High Density Polyethylenes Bearing Isolated In-Chain Carbonyls

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Abstract

Polyethylene materials are highly important polymers which are produced in the largest volume among all plastics. Due to the chemical inert property of saturated carbon-carbon bonds, the degradation of polyethylene is extremely challenging, which prevents them from efficient chemical recycling. Installing functional groups in the main chain of polyethylenes may facilitate the degradation and following chemical recycling of polyethylene materials. Here we report a highly selective approach for the synthesis of high-density polyethylenes bearing isolated in-chain carbonyls. Linear high-molecular weight polyethylene chains are synthesized via the palladium catalyzed copolymerization of ethylene with metal carbonyls. Different from traditional ethylene/CO copolymerization reactions, excellent non-alternating selectivity has been achieved. While the properties of polyethylene have been retained in the copolymer, faster degradation compared with that of polyethylene was observed upon UV light irradiation. The synthesized materials may therefore serve as more environmentally friendly alternative plastics than traditional polyethylene materials.

Background

Polyolefin plastics are fundamental materials, which have been used in numerous areas of modern society. Specifically, polyethylene plastics are produced in the largest amount in volume among all polymer materials,[1,2] but their remarkable chemical inertness has led to serious environmental plastic pollution issues (Fig. 1a).[3,4] Accordingly, efficient chemical recycling of polyolefins became an emerging hot topic.[5,6] One potential solution to overcome the problem of the high chemical inertness of polyethylene plastics is to install a small amount of cleavable functional groups in the main chain of polyethylenes.[7] It is known that in-chain carbonyl units can enable chain scission through Norrish-type photochemical reactions.[8-10] Since the 1950s, radical copolymerization of ethylene and carbon monoxide (CO) to yield low-density polyketone materials was developed providing either alternating or ethylene rich non-alternating copolymers both with branched structures.[11,12] Later, the coordination-insertion copolymerization using group 10 metal complexes was developed to give completely alternating linear copolymers.[13,14] The high content of carbonyl groups alters the physical property of these materials in a way in which they do not serve as an alternative to polyethylene plastics (Fig. 1b).[15-17] Consequently, efforts have been paid to develop methods for synthesizing polyethylenes with a low-content of carbonyl groups that would allow to retain the bulk material properties of polyethylene while adding further functionality such as photodegradablity.[18-24] Especially the so far unachieved spread-out incorporation of the carbonyl groups into the polymer chain is highly desired over accumulated alternating structural units in order to maximize the breakdown of the polymer chains into smaller pieces (Fig. 1c).

Nearly thirty years ago, a seminal report by Drent *et al.* described the palladium catalyzed synthesis of modestly non-alternating copolymers of ethylene and CO by employing a phosphine sulfonate (P/S) ligand (up to 18.4 mol% extra ethylene units with 40.8 mol% CO content).[18] While later studies by the groups of Sen and Müller employing monomer feeds with high ethylene-to-CO ratio could further lower

the CO incorporation down to 1.5 mol%,[22,25] a clustering of the CO units in the polymer chain remained so far mechanistically unavoidable due to formation of a strong chelate after CO insertions (Fig. 1d).[20,26] More recently, the group of Mecking reported a radical copolymerization strategy for the synthesis of highly branched polyethylenes with low content in-chain carbonyl groups.[23] While a high selectivity towards isolated carbonyls was achieved, compared to coordination-insertion copolymerization, much higher initial ethylene pressures (> 300 bar) were required for the successful radical copolymerization.

Here we report a new reaction protocol for the synthesis of high-density polyethylene (HDPE) with low content in-chain isolated carbonyl groups. By employing metal carbonyls instead of CO gas for the palladium catalyzed coordination-insertion copolymerization with ethylene, highly selective incorporation of isolated carbonyls in the main chain of polyethylene was achieved. The physical property of HDPE is retained in the obtained copolymer. Importantly, better photodegradability compared with polyethylene was observed upon UV light irradiation.

