

Supporting Information

Nanocrystal Formation in Aqueous Insertion Polymerization

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Influence of the TPPTS ligand on aqueous ethylene polymerization	S2
Catalyst pre-exposure experiments in aqueous solution	S5
Influence of the surfactant concentration and surfactant nature	S6
Studies using ¹³C-labeled 1-TPPTS	S11
Influence of the pressure and temperature on catalytic aqueous ethylene polymerization	S22
Polyethylene analysis	S25
Polymerization in deuterium oxide	S26
Influence of pH on catalytic aqueous ethylene polymerization	S27
Catalyst-Stabilizing additives	S32
Sampling system	S41
Validation of the sampling system	S45
Analyses of particles obtained with the sampling system by TEM	S49
AUZ measurements	S56
Particle thickness measurements	S59
Additional TEM micrographs	S61
References	S62

Influence of the TPPTS ligand on aqueous ethylene polymerization

Table S1. Influence of TPPTS and TPPTS-oxide on ethylene polymerization in water catalyzed by **1-TPPTS**.

entry ^a	time [h]	additives	polymer [%] ^b	TOF ^c	particle size [nm] ^d	T _m [°C] (crystallinity [%]) ^e
S1-1	0.5	-	1.26	16964	14	nd
S1-2	1	10 μ mol 1-TPPTS after 30 min	2.91	10054	40 (25%), 14	132 (71)
S1-3	1	-	1.37	9747	8	137 (75)
S1-4	0,5	20 μ mol 1-TPPTS	2.33	16479	7	132 (62)
S1-5	1	10 eq TPPTS	2.27	15736	40 (49%), 10	134 (67)
S1-6	0,5	10 eq TPPTS-oxide	-	-	-	-
S1-7	1	+ 10 eq TPPTS (6 % TPPTS-oxide)	1.70	12175	14	nd

^a Reaction conditions: 50 μ mol L⁻¹ **1-TPPTS**, 200 mL water 26 mmol L⁻¹ SDS, 15 °C, 40 bar. ^b Determined by precipitation. ^c [mol ethylene $\times$ mol cat.⁻¹ h⁻¹]. ^d Determined by DLS.

^e Determined by DSC.

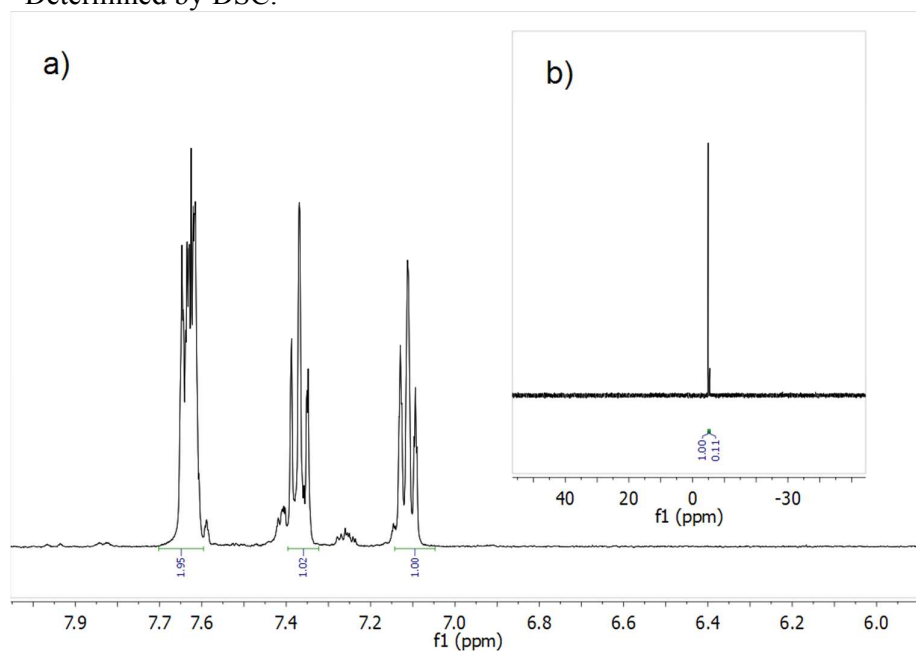


Figure S1. a) ¹H and b) ³¹P NMR of oxide free TPPTS purchased from abcr. The spectrum is recorded on 400 MHz Bruker Avance 400 device in dmsd-d₆.

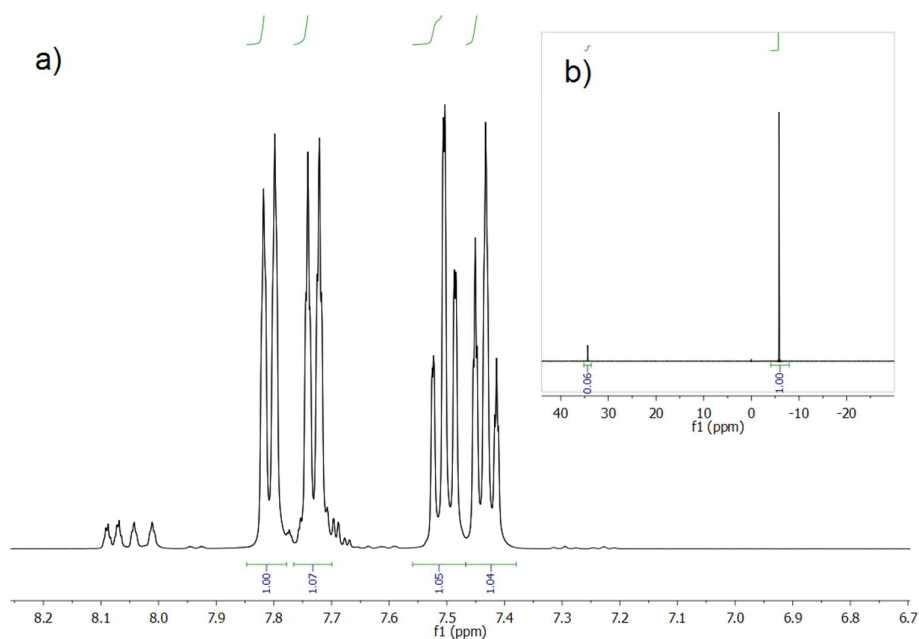


Figure S2. a) ^1H and b) ^{31}P NMR of TPPTS with 6 % TPPTS-oxide. The spectrum is recorded on 400 MHz Bruker Avance 400 device in D_2O .

