

Catalytic Chemical Recycling of Post-Consumer Polyethylene

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Cite This: *J. Am. Chem. Soc.* 2022, 144, 23280–23285



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ABSTRACT: Among commercial plastics, polyolefins are the most widely produced worldwide but have limited recyclability. Here, we report a chemical recycling route for the conversion of post-consumer high-density polyethylene (HDPE) into telechelic macromonomers suitable for circular reprocessing. Unsaturation was introduced into HDPE by catalytic dehydrogenation using an Ir-POCOP catalyst without an alkene acceptor. Cross-metathesis with 2-hydroxyethyl acrylate followed by hydrogenation transformed the partially unsaturated HDPE into telechelic macromonomers. The direct repolymerization of the macromonomers gave a brittle material due to the low overall weight-average molecular weight. Aminolysis of telechelic macromonomers with a small amount of diethanolamine increased the overall functionality. The resulting macromonomers were repolymerized through transesterification to generate a polymer with comparable mechanical properties to the starting post-consumer HDPE waste. Depolymerization of the repolymerized material catalyzed by an organic base regenerated the telechelic macromonomers, thereby allowing waste polyethylene materials to enter a chemical recycling pathway.

The production of polyolefins has increased dramatically in the last few decades due to their low cost, chemical robustness, thermal stability, and high mechanical strength.¹ These features make polyolefins ubiquitous in single-use applications, such as packaging films and containers.^{1,2} However, most post-consumer plastic waste is incinerated or ends up in landfills or the environment, instead of being reused or recycled.^{3–7} Therefore, considerable efforts have focused on developing technologies such as pyrolysis, gasification, and hydrogenolysis to convert waste polyolefins to monomers or chemical feedstocks.^{8–15} The C–C bond cleavage of polyethylene is an energy intensive process that is industrially accomplished through noncatalytic pyrolysis and gasification at very high temperatures (>500 °C) but gives rise to an uncontrolled distribution of products.^{9–11} Catalytic hydrogenolysis cleaves polyolefins into shorter hydrocarbons that can be utilized as chemical feedstocks and fuels.^{12–14} An alternative approach is outlined in Figure 1, which addresses the end-of-life dilemma of plastics by transforming post-consumer waste into a new polymer with chemical recyclability and biodegradability, while retaining its original material properties.

In particular, HDPE is one of the most used commodity plastics with excellent thermal and mechanical properties, but in 2018, only 9% of HDPE was recycled.^{1,7,9} Fully reprocessed HDPE from mechanical recycling methods rarely makes its way back to its original intended applications, since degradation of material properties and contamination occurs.^{16,17} A more controllable approach to chemically recycle polyolefins is through the installation of cleavable linkages along the polymer backbone that allow selective deconstruction. In contrast to polyolefins, poly(ethylene terephthalate) (PET) can be chemically recycled due to the presence of ester functionality in the backbone.^{18,19} Facile

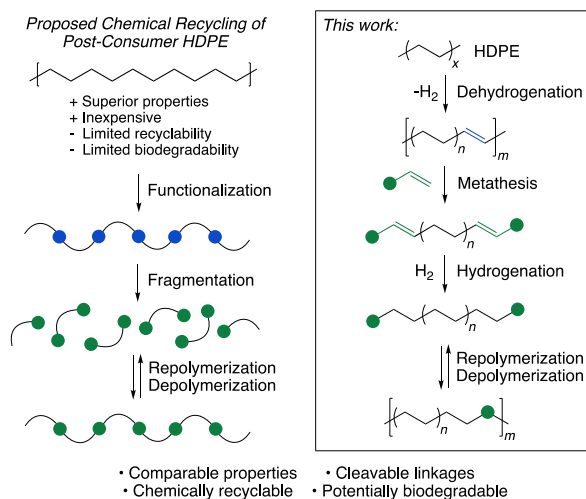
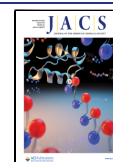


Figure 1. Proposed chemical recycling of waste polyolefins and this work on transformation of post-consumer waste polyethylene into chemically recyclable materials.

glycolysis at these ester linkages leads to the formation of monomers, dimers, and oligomers which after purification can be recombined through esterification to regenerate commercial-grade PET.^{17–19} We envision that the cleavage of reactive linkages incorporated into HDPE would result in telechelic

