*Erschienen in: ACS Macro Letters ; 11 (2022), 10. - S. 1207-1211*
*https://doi.org/10.1021/acsmacrolett.2c00459*

# Polyethylenes with combined in-chain and side-chain functional groups from catalytic terpolymerization of carbon monoxide and acrylate

Maximilian Baur [a] and Stefan Mecking* [a]

a) Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, 78464 Konstanz, Germany.

**ABSTRACT** Linear polyethylenes with a combination of incorporated in-chain keto as well as side-chain ester groups are formed by Ni(II)-catalyzed terpolymerization of ethylene, carbon monoxide and methyl acrylate. These possess a random structure, with largely isolated non-alternating in-chain keto groups as well as ester-substituted units adjacent to the polyethylene chain, whereas the solid state structure of polyethylene is retained. Molecular weights of the terpolymers ($M_n$ ~ 20.000 g $mol^{-1}$) are predominantly determined by chain transfer after acrylate incorporation.

## Introduction

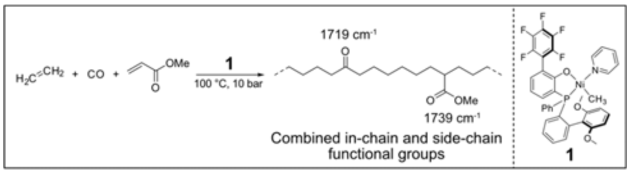
An introduction of polar groups into otherwise apolar polyethylene (PE) is frequently employed to increase the PEs polarity to achieve, e.g., compatibility with other polar materials. This can be achieved by post-polymerization modifications, or directly by copolymerization of ethylene with vinyl monomers like acrylates, vinyl ketones or others.[1-7] The later approach yields side-chain functional groups. By comparison, incorporation of carbon monoxide during polyethylene chain growth can afford in-chain keto groups. Amongst others, small amounts of such keto-units can impart the material with desirable photodegradability, to reduce the problematic environmental persistency of mismanaged polyethylene waste.[8] An access to linear HDPE-type polyethylenes with in-chain keto units (Keto-PEs) by incorporation of small amounts of carbon monoxide during ethylene polymerization had been long-sought for, as usually ethylene-CO copolymerization results in alternating polyketones due to the preference for CO incorporations. [9,10] Such Keto-PE materials have been enabled only recently by non-alternating copolymerization[11-13] catalyzed by advanced phosphinophenolato[14-20] Ni(II) complexes. Amongst others due to their high molecular weights (up to $M_w$ 400.000 g $mol^{-1}$; $M_n$ 200.000 g $mol^{-1}$) these polymers are processable and on par in their mechanical properties with commercial high density polyethylene (HDPE).[188] At the same time these materials are rendered photodegradable by the incorporated in-chain carbonyl groups.[11,18]

Polyethylenes with both in-chain and side-chain functional groups have so far only been accessible by free-radical terpolymerization of carbon monoxide and acrylates. This requires harsh conditions (≥ 300 atm) and yields branched products.[21]

We now report catalytic terpolymerizations of ethylene with carbon monoxide and acrylate under mild condtions that yield linear polyethylenes with in-chain as well as side-chain functional groups.

## Results and Discussion

Exposure of a phosphinophenolato Ni(II) catalyst precursor (**1**) to ethylene (10 atm) and small amounts of carbon monoxide in the presence of methyl acrylate (MA) results in the formation of solid polymers (Table 1). The presence of CO and MA substantially decrease catalytic activity of **1** and, therefore, polymerization yields when compared to an ethylene homo-polymerization with the same catalyst under identical conditions (Table 1, entry 6). This is in line with expected effects of the polar comonomers reversibly coordinating to catalytically active sites, thus competing with ethylene coordination and insertion.




**Scheme 1**. Catalytic terpolymerization of ethylene with CO and acrylate to in- and side-chain functionalized polyethylene.

The IR spectroscopic analysis of the formed polymers reveals these to be polyethylenes with incorporated keto- as well as ester-carbonyl units, which show absorption maxima for backbone-adjacent ester groups (1739 $cm^{-1}$) and in-chain ketones (1719 $cm^{-1}$) (Figure 1 and Scheme 1). This is concluded from comparison of the carbonyl absorption bands to corresponding ethylene-CO and ethylene-acrylate copolymers, respectively. (Figure 1). The observed IR absorption maximum at 1719 $cm^{-1}$ further shows the predominantley isolated/non-alternating nature of the in-chain carbonyl groups formed by CO incorporation. Deconvolution of the terpolymer absorption bands enables quantification of the incorporation ratios of functionalized repeat units in these terpolymers, which are confirmed by $^{1}$H NMR spectroscopy (Table 1). Incorporation ratios of either comonomer can be influenced by variation of CO or acrylate concentration in the reaction mixture, respectivley.

