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Authors

Conk, Richard

Hanna, Steven

Shi, Jake

et al.

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Catalytic deconstruction of waste polyethylene with ethylene to form propylene

Richard J. Conk[1,2,†], **Steven Hanna**[1,2,†], **Jake X. Shi**[1,2], **Ji Yang**[2], **Nicodemo R. Ciccia**[1,2], **Liang Qi**[2,3], **Brandon J. Bloomer**[1,2], **Steffen Heuvel**[1], **Tyler Wills**[1], **Ji Su**[2], **Alexis T. Bell**[2,3], **John F. Hartwig**[1,2,*]

[1]Department of Chemistry, University of California, Berkeley, Berkeley, CA 94720, USA.

[2]Division of Chemical Sciences, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

[3]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, Berkeley, CA 94720, USA.

Abstract

The conversion of polyolefins to monomers would create a valuable carbon feedstock from the largest fraction of waste plastic. However, breakdown of the main chains in these polymers requires the cleavage of carbon–carbon bonds that tend to resist selective chemical transformations. Here, we report the production of propylene by partial dehydrogenation of polyethylene and tandem isomerizing ethenolysis of the desaturated chain. Dehydrogenation of high-density polyethylene with either an iridium-pincer complex or platinum/zinc supported on silica as catalysts yielded dehydrogenated material containing up to 3.2% internal olefins; the combination of a second-generation Hoveyda-Grubbs metathesis catalyst and $[PdP(^tBu)_3(\mu\text{-}Br)]_2$ as an isomerization catalyst selectively degraded this unsaturated polymer to propylene in yields exceeding 80%. These results show promise for the application of mild catalysis to deconstruct otherwise stable polyolefins.

The mechanical durability and chemical inertness of commercial plastics have led to their widespread use in everyday life, but these same properties make them difficult to recycle. Polyolefins, which account for 36% of global plastic production (1), are particularly

SUPPLEMENTARY MATERIALS
science.org/doi/10.1126/science.add1088
Figs. S1 to S23
Tables S1 to S7
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durable and inert, and only a small proportion of polyethylene (PE) waste is recovered by recycling (~14% in 2015) (2). Polyolefins are prepared with distinct molecular weights, molecular weight distributions, and microstructures for specific applications. Thus, a mixture of polyolefins individually produced for diverse applications lacks the properties of any one component; moreover, accumulated additives and contaminants, as well as chain scission induced by mechanical recycling, can degrade performance (2). Given the social, economic, and ecological threats from the accumulation of mixed polyolefin waste, innovative approaches to use this material as a carbon feedstock are needed (2–4).

Our group (5) and others (6–8) have been investigating catalytic chemistry that could occur with these polymers that contain only alkyl C–H and C–C bonds. Because the C–H bonds are more reactive than the C–C bonds, many efforts have focused on the introduction of functional groups onto the polymer chain to tune the properties of the plastic (5, 7, 8). More challenging are methods for "chemical recycling" of polyolefins, which entails the cleavage of polymer chains to regenerate monomers that can be repolymerized (6, 9). Whereas processes are well established to cleave the C–O bonds of polyesters (10), methods to cleave the alkyl C–C bonds of PE are more limited. Pyrolysis (4), catalytic cracking (11), hydrogenolysis (12–15), tandem hydrogenolysis-aromatization (16), and alkane metathesis (17, 18) have been reported for cleavage of PE chains. However, these processes form complex mixtures of hydrocarbons that are difficult to separate and have varying levels of utility (Fig. 1A). A process is needed by which PE undergoes depolymerization to form a single product for which the demand approaches the supply of PE waste. A method for the selective production of a commodity olefin from PE could thus render PE a valuable hydrocarbon feedstock.

We envisioned a cascade of catalytic processes that would introduce unsaturation to a PE chain and then unravel the chain to propylene. More specifically, dehydrogenation could be used to enable subsequent C–C bond cleavage by a combination of olefin metathesis and isomerization to form propylene (Fig. 1B) (19, 20). We show that the combination of dehydrogenation of high-molecular-weight PE having high density (HDPE) or low density (LDPE) and subsequent isomerizing ethenolysis (I/E) of the resulting crude polymer containing internal alkenes converts PE with commercially relevant molecular weights to propene in yields as high as 80%. This dehydrogenation and isomerizing ethenolysis (DIE) process was successfully tested on both postconsumer and virgin PE dehydrogenated by either homogeneous or heterogeneous catalysts.