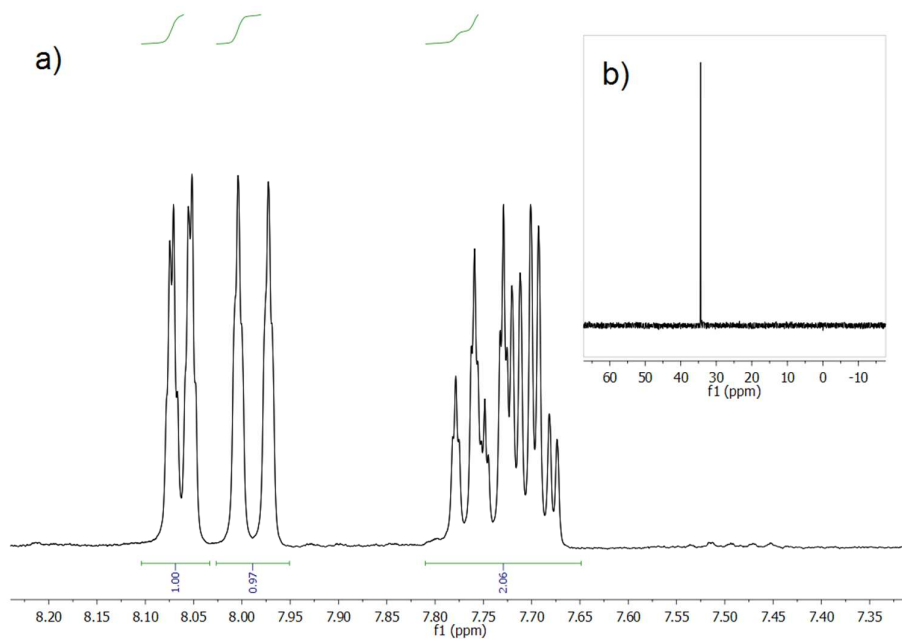


Figure S3. a) ^1H and b) ^{31}P NMR of TPPTS-oxide. The spectrum is recorded on 400 MHz Bruker Avance 400 device in D_2O .

Addition of an excess of the free labile ligand L can potentially increase the concentration of the dormant species and decrease the catalyst deactivation. Addition of 10 eq of the free

TPPTS ligand leads to increased overall productivity of the catalyst at 40 bar and 15 °C (Table S1, entry S1-5). However, only oxide free TPPTS is applicable (Figure S1). Addition of 10 eq of TPPTS oxide (Figure S3) deactivates the catalyst completely (entry 2-6). When using TPPTS with 6 % oxide (typical commercial purity grade, Figure S2), the catalyst productivity is only slightly higher than without additional TPPTS (compare Table S1, entry S1-1, S1-5 and S1-7) which is due to the TPPTS-oxide impurities.

Catalyst pre-exposure experiments in aqueous solution

The reaction mixture consisting of water, catalyst precursor **1-TPPTS** and optionally the surfactant were stirred together at 15 °C for a given time at ambient pressure prior to the polymerization for 30 min at 40 bar and 15 °C. When required, surfactant was added just before the polymerization.

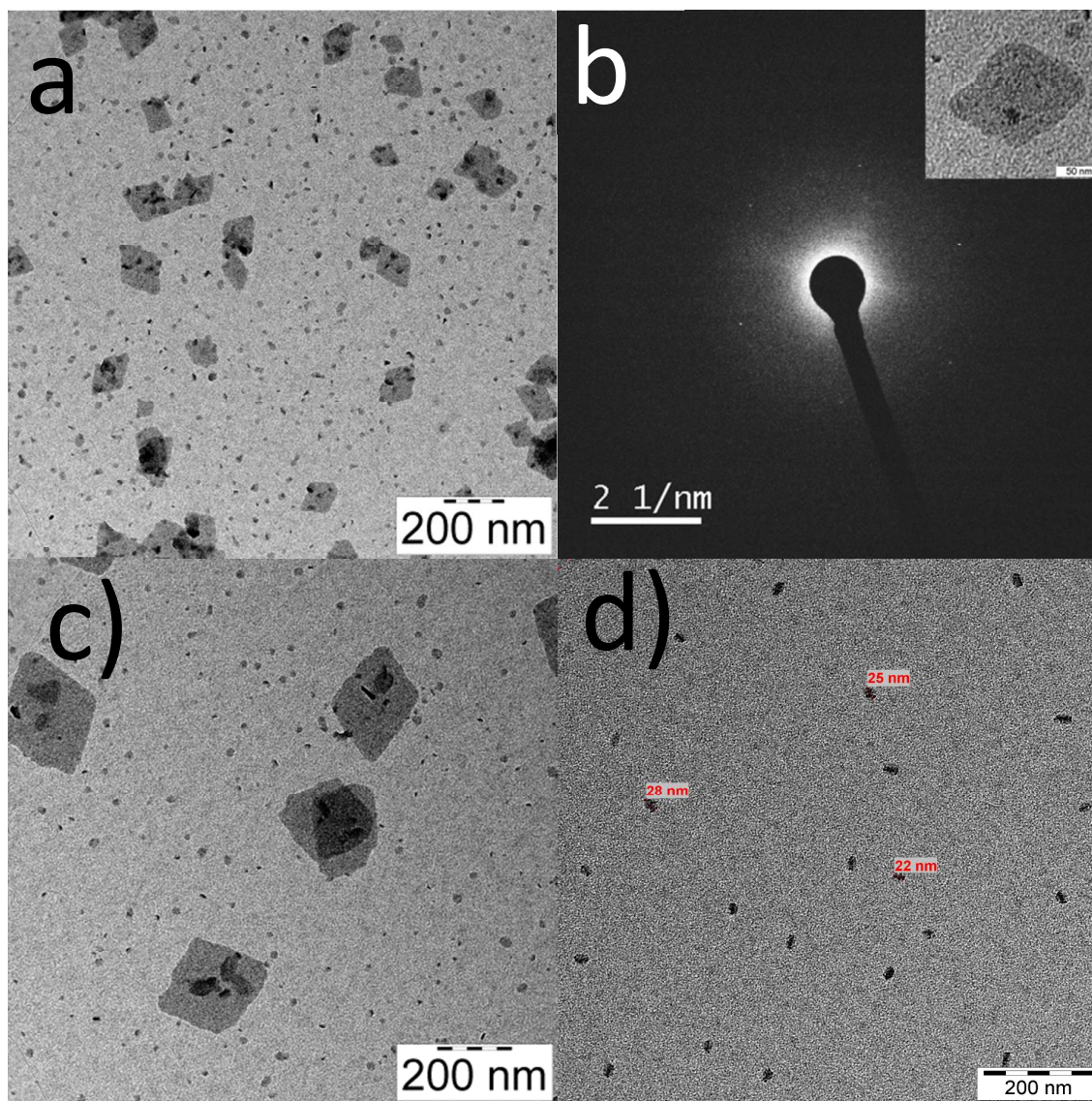


Figure S4. TEM micrographs and SAED of the dispersions obtained by aqueous ethylene polymerization at 40 bar ethylene and 15 °C for 30 min polymerization time using pre-exposed solutions of 10 $\mu\text{mol L}^{-1}$ **1-TPPTS** catalyst precursor. (a) and (b) pre-exposure for 30

min without SDS, 26 mmol L⁻¹ SDS were added just before the polymerization, (c) pre-exposure for 60 min without SDS, 26 mmol L⁻¹ SDS were added just before the polymerization and (d) pre-exposure for 30 min in presence of 26 mmol L⁻¹ SDS.

Influence of the surfactant concentration and surfactant nature

The nature of the surfactant plays an important role in terms of the catalyst dissolution as well as for the fact that the surfactant can interact with the additives like cesium hydroxide. Ethylene can be polymerized in water without addition of any surfactant (Table S2). In this case, large multilamellar particles are obtained at low yields (entry S2-2, Table S2 and Figure S5).