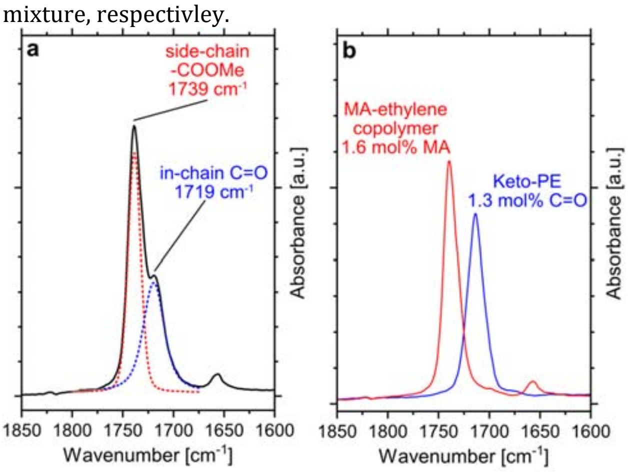



**Figure 1**. Carbonyl regime of ATR-IR spectra of **a.** A terpolymer (Table 1, entry 2) with deconvolution shown that allows for quantification of the keto and acrylate content (cf. SI for details). **b.** A Keto-PE (Table 1, entry 4) and ethylene-acrylate copolymer (Table 1, entry 5). Full ATR-IR spectra of terpolymers and reference copolymers are provided in the Supporting Information.

**Table 1.** Polymerization results.

| # | CO/$C_2H_4$ feed* [%] | Conc. MA† [mol $L^{-1}$] | Yield [g] | X (CO)‡ [mol%] | X (MA)‡ [mol%] | $M_n$ ($M_w/M_n$)# [$10^3$ g $mol^{-1}$] | $T_m$ [°C]** |
|---|---|---|---|---|---|---|---|
| 1 | 0.6 | 0.05 | 0.98 | 0.8 | 0.9 | 21 (1.5) | 126 |
| 2 | 0.6 | 0.1 | 0.30 | 1.0 (1.3) | 1.4 (1.5) | 13 (1.6) | 116/ 128 |
| 3 | 0.8 | 0.1 | 0.21 | 2.0 (2.3) | 1.7 (1.7) | 13 (1.5) | 117/ 125 |
| 4 | 0.6 | 0 | 2.15 | 1.3 (1.6) | - | 140 (1.6) | 136 |
| 5 | 0 | 0.1 | 1.07 | - | 1.6 (1.3) | 20 (2.0) | 116/ 129 |
| 6§ | 0 | 0 | 10.5 | - | - | 21 (1.9) | 131 |

Polymerization conditions: 10 µmol precat. **1**, 10 atm, 100 °C, 1000 rpm, 75 min, 100 mL toluene. * ratio of CO in an ethylene-CO gas feed. † concentration of MA in initial reaction solution. ‡ calculated from ATR-IR spectroscopy (cf. SI for details). In brackets: Incorporation calculated from $^{1}$H NMR spectroscopy by integration of the $^{1}$H signals of $\alpha$-carbonyl $CH_2$ (CO) or $OCH_3$ (MA) in relation to the overall integral. # determined by SEC in 1,2-dichlorobenzene at 160 °C via universial calibration against PS standards. ** Determined by DSC, second heating cycle. § 500 rpm stirring rate. 20 minutes reaction time accounting for high activity of **1** in ethylene homopolymerization. Reference homopolymerization data adopted from our previously reported work.[15]

Analysis of molecular weights by high tempature SEC (Table 1 and Figure 2) reveals considerably lower molecular weights of the terpolymers when compared to an ethylene-CO copolymer formed under identical conditions (Table 1, entry 4). However, the molecular weights of terpolymers are similar to an ethylene-MA reference copolymer synthesized under the same conditions at 10 atm, 100 °C. The observed narrow molecular weight distributions further indicate that a terpolymer and no mixture of Keto-PE and ethylene-acrylate copolymer is formed.