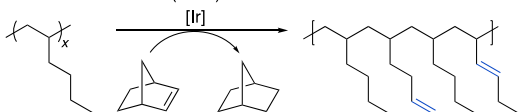
Received: November 9, 2022
Published: December 16, 2022



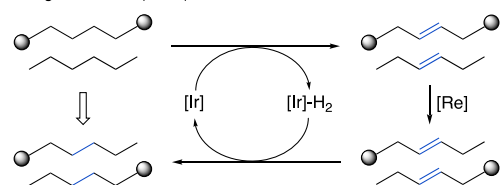
polyethylene segments capable of repolymerization. This would allow the mechanical properties to be controlled by tuning the spacing between linkages.^{20,21} Note that polyethylene with polar functional groups and molecular weights below 5 kDa has been shown as biodegradable, under specific conditions.^{22–25}

Incorporating cleavable linkages into HDPE can be achieved by introducing tunable amounts of unsaturation. Subsequent C=C bond cleavage via oxidation, metathesis, and other approaches would produce telechelic polymers.^{21,26–44} We have previously demonstrated the copolymerization of propylene and butadiene to incorporate internal C=C bonds into the polyolefin backbone and subsequently converted the copolymer into a chemically recyclable ester-linked polypropylene.⁴⁵ The catalytic transfer dehydrogenation of polyolefins was reported by Goldman, Coates and co-workers using iridium pincer catalysts and norbornene as a sacrificial hydrogen acceptor (Figure 2a).⁴⁶ Huang, Guan and

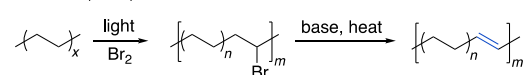
a. Goldman and Coates (2005):



b. Huang and Guan (2016):



c. Abu-Omar (2021):



d. Hartwig, Guironnet and Scott (2022):

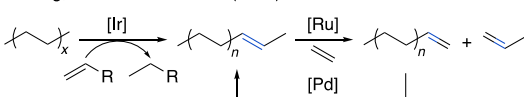


Figure 2. Previous advances on introducing unsaturation into saturated polyolefins.

co-workers utilized catalytic dehydrogenation coupled with olefin metathesis and then hydrogenation to degrade waste polyethylene into light hydrocarbons (Figure 2b).⁴⁷ Abu-Omar and co-workers incorporated unsaturation into commercial polyethylene via stoichiometric bromination and dehydrobromination, followed by ethenolysis to form low-molecular-weight divinyl-terminated polyethylene as value-added products (Figure 2c).⁴⁸ Recently, Hartwig and co-workers, and Guironnet, Scott and co-workers catalytically deconstructed polyethylene through transfer dehydrogenation, isomerization, and metathesis into propylene (Figure 2d).^{49,50} In this work, dehydrogenated HDPE was used to develop recyclable-by-design polyethylene-like materials from hard-to-recycle waste HDPE (Figure 1).

Partial unsaturation of polyethylene from post-consumer waste was achieved under hydrogen acceptorless dehydrogenation conditions. This method is an atom-economic alternative to catalytic transfer dehydrogenation in solution-phase chemistry.^{51–54} The iridium POCOP ethylene complex (**1**,

POCOP-H: 1,3,5-[(^tBu₂PO)₃C₆H₃) was selected as the dehydrogenation catalyst due to its known ability to dehydrogenate alkanes in solution.^{47,55} The Ir-POCOP species demonstrates a preference for dehydrogenation at the internal position of *n*-alkanes.⁵⁶ Additionally, Ir pincer complexes are also known to isomerize terminal olefins into internal olefins.^{57,58} A post-consumer water jug (HDPE) was used without any treatment. Shredded HDPE and catalyst **1** in a minimum amount of toluene were combined and heated at 200 °C under vacuum to remove the hydrogen generated (Table 1).

Table 1. Dehydrogenation of Post-Consumer HDPE^a

Entry	<i>t</i> (h)	Internal Olefin (mol %) ^b	<i>n</i> ^b	<i>M</i> _n (kDa) ^c	<i>M</i> _w (kDa) ^c	<i>Đ</i> ^c
HDPE	0	0	–	18.1	120	6.6
DH1	24	0.49	203	18.0	113	6.3
DH2	48	0.57	173	18.2	115	6.3
DH3	72	0.69	145	17.8	122	6.9
DH4	96	0.79	125	17.7	123	7.0

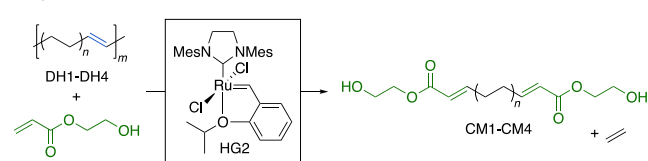
^aConditions: 3.30 × 10^{−4} equiv of **1** relative to ethylene units, vacuum, 200 °C. ^bDetermined by ¹H NMR spectroscopy; see S1 for calculations. ^cDetermined by gel permeation chromatography (GPC) in 1,2,4-C₆H₃Cl₃ at 150 °C versus polyethylene standards.

