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C−H Functionalization of Polyolefins to Access Reprocessable Polyolefin Thermosets

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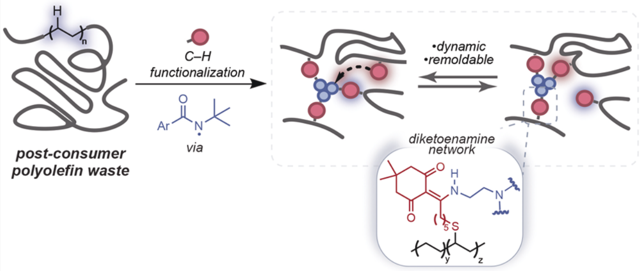
ABSTRACT: Upcycling plastic waste into reprocessable materials with performance-advantaged properties would contribute to the development of a circular plastics economy. Here, we modify branched polyolefins and postconsumer polyethylene through a versatile C−H functionalization approach using thiosulfonates as a privileged radical group transfer functionality. Cross-linking the functionalized polyolefins with polytopic amines provided dynamically cross-linked polyolefin networks enabled by associative bond exchange of diketoenamine functionality. A combination of resonant soft X-ray scattering and grazing incidence X-ray scattering revealed hierarchical phase morphology in which diketoenamine-rich microdomains phase-separate within amorphous regions between polyolefin crystallites. The combination of dynamic covalent cross-links and microphase separation results in useful and improved mechanical properties, including a ∼4.5-fold increase in toughness, a reduction in creep deformation at temperatures relevant to use, and high-temperature structural stability compared to the parent polyolefin. The dynamic nature of diketoenamine cross-links provides stress relaxation at elevated temperatures, which enabled iterative reprocessing of the dynamic covalent polymer network with little cycle-to-cycle property fade. The ability to convert polyolefin waste into a reprocessable thermoformable material with attractive thermomechanical properties provides additional optionality for upcycling to enable future circularity.



polyolefin C–H functionalization • upcycling to reprocessable thermosets • tunable properties

■ INTRODUCTION

Accumulation of plastic in the environment is a contemporary societal and ecological problem as a result of end-of-life plastic waste management that is poorly matched with the scale of global plastic production.[1−5] Using plastic waste as a starting material to synthesize performance-advantaged materials (i.e., upcycling) has the benefit of diverting waste from landfills and lowering the dependence on petrochemical resources.[4,6−9] Polyolefins in particular represent advantageous substrates for polymer upcycling because they account for a large fraction (>50%) of global plastic production and are particularly challenging to recycle.[1,10−13] The C−H functionalization of polyolefins has resulted in materials that have diversified properties.[14−25] Upcycling polyolefins into reprocessable substitutes for materials that are currently nonrecyclable would provide an approach for enhanced waste utilization.[26]

Cross-linked polymers are robust high-volume materials with permanent covalent bonds between polymer chains, which preclude reprocessing; therefore, these materials are landfilled after use.[27,28] Polymer networks whose cross-links undergo reversible exchange reactions have been proposed as versatile replacements for many difficult-to-recycle thermoplastics and thermosets.[28−46] Polydiketoenamine (PDK) dynamic covalent networks in particular are a versatile class of materials whose chemistry can be tailored to access a range of properties while remaining mechanically reprocessable and chemically recyclable.[47−51] Dynamic covalent polymer networks, however, are often built from petrochemical resources and yield under applied strain (i.e., creep) at temperatures relevant to their desired application.[52]

We envisioned that placing dynamic diketoenamine functional groups onto polyolefins could enable access to performance-advantaged reprocessable polyolefin thermosets and would represent an example of upcycling plastic waste to a next generation of reprocessable polymeric materials (Figure 1A). A key challenge to placing regenerative functionality onto polyolefins postproduction is the high bond strength of aliphatic C−H bonds.[22] This has traditionally been overcome by using peroxide-mediated hydrogen atom transfer (HAT) under harsh reaction conditions, which leads to a deterioration in polymer properties (Figure 1B).[28,53−55] Consequently,