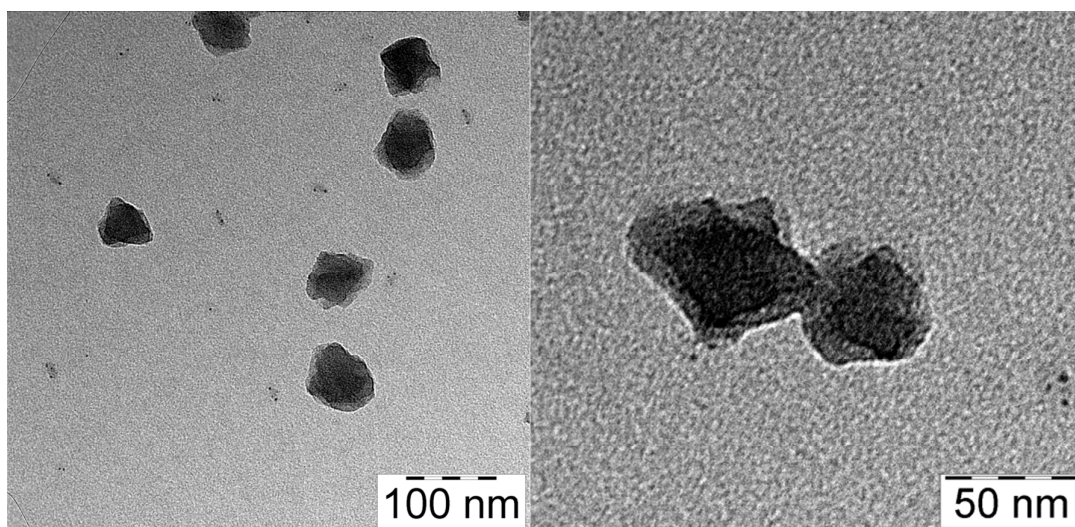


Figure S5. Multilamellar nanoparticles which are obtained in aqueous ethylene polymerization at 15 °C and 40 bar using 50 μmol L⁻¹ catalyst precursor **1-TPPTS** without addition of SDS.

The molecular weight distribution is bimodal indicating a non-uniform polymerization mechanism. To obtain smaller and more uniform particles a surfactant like SDS must be added. Krafft temperature of SDS $T_{K,SDS} = 15\text{ °C}$, meaning that the reaction is performed at the borderline of stability of the surfactant micelles. The SDS concentration that has been

applied in all previous studies reported in the literature is higher than the critical micelle concentration ($\text{cmc}_{\text{SDS}} = 8 \times 10^{-3} \text{ mol L}^{-1}$ or 0.23 wt.-% SDS¹).^{2,3} The surfactant is rapidly adsorbed on the surface of the particles formed and any micelles disappear at the very early stages of the reaction. The surfactant stabilizes those newly formed small particles. Dispersions formed at 40 bar at 15 °C (26 mmol L⁻¹ SDS) have a surface tension > 50 mN m⁻¹ which is far above the surface tension at the cmc (37 mN m⁻¹). When much higher surfactant concentrations (> 104 mmol L⁻¹ SDS) are applied, increased ethylene consumption is observed resulting in dispersions with up to 4.5 wt.-% polymer content. In this case the surfactant concentration at the end of the reaction is above cmc (indicated by the surface tension of 37 mN m⁻¹), meaning that during the polymerization free surfactant molecules were present at all time. The obtained particles do not significantly differ in the microstructure of the polymer from particles obtained at 26 mmol L⁻¹ SDS at 15 °C and 40 bar. Further increase of the surfactant concentration to 173 mmol L⁻¹ SDS has no significant influence on the catalyst activity (Figure S6) and the polymer yield.

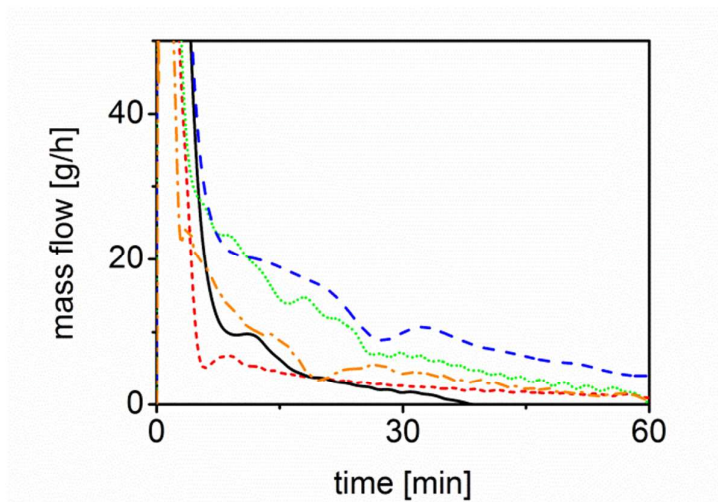
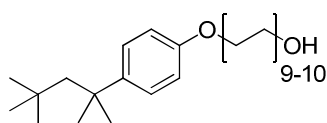
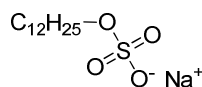


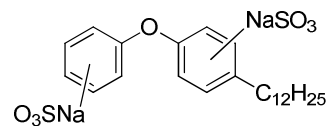
Figure S6. Influence of the SDS concentration on the ethylene consumption. (---) no SDS, (—) 26 mmol L⁻¹ SDS, (···) 104 mmol L⁻¹ SDS, (- - -) 173 mmol L⁻¹ SDS, (- · -) 26 mmol L⁻¹ DOWFAX 2A1.



Triton X-100



SDS



Dowfax 2A1

Figure S7. Surfactants applied in aqueous ethylene polymerization.

Other surfactants, namely, the nonionic Triton X-100 as well as the anionic DOWFAX 2A1 were used for ethylene polymerization in aqueous dispersion using complex **1-TPPTS** (Figure S7). No sufficient particle stabilization was observed using the non-ionic Triton X-100. Only precipitates could be obtained at 15 °C and 40 bar ethylene. Obviously, surface stabilization by ionic groups is necessary. DOWFAX 2A1, an anionic surfactant with high charge density due to the two sulfonate groups located at the head of the molecule, was used for the ethylene polymerization in water. The advantage of this surfactant compared to SDS besides the higher charge density is the better solubility in water (complete solubility also below 5 °C) and its resistivity to hydrolysis. In ethylene polymerization at 15 °C and 40 bar significantly higher catalyst stability was observed. Also in presence of CsOH and DOWFAX 2A1 the catalyst is more stable compared to experiments which were performed in presence of CsOH and SDS (Figure S8). However, the ethylene consumption per time unit is lower.

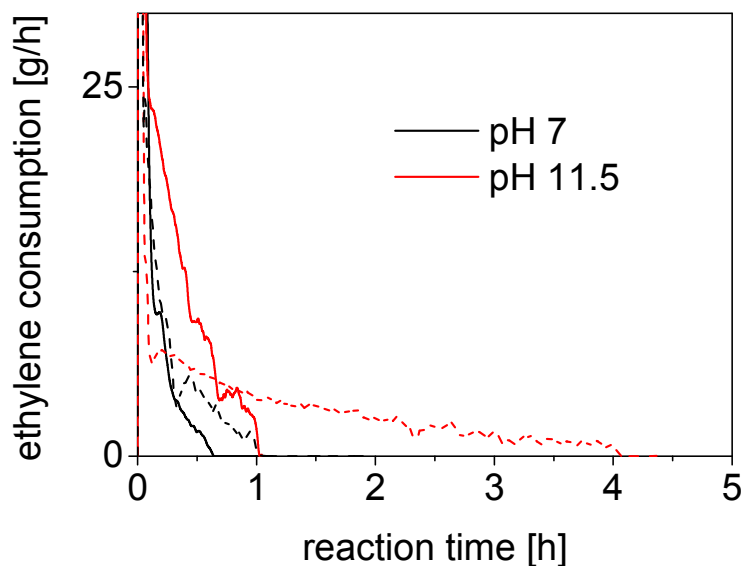


Figure S8. Ethylene consumption in polymerization at 15 °C, 40 bar ethylene using 50 $\mu\text{mol L}^{-1}$ **1-TPPTS** and (—) SDS or (- - -) DOWFAX 2A1 as surfactants in presence of CsOH.

