

Polyethylene Materials with In-Chain Ketones from Catalytic Copolymerization

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ABSTRACT: The world's most important plastic, polyethylene, consists of inert hydrocarbon chains. An introduction of reactive polar groups in these chains is much sought-after, to overcome the problematic environmental persistency and enhance compatibility with other materials. However, with state of the art catalytic polymerization processes this has not been possible. Here, we show how a low density of individual in-chain keto groups can be generated in the high molecular weight polyethylene chains by catalytic copolymerization with carbon monoxide. Most importantly, the desirable materials' properties of high density polyethylene (HDPE) are retained. Processing can be performed by common injection molding and mechanical characteristics are on a par.

Introduction

Plastics materials are used on a vast scale, and they are an essential component of any modern technology. Polyethylene is the most important polymer material by scale. It combines facile processing and low-cost production with excellent mechanical properties.¹ The latter arise from crystalline ordering of stretched hydrocarbon chains. This is particularly pronounced for HDPE (high density polyethylene), as it is composed of linear chains devoid of branches that would disturb this crystalline packing.² Their hydrocarbon nature also makes polyethylenes hydrophobic and apolar. They will not easily adhere to polar materials like metals or wood. Due to the chemically inert nature of the hydrocarbon chains, polyethylenes are not susceptible to degradation reactions. This renders them persistent when released to the environment.

A possible approach to in-chain functionalized crystalline polyethylene materials is catalytic copolymerization with carbon monoxide, in theory. The resulting keto groups in the polyethylene chain can provide an array of desirable reactivities, including photodegradability as demonstrated for branched LDPEs (low density polyethylenes) with ca. 1 mol% of keto groups from free-radical high pressure copolymerization.³⁻⁵ Due to their ability to accommodate into the polyethylene crystal lattice,⁶ low concentrations of keto groups are anticipated to not disturb the crystalline order in linear polyethylenes.

However, such materials have remained elusive to date despite numerous efforts. The much stronger binding of carbon monoxide (CO) vs. ethylene monomer to the catalyst prevents consecutive incorporation of olefin.⁷ Thus,

rather than a polyethylene chain, alternating polyketones are formed. These are high-melting engineering thermoplastics with entirely different applications and processing properties than polyethylenes.⁸

We report how the long-sought non-alternating catalytic copolymerization of ethylene and CO can be achieved with Ni(II) catalysts. Materials with a desirable low content of keto groups in high molecular weight polyethylene chains are formed, that can be melt processed and feature tensile properties like commercial HDPE.

Results and Discussion

Considering guidelines for catalyst choice and design, compatibility with polar reagents is an essential prerequisite. This excludes traditional electron-deficient d^0 -metal sites, as used in production of polyolefins¹, which are deactivated by polar molecules like carbon monoxide. In fact, quenching with carbon monoxide is an established method to deactivate such olefin polymerization catalysts.⁹ Catalytic processes involving CO, such as olefin carbonylation, generally rely on d^8 -metal centers,¹⁰ and the aforementioned alternating polyketones are produced commercially with cationic palladium catalysts.⁸ Further, the strong binding affinity of CO – widely used as a ligand in organometallic chemistry – has to be controlled. Especially irreversible displacement of other essential ligands, thus destroying active sites, must be prevented. In addition, the coordination of CO or formed keto-groups in the growing chain can potentially block coordination sites reversibly for further chain growth. Most importantly, the kinetic preference for CO incorporation, which promotes the formation of alter-

nating polyketones, needs to be overcome. Note that in this sense the target CO copolymerizations are opposite to catalytic copolymerizations of ethylene with polar vinyl comonomers like acrylates¹¹⁻¹⁴ in which the comonomer reactivity can be problematically low.

These arguments underline neutral late transition metal catalysts with strongly bound chelating ligands as promising objective. Compared to the common cationic polymerization catalysts, in neutral active sites the preference for binding of CO vs. other ligands, including olefinic mono-

mer, is less pronounced. Indeed, the only precedence for the occurrence of consecutive ethylene insertions in CO copolymerization has been observed with neutral phosphinesulfonato palladium catalysts.¹⁵⁻¹⁸ However, low molecular weight brittle waxes with $M_n \leq 3.000 \text{ g mol}^{-1}$ (and likely heterogeneous compositions) were formed¹⁹ and no polyethylene plastics materials could be obtained despite extensive studies by different joint industrial and academic ventures.