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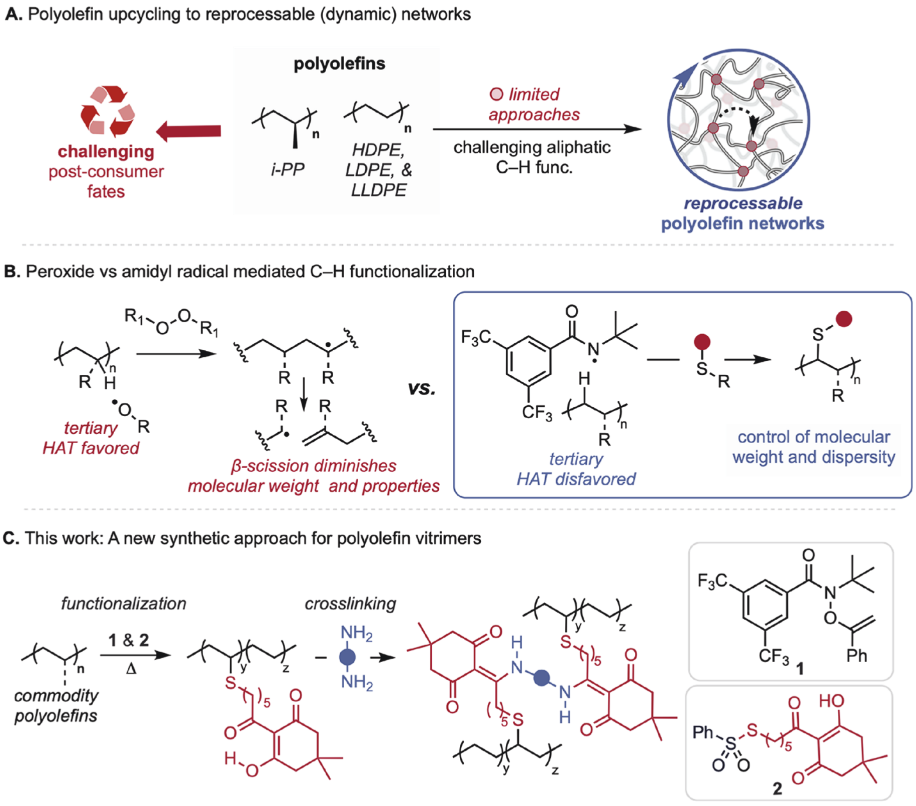


Figure 1. C−H functionalization of polyolefins to access dynamic networks. (A) Upcycling to dynamic polyolefin networks as an alternative to nonrecyclable permanent thermosets is a desirable but understudied approach. (B) Amidyl radical mediated C−H functionalization has advantages compared to peroxide mediated C−H functionalization. (C) Diketoenamine dynamic covalent polyolefin networks (DCPNs) through selective C−H functionalization to access reprocessable polyolefin thermosets.

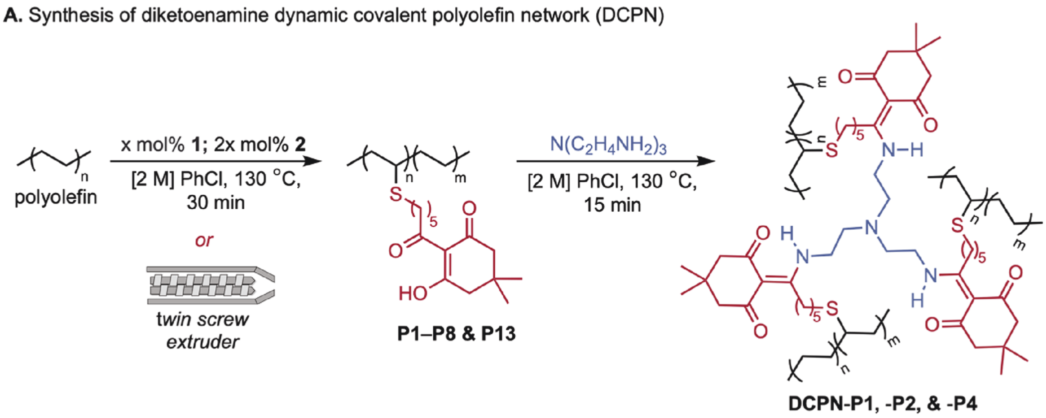
approaches to dynamic covalent polyolefin networks through post polymerization modification have been limited and, when pursued, have yielded thermosets with partial network connectivity and a corresponding high density of plasticizing chains due to peroxide mediated HAT.[56−60] The lack of structural control inherent to peroxide mediated HAT has convoluted studies to understand how dynamic cross-links impact the phase behavior, crystallinity, mechanical properties, and reprocessability of dynamic covalent polyolefin networks (DCPNs).

We recently identified an *O*-alkenylhydroxamate reagent (**1**) whose steric demand around nitrogen and strong thermodynamic driving force for HAT result in selective and efficient functionalization, with an observed lack of chain coupling and scission events (Figure 1B).[16,61] We hypothesized that **1**, when combined with a triketone radical trap with fast chain-transfer kinetics (**2**), would provide a platform to access DCPNs with discrete control over polymer structure and high network connectivity (Figure 1C). Controlled placement of diketoenamine functionality would enable a more holistic understanding of structure−property−performance relationships of DCPNs and evaluation of their potential as sustainable alternatives to current single-use polyolefin thermoplastics and thermosets.

