

Supporting Information

Compartmentalized polymerization in aqueous and organic media to low-entangled ultra high molecular weight polyethylene

Florian P. Wimmer, Viktoria Ebel, Felix Schmidt and Stefan Mecking*

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

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1 Materials and General Considerations

All manipulations involving air/moisture sensitive compounds were carried out under nitrogen as inert gas atmosphere using standard Glovebox/Schlenk techniques. All glassware was dried under vacuum prior to use.

1.1 Solvents and reagents

Solvents were dried and degassed using standard laboratory techniques.¹ Pentane and heptane were distilled from CaH₂ whereas THF and toluene were distilled from sodium benzophenyl ketyl. Mesitylene and m-xylene were degassed by three consecutive freeze-pump-thaw cycles and dried by storing over 4 Å molecular sieve. Ethylene for polymerization experiments (3.5 grade) was supplied by AirLiquide and used as received. CDCl₃ was supplied by Sigma Aldrich. All other deuterated solvents were supplied by Eurisotop. Deuterated solvents were stored over 3 Å molecular sieves.

Dimethyl-1,48-octatetracontanedioate and dimethyl-1,18-octadecanedioate were prepared according to reported procedures.² PBDD (GI-2000) was donated by Nisso Chemicals Europe. Ti(O^{*n*}Bu)₄, common organic solvents, acetic anhydride and sodium laurylsulfate were purchased from Sigma-Aldrich. Hexafluorobenzene and CsOH were purchased from ABCR. An ethylene-octene copolymer (Engage 8400, 40 wt.-% octene. Designated here as ran-EO48) was supplied by DOW Chemicals.

All Ni(II) salicylaldiminato catalysts, the corresponding salicylaldimines and [(tmeda)NiMe₂] applied in this work were synthesized according to reported procedures.³⁻⁵

1.2 Analytical methods and techniques

NMR spectra were recorded on a Bruker Avance III 400 spectrometer, a BRUKER Avance III HD 400 (¹H: 400.1 MHz, ¹³C: 100.6 MHz) or a BRUKER Avance III 600 spectrometer (¹H: 600 MHz, ¹³C: 151 MHz). ¹H and ¹³C chemical shifts were referenced to the solvent signals. NMR spectra of stabilizers were acquired in tetrachloroethane-*d*₂ at 383 K sample temperature for better solubility. ¹³C{¹H} NMR spectrum of the **ran-EO** stabilizer was acquired at 10-20wt.% polymer content in tetrachloroethane-*d*₂ (TCE), inverse gated decoupling with a relaxation delay of 2.0 s, an acquisition time of 1.8 s and about 25000 accumulated scans. As paramagnetic relaxation aid, 5 mg [Cr(acac)₃] per mL TCE-*d*₂ was added to the sample.

NMR spectral data are reported as follows: chemical shift (δ in ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are given as follows (or combinations thereof): s:

singlet, d: doublet, t: triplet, q: quartet, quint: quintet, sept: septet, m: multiplet, v: virtual, br.: broad. Acquired data were processed and analyzed using MestReNova software.

DSC analysis was performed on a Netzsch Phoenix 204 F1 instrument at heating and cooling rates of 10 K min⁻¹, unless noted otherwise. Data is reported from first and second heating cycles. Crystallinities were calculated by dividing the heat of fusion by 293 J g⁻¹ as the heat of fusion of 100% crystalline PE.⁶

Molecular weights of synthesized polyethylenes were determined by high temperature gel permeation chromatography (GPC). Polymer samples were dissolved at 160 °C in the respective solvent by gentle shaking over 120 min. Unless stated otherwise, a PolymerChar GPC-IR instrument, equipped with an IR (model IR5) and a viscosity detector, and with Olexis columns was employed. Measurements were conducted at 160 °C in 1,2-dichlorobenzene at a flow rate of 0.5 ml min⁻¹. Separate IR detection of CH₃ and CH-total (that is all CH_X) signals allowed for online measurement of the number of methyl branches. Universal calibration with linear polystyrene standards was employed. Samples of Table 4 were measured on a Polymer Laboratories 220 instrument (software: Cirrus Multi Offline GPC/SEC software, version 3.3) equipped with PLgel Olexis columns at 160 °C in 1,2,4-trichlorobenzene (1.0 mL minute⁻¹ flow rate) with refractive index (concentration signal), viscosity and light scattering detection (15° and 90°). Molecular weights were determined using the triple detection method calibrated with narrow polystyrene standards.

