

Polyethylene Materials Bearing In-chain Mechanophores

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ABSTRACT: Polyethylenes are recognized as fundamental plastic materials that are manufactured in the largest quantities among all synthetic polymers. The chemical inert nature of the saturated hydrocarbon chains is important for the storage and usage of polyolefin plastics, whereas has given rise to significant environmental challenges regarding plastic pollution. Here we report the synthesis of polyethylene materials bearing in-chain mechanophores via catalytic copolymerization of ethylene with cyclobutene-fused polar comonomers. Cyclobutane-fused mechanophores serve as mechanical gates to regulate the degradability of the polyethylene materials. Upon ultrasonication treatment, saturated hydrocarbon chains will transform to degradable backbones bearing acyclic imide units. Subsequent hydrolysis enables polymer chemical recycling to bifunctional small molecules. Such polyethylene materials possess an ideal combination of stability and accessible degradability.

Due to their outstanding mechanical properties, low cost, easy processibility and high chemical resistance, polyolefins are the most extensively produced synthetic polymers, and have found broad applications in modern society.¹ However, most polyolefins are derived from inert hydrocarbons, rendering them hydrophobic and nonpolar. Furthermore, improper handling of polyolefin waste has resulted in 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 improve their surface properties including adhesion, dyeability, printability, and compatibility, therefore expanding the application of these materials.³⁻⁵ Copolymerization of ethylene with polar monomers via coordination/insertion and radical mechanisms represents the most straightforward way to produce polar-functionalized polyethylenes (Fig. 1a).⁶⁻⁸ In most cases, the polar groups were incorporated as pendent functional groups, leading to the production of undegradable polyethylene materials (Fig. 1b).

Though with considerable interests, only a few methods have been developed for incorporating polar functional groups into the main backbone of polyethylenes via ethylene copolymerization. Since the 1950s, copolymerization of CO and ethylene is known to produce polyketones through either radical copolymerization or coordination/insertion copolymerization.⁹⁻¹¹ However, polyethylene copolymers with high carbonyl content generally suffer from poor processability due to its insolubility in common solvents and high melting temperatures. Over the past few years, significant attention was paid to produce polyethylene materials bearing low content carbonyls to attain both the good mechanical properties and photodegradability.¹²⁻²² Despite of the insertion of carbonyl units, Zeng *et al.* reported the incorporation of degradable ester units into the main backbone of polyethylene via cobalt mediated radical copolymerization (CMRP) of ethylene with 2-methylene-1, 3-dioxepane.²³ More recently, Coates and co-workers reported the incorporation of unsaturated carbon-carbon double bonds using a cascade coordination copolymerization/retro-Diels-Alder reaction protocol, making it possible to recycle the polyethylene materials via cross metathesis.²⁴ Notably, incorporating degradable

functionalities on the polyethylene backbone are crucial for reducing their environmental persistence, but also lead to decreased stability during the storage and usage of polyolefin plastics (Fig. 1c).

Mechanophores, units that respond to mechanical force, have been shown to enable site selective polymer chain scission or functional group transformation upon mechanochemical activation.^{25,26} In this regard, cyclobutane-fused mechanophores have been demonstrated to undergo force-induced ring opening reaction, resulting in the formation of unsaturated linear polymers.²⁷⁻³⁴ In 2020, Craig *et al.* demonstrated the synthesis of polymers bearing cyclobutane-fused cyclic ketal units,³⁵ while Wang *et al.* reported the construction of polymers bearing repeating cyclobutane-fused lactone units.³⁶ In both cases, the cyclobutane units ensure the polymer backbone stability under the chemical conditions for cyclic ketal or ester group cleavage, whereas mechanochemical activation of the cyclobutane units makes the backbone degradable. Later on, tetrasubstituted [4.2.0]bicyclooctene, cyclic ether fused bicyclohexane and cyclobutane-fused tetrahydrofuran were subsequently used as mechanophores by Craig,³⁷ Xia³⁸ and Wang³⁹ in the synthesis of mechanically gated degradable polymers. Inspired by these studies, we envisioned that the incorporation of cyclobutane-fused mechanophores might provide an avenue to regulate the degradability of the most widely used polyethylene materials.⁴⁰

