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Polymer Chemistry Hot Paper

Photooxidation of Polyolefins to Produce Materials with In-Chain Ketones and Improved Materials Properties

Xin Liu[+], *Zhitao Hu*[+], *Brandon S. Portela, Emma M. Rettner, Agustin Pineda, Joel Miscall, Nicholas A. Rorrer, Amber T. Krummel,* Robert S. Paton,* and Garret M. Miyake**

Abstract: Herein, we report a selective photooxidation of commodity postconsumer polyolefins to produce polymers with in-chain ketones. The reaction does not involve the use of catalyst, metals, or expensive oxidants, and selectively introduces ketone functional groups. Under mild and operationally simple conditions, yields up to 1.23 mol % of in-chain ketones were achieved. Installation of in-chain ketones resulted in materials with improved adhesion of the materials and miscibility of mixed plastics relative to the unfunctionalized plastics. The introduction of ketone groups into the polymer backbone allows these materials to react with diamines, forming dynamic covalent polyolefin networks. This strategy allows for the upcycling of mixed plastic waste into reprocessable materials with enhanced performance properties compared to polyolefin blends. Mechanistic studies support the involvement of photoexcited nitroaromatics in consecutive hydrogen and oxygen atom transfer reactions.

Polyolefins are the most widely used plastics due to their versatility, durability, and cost-efficiency.[1] These polymers are crucial in various applications including packaging, automotive components, textiles, and medical devices.[2] However, their durability has led to significant global environmental challenges.[3] The resistance to degradation of polyolefins burdens waste management systems and poses long-term environmental risks, including threats to wildlife from entanglement and ingestion.[4] Persistent pollutants from these plastics can cause bioaccumulation and biomagnification, potentially impacting human health.[5] Therefore, addressing the sustainability issues associated with polyolefins is urgent, necessitating innovative approaches to recycling, and degradable alternatives aimed at reducing plastic pollution and its environmental footprint.

Polyethylene (PE)-like materials with in-chain ketones have attracted significant attention due to their distinct properties.[6] Introducing low densities of in-chain ketones preserves the crystal structure and overall properties of PE, while also conferring ultraviolet photodegradability through Norrish-type chain scission.[7] These materials exhibit physical properties not found in unmodified PEs, such as enhanced adhesion and compatibility with common waterborne latex paints.[7] Additionally, the in-chain ketone groups offer opportunity for a variety of potential chemical modifications and serve as a platform to make PE more amenable to subsequent chemical deconstruction.[8] As a result, multiple strategies have been developed for incorporating ketone groups into the PE backbone include copolymerizing ethylene with carbon monoxide (Scheme 1A, i)[9] or polymerizing ketone-containing monomers.[10]

Alternatively, ketone groups can be installed on the PE backbone in a two-step post-polymerization functionalization strategy (Scheme 1A, ii).[11] In these strategies, ruthenium and nickel catalysts oxidize PE materials to install both ketone and hydroxyl groups. Then, catalytic dehydrogenation of the in-chain alcohols with iridium complexes increases the ketone content of the materials. While this strategy makes strides toward the upcycling of waste polyolefins, the use of precious metal catalysts is undesirable. Additionally, a one-step functionalization strategy using a copper catalyst has been developed, however, the oxidation results in a significant reduction in molecular weight relative to the original materials.[12]

Our group has been focused on developing light-driven synthetic methodologies for small molecule and polymer syntheses as well as in the realization of chemically recyclable plastics.[13] As such, we have been motivated to develop light-driven methods to use plastic waste as a valuable feedstock for value-added chemicals and materials. Inspired by advances in the work of light excitation of nitroarenes for chemical synthesis using the triplet biradical

