Catalytic closed-loop recycling of bio-based polyethylene-like materials

Xin Liu[1†], Zhitao Hu[1†], Emma M. Rettner[2], Katherine L. Harry[1], Joel Miscall[3,4], Nicholas A. Rorrer[3,4], and Garret M. Miyake[1,2]*

[1]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States.

[2]School of Advanced Materials Discovery, Colorado State University, Fort Collins, Colorado 80523, United States.

[3]Renewable Resources and Enabling Sciences Center, National Renewable Energy Laboratory; Golden, CO 80401, United States

[4]BOTTLE Consortium; Golden, CO 80401, United States.

†These authors contributed equally: Xin Liu and Zhitao Hu

*Corresponding author e-mail: garret.miyake@colostate.edu

Summary Paragraph: Renowned for their important materials properties and cost-effectiveness, polyolefins have become indispensable across diverse applications.[1-5] Despite their numerous benefits, the environmental toll of polyolefins is significant due to their extensive production, single-use nature, and slow decomposition rates.[6-8] As the production of polyolefins continues to surge, far exceeding the global capacity for effective management, the urgency for a sustainable circular plastics economy becomes increasingly critical.[9-10] Promising strategies to recapture the value of polyolefins include advanced recycling, where plastic waste is transformed into raw materials for value-added products[11-13] or developing polyethylene (PE)-like materials which can be chemically recycled back to building blocks.[14] Herein, we report a family of bio-based PE-like materials synthesized by acceptorless dehydrogenative polymerization from linear and branched diols. These materials exhibit a wide range of mechanical

properties, encompassing thermoplastics to plastomers to elastomers. The branched diols, produced through a thiol-ene click reaction, can lead to plastics with significantly enhanced tensile properties, toughness, and adhesive properties. Furthermore, these materials could be depolymerized back to monomer through hydrogenation and were separatable with a monomer recovery up to 99%, unaffected by the presence of dyes and additives. Both the polymerization and depolymerization processes utilize earth-abundant manganese (Mn) complexes as catalysts.

Main Text: Chemically recyclable polyethylene-like materials represent a critical goal for environmentally sustainable commodity plastics.[14-15] These materials mimic the properties of traditional polyolefins, such as high-density polyethylene (HDPE) and linear-low density polyethylene (LLDPE) but are designed for depolymerization through incorporation of functional groups (e.g., esters, and amides) that serve as breaking points in their molecular structure. The low density of in-chain breaking points allows these materials to be recycled back to monomers, while preserving the intrinsic structure and important properties of PE.[14] The chemical recycling of PE-like materials represents an advantage over existing valorization methods for PE such as pyrolysis or steam cracking, which typically yield limited quantities of ethylene (around 10% at temperature up to 800 ºC),[16-17] while the chemical recycling of PE-like polymers can be carried out under milder conditions (below 200 ºC), resulting in a high yield of monomers suitable for repolymerization.[14] Telechelic polyethylene macromonomers can be used to create recyclable plastics with lower ester content via polycondensation and obtain materials with similar materials properties of commercial PE.[18-22] However, multistep macromonomer syntheses and the reliance on precious metals in these transformations constrains the commercial viability of these approaches. Ring-opening metathesis polymerization (ROMP) of cyclooctene and comonomers with breaking points (e.g., ester, or Si–O bonds) has been used to generate chemically recyclable PE-like materials, but this approach relies on the use of the precious metals (e.g., ruthenium) for polymerization.[23-24] Significantly, the step-

growth condensation polymerization of bio-based long-chain dicarboxylic acids (or diesters) with diols using an inexpensive and abundant metal catalyst can result in recyclable plastics using which have similar solid-state structure and ductility to HDPE.[25-26] However, traditional condensation polymerizations require precisely balanced stoichiometric ratios between the complimentary functional groups and even minor imbalances can lead to significant reductions in polymer molecular weight and related properties.[27] As such, the materials properties of the plastics cannot be easily tunable through simple modulation of the monomer ratios. Recently, our group reported an approach to the production of diverse polyolefin-like plastics that possess a closed-loop recycling strategy based on ruthenium pincer catalyst.[28] The highly tunable multiblock PE-like materials can be synthesized from two different hydroxy-telechelic olefinic oligomers via acceptorless dehydrogenative polymerization (ADP). The use of ADP enabled the direct coupling of diols, overcoming synthetic limitations of stoichiometry in step-growth polymerization.

Reflecting upon these advancements, we recognized that further focus on cost-effective catalysts, easily separatable monomers, and economical feedstocks is needed. Herein, we report a series of bio-based PE-like materials synthesized from linear and branched diols via ADP, offering highly modular material properties (e.g., tensile strength, 3D printability, and adhesion) dependent on the proportion of these two monomers. Both linear and branched monomers could bedirectly and efficiently synthesized from renewable resources (Fig. 1a) while an earth-abundant manganese complex mediates both the polymerization and depolymerization processes (Fig. 1b). These materials were effectively depolymerized to monomer through hydrogenation, even in the presence of commercial or waste plastics, and these two monomers can be separated via selective crystallization, demonstrating their applicability within a circular economy framework.