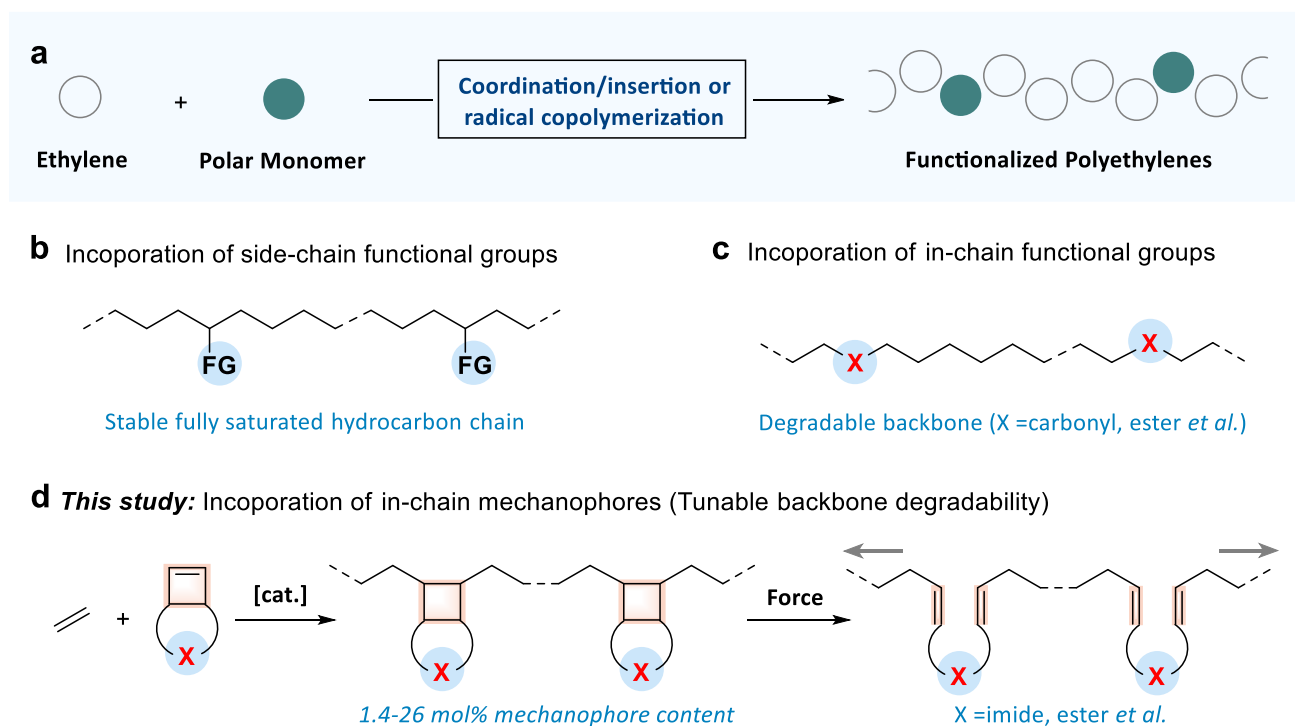


Figure 1. Polar-functionalized polyethylene materials. **a**, Synthesis of polar-functionalized polyethylenes via copolymerization of ethylene with polar monomers. **b**, Polyethylene material bearing pendant functional groups. **c**, Polyethylene materials bearing in-chain degradable functional groups. **d**, Polyethylene materials bearing in-chain mechanophores: tunable backbone degradability via mechanochemical activation (*This study*).

Herein, we report the first preparation of polar polyethylene materials bearing in-chain mechanophores (Fig. 1d). 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 during storage and usage, and degradable functional units will be introduced into the main polymer chain upon mechanochemical activation by ultrasonification. Several cyclobutane-fused mechanophores were successfully incorporated with varied insertion ratios (4.5-26 mol%) via direct coordination/insertion copolymerization of ethylene with cyclobutene-fused polar monomers.

In the case of cyclobutane-fused succinimide mechanophores, fully saturated hydrocarbon chains will transform to degradable backbones bearing acyclic imide units upon ultrasonication treatment. Significantly, the cyclic imide groups are relatively stable under acidic conditions, while the conjugated unsaturated acyclic imides obtained after mechanochemical activation are hydrolyzed easily to enable the efficient chemical recycling of high molecular weight polyethylene materials into bifunctional small molecules.