Herein, we synthesized triketone functionalized polyolefins through amidyl radical mediated C−H functionalization by using thiosulfonates as an enabling triketone group transfer functionality.[62] Subsequent cross-linking with a polytopic amine provided diketoenamine cross-linked dynamic covalent polyolefin networks (DCPNs) that demonstrate high network connectivity, efficient remoldability, and enhanced mechanical properties even at very low cross-linker content (∼1 diketoenamine every 200 repeat units). Resonant soft X-ray scattering (RSoXS) revealed hierarchical phase behavior in the materials, where polar diketoenamine-rich domains resided in the amorphous phase between polyolefin crystallites and contributed to their improved thermomechanical properties. Dynamic cross-links imparted resistance to creep at temperatures relevant to applications of cross-linked polyolefins, and the associative exchange of diketoenamine functional groups enabled reprocessing with little cycle-to-cycle property fade.

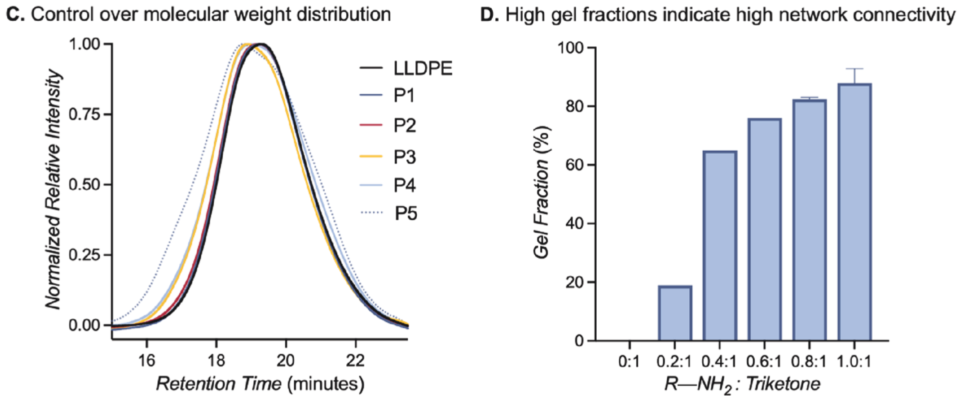
■ RESULTS AND DISCUSSION

To add triketone groups onto polyolefins, we identified thiosulfonates as a functional group that rapidly transfers desirable functionality to alkyl radicals. When combined with the *O*-alkenylhydroxamate reagent (**1**), we hypothesized that a custom-synthesized thiosulfonate appended with a triketone (**2**) would provide efficient group transfer of functionality that would enable access to DCPNs (Figure 2A). We propose that thermally induced N−O bond homolysis of **1** initiates the formation of amidyl radical, which is competent for hydrogen atom abstraction from the polymer.[21] The polymer-centered radical subsequently reacts with thiosulfonate to generate functionalized polymer and 1 equiv of phenyl sulfonyl radical, which reacts with **1** to generate another equivalent of amidyl radical and 1 equiv of *α*-sulfone phenyl ketone. As support for this mechanistic hypothesis, we observed the *α*-sulfone phenyl ketone as a reaction byproduct (Figure S17).[21]


A. Synthesis of diketoenamine dynamic covalent polyolefin network (DCPN)

B. Triketone functionalized polyolefins

Entry	Substrate	Mol% **1**	Func. (mol%)^b	M_n (kg mol^{-1})^c	$Đ$
P1*	LLDPE	0.25	0.1	22	3.4
P2*	LLDPE	1	0.5	22	3.6
P3	LLDPE	2	1.0	24	3.9
P4*	LLDPE	5	2.2	22	4.3
P5	LLDPE	10	3.1	22	6.0
P6	HDPE	10	3.4	39	4.0
P7	*i*-PP	10	0.4	61	6.5
P8	PCPE	10	3.0	26	5.5


C. Control over molecular weight distribution

D. High gel fractions indicate high network connectivity

Figure 2. C−H functionalization of commodity polyolefins yields diketoenamine dynamic covalent polyolefin networks (DCPNs). (A) Reaction scheme for C−H functionalization to provide DCPNs. (B) Results demonstrating the ability to tune functionalization density (**P1**−**P5**) and polymer substrate (**P6**−**P8**); * indicates substrates for the synthesis of DCPNs. (C) Size-exclusion chromatography (SEC) chromatographs of triketone functionalized LLDPE compared to LLDPE demonstrate minimal change in molecular weight distribution and dispersity. (D) Gel fractions of 0.5 mol % functionalized diketoenamine cross-linked LLDPE (**DCPN-P2**) when varying the ratio of cross-linker to triketone. Gel fraction is calculated gravimetrically by comparing the mass of polymer before and after Soxhlet extraction. ^{a}mol % refers to mol % compared to polymer repeat unit; ^{b}percent functionalization calculated by integration of high temp ^{1}H NMR relative to aliphatic polyolefin protons; ^{c}M_n and $Đ$ values calculated from RI detection in 1,2,4-trichlorobenzene at 140 °C. LLDPE (M_n= 21 kg/mol; $Đ$ = 3.6), HDPE (M_n= 35 kg/mol; $Đ$ = 4.0), iPP (M_n= 62 kg/mol; $Đ$ = 5.1), and PCPE (M_n= 23 kg/mol; $Đ$ = 7.6).

