Dehydrogenated Polyethylene from Discarded Plastics as a Synthon for Functional Polyolefins

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ABSTRACT: Many valuable specialty chemicals and drug candidates rely on synthesizing reactive intermediates to generate the final product(s). An approach that leverages C–H activation chemistry to achieve chemically active reactive handles for polymer diversification is desirable. This report describes the synthesis and functionalization of dehydrogenated high-density polyethylene (HDPE) from discarded post-consumer plastic via acceptor-less Ir-pincer-catalyzed non-oxidative dehydrogenation followed by acid-catalyzed hydroamination and hydroalkoxylation. The final products show significant material property changes with tunability and scalability through the incorporation of the olefin. This method highlights the potential value of dehydrogenated intermediates as platforms to enable carbon circularity and polyolefin end-of-life management strategies.

End-of-life management of plastic waste is a grand challenge in sustainability.[1] Given the scale of waste polyolefins, in particular, there exists an opportunity for waste polyethylene as a feedstock in chemical manufacturing.[2] Traditionally, functional polyolefins are synthesized through the copolymerization of ethylene and a polar vinyl monomer[3] (**Figure 1A**) or post-polymerization modification (PPM)[4] of virgin polyethylene. There are ample reports for obtaining specific materials; however, both processes have downsides. Namely, radical copolymerization strategies suffer limited comonomer variety, catalyst stability, and uncontrolled branching,[3] while catalytic processes possess greater comonomer variability and control they are limited in their reactivity such as polar vinyl coordination to the metal center and greatly retarded rates of chain growth.[5] PPM strategies rely on C–H activation and are often nonselective,[6] limited in functional group scope, and potentially deconstructive regarding polymer size fidelity.[6] Approaches that address some of these problems include amidyl radical functionalization[7] (**Figure 1B**) and Ru-catalyzed oxidation[8] (**Figure 1C**), or pre-installed functional handles for PPM from specialized monomers (**Figure 1D**) via ring-opening metathesis polymerization (ROMP).[9, 10] However, synthesizing monomer, reagent or catalyst is often limiting.[11] A permutational method that combines the benefits of both processes is thus desirable. An example of this strategy is the functionalization of oxidized low-density polyethylene (LDPE) (**Figure 1C**).[12] This approach identifies a key workaround for valorizing waste plastic material through a reactive chemical intermediate. Recent work showed that Ir-pincer catalysts dehydrogenate untreated waste HDPE to form unsaturated HDPE (deHDPE, **P0**) with tunable degrees of unsaturation and negligible formation of aromatic products.[13] The degree of unsaturation is variable based on reaction time and catalyst loading and readily undergoes metathesis to form telechelic polyethylene macromonomers capable of poly-esterification for fully recyclable HDPE-like materials.[14] Thus, **P0** presents a unique opportunity for functionalizing polyolefins via a reactive intermediate (**Figure 1E**).

There is a library of olefin functionalization reactions[15-17] with activated olefins or intramolecular cyclizations predominating.[15] Acid-catalyzed additions of alcohols to olefins are a classic reaction in organic

