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Polymerization *Hot Paper*

Polyethylene Incorporating Diels–Alder Comonomers: A "Trojan Horse" Strategy for Chemically Recyclable Polyolefins

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Abstract: Polyolefins with periodic unsaturation in the backbone chain are sought after for synthesizing chemically recyclable polymers or telechelic polyolefin macromonomers. Here we introduce a bottom-up synthesis of unsaturated high-density polyethylene (HDPE) via copolymerization of ethylene with dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-3,5-dicarboxylate followed by post-polymerization retro-Diels–Alder to unveil hidden double bonds in the polymer backbone. The incorporation of this "Trojan Horse" comonomer was varied and a series of unsaturated HDPE polymers with block lengths of 1.2, 1.9, and 3.5 kDa between double bonds was synthesized. Cross metathesis of unsaturated HDPE samples with 2-hydroxyethyl acrylate yielded telechelic ester terminated PE macromonomers suitable for the preparation of ester-linked PE. These materials were depolymerized and repolymerized, making them suitable candidates for chemical recycling. The ester-linked PE displayed thermal and mechanical properties comparable to commercial HDPE.

Polyolefins are strong, lightweight, versatile, and inexpensive, making them ubiquitous in modern life. The high mechanical strength and chemical stability that make polyolefins so desirable have negative consequences when these materials are landfilled or inevitably leaked into the environment.[1–4] Relying on mechanical recycling of polyolefins as an end-of-life solution is problematic because waste arrives at recycling plants as a contaminated mixture of various types of polyolefins and unknown composition with respect to colorants, plasticizers, and other additives.[1] The result is a low-value recycled product with poor thermal and mechanical properties.[1] A more sustainable solution is to establish a circular economy based on polyolefins that have been designed to undergo chemical recycling and are capable of biodegradation should they end up in the environment.[2–4]

It is difficult to implement lifetime circularity for polyolefin materials because their high stability prohibits depolymerization back to monomer. Various solutions to the end-of-life problem have been proposed including energy recovery, recycling to alternative feedstocks, and more recently, recycle-by-design techniques.[3,4] To chemically recycle a polyolefin, cleavable functional groups must be built into the polymer chain to allow it to be broken into smaller pieces[5–20] that can be purified and repolymerized to yield recycled materials with properties similar to the original material.[21–24] Long-spaced aliphatic polyesters and polyamides have been explored as degradable polyethylene (PE) mimics[10,13,18,20,21,25] and it was observed that the longer the methylene chain spacing between functional groups, the more similar the material's thermal and mechanical properties were to PE.[26]

The inclusion of a small amount of unsaturation dispersed within a polyolefin chain gives sites at which the backbone can be cleaved or further functionalized by methods such as olefin metathesis.[27,23,24] Unsaturated polyolefins can be made via bottom-up syntheses including acyclic diene metathesis polymerization (ADMET),[28–31] ring-opening metathesis polymerization (ROMP),[32–34] and copolymerization of α-olefins and conjugated dienes.[35–38] Alternatively, top-down syntheses can be used such as dehydrogenation[39] and sequential bromination-dehydrobromination (Figure 1).[27]

We envisioned introducing unsaturation into polyolefins via a thermally triggered reaction to reveal small amounts of masked double bonds. This might be achieved in a bottom-up synthesis by copolymerization of ethylene with small amounts of a "Trojan Horse" monomer that would undergo a post-polymerization retro-Diels–Alder (rDA) reaction at

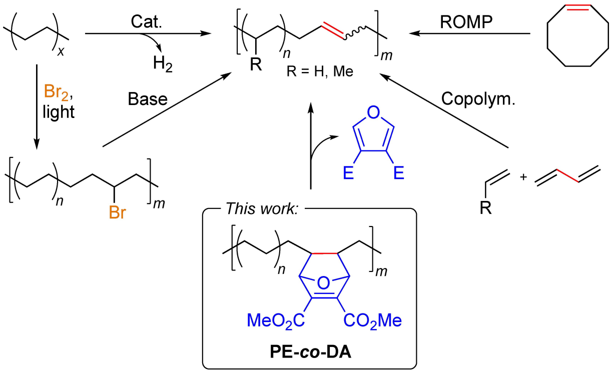

Figure 1. Strategies to introduce unsaturation into the backbones of polyolefins.