Molecular weights of the precise block length copolymers (used as stabilizers) were measured in THF at 35 °C on a PSS SECcurity² GPC System with two PSS SDV linear M 3 μm columns using refractive index detection directly vs. polystyrene standards at a flow rate of 1 ml min⁻¹.

Dynamic light scattering (DLS) was performed on diluted polyethylene dispersions using a Malvern Zetasizer Nano-ZS ZEN 3600 instrument (633 nm) in backscattering mode (173°) at 25 °C. The data was analyzed to yield particle size distributions and polydispersity indices (PDIs; dimensionless number between 0 (monodisperse) and 1 (highly disperse); determined from gradient of cumulants analysis) using the Malvern Zetasizer Software, version 7.12.

Transmission electron microscopy (TEM) images were recorded on a Zeiss Libra 120 FE-TEM instrument. TEM images were analyzed using ISP Viewer and ImageJ/Fiji software.

Scanning electron microscopy (SEM) images were recorded on a Zeiss Auriga 40 Crossbeam FE-SEM instrument. SEM images were analyzed using ImageJ/Fiji software.

Polyethylene dispersion samples were dialyzed versus demineralized water using Spectra/Por Dialysis Membranes 2, MWCO 12 – 14 kD and electron microscopy samples prepared by drop casting (diluted to 0.01 wt-%) directly on the respective sample holder. The decrease of surfactant content during dialysis was monitored by tensiometry measurements.

Samples for SEM were Au sputtered for 25 seconds using an Edwards Scancoat Six prior to imaging.

2 General Polymerization Procedure

Ethylene polymerization was carried out in a 300 mL stainless steel pressure reactor equipped with a mechanical stirrer (three-blade axial current propeller stirrer, approx. 30 mm diameter) and a heating/cooling jacket supplied with a thermostat controlled by a thermocouple dipping into the reaction mixture. The pressure reactor was prepared by heating to an internal temperature of >60 °C and passing through three cycles of applying vacuum for at least five minutes followed by flushing with inert gas.

2.1 General Procedure for Polymerization with Aqueous Mini-Emulsions

The desired amounts of sodium laurylsulfate and CsOH were degassed and dissolved in 100 mL of degassed water. The corresponding amounts of [(tmeda)NiMe₂] and salicylaldehyde were weighed into an 8 mL vial in a nitrogen filled glovebox and dissolved in the respective amounts of organic solvents and transferred to the aqueous surfactant solution (for details see section 3.1). The components were emulsified by ultrasonication for 2 minutes using a Bandelin GM3200 ultrasonotrode with a KE76 tip, operated at 120 W with 70% amplitude. During emulsification the reaction mixture was cooled in an ice bath to prevent a temperature increase upon ultrasonication. The mixture was subsequently transferred into the autoclave and pressurized to 40 bars of ethylene pressure (within 1 minute). A constant pressure was maintained by feeding ethylene. At the end of the desired reaction time, the ethylene flow was interrupted, and the autoclave was vented. The obtained dispersion was subjected to DLS analysis. Polymer yields were determined by precipitating a 20 g aliquot of the dispersion in ethanol. The resulting polymer was washed thoroughly with water and ethanol and the residual polymer was dried at least 18 h at 60 °C, 4 mbar.

2.2 General Procedure for Polymerization in non-Aqueous Media

The desired amount of block- or random copolymer stabilizer was degassed thoroughly by dissolution in previously distilled THF and removal of the solvent in vacuo at slightly elevated

temperatures. Subsequently the stabilizer was dissolved again in THF and the obtained clear solution was transferred to the autoclave. The appropriate amount of catalyst was dissolved in THF in a nitrogen filled glovebox and transferred to the autoclave, followed by pressurization to 40 bars. A constant pressure was maintained by feeding ethylene. At the end of the desired polymerization time the ethylene feed was interrupted, and the autoclave was vented. The obtained dispersion was subjected to DLS analysis. Polymer yields were determined by precipitating a 20 g aliquot of the dispersion in ethanol. The resulting polymer was washed thoroughly with water and ethanol and the residual polymer was dried at least 18 h at 60 °C, 4 mbar.

3 Additional Data on Mini-Emulsion Polymerization

3.1 Amount of Lipophilic Solvent

Table S1. Polymerization experiments with variable amounts of benzene as lipophilic solvent.