To determine whether the conversion of PE to propylene could be achieved by a cascade comprising DIE, a reliable dehydrogenation reaction was first needed. The formation and isolation of desaturated PE by catalytic dehydrogenation has been reported only with materials of low molecular weight [number-average molecular weight (M_n) = 606] to ensure solubility (21, 22). Even a recently reported combination of stoichiometric halogenation and elimination was conducted with material with an M_n below 6.6 kDa (18). Many alkane dehydrogenation catalysts have been reported since these initial reports, and we investigated those containing phosphinous acid, bis(1,1-dimethylethyl)-, 5-methoxy-1,3-phenylene ester, which is a symmetric phosphinite pincer ligand containing an aryl backbone known as [tBu]POCOP, and related pincer ligands (23). Dehydrogenations of virgin HDPE

and LDPE with more commercially relevant molecular weights (M_n 26.1 kDa,   = 3.31 and M_n = 35.1 kDa,   = 6.54, respectively) catalyzed by **Ir-^{tBu}POCOP** with *tert*-butyl ethylene (TBE) as the hydrogen acceptor in *p*-xylene solvent yielded unsaturated polymer containing exclusively internal olefins (<0.1% terminal and up to 3.2% internal), along with small amounts (<0.75%) of alkylarenes (Fig. 2A), as determined by ^{1}H nuclear magnetic resonance spectroscopy. The isomerization of terminal olefins (which might be the kinetic product) to internal olefins is well known from dehydrogenation of liquid alkanes with this catalyst (24). The 3.2% of unsaturated units corresponds to a modest 7.6 turnovers but was limited by consumption of the acceptor and generated sufficient alkene units for the subsequent steps of the DIE process. Analysis of the molecular weight by gel-permeation chromatography revealed a decrease in M_n of the HDPE from 26.1 to 18.2 kDa upon dehydrogenation, but this change was not detrimental to our envisioned degradation to propylene.

To determine whether heterogeneous catalysts also could desaturate polyolefins, we investigated the dehydrogenation of PE with catalysts inspired by those in the Oleflex process of Honeywell UOP (formerly Universal Oil Products) for the dehydrogenation of long-chain paraffins (25). We tested the dehydrogenation of HDPE with established Pt/Sn (25) and a new type of heterogeneously supported Pt/Zn catalyst (26). Heating of the polymer melt over such catalysts under a flow of Ar at 350°C furnished unsaturated PE containing up to 0.6% olefins, along with ~0.25% arenes (Fig. 2B). Again, just a slight reduction in M_n was observed (from 26.1 to 21.7 kDa), and all of the olefin units were internal.

Having demonstrated the feasibility of the dehydrogenation of high-molecular-weight PE, we synthesized a series of dehydrogenated PEs with varying levels of unsaturation. To do so, we subjected laboratory-grade HDPE to dehydrogenation with Ir-^{tBu}POCOP and varying loadings of TBE as the sacrificial H_2 acceptor (see table S2 for full details). These reactions produced PE with degrees of unsaturation ranging from 0.6 to 3.2%.

It was unclear whether high-molecular-weight, unsaturated PE would undergo ethenolysis to form long-chain terminal alkenes for subsequent I/E. Subjecting the unsaturated HDPE containing 1.09% olefin units to ethenolysis with 3.6 mol % of second-generation Hoveyda-Grubbs catalyst **M1** resulted in a reduction of the M_n from 18.1 to 1.6 kDa. The M_n of the cleaved product corresponds to an average chain length of 114 carbons (Fig. 2C). To model the process of dehydrogenation and ethenolysis on a pure reactant and to gain information on the position of the alkene units and the resulting chain lengths, we conducted these reactions on tetracosane ($C_{24}H_{50}$), a pure, long-chain alkane. Initial dehydrogenation of tetracosane with 1 equivalent of TBE converted >95% of the acceptor to *tert*-butyl ethane and converted ~15% of the alkane to internal tetracosenes. Subsequent ethenolysis of the reaction mixture catalyzed by **M1** under 25 bar of ethylene formed the distribution of olefins, including a wide range of chain lengths shown in Fig. 2D. This result indicates that dehydrogenation of this long alkane with Ir-tBuPOCOP produces predominantly internal alkene, rather than terminal alkene, units.

Having shown that we could generate long-chain alkenes from PE, we investigated conditions for I/E of the resulting chains. I/E of hydrocarbons is known for the conversion of unsaturated alkylarenes to vinylarenes and for the conversion of 1-octadecene to propylene at low conversions. We sought an I/E that would transform the long-chain PE fragments to propylene in high yield by first seeking conditions for high conversion of 1-octadecene (**1a**) (19). Several combinations of complexes known to catalyze either olefin metathesis or isomerization were tested, and the results are summarized in table S1. The reaction of 1-octadecene with ethylene catalyzed by the combination of Hoveyda-Grubbs catalyst **M1** (6 mol % relative to alkene chains, 0.67 mol % relative to ethylene subunits) and the dimeric Pd(I) bromide catalyst **I1** (3 mol %, 0.33 mol % relative to ethylene subunits) at 60°C for 16 hours formed propylene in 95% yield.