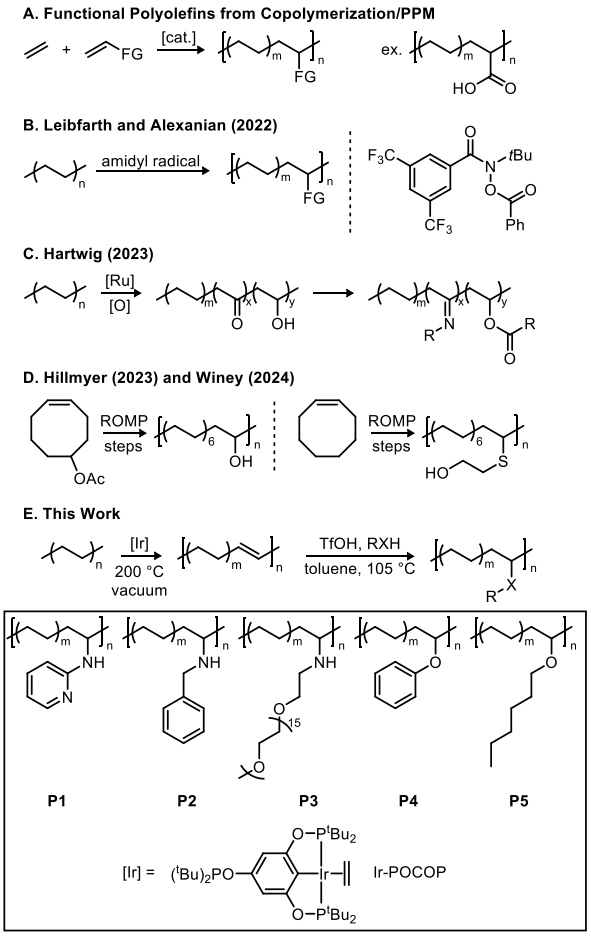

Figure 1. (A) Synthesis of functional olefins via copolymerization, (B) radical functionalization, (C) ROMP of functional cyclooctenes, (D) transition metal-catalyzed oxidation, and (E) dehydrogenated HDPE as an intermediate.