Entry	Amount Lipophilic Solvent [ml]	Yield ^a [g]	activity ^b	T _m ^c [°C]	χ ^c [%]	M _n ^d [x 10 ⁶ g mol ⁻¹]	M _w /M _n ^d
1	1.9	3	16	139(135)	68(46)	1.3	2.6
2	2.9	2.9	16	141(134)	69(42)	1.9	2.4
3	4.9	3.3	17	140 (134)	70 (47)	1.3	2.7

Polymerization conditions: 40 bar ethylene, 100 mL water, 750 rpm. 5 g sodiumlaurylsulfate, 550 mg CsOH, 15 °C, 30 min. Experiments were conducted in mixtures of the appropriate amount of lipophilic solvent and 0.1 mL hexafluorobenzene. 15 μmol [(tmeda)NiMe₂] and 9 μmol salicylalimine. Reaction mixtures were emulsified by 2 min of ultrasonication, transferred to the autoclave and pressurized. Reaction time was started at the moment of reaching 40 bar. a) Yields were determined by precipitating a 20 g aliquot of the dispersion after polymerization. b) average activity in units of × [10³ mol_E mol_{Ni}⁻¹ h⁻¹] c) Determined by DSC at a heating/cooling rate of 10 K min⁻¹. Data is reported from first heating cycles. Data from second heating cycles is given in brackets. d) Determined by gel permeation chromatography in o-DCB at 160 °C via universal calibration versus polystyrene standards.

Increased amounts of lipophilic solvents did not have a significant impact on the outcome of polymerization with aqueous miniemulsions. Notably at volumes of 5 mL of lipophilic solvent, phase separation between aqueous and lipophilic phase occurred during polymerization as evidenced by a layer of lipophilic solvent on top of the dispersion after polymerization.

3.2 Additional Data on Solvent Optimization

Table S2. Summary of polymerization conditions, catalytic activity and polymer analytics and their solvent dependency.

Entry	Lipophilic Solvent		[(tmeda)NiMe ₂] [μmol]	Salicylaldimine Ligand [μmol]	T _{reaction} [min]	Yield ^a [g]	activity ^b	T _m ^c [°C]	χ ^c [%]	M _n ^d [x 10 ⁶ g mol ⁻¹]	M _w /M _n ^d
	Solvent 1 [mL]	Solvent 2 [mL]									
1	Benzene	C ₆ F ₆	7.5	4.5	90	3.8	20	139(134)	62(47)	1.6	2.1
	1.1	0.5									
2	Toluene	C ₆ F ₆	10	9	90	5.1	13	139 (135)	69(45)	1.5	2.3
	1.9	0.1									
3	m-Xylene	C ₆ F ₆	10	9	90	5.8	15	141(134)	69(42)	1.9	2.4
	1.9	0.1									
4	Mesitylene	C ₆ F ₆	10	9	90	2.3	6.0	143(136)	70(44)	1.7	2.4
	1.9	0.1									

Polymerization conditions: 40 bar ethylene, 100 mL water, 750 rpm. 5 g sodiumlaurylsulfate, 550 mg CsOH, 15 °C. Reaction mixtures were emulsified by 2 min of ultrasonication, transferred to the autoclave and pressurized. a) Yields were determined by precipitating a 20 g aliquot of the dispersion after polymerization. b) average activity in units of $\times [10^3 \text{ mol}_E \text{ mol}_{Ni}^{-1} \text{ h}^{-1}]$ c) Determined by DSC at a heating/cooling rate of 10 K min⁻¹. Data is reported from first heating cycles. Data from second heating cycles is given in brackets. d) Determined by gel permeation chromatography in o-DCB at 160 °C via universal calibration with polystyrene standards.

4 Additional Data on Particle Size *versus* Polymer Yield

To further underline the dependency of particle size and polymer yield, experiments at different reaction times and otherwise identical reaction conditions were performed. In all cases an increase in polymer yield led to an increase in particle size.

Table S3. Correlation of polymer yield and particle sizes.

Benzene		Toluene		<i>m</i> -Xylene		Mesitylene	
Yield PE [g]	d _{Particle} (DLS) [nm]	Yield PE [g]	d _{Particle} (DLS) [nm]	Yield PE [g]	d _{Particle} (DLS) [nm]	Yield PE [g]	d _{Particle} (DLS) [nm]
0.6	201	2.4	348	3	659	1.4	265
3.1	271	5.1	418	5.8	791	2.3	284

Figure S1 compares the droplet size of the initial miniemulsion prior to polymerization with the particle size of the obtained UHMWPE dispersion.