Catalyst systems created from other combinations of individual metathesis and isomerization catalysts led to lower yields of propylene than those with **M1** and **I1**. Systems containing three alternative metathesis catalysts (**M2** to **M4** in table S1) with **I1** formed <60% propylene. Those containing the combination of **M1** and one of three other isomerization catalysts (**I2** to **I4** in table S1) formed <10% propylene. All of the isomerization catalysts furnished exclusively internal octadecenes from 1-octadecene in high or quantitative yield after 16 hours at 60°C in *p*-xylene, implying that incompatibility of the isomerization catalysts with the metathesis catalyst or with ethylene is the cause of the lower yields of propylene with alternative isomerization catalysts **I2** to **I4** (see table S1 for details).

The free energy of isomerizing ethenolysis is estimated to be negative but small (−1.52 kcal/mol of propylene formed under standard conditions; see the supplementary materials for details). Thus, our standard reactions that gave 95% yield of propylene were conducted in a pressure vessel with sufficient headspace to provide a large excess (64 equivalents per methylene unit) of ethylene to favor full consumption of the alkene chain. Consistent with the estimated thermodynamics, reactions with a smaller headspace providing just 3.5 equivalents of ethylene in the system also led to a high, albeit slightly lower, 72 ± 6% yield of propylene.

Finally, we tested the formation of propylene from ethylene and the unsaturated PE samples that we produced by dehydrogenation. The reactions of ethylene with the material from HDPE catalyzed by the two complexes in our I/E system formed propylene in yields shown in Fig. 3B. Reactions with HDPE containing only 0.68% unsaturation formed propylene in nearly 60% yield [turnover numbers (TONs) of 34 and 55 in **M1** and **I1**, respectively]. Reaction of the polymer in which 1.9% of the monomer units were unsaturated led to the formation of propylene in 87% yield (48 and 79 TON in **M1** and **I1**, respectively). The conversion of unsaturated LDPE to propylene also occurred under these conditions in yields up to 70% (39 and 64 TON in **M1** and **I1**, respectively).

We considered that ethylene could undergo dimerization or oligomerization, followed by ethenolysis, to form propylene without contribution from the polymer chains. Indeed, we did observe this background reactivity in the absence of long-chain olefins to form 0.13 mmol of propylene under our reaction conditions after 16 hours at 60°C and to form 1.01 mmol of propylene after the same reaction time at 130°C. Thus, to determine whether the

observed propylene from the reactions with PE originated from dehydrogenated polymer or from the background conversion of ethylene to propylene, we designed an isotope-labeling experiment in which the production of propylene could be observed more directly. Because both dehydrogenation and I/E scramble ^{2}H labels, we conducted experiments with ^{13}C-labeled PE to assess the extent of formation of propylene from polymer clearly. The propylene arising from dehydrogenated PE by the proposed scheme would consist entirely of the singly ^{13}C-labeled isotopomer. This isotopic composition would be observed because scrambling would occur at the termini of propylene by olefin metathesis during the I/E, but scrambling at the 2 position would not (Fig. 3C). Accordingly, we subjected ^{13}C-labeled (99.9% ^{13}C) HDPE to DIE and characterized the resulting propylene by mass spectrometry. The mass spectrum revealed an isotopic enrichment of the propylene >70%, demonstrating that most of the propylene observed from the DIE of PE results from polymer chain degradation. Small amounts of propylene containing two ^{13}C carbons that results from metathesis of the initial propylene product with the ^{13}C ethene formed in situ were also detected, but this material accounted for just 1% of the propylene product.

We also conducted DIE on samples of post-consumer PE (Fig. 3E). Substantial yields of propylene were observed in all cases. Moreover, HDPE from a milk jug yielded 57% propylene, which is only 20% lower than the yield from virgin HDPE with a similar degree of unsaturation, and LDPE food packaging generated >50% yield of propylene. To investigate the effect of additives on the performance of the catalytic system, these experiments were conducted by two methods. In the first method, postconsumer samples were coarsely cut with scissors and dehydrogenated directly using Ir-^{tBu}POCOP under the conditions specified in Fig. 2A. In the second method, the cut samples were first dissolved in boiling xylenes and then precipitated from acetone to remove additives and impurities. In some cases, the additives and impurities had no effect, and in some cases, such as those from can tops and food packaging, the simple precipitation was needed for dehydrogenation to occur. These results show that postconsumer products comprising HDPE or LDPE can be converted to propylene by this protocol, and that our system is sufficiently robust to tolerate the additives present in postconsumer products while still furnishing substantial amounts of propylene.