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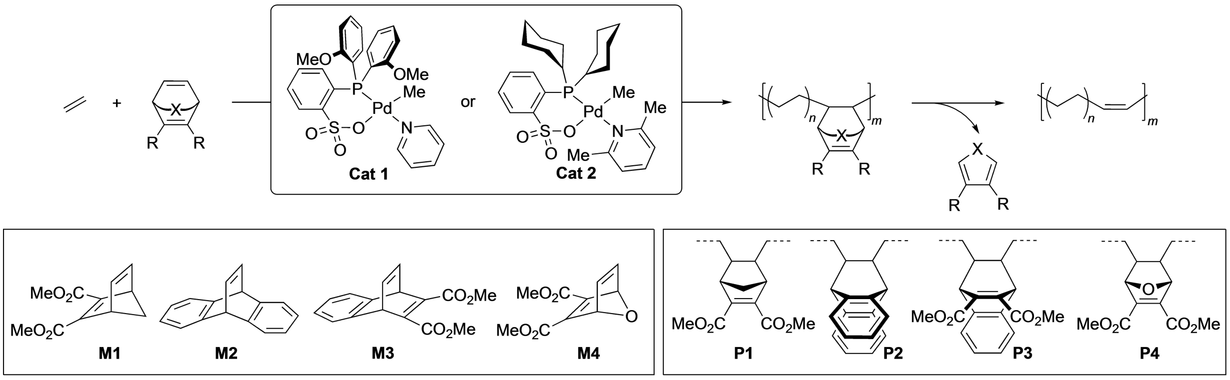


Scheme 1. Copolymerization of **M1–M4** with ethylene to produce **P1–P4** using palladium phosphine sulfonate catalysts **Cat 1** or **Cat 2**.

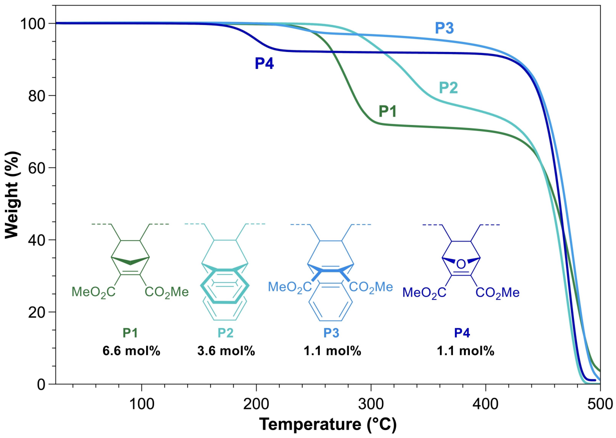


Figure 2. TGA curves of polymers **P1–P4** indicating a lower retro-Diels–Alder temperature for **P4**.

elevated temperatures. In the 1980's, Feast and Winter reported a two-stage synthesis of polyacetylene via ROMP to a soluble precursor polymer followed by rDA to yield benzene byproducts and polyacetylene.[40–42] Novak and co-workers developed a simpler route to polyacetylene homopolymers and copolymers using Pd-catalyzed 1,2-olefin-insertion polymerization of an oxa-norbornadiene-based monomer followed by rDA.[43–45] Nozaki and co-workers copolymerized ethylene and [2.2.1]oxabicyclic alkene-based monomers, followed by dehydration, to obtain *o*-arylene units in the polymer main chain.[46,47] We combined these strategies by polymerizing ethylene in the presence of a Diels–Alder-functional comonomer to yield polyethylene with masked double bonds (Scheme 1).

This method enables tunable spacing of double bonds in the polymer backbone and these double bonds provide sites for further functionalization. For example, cross metathesis has been used to cleave double-bond containing polypropylene into smaller segments with controllable end groups enabling telechelic properties.[23] We applied this strategy to generate high-density polyethylene with an ethylene glycol ester linkage at roughly equal spacing along the polymer backbone and studied the effects of ester spacing on the thermal and mechanical properties of the polyethylene.