Results And Discussion

Previously reported methods for the non-alternating ethylene/CO copolymerization generally led to the formation of polyethylenes containing both isolated and alternating carbonyl groups with low selectivities,[18-23] while the incorporation of CO often lowered the molecular weights of the obtained polymers.[22] Here we aimed improvement of both the selectivity for isolated CO insertion and molecular weight of the non-alternating ethylene/CO copolymers for practical applications of these materials as potential environmentally friendly plastics. Intriguingly metal carbonyls, which are industrially produced in the context of metal refinement by transport reactions, have been used as alternative CO sources in transition metal catalyzed carbonylation reactions[27-29] We wondered whether metal carbonyls could be used as a CO source for accessing polyethylenes with low contents of in-chain carbonyl groups.

Different metal carbonyls were tested as comonomers in the polymerization of ethylene using a common palladium phosphine-sulfonate (P/S) catalyst, **[Pd]-1** (Table 1, entries 1-4). When $Fe_2(CO)_9$, $Mn_2(CO)_{10}$ and $Fe(CO)_5$ were used as the CO sources (Bond enthalpies of metal carbonyls were discussed in Supplementary Table 1), polymers were obtained after precipitation with MeOH and washing with diluted hydrochloric acid to remove metal residues (Table 1, entries 1-4). ^1H and ^{13}C NMR analysis of the obtained polymers clearly supported the presence of carbonyl groups in the polyethylene main-chain. The ^1H NMR spectrum of the copolymer corresponding to entry 1 (Fig. 1a) showed a characteristic triplet of the isolated ketone unit at δ = 2.42 ppm (**B**), which was also observed at 210.5 ppm (**A**) in the $^{13}C\{^1H\}$ NMR spectrum (Fig. 2b). A weak signal for alternating ketone unit was found at δ = 2.70 ppm (s; **H**) in the ^1H NMR spectrum (Fig. 2a). The highest CO incorporation ratio (1.6 mol%, corresponding to about 2.3 ketone units per chain) was observed with $Fe_2(CO)_9$ and in-chain isolated carbonyls were observed as the predominant insertion moiety [Isolated carbonyls/Alternating carbonyls (I/A) = 96:4]. The choice of metal carbonyls had a significant effect on the incorporation of CO. Significantly lower CO incorporation ratios were observed in the case of $Fe(CO)_5$ and $Mn_2(CO)_{10}$ (0.16 and 0.14 mol% respectively), while almost no

alternating carbonyls were observed in the obtained copolymer and the polymer yields and molecular weights were increased in comparison to the copolymer in entry 1 (Table 1, entries 2 and 3). No polymer was obtained when $Co_2(CO)_8$ was employed as the comonomer, which was likely due to the catalyst deactivation by $Co_2(CO)_8$ (Table 1, entry 4). Control experiments were carried out to confirm an interaction between the palladium catalyst and metal carbonyls. When $Fe_2(CO)_9$ was added outside the glass tube in the reaction autoclave, a high yield of polymer was obtained while less than 0.01 mol% CO incorporation was observed (Table 1, entry 5). When CO gas was used as the carbonylation source instead of metal carbonyls, a copolymer was obtained in a high yield but with a low molecular weight and poor PDI (Table 1, entry 6). Though with a low CO incorporation ratio (0.31 mol%), a poor selectivity of isolated over alternating carbonyl units was observed (I/A = 67:33), which was in stark contrast to the experiments employing metal carbonyls as a CO source. A stoichiometric experiment was then performed to further confirm the CO transfer from $Fe_2(CO)_9$ to **[Pd]-1** (Fig. 3). As was expected, slow CO insertion to **[Pd]-1** was observed after mixing an excess amount of $Fe_2(CO)_2$ with **[Pd]-1** at room temperature (Supplementary Fig. 1).