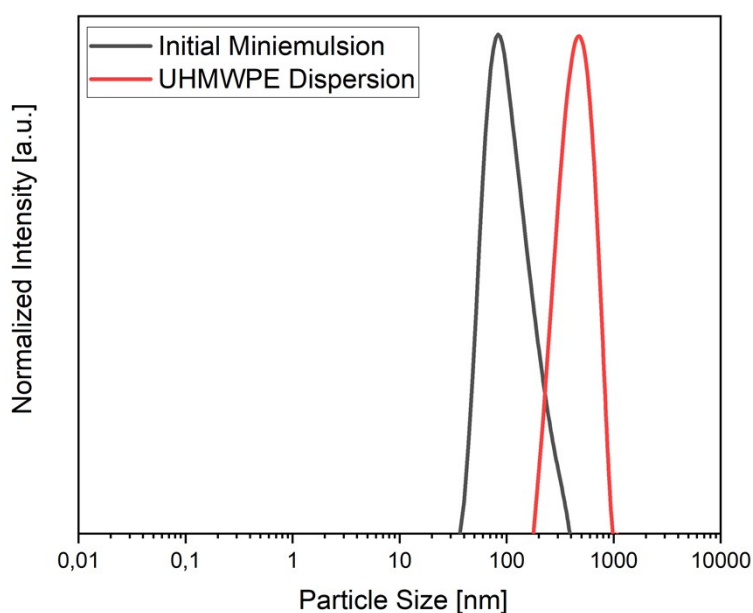


Figure S1. Comparison of the particle size of the obtained polymer dispersion (red, **Table S2**, Entry 3) and the droplet size of the corresponding initial miniemulsion prior to polymerization (black). Note that the miniemulsion shown here was generated in the absence of catalyst, by an otherwise identical protocol.

5 Determination of Chains per Particle

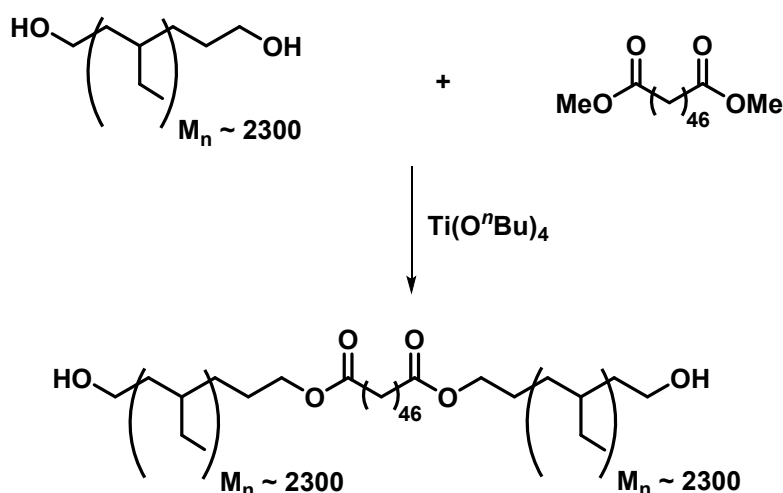
The number of chains per particle was determined on the polymer dispersion from Entry 3, Table S1. A dialyzed and diluted polymer dispersion (cf. preparation of TEM samples) was

heated to 160 °C for 60 minutes in a pressure-tight glass vial. Subsequent TEM analysis revealed the obtained particles to be spherical in shape. The size of the spherical particles was determined by dynamic light scattering. The number of chains per particle were calculated assuming a polymer density of 970 kg m⁻³.⁷

$$N_{\text{particles/chain}} = \frac{m_{\text{particle}}}{M_n(\text{GPC})} = \frac{V_{\text{particle}} \times \rho_{\text{UHMWPE}}}{\frac{M_n(\text{GPC})}{N_A}} = \frac{\frac{4}{3} \times \left(\frac{d_{\text{particle}}(\text{DLS})}{2} \right)^3 \times \pi \times \rho_{\text{UHMWPE}}}{\frac{M_n(\text{GPC})}{N_A}}$$

6 Synthesis of Block Copolymers used as Stabilizers

Scheme S1. General Scheme for the Synthesis of Block Copolymers used as Stabilizers.