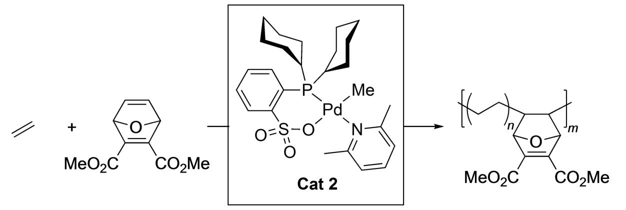
Our system required a suitable norbornene-like monomer that could undergo coordination-insertion copolymerization with ethylene to yield a copolymer that would undergo rDA at a low enough temperature to avoid undesired side reactions.[48] We began by evaluating monomers **M1–M4** for copolymerization with ethylene to produce **P1–P4** using palladium phosphine-sulfonate catalysts (Scheme 1). **Cat 1** and **Cat 2** were used because they are known to undergo insertion copolymerization of norbornene and ethylene and tolerate oxygen-containing functionality (Scheme 1, Table S1).[46,47,49–54]

Thermogravimetric analysis (TGA) was used to estimate the rDA temperatures for polymers **P1–P4** (Figure 2). The observed mass loss by TGA matches with the theoretical mass of rDA byproducts calculated for each polymer based on its comonomer % incorporation calculated using ^{1}H NMR spectroscopy. **P1–P3** exhibited rDA temperatures above 250 °C and attempts at conducting rDA of bulk polymer samples above 180 °C produced insoluble products, indicative of cross-linking or decomposition. Gratifyingly, TGA of **P4** indicated clean rDA at 160 °C (Figure 2).

Using **Cat 2**, we were able to copolymerize ethylene and **M4** to give low to moderate molecular weights and incorporation levels of <5 mol %. We observed that the yield of **P4** could be increased significantly by running the polymerization at a high ethylene pressure (27.2 atm) and the molecular weight of **P4** was highest at a temperature of 30 °C (Table S3). With optimized copolymerization conditions in hand, we targeted a series of **P4** copolymers with segments of HDPE of 1.0, 2.0, and 3.0 kDa in between **M4** units which corresponds to 2.8, 1.4, and 0.9 mol % incorporation of **M4**. We varied the comonomer feed concentration to tune the PE segment lengths in **P4** (Table 1).

Preparative scale rDA reactions were performed by heating **P4** at 165 °C in Ph_2O for 5 hours. $NaHCO_3$ (4 wt %) was added to prevent an undesired dehydration side reaction that was originally observed.[46,47] ^{1}H NMR analysis of the product, **P5**, revealed the presence of cis-unsaturated PE (5.41 ppm). **P4a**, **P4b**, and **P4c**, with PE segments of 1.2, 1.9, and 3.5 kDa, respectively, were converted to **P5a**, **P5b**, and **P5c** with high conversion by NMR and quantitative product recovery. The rDA reaction can also be performed by melt processing **P4** in the absence of solvent at 180 °C for

Table 1: Synthesis of PE-*co*-DA copolymers **P4a**–**P4c** with tunable PE block lengths.



Entry [a]	[M4] (mM)	Yield (g)	mol (%) [b]	PE Block Length (kDa) [b]	M_n (kDa) [c]	$Đ$ [c]	T_m (°C) [d]
P4a	65.3	1.87	2.24	1.2	28.9	2.2	117
P4b	50.0	2.34	1.48	1.9	28.7	2.3	123
P4c	46.3	2.33	0.79	3.5	28.7	2.4	128