Next, the effect of different reaction parameters on the copolymerization were explored. Decreasing the amount of $Fe_2(CO)_9$ lowered the CO incorporation ratio but increased CO insertion selectivity and molecular weight of the copolymer (Table 1, entry 7). On the contrary, increasing the amount of $Fe_2(CO)_9$ led to a high CO incorporation ratio but decreased molecular weight and CO insertion selectivity (Table 1, entry 8). The effect of different palladium catalysts was also explored. First, palladium P/S complexes bearing different substituents on phosphine were tested. Similar molecular weights were observed in the case of **[Pd]-2** and **[Pd]-3** (Table 1, entries 9 and 10). Notably, **[Pd]-4** afford much higher molecular weights of the copolymer with an excellent selectivity toward non-alternating copolymerization (Table 1, entry 12). The effect of temperature on the copolymerization was investigated using **[Pd]-4** as the catalyst (Table 1, entries 11-13). Increasing the reaction temperature had a positive effect on the incorporation of CO, still the highest molecular weight (58 kg mol^{-1}, about 8 ketone units per chain) of the copolymer was obtained at 80 °C (Table 2, entry 12). According to ^{1}H NMR analysis, more than 99% selectivity towards the incorporation of isolated carbonyls was observed for this copolymer (Fig. 2b). At the same time, only one carbonyl signal was observed in the ^{13}C NMR spectrum (Fig. 2e).

Aside from the palladium P/S catalysts, a palladium NHC-phenolate (**[Pd]-5**) and a bisphosphine-monoxide catalyst (**[Pd]-6**) were also tested under similar reaction conditions (Table 1, entries 14 and 15). Less than 0.05 mol% of CO incorporation was observed in the obtained polymers, which suggests that only high-density polyethylenes were obtained (See Fig. 2c for the ^{1}H NMR spectrum of the polymer in Table 1, entry 15). It is known that diphosphine ligands such as dppp or dppb have been widely used in the palladium catalyzed alternating ethylene/CO copolymerization,[13] but no polymer was obtained with both ligands when $Fe_2(CO)_9$ was used as the carbonyl source (See Supplementary Information for details). These results suggest that an interaction between the palladium P/S catalyst and the metal carbonyls are important for achieving the copolymerization, and that the metal carbonyls are crucial for

allowing highly selective non-alternating ethylene/CO copolymerization. A plausible mechanism for CO transfer from $Fe_2(CO)_9$ to [Pd]-1 is presented in Supplementary Fig. *S12*.

Differential scanning calorimetry (DSC) analysis of the copolymer in entry 12 in Table 1 revealed an endothermic peak at T_m = 130 $^{\circ}$C (Fig. 4a), closely resembling the HDPE obtained for entry 15 in Table 1 which demonstrated an endothermic peak at T_m = 131 $^{\circ}$C (Fig. 4b). These results indicate the melt property of the copolymer is not compromised by the incorporation of a low quantity of CO. Moreover, the thermogravimetric analysis of the polymers in entry 12 and 15 gave similar results for T_d = 437 and 434 °C respectively (Fig. 4c and 4d). Thus, the obtained copolymer is stable for thermal processing, which serves as another advantage compared with alternating polyketone materials. As a proof of concept, the photodegradability of the copolymer in Table 1, entry 12 was explored upon 275 nm UV light irradiation. The decomposition of the polyethylene in Table 1, entry 15 was also investigated under similar conditions to demonstrate the importance of low content CO incorporation. After irradiating the polymer at 30 °C for 50 h, the molecular weight of the copolymer (0.41 mol% CO incorporation) decreased significantly from 58 kg/mol to 22 kg/mol and the molecular weight distribution was broadened to M_w/M_n = 2.6 (Fig. 4e). In the control experiment, only slight molecular weight change was observed, and the initial molecular weight distribution was maintained (Fig. 4f). These results support our assumption that the incorporated low content carbonyl groups facilitate the degradation of polyethylene materials.