Photochemical [2+2] cycloaddition of succinimides with acetylene or 1,2-Dichloroethylene was reported to produce cyclobutene-fused succinimides in high efficiency.^{41,42} However, little was known regarding its reactivity in polymerization reactions. We were inspired by the fact that the cyclic imide groups were relatively stable, while acyclic imides exhibit much higher activity in hydrolysis to cleave the C-N bonds. Therefore, we envisioned the incorporation of cyclobutane-fused succinimide mechanophores to regulate the stability and degradability of a polymer upon mechanochemical activation by ultrasonication. Taking advantage of the reactivity of the highly strained cyclobutene rings, *N*-methyl cyclobutene-fused succinimide (**M1a**) was first tested as a comonomer with ethylene to synthesize polyethylene materials bearing cyclobutane-fused succinimide units (**poly-1**). Palladium phosphine-sulfonate complexes⁴³ demonstrated excellent tolerance towards polar cyclic imide groups in the copolymerization of ethylene with **M1a**. The substituents on the phosphine ligands played a crucial role in the incorporation of cyclobutane-fused succinimide units and influenced the molecular weights of the resulting polymers (Fig. 2b, **[Pd]-1-4**). The palladium phosphine-sulfonate complex with two isopropyl groups on phosphine (**[Pd]-1**) showed the highest activity, but furnished **poly-1** with a low molecular weight and broad dispersity. Strong sterically hindered complex **[Pd]-2** gave a low comonomer incorporation ratio (0.35 mol%) along with a high molecular weight ($M_n = 44$ kg/mol). With a high incorporation ratio (18 mol%), complex **[Pd]-4** furnished copolymers with the highest molecular weight ($M_n = 80$ kg/mol) and narrowest dispersity ($M_w/M_n = 1.11$). In contrast, palladium carbene-phenolic complexes⁴⁴ or nickel phosphine-phenolic complexes⁴⁵, which have been used for copolymerization of ethylene with polar monomers, exhibited little polymerization activity in the presence of **M1a** (Fig. 2b, **[Pd]-5** and **[Pd]-6**).

In the ¹H 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**) (Fig. 3c). 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** (See Supplementary Fig. 53). In the ¹³C{¹H} NMR spectrum (See Supplementary Fig. 21), the resonance of the carbonyl carbon was observed around 179.5 ppm (m) while the sp³-carbon of the *N*-methyl group was determined at 25.0 ppm (m). Moreover, the sp³-carbons of the cyclobutane ring were found at 42.7 ppm (m) and 40.2 ppm (m). Given the crucial role of high molecular weight in effective mechanochemical activation,^{25,46} complex **[Pd]-4** was selected as the optimized catalyst for further investigation. Decreasing the amount of **M1a** resulted in reduced mechanophore incorporation, while increasing the amount of **M1a** promoted the mechanophore incorporation (Fig. 2c). Decreasing the reaction temperature to 80 °C significantly decreased polymerization activity, yielding **poly-1** with lower molecular weight and broader dispersity (See Supplementary Table 1, entry 11). As was expected, increasing the reaction temperature promoted the incorporation of **M1a** (25-26 mol%) (See Supplementary Table 1, entries 12 and 13). Utilizing palladium phosphine-sulfonate complexes as catalysts, efforts to obtain homopolymers of **M1a** were proven to be unsuccessful in the absence of ethylene. No polymer could be precipitated under high monomer concentration while only oligomers were precipitated under low concentrations of **M1a** (See supplementary Table 2). It is worth noting that other cyclobutane-fused mechanophores can also be incorporated into polyethylene materials through the current copolymerization protocol. A decreased

polymerization activity was also observed in the case of unprotected cyclobutene-fused succinimide, producing **poly-3** with both decreased molecular weight ($M_n = 22$ kg/mol) and mechanophore incorporation ratio (7.0 mol%) (Fig. 2d, **M1b**). Possibly due to the poisoning coordination of amide group with **[Pd]-4**, no polymer was precipitated in the case of β -lactam-fused cyclobutene (Fig. 2d, **M2**). A cyclobutene-fused lactone showed a high activity in the copolymerization with ethylene. Compared to cyclobutene-fused succinimides, it achieved a much higher insertion ratio under the same comonomer concentration (Fig. 2d, **M3**).