Block copolymers were synthesized by modification of a procedure reported by Stempfle *et al.*⁸ The respective amount of both (macro-) monomers were weighed into a Schlenk tube equipped with an overhead stirrer and a screw type agitator. The mixture was degassed in vacuum. 0.1 mol% of [Ti(OⁱBu)₄] (5 µm/mL stock solution in dry toluene) were added and the mixture was heated to 230 °C under vacuum and gentle stirring for 18 h. After cooling to room temperature, the crude product was dissolved in THF, precipitated in cold methanol and dried at 5 mbar and 60 °C for at least 24 h. The exclusive presence of the desired endgroup (i.e. OMe endgroups for stabilizer **MB34-OMe** and OH endgroups for stabilizer **MB29-OH**) was shown by ¹H-NMR spectroscopy (singulett at 3.66 ppm for OMe or triplett at 3.62 ppm for CH₂OH). (cf. **Figure S2**).

Table S4. Analytical data for precise block length block copolymers.

	eq _{C48-OMe2} used in synthesis	eq _{PBDD} used in synthesis	M _n (GPC) [× 10 ³ g mol ⁻¹]	M _w /M _n	Endgroups from NMR
MB29-OH	1	1.01	29	4.6	OH
MB34-OMe	1.01	1	29	4.4	OMe
TB9-OH	1	2.2	9	1.5	OH