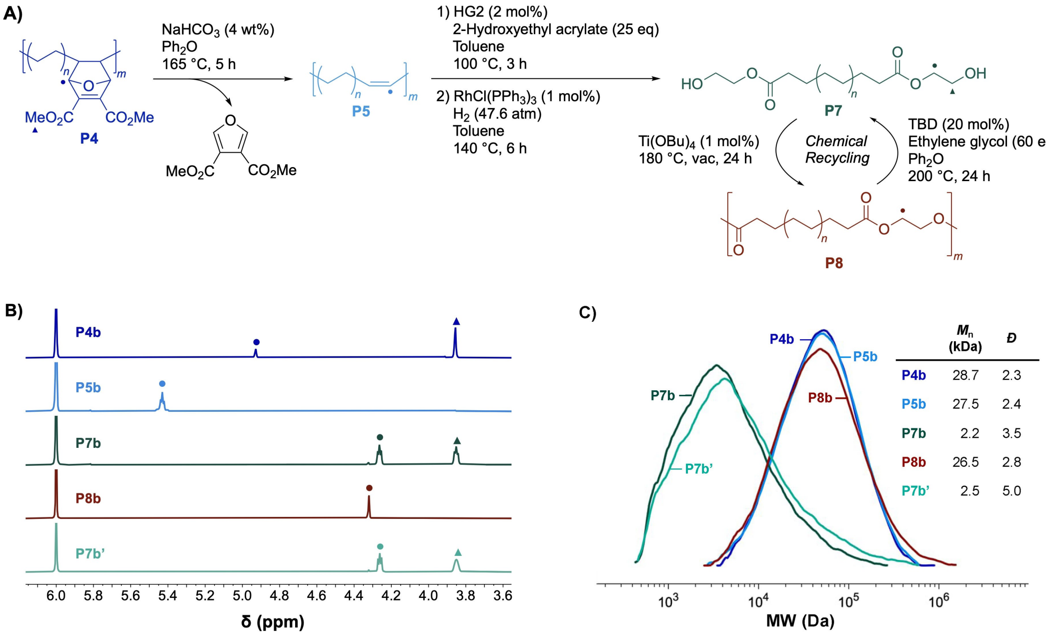
[a] Conditions: 43 μmol **Cat 2**, 27.2 atm ethylene, 100 mL toluene, 30 °C, 24 h. [b] Molar incorporation of **M4** determined by ^{1}H NMR at 130 °C in 1,1,2,2-tetrachloroethane-d_2. [c] Determined by gel permeation chromatography (GPC) at 150 °C in 1,2,4-trichlorobenzene versus PE standards. [d] Determined by differential scanning calorimetry (DSC) using the second heating cycle.

30 minutes (Figure S48a). The rDA furan byproduct remains in the unsaturated polymer and can be carried over to the following step without reacting with the alkene functionality and is removed during polymer isolation and purification (Figure S48b). This method requires no solvent or $NaHCO_3$ additive and is convenient for bulk processing.

Next, we sought to investigate the relationship between material properties and polyolefin segment length in chemically recyclable ester-linked polyethylene. **P5a**–**P5c** were first subjected to cross metathesis with 2 mol % Hoveyda-Grubbs II (HG2)[55] and an excess of 2-hydroxyethyl acrylate at 100 °C to produce telechelic 2-hydroxyethyl acrylate-terminated PE macromonomers **P6a**–**P6c**. Hydrogenation of **P6a**–**P6c** with $RhCl(PPh_3)_3$ and 47.6 atm hydrogen at 140 °C yielded **P7a**–**P7c** (Figure 3A).[56] **P7a**–**P7c** were repolymerized via $Ti(OBu)_4$-catalyzed step growth polymerization to generate **P8a**–**P8c**.[57] GPC and ^{1}H NMR were used to monitor the intermediates. The conversion of **P4** to **P5** results in the appearance of an internal olefin signal at 5.41 ppm and minimal change in the molecular weight. After cross metathesis and hydrogenation, this olefin signal disappears and is replaced with signals at 3.85 and 4.26 ppm indicating complete conversion to ester-capped **P7**. GPC analysis of **P7a**–**P7c** indicated M_n values matching the expected PE segment lengths estimated in **P4** and **P5** using the **M4** mol % incorporation calculated by ^{1}H NMR spectroscopy and assuming random incorporation of **M4** (Figure 3C). Upon polymerization to **P8**, an increase in molecular weight back to the original value for **P4** and **P5** is observed.

To demonstrate the chemical recyclability of our ester-containing polyethylene, **P8** was depolymerized using triazabicyclodecene (TBD)[58] and an excess of ethylene glycol to regenerate **P7**. This recycled **P7**, or **P7′**, was polymerized back to **P8′** using the original conditions.