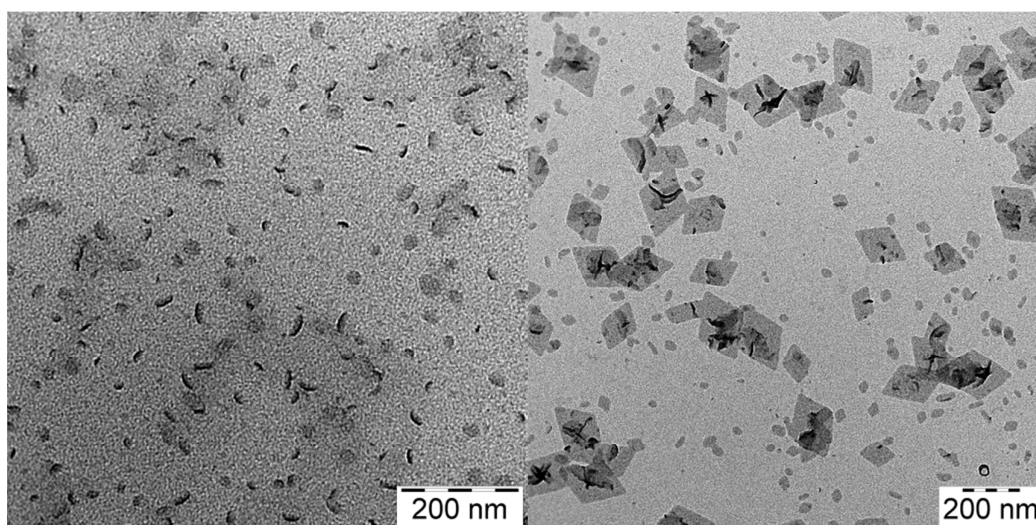


Figure S9. Polyethylene particles obtained in presence of DOWFAX 2A1 (left) without or (right) with CsOH at 15 °C and 40 bar ethylene. Samples from Table S2, entry S2-7 and S2-8, respectively.

Table S2. Influence of surfactant concentration and surfactant nature on aqueous ethylene polymerization using **1-TPPTS** as catalyst precursor.

entry ^a	t [h]	T [°C]	surfactant [mmol L ⁻¹]	p [bar]	polymer [%] ^b	TOF ^c	d _{part} [nm] ^d	T _m [°C] (crystallinity [%]) ^e	M _n [10 ⁵ g mol ⁻¹] (M _w /M _n)
S2-1	1	15	26 (SDS)	40	1.37	9747	8	137 (75)	0.9 (2.1)
S2-2	1	15	0 (SDS)	40	0.55 + coagulates	3913	65	128 (70)	0.1 (3.5); 11 (1.9)
S2-3	1	15	52 (SDS)	40	1.86	14222	16	n.m.	n.m.
S2-4	1	15	104 (SDS)	40	4.47	33201	11	135 (68)	2.7 (1.6)
S2-5	2	15	173 (SDS)	40	4.74	37565	17	135 (79)	2.4 (1.5)
S2-6	1	15	13 (Triton-X)	40	2.64 g coagulates	n.e.	n.e.	n.m.	n.m.
S2-7	1	15	25 (DOWFAX 2A1)	40	2.64	14526	29	139 (80)	n.m.
S2-8 ^f	4	15	41 (DOWFAX 2A1)	40	7.80	13387	21	137 (79)	n.m.

^a Reaction conditions: 50 $\mu\text{mol L}^{-1}$ complex **1**, 200 mL water. ^b Determined by precipitation. ^c [mol ethylene mol cat.⁻¹ h⁻¹]. ^d Particle diameter determined by DLS. ^e Determined by DSC. ^f In presence of 1.7×10^{-2} mol L⁻¹ CsOH.

Studies using ^{13}C -labeled 1-TPPTS

^{13}C -labeled catalyst precursor

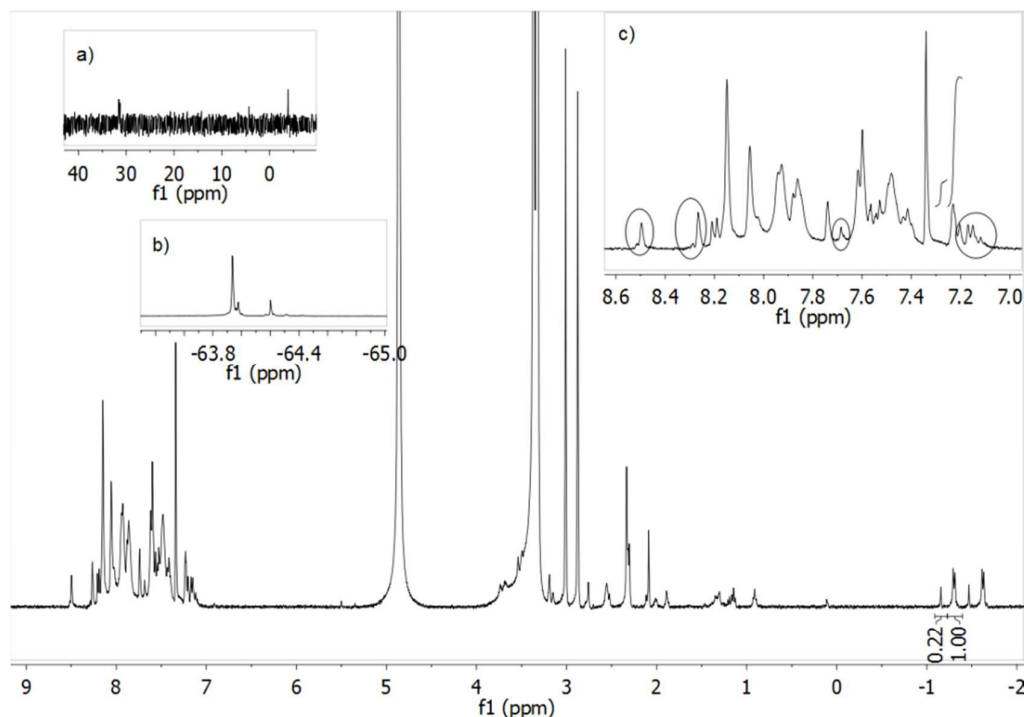


Figure S10. ^1H NMR spectrum of the ^{13}C -labeled **1-TPPTS**. Inlet: a) ^{31}P - and b) ^{19}F -NMR spectra of the ^{13}C -labeled catalyst; c) enlargement of the aromatic area of ^1H NMR, impurities are marked with a circle.

Short-term experiments using ^{13}C -labeled catalyst precursor **1- ^{13}C -TPPTS**.