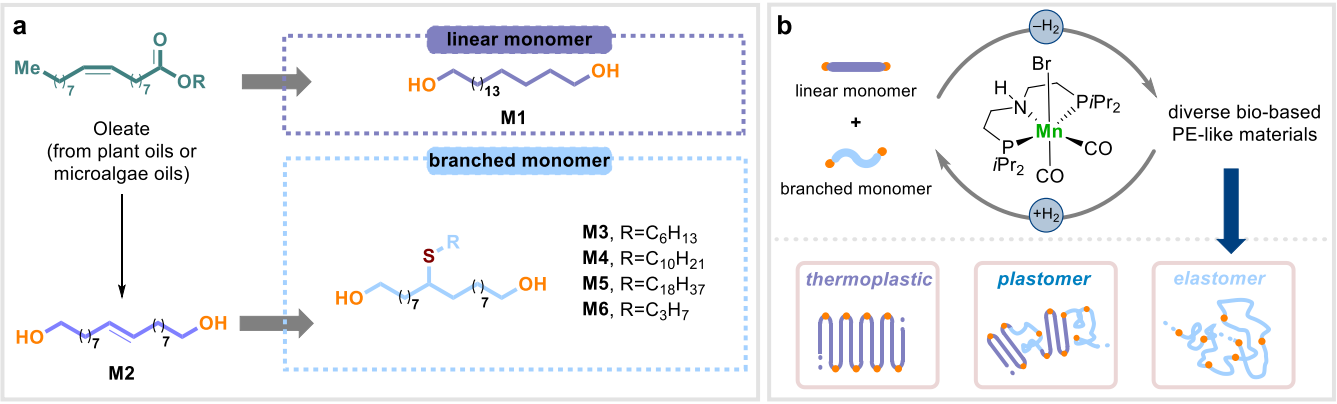

Fig.1 | Overview of the catalytic closed-loop recycling of polyethylene-like materials with tunable properties from polymerization of bio-based linear and branched diols. a, Linear and branched monomers synthesized from biorefining of plant or microalgae oils. **b**, This work developed a straightforward approach to the closed-loop polymerization and recycling bio-based of PE-like materials with highly tunable mechanical properties from long-chain linear and branched diols using an earth abundant manganese complex.

Results and discussion

Monomer synthesis. Unsaturated fatty acids are attractive bio-sourced starting materials for synthesizing linear and branched C18 monomers (18 carbons between the alcohols) as they already contain long linear methylene sequences to impart PE-like properties yet can be readily functionalized for installing diverse structural modifications. Notably, the transformation of unsaturated fatty acids (from plant oil) to C18 products has been employed as a known process in biorefining.[29-30] The long-chain 1,18-octadecanediol (**M1**) and 1,18-octadec-9-enediol (**M2**) can be obtained from fatty acids using established techniques.[31] **M1** serves as a crystallizable monomer with long linear methylene sequences, intended to imbue a high melting temperature (T_m) and modulus to the polymer. The functionalized soft monomers **M3**-**M6** were efficiently synthesized via radical thiol-ene click chemistry from **M2** (see supporting information for

details),[32] which was designed to install amorphous and elastomeric soft domains in the polymer. The simple and efficient thiol-ene reaction between **M2** with thiols (yield >99%) allowed for synthesis of monomers possessing various branched groups, influencing the chain architecture, morphology, and consequently the thermal and mechanical properties of the polymers.[33]

Table 1. Characteristics of PE-like polymers.

entry	Sample	M_w (kDa)	$Đ$ (M_w/M_n)	T_c (°C)	T_m (°C)	T_{d5} (°C)	E (MPa)	σ_{UTS} (MPa)	ε_b (%)	U_T (MJ•m^{-3})
1	**PE-18-0**	67.9	1.99	78	94	395	680 ± 20	22 ± 2	730 ± 40	130 ± 10
2	**PE-18-S6-3**	185.1	1.26	77	93	398	500 ± 10	26 ± 2	910 ± 30	150 ± 20
3	**PE-18-S6-5**	133.9	1.76	76	90	393	440 ± 20	25 ± 3	930 ± 20	140 ± 10
4	**PE-18-S6-10**	118.4	1.20	73	85	387	380 ± 10	26 ± 2	960± 30	150 ± 20
5	**PE-18-S6-20**	132.0	1.65	65	76	386	140 ± 5	25 ± 3	1120 ± 30	180 ± 20
6	**PE-18-S6-40**	142.8	1.41	49	66	382	46 ± 3	23 ± 2	1240 ± 40	170 ± 30
7	**PE-18-S6-60**	116.2	1.71	23	41	377	1.4 ± 0.3	17 ± 2	1610 ± 60	150 ± 20
8	**PE-18-S6-80**	69.9	1.31	–	–	363	–	–	–	–
9	**PE-18-S3-20**	108.2	1.65	68	79	388	130 ± 5	16 ± 3	710 ± 40	110 ± 10
10	**PE-18-S10-20**	109.4	1.42	67	80	386	160 ± 7	23 ± 4	930 ± 30	140 ± 20
11	**PE-18-S18-20**	81.2	1.56	67	78	382	150 ± 10	21 ± 4	640 ± 30	100 ± 10
12	**HDPE**	91.6	5.32	114	127	431	720 ± 40	18 ± 1	650 ± 50	110 ± 10
13	**LLDPE**	80.7	2.91	102	120	433	230 ± 10	21 ± 2	850 ± 40	130 ± 10

See supplementary materials for polymerization details. Sample naming following the format: **PE-18-S6-20**, PE represents polyethylene-like, 18 is the number of carbons between each ester, S6 represents the branch in the monomers (one sulfur and six carbon atoms), and 20 represents the incorporation of branched comonomer in the copolymers in percentage. Weight average molecular weight, M_w; dispersity, $Đ$; crystallization temperature, T_c; melting transition temperature, T_m; decomposition temperature at 5% weight loss, T_{d5}; Young's modulus, E; tensile strength, σ_{UTS}; elongation at break, ε_b; tensile toughness, U_T. Average values for E, σ_{UTS}, ε_b, and U_T are provided with standard deviations from the mean value of four samples.

Polymerization. As Mn pincer complexes have proven successful in the acceptorless dehydrogenative coupling of alcohols to esters in small molecule synthesis,[34-35] we were motivated to explore the potential

of earth-abundant Mn complexes to transform diols into PE-like polymers through ADP. Mn based catalysts are attractive relative to Ru catalysts because of the greater natural abundance and lower-toxicity [36-37]. We investigated a series of Mn pincer complexes (Fig. S1)[38-39] for the ADP of **M1** to **PE-18-0** under varying conditions (Table S2–S5). Under optimized conditions (3.0 mol% ***i*Pr-PNP-Mn** complex, 9.0 mol% KO^{t}Bu, and toluene at 130 °C), a high molecular weight **PE-18-0** (M_w = 67.9 kDa, $Đ$ = 1.99) was synthesized (Table 1, entry 1). Owing to the high reactivity of this Mn complex, it was employed for further polymerization studies. We synthesized copolymers using the branched monomer **M3** in varying ratios (3 to 80%) with **M1** to access a range of thermal and mechanical properties (entries 2-8). High-molecular weight copolymers (M_w = 69.9 to 185.1 kDa) with moderate dispersities ($Đ$ < 1.76) were obtained after precipitation into methanol. In the copolymerization using branched monomers with different branching patterns (entries 9-11), a lower molecular weight was observed when the branching length reached a size of C18.