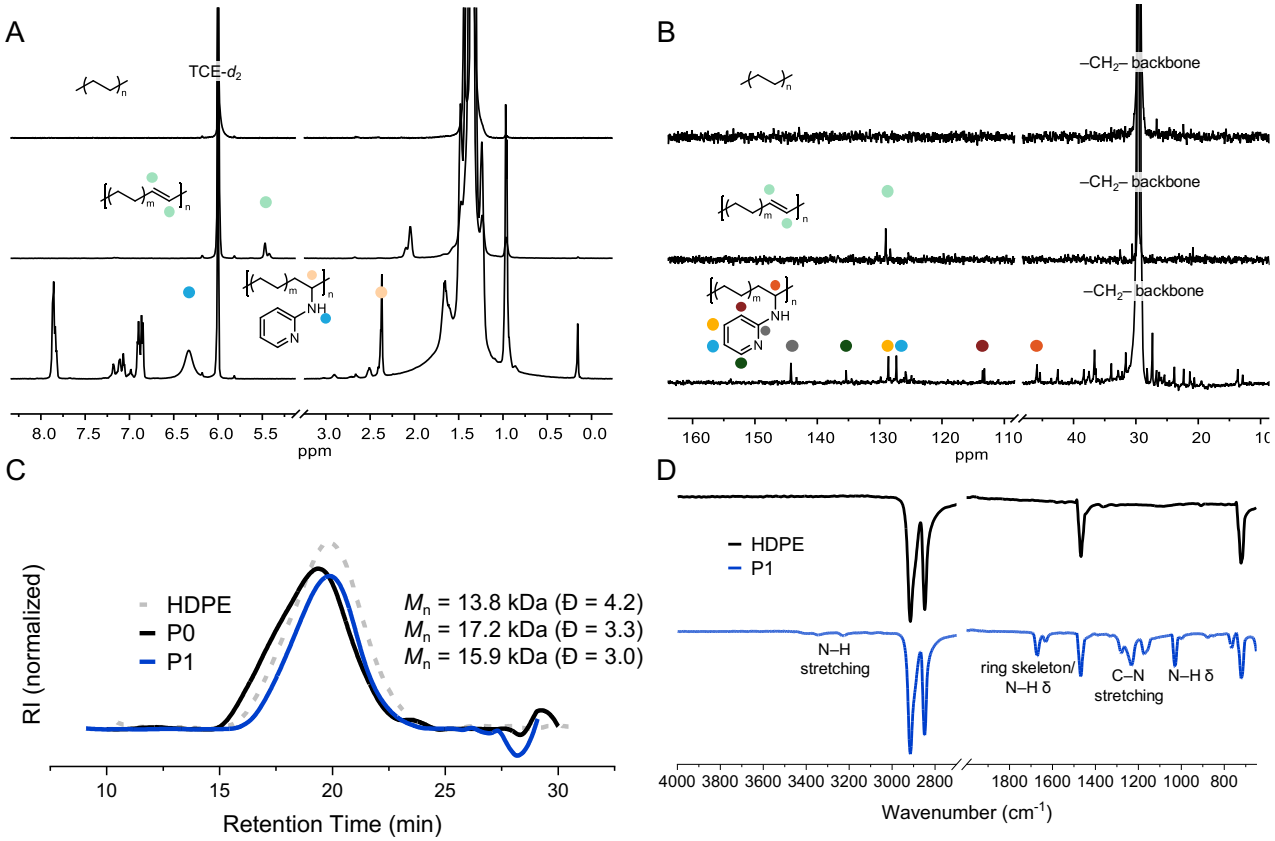

Figure 2. (A) ^{1}H NMR of **P1**, **P0**, and HDPE. (B) ^{13}C NMR of **P1**, **P0**, and HDPE. (C) GPC Chromatogram of **P1**, **P0**, and HDPE; signal after 25 min is the sample injection. (D) FTIR of **P1** and HDPE (see **Figure S29** for FTIR of **P0**).

chemistry,[18] and their amine counterpart was identified by Hartwig et al. for aliphatic olefins.[19, 20] Note that the amination of polyolefins has commercial relevance demonstrated by their use as blend compatibilizers,[21] corrosion inhibitors[22], and as polar additives,[23] thus drawing attention to the acid-catalyzed functionalization of **P0**.

Dehydrogenated HDPE (**P0**) was synthesized via a previously reported Ir-pincer complex (Ir-POCOP, **Figure 1E**) from untreated waste HDPE sourced from a water jug.[13] This one-step, solvent-free reaction occurs at 200 °C under vacuum to remove H_2 and yields approximately 0.60 mol % olefins per chain via ^{1}H NMR analysis (See SI for calculation details). The Ir-POCOP was resistant to any additives or impurities present in the untreated waste HDPE. **P0** was combined with 5 equivalents of TfOH and 10 equivalents of 2-aminopyridine (**1**) (with respect to olefin) in toluene ([**P0**] = 1.0 M) at 105 °C for 12 hours. ^{1}H NMR spectroscopy showed the disappearance of the internal olefin signals (**Figure 2A**), while ^{13}C NMR demonstrated the appearance of the methylene carbon at 45.89 ppm (**Figure 2B**), supporting hydroamination product formation. Despite the high loadings of TfOH to olefin, the process was non-destructive via GPC (**Figure 2C**). FTIR demonstrated characteristic secondary N–H stretching at ~3200 cm^{-1}, an admixture of pyridinyl ring skeleton stretching and secondary N–H δ (deformation) stretching at ~1650 cm^{-1}, and strong sharp bands at ~1200 cm^{-1} indicative of C–N stretching, consistent with secondary amines (**Figure 2D**).[24] Various hydroarylation, hydroamination, and hydroalkoxylation reactions use early transition metal triflates as catalysts[19]; $Zn(OTf)_2$, $Cu(OTf)_2$, and $Sc(OTf)_3$), were screened for the hydroamination of **P0** (**Table S1**) with **1** at 105 ° C for 12 hours in toluene in air with no reaction.[19]