We initiated the study using linear low-density polyethylene (LLDPE), a branched commodity polyolefin substrate that is relevant to plastic recycling. Triketone group transfer occurred in 30 min at 130 °C in chlorobenzene. For LLDPE, stoichiometry targeting 10 mol % functionalization relative to polymer repeat unit provided **P5** with 3.1 mol % of triketone on the polymer, as quantified by high temperature ^{1}H NMR. The degree of functionalization could be systematically varied, allowing for tunable functionalization between 0.1 and 3.1 mol % (from 1 to 18 triketones per chain on average) (**P1**−**P5**) by altering the stoichiometry of **1** and **2** relative to repeat unit (Figure 2B). Similar levels of functionalization were observed for high density polyethylene (HDPE) (**P6**), whereas isotactic polypropylene (iPP) demonstrated a lower efficiency of functionalization (0.4 mol %) (**P7**), which is in-line with our previous observations.[33] The molecular weight distribution demonstrated minimal change after functionalization, indicating a lack of observed chain scission, which we hypothesized was a result of reagent controlled regioselectivity (Figure 2C, Figures S8−S11).[15,16,21,61] We were able to translate the approach to functionalization of postconsumer polyethylene (PCPE) obtained from packaging waste at a similar efficiency to HDPE and LLDPE (**P8**). To further demonstrate the scalability and translational potential of the method, the C−H