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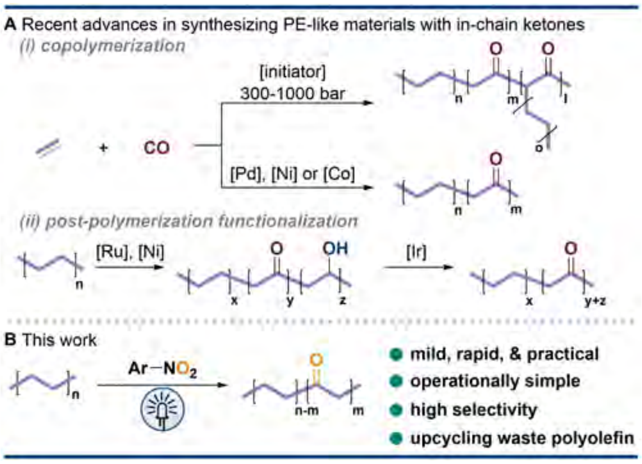
[*] Dr. X. Liu,[+] Dr. Z. Hu,[+] B. S. Portela, A. Pineda,
Prof. Dr. A. T. Krummel, Prof. Dr. R. S. Paton, Prof. Dr. G. M. Miyake
Department of Chemistry, Colorado State University
Center Ave, Fort Collins, CO 80523, United States
E-mail: amber.krummel@colostate.edu
robert.paton@colostate.edu
garret.miyake@colostate.edu

E. M. Rettner, Prof. Dr. G. M. Miyake
School of Materials Science and Engineering
Colorado State University, Fort Collins, CO 80523, United States

J. Miscall, Dr. N. A. Rorrer
Renewable Resources and Enabling Science Center,
National Renewable Energy Laboratory; Golden, CO 80401, United States

J. Miscall, Dr. N. A. Rorrer
BOTTLE Consortium; Golden, CO 80401, United States

[+] These authors contributed equally to this work.



Scheme 1. (A) Recent methods for producing PE with in-chain ketones including copolymerization and post functionalization. (B) This work: photooxidation of polyolefin to produce materials with in-chain ketones.

intermediate,[14] we envisioned a low energy light driven oxidation pathway to introduce ketone group into the backbone of the polyolefins. Irradiation of nitroarenes for the anaerobic hydroxylation of small molecules at room temperature is an established process via hydrogen atom transfer (HAT) and radical recombination.[15] Furthermore, photoexcitation of nitroarenes can also result in the anaerobic alcohol oxidation to ketones.[16] In light of these findings, we hypothesized that the resulting triplet biradical excited state can hydroxylate polyolefins at high temperatures, while the formed hydroxyl group on the backbone can be further oxidized to ketones through a double HAT process (Scheme 1B).

We began our studies investigating the photooxidation of low-density polyethylene (LDPE, $M_n = 15.7$ kDa, $M_w = 37.2$ kDa) in chlorobenzene at 90 °C with irradiation using a 390 nm LED light for 16 h in the presence of 20 mol % different nitroarenes (**1–10**) (Figure 1A). The level of functionalization (LOF) could be quantified by high temperature ^{1}H NMR . We found that 2,4,6-trichloronitrobenzene **6** gave the highest level of functionalization (LOF = 0.71 mol %). In contrast to the transition metal catalyzed oxidation of PE, the ^{1}H NMR spectra indicates that this system did not in-corporate chlorine or hydroxyl units (Figure 1B). The oxidation content of the PE materials were also measured by attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) and confirmed the presence of ketone groups (1720 cm^{-1}) in the polymer mainchain (see Figures S6 and S7). We also examined other light sources, additives, and solvents but did not observe higher LOF (see Tables S3–S7). Increasing the temperatures (> 140 °C) did not result in a higher LOF while insoluble cross-linked products were obtained (see Table S6). When classical C–H activation photoredox catalyst tetra-n-butylammonium decatungstate (TABDT) is added into the system, a higher LOF (1.09 mol %) can be obtained (see Table S9). Inspired by recent advancements in this field, we explored the use of co-solvents as a strategy to improve the LOF.[16a] We found that using *tert*-Amyl alcohol (*t*AmylOH) as a co-solvent could further increase the LOF up to 1.23 mol % (see Table S8). Analysis by high-temperature gel permeation chromatography revealed a slight decrease in the number-average molecular weight (M_n) of the material after functionalization (virgin PE, $M_n = 15.7$ kDa; after functional-