Table 1. Polymerization experiments.^a

#	Cat.	T [°C]	p [bar]	t [min]	CO in feed [mol%] ^b	yield [g]	TOF ^c	χ^d [mol%]	I / NA / A ^e [mol-%]	M_n^f [10^3 g mol^{-1}]	M_w/M_n^f	T_m [°C] (% Cryst) ^g
1	1	50	10	60	0.2	0.06	0.2	50 ^h	0 / 0 / 100 ^h	n.d. ^h	n.d. ^h	243 ⁱ
2	2	100	5	10	0.2	0.80	15.6	0.3 (0.4)	69 / 11 / 20	54	1.7	133 (71)
3	2	100	5	60	0.2	2.07	7.41	0.3 (0.4)	70 / 22 / 8	102	1.5	135 (66)
4	2	100	5	120	0.2	4.26	7.61	0.3 (0.3)	79 / 21 / 0	140	1.6	134 (68)
5	2	110	5	60	0.2	1.07	3.81	0.5 (0.5)	61 / 27 / 12	84	1.7	133 (65)
6	2	120	5	30	0.2	0.06	0.41	1.7 (1.7)	31 / 49 / 20	3	8.9	110 (65)
7	2	100	40	10	0.2	1.20	23.4	1.1 (2.7)	9 / 37 / 54	42	2.9	133 (68)
8	2	70	40	90	0.2	0.05	0.12	50 ^h	0 / 0 / 100 ^h	n.d. ^h	n.d. ^h	228 ⁱ
9	2	100	5	120	0.6	1.98	3.53	0.8 (1.1)	32 / 36 / 32	147	1.8	135 (62)
10	2	100	10	60	0.6	2.35	8.39	0.6 (1.4)	27 / 33 / 39	154	1.9	134 (63)
11	2	100	10	120	0.6	3.01	5.38	0.6 (1.3)	27 / 27 / 46	210	1.8	138 (61)
12	2	100	10	240	0.6	3.31	2.95	0.6 (1.0)	43 / 33 / 24	216	1.8	136 (60)
13	2	100	5	120	2.6	0.06	0.08	50 ^h	0 / 0 / 100 ^h	n.d. ^h	n.d. ^h	230 ⁱ
14	5	100	5	120	2.6	0.03	0.06	50 ^h	0 / 0 / 100 ^h	n.d. ^h	n.d. ^h	228 ⁱ
15	5	100	5	60	0.2	1.04	3.73	0.4 (0.4)	62 / 29 / 9	88	1.6	133 (70)
16	3	100	5	120	0.6	0.05	0.08	50 ^h	0 / 0 / 100 ^h	n.d. ^h	n.d. ^h	229 ⁱ
17	4	100	5	120	0.6	1.13	2.02	1.0 (1.4)	21 / 29 / 49	60	1.7	133 (69)
18	5	100	5	120	0.6	0.26	0.46	3.7 (4.4)	28 / 34 / 38	84	1.7	134 (63)
19	6	100	5	120	0.6	0.44	0.79	1.6 (3.0)	7 / 34 / 59	45	1.6	133 (69)
20	7	100	5	120	0.6	0.82	1.47	1.1 (2.5)	18 / 33 / 49	90	1.7	135 (67)
21	8	100	5	120	0.6	0.01	0.02	50 ^h	0 / 0 / 100 ^h	n.d. ^h	n.d. ^h	232 ⁱ
22	1	90	40	60	0.1 ^m	0.05	0.2	50 ^h	0 / 0 / 100 ^h	n.d. ^h	n.d. ^h	240 ⁱ
23 ^k	2	100	5	20	-	10.8	231.2	-	-	17	1.9	131 (71)
24 ^k	2	70	10	10	-	3.16	135.1	-	-	548	2.3	138 (58)