After 24 h, dehydrogenated HDPE (DH1) resulted in 0.49 mol % internal olefins (5.43 and 5.48 ppm, *cis* and *trans* isomers, respectively) as determined by ¹H NMR spectroscopy. GPC showed no significant change in molecular weights for HDPE and DH1 (*M*_n: 18.1 kDa, *M*_w: 120 kDa and *M*_n: 18.0 kDa, *M*_w: 113 kDa, Table 1 and Figure S40) indicating that no C–C bond cleavage occurred. The mole percent of internal olefins produced increased linearly as the reaction time increased (Table 1). There was also no chain scission observed for DH2–DH4. In addition, acceptorless dehydrogenation of polyethylene can be applied to different molecular weights and polydispersities. The reactions of two polyethylene standards PE-std1 (*M*_n: 11.6 kDa, *M*_w: 30.7 kDa) and PE-std2 (*M*_n: 97.7 kDa, *M*_w: 210 kDa) with **1** produced 0.76 mol % and 0.46 mol % internal olefins, respectively (Figures S30, S34) at 72 h. Given one of the most common contaminants of HDPE is isotactic polypropylene (*i*PP), the dehydrogenation of HDPE in the presence of 10 wt % of this impurity was examined. After 72 h, dehydrogenation of an *i*PP contaminated HDPE sample resulted in 0.68 mol % internal olefins (Figure S38), almost identical to the dehydrogenation of pure HDPE (Table 1, entry DH3).

To obtain repolymerizable segments, the dehydrogenated polyethylene (DH1–DH4, Table 1) was subjected to cross-metathesis with excess 2-hydroxyethyl acrylate in the presence of 1 mol % Hoveyda–Grubbs II (HG2) catalyst.⁵⁹ After 6 h, the reactions went to completion, as the internal olefin signals at 5.4–5.5 ppm disappeared and new peaks were observed around 3.88, 4.32, 5.91, and 7.05 ppm, assigned to the corresponding 2-hydroxyethyl acrylate chain ends. The *M*_n of the telechelic macromonomer ranged from 2.6 kDa to 4.3 kDa for CM1–CM4 (Table 2). By tuning the degree of

dehydrogenation, telechelic macromonomers with different molecular weights can be obtained.

Table 2. Cross-Metathesis of Dehydrogenated HDPE (DH-PE)^a



Entry	DH-PE	M_n (kDa) ^b	M_w (kDa) ^b	\mathcal{D}^b	T_m (°C) ^c
CM1	DH1	4.3	9.5	2.2	132
CM2	DH2	3.8	8.1	2.1	128
CM3	DH3	3.5	7.7	2.2	127
CM4	DH4	2.6	5.6	2.2	126

^aConditions: 10 equiv of 2-hydroxyethyl acrylate, 1 mol % Hoveyda–Grubbs II (HG2) catalyst, toluene, 100 °C, 6 h. ^bDetermined by GPC in 1,2,4- $C_6H_3Cl_3$ at 150 °C versus polyethylene standards. ^cDetermined by differential scanning calorimetry (DSC).

Telechelic macromonomer **CM3** (M_n : 3.5 kDa and M_w : 7.7 kDa) was chosen for chemical recycling of waste polyethylene, based on previous reports that low molecular weight polyethylene can be potentially biodegradable. **CM3** was hydrogenated to remove C=C bonds to prevent cross-linking at the acrylate unsaturation.⁴⁵ The hydrogenation was performed using 1 mol % of Wilkinson's catalyst ($RhCl(PPh_3)_3$) and minimal toluene at 140 °C and 48 atm H_2 for 6 h.⁶⁰ The alkene signals around 5.91 and 7.05 ppm disappeared, indicating complete hydrogenation to generate telechelic macromonomer **P1** (Figure 3). The molecular weights of **P1**

(M_n : 3.5 kDa and M_w : 7.9 kDa) remained relatively unchanged compared to **CM3** (M_n : 3.5 kDa and M_w : 7.7 kDa). Less than 5% repolymerization was observed after hydrogenation, indicated by the signal at 4.32 ppm.