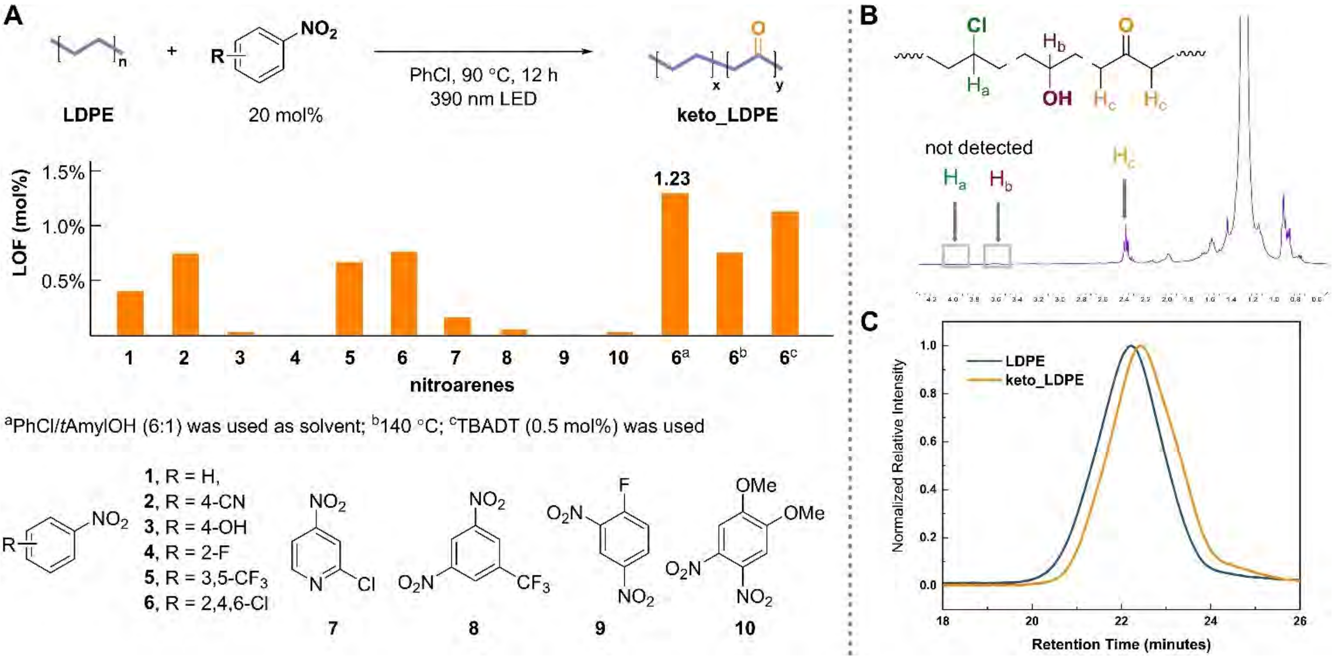
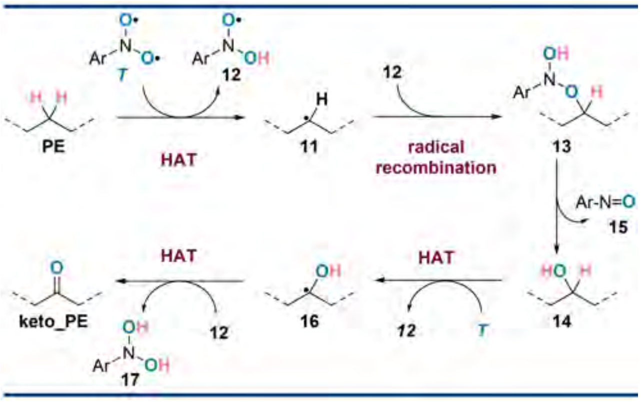


Figure 1. (A) Optimized conditions for the photooxidation of LDPE. (B) ^{1}H NMR of the functionalized LDPE. (C) High temperature gel permeation chromatography (HT-GPC) of the LDPE before (LDPE) and after photooxidation (**keto_LDPE**).

ization, $M_n = 13.3$ kDa), indicating that there was minimal chain scission under these conditions (Figure 1C). Although extending the reaction time and increasing the concentration of nitroarenes can result in higher LOF, it simultaneously leads to a significant reduction in the molecular weight of the polymer (see Table S10 and S11).