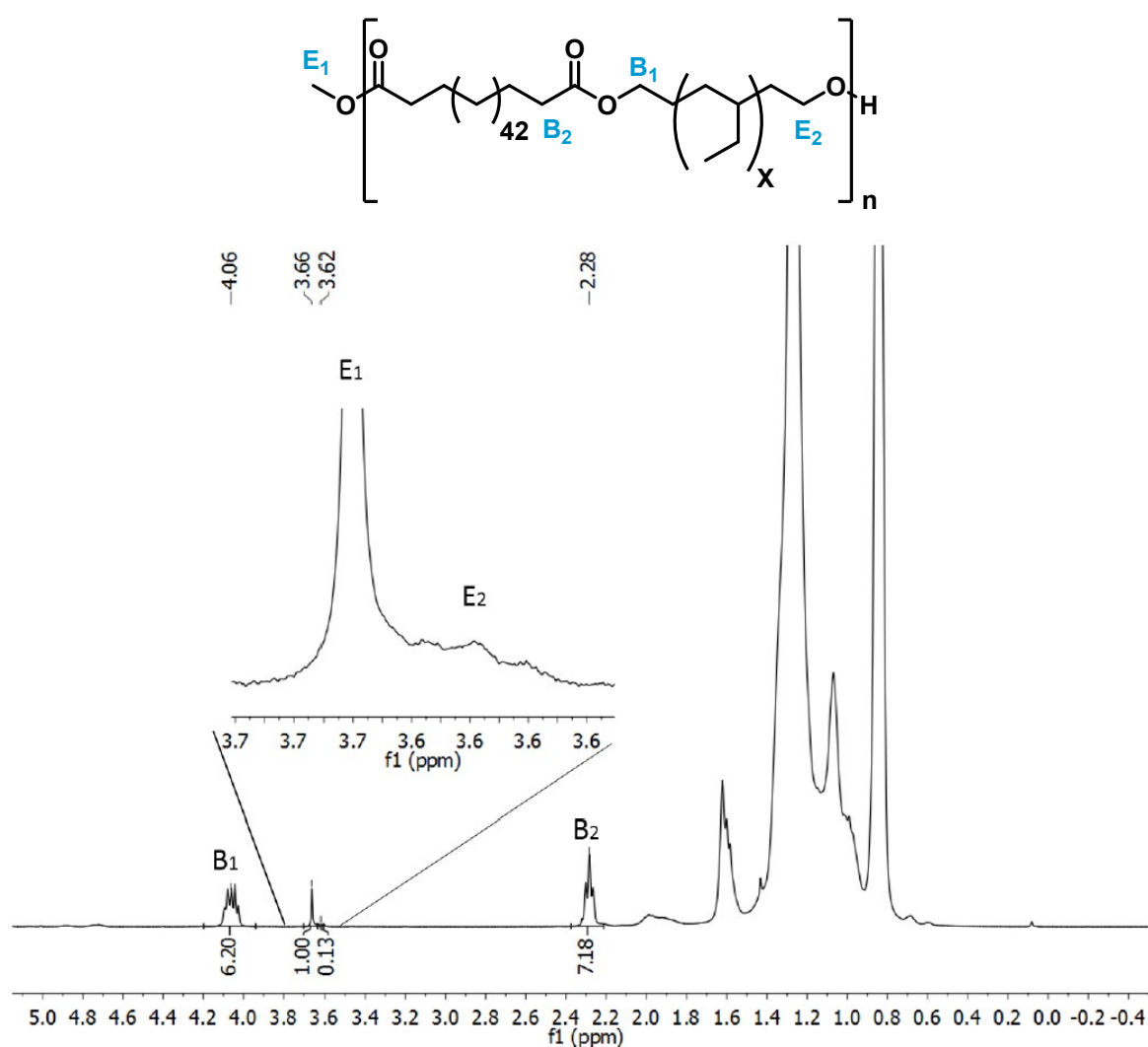


Figure S2. ¹H-NMR Spectrum (400 MHz, C₂D₂Cl₄, 383 K) of precise chain length block copolymer MB34-OMe.

7 Block Length Distribution of Random Copolymer

Weight averaged block length distributions for random copolymers were calculated according to:

$$P_i = p_{aA}^{i-1} \times (1 - p_{aA}) \times i \times (1 - p_{aA})^2$$

(i: block length, p_{aA} : mole fraction of ethylene repeat units in polymer).

$$p_{aA} = \frac{[E]}{[E] + [O]}$$

The following values for p_{aA} were considered: 0.72 (60 wt.% octene), 0.85 (40 wt.% octene) and 0.94 (20 wt.% octene). The assumption of a random copolymer nature is reasonably fulfilled for these copolymers as evidenced by analysis of ethylene 1-octene copolymers obtained by constrained geometry catalysts.⁹

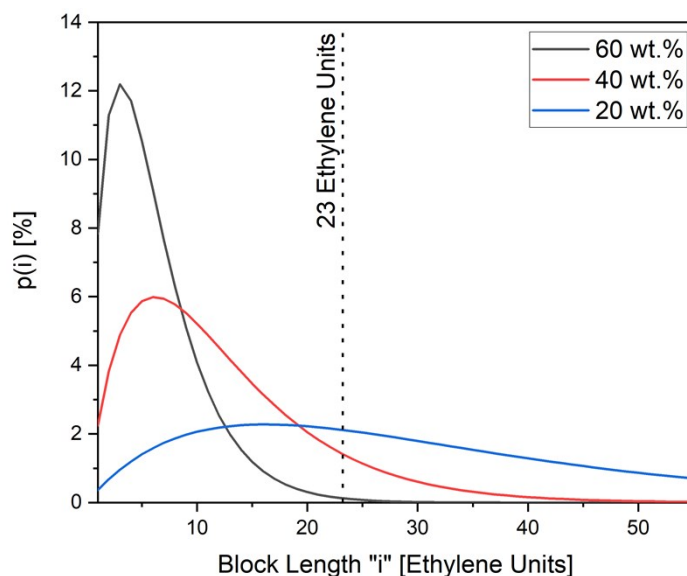


Figure S3. Calculated block length distribution of random ethylene 1-octene copolymers with different 1-octene contents.

The underlying assumption that **ran-EO48** can be considered a random copolymer is underlined by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy (**Figure S4**).