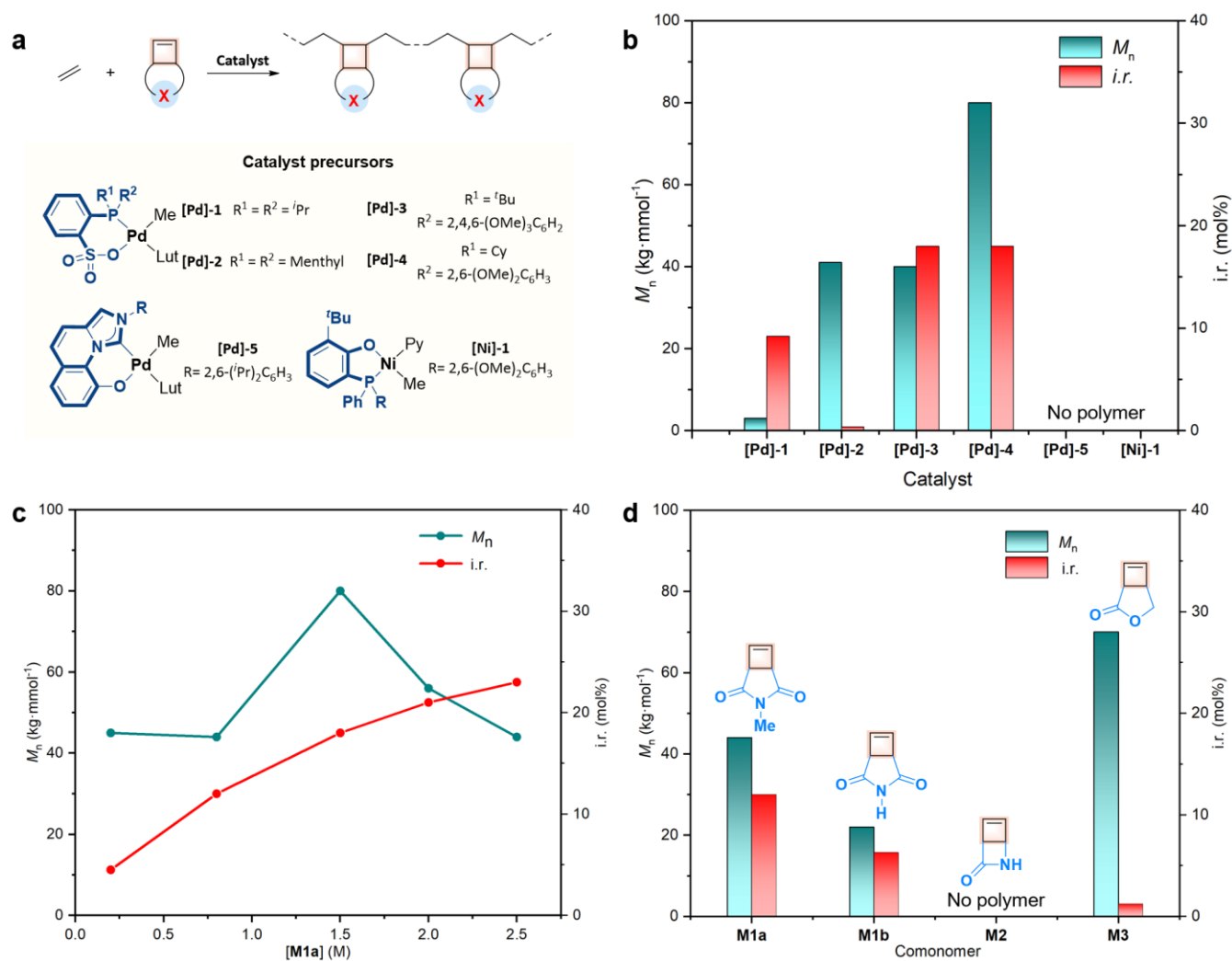


Figure 2. Copolymerization of ethylene with cyclobutane-fused comonomers. **a**, Studied catalyst precursors for the synthesis of polyethylene material bearing in-chain mechanophores. **b**, The effect of different metal catalysts on the molecular weight and mechanophore incorporation ratio (i.r.) in copolymerization of ethylene with **M1**. **c**, The effect of initial concentration of **M1a** on the molecular weight and mechanophore content in **poly-1** using **[Pd]-4**. **d**, The effect of cyclobutane-fused comonomers on the polymer molecular weight and mechanophore incorporation ratio (See Supplementary Table 1 for the detailed polymerization results).