Having established the optimized reaction conditions, we sought to elucidate a plausible mechanism for the in-chain ketone formation. In this study, we used small alkanes as model substrates for this transformation and photooxidized them under the same optimized reaction conditions as the LDPE system (see Figures S15 and S16). For cyclohexane and cyclooctane, cyclohexanone and cyclooctanone were obtained in high yields (86 and 71 %, respectively). Notably, ketone was the only functional group detected. Next, we observed that ketone products are selectively obtained from oxidizing secondary alcohols under the same reaction conditions (see Figures S17 and S18). We hypothesized that the photoexcited nitroarenes activate the aliphatic C(sp^3)–H bond to form a hydroxyl intermediate, which can undergo another HAT event to generate an *α*-hydroxyl radical. Subsequently, the *α*-hydroxyl radical can be further oxidized via HAT to yield the corresponding ketone product. We performed density functional theory calculations (DFT) to investigate the thermodynamics and kinetics of this transformation. The full computational methodology is detailed in the Supporting Information and the detailed free-energy surface is shown in Figure S20. We predicted the generation of a hydroxyl intermediate using the photo-excited nitroarene and aliphatic small alkane to be exergonic ($\triangle G_{rel} = -12.5$ kcal/mol). Furthermore, an HAT event be-tween the hydroxyl intermediate and excited nitroarene generates an α-hydroxyl radical, which is exergonic ($\triangle G_{rel} = -29.5$ kcal/mol) and kinetically feasible ($\triangle G_{\ddagger} = 15.8$ kcal/mol). The *α*-hydroxyl radical undergoes another HAT event to afford the ketone product, which is predicted to occur favorably ($\triangle G_{rel} = -74.9$ kcal/mol). Additionally, we monitored the reaction conversion over time for the LDPE oxidation, revealing that hydroxyl groups initially form in the LDPE main chain within the first 4 hours, but over the course of the reaction ketones become the only functional groups in the backbone (see Figure S19).

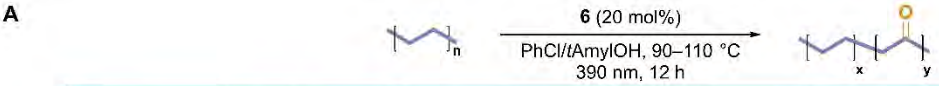
Based on the above studies and previous literature reports,[14–16] we propose a plausible reaction mechanism (Scheme 2). Under irradiation, nitroarenes form a singlet excited state, which then undergoes intersystem crossing to produce a long-lived triplet biradical state. The triplet biradical intermediate engages in HAT process with the C(sp^3)–H bonds of PE, producing an alkyl radical intermediate **11** and the oxygen-centered dihydroxyaniline radical **12**. Subsequently, radical recombination of **11** and **12** leads to intermediate **13**. Next, fragmentation of 13 leads to oxygen atom transfer to generate a hydroxyl intermediate **14** and the nitroso byproduct **15**. Additionally, **14** undergoes HAT with a triplet biradical intermediate to generate an α-hydroxyl radical intermediate **16**. Lastly, **16** undergoes HAT with **12** to form the respective ketone product and dihydroxylamine **17** as the byproduct. The byproduct **17** decomposes to the nitroso intermediate **15** which can rapidly decompose under the reaction conditions to form side products such as amine, azobenze, or azoxybenzene.



Scheme 2. Proposed mechanism.

Given our optimized conditions and mechanistic rationale, we envisioned our strategy should be amenable to oxidation of commercial polyolefin materials. Functionalization of high-density PE (HDPE) and linear low-density PE (LLDPE) are both successfully functionalized, but reactions with these polymers required higher temperatures (100 and 110 °C, respectively) than reactions of LDPE for functionalization due to solubility. With these modified conditions, both HDPE and LLDPE underwent oxidation to yield functional materials with 1.15 and 0.59 mol % LOF, respectively (Figure 2A). As anticipated, these in-chain ketone motifs do not greatly reduce many of the desirable material properties of polyolefins. We evaluated the feasibility of our system on a large-scale reaction (see Table S13). The reaction was successfully performed on a 10 to 20 g scale, and the LOF up to 0.94 mol %. Furthermore, in each case, the wide-angle X-ray diffraction (WAXD) patterns before and after functionalization are similar (Figure 2B), underlining a solid-state structure dominated by crystallization of aligned hydrocarbon segments. The decomposition temperature at 5 % weight loss (T_{d5}), crystallization temperature (T_c), melting temperature (T_m), and degree of crystallinity (X_c) were slightly lower in the functionalized polymers compared to the virgin mate-rials (Figure 2A and 2C). Tensile testing results indicate that the oxidized materials exhibit a noticeable reduction in elongation at break, tensile strength, and Young's modulus compared to the virgin plastic, likely due to a decrease in molecular weight induced by the functionalization process (Figure 2D). In the absence of nitroarenes, no appreciable functionalization was observed (Figure S21) while the mechanical properties of the polymer before and after exposure to the reaction conditions was similar (see Figure S22). Under reaction conditions between 90–110 °C, we did not observe any evidence of cross-linking that could impede melt processing. Cross-linking promoted by in-chain ketones has been reported as an issue for thermoplastic processing of commercial polyketone resins.[17]