The hydroamination scope was extended to aliphatic amines such as methylbenzylamine which exhibited similar reactivity (**Table 1**) with the formation of the internal methylene carbon adjacent to the amine nucleophile at 38.34 ppm (**Figure S5**). The direct reaction of aliphatic amines contrasts with other reports where the inherently lower reactivity of aliphatic amines precludes their reactivity.[25] The extension to amine-PEGylated **3**, resulted in complete conversion of the olefin as confirmed via ^{1}H and ^{13}C NMR spectroscopy (**Figure S7-S9**). Additionally, FTIR spectroscopy exhibited characteristic ether asymmetric stretching at 1164 cm^{-1} of the H_2C–O–CH_2 moiety in noncyclic ethers and secondary amine C–N asymmetric stretching at 1246 cm^{-1} (**Figure S31**).[24]

Other substrates such as benzamides, carboxylic acids, alcohols, and more hindered amines were investigated. Phenol and 1-hexanol underwent complete conversion as evidenced by ^{1}H and ^{13}C NMR spectroscopy (**Figure S10-S13**). FTIR analysis indicates the formation of ether linkages with distinctive stretching at 1250 cm^{-1} for both **P4** and **P5** (**Figure S32** and **Figure S33** respectively). Additionally, for **P4**, there are clear

Table 1. Amination optimization and catalyst study.[a]

Entry	M_n (kg mol^{-1})[b]	$Đ$[b]	Conversion[c]
HDPE	13.9	4.2	–
P0	17.2	3.3	–
P1	15.9	3.0	100 %
P2	12.8	3.1	100 %
P3	13.8	3.8	75 %

[a] General conditions: 5 equiv of catalyst to olefin, 10 equiv of nucleophile to olefin, 105 °C, 12 hours, [polymer] = 1 M. [b] Calculated from narrow standard calibration with GPC. [c] Calculated from initial olefin content via ^{1}H NMR.

aromatic overtones at ~1710 cm^{-1} that are blue-shifted due to the increased substitution following functionalization (**Figure 3** bottom) (See SI for full characterization). Secondary aromatic amines such as *p*-tolueneamine did not react with **P0**; additionally, carboxylic acids and benzamides results in no reaction as supported by ^{13}C NMR, contrasting with a prior report.[26] The addition of benzoic acid, 4-hydroxybenzoic acid, and benzamide resulted in the precipitation of the unfunctionalized polymer, most likely inhibiting any reactivity with the acidic functionality.

The thermal properties of the materials were evaluated via differential scanning calorimetry (DSC). DSC indicated that introducing aromatic functionality directly a to the backbone resulted in a negligible change in the melting temperature (T_m) of the polymer but resulted in a decrease in the enthalpy of melting from 272 J g^{-1} for HDPE to 179 J g^{-1} and 170 J g^{-1} for **P1** and **P4** respectively (Figure 4A). Introducing polyethylene glycol and longer-chain polar aliphatic functionality resulted in significant shifts to lower T_m of 127 °C and 131 °C for **P3** and **P5**, respectively. The presence of short chain branching also induced slight decreases in the degree of crystallization (163 J g^{-1} and 143 J g^{-1} for **P3** and **P5**, respectively); however, the PEGylated **P3** showed less of a decrease than the bulky, planar, **P1** and **P4** materials. In total, the introduction of polar functionality to dehydrogenated HDPE results in disparate changes to the thermal profile of the resultant materials. The general trend indicates that the T_m of the material is dependent on the flexibility of the added pendant group as seen with a methylene spacer in **P2** versus the more planar **P1**.

Given the high selectivity, the easy tunability of the Ir-catalyzed dehydrogenation was hypothesized to enable varying degrees of functionalization for **P5**. By increasing the catalyst loading from 0.033 mol% to 0.132 mol% the degree of unsaturation increased from 0.26 % to 0.45 %. Upon functionalization of the modulated materials, the T_m decreased from 130 °C to 126 °C (**Figure 4B** top). Dynamic storage (G') and loss moduli (G") were determined from a flat punch nanoindentation testing. The modulated **P5** materials were prepared by melt pressing into a puck followed by gluing them to the indenter holder (see SI). The modulated **P5** materials showed an increase in the storage moduli concurrent with increasing functionalization at room temperature. Interestingly, the loss moduli of the material decreased as the degree of functionalization increased, with the highest degree of functionalization (0.45 %) showing