The thermal properties of the resulting polyethylene materials were assessed through differential scanning calorimetry (DSC) and thermogravimetric (TGA) analyses. In the DSC analysis of the polyethylene material with only 4.5 mol% incorporation of **M1a**, a clear endothermic peak at $T_m = 107$ °C was detected (Fig. 3a, orange line). As the incorporation ratio of **M1** increased to 12 mol%, both the glass transition temperature ($T_g = 67$ °C) and melting point ($T_m = 125$ °C) were observed (Fig. 3a, red line). Interestingly, no discernible melting points were detected as the incorporation ratio of

M1 exceeded 18 mol%, possibly due to increasing incorporation ratio of polar groups undermine the crystalline region of the polyethylenes, resulting the transformation from crystalline to semi-crystalline and amorphous states. With an increase in the **M1** incorporation ratio from 18 to 26 mol%, the glass transition temperatures of the polyethylene materials rose from 61 to 104 °C, respectively (Fig. 3a, blue, green and purple lines). As illustrated in Fig. 3b, TGA curves for the polyethylene materials demonstrated high thermal decomposition temperatures ($T_d > 419$ °C), close to the commercially available HDPE. 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. To verify the chemical stability, **poly-1** was treated with trifluoroacetic acid and water (TFA/H₂O = 10:1) for 24 h. Based on the ¹H NMR analysis, there were no observed changes in the chemical shifts of the *N*-methyl group or the cyclobutane ring (Fig. 3c). Furthermore, there was no discernible alteration in the SEC traces of **poly-1** before and after acid treatment (Fig. 3d). These results suggest that, in addition to the backbone's high acid resistance, the cyclic imides groups remained relatively stable during acid treatment.