With the successful addition of ketone groups into the different polyolefins, we investigated whether these materi-



sample	LOF (mol%)	M_n (KDa)	Đ (M_w/M_n)	T_c (°C)	T_m (°C)	T_{d5} (°C)	E (MPa)	σ_{UTS} (MPa)	ε_b (%)
LDPE	–	15.7	2.37	95	109	430	220 ± 30	10 ± 1	130 ± 30
LLDPE	–	21.8	4.28	102	120	433	210 ± 20	21 ± 3	710 ± 20
HDPE	–	36.2	2.64	114	127	431	630 ± 30	22 ± 2	630 ± 10
keto_LDPE	1.22	13.3	1.90	90	107	428	280 ± 30	12 ± 3	180 ± 20
keto_LLDPE	1.15	18.3	2.79	101	112	425	160 ± 20	14 ± 3	410 ± 30
keto_HDPE	0.59	27.4	1.92	109	120	426	600 ± 20	16 ± 2	430 ± 30

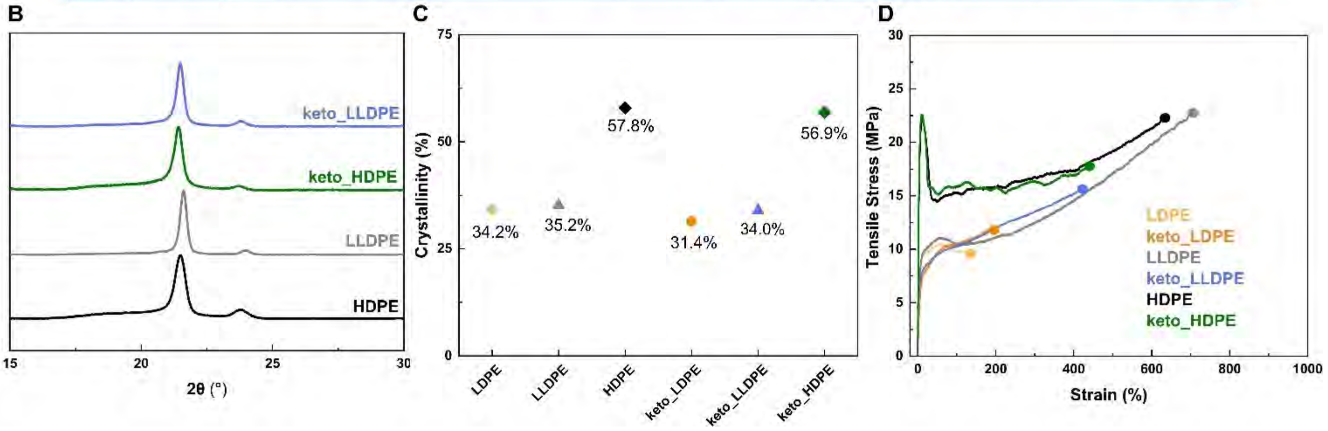


Figure 2. (A) Photooxidation of polyethylenes and their materials properties data. (B) WAXD profiles of functionalized materials, HDPE and LLDPE. (C) Comparison of crystallinity before and after the reaction. (D) Representative stress-strain curves. M_n, number average molecular weight; Đ, dispersity; T_c, crystallization temperature; T_m, melting transition temperature; T_{d5}, decomposition temperature at 5% weight loss; E, Young's modulus; σ_{UTS}, tensile strength; ε_b, elongation at break; Average values for E, σ_{UTS}, and ε_b, are provided with standard deviations from the mean value of four samples.