In conclusion, a highly selective reaction protocol for the synthesis of non-alternating, linear ethylene/CO copolymers has been developed. Incorporation of a low CO content in the main-chain of polyethylene along with remarkable isolated carbonyl selectivity was achieved via palladium catalyzed copolymerization of ethylene with metal carbonyls. This polyethylene copolymer retained the main physical properties of high-density homopolyethylene, while treating the obtained copolymer with UV light resulted in partial degradation. Therefore, the synthesized materials may serve as more environmentally friendly alternative plastics than traditional polyethylene materials.

Declarations

Data availability

All data supporting the findings of this study are available within the article and its Supplementary Information.

Acknowledgements

Author Contributions

K.N., F.W.S. and S.T. contributed to the conception and design of the experiments. S.T., and F.W.S. performed the experiments. S.T., F.W.S. and K.N. co-wrote the manuscript. All authors participated in discussion and K.N. directed the project.

Competing financial interests

The authors declare no competing financial interests.

Additional Information

Supplementary information and chemical compound information are available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to K.N.

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Table

Due to technical limitations, table 1 is only available as a download in the supplementary files section.
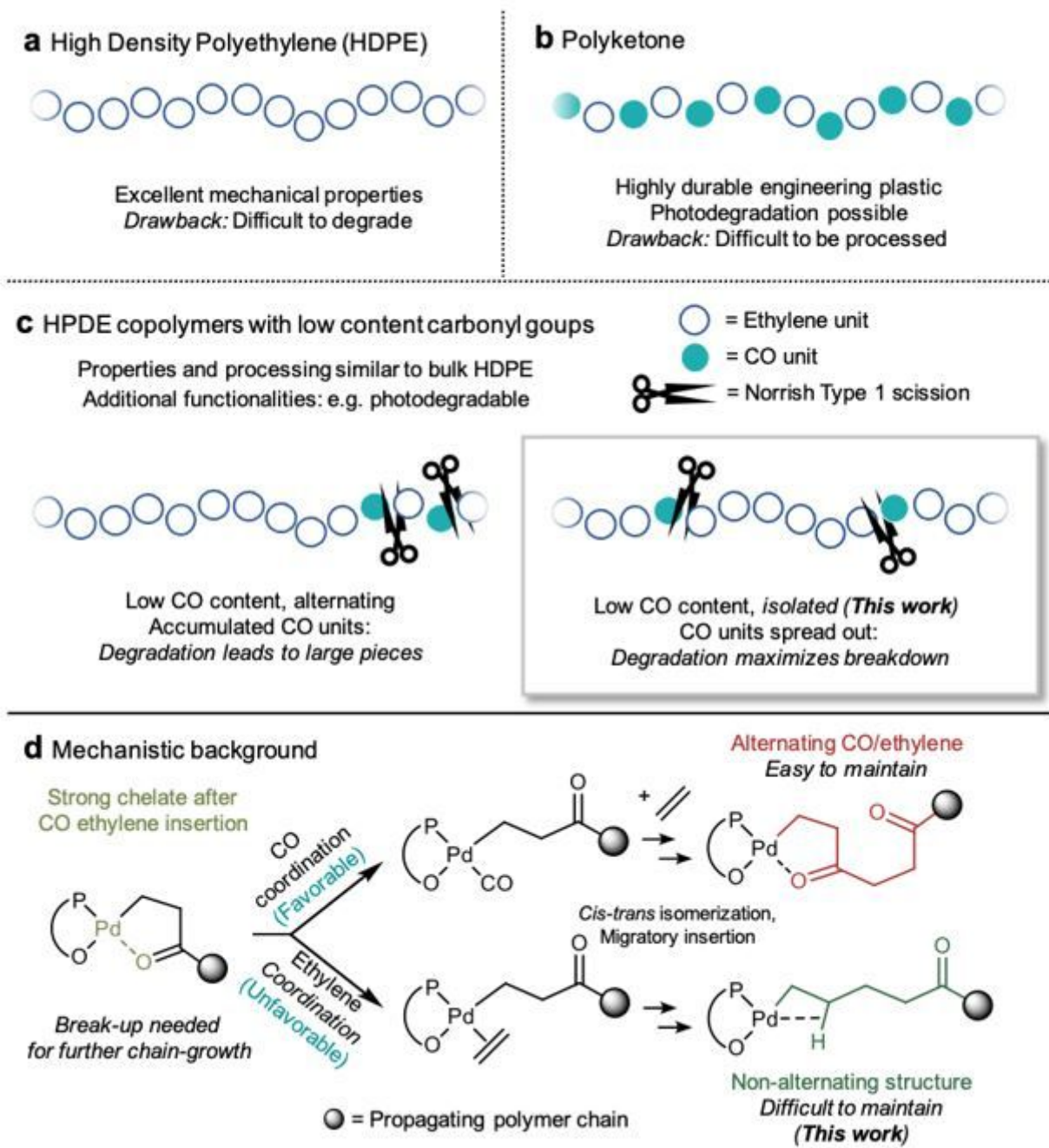
Figures