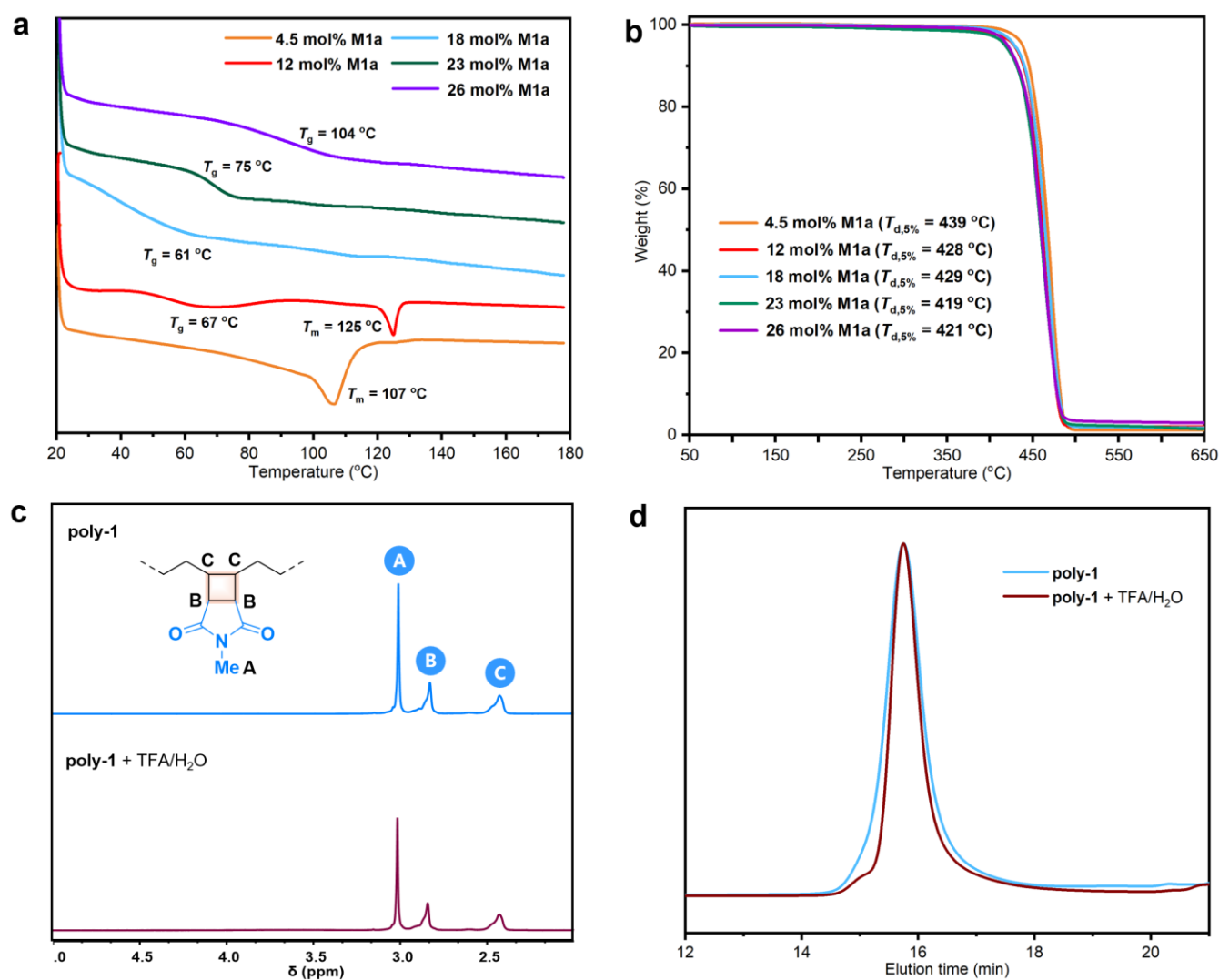


Figure 3. Properties and stability of the polyethylene materials. **a**, DSC traces of the polyethylene materials with varied **M1a** insertion ratios. **b**, TGA curves of the polyethylene materials with varied **M1a** insertion ratios. **c**, ¹H NMR spectra of **poly-1** (18 mol% **M1a**) and TFA treated **poly-1**. **d**, Comparison of the SEC traces of **poly-1** (18 mol% **M1a**) and TFA treated **poly-1**.

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 ($M_n = 80 \text{ kg}\cdot\text{mmol}^{-1}$ and $M_n = 40 \text{ kg}\cdot\text{mmol}^{-1}$), but the same mechanophore content (18 mol%), were activated by pulsed ultrasonication at 0°C (Fig. 4). Aliquots were taken at designated time intervals from the reaction solution for ^1H NMR and SEC analyses to monitor the mechanochemical activation process. The initial molecular weight of **poly-1** has significant effect on the mechanochemical activation efficiency. As shown in Fig. 4a, the cyclobutane ring opening ratio of the high molecular weight **poly-1** increased more rapidly than that of the low molecular weight **poly-1**. After 48 hours of ultrasonication, the cyclobutane ring opening ratios 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.⁴⁷ Concurrently with the cyclobutane ring opening, a noticeable reduction in polymer molecular weight was observed with increased ultrasonication time (Fig. 4b). Despite differing ring-opening ratios, both polymers with initial molecular weights of $M_n = 80 \text{ kg}\cdot\text{mmol}^{-1}$ and $M_n = 40 \text{ kg}\cdot\text{mmol}^{-1}$ reached an identical molecular weight of $35 \text{ kg}\cdot\text{mmol}^{-1}$ after 36 hours of ultrasonication. Since these activated polymers are approaching the limiting molecular weight (around $30 \text{ kg}\cdot\text{mmol}^{-1}$)^{25,46} via ultrasonication activation, both exhibited a slight molecular weight decrease to $32 \text{ kg}\cdot\text{mmol}^{-1}$ after an additional 12 hours of ultrasonication. Due to the poor solubility of polyethylene materials with low mechanophore content in THF, their mechanochemical activation through pulsed ultrasonication need to be performed in toluene. After 24 hours of ultrasonication at room temperature, 32% of cyclobutane ring opening was determined in the case of **poly-1** with 4.5 mol% **M1a** insertion ($M_n = 45 \text{ kg}\cdot\text{mmol}^{-1}$).