als could be cross-linked with diamines to form cross-linked dynamic covalent polyolefin networks (DCPNs) (Figure 3A).[18] We formed a DCPN material (**DCPN_LDPE**) by reacting a **keto_HDPE** (LOF = 0.51 mol%) with a 1,6-diaminohexane for 120 min in chlorobenzene at 130 °C. The stoichiometry of amine relative to ketone group was systematically varied to probe the efficiency of cross-linking. The gel fraction increased as the equivalents of diamine approached that of ketone, which reached a maximum of 91% at an equimolar ratio (Figure 3B). Compared to HDPE ($X_c = 57.8\,\%$, $T_m = 127\,°C$) and **keto_HDPE** ($X_c = 56.9\,\%$, $T_m = 120\,°C$), the thermal properties and crystallinity of **DCPN_HDPE** showed a moderate decrease ($X_c = 49.6\,\%$, $T_m = 109\,°C$), similar to previous studies using branched triketone to build DCPN materials (see Table S18).[19] Compared to HDPE, **DCPN_HDPE** retains a significant degree of crystallinity and thermal properties, which we speculate is due to the low cross-linking density (0.51 mol%). Furthermore, we sought to understand the mechanical properties of these DCPN materials. **DCPN_HDPE** exhibits a pronounced elastic region with no observed yield point (Figure 3C). Although the ductility of these cross-linked materials decreased, the toughness is improved relative to the parent HDPE material. We believe this performance is the result of the combined effects of the semicrystalline structure and dynamic cross-linking.[19a] Additionally, the **DCPN_HDPE** can be completely solubilized by the addition of a monofunctional amine (see Figure S10). This experiment demonstrated that the network materials can be efficiently deconstructed without forming permanently cross-linked materials.

Lastly, we sought to demonstrate that this process is also applicable to upcycling postconsumer materials. Real-world upcycling of plastic waste requires that the process be tolerant of the presence of dyes, plasticizers, and stabilizers.[20] Recent studies have shown some performance limitations of PE, such as poor surface adhesion, can be overcome via post-polymerization functionalization, without sacrificing processability and thermal stability.[11] Therefore, we carried out the photooxidation of post-consumer LDPE (food packaging) and HDPE (milk jug), which yielded functionalized materials with 0.59 or 0.35 mol% LOF, respectively. Then, we tested the adhesion of these functionalized materials using single-lap-shear tests and found that **keto_waste_HDPE** adhered most strongly to aluminum (3.7 ± 0.4 MPa) and adhered to both copper (2.7 ± 0.6 MPa) and stainless steel (3.3 ± 0.3 MPa) surfaces (Figure 3D). In comparison, unfunctionalized PEs show very poor adhesion to these metals (< 0.3 MPa).

Next, we sought to use this method to address a more complex challenge of polyolefin municipal waste (typically, PE : PP = 70 : 30), because these two plastics together constitute approximately half of the world's polymer production.[1b] In plastic recycling, due to the similar