Reaction conditions: The reactor was charged with 188 mL dest. water. A freshly prepared aqueous solution of 1.5 g SDS in 10 mL water was added under stirring. The catalyst precursor **1- ^{13}C -TPPTS** (NMR spectrum cf. Figure S10) was dissolved in 2 mL water. The solution was stirred for 2 min and added into the reactor. The reactor was sealed and immediately pressurized (Pressure curves cf. Figure S11). The polymerization was carried out at 15 °C and 40 bar. To enable the unloading of the reactor the stirrer was turned off 10 seconds before the end of the reaction. The reactor was unloaded immediately vs. ambient pressure via the bottom valve of the reactor vessel. The sample was collected into a beaker

and precipitated in methanol. The pressure inside the empty reactor remained at ~ 30 bar. The obtained dispersions were precipitated in methanol, washed, dried and analyzed by high-temperature NMR-spectroscopy. The polyethylenes obtained **1- ^{13}C -TPPTS** and **1-TPPTS** are comparable (Figures S12, S13, S15 and S16). The polymerization was performed using $50\ \mu\text{mol L}^{-1}$ and $100\ \mu\text{mol L}^{-1}$ **1- ^{13}C -TPPTS**. In both cases after the polymerization for 30 sec solid polymer with the molecular weight of $4 \times 10^3 - 6 \times 10^3\ \text{g mol}^{-1}$ was obtained. No dependence of the catalyst activation on the initial concentration of the **1- ^{13}C -TPPTS** was observed. The polymer obtained after 2 min polymerization time has a molecular weight of $9 \times 10^3\ \text{g mol}^{-1}$. The ^{13}C -labeled methyl group is incorporated at the end of the ethylene chain (**Figure S14**). The label can be identified as a part of the S1 signal in ^{13}C -NMR spectra and the amount of the activated catalyst can be determined (Figures S16, S18 and S20). Polymer yields, molecular weights, amount of the initiated catalyst, proportion of the labeled chain ends and branch content were calculated using Equations (S1)-(S7) (Table 1). According to the NMR, ca 20-30 % of the chain ends are labeled after 30 sec and after 2 min the amount of transferred ^{13}C -label is similar. Label transfer analysis of the polymer at longer polymerization times was not possible due to very high dilution of the labeled end groups.

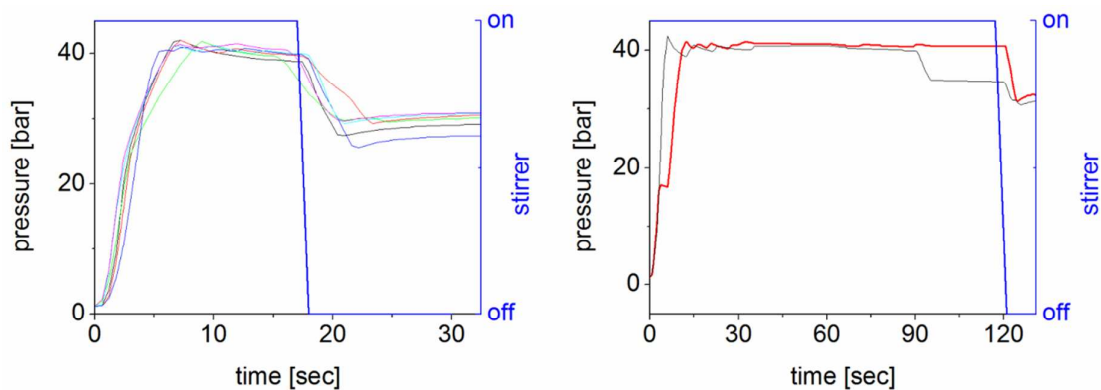


Figure S11. Pressure evolution during the ethylene polymerization for 30 s and 2 min (from Table 1). Before depressurizing the reactor the stirrer was turned off. The reactor content was unloaded 40 bar using a bottom valve. The pressure inside the empty reactor remained at ~ 30 bar. a) 30 s experiment: stable reaction conditions for ~ 10 sec, b) 2 min experiment: stable reaction conditions for ~ 110 s.

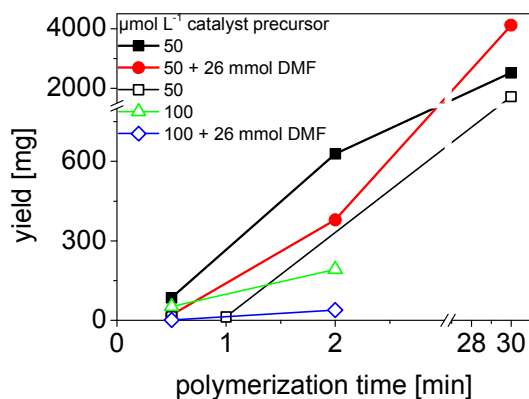


Figure S12. Polymer yields obtained after ethylene polymerization using (□) $1\text{-}^{13}\text{C}$ -TPPTS and (■) 1-TPPTS as catalyst precursor at 40 bar and 15 °C.

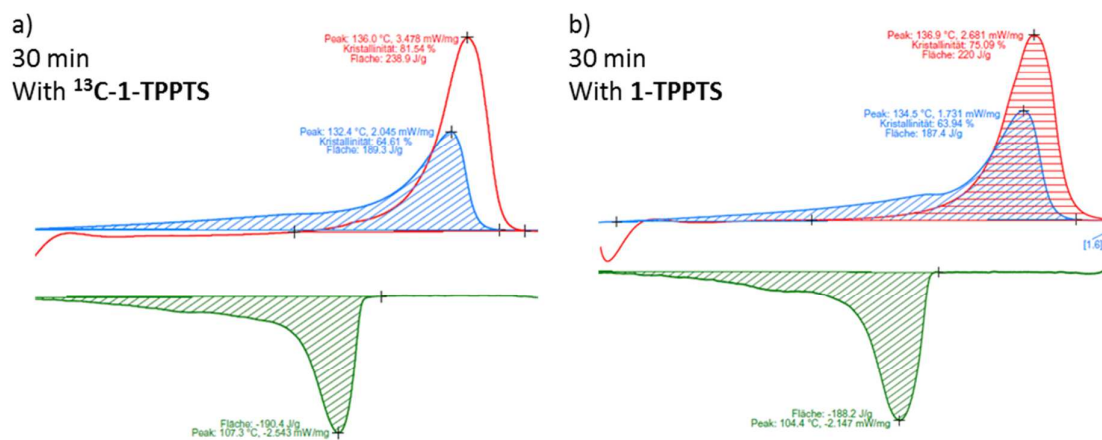
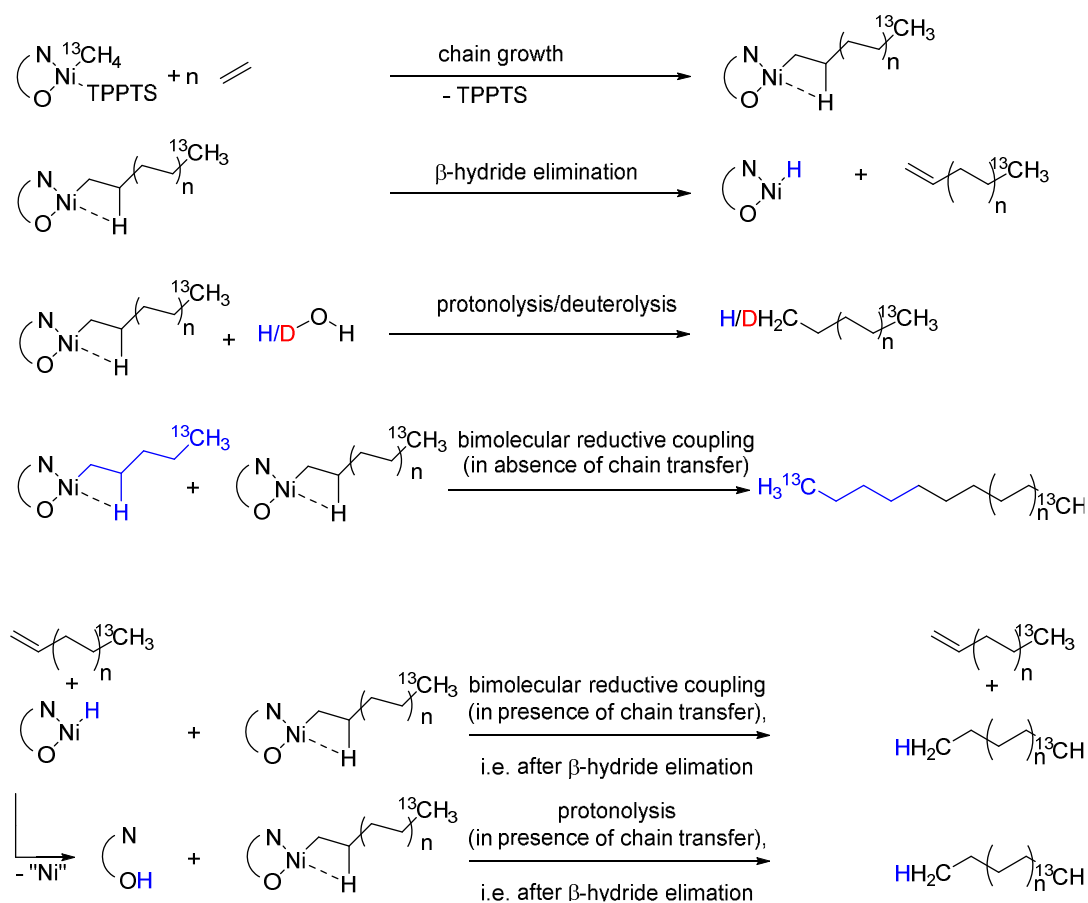