The time courses of reactions for degrading octadecene at 60°C and degrading HDPE at 130°C are displayed in Fig. 4, A and B, respectively. These data revealed a lengthy induction period for the reaction of octadecene at 60°C, presumably because of the multiple stages of catalyst activation necessary for the reaction to occur at an appreciable rate. This plot fit well to an exponential formation of catalyst and a zero-order appearance of product until the substrate was depleted. The reaction of the unsaturated HDPE at 130°C occurred with a shorter induction period despite the need to first cleave the internal alkenes of the unsaturated HDPE, and a constant rate was then observed up to 85% of the total conversion. Presumably, the higher temperature diminishes the induction period. The linear formation of propylene suggest that the process occurs by a rate-determining reaction with the excess ethylene.

Additional data that we gathered on the degradation of PE by DIE point to future challenges. First, samples of dehydrogenated LDPE consistently furnished propylene in lower yields

than did dehydrogenated HDPE with the same degree of unsaturation. We hypothesized that the significant degree of branching in LDPE led to the formation of trisubstituted alkenes during IE, and these more hindered alkenes underwent slower isomerization or slower ethenolysis. To test this hypothesis, we synthesized several substituted olefins and subjected them to I/E under conditions identical to those we used for the I/E of 1-octadecene (Fig. 4C). The I/E of substrates **1a** to **1d** demonstrate a clear trend of decreasing propylene yield with increasing olefin substitution.

Second, our experiments with virgin PE (Fig. 3B) showed that a high degree of unsaturation of PE chains was detrimental to the yield of I/E. We hypothesized from this observation that a high degree of polymer unsaturation leads to dienes and polyenes that isomerize during the I/E process to conjugated dienes that could poison the catalyst. Because there are multiple sites of unsaturation on each polymer chain, **I1** could isomerize such olefins to conjugated 1,3-dienes within the polymer, and such conjugated dienes could poison one or both catalysts. To test this hypothesis, we conducted I/E on one α,ω-diene, **1e** (1,9-decadiene), and one conjugated diene, **1f** (1,3-tetradecadiene) (Fig. 4D). These experiments showed that α-ω dienes separated by six methylene units (**1e**) formed propylene in much higher yields than did 1,3-dienes. Consistent with our hypothesis, the addition of catalytic amounts of catalyst **I1** to conjugated diene **1f** without ethylene or the metathesis catalyst led to the immediate formation of a black precipitate (Fig. 4D).

We assessed this hypothesis further by applying I/E to poly(cyclooctene) (PCO). We synthesized PCO (M_n = 5.2 kDa, = 1.64) by ring-opening metathesis polymerization of cyclooctene (27). I/E of this substrate furnished propylene in significantly diminished yield, but I/E of a partially hydrogenated PCO (28) (with an olefin content of 12.2% versus 25% for the original polymer) furnished propylene in 38.5% yield (Fig. 4D). We concluded from these data that the formation of 1,3-dienes in situ was likely responsible for the lower yields of propylene from the more highly unsaturated polymers.

Propylene is used as a precursor to multiple commodity chemicals, including acrylic acid, acrylonitrile, and cumene, in addition to its use in the production of polypropylene plastic (28). Although it is produced primarily as a by-product of steam cracking or fluid catalytic cracking, the increasing demand for propylene since the 1990s has motivated its "on-purpose" production through methanol-to-olefins technology, propane dehydrogenation, or the conproportionation of butene and ethylene (29). This on-purpose production is only expected to increase as increasing populations and standards of living heighten the demand for polypropylene.

The constituent reactions of the DIE process that we report on laboratory scale with homogeneous catalysts are closely related to reactions conducted on industrial scales with heterogeneous catalysts, and their combination draws analogies to the combination of reactions in the commodity-scale shell higher olefin process (SHOP) that forms long-chain alkenes from ethylene (29). The olefin metathesis and isomerization by which this degradation of the unsaturated polymer occurs are some of the most practiced industrial transformations and are routinely performed on commodity scales with heterogeneous catalysts (30, 31). Thus, the capacity of such systems to catalyze the DIE processes would

allow dehydrogenation and I/E to be conducted in continuous flow with less ethylene while removing the propylene product. The separation of propylene from ethylene is already conducted on the industrial scale by various methods, including low-temperature and extractive distillation (32). Thus, this initial report charts a path by which a DIE sequence could render polyolefin waste a hydrocarbon feedstock to generate a commodity chemical for which the demand is comparable to the available supply of recovered polyolefins. The use of heterogeneous catalysts is under development.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

Data and materials availability:

All data are available in the main text or the supplementary materials.