Polymer properties. The synthesized thermoplastic **PE-18-0** (Table 1, entry 1) was found to exhibit a decomposition temperature at 5% weight loss (T_{d5}) of 395 °C, being lower than commercially available HDPE (T_{d5} = 431 °C) or LLDPE (T_{d5} = 433 °C) samples. The T_m of **PE-18-0** (94 °C) was found to be highly comparable to that of PE-like materials (T_m = 97 °C) obtained from step-growth condensation polymerization of 1,18-dimethyl octadecanedioate and 1,18-octadecane diol.[25] The crystallinity of the polymers decreased (from 43 to 0%, Fig. 2a) with increasing comonomer content (from 3 to 80%), similar as observed in LLDPE with respect to HDPE. The increase in branching content leads to a decrease in crystallinity due to the decrease in crystallizable content combined with the increasing difficulty for the polymer chains to undergo crystallization.[33] Miscibility between the different polymer domains likely also decreases the observed T_m. Wide-angle x-ray diffraction (WAXD) revealed that copolymers with branched monomers lower than 20% exhibit sharp and intense reflections, indicating the orthorhombic

crystal packing of the alkane segments, resembling HDPE and LLDPE (Fig. 2b). These findings are in agreement with previous studies which found introducing ester, thioether, or hydroxyl groups into PE at lower concentrations does not significantly perturb the crystal structure.[25, 33]Additionally, small-angle x-ray scatting (SAXS) of the homopolymer **PE-18-0** showed a broad peak at low scattering vector *q* of 0.04 $Å^{-1}$ characteristic of the long period, or average distance between lamellae in semicrystalline polyolefins (Fig. S7).[40] The long period decreased with increasing incorporation of comonomer, as is expected when reducing the crystallizable volume by including branching.[41]

Uniaxial tensile testing was used to investigate the mechanical properties of the materials, and representative stress-strain curves of the polymers are shown in Fig. 2c. All samples exhibited excellent extensibility with the average strain at break (ε_b) for all polymers exceeding 700%, and polymers with over 20% comonomer exceeding 1100% . Also observed with increasing incorporation of branched comonomer were decreased yield stress (Fig. S8) and the Young's modulus (E) (E = 680 MPa for **PE-18-0** to 1.4 MPa for **PE-18-S6-60**) until the materials behaved as elastomers (Fig. 2d). Independent of composition, all the materials exhibit both high ultimate tensile strength (σ_{UTS}= 16 to 27 MPa) and high toughness (U_T= 100 to 180 $MJ•m^{-3}$). Compared to commercial plastics such as HDPE, LLDPE, commercial 3D printing materials (SemiFlex and T-Lyne), synthetic fibers, polycarbonate (PC), and polyvinyl butyral (PVB), as well as tough engineering plastics (>100 $MJ•M^{-3}$)[28], these PE-like materials demonstrate equivalent or even superior toughness (Fig. 2e).

Inspired by the exceptional metal adhesion properties of sulfur-containing polymers,[42-43] we investigated the interfacial adhesion of these PE-like materials to metal surfaces. Single-lap-shear tests were performed on stainless steel substrates to assess their adhesive strength (Fig. 2f). Excitingly, **PE-18-S6-10** and **PE-18-S6-20** showed strong adhesion to stainless steel surfaces (4.8 ± 0.2 MPa and 5.0 ± 0.2 MPa, respectively), comparable to the commercially available J-B Kwik adhesive (5.0 ± 0.4 MPa). To validate

the role of the thioether comonomer in adhesion, we compared copolymers with different functional groups at the branching point such as -CH_2- and -SO_2-, which showed significantly lower adhesion to metal surfaces (Fig. 2f, green inverted triangle for -SO_2-, blue round for -CH_2-) even though the thermal properties and crystallinity of copolymers with these different branch-point functional groups are comparable to their thioether copolymer counterpart (Table S11).