Figure S13. DSC thermograms of a polyethylene obtained using a) 1- ^{13}C -TPPTS and b) 1-TPPTS as catalyst precursor at 40 bar and 15 °C.

NMR Spectra of polyethylene

In addition to chain walking reactions, the following chain propagation, chain transfer, and chain termination reactions have been considered to potentially account for characteristic NMR signals of the obtained polyethylenes using **1-¹³C-TPPTS**.



Scheme S1. Possible propagation, transfer and termination reactions based on ¹³C-labeled catalyst precursor **1-¹³C-TPPTS** in aqueous ethylene polymerization.

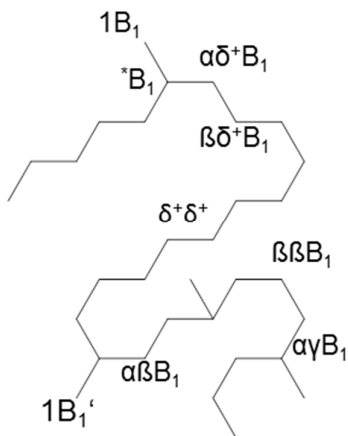


Figure S14. Assignment of ^{13}C peaks for the different Me-branch positions.

$$\text{catalyst initiated [\%]} = \frac{\frac{\text{polymer yield [g]}}{\frac{\text{overall integral} \cdot \frac{28}{2} [\frac{\text{g}}{\text{mol}}]} * \frac{1S_{\text{labeled}}}{1S_{\text{real}}}}}{\text{catalyst [mol]} * 100} \quad (\text{S1})$$

$$1S_{\text{labeled}} = \frac{1S - 2S}{100} \quad (\text{S2})$$

$$1S_{\text{real}} = 2S + 1S_{\text{labeled}} \quad (\text{S3})$$

$$\chi = \text{labeled chain ends [\%]} = \frac{1S_{\text{labeled}}}{1S_{\text{real}}} * 100 \quad (\text{S4})$$

$$\frac{\text{transfer}}{\text{polymerization}} = \text{nb. monomer units per chain} * \frac{\text{nb. chains}}{\text{nb. transfers}} =$$

$$\frac{M_n [\frac{\text{g}}{\text{mol}}]}{28 [\frac{\text{g}}{\text{mol}}]} * \frac{1 + \frac{1}{\text{labeled chains [\%]}/100}}{1/\text{labeled chains [\%]}/100} \quad (\text{S5})$$

$$\frac{(\text{methyl})\text{branches}}{1000\text{C}} = (0,5 * \alpha B_1 / \delta^+ \delta^+) * 1000 \quad (\text{S6})$$

$$M_n = \frac{\text{overall integral} - 1S + 1S_{\text{real}}}{1S_{\text{real}}} * \frac{28}{2} \text{ g/mol} \quad (\text{S7})$$

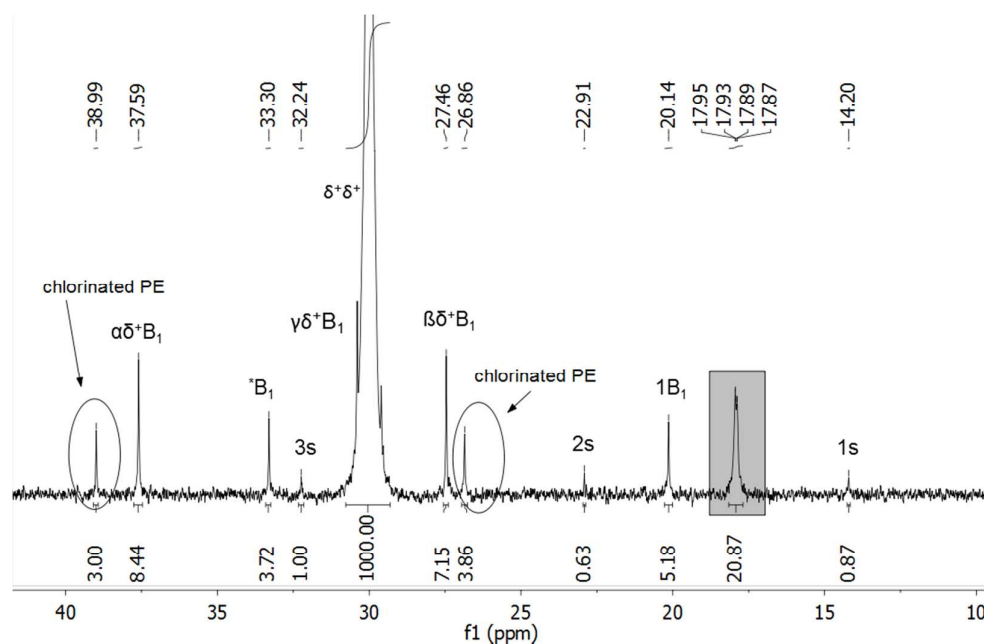


Figure S15. ^{13}C NMR spectrum (inverse gated decoupling, 403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 30 sec polymerization time (entry 1-1, Table 1). Signals highlighted with a circle are the result of the prolonged heating of the sample in tetrachloroethane.⁴ Not assigned peak is marked with the grey square.