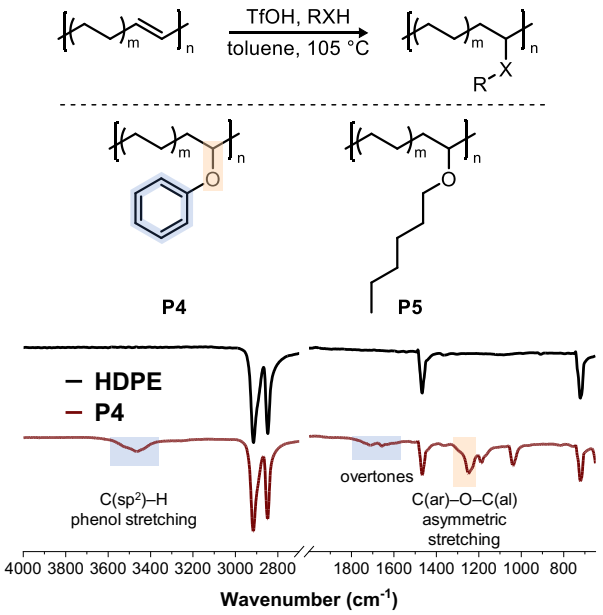

Figure 3. (Top) Substrate scope for TfOH catalyzed dehydrogenated polyolefin functionalization strategy. (Bottom) FTIR of **P4** and **P5**.

significant deviations from the lightly (0.26 %) functionalized material. This shift is also in line with the decrease in T_m (**Figure 4B** top). Additionally, the indentation modulus (approximately Young's Modulus) and hardness (reported as Vickers hardness) were determined from unload and load curves using the ISO 14577 method drawing on Oliver and Parr's work.[27, 28] The modulated **P5** materials showed a distinct trend in line with the viscoelastic property changes and T_m modulation with the more functionalized materials possessing greater indentation moduli and hardness.

The tensile properties of **P1** and **P2** showed a marked increase in the tensile strength from HDPE, with a final tensile strength of 1.40 and 1.19 times greater than HDPE for **P1** and **P2**, respectively. The elongation at break for **P1** (890 ± 170%) and **P2** (963 ± 114%) was significantly greater than that for HDPE (790 ± 298%) (**Figure 4D**). **P4** also demonstrated similar tensile strength with decreased elongation at break (1.28 times greater and 689 ± 370% respectively). The softer **P3** and **P5** showed decreased tensile strength (0.78 and 0.74 times lesser, respectively) and elongation at break (298 ± 136% and 205 ± 87% respectively) compared to HDPE. Further mechanical testing indicates that the introduction of bulky substituents to HDPE resulted in a significant increase in indentation modulus and hardness, as seen by **P1** and **P4** (**Figure 4E**). The functionalization of HDPE with flexible **P2**, **P3**, and **P5** resulted in either minimal changes to the indentation modulus and hardness or mild decreases. Interestingly, there was a limited correlation between the indentation modulus and the hardness of the materials. **P2** demonstrated a sizable decrease in the indentation modulus but an increase in the hardness of the material. The modulus of elasticity is an intrinsic material property that is related to how the polymer chain interacts with itself in the bulk, whereas the hardness is a result of processing conditions and parameters. Thus, given that these materials were processed identically, it is apparent that there is a multi-pronged effect of