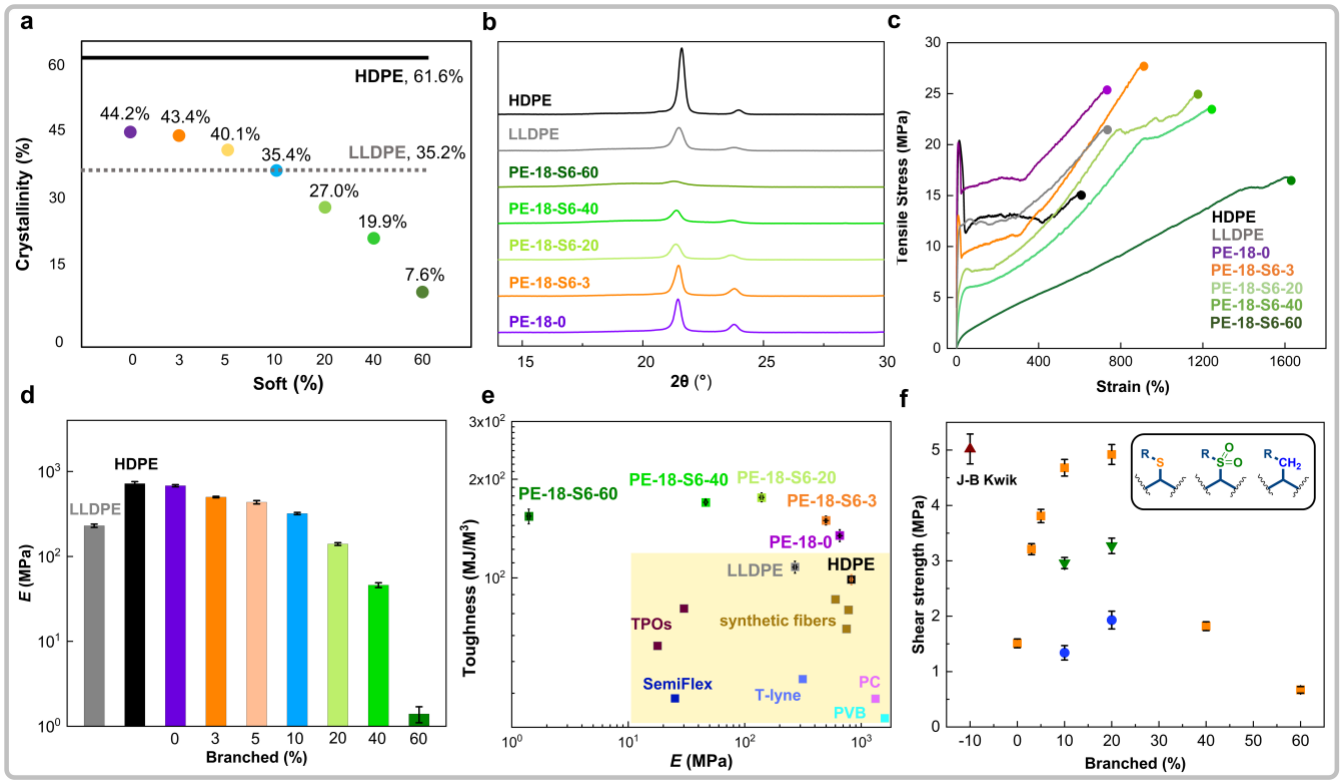

Fig.2 | Properties of the polymers are modulated over diverse regimes. a, Crystallinity measured from the melting endotherms obtained by differential scanning calorimetry (DSC). **b**, WAXD patterns of PE-like materials, HDPE, and LLDPE. **c**, Representative stress-strain curves. **d**, Young's modulus of the polymers as a function of branching content. **e**, Comparison between synthesized polymers and commercial materials as a function of toughness and modulus. **f**, Lap-shear adhesion tests, produced materials and commercial adhesive as the adhesive interlayers, R= hexane. Error bars represent standard deviations from the mean value of four samples.

Catalytic closed-loop recycling studies. In current waste management processes, different types of plastics need to be sorted before they can be effectively recycled, which is a complex and labor-intensive process.[44] Contamination from additives and dyes can also challenge the recyclability of plastics. Even if separation is achieved, mechanical recycling will result in plastics with deteriorated materials properties. Therefore, in the chemical recycling process efficiently converting the target materials back to monomers from mixed plastics is desirable. To this end, we investigated the depolymerization of **PE-18-S6-20** driven by hydrogen gas (H_2) and the ***i*Pr-PNP-Mn** complex in the presence of various commercial plastics such as polypropylene (PP), HDPE, polystyrene (PS), Nylon-66 (PA-66), Teflon (PTFE), polyethylene terephthalate (PET), polyurethane (PU), and polyvinyl chloride (PVC) (Fig. 3a). Both linear and branched monomers were recovered in high yields (91 to 99%), while the commercial polymers remained intact under these conditions for facile separation. Importantly, the polyester PET, a major contaminant in PE waste streams and contains a high concentration of ester groups[45], remained unconverted at 110 ºC, while **PE-18-S6-20** depolymerized fully (>99%). Once the non-depolymerized commercial plastic is separated by filtration, the depolymerization residue is ready for polymerization without any need for post-treatment or additional catalysts (Fig. S12). While the molecular weight of the resulting polymer was lower (starting: M_w=59.9 kDa, repolymerization: M_w=17.3 kDa), the capacity to repolymerize without additional catalysts demonstrates promise.

To further probe the feasibility of chemically recycling these materials in real-life conditions, **PE-18-S6-20** was chemically recycled in the presence of postconsumer plastics (e.g., milk bottle, plastic bag, and centrifuge tube). In all instances, both monomers could be isolated in high yields (>95%) while the commercial plastics were recovered in their original unaltered state (Fig. 3b). The corresponding monomers **M3** and **M1** were almost quantitatively recovered from the filtrate by recrystallization at 0 ºC. Any potential additives or plasticizers contained in the commercial plastics do not affect the hydrogenation

process. Subsequently, we evaluated the viability of this recycling system at larger-scale. As shown in Fig. 3c it is possible to conveniently run (de)polymerization reactions on 10 to 30 g scale, with the only limitation being the size of the reactor vessel and autoclave. These results further demonstrate the potential for scalability with this approach.