Figure 1

Background. (a) Properties of high-density polyethylene. (b) Properties of alternating polykeone. (c) Potential properties of high-density polyethylene with low-content carbonyl groups. (d) Mechanistic background of the difficulty in generating non-alternating CO/ethylene copolymer structures through palladium-catalyzed coordination/insertion copolymerization.
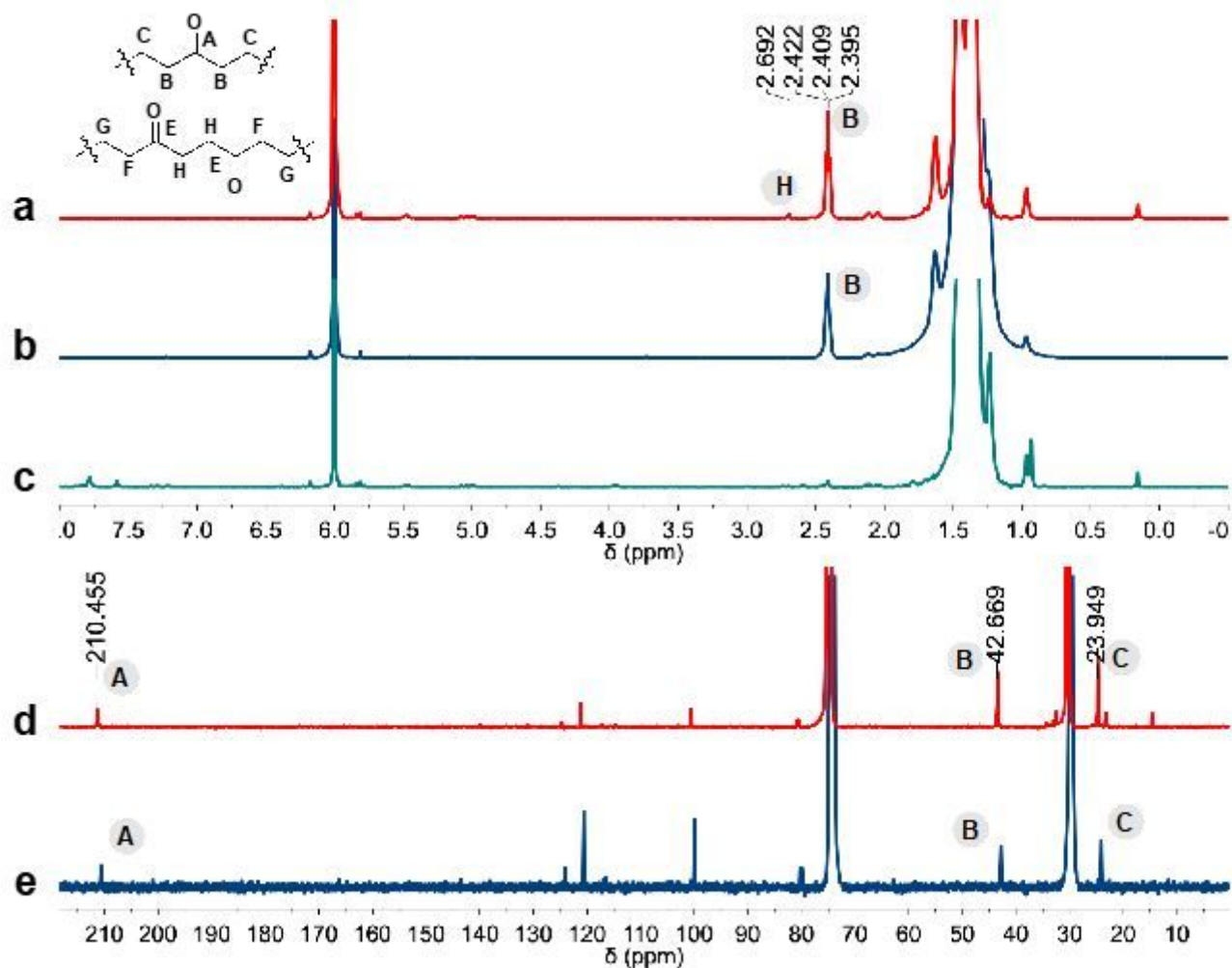
Figure 2