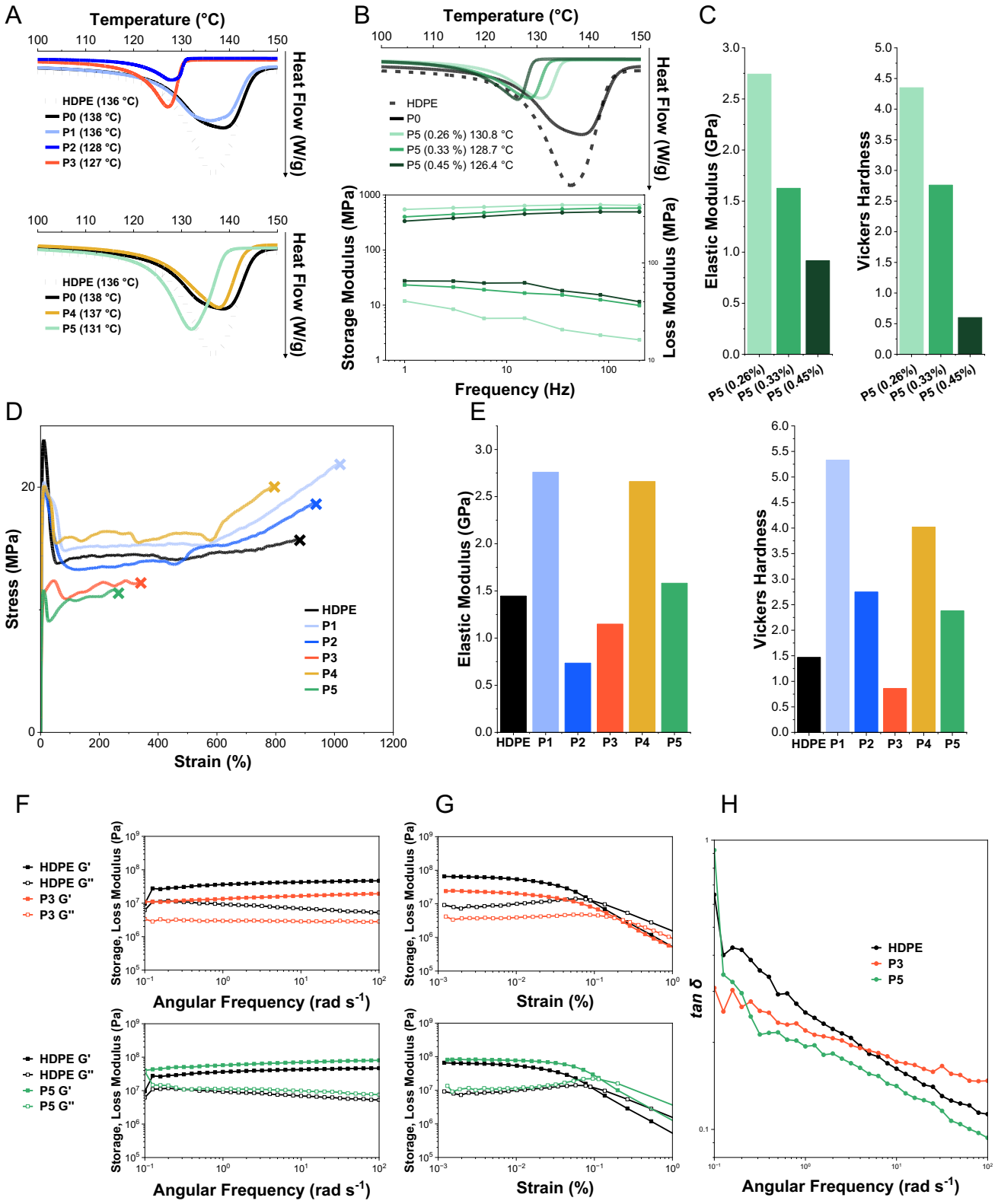

Figure 4. (A) Differential scanning calorimetry (DSC) thermogram of **P0** – **P5**. (B) DSC thermogram of **P5** modulation. (C) Storage and loss moduli versus frequency for **P5** modulation study as assessed by nanoindentation. (D) Tensile testing of **P1** and **P2**. (E) Hardness and elastic modulus analysis of functional polyolefins as assessed by nanoindentation. (F) Amplitude sweeps of **P3** and **P5** via rheology with angular frequency fixed at 10 rad s^{-1} at 40 °C. (G) Frequency sweep of **P3** and **P5** via rheology fixed at 0.01 % strain rate at 40 °C. (H) tan δ plot of HDPE, **P3**, and **P5**.