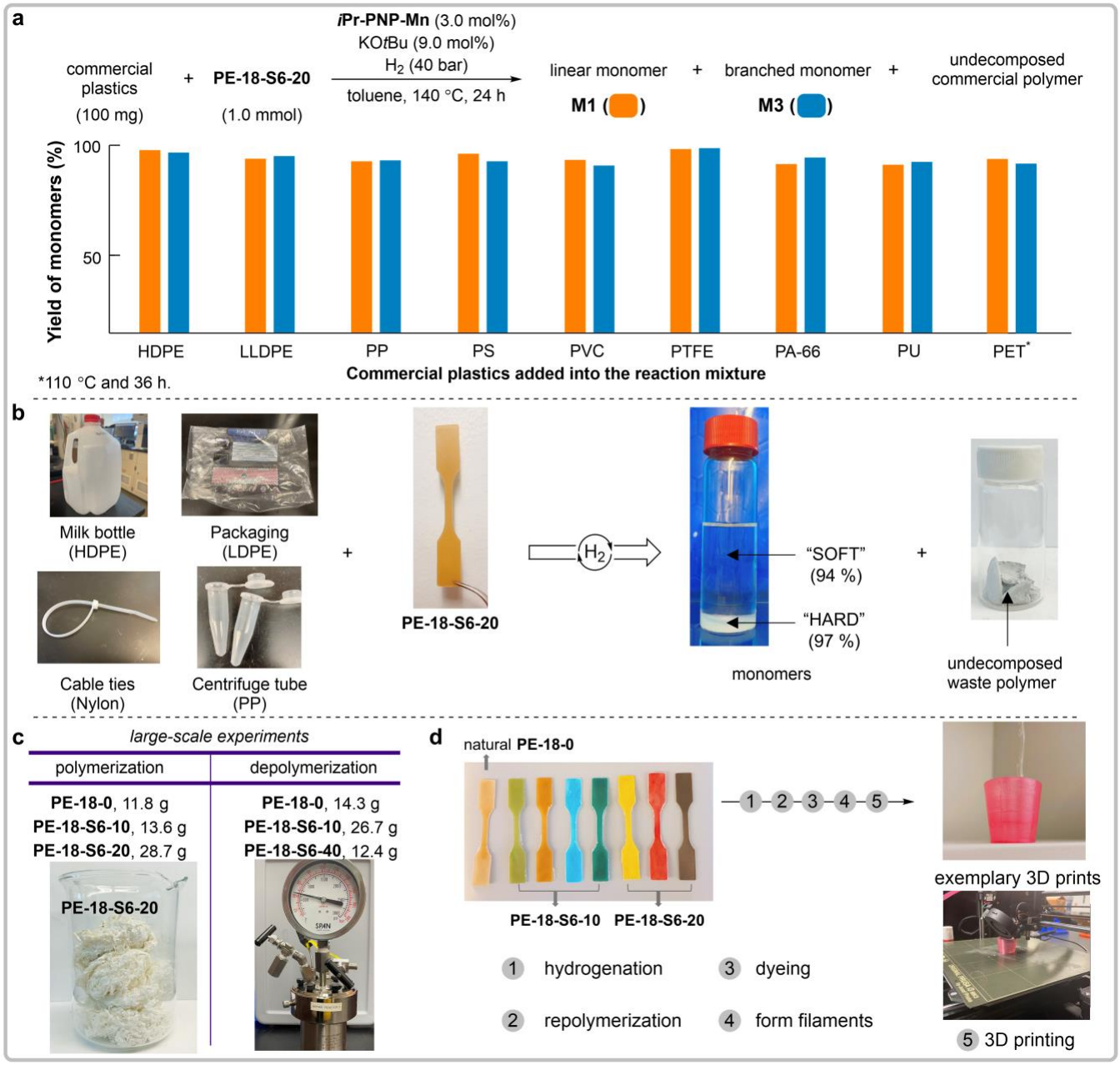

Fig.3 | Catalytic recycling of PE-like materials. **a**, depolymerization of **PE-18-S6-20** with different commercial polymers. The yield was determined by GC using mesitylene as the internal standard **b**, recycling of a mixture of **PE-18-S6-20** with postconsumer polymers. Isolated yields are given. **c**, large-scale synthesis and depolymerization. See supporting information for more details. **d**, recycling a variety of dyed polymers including **PE-18-0**, **PE-18-S6-10**, and **PE-18-S6-20**, which are extruded to make filaments for 3D printing.

Lastly, the capability for 3D printing these PE-like materials was investigated to establish the processability of these materials (Fig. 3d). HDPE can be challenging to 3D print due to shrinkage and poor adhesion to standard build plates.[46] Firstly, the colored tensile testing bars were recycled back to the monomers via catalytic hydrogenation. The dye additives did not interfere with the depolymerization process and both monomers were recovered in excellent yield (>90%) (Fig. S11). Next, the monomers were repolymerized in a new ratio, and the resulting material was used for producing filament. The addition of colorants did not affect the quality of the filament (Fig. S19). The extruded filament was used to 3D print a cup from light-red-colored **PE-18-0** (Fig. 2d and Fig. S22). Notably, the 3D printed products can be completely depolymerized back to the corresponding monomers (Fig. S22). While the softening point of this material is insufficient for high-temperature applications, the feasibility for chemical recycling could increase the sustainability of plastic materials.

Conclusions

We have developed a robust approach to synthesize bio-based PE-like materials with highly tunable thermal and mechanical properties from long-chain linear and branched diols. The circular lifecycle of these plastics was driven by the reversible loading and discharge of hydrogen, the smallest molecule possible for polycondensation, representing a highly atom- and mass-economical strategy. Both linear and branched monomers are easily sourced from plant oils. Their closed-loop recycling process is effective

even in the presence of other commercial plastics. Employing non-precious metal Mn as catalysts facilitates the creation of a low-cost and sustainable recycling platform. Our continuing goals seek establishment of more efficient non-precious metal catalysts to mediate the polymerization and depolymerization steps while we posit that employing bio-based diols to create closed-loop materials will be a pivotal strategy in advancing the development of the circular plastic economy that have the potential for biodegradability in the advent that the plastics are undesirably discarded and prevent the buildup of plastic waste or microplastics.

Methods

Materials

All chemicals were used as received without further purification unless otherwise noted. All air-sensitive manipulations were conducted under an inert atmosphere in a nitrogen-filled gloveboxes or by standard Schlenk techniques under nitrogen. The procedures for the synthesis of **M1**-**M8** and corresponding spectra are provided in the respective section of the Supplementary Information. Tetrahydrofuran (THF), dichloromethane (DCM), and toluene were dried using a solvent purification system from MBRAUN Inertgas-Systeme GmbH. Dry dimethyl sulfoxide (DMSO), acetone, anisole, *n*-hexane, methanol (MeOH), ethyl acetate (EtOAc), and 1,4-dioxane were purchased from Acros Organics, degassed, and purged with nitrogen prior to use. Deuterated solvents for NMR spectroscopy were ordered from Oakwood Chemical and stored over molecular sieves. The dyes were purchased from MONOCURE 3D company. All the manganese complexes were prepared according to the literature procedure (see supporting information for details).