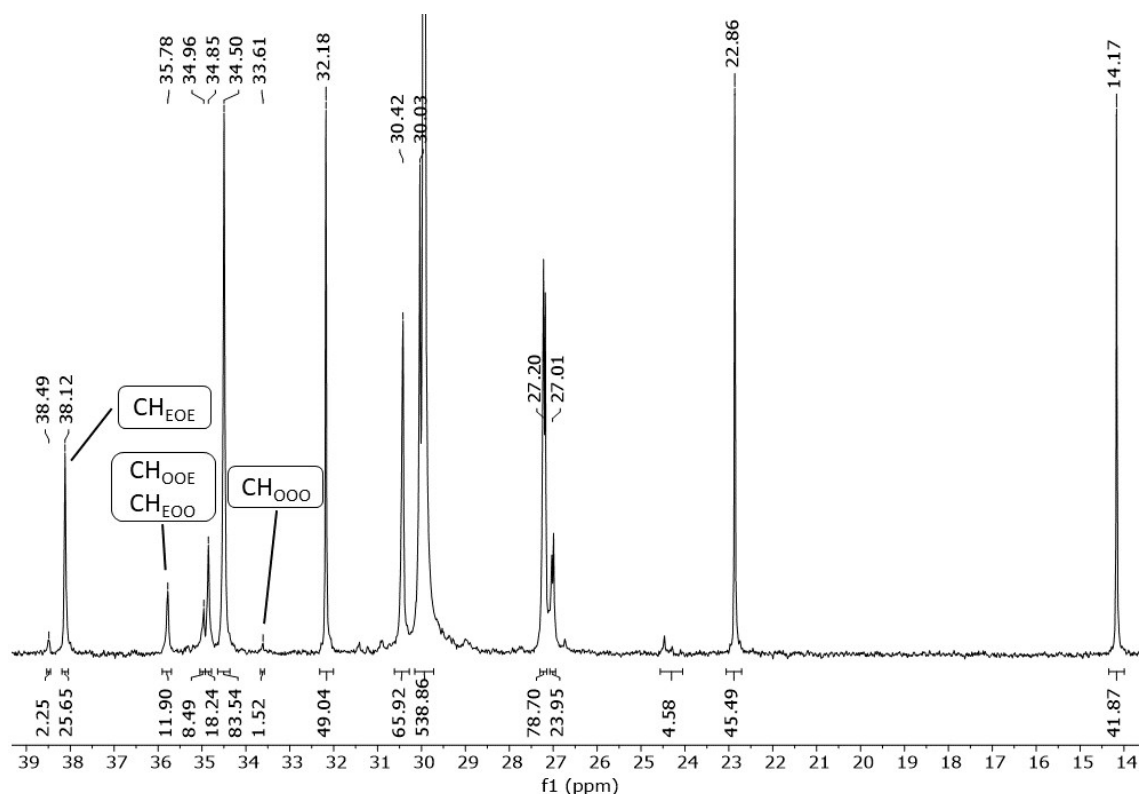


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (383 K, 151 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$) of the ethylene-octene copolymer employed as a stabilizer (**ran-EO48**). Assignments according to ^{10,11}.

8 Additional Data on Polymerizations in THF in the Presence of Block Copolymer Stabilizers

To elucidate the role of the stabilizers, reference experiments were performed with the building blocks employed for stabilizer synthesis (cf. **Figure S5**), representing the individual blocks of the stabilizer multiblock copolymers (**Table S5**). Furthermore, multiblock copolymers with shorter co-crystallizable segments were synthesized and studied in ethylene polymerization (**Table S5**).

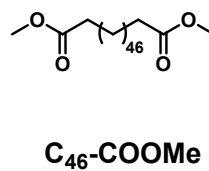
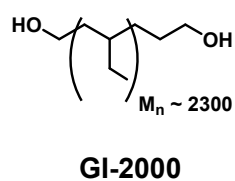
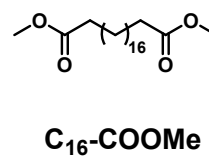


Figure S5. Compounds studied as stabilizers in reference polymerization experiments.

Table S5. Additional Polymerization Data with reference stabilizers.

Entry	Additive	Amount Additive [mg]	Yield ^a [g]	activity ^b	T _m ^c [°C]	χ ^c [%]	M _n ^d [x 10 ⁶ g mol ⁻¹]	M _w /M _n ^d
1	MB¹⁶36-OMe	100	1.8	6.6	140 (135)	51 (43)	0.2	2.3
2	MB¹⁶36-OMe	200	1.9	6.6	140 (132)	56 (41)	0.6	1.3
3	C₄₆-COOMe	100	3.6	12.4	139 (131)	57 (31)	1.0	1.2
4	C₁₆-COOMe	100	No polymer obtained.					
5	GI-2000	100	1.8	5.8	140 (133)	57 (41)	0.2	2.3

Polymerization conditions: 5 μmol 2-Py precatalyst, 40 °C, 30 min. Additives were degassed by three consecutive cycles of dissolving in oxygen-free THF and removal thereof under inert gas condition. Reaction time was started at the moment of reaching 40 bar. a) Yields were determined by precipitating a 20 g aliquot of the dispersion after polymerization. b) average activity in units of $\times [10^3 \text{ mol}_E \text{ mol}_{Ni}^{-1} \text{ h}^{-1}]$ c) Determined by DSC at a heating/cooling rate of 10 K min⁻¹. Data is reported from first heating cycles. Data from second heating cycles is given in brackets. d) Determined by gel permeation chromatography in o-DCB at 160 °C via universal calibration with polystyrene standards.

9 Additional Data on Melting Transitions of Stabilized UHMWPE

DSC analysis of a neat multiblock copolymer, stabilized UHMWPE as obtained from polymerization, and stabilizer-free UHMWPE shows a lower peak melting temperature for the stabilizer-containing UHMWPE vs. neat UHMWPE (142-136 °C, **Figure S6**). This may indicate a certain extent of co-crystallization of the stabilizer multiblock copolymer with the UHMWPE.