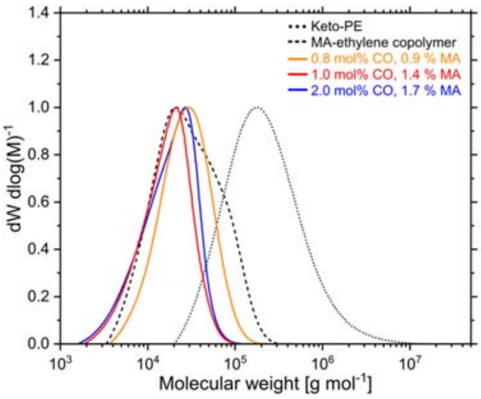



**Figure 2**. SEC traces of terpolymers, and a Keto-PE and ethylene-acrylate copolymer for comparison.

In depth analysis of polymer microstructures by 1D and 2D NMR spectroscopy (Figure 3 and Supporting Information) reveals the in-chain keto groups to be largely isolated, with additional motifs of adjacent carbonyl groups seperated by one or several ethylene units and only minor amounts of alternating segments. The same in-chain carbonyl microstructures are observed for the Keto-PE generated in the absence of acrylate under otherwise identical polymerization conditions (cf. Figure S4). These in-chain carbonyl motifs and the acrylate-based repeat units are arranged in the polyethylene chains in a random fashion and no evidence for e.g. a propensity for adjacent keto and ester incorporation or other effects of incorporated functional groups on the incorporation of the other polar comonomer is observed. This suggests that the chelates,[7,14,15,19] which are formed by reversible coordination of the functional groups incorporated in the chain to the active sites, are opened much the same way as in corresponding copolymerizations of ethylene with only CO or acrylate, respectively. Therefore, no evidence for a conceivable strong preference for opening of chelates from acrylate incorporation by CO is observed.[22] Unsaturated endgroups formed by $\beta$-H elimination after an acrylate incorporation prevail and only a small amount of non-functionalized, unsaturated endgroups are observed (Figure 3), despite the chains being largely formed by ethylene incorporation (Table 1). This observation qualitatively agrees with previous observations of the relative high propensity for chain transfer vs. chain growth after acrylate incorporation with different catalysts.[15,16] The decrease of molecular weights by acrylate comonomer is in contrast to CO-ethylene copolymerization with phosphinophenolato Ni(II) catalysts, where the formed in-chain ketones do not promote β-H elimination but rather increase molecular weights of the formed Keto-PE compared to homopolymerization under the same conditions (Table 1, entry 4 and 6) due to blocking of free coordination sites thus reducing β-H elimination rates.[18] Therefore, molecular weights of the formed terpolymers are predominantley determined by the presence of acrylate and limited by chain transfer reactions after respective acrylate insertions. The true terpolymer nature of the materials is further underlined by 2D DOSY NMR spectroscopy, featuring identical diffusion coefficients for the resonances indicative of the two different types of incorporated functional groups as well as endgroups and the polyethylene backbone (Figure S2).

In line with the linear structures devoid of branches observed by NMR spectroscopy, the terpolymers are crystalline according to DSC analyses (cf. Figure S11). Analysis by WAXS further revealed that the orthorombic solid state structure of polyethylene is fully retained in the formed terpolymer despite an overall incorporation of approx. 2 – 4 mol% polar comonomers. The incorporation of these reported low amounts of side-chain ester and in-chain keto groups (1 – 2 mol% of each polar comonomer) does therefore not significantly influence or disturb the crystal packing of the hydrocarbon backbone of the polyethylene chain (cf. Figure S12).

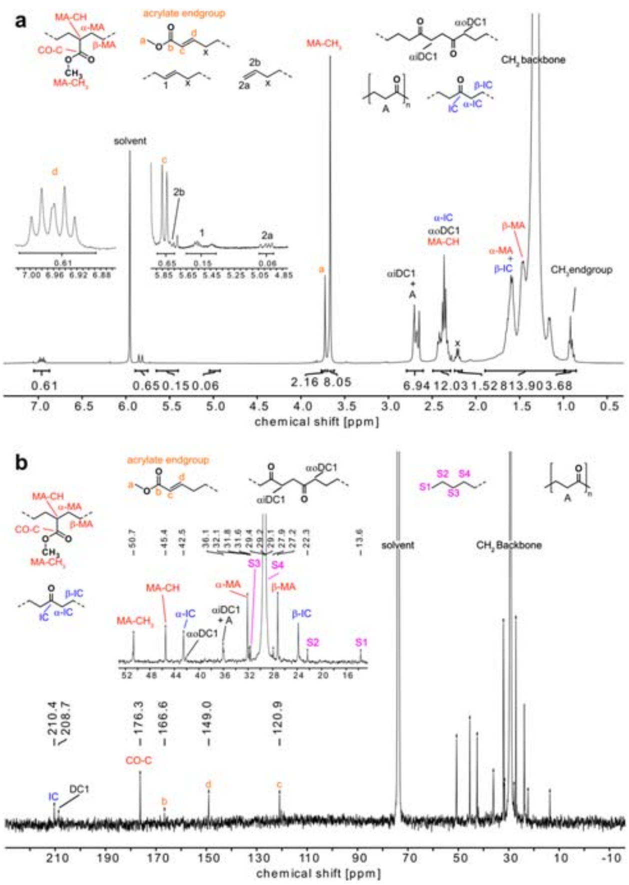



**Figure 3**. $^{1}H$ NMR spectrum (**a**) and $^{13}C\{^{1}H\}$ NMR spectrum (**b**) of a terpolymer (Table 1, entry 3) with full assignments. Acquired in tetrachloroethane-$d_2$ at 110 °C.