The repolymerization of **P1** was catalyzed by 1 mol % $Ti(OBu)_4$ under vacuum at 180 °C to remove ethylene glycol produced.⁶¹ The 1H NMR spectrum of repolymerized product **RP1** exhibited a signal at 4.32 ppm for the ester-linkage along with the disappearance of the hydroxyethyl moiety (Figure S21) and had an M_n of 16 kDa and M_w of 33 kDa. The melting temperatures of the products for each transformation were monitored by DSC and remained between 125 and 132 °C (Figures S49, S57, S59, S60), which are comparable with the T_m of **HDPE** (130 °C). The uniaxial elongation experiment performed on the repolymerized material **RP1** showed poor tensile behavior (Figure 4, inset). The initial **HDPE** and **RP1** had similar M_n , but the M_w of **RP1** (33 kDa) was significantly lower than the M_w of waste polyethylene (120 kDa). The statistical basis of this phenomenon was recently described by Johnson and co-workers for polystyrene. Due to the presence of monofunctional macromonomers formed from the chain ends, the dispersity of the repolymerized polymer is dependent on the distribution of the macromonomers rather than the starting polymer.⁶²

A polyethylene sample with a higher fraction of long polymer chains tends to have higher stress and greater chain alignment, leading to enhanced toughness and elongation.^{63,64} In order to increase the M_w and thus improve the mechanical properties of the chemically recyclable material, a trifunctional cross-linker was used to provide a controlled amount of branching in the repolymerized material (Figure 3a). Therefore, **P1** was subjected to 10 equiv of diethanolamine to form a