Commercial polymers were purchased from Sigma Aldrich (see Table S1 for CAS number and details) and used as received without further purification. J-B Weld 8271 Kwik was purchased from Amazon, which is used as an adhesive to steel. All post-consumer samples were first cleaned of external contamination by washing the surface thoroughly with soap and water, followed by acetone. These samples were then cut with scissors to form sheets measuring approximately 5 mm on a side. These pieces of the object were used directly as waste plastics in the hydrogenation reaction.**Characterization and processing techniques:**

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker 400 MHz NMR Spectrometer at 298 K and a Varian 500 MHz NMR Spectrometer at 383 K. All **^{1}H-NMR** experiments are reported in parts per million (ppm) and were measured relative to the signals for residual chloroform (δ = 7.26 ppm) in deuterated chloroform, or toluene (δ = 2.09 ppm) in deuterated toluene. **^{13}C-NMR** quantitative spectra were obtained at 403 K and reported in ppm are relative to tetrachloroethane (δ = 73.78 ppm) and were obtained with ^{1}H decoupling. Gas chromatography (GC) analyses were performed on a Trace 1310 chromatograph with a 29 m HP5 column. The reported GC yields, and conversions are based on a calibrated area of mesitylene as the internal standard. Molecular weights of the **PE-18-0** were determined by High Temperature Size Exclusion Chromatography (HT-SEC) analysis of the polymer samples were performed using a Tosoh EcoSec HLC-8321 High Temperature SEC System with autosampler and a differential refractive index (DRI) detector. The mobile phase used was 1,2,4-trichlorobenzene (TCB) (Fischer Scientific-HPLC Grade) which was used as-received with no inhibitor added. Other copolymers were determined by room temperature Gel Permeation Chromatography (GPC) coupled with multi-angle light scattering (MALS) using an Agilent HPLC fitted with one guard column, three PL-gel 5 μm MIXED-C gel permeation columns, a Wyatt Technology T-rEX differential refractometer, and a Wyatt Technology mini-DAWN TREOS light scattering detector (MALS). Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Auto Q20 in N_2 atmosphere. All values of T_m, T_g and ΔH_f were obtained from the second heating cycle. All cycles used heating and cooling rates of 10 °C/min. Degrees of crystallinity were calculated from ΔH_f integrations compared to the equilibrium heat of fusion for fully crystalline polyethylene of relevant molecular weight (M_w = 60.7 kDa). Thermogravimetric Analysis (TGA) was performed using a Mettler-Toledo TGA/SDTA851. Samples were heated in platinum pans from ambient temperatures to 500 °C using a heating rate of 10 °C/min under N_2 purge. Wide-Angle X-Ray Diffraction (WAXD) data was collected using a Bruker D-8 Discover DaVinci X-ray diffractometer (Cu-Kα X-ray source, line focus). A 0.6 mm divergent slit was placed on the primary beam side and a high-resolution energy-dispersive LYNXEYE-XE-T detector on the diffracted beam side during the WAXS measurements. WAXS measurements were performed with soller slits on the primary and diffracted beam side (2.5° separation). The instrument alignment was verified with NIST 1976b SRM. Small-Angle X-Ray Scattering (SAXS) data were collected using a Xenocs Xeuss 3.0 (GI)- SAXS/WAXS/USAXS with Cu- Ka X-ray source. Compression molded thin films (quenched to room temperature at ~35 °C/min) of each sample were fixed to the XY sample stage using Kapton tape. Tensile tests were performed on an Instron 5966 Universal Testing System equipped with a 10 kN load

cell using a crosshead speed of 5 mm/min until sample failure. Specimens were prepared according to ASTM D638 for Type-V standard tensile bar specimens (cross-section w = 3.18 mm). Tensile toughness (U_T; MJ m^{-3}) was determined by integration of the tensile curve. Tensile statistics were reported according to the average and standard deviation (to one significant figure) of all tensile tests, typically between four to six specimens per sample. The filaments (1.75 mm diameter) were made using a 3Devo Composer 350. The polymer is cut into small pieces and fed into the machine for processing. Heat is applied from four Heaters around the outside of the barrel. 3D printing of demonstration objects was conducted using an Original Prusa i3 MK3.

Acceptorless dehydrogenative polymerization experiments:

A Schlenk tube equipped with a stir bar was charged with ***i*Pr-PNP-Mn** (3.0 mol%), KO^{t}Bu (9.0 mol%), and toluene. The mixture was stirred at room temperature (23 ˚C) for 5 min. Subsequently, monomer was added in one portion. The Schlenk tube was placed in a preheated oil bath at 130 ºC and the mixture was stirred under nitrogen protection for 48 h. After the indicated time, the reaction mixture was precipitated by pouring the solution into methanol at room temperature, washed with methanol three times and dried in a vacuum oven at 100 ˚C to obtain the pure polymers.

Chemical depolymerization experiments:

A glass vial containing a stir bar was sequentially charged with polymer, ***i*Pr-PNP-Mn** (3.0 mol%**)**, KO^{t}Bu (9.0 mol%), and toluene under nitrogen atmosphere. Then, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate, which was then placed into a 300 mL autoclave. Once sealed, the autoclave was purged 5 times with hydrogen, then pressurized to 40 bar of H_2 and placed into an aluminum block, then heated to 140 ºC. After 24 h, the autoclave was cooled in an ice bath, and the remaining gas was carefully released. Finally, the reaction mixture was diluted with ethyl acetate and analyzed by GC using mesitylene as internal standard.

Large-scale depolymerization necessitates the use of a 2.0 L autoclave, with elevated hydrogen pressure and intensified reaction conditions. For the depolymerization of colored polymers, a higher reaction temperature and pressure were required (150 ºC and 50 bar of H_2). See supporting information for more details.

Separation from commercial/waste plastics:

A glass vial containing a stir bar was sequentially charged with waste/commercial plastic, our synthesized polymers, ***i*Pr-PNP-Mn** (3.0 mol%), KO^{t}Bu (9.0 mol%), and toluene under nitrogen atmosphere. Then,

the reaction vial was placed into a 2.0 L autoclave. Once sealed, the autoclave was purged 5 times with hydrogen, then pressurized to 40 bars of H_2 and placed into an oil bath, then started heating to the desired temperature. After 48 h, the autoclave was cooled to room temperature, and the remaining gas was carefully released. The reaction mixture is filtered under nitrogen protection to obtain decomposed waste polymers and reduced monomers. Neat linear and branched diol can be recovered by crystallization at 0 ºC.

PET exhibited minimal depolymerization products at 140˚C while the other waste/commercial plastics remained unaltered and can be removed from the monomer solution. However, upon reducing the reaction temperature to 110˚C, no depolymerization of PET was observed.