^aReaction conditions: 10 μmol precatalyst loading, 100 mL of toluene, 500 rpm pitched blade stirrer. ^bCarbon monoxide content in the feed gas. ^cTOF given in units of $10^3 \text{ mol}[\text{C}_2\text{H}_4] \text{ mol}^{-1}[\text{Ni}] \text{ h}^{-1}$. ^dCarbon monoxide incorporation determined by IR spectroscopy. In brackets: Carbon monoxide incorporation calculated from ^{13}C NMR spectroscopy by integration of the ^{13}C labeled C=O signals in relation to the overall integral, considering natural abundance of ^{13}C vs. ^{12}C . ^eI: isolated carbonyls, NA: non-alternating adjacent carbonyls (cf. Fig. 2 for specification), A: alternating polyketone segments. Determined by ^{13}C NMR spectroscopy. ^fDetermined by GPC in 1,2-dichlorobenzene at 160°C via universal calibration vs. polystyrene standards. ^gDetermined by DSC, second heating cycle. ^hAlternating polyketone obtained. ⁱObserved in first heating cycle. ^k5 μmol precatalyst loading. ^m0.05 atm CO introduced to reactor prior to ethylene addition, 200 mL toluene, catalyst precursor added by means of a dosing pump after pressurization and heating to reaction temperature. This procedure was used to account for the limited temperature stability of 1.

Neutral N,O-coordinated salicylaldiminato and P,O-coordinated phosphinoenolato Ni(II) catalysts in ethylene homopolymerization can produce linear semicrystalline PE with several million g mol^{-1} molecular weight.²⁰ To favor non-alternating chain growth, high polymerization temperatures are also expected to be favorable. For the general case of two competing pathways, the preference for the energetically favored one decreases with increasing temperature according to $k_a/k_b \sim \exp(\Delta\Delta G^\ddagger/RT)$ assuming a given difference $\Delta\Delta G^\ddagger$ between the barriers for both pathways. The robust nature of P,O-coordinated nickel(II) catalysts is advantageous in this regard. They are applied at 140 °C for industrial ethylene oligomerization.²¹ However, due to their propensity for chain transfer by β -hydride elimination events, traditional P,O-coordinated catalysts even at lower reaction temperatures yield oligomers or low molecular weight polymers with $M_n < 10^4 \text{ g mol}^{-1}$.²²⁻²⁴ Only recently this long prevalent picture has been revised by the finding that appropriate bulky substituents can strongly suppress chain transfer to afford high molecular weight polyethylenes.^{25,26}

Notwithstanding the literature consensus that such catalysts are rapidly deactivated by CO and at most form only

alternating polyketones with low activity,^{23,27} a state-of-the-art salicylaldiminato (**1**) and phosphinophenolato catalyst precursor (**2**) were exposed to ethylene (E)/CO mixtures with low partial pressures of CO (Table 1), at polymerization temperatures found to be optimum in the established ethylene polymerizations with these catalysts. With **1**, only small amounts of polymer were obtained even at an E/CO ratio of $> 10^2$ (entry 1). The polymer product features the IR spectrum of an alternating polyketone. By contrast, with **2** substantial amounts of a polymer were obtained which features IR bands of polyethylene and a carbonyl band with a distinctly different wavelength compared to an alternating polyketone (entry 2, Fig. 2b).

Encouraged by these findings, a series of novel and also state-of-the-art known neutral P,O-chelated catalyst precursors with bulky substituents on the phenolate moiety as well as aryl groups shielding one or both apical positions were explored (Figure 1. For details of synthesis and full characterization data cf. the Supporting Information, SI). Notably, catalyst precursors **2** - **7** are polymerization active in the presence of CO and, at high E/CO ratios on the order of 100, form polymers that are not alternating polyketones according to IR spectroscopy (Table 1).