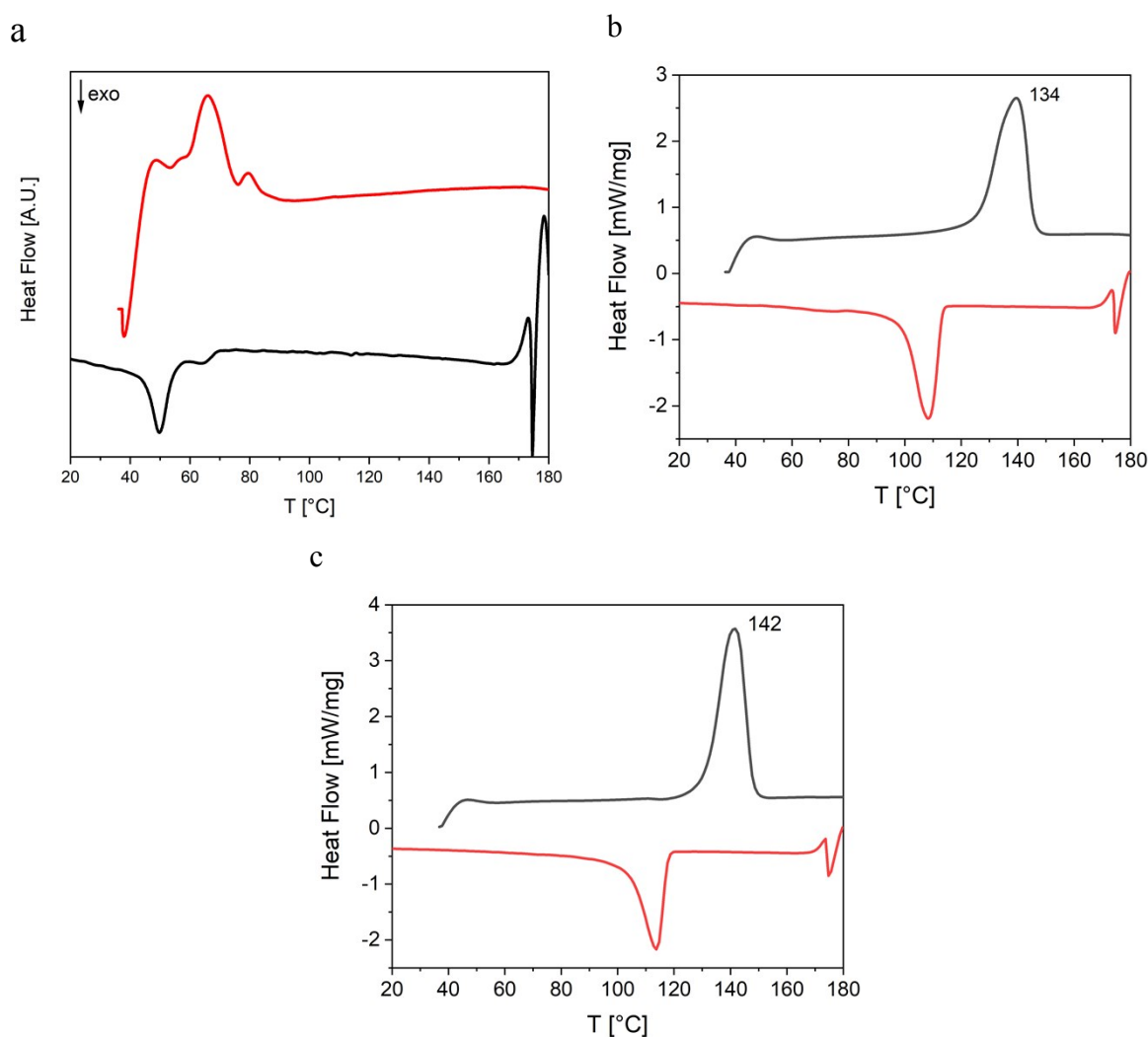


Figure S6. DSC traces (heating/cooling rate: 10 K/min) of a) stabilizer **MB34-OMe**, b) **MB34-OMe** stabilized UHMWPE as obtained from polymerization (Table 3, Entry 4) and c) UHMWPE obtained from aqueous emulsion polymerization (i.e. without steric stabilizer, Table 2, Entry 5).

10 References

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