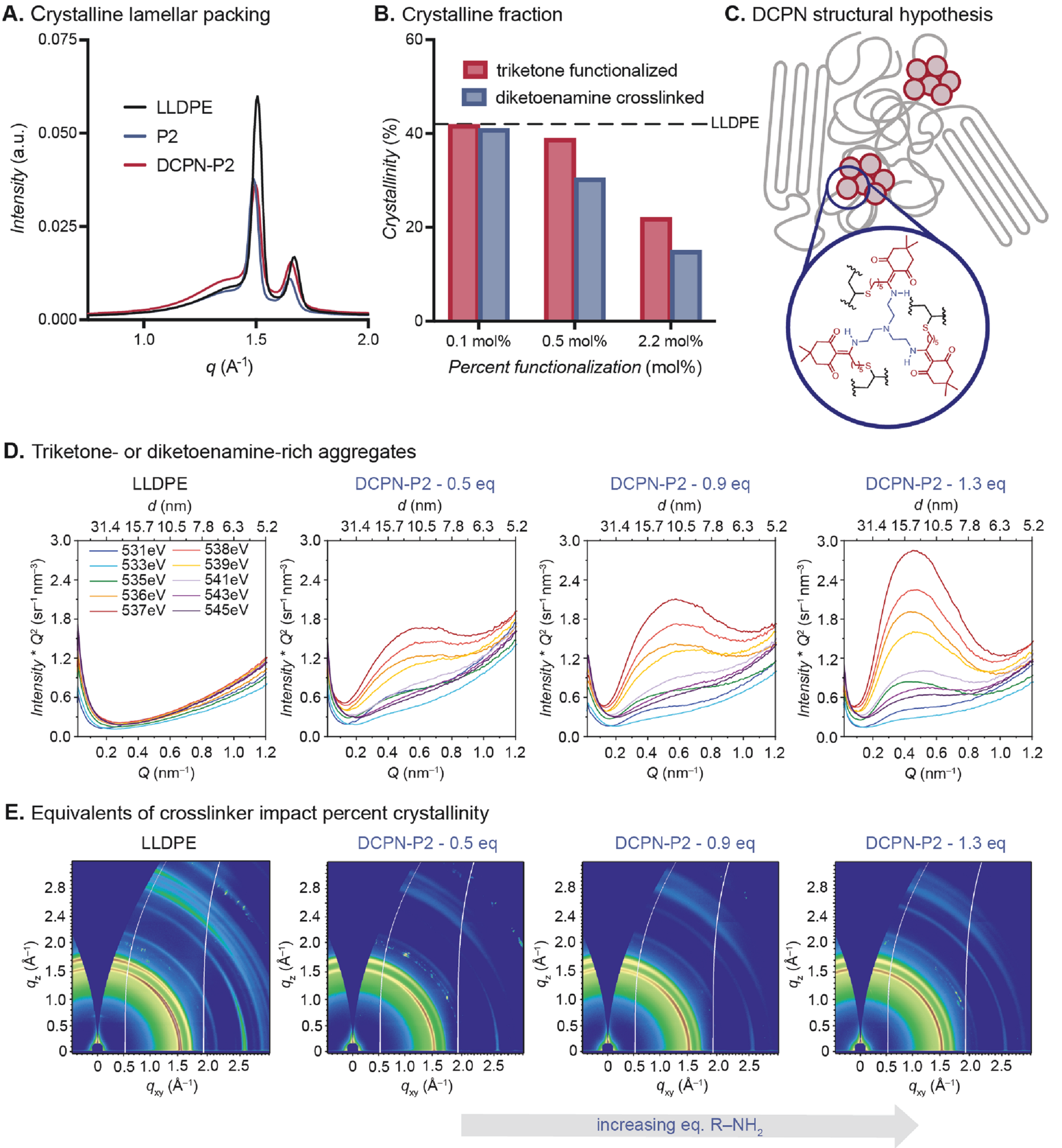


Figure 3. Structural characterization of the diketoenamine dynamically cross-linked polyolefin (DCPN). (A) The WAXS profiles indicate scattering that corresponds to polyethylene chain packing into crystallites for LLDPE, 0.5 mol % functionalized LLDPE (**P2**), and the resultant DCPN (**DCPN-P2**). B) Comparison of crystallinity (%) for 0.1, 0.5, 2.2 mol % functionalized LLDPE and the resultant DCPN shows decreases in crystallinity as functionalization increases determined by WAXS. (C) Proposed DCPN macrostructure is comprised of crystalline, amorphous, and cross-link-rich domains. (D) Diketoenamine-rich domains in **DCPN-P2** were characterized by RSoXS as the number of equivalents of R—NH_2 relative to triketone were increased from 0 to 1.3. (E) The crystallinity of **DCPN-P2** was characterized by GIWAXS as the number of equivalents of R—NH_2 relative to triketone was increased from 0 to 1.3.

functionalization was conducted in a twin screw extruder, which is common infrastructure used to process polymers in industry.[63] Preliminary experiments indicate the successful reaction of LLDPE with reagents **1** and **2** in the melt state (i.e., without the use of solvents) to form **P13** with moderate efficiencies and minimal change in molecular weight distribution (Figure S13).

With access to triketone-functionalized polyolefins, we sought to understand the reactivity of the polymer-bound triketones with monofunctional amines to access diketoenamines as soluble surrogates for cross-linked diketoenamine polyolefins. LLDPE functionalized with 3.1 mol % triketone (**P5**) was heated to 130 °C in chlorobenzene in the presence of excess hexylamine, which resulted in full conversion to hexyl