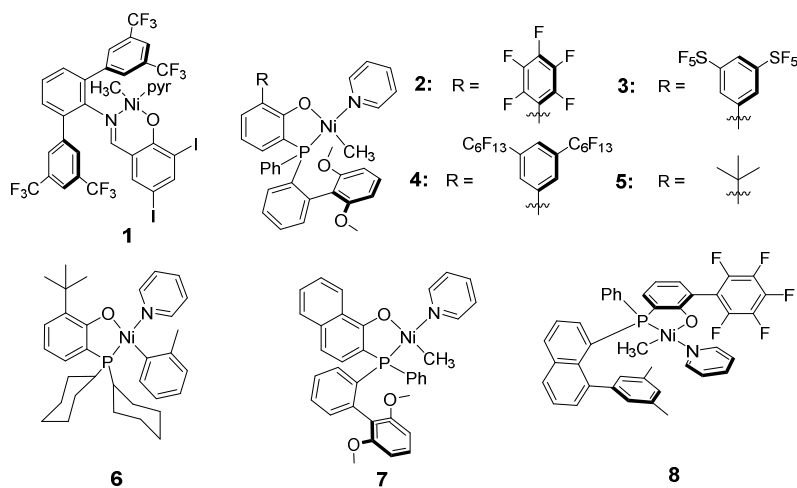


Fig. 1. Catalyst precursors studied. Salicylaldiminato complex **1**, and phosphinephenolato complexes **2** to **8**.

Polymer microstructure and materials properties. The microstructure of the novel polymers was elucidated by ¹³C NMR spectroscopic methods. To enhance sensitivity, copolymers from pressure reactor experiments with ¹³CO were utilized. By a combination of 1D and 2D NMR methods and reference to literature data, ¹H and ¹³C NMR spectra could be assigned fully (cf. Supporting Information, SI, for details). This reveals the presence of isolated ketone groups in the polyethylene chain (Fig. 2a). Further, non-alternating motifs of ketone groups in proximate positions along the chain can be differentiated, and alternating motifs are observable. Most notably, at desirable values of the CO incorporation of ca. 1 %, the majority of keto groups are not alternating, and moreover amongst these the isolated

keto groups prevail. The overall keto contents determined by quantitative NMR spectroscopy are confirmed by IR spectroscopy (Table 1 and Fig. 2b. For details of reference data and discussion of the IR spectra of keto-functionalized polyethylenes cf. the SI). As anticipated, these in chain keto-motifs do not compromise the desirable materials properties of polyethylene. Wide angle X-ray scattering (WAXS) diffractograms of the materials are virtually identical to that of HDPE (Fig. 3a), underlining the solid-state structure is retained. Also, melting and crystallization points are virtually unaltered (Fig. 3c). Most notably, the keto-modified polyethylenes possess high molecular weights (up to $M_w \sim 400.000 \text{ g mol}^{-1}$, $M_n \sim 220.000 \text{ g mol}^{-1}$). This is remarkable in view of the very low molecu-

lar weights formed in ethylene-CO copolymerizations yielding any partially non-alternating motifs to date,¹⁹ and it is crucial to obtain useful mechanical properties. Indeed, tensile tests on injection molded test bars show a ductile behavior that compares to commercial HDPE (Fig. 3d).

The modulus of elasticity and tensile strength compares to that of typical linear polyethylenes ($E = 995$ MPa and $\sigma_y = 29$ MPa, compared to literature values of $E = 900$ MPa and $\sigma_y = 27$ MPa for HDPE and for LDPE $E = 240$ MPa, $\sigma_y = 12$ MPa).²⁸