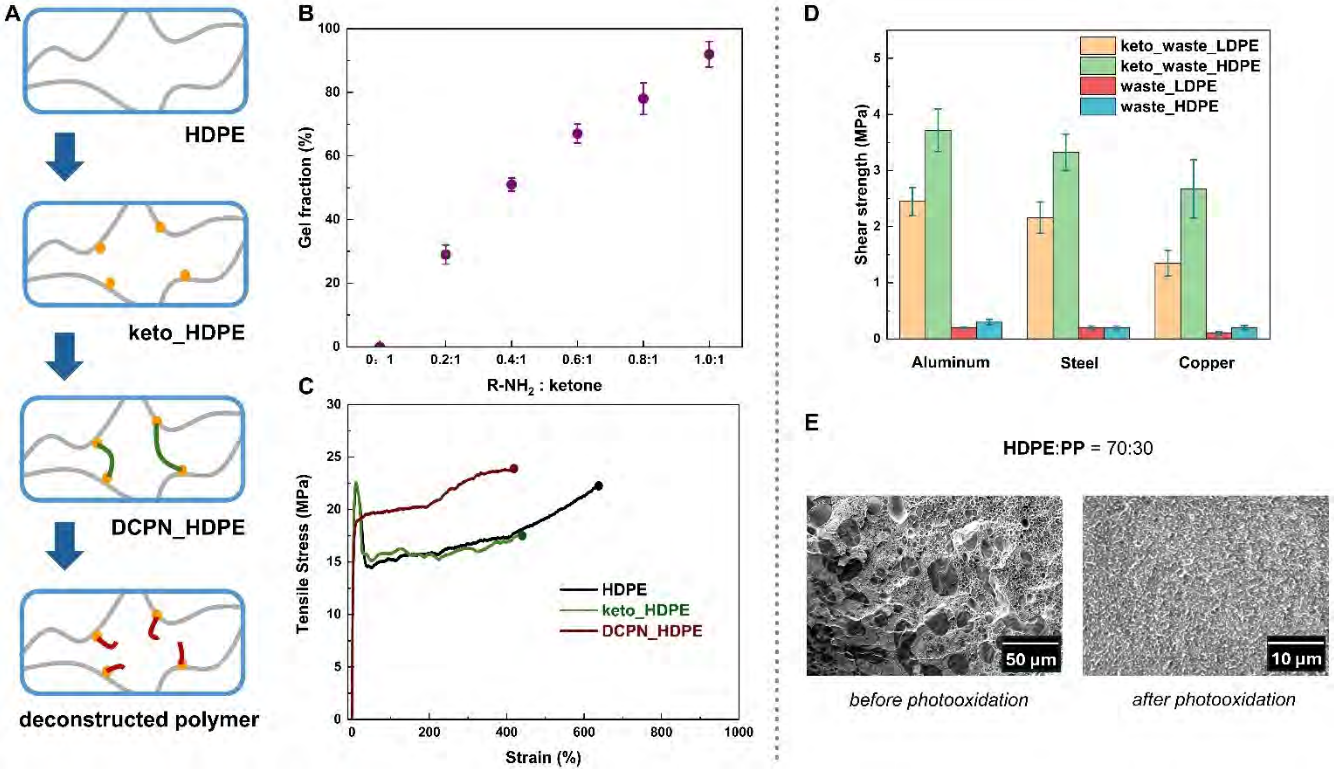


Figure 3. (A) Schematical representation for the synthesis of cross-linked dynamic covalent polyolefin networks from HDPE. (B) Gel fractions of cross-linked **keto_HDPE** (LOF = 0.56 mol %) when varying the ratio of cross-linker to ketone group. (C) Uniaxial tensile experiments demonstrated the enhanced mechanical properties of HDPE, **keto_HDPE** and **DCPN_HDPE**. (D) Lap-shear-adhesion testing of functionalized waste PE materials on various substrates. (E) SEM images of HDPE-PP mixture before and after photooxidation. Error bars represent standard deviations from the mean value of four samples.

chemical nature of HDPE and polypropylene (PP), they cannot be efficiently sorted in a cost-effective way, and untreated blends are generally too brittle for use because of phase segregation.[21] We hypothesized that oxidation of both plastics in the mixture would promote miscibility and improve the properties of the blend. Therefore, we obtained a mixture of PE and PP from post-consumer plastic spray bottles and conducted an oxidation reaction at 120 °C for 16 hours without *t*AmylOH as a co-solvent. Excitingly, the oxidized mixture of the materials exhibited a significant improvement in mechanical properties, with the elongation at break increasing tenfold relative to the unfunctionalized PE:*i*PP mixture (see Figure S12). Microstructural investigation by Scanning Electron Microscopy (SEM) shows that the mixture of PP and PE exhibit obvious phase segregation, whereas the oxidized mixture shows increased homogeneity between phases (Figure 3E). These data demonstrate the improved compatibility between oxidized **PP** and **HDPE** relative to unfunctionalized PP and HDPE mixtures. Notably, we observed a substantial reduction in the molecular weight of PP following photooxidation (before: M_w = 247.3 kDa, M_n = 67.0 kDa; after: M_w = 12.9 kDa, M_n = 3.2 kDa), accompanied by a pronounced decrease in the associated T_c, T_m, and overall crystallinity (see Figures S15–S16). The ATR-FTIR confirmed the presence of ketone groups in the PP backbone (see Figure S14). However, their formation was not detected via NMR, likely due to the extremely low concentration. It remains unclear whether this improved compatibility is primarily due to the introduction of carbonyl groups or the reduced molecular weight of PP after oxidation. Further studies on these polyolefin blends are ongoing in our laboratory.

In sum, we have developed a mild, metal-free, and highly selective photooxidation methodology for the functionalization of variety of polyolefin substrates including post-consumer mixed plastic waste to produce materials with in-chain ketones. These materials can serve as precursors to DCPNs which have higher toughness compared to the parent PEs. Importantly, this protocol has the potential to upcycle plastic waste into reprocess able materials with enhanced performance.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Plastic Upcycling · Polyolefins · Plastic Functionalization · Photochemistry · Oxidation

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