: A Compromise between Two Mechanisms. *Angew. Chem., Int. Ed.* **2017**, *56*, 6975−6979.
(16) Parke, S. M.; Lopez, J. C.; Cui, S.; LaPointe, A. M.; Coates, G. W. Polyethylene Incorporating Diels−Alder Comonomers: A "Trojan Horse" Strategy for Chemically Recyclable Polyolefins. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202301927.
(17) May, P. A.; Moore, J. S. Polymer Mechanochemistry: Techniques to Generate Molecular Force via Elongational Flows. *Chem. Soc. Rev.* **2013**, *42*, 7497−7506.
(18) Versaw, B. A.; Zeng, T.; Hu, X.; Robb, M. J. Harnessing the Power of Force: Development of Mechanophores for Molecular Release. *J. Am. Chem. Soc.* **2021**, *143*, 21461−21473.
(19) Kean, Z. S.; Black Ramirez, A. L.; Yan, Y.; Craig, S. L. Bicyclo[3.2.0]Heptane Mechanophores for the Non-Scissile and Photochemically Reversible Generation of Reactive Bis-Enones. *J. Am. Chem. Soc.* **2012**, *134*, 12939−12942.
(20) Kean, Z. S.; Niu, Z.; Hewage, G. B.; Rheingold, A. L.; Craig, S. L. Stress-Responsive Polymers Containing Cyclobutane Core Mechanophores: Reactivity and Mechanistic Insights. *J. Am. Chem. Soc.* **2013**, *135*, 13598−13604.
(21) Wang, J.; Kouznetsova, T. B.; Boulatov, R.; Craig, S. L. Mechanical Gating of a Mechanochemical Reaction Cascade. *Nat. Commun.* **2016**, *7*, 13433.
(22) Chen, Z.; Mercer, J. A. M.; Zhu, X.; Romaniuk, J. A. H.; Pfattner, R.; Cegelski, L.; Martinez, T. J.; Burns, N. Z.; Xia, Y. Mechanochemical Unzipping of Insulating Polyladderene to Semiconducting Polyacetylene. *Science* **2017**, *357*, 475−479.
(23) Chen, Z.; Zhu, X.; Yang, J.; Mercer, J. A. M.; Burns, N. Z.; Martinez, T. J.; Xia, Y. The Cascade Unzipping of Ladderane Reveals Dynamic Effects in Mechanochemistry. *Nat. Chem.* **2020**, *12*, 302−309.
(24) Zhou, J.; Hsu, T.-G.; Wang, J. Mechanochemical Degradation and Recycling of Synthetic Polymers. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202300768.
(25) Lin, Y.; Kouznetsova, T. B.; Craig, S. L. Mechanically Gated Degradable Polymers. *J. Am. Chem. Soc.* **2020**, *142*, 2105−2109.
(26) Hsu, T.-G.; Zhou, J.; Su, H.-W.; Schrage, B. R.; Ziegler, C. J.; Wang, J. A Polymer with "Locked" Degradability: Superior Backbone Stability and Accessible Degradability Enabled by Mechanophore Installation. *J. Am. Chem. Soc.* **2020**, *142*, 2100−2104.
(27) Yang, J.; Xia, Y. Mechanochemical Generation of Acid-Degradable Poly(Enol Ether)s. *Chem. Sci.* **2021**, *12*, 4389−4394.
(28) Liu, P.; Jimaja, S.; Immel, S.; Thomas, C.; Mayer, M.; Weder, C.; Bruns, N. Mechanically Triggered on-Demand Degradation of Polymers Synthesized by Radical Polymerizations. *Nat. Chem.* **2024**, *16*, 1184−1192.
(29) Li, Z.; Zhang, X.; Zhao, Y.; Tang, S. Mechanochemical Backbone Editing for Controlled Degradation of Vinyl Polymers. *Angew. Chem., Int. Ed.* **2024**, *63*, No. e202408225.
(30) Steglich, W.; Bauer, H.; Große-Bley, M.; Jeschke, R.; Josten, J.; Klein, J. Azepine Derivatives from Toadstools: The Development of New Syntheses for 3H- and 4H-Azepines. *J. Heterocycl. Chem.* **1990**, *27*, 107−110.
(31) Liang, Z.; Wang, L.; Wang, Y.; Wang, L.; Chong, Q.; Meng, F. Cobalt-Catalyzed Diastereo- and Enantioselective Carbon−Carbon Bond Forming Reactions of Cyclobutenes. *J. Am. Chem. Soc.* **2023**, *145*, 3588−3598.
(32) Testa, B.; Mayer, J. M. *Hydrolysis in Drug and Prodrug Metabolism: chemistry, Biochemistry, and Enzymology*; Wiley-VCH: Weinheim, 2003.

(33) Zhang, Y.; Mu, H.; Pan, L.; Wang, X.; Li, Y. Robust Bulky [P,O] Neutral Nickel Catalysts for Copolymerization of Ethylene with Polar Vinyl Monomers. *ACS Catal.* **2018**, *8*, 5963−5976.
(34) Yasuda, H.; Nakano, R.; Ito, S.; Nozaki, K. Palladium/Izqo-Catalyzed Coordination−Insertion Copolymerization of Ethylene and 1,1-Disubstituted Ethylenes Bearing a Polar Functional Group. *J. Am. Chem. Soc.* **2018**, *140*, 1876−1883.
(35) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. Ortho-Phosphinobenzenesulfonate: A Superb Ligand for Palladium-Catalyzed Coordination−Insertion Copolymerization of Polar Vinyl Monomers. *Acc. Chem. Res.* **2013**, *46*, 1438−1449.
(36) Nguyen, T. Q.; Kausch, H.-H. Mechanochemical Degradation in Transient Elongational Flow. In *Macromolecules: synthesis, Order and Advanced Properties*; Springer: Berlin, Heidelberg, 1992; pp. 73182.
(37) Lenhardt, J. M.; Black Ramirez, A. L.; Lee, B.; Kouznetsova, T. B.; Craig, S. L. Mechanistic Insights into the Sonochemical Activation of Multimechanophore Cyclopropanated Polybutadiene Polymers. *Macromolecules* **2015**, *48*, 6396−6403.
(38) Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S. Mechanically-Induced Chemical Changes in Polymeric Materials. *Chem. Rev.* **2009**, *109*, 5755−5798.

https://doi.org/10.1021/jacs.4c07445
J. Am. Chem. Soc. 2024, 146, 24024−24032