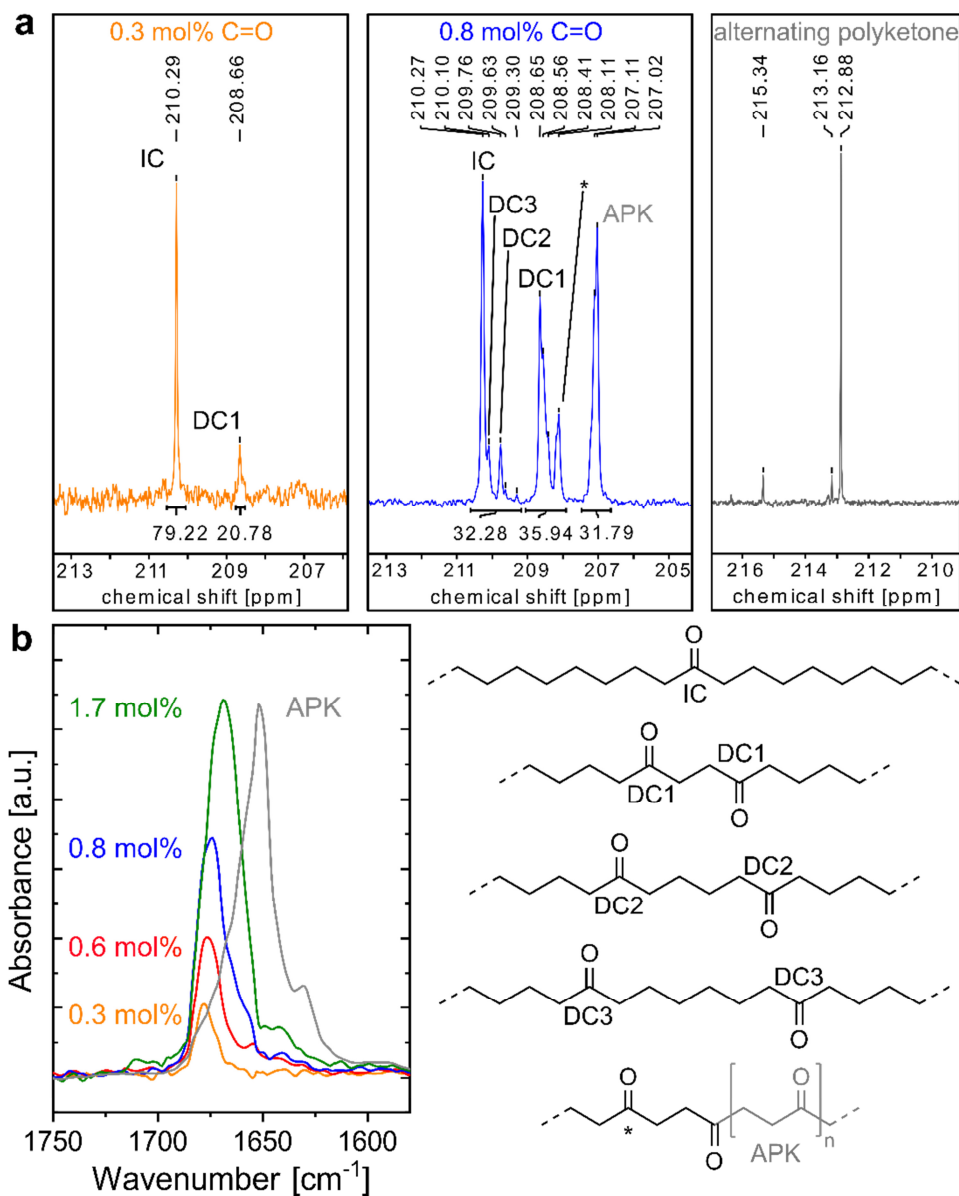


Fig. 2. Microstructure Characterization of Copolymers. **a**, Carbonyl regime of ¹³C NMR spectra of ¹³CO copolymers with different keto contents (C₂D₂Cl₄ solvent, 383 K) and an alternating polyketone (hexafluoroisopropanol/C₆D₆ solvent, 273 K) for comparison. IC: Isolated carbonyl, DCX: Double carbonyl separated by X repeat units of ethylene, APK: Alternating polyketone, *: Carbonyl adjacent to an alternating sequence **b**, IR spectra of copolymers with different keto contents, and alternating polyketone for comparison. The absorbance intensity of alternating polyketone is adjusted for clarity. Note these are ¹³CO copolymers as in **a**, which shifts the absorption frequency compared to non-labelled polymers (cf. the Supporting Information for IR spectra of the latter).

No evidence for undesirable cross-linking that could hamper melt processing was observed. This is notable as cross-linking promoted by the keto motifs is an issue in the thermoplastic processing of commercial polyketone resins.²⁹

Mechanistic features of the catalytic polymerization.