References

1. Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, e1700782 (2017).
2. Galli, P. & Vecellio, G. Polyolefins: The most promising large-volume materials for the 21st century. *J. Polym. Sci. A Polym. Chem*. **42**, 396–415 (2004).
3. Westlie, A. H., Chen, E. Y. -X., Holland, C. M., Stahl, S. S., Doyle, M., Trenor, S. R. & Knauer, K. M. Polyolefin innovations toward circularity and sustainable alternatives. *Macromol. Rapid. Commun.* **43**, 2200492 (2022).
4. Qiao, J., Guo, M., Wang, L., Liu, D., Zhang, X., Yu, L., Song, W. & Liu, Y. Recent advances in polyolefin technology. *Polym. Chem*., **2**, 1611–1623 (2011).
5. Yeung, C. W. S., Teo, J. Y. Q., Loh, X. J. & Lim, J. Y. C. Polyolefins and polystyrene as chemical resources for a sustainable future: challenges, advances, and prospects. *ACS Materials Lett.* **3**, 1660–1676 (2021).

6. Chamas, A., Moon, H., Zheng, J., Qiu, Y., Tabassum, T., Jang, J. H., Abu-Omar, M., Scott, S. L. & Suh, S. Degradation rates of plastics in the environment. *ACS Sustainable Chem. Eng.* **8**, 3494–3511 (2020).
7. MacLeod, M., Arp, H. P. H., Tekman, M. B. & Jahnke, A. The global threat from plastic pollution. *Science* **373**, 61–65 (2021).
8. Pabortsava. K. & Lampitt, R. S. High concentrations of plastic hidden beneath the surface of the atlantic ocean. *Nat. Commun.* **11**, 4073 (2020).
9. Lebreton, L. & Andrady, A. Future scenarios of global plastic waste generation and disposal. *Palgrave Commun.* **5**, 6 (2019).
10. Stubbins, A., Law, K. L., Muñoz., S. E., Bianchi, T. S. & Zhu, L. Plastics in the Earth system. *Science* **373**, 51–55 (2021).
11. Jehanno, C., Alty, J. W., Roosen, M., Meester, S. D., Dove, A. P., Chen, E., Y.-X., Leibfarth, F. A. & Sardon, H. Critical advances and future opportunities in upcycling commodity polymers. *Nature* **603**, 803–814 (2022).
12. Zhao, X., Korey, M., Li, K., Copenhaver, K., Tekinalp, H., Celik, S., Kalaitzidou, K., Ruan, R., Ragauska, A. J. & Ozcan, S. Plastic waste upcycling toward a circular economy. *Chem. Eng. J.* **428**, 131928 (2022).
13. Chen, X., Wang, Y. & Zhang, L. Recent progress in the chemical upcycling of plastic wastes. *ChemSusChem* **14**, 4137–4151 (2021).
14. Schwab, S. T., Baur, M., Nelson, T. F. & Mecking S. Synthesis and deconstruction of polyethylene-type materials. *Chem. Rev.* **124**, 2327–2351 (2024).

15. Li, X., Mahadas, N. A., Zhang, M., DePodesta, J., Stefik, M. & Tang, C. Sustainable high-density polyethylene via chemical recycling: From modification to polymerization methods. Polymer 295, 126698 (2024).

16. Lopez, G., Artetxe, M., Amutio, M., Bilbao, J. & Olazar, M. Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review. *Renew. Sust. Energ. Rev.* **73**, 346–368 (2017).

17. Galadima, A., Masudi, A. & Muraza. O. Towards low-temperature catalysts for sustainable fuel from plastic: A review. *J. Environ. Chem. Eng.* **9**, 106655 (2021).

18. Arroyave, A., Cui, S., Lopez, J. C., Kocen, A. L., LaPointe, A. M., Delferro, M. & Coates, G. W. Catalytic chemical recycling of post-consumer polyethylene. *J. Am. Chem. Soc.* **144**, 23280–23285 (2022).

19. Kocen, A. L., Cui, S., Lin, T. -W., LaPointe, A. M. & Coates, G. W. Chemically recyclable ester-linked polypropylene. *J. Am. Chem. Soc.* **144**, 12613–12618 (2022).

20. Jang, Y., Nguyen, S. & Hillmyer, M. A. Chemically recyclable linear and branched polyethylenes synthesized from stoichiometrically self-balanced telechelic polyethylenes. *J. Am. Chem. Soc.* **146**, 4771–4782 (2024).

21. Han, X.-W., Zhang, X., Zhou, Y., Maimaitiming, A., Sun. X.-L., Gao, Y., Li, P., Zhu, B., Chen. E. Y.-X., Kuang, X. & Yong, T. Circular olefin copolymers made de novo from ethylene and α-olefins. *Nat. Commun.* **15**, 1462 (2024).

22. Si, G., Li, C., Chen, M. & Chen, C. Polymer multi-block and multi-block^{+} strategies for the upcycling of mixed polyolefins and other plastics. *Angew. Chem. Int. Ed.* **62**, e202311733 (2023).

23. Johnson, A. M. & Johnson, J. A. Thermally robust yet deconstructable and chemically recyclable high-density polyethylene (HDPE)-like materials based on Si−O bonds. *Angew. Chem. Int. Ed.* **135**, e202315085 (2023).

24. Si, G. & Chen, C. Cyclic–acyclic monomers metathesis polymerization for the synthesis of degradable thermosets, thermoplastics and elastomers. *Nat. Synth*. **1**, 956–966 (2022).

25. Häußler, M., Eck, M., Rothauer, D. & Mecking, S. Closed-loop recycling of polyethylene-like materials. *Nature* **590**, 423–427 (2021).

26. Nelson, T. F., Rothauer, D., Sander, M. & Mecking, S. Degradable and recyclable polyesters from multiple chain length bio- and waste-sourceable monomers. *Angew. Chem. Int. Ed.* **62**, e202310729 (2023).