functionality on the material properties. Specifically, bulky, inflexible functionality increases the ability of the material to resist elastic deformation and surface penetration, while greater flexibility has the opposite effect. The increase in elastic modulus and hardness for **P1** and **P4** is postulated to arise due to the decreased free rotation and minimal crystallinity changes

compared to **P2**, **P3**, and **P5**.[29] The increased flexibility and polar side chain interaction are postulated to decrease the elastic modulus and hardness for **P2**, **P3**, and **P5** compared to HDPE, **P1**, and **P4** via hindering crystallization resulting in softer materials.

Rheological studies were conducted at three temperatures, 25 °C, 40 °C, and 80 °C with a twin plate apparatus. **P3** and **P5** possessed a linear viscoelastic region at slightly higher strains than HDPE, indicating that the materials have slightly more elastic characteristics than HDPE. Frequency sweeps of the material showed little to no change in viscoelastic properties from the parent material, demonstrating that the functional materials possess similar solid-like characteristics. Analysis of the tan δ values shows a negligible difference between **P5** and **HDPE**. However, the softer **P3** showed greater dampening at higher frequencies, indicating a greater ability to dissipate elastic strain during deformation. This is consistent across the entire temperature range (see SI) and is hypothesized to arise from the flexibility and ability to rearrange under deformation, like the changes in elastic moduli.

Past reports of polyolefin functionalization processes have shown that the incorporation of polar functionality into polymers can have mixed effects. For example, Hartwig et al. focused on the modification of LDPE and found that the presence of free polar functionality is not always indicative of material properties changes.[12, 30] Specifically, generic alcohol containing LDPE showed no discernible difference in tensile strength, elongation at break, or toughness compared to pure LDPE. However, the introduction of a carbonyl functionality, regardless of steric bulk or planarity (propyl side chain versus phenyl ring), resulted in significant increases in toughness and elongation at break. This report, however, suggests that for HDPE, the variation from phenol functional to pyridinyl functional does not lead to meaningful mechanical changes, indicating that any comparison across different parent polymers is moot. Additionally, rheological measurements indicate similar reports to this work where the addition of polar functionalization does not fundamentally change the viscoelastic behavior. It is important to note that there is no discernible trend or structure-property relationship in the literature, which further underscores the complexity of this topic.[31]

In conclusion, these results demonstrate the facile ability to vary the thermal and mechanical properties via **P0** synthon. Notably, further work will focus on improving catalyst reactivity, scalability, and reactor design. Additionally, it should be noted that upcycling plastic waste faces several hurdles; most notably the requirement to enter the recycling pathway regardless, upcycled materials would be a significantly smaller product area, and general chemical upcycling most likely will have greater net costs (energy, environmental, etc.) than virgin materials.[32] Critically, this work highlights how bulky, sterically hindered functional materials generally possess equivalent thermal properties to their parent material while being tougher, having greater elongation at break, and generally greater tensile strength. At the same time, more flexible and freely rotating functionality decreases the thermal properties of the parent polymer (specifically T_m) to a point where prior reports indicate that regularly functional materials with high degrees of functionalization vary dramatically. Additionally, flexible polymers possess significantly different mechanical properties than their parent material. This report indicates the viability of dehydrogenated polyolefins from abundant plastic waste as an intermediate for functional materials with easy tunability and potentially wide-ranging thermal and mechanical properties.

ASSOCIATED CONTENT

The Supporting information is available free of charge on the Publications website. Experimental details; materials and methods; NMR spectra; GPC chromatograms; DSC thermograms; DMA thermograms; rheometry thermograms; nanoindentation thermograms.

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Author Contributions

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