At given initial reaction conditions, the composition of the formed polymer does not vary significantly with increasing reaction time and increasing polymer yield (entries 2 to 4 and 10 to 12). A homogeneous material is formed, as op-

posed to a conceivable drift of microstructure and composition due to e.g. a significant alteration of the monomers' relative concentrations. Compared to ethylene homopolymerization the copolymerization yields and average activities are lowered (entry 2 vs. 23, cf. Table S1 in the Supporting Information for further homopolymerization data). However, this is not due to a conceivable problematic rapid catalyst deactivation. Catalysts are stable for hours in CO copolymerizations (entries 2 to 4). Presumably, in addition to CO binding, reversible chelating binding of formed keto groups slows down chain growth to a certain extent as concluded from the observation of overall increased productivities with increasing monomer concentration at a given E/CO ratio (entries 2 vs. 7 and 9 vs. 11. Cf. Figure S33 in the SI for a scheme of reversible deactivation path-

ways). A certain polymerization reaction temperature is required to overcome this retardation. Thus, efficient copolymerization with **2** requires ca. 100 °C, while homopolymerizations proceed rapidly also at lower temperatures (entry 24). As anticipated, higher polymerization reaction temperatures also decrease the CO incorporation and in fact are necessary to achieve non-alternation (entry 8 vs. 2 to 7). This underlines the role of the temperature stability of catalysts **2** to **7** in enabling the non-alternating copolymerizations to keto-modified polyethylenes. Beyond this, the underlying phosphinophenolate motif also appears particularly suited for non-alternating copolymerization. By comparison, **1** also at an elevated polymerization temperature only formed alternating polyketone (entry 22).