The thermal and mechanical properties of **P8a**–**P8c** were studied by TGA, DSC, and uniaxial tensile elongation and compared to commercial HDPE. **P8a**, **P8b**, and **P8c** were observed to have T_m values of 127.4, 130.6, and 133.9 °C, respectively, and ΔH_m values of 150.7, 120.6, and 110.4 J g^{-1}, respectively (our commercial HDPE reference has a T_m of 136.7 °C and a ΔH_m of 200.4 J g^{-1}). We observe an increase in the T_m correlating with a decrease in the number of ester groups. However, the effect of these ester



	M_n (kDa)	$Đ$
P4b	28.7	2.3
P5b	27.5	2.4
P7b	2.2	3.5
P8b	26.5	2.8
P7b'	2.5	5.0

Figure 3. A) Multistep synthesis of ester-linked polyethylene **P8**. B) ^{1}H NMR spectra of polymer intermediates (**P4b**–**P7b**) and ester-linked polyethylene **P8b** (TCE-d_2 at 130 °C) and C) GPC chromatographs of polymer intermediates (**P4b**–**P7b**) and ester-linked polyethylene **P8b**.

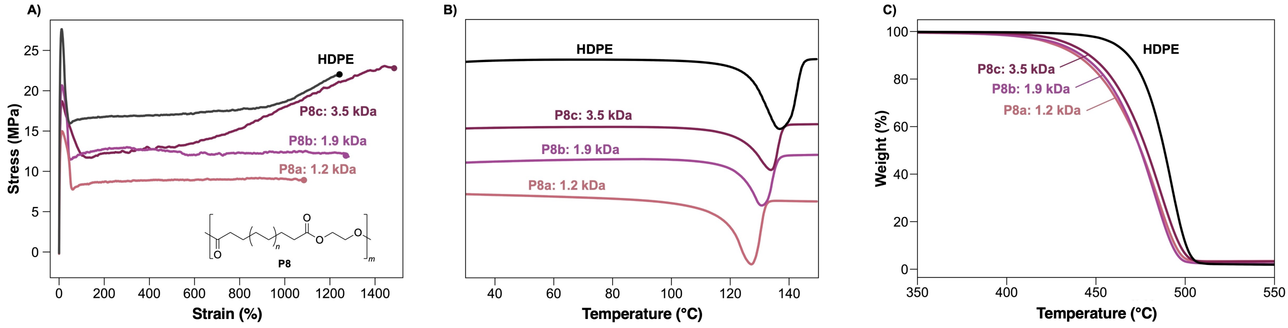


Figure 4. A) Representative stress-strain curves, B) DSC thermograms obtained from the second heating cycles, and C) TGA curves for commercial HDPE and **P8** with varying aliphatic spacings.

groups on the ΔH_m and on the crystallization of polyethylene is less straightforward but has been studied more closely in similar systems.[26] The strain at break, toughness, and thermal stability of these materials is comparable to HDPE (Figure 4, Table S4). Ester-linked polyethylenes, **P8a**–**P8c**, had a lower yield point and lower modulus values (stress) between the plastic deformation region than commercial HDPE. Improved toughness and an increase in the strain at break was observed with an increase in the polyethylene spacing. Furthermore, **P8c** with a spacing of 3.5 kDa demonstrated strain hardening, a phenomenon that is observed in semicrystalline polyolefins and results from the realignment of chains during continued applied force.[59,60]

In conclusion, we have introduced a strategy for obtaining polyethylene with periodic unsaturation in the polymer backbone using the sequential incorporation of a Diels–Alder comonomer followed by a thermally induced retro-Diels–Alder reaction. We were able to unmask the double bonds during melt processing conditions, suggesting scalability of the method. The spacing of double bonds in the PE was easily tuned by controlling the DA comonomer concentration during the polymerization and unsaturated PE with block lengths of 1.2, 1.9, and 3.5 kDa were synthesized. Finally, we demonstrated the synthesis of ester-linked HDPE with thermal and mechanical properties comparable to those of commercial HDPE, but one that can undergo depolymerization to macromonomers and subsequent repolymerization.

This strategy to generate HDPE with double bonds at controllable spacing provides a simple method to make telechelic HDPE chains with two reactive end groups and avoids the complications that often accompany the introduction of C=C bonds in polyolefin synthesis. Additionally, this method is expected to have a greater tolerance towards the incorporation of polar comonomers, enabling the synthesis of telechelic ethylene copolymers that may be inaccessible via the top-down synthetic approach of dehydrogenating HDPE. Finally, our method will provide a convenient route to make olefin block copolymers or to install a variety of different linkage types into the backbone of polyolefins.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

Keywords: Copolymerization · Degradable · Diels–Alder · Polyolefin · Protecting Groups

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