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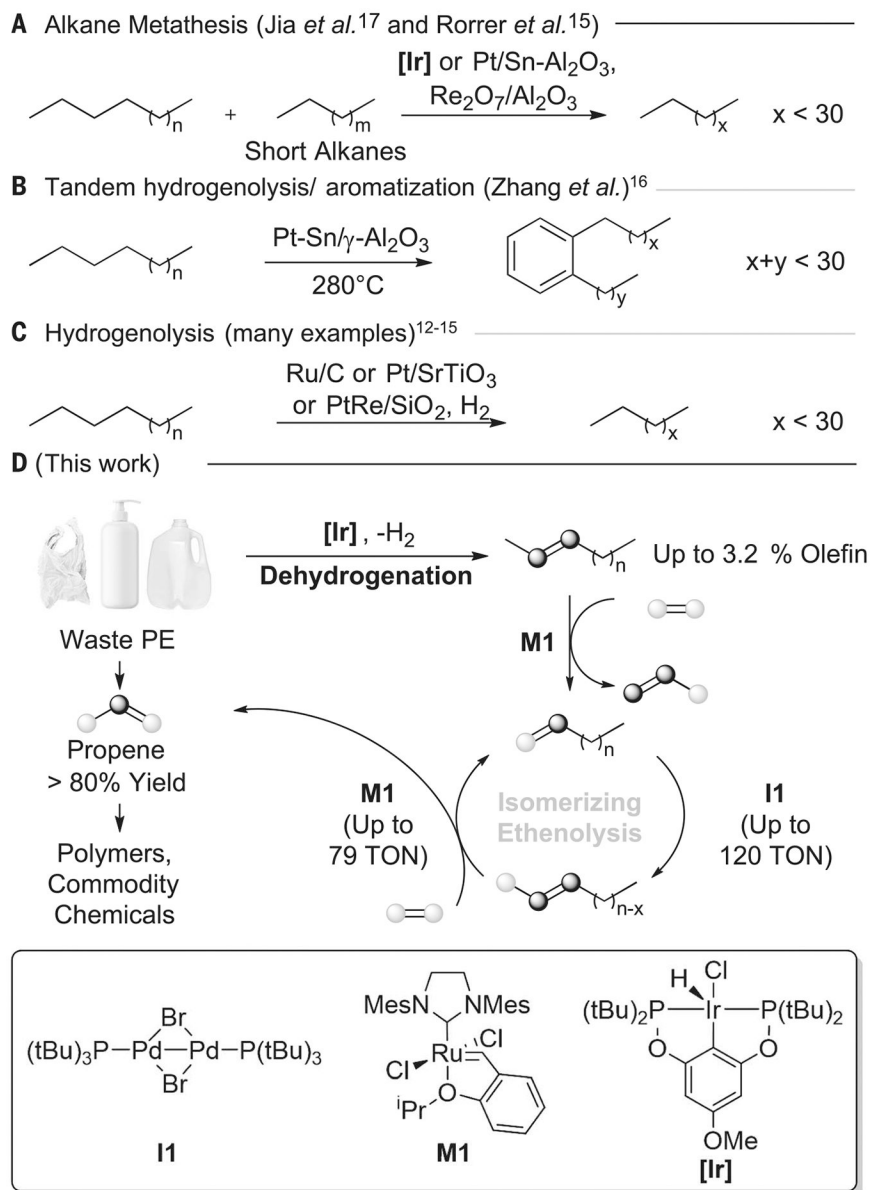**Fig. 1. Strategies for the valorization of PE waste.**
(**A**) Degradation of PE by alkane metathesis with n-hexane. (**B**) Conversion of PE to alkyl aromatics by tandem hydrogenolysis/aromatization. (**C**) Degradation of PE by hydrogenolysis. (**D**) Conversion of PE to propylene by DIE (where x is the number of I/E turnovers). Mes, mesitylene (2,4,6-trimethylbenzene).
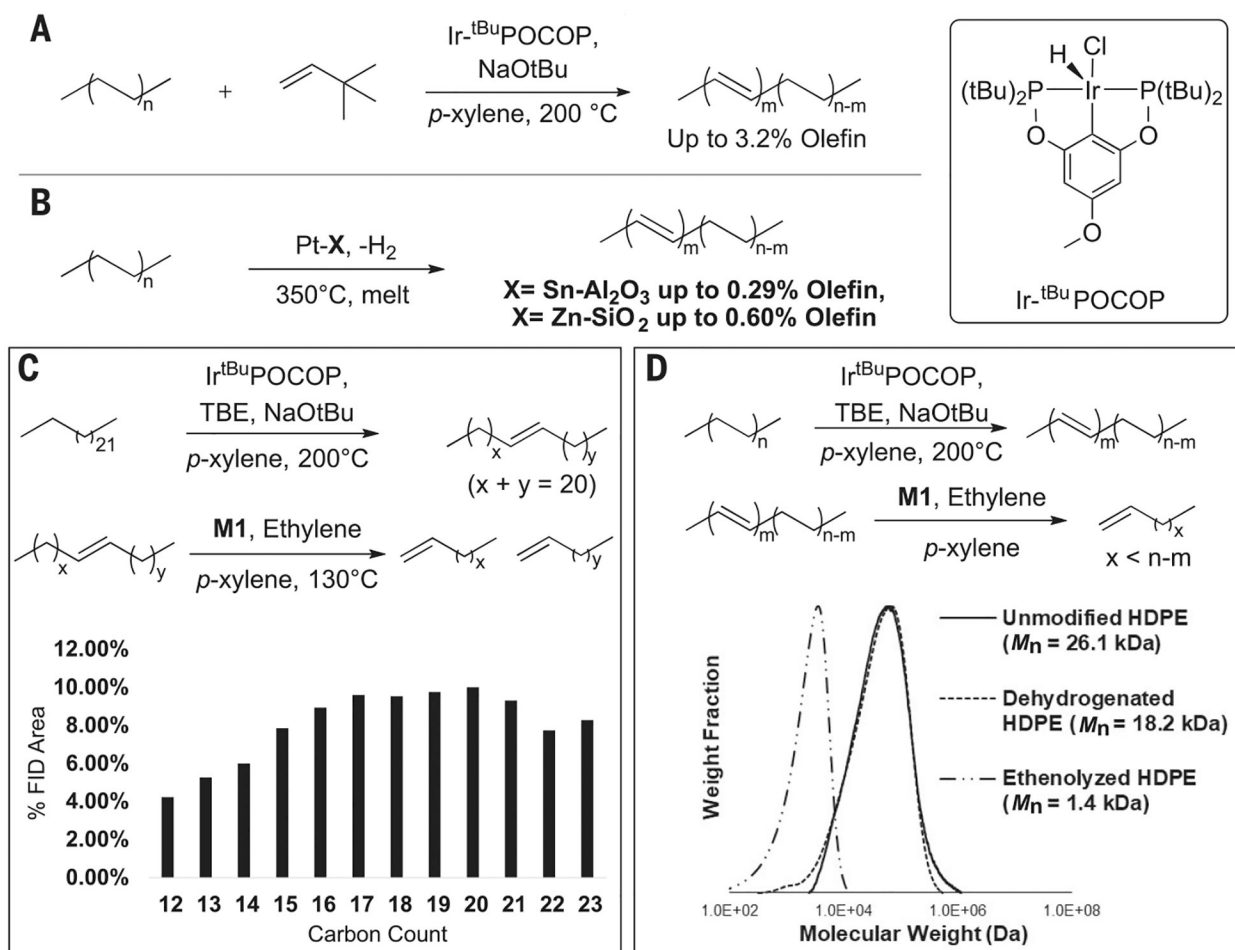
Fig. 2. Conditions tested for DIE.