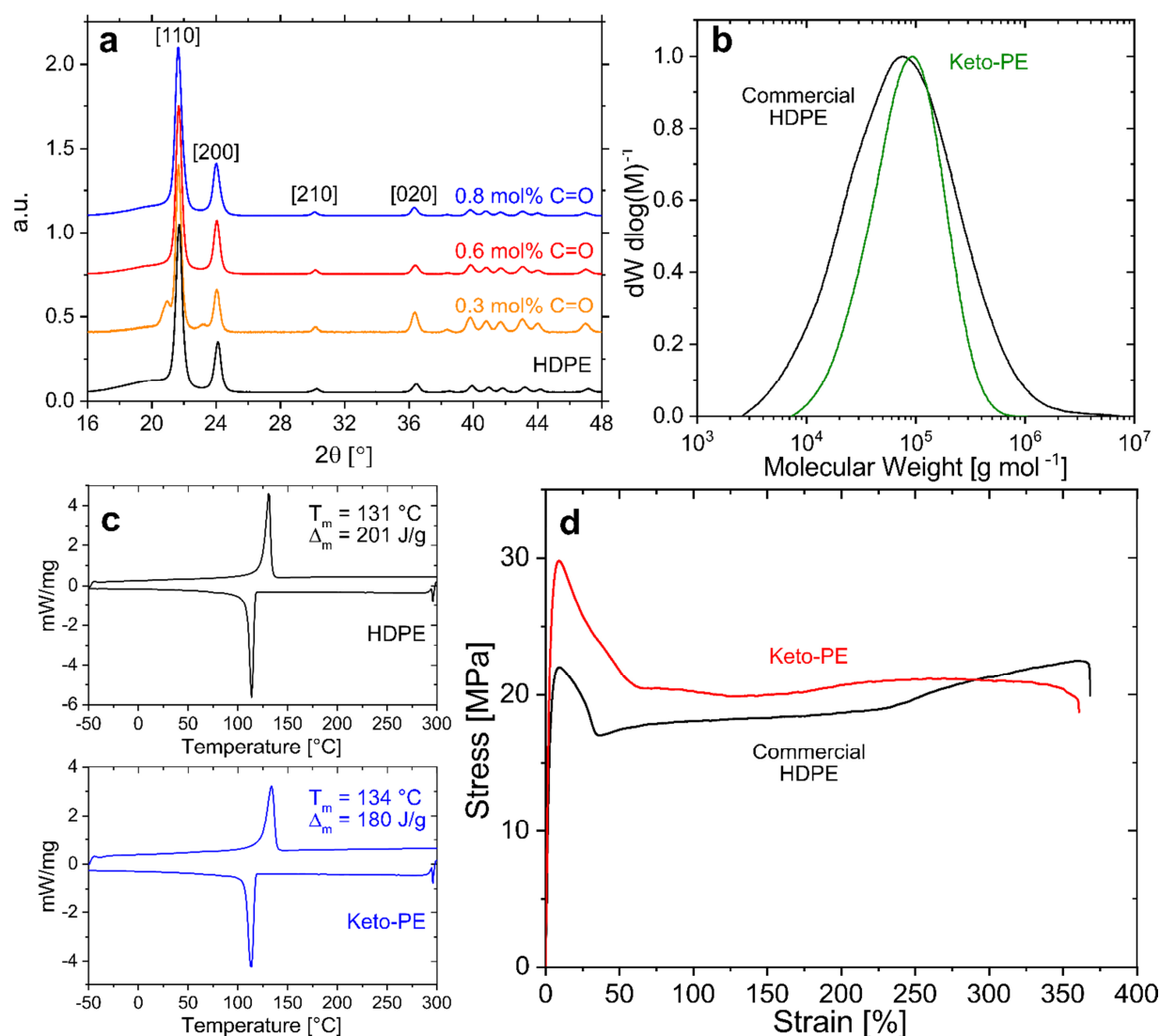


Fig. 3. Materials Characterization of Copolymers. **a**, WAXS of copolymers with different keto contents and commercial HDPE. Reflexes correspond to the orthorhombic unit cell of polyethylene. **b**, GPC trace of copolymer (1.0 mol% keto repeat units), and commercial HDPE for comparison. **c**, DSC trace of copolymer (0.8 mol% keto repeat units), and commercial HDPE for comparison. **d**, Representative stress-strain curves of injection molded keto-modified polyethylene (0.6 mol% keto repeat units) in comparison to commercial HDPE.

The high molecular weights of the keto-modified polyethylenes suggest that the presence and incorporation of CO does not promote any problematic chain transfer reactions. Indeed, an analysis of the polymers' endgroups shows only those types of endgroups also found in homopolyethylenes, namely olefinic endgroups originating from β -hydrogen transfer of the Ni-polymeryl species (Figure S19). This confirms no undesired additional chain transfer pathways are operative in CO copolymerizations. Rather, the presence of CO appears to hinder chain transfer and branching as concluded from higher molecular weights and the complete absence of branches in copolymers compared to ethylene homopolymers (entry 23 vs. 2 to 4 and 9; and Figures S19, S20, S24 and S25), possibly by blocking of coordination sites for β -hydrogen transfer by CO.

Conclusion

In summary, the non-alternating copolymerization of ethylene with carbon monoxide to in-chain keto functionalized polyethylene materials can be achieved with catalysts based on nickel as the active sites. Remarkably, this long-sought reaction proceeds under mild conditions, namely ethylene pressures of 5 to 10 atm or lower. The high catalyst stability and well-behaved single site nature of the catalysts in the presence of the carbon monoxide monomer – which usually deactivates olefin polymerization catalysts rapidly and irreversibly – during the generation of the target polymers is encouraging for the further prospects of this reaction. The earth-abundant nature of nickel compared to noble metal catalysts, as used e.g. for polyketone production, is further beneficial. The ability to polymerize at elevated temperatures is identified to be a key feature of suitable catalysts for non-alternating copolymerization, which can guide further catalyst development. Other than apprehended from polar vinyl monomer copolymerizations,^{14,25,26} the incorporation of carbon monoxide does not compromise polymer molecular weights. On the contrary, the presence of carbon monoxide suppresses chain transfer and branching. This is important and encouraging for further development of these novel materials, given the paramount role of sufficient molecular weight in attaining desirable mechanical properties. The now provided access to in-chain functionalized polyethylene which possess the desirable materials properties of HDPE offers perspectives for environmentally less persistent polyolefins in enabling photolytic and oxidative chain breakdown.

ASSOCIATED CONTENT

Supplementary Information. Precatalyst synthesis and characterization, experimental methods and additional copolymer analysis data Fig. S1 – Fig. S33.

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Author Contributions

S.M. conceived the concept. M.B., F.L., T.M., L.O and S.M. jointly devised the experimental program. F.L., M.B. and T.M. synthesized and characterized catalyst precursors. M.B. and T.M. performed polymerization experiments with phosphinenolato catalysts. L.O. performed experiments with salicylaldimine catalysts. M.B. and T.M. performed microstructure analysis, and experiments on materials properties. All authors jointly wrote the manuscript.

Notes

The authors declare no competing financial interests.

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