In the ^1H NMR spectra of the precipitated **poly-1S** (initial $M_n = 80 \text{ kg}\cdot\text{mmol}^{-1}$, 48 h), characteristic resonances of conjugated cyclic imide groups were identified at 7.00 ppm (m, **I**), 6.40 ppm (m, **J**), and 3.26 ppm (d, **G**) (Fig. 3c, **poly-1S**). 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 Supplementary Fig. 54). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (See Supplementary Fig. 34), the resonance of the carbonyl carbon was observed around 169.3 ppm (m). Notably, the sp^2 -carbons of the C=C double bonds appeared at 149.5 ppm and 123.8 ppm. Next, the degradability of the activated polymer was explored by treating it with a TFA/ H_2O (10:1) solution at room temperature for 24 hours. Following the removal of all volatiles, the reaction mixture underwent analysis via ^1H NMR and SEC. According to ^1H NMR analysis, characteristic signals of conjugated cyclic imide at 6.40 ppm (m, **J**) and 3.26 ppm (d, **G**) completely disappeared (See Supplementary Fig. 2). In contrast to **poly-1** and **poly-1S** (48 h), the SEC trace of hydrolyzed **poly-1S** (48 h) displayed a broad bimodal distribution (Fig. 4d). The low molecular weight peak, representing the main component, corresponded to the oligomers produced from hydrolysis. Meanwhile, the peak with high molecular weight was identified as the unactivated fraction of the copolymer, likely situated toward the ends of the unactivated polymer. Attempts were undertaken to characterize the degraded oligomers and unactivated fraction. In the crude ^1H NMR spectrum of the mixture (See supplementary Fig. 2), a clear resonance of carboxylic acid was observed at 12.08 ppm (bs). Moreover, multiple signals, corresponding to the olefinic and amide protons, appeared at 7.90-6.40 ppm. In the HR-ESI-MS spectra (See supplementary Tables 3 and 4), unsaturated bifunctional small molecules including diacids, acid-amides and diamides were detected. Only a very small amount of polymer was reprecipitated from the reaction mixture by methanol (11% yield). In its ^1H NMR spectrum of the precipitated polymer (Fig. 4c, **poly-1'**), only signals corresponding to the unactivated cyclobutane-fused succinimide groups were observed. Overall, the combination of ultrasonication activation and acid hydrolysis

facilitated the efficient chemical recycling of high molecular weight polyethylene materials into bifunctional small molecules.