(**A**) Homogeneous dehydrogenation of PE: 0.42 mol % Ir-^{tBu}POCOP (9.8 wt %), 0.46 mol % NaOtBu, 0.6 M in PE; reactions were run for 12 hours with 0.4 equivalents of TBE. Mol %, equivalents. TBE and M of PE were calculated relative to PE monomer units. (**B**) HDPE (M_n = 26.1 kDa) with bimetallic catalysts supported on alumina. Conditions: 20 wt % catalyst, 350°C. Catalysts were first activated under H_2 flow for 1 hour, and then dehydrogenation was conducted for 16 hours under Ar flow. (**C**) Gel-permeation chromatogram of HDPE before and after ethenolysis with **M1**. Conditions for ethenolysis were 0.36 M in unsaturated PE 3.6 mol % **M1** in p-xylene (relative to PE monomer units), heated at 130°C for 16 hours under 25 bar ethylene. (**D**) Sequential dehydrogenation and ethenolysis of a long-chain paraffin (tetracosane). Initial dehydrogenation yields olefins in 10% yield, and subsequent ethenolysis with **M1** yields a statistical distribution of shorter-chain olefins.
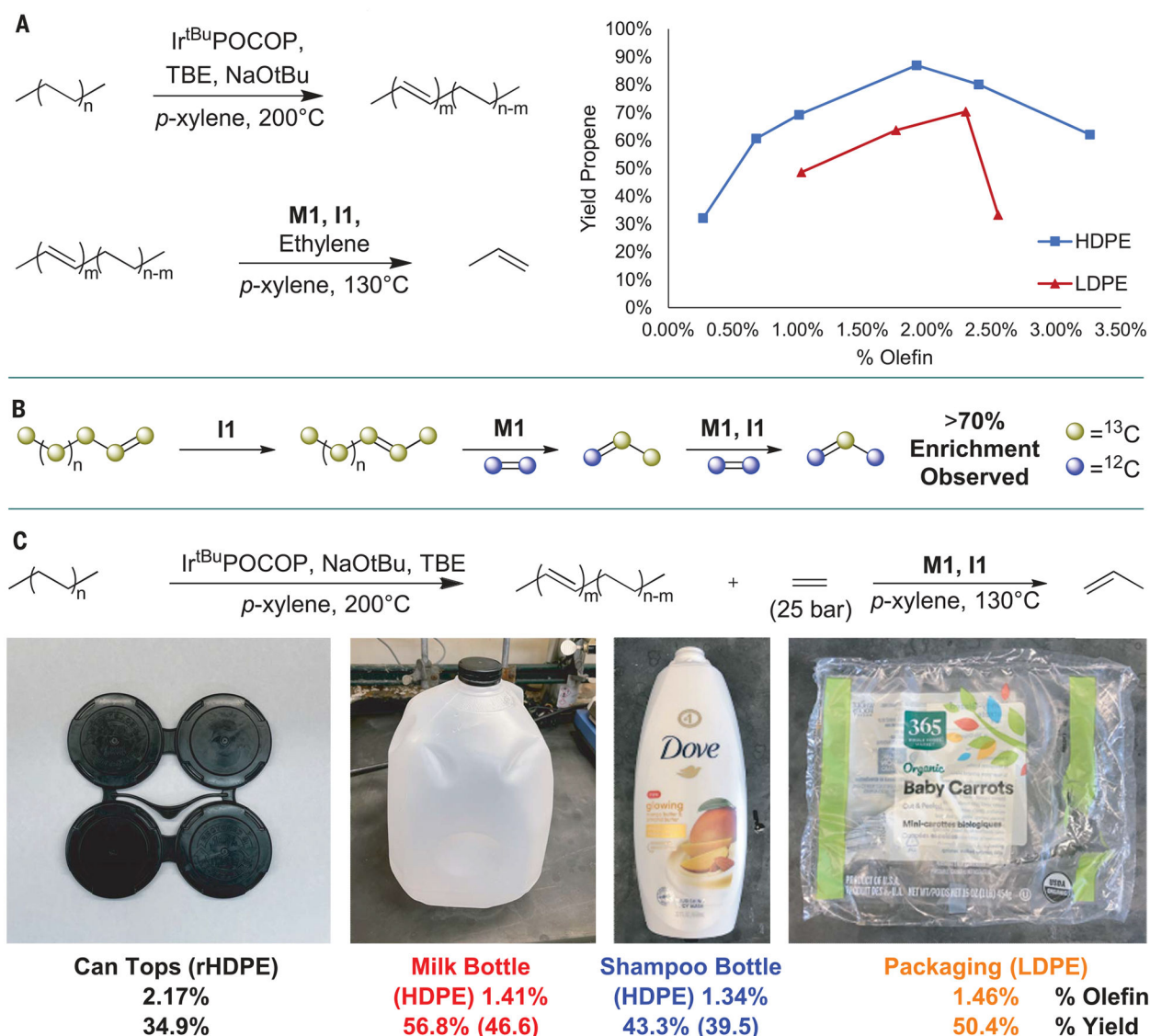
Fig. 3. Development of conditions for DIE of PE.
(**A**) Application of I/E to dehydro-PE, with dehydro-HDPE yielding a maximum of 80% propylene with 1.96% dehydrogenation. Conditions for I/E of dehydrogenated PE: 3.6% **M1**, 2.2% **I1**, 1.78 M in PE, heated at 130°C in *p*-xylene for 16 hours under 25 bar of ethylene. Catalyst loadings are reported as mol % relative to total PE repeat units. (**B**) DIE of ^{13}C-labeled HDPE to check for background reactivity [conditions identical to those in (A)]. (**C**) DIE of postconsumer PE [conditions identical to those in (B)]. Propylene yields are reported as X% (Y) where X is the yield obtained from polymer purified by precipitation from acetone and Y is the yield obtained from unmodified polymer. Where a single yield is reported, dehydrogenation on unpurified samples failed.
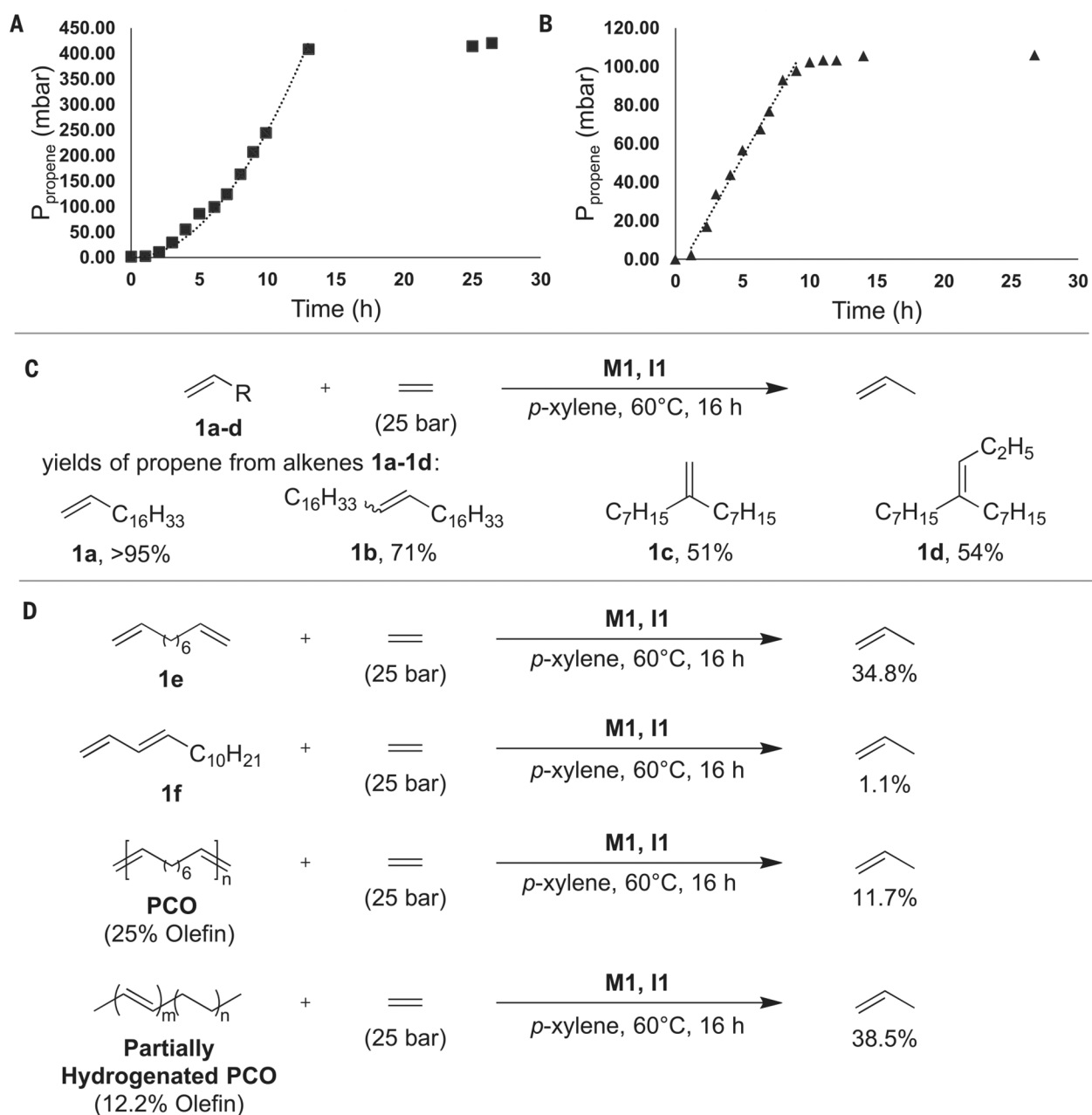
A