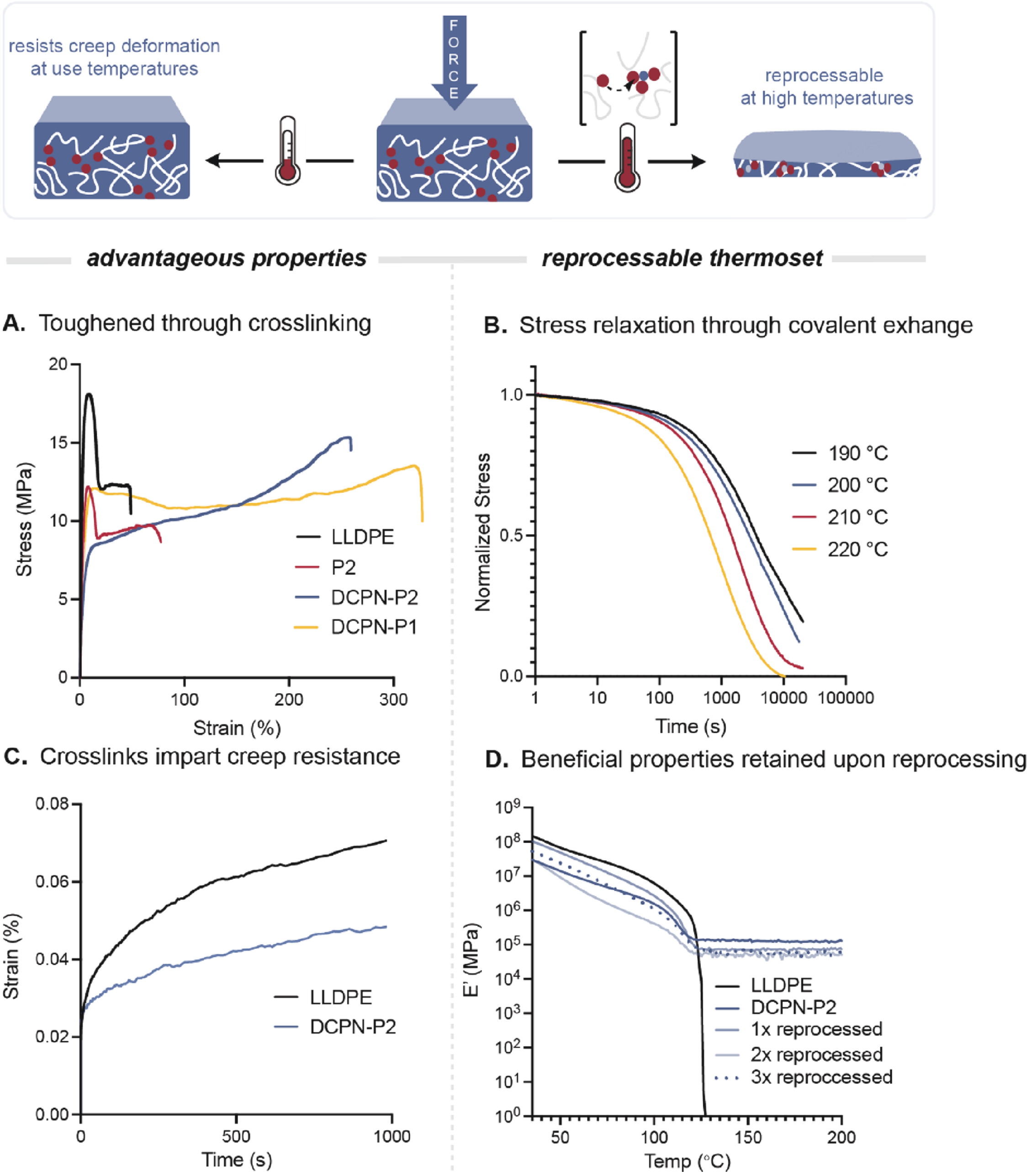


Figure 4. DCPN demonstrated attractive mechanical properties. (A) Uniaxial tensile experiments demonstrated the enhanced mechanical properties of diketoenamine **DCPN-P1** and **DCPN-P2**. Representative stress−strain curves are shown (strain rate = 0.005 s^{-1}). (B) tress relaxation experiments at elevated temperatures demonstrate dissipation of stress over time enabled by dynamic covalent bond exchange. (C) Resistance to deformation increases in the diketoenamine **DCPN-P2** compared to LLDPE in creep experiments under applied stress of 1 kPa; (D) **DCPN-P2** was reprocessed three times; oscillatory temperature sweeps indicate little cycle-to-cycle property fade under constant strain of 2% and a constant frequency of 1 Hz.

diketoenamine (Figure S14). We subsequently investigated the potential of amine exchange. Heating the hexyl diketoenamine LLDPE in the presence of excess benzyl amine fully converted the material into a benzyl diketoenamine functionalized polymer (Figure S14). These data provided evidence that the polymer-bound triketones undergo dynamic covalent exchange in the presence of amines, which is necessary for the realization of thermal reprocessability.

With the understanding of the reactivity of polymer bound triketone, we fabricated a diketoenamine DCPN by reacting a 0.5 mol % triketone functionalized LLDPE (**P2**) with a tritopic amine, *tris*(2-aminoethyl)amine (TREN), for 15 min in chlorobenzene at 130 °C (Figure 2A). The stoichiometry of primary amine relative to polymer bound triketone was systematically varied to probe efficiency of cross-linking. Gel fraction increased as the equivalents of amine approached that of triketone, which reached a maximum of 85% at an equimolar ratio (Figure 2D). This high network participation at a low density of polymer functionalization is a significant advantage over strategies that rely on peroxide-mediated polyolefin functionalization, where a high density of uncross-linked chains act as diluents and complicate structure−property studies. We hypothesized that high levels of network connectivity would contribute to efficient stress redistribution throughout the dynamic network with the potential to contribute to beneficial mechanical properties.