## Conclusions

By catalytic terpolymerization of ethylene with carbon monoxide and acrylates, linear polyethylenes with a combination of in-chain keto and ester side groups are accessible. This can be achieved with catalysts based on earth-abundant nickel as the active sites. Terpolymerization proceeds under mild conditions of 10 atm ethylene pressure and 100 °C. The formed terpolymers possess a random nature, and in terpolymerization no adverse effect of either polar comonomer on activity and incorporation ratio compared to the corresponding ethylene copolymerizations is observed and solid state structure of polyethylene is retained. Compared to the Keto-PEs from ethylene-CO copolymerization, the molecular weights of terpolymers are lowered due to the propensity for chain transfer after an acrylate insertion. This may be an issue for potential applications requiring certain minimum molecular weights, e.g. to achieve ductility and mechanical strength. The incorporation of additional polar functional groups can be beneficial to achieve a higher surface free energy and thus compatibility with polar materials. Also, in-chain and side-chain carbonyl groups can promote different, possibly synergistic photodegradation pathways.[8,23]

### ASSOCIATED CONTENT

The Supporting Information is available free of charge via the Internet at http://pubs.acs.org."

Experimental procedures, polymer characterization data (PDF).

### AUTHOR INFORMATION


#### Corresponding Authors

Stefan Mecking – Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany; orcid.org/0000-0002-6618-6659;
Email: stefan.mecking@uni-konstanz.de

#### Authors

Maximilian Baur – Chair of Chemical Materials Science, Department of Chemistry, University of Konstanz, 78457 Konstanz, Germany; orcid.org/0000-0001-8222-9500.
Email: maximilian.baur@uni-konstanz.de


#### Author Contributions

M.B. performed all experiments. M.B. and S.M. devised the research program and wrote the manuscript.

#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENT

The authors thank M. Birkle for WAXS measurements and A. Kartheiser for contribution to this work as part of his undergraduate studies. Financial support of part of this work by the ERC (Advanced Grant 'DEEPCAT', 832480 to S.M.) is gratefully acknowledged.

## REFERENCES

(1) Keyes, A.; Basbug Alhan, H. E.; Ordonez, E.; Ha, U.; Beezer, D. B.; Dau, H.; Liu, Y.-S.; Tsogtgerel, E.; Jones, G. R.; Harth, E. Olefins and Vinyl Polar Monomers: Bridging the Gap for Next Generation Materials. *Angew. Chem. Int. Ed.* **2019**, *58*, 12370–12391.

(2) Walsh, D. J.; Hyatt, M. G.; Miller, S. A.; Guironnet, D. Recent Trends in Catalytic Polymerization. *ACS Catal.* **2019**, *9*, 11153-11188

(3) Tan, C.; Chen, C. Emerging Palladium and Nickel Catalysts for Copolymerization of Olefins with Polar Monomers. *Angew. Chem. Int. Ed.* **2019**, *58*, 7192–7200.(4) Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leeuwen, P. W. N. M.; Nozaki, K. *Ortho*-Phosphinobenzenesulfonate: A Superb Ligand for Palladium-Catalyzed Coordination-Insertion Copolymerization of Polar Vinyl Monomers. *Acc. Chem. Res.* **2013**, *46*, 1438–1449.

(5) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. Mechanistic Studies of the Palladium-Catalyzed Copolymerization of Ethylene and α-Olefins with Methyl Acrylate. *J. Am. Chem. Soc.* **1998,** *120* (5), 888–899.

(6) Williamson, J. B.; Lewis, S. E.; Johnson, R. R.; Manning, I. M.; Leibfarth, F. A. C-H Functionalization of Commodity Polymers. *Angew. Chem. Int. Ed.* **2019,** *58* (26), 8654–8668.

(7) Chen, L.; Malollari, K. G.; Uliana, A.; Sanchez, D.; Messersmith, P. B.; Hartwig, J. F. Selective, Catalytic Oxidations of C–H Bonds in Polyethylenes Produce Functional Materials with Enhanced Adhesion. *Chem* **2021,** *7* (1), 137–145.