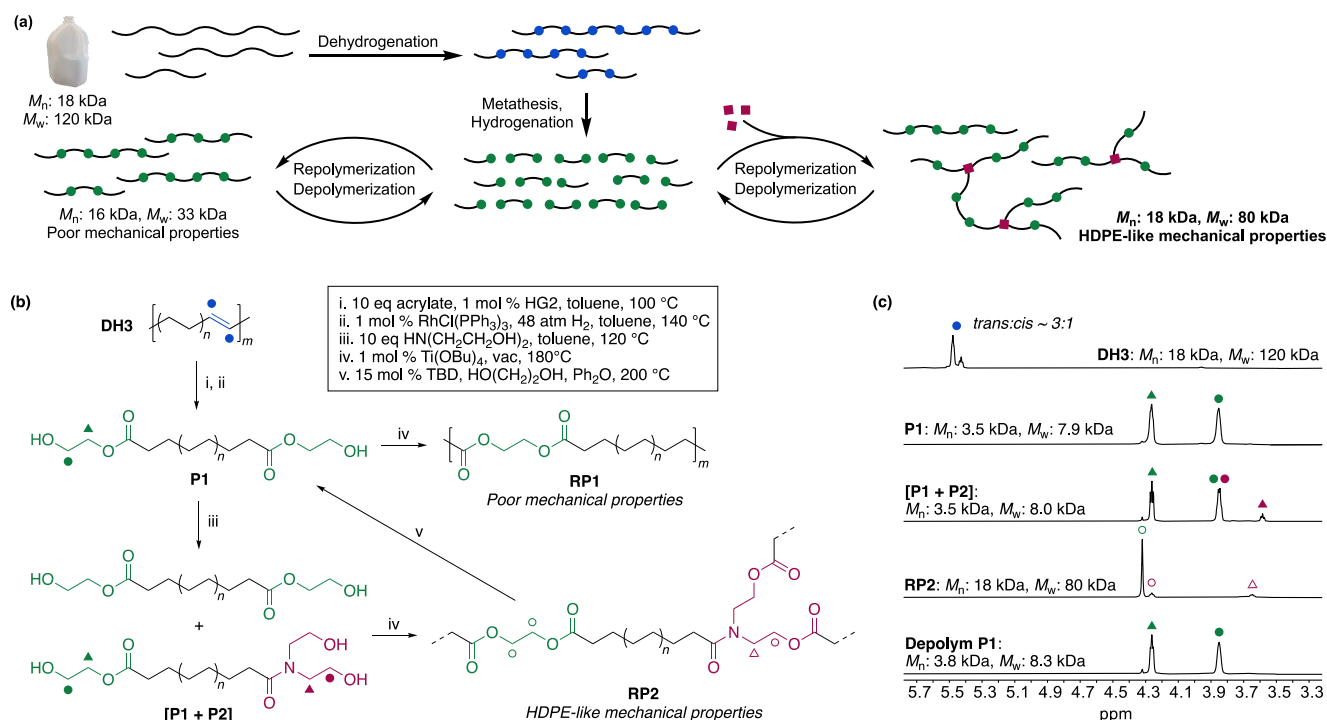


Figure 3. (a) Overall schematics of chemical recycling of post-consumer waste HDPE into a chemically recyclable material with good mechanical properties. (b) Reaction conditions and key intermediates of chemical recycling process. See Supporting Information for detailed experimental conditions. (c) 1H NMR spectra and GPC results of key intermediates to show the chemical transformations between dehydrogenated HDPE, macromonomers, and repolymerized material.

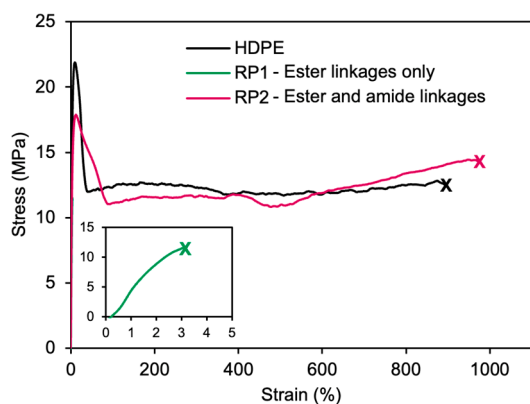


Figure 4. Mechanical properties of post-consumer waste **HDPE**, **RP1** (ester linkages; $M_w = 33$ kDa), and **RP2** (ester and amide linkages; $M_w = 80$ kDa).

mixture of macromonomers ($[P1 + P2]$, 8 mol % amide incorporation relative to overall functionalities, Figure 3b). The signals around 3.85 and 4.26 ppm were attributed to the diethanolamine functionality (Figure 3c). $[P1 + P2]$ was then polymerized to generate **RP2** (Figure 3b). The resulting material (M_n : 18.2 kDa, M_w : 80.3 kDa, T_m : 132 °C) exhibited a yield strength of 18 MPa and a strain at break of 970%, comparable to starting post-consumer waste **HDPE** (Figure 4). Depolymerization of **RP2** back to **Depolym P1** was achieved in the presence of a catalytic amount of triazabicyclodecene (TBD) and an excess of ethylene glycol, with conversion greater than 95%.^{65,66} This allows the chemical recycling of post-consumer HDPE waste to a polyethylene-like material with comparable thermal and mechanical properties.

In conclusion, we have shown that the Ir-POCOP pincer catalyst, **1**, can introduce unsaturation into polyethylene chains from post-consumer HDPE waste under hydrogen acceptorless conditions at low catalyst loadings. The partially dehydrogenated polyethylene provides access to novel polymer-to-polymer transformations. The dehydrogenated HDPE waste undergoes cross-metathesis to form macromonomers with molecular weights dependent on the degree of unsaturation. After hydrogenation and partial aminolysis, these macromonomers may be polymerized to yield a material with comparable mechanical and thermal properties to HDPE. We have demonstrated that incorporation of main-chain ester functionalities in polyethylene enables the chemical recycling of waste polyethylene and envision that this methodology will offer a pathway to functionalize and recycle waste polyolefin materials. Future work will focus on developing more scalable catalysts for hydrocarbon dehydrogenation, applying this strategy to other commodity polyolefins, and studying the chemical, physical, and mechanical properties of these ester-linked polymers, along with their potential biodegradability.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c11949>.

General information, materials, experimental details, NMR spectra, GPC chromatograms, DSC thermograms, tensile test data, and additional supporting data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported through a subcontract from the Ames Laboratory with funding from the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-07CH11358 as part of the Energy Frontier Research Center titled the Institute for Cooperative Upcycling of Plastics (iCOUP). Work at Argonne National Laboratory was supported as part of the Institute for Cooperative Upcycling of Plastics (iCOUP), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. Argonne National Laboratory is operated by UChicago Argonne LLC under Contract DE-AC-02-06CH11357 for the United States Department of Energy. This work made use of the NMR Facility at Cornell University, supported by the NSF under Award CHE-1531632. The authors thank Dr. Zhiyao Zhou for helpful discussions.

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