Assignment of characteristic NMR resonances. (a) 1H NMR spectrum of the copolymer in Table 1, entry 1. (b) 1H NMR spectrum of the copolymer in Table 1, entry 12. (c) 1H NMR spectrum of the polymer in Table 1, entry 15. (d) 13C NMR spectrum of the copolymer in Table 1, entry 1. (e) 13C NMR spectrum of the copolymer in Table 1, entry 12.
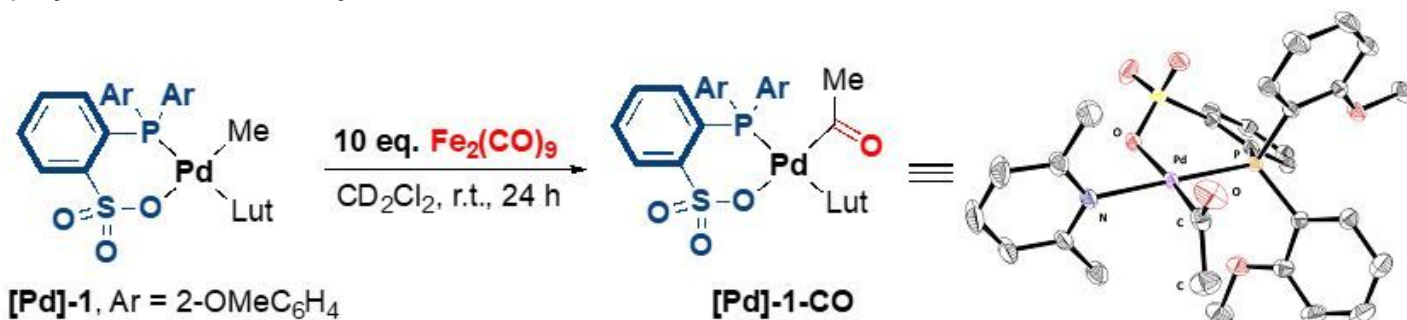