(8) Hartley, G. H.; Guillet J. E. Photochemistry of Ketone Polymers. I. Studies of Ethylene-Carbon Monoxide Copolymers. *Macromolecules.* **1968,** *1*, 165–170.

(9) Rix, F. C.; Brookhart, M.; White, P. S. Mechanistic Studies of the Palladium(II)-Catalyzed Copolymerization of Ethylene with Carbon Monoxide. *J. Am. Chem. Soc.* **1996**, *118*, 4746-4746.

(10) Shultz, S. C.; Ledford, J.; DeSimone, J. M.; Brookhart, M. Kinetic Studies of Migratory Insertion Reactions at the (1,3-Bis(diphenylphosphino)propane)Pd(II) Center and Their Relationship to the Alternating Copolymerization of Ethylene and Carbon Monoxide. *J. Am. Chem. Soc.* **2000**, *122*, 6351-6356.

(11) Tang, S.; Seidel, F. W.; Nozaki, K. High Density Polyethylenes Bearing Isolated In-Chain Carbonyls. *Angew. Chem. Int. Ed.* **2021**, *60*, 26506–26510.

(12) Chen, S.-Y.; Pan, R.-C.; Chen, M.; Liu, Y.; Chen, C.; Lu, X.-B. Synthesis of Nonalternating Polyketones Using Cationic Diphosphazane Monoxide-Palladium Complexes. *J. Am. Chem. Soc.* **2021**, *143*, 10743-10750.

(13) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oorta B.; Pugh, R.I. The first example of palladium catalysed non-perfectly alternating copolymerisation of ethene and carbon monoxide. *Chem. Commun.* **2002**, 964-965.

(14) Xin, B. S.; Sato, N.; Tanna, A.; Oishi, Y.; Konishi, Y.; Shimizu, F. Nickel Catalyzed Copolymerization of Ethylene and Alkyl Acrylates. *J. Am. Chem. Soc.* **2017**, *139*, 3611–3614.

(15) Zhang, Y.; Mu, H.; Pan, L.; Wang, X.; Li, Y. Robust Bulky [P,O] Neutral Nickel Catalysts for Copolymerization of Ethylene with Polar Vinyl Monomers. *ACS Catal.* **2018**, *8*, 5963–5976.

(16) Xiong, S.; Shoshani, M. M.; Zhang, X.; Spinney, H. A.; Nett, A. J.; Henderson, B. S.; Miller, T. F.; Agapie, T. Efficient Copolymerization of Acrylate and Ethylene with Neutral P, O-Chelated Nickel Catalysts: Mechanistic Investigations of Monomer Insertion and Chelate Formation. *J. Am. Chem. Soc.* **2021**, *143*, 6516–6527.

(17) Lin, F.; Morgen, T. O.; Mecking, S. Living Aqueous Microemulsion Polymerization with Robust Ni(II) Phosphinephenolato Catalysts. *J. Am. Chem. Soc.* **2021**, *143*, 20605–20608.

(18) Baur, M.; Lin, F.; Morgen, T. O.; Odenwald, L.; Mecking, S. Polyethylene materials with in-chain ketones from nonalternating catalytic copolymerization. *Science* **2021**, *374*, 604–607.

(19) Voccia, M.; Odenwald, L.; Lin, F.; Baur, M.; Falivene, L.; Mecking, S.; Caporaso, L. *J. Am. Chem. Soc.* **2022**, *144*, 15111 – 15117.

(20) Mecking, S.; Schnitte, M. Neutral Nickel(II) Catalysts: From Hyperbranched Oligomers to Nanocrystal-Based Materials. *Acc. Chem. Res.* **2020**, *53*, 2738–2752.

(21) Morgen, T. O.; Baur, M.; Mecking, S. Photodegradable branched polyethylenes from carbon monoxide copolymerization under benign conditions. *Nat. Commun.* **2020**, *11*, 3693.

(22) Nakamura, A.; Kageyama, T.; Goto, H.; Carrow, B. P.; Ito, S.; Nozaki, K. Pd-Catalyzed Copolymerization of Methyl Acrylate with Carbon Monoxide: Structures, Properties and Mechanistic Aspects toward Ligand Design. *J. Am. Chem. Soc.* **2012**, *134*, 12366–12369.

(23) Amerik, Y.; Guillet J. E. Photochemistry of Ketone Polymers. IV. Photolysis of Methyl Vinyl Ketone Copolymers. *Macromolecules.* **1971,** *4*, 375–379.