B

C

1a-d   (25 bar)   *p*-xylene, 60°C, 16 h

M1, I1

yields of propene from alkenes **1a-1d**:

1a, >95%   **1b, 71%**   **1c, 51%**   **1d, 54%**

D

1e   (25 bar)   **M1, I1**   *p*-xylene, 60°C, 16 h   34.8%

1f   (25 bar)   **M1, I1**   *p*-xylene, 60°C, 16 h   1.1%

PCO (25% Olefin)   (25 bar)   **M1, I1**   *p*-xylene, 60°C, 16 h   11.7%

Partially Hydrogenated PCO (12.2% Olefin)   (25 bar)   **M1, I1**   *p*-xylene, 60°C, 16 h   38.5%

Fig. 4. Investigation of reaction scope and kinetics.
(**A**) Time course of I/E with 1-octadecene (100% yield = 458.3 mbar). Conditions for I/E of 1-octadecene: 6.0 mol % **M1** (0.67 mol % relative to ethylene subunits), 3.0 mol % **I1** (0.33 mol % relative to ethylene subunits), 0.500 M in olefin, heated at 60°C in p-xylene for 16 hours under 25 bar of ethylene. A fit for the time course was conducted using COPASI by simulating an exponential appearance of catalyst and a zero-order reaction ($R^2 = 0.993$, $k_{cat} = 0.071$ s^{-1}, $k_{propylene} = 18.0$ s^{-1}). (**B**) Time course of I/E with dehydrogenated HDPE (1.41% olefin) (100% yield = 193.5 mbar). A linear fit has been added to (B) to show the zero-order reaction after the short induction period and completion of the reaction ($R^2 = 0.989$). (**C**) Yields of I/E on small molecules **1a** to **1d** designed to assess the effect of

branching on I/E. (**D**) Yields of I/E on small molecules **1e** and **1f** designed to test the effect of dienes on I/E [conditions identical to those specified in (A)] and on PCO (M_n= 5.2 kDa) designed to demonstrate the effect of polymer unsaturation on I/E yield in the absence of branching. Conditions for I/E in (C) and (D) were identical to those in Fig. 3C.