Figure 3

Stoichiometric experiment. CO transfer between [Pd]-1 and Fe2(CO)9.
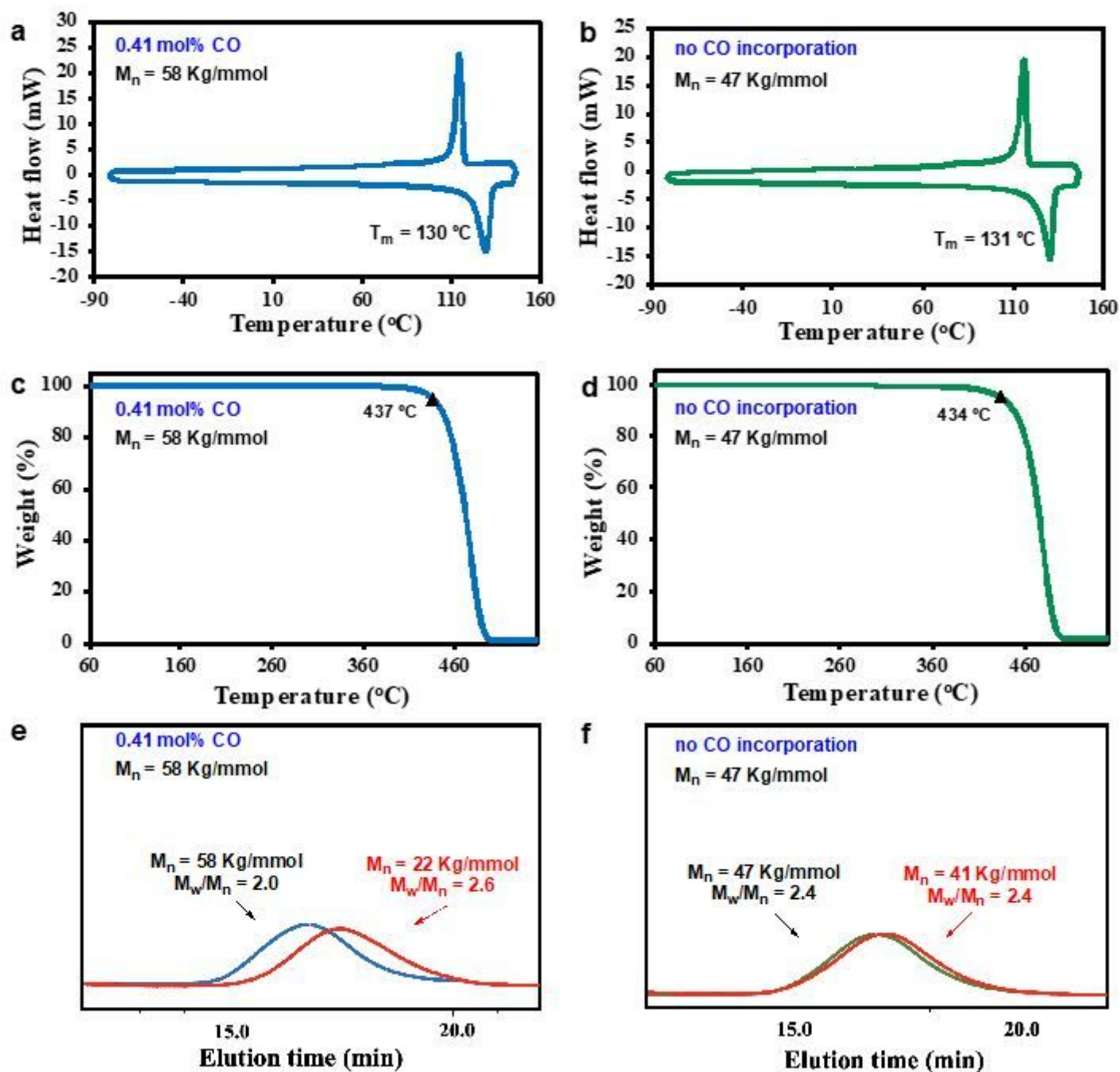
Figure 4

Physical property of the copolymers. (a) DSC trace of the copolymer in Table 1, entry 1 (1.6 mol% CO). (b) DSC trace of the copolymer in Table 1, entry 7 (1.1 mol% CO). (c) DSC trace of the copolymer in Table 1, entry 11 (0.41 mol% CO). (d) DSC trace of the polyethylene in Table 1, entry 15. (e) SEC trace of the copolymer in Table 1, entry 12 before (Blue line) and after (Red line) UV irradiation (275 nm at 30°C for 50 h). (f) SEC trace of the polyethylene in Table 1, entry 15 before (Green line) and after (Red line) UV irradiation (275 nm at 30°C for 50 h).

Supplementary Files

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