An understanding of the impact of polymer functionalization on the crystallinity was assessed by wide-angle X-ray scattering (WAXS) because functionalization typically results in defects that disrupt polyolefin crystallization and, accordingly, the mechanical properties. Both LLDPE and functionalized polymers showed two primary scattering peaks at scattering vector, q, of 1.5 and 1.7 A^{-1} which correspond to the reflections of the orthorhombic crystal lattice due to the regular packing of polyethylene chains to form lamellae (Figure 3A). The intensity of the scattering peaks decreases upon functionalization (**P2**) and cross-linking (**DCPN-P2**). The crystalline fraction was quantitatively determined by comparing the integration of the crystalline and amorphous phases with WAXS (Figure 3B). A significant fraction of the crystallinity was preserved for **DCPN-P1** (41%) relative to LLDPE (42%), which we hypothesized was due to the low areal density of cross-linking sites (0.1 mol %). Increasing the density of functionalization to 0.5 mol % for the formation of the **DCPN-P2** showed a decrease in crystallinity to 30%. Further increasing the density of cross-linking to 2.2 mol % functionalization for **DCPN-P4** resulted in a 15% crystalline material. To calculate the percent crystallinity through a complementary technique, the enthalpies of melting were determined by differential scanning calorimetry (DSC), whose trends fit with the WAXS data (Figure S24). From these data, we propose that a lower degree of cross-linking results in longer chain segments that can participate in crystallization and, thus, a higher degree of crystallinity compared to DCPNs with a higher degree of functionalization.

With the addition of polar diketoenamines into the nonpolar polyolefin matrix, we hypothesized that microphase separation may have occurred to generate more complex phase behavior, where diketoenamine domains are dispersed within the amorphous phase of the semicrystalline polyolefin (Figure 3C). The elementally weighted distribution of microstructures in **DCPN-P2** was characterized by RSoXS. RSoXS exploits X-ray radiation that is resonant with atomic electronic transition and enables the identification of not only spacing, but also elemental composition of microphase separated domains.[41,42] With the triketone group being the only oxygen-containing functionality in the cross-linked material, triketone- or diketoenamine-rich domains were expected to show enhanced scattering at X-ray energies that approach the characteristic absorption energy of oxygen at 537 eV, according to the near edge absorption fine structure (NEXAFS) spectra for triketone functionalized polymers (Figure S20).

Both LLDPE and triketone-modified LLDPE (**P2**) did not show evidence of microphase separation, indicating that no observed phase separation of triketones was occurring in the non-cross-linked polymers (Figure 3D, Figure S21). After cross-linking with TREN, however, scattering was significantly enhanced as the X-ray energy approached 537 eV. The scattering peak in the integrated spectrum indicated the clear formation of diketoenamine-rich domains with a spacing of 10−15 nm. Additionally, the spacing of diketoenamine-rich domains increased as equivalents of amine cross-linker increased (Figure 3D). Grazing-incidence wide-angle X-ray scattering (GIWAXS) showed that the relative degree of crystallinity increased as cross-linking increased for **DCPN-P2** (i.e., as more TREN was added), which suggests that phase separation of diketoenamine-rich domains helps to recover the loss of crystallinity that would otherwise result from cross-linking and potentially contributes to retaining the beneficial properties of polyolefins within the DCPN (Figure 3E, Figure S23). Taken together, these characterizations of structure indicate that DCPNs comprised a complex combination of physical crystalline cross-links, dynamic covalent chemical cross-links, and polar triketone-rich domains, all of which contribute to material properties (Figure 3C).

With an understanding of the chemical structure and phase behavior of DCPNs, we sought to understand the impact of the mechanical properties of the DCPN. The performance of **DCPN-P2** was assessed under uniaxial strain (Figure 4A, Figure S34). LLDPE demonstrated typical thermoplastic behavior, with high yield stress (∼18 MPa) at low strain and a strong yield followed by necking of the material until failure. The 0.5 mol % triketone modified LLDPE (**P2**) showed similar behavior, suggesting that the lower strength and higher ductility were due to the lower % crystallinity as a result of functionalization. **DCPN-P2** demonstrated a clear elastic region and yield at low strain, which we attribute to the crystalline regions of the material. After yielding, **DCPN-P2** demonstrated a pronounced strain stiffening behavior and elongated approximately 2.5 times its original length before failure. We hypothesize that the observed strain stiffening behavior is attributed to an interplay between the finite extensibility of polymer chains and redistribution of stress throughout the material by the dynamic network cross-links. This material performance, which is a result of both the semicrystalline structure and dynamic covalent cross-links, yielded a material that is 4.5-times tougher compared to the parent LLDPE material. To understand the effect of cross-linking density, we compared 0.5 mol % functionalized **DCPN-P2** and 0.1 mol % functionalized **DCPN-P1**. The DCPN with lower cross-linking density showed greater yield stress, higher ductility, but less strain-stiffening. Greater yield stress is consistent with less disruption of crystallinity as a result of a lower percent functionalization. Higher ductility is attributed to longer network strands that increase the network extensibility at larger strains. These data indicated to us that controlled dynamic network synthesis enabled tunable performance-advantage properties from commodity polyolefin substrates.