27. Stille, J. K. Step-growth polymerization. *J. Chem. Educ.* **58**, 862–866 (1981).

28. Zhao, Y., Rettner, E. M., Harry, K. L., Hu, Z., Miscall, J., Rorrer, N. A. & Miyake, G. M. Chemically recyclable polyolefin-like multiblock polymers. *Science* **382**, 310–314 (2023).

29. Beuhler, A. A "Game-Changing" C18 Diacid for the Plastics Industry? *Plast. Eng.* **70**, 32– 35 (2014).

30. Chikkali, S. & Mecking, S. Refining of plant oils to chemicals by olefin metathesis. *Angew. Chem., Int. Ed.* **51**, 5802– 5808 (2012).

31. Gonzalez-de-Castro, A., Cosimi, E., Aguila, M. J. B., Gajewski, P., Schmitkamp, M., de Vries, J. G. & Lefort, L. Long-chain α–ω diols from renewable fatty acids via tandem olefin metathesis–ester hydrogenation. *Green Chem.,* **19**, 1678-1684 (2017).

32. Hoyle, C. E. & Bowman, C. N. Thiol–ene click chemistry. *Angew. Chem. Int. Ed.* **49**, 1540–1573 (2010).

33. Pepels, M. P. F., Koeken, R. A. C., der Linden, S. J. J., Heise, A. & Duchateau, R. Mimicking (linear) low-density polyethylenes using modified polymacrolactones. *Macromolecules* **48**, 4779–479 (2015).33

34. Nguyen, D. H., Trivelli, X., Capet, F., Paul, J., Dumeignil, F. & Gauvin, R. M. Manganese pincer complexes for the base-free, acceptorless dehydrogenative coupling of alcohols to esters: development, scope, and understanding. *ACS Catal* **7**, 2022–2032 (2017).

35. Das, U. K., Ben-David, Y., Leitus, G., Diskin-Posner, Y. & Milstein, D. Dehydrogenative cross-coupling of primary alcohols to form cross-esters catalyzed by a manganese pincer complex. *ACS Catal*. **9**, 479–484 (2019).

36. Gandeepan, P., Müller, T., Zell, D., Cera, G., Warratz, S. & Ackermann, L. 3d transition metals for C–H activation. *Chem. Rev.* **119**, 2192–2452 (2019).

37. Ysart, G., Miller, P., Crews, H., Robb, P., Baxter, M., De L'Argy, C., Lofthouse, S., Sargent, C. & Harrison, N. Dietary exposure estimates of 30 elements from the UK Total Diet Study. *Food Additives & Contaminants* **16**, 391–403 (1999).

38. Filonenko, G. A., Putten, R., Hensen, E. J. M. & Pidko, E. A. Catalytic (de)hydrogenation promoted by non-precious metals – Co, Fe and Mn: recent advances in an emerging field. *Chem. Soc. Rev.*, **47**, 1459-1483 (2018).

39. Mukherjee, A. & Milstein, D. Homogeneous catalysis by cobalt and manganese pincer complexes. *ACS Catal*. **8**, 11435–11469 (2018).

40. Tran, Q. H., Neidhart, E. K., Sheiko, S. S., Bras, W. & Leibfarth, F. A. Polyolefin ionomer synthesis enabled by C–H thioheteroarylation. *Macromolecules* **56**, 8920–8927 (2023).

41. Tsvankin, D. Y., Zubov, A. & Kitaigorodskii, A. I. Calculation of long periods in polymers and determination of the sizes of crystallites and amorphous regions. *J. Polym. Sci., Part C: Polym. Symp.* **16**, 4081–4091 (1967).

42. Herrera, C., Ysinga, K. J. & Jenkins, C. L. Polysulfides synthesized from renewable garlic components and repurposed sulfur form environmentally friendly adhesives. *ACS Appl. Mater. Interfaces* **11**, 35312–35318 (2019).

43. Ellison, M. M. & Taylor, L. T. Sulfur versus non-sulfur containing polyimide adhesives for bonding steel. *J. Adhes.* 60, 51–69 (1997).

44. Ragaert, K., Delva, L. & van Geem, K. Mechanical and chemical recycling of solid plastic waste. *Waste Manag.* **69**, 24–58 (2017).

45. Barnard, E., Arias, J. J. R. & Thielemans, W. Chemolytic depolymerisation of PET: a review. *Green Chem*. **23**, 3765–3789 (2021).

46. Schirmeister, C. G., Hees, T., Licht, E. H. & Mülhaupt, R. 3D printing of high density polyethylene by fused filament fabrication. *Addit. Manuf.* **28**, 152–159 (2019).

Data availability Full experimental details and the data supporting the findings of this study are available within the article and its Supplementary Information. Source data are provided with this paper.

Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests.

Correspondence and requests for materials/raw data should be addressed to the corresponding authors (garret.miyake@colostate.edu).

Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements We thank Dr. Z. Zhang for insightful discussions throughout the lap-shear adhesion testing. This work was supported by the National Institutes of Health under award no. R35GM144356 and RePLACE (Redesigning Polymers to Leverage a Circular Economy) funded by the Office of Science of the US Department of Energy through award no. DE-SC0022290. Funding for N.A.R. and J.M. was provided in part by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office (AMO) and Bioenergy Technologies Office (BETO). This work was performed as part of the BOTTLE™ Consortium and was supported by AMO and BETO under contract no. DE-AC36-08GO28308 with the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC. The authors thank the Analytical Resources Core (RRID: SCR_021759) and the SAMD Core (RRID: SCR_022002) at Colorado State University for instrument access and training. G.M.M. acknowledges support from The Camille & Henry Dreyfus Foundation through a Camille Dreyfus Teacher-Scholar Award and the Dr. Robert Williams Professorship in Organic Chemistry at Colorado State University.

Author contributions X. L., Z.H., and G.M.M. conceived the idea. X.L. and Z.H. designed and conducted experiments and analyzed results. X.L., Z. H., E. M. R., J.M., and N.A.R. performed characterization and analyzed results. X.L. and K.L.H synthesized the required complexes. X.L. wrote initial manuscript and supplemental materials. All authors read and edited the manuscript. G. M. M. directed the project. X.L. and Z.H. contributed equally.