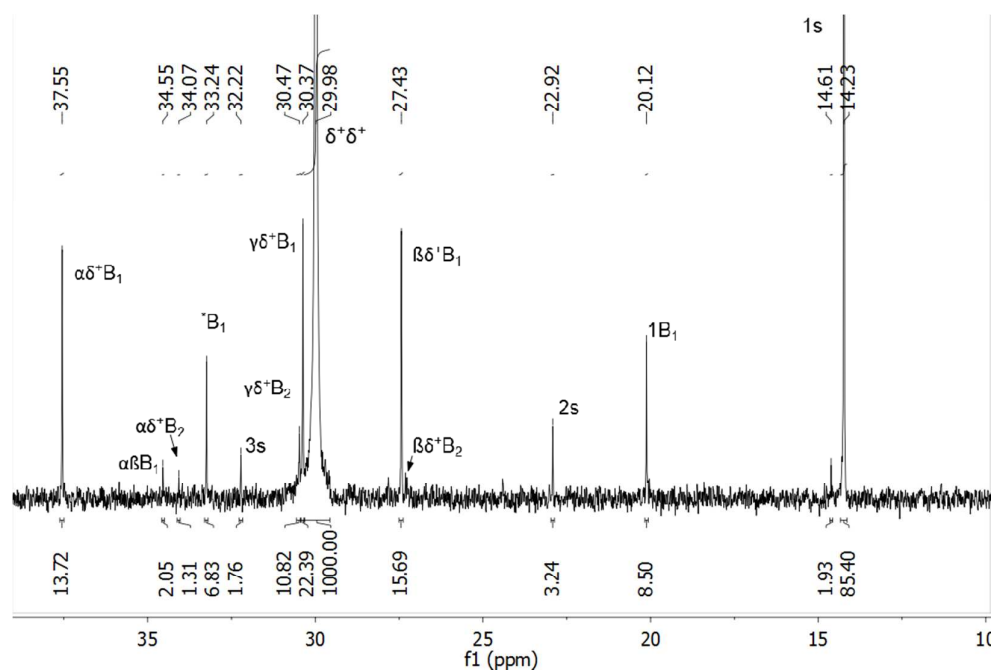


Figure S16. ^{13}C NMR spectrum (inverse gated decoupling, 403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 30 sec polymerization time (entry 1-2, Table 1).

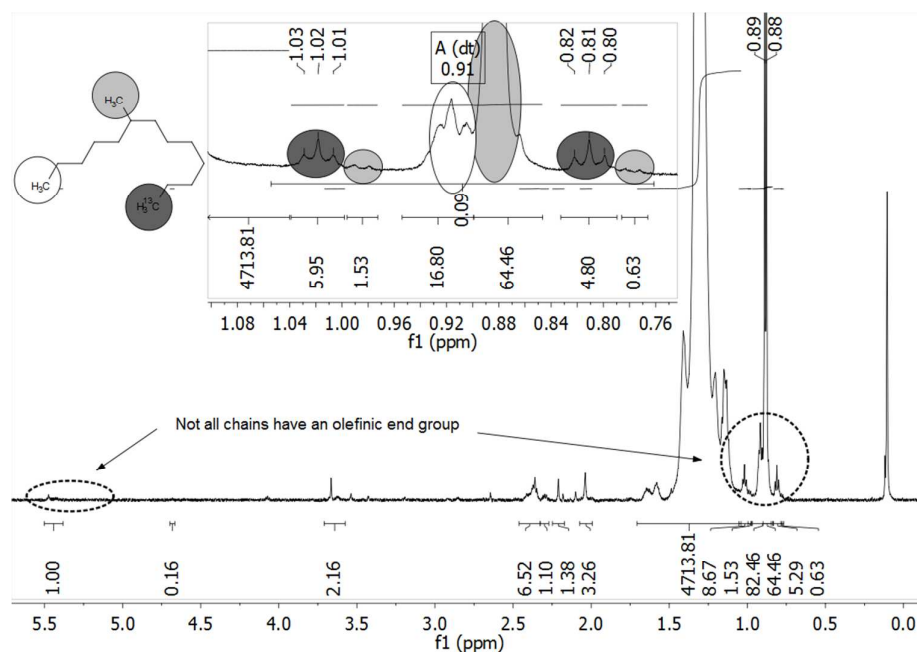


Figure S17. ^1H NMR spectrum (403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 30 sec polymerization time (entry 1-2, Table 1). The assignment of the methyl end groups and methyl branches is highlighted in the inlet.

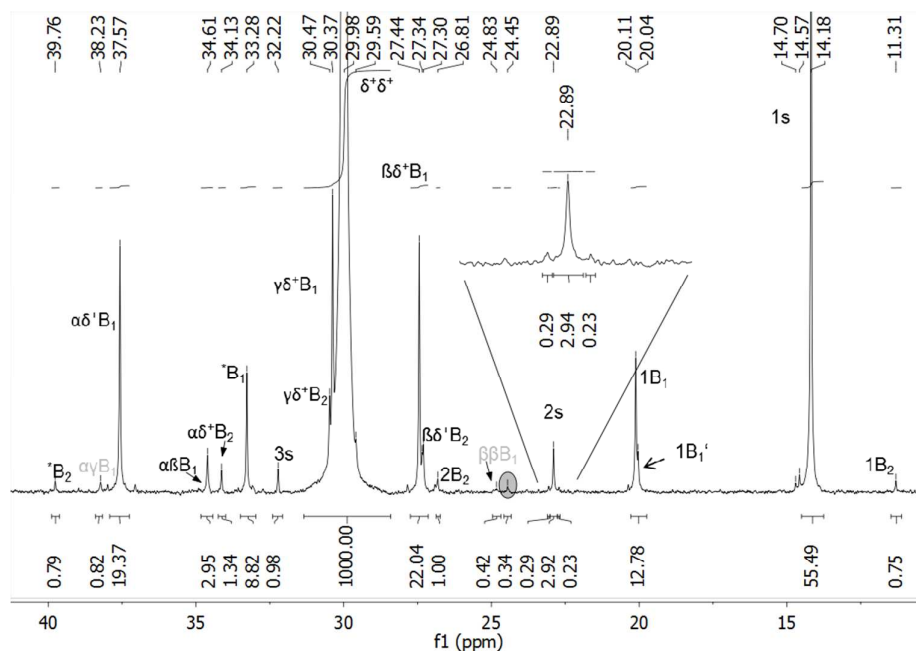


Figure S18. ^{13}C NMR spectrum (inverse gated decoupling, 403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 30 sec polymerization time (entry 1-6, Table 1). Ambiguous assignment is shown in grey. Not assigned peak is highlighted with a grey circle.