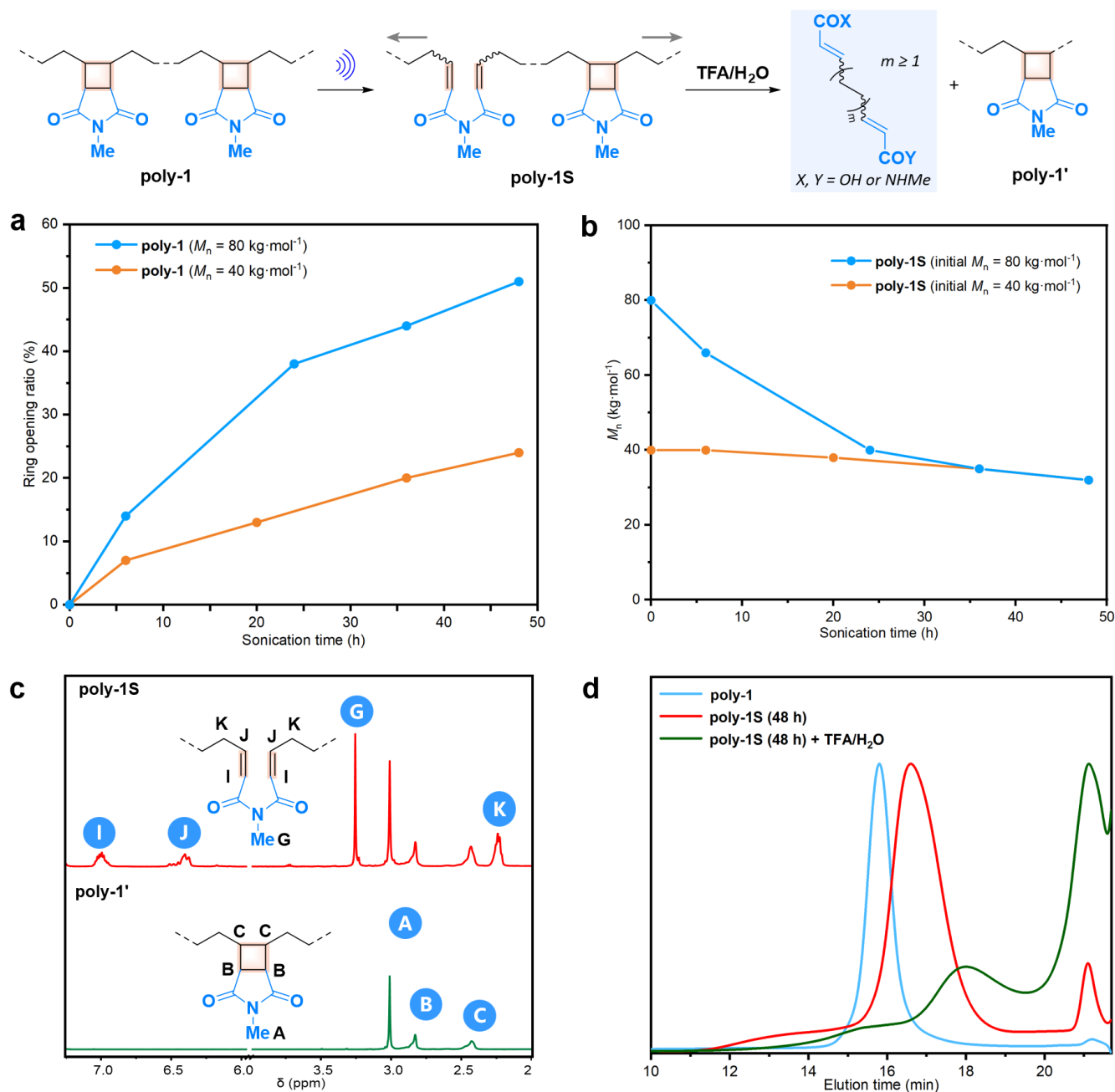


Figure 4. Mechanochemical activation and degradation of poly-1. **a**, Ring-opening ratios of **poly-1s** over ultrasonication time. **b**, Molecular weights (M_n) of **poly-1S**s over ultrasonication time. **d**, ¹H NMR spectra of precipitated **poly-1S** (48 h) and **poly-1'**. **c**, Comparison of the SEC traces of **poly-1** ($M_n = 80 \text{ kg} \cdot \text{mol}^{-1}$), **poly-1S** (48 h) and hydrolyzed **poly-1S** (48 h).

We have reported for the first time on the preparation of polar polyethylene materials bearing in-chain mechanophores. Using palladium catalysis, several cyclobutane-fused mechanophores were successfully incorporated with varied insertion ratios (4.5-26 mol%) via direct coordination/insertion copolymerization of ethylene with cyclobutene-fused comonomers. The obtained polyethylene materials with in-chain mechanophores exhibits both high thermal stability and acid resistance. All saturated hydrocarbon chains of the copolymer ensure the backbone stability of polyethylene materials during storage and usage, while degradable conjugated unsaturated acyclic imides will be introduced into the main

polymer chain upon mechanochemical activation by ultrasonification. Subsequent hydrolysis of the sonicated copolymers under acidic conditions enables chemical recycling of the high molecular weight polyethylene material into bifunctional small molecules. Such polyethylene materials possess an ideal combination of stability and accessible degradability.

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Data availability

All the other data supporting the findings of this study are available within the article and its Supplementary Information.

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Author Contributions

S.T. and Y.Z. contributed to the conception and design of the experiments. X.Z. and Y.Z. performed the polymer synthesis and characterization. X.Z. and M.C. conducted the polymer mechanochemical activation and degradation. S.T. and Y.Z. co-wrote the manuscript. All authors participated in discussion and S.T. directed the project.

Competing financial interests

The authors declare no competing financial interests.