We next sought to understand how the structure of DCPNs influenced the reprocessability of the bulk materials by probing their stress relaxation through rheological measurements. An initial step strain was applied to **DCPN-P2** at temperatures ranging from 190 to 220 °C, resulting in stress that decayed to zero over 2 h, which is consistent with bond exchange at elevated temperatures that dissipates stress (Figure 4B). We anticipated that this stress relaxation would enable reprocessing of the DCPN. The activation energy to bond exchange was extrapolated from the stress relaxation time for each temperature using Arrhenius analysis (Figure S31). **DCPN-P2** exhibited an activation energy to bond exchange of 115 kJ mol^{-1}, which is considerably higher than the activation energy of 49 kJ mol^{-1} for diketoenamine networks comprised of TREN and a small molecule bis-triketone.[17] The difference in activation energies may be a consequence of the reorganization energy required for cross-linkers to diffuse through the hydrophobic polyolefin to access other diketoenamine-rich domains for bond exchange.[38]

While numerous dynamic covalent networks demonstrate attractive mechanical properties under rapid deformation, the dynamic exchange of cross-links typically results in a loss in structural integrity under ambient conditions due to creep deformation over longer time scales. To understand the creep behavior of DCPNs, a constant stress of 1.0 kPa was applied to both the semicrystalline LLDPE and **DCPN-P2** at 60 °C and the strain deformation was measured as a function of time (Figure 4C, Figures S32 and S33). These data clearly show that the DCPN creeps very little and deforms at a slower rate than the LLDPE, despite LLDPE having higher % crystallinity. We propose that the hierarchical organization of the DCPN, with cross-links organized into discrete domains and separated by crystalline regions, reduces creep compared to other dynamic covalent networks and even semicrystalline polyolefins.

To further understand the impact of dynamic chemical cross-links on network integrity, oscillatory temperature sweeps under uniaxial extension were conducted through the melting temperature of the materials. As expected for a thermoplastic, the modulus of LLDPE dropped quickly to zero above its melting temperature (T_m). **DCPN-P2**, in contrast, showed a decrease in modulus through its melting point and a plateau at ∼0.1 MPa (Figure 4D). These results indicate that the diketoenamine cross-links support network integrity and sample shape at elevated temperatures above T_m.

To assess whether bond exchange in the DCPN results in reprocessability, the **DCPN-P2** was cut into pieces and compression molded at 200 °C for 2 h to yield smooth, transparent films that had similar mechanical properties to the virgin material, even after three rounds of reprocessing (Figure 4D, Figure S35). In contrast, a permanently cross-linked material was synthesized by C−H functionalization of LLDPE and was not reprocessable under the same conditions (see Supporting Information for details). To demonstrate the potential for circularity, the polymer network after three rounds of reprocessing was completely solubilized by the addition of a monofunctional amine (Figure S36). This experiment demonstrated that no observed permanent cross-links were formed during iterative mechanical reprocessing and that the network can be efficiently deconstructed for subsequent reactivity.

CONCLUSIONS

We demonstrated a new class of polyolefin thermosets that are reprocessable over multiple cycles and resist creep deformation at use temperatures. Amidyl radical-mediated C−H functionalization enabled the placement of triketone groups onto a variety of polyolefin substrates, including postconsumer plastic waste, which serve as precursors to diketoenamine DCPNs. The selectivity and efficiency of this approach provided high network connectivity even at low cross-linking densities, which enabled an understanding of how dynamic exchange of cross-linkers contribute to material properties. Cross-linking using dynamic diketoenamines significantly improved the toughness of the material and resulted in improved resistance to creep compared to LLDPE. Structural characterization revealed that the changes in crystallinity, dynamic covalent exchange reactions, and phase separation contributed to the performance of the material. We anticipate that the ability to upcycle postconsumer plastic waste into useful reprocessable thermosets with well-defined structure and attractive thermomechanical properties will expand the options for polyolefins to enter a more circular plastics economy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c08682.

Synthesis, experimental procedures, characterization data, and supplementary figures (PDF)

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Notes

The authors declare the following competing financial interest(s): F.A.L., B.A.H., E.K.N., and M.H. are inventors on the U.S. provisional patent application 63/603,965 submitted by Lawrence Berkeley National Laboratory and the University of North Carlina at Chapel Hill that covers DCPNs, as well as aspects of their use and recovery. B.A.H. is inventor on the U.S. provisional patent application 62/587,148 submitted by Lawrence Berkeley National Laboratory that covers PDKs, as well as aspects of their use and recovery. F.A.L. is an inventor on a U.S. patent application 63/188,215 submitted by UNC Chapel Hill that covers the amide reagents and their use in polymer functionalization. B.A.H. has a financial interest in Cyklos Materials and Sepion Technologies. The other authors declare that they have no other competing interests.

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