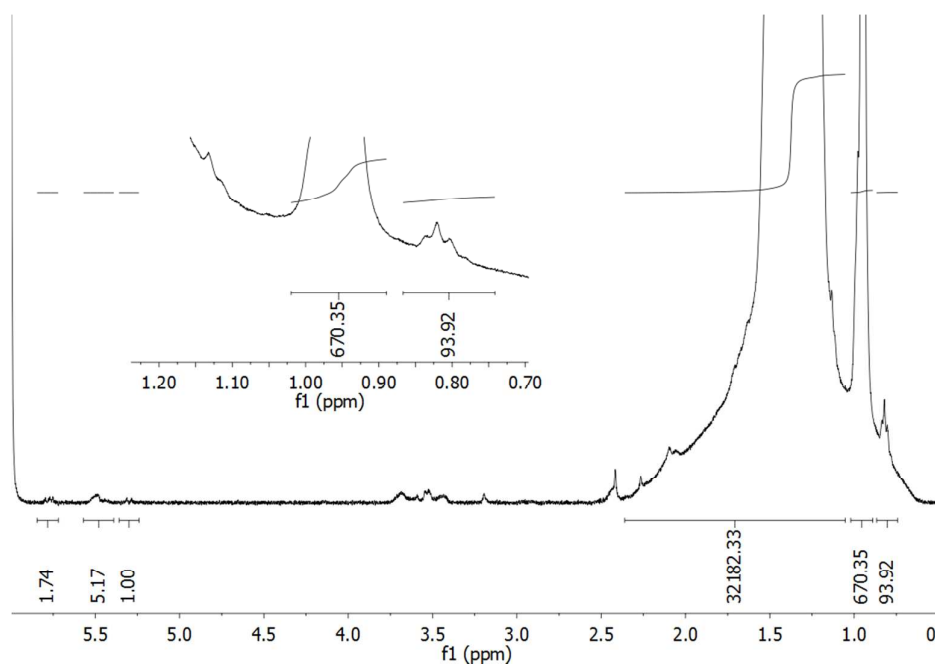


Figure S19. ^1H NMR spectrum (403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 30 sec polymerization time (entry 1-6, Table 1). The splitting of the methyl signal into a doublet of triplet is shown in the inlet.

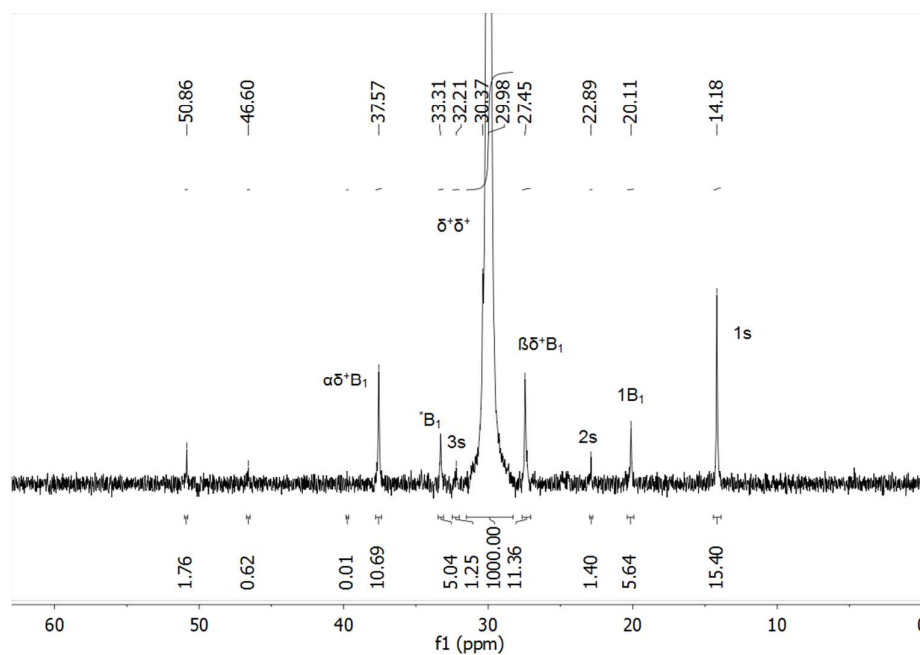


Figure S20. ^{13}C NMR spectrum (inverse gated decoupling, 403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 2 min polymerization time (entry 1-7, Table 1).

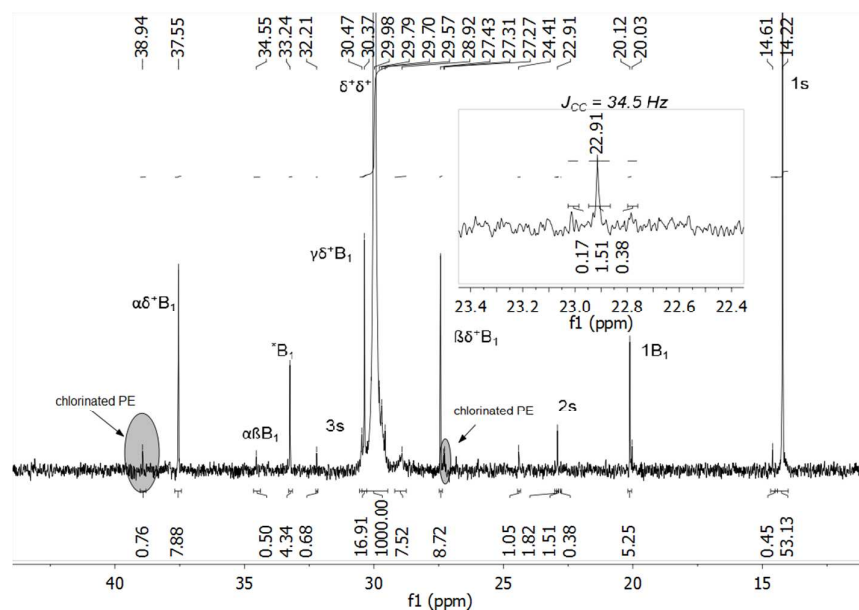


Figure S21. ^{13}C NMR spectrum (inverse gated decoupling, 403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 2 min polymerization time (entry 1-9, Table 1). The region of the 2S signal is shown in the inlet. Signals highlighted with a grey circle result from prolonged heating of the sample in tetrachloroethane.⁴

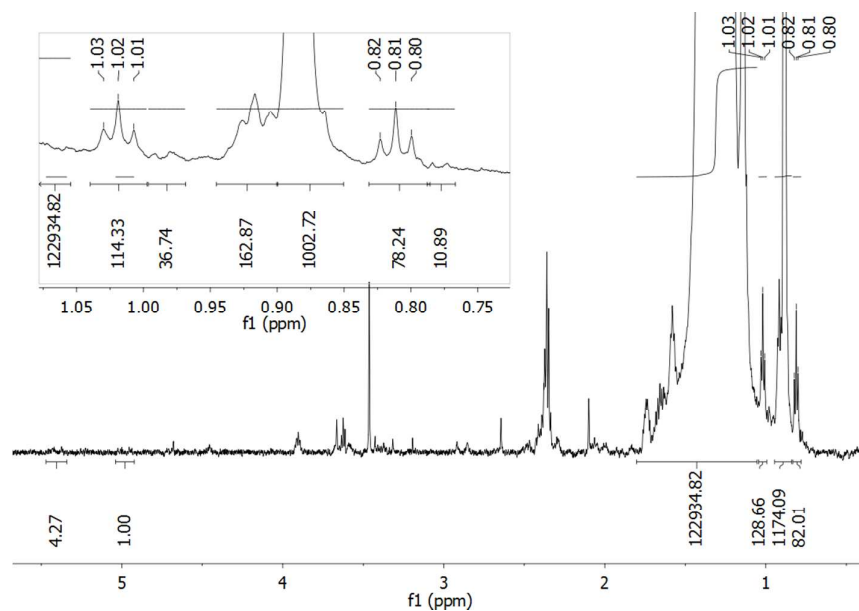


Figure S22. ^1H NMR spectrum (403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 2 min polymerization time (entry 1-9, Table 1). The splitting of the methyl signal into a doublet of triplet is shown in the inlet. $^{13}\text{CH}_3$ -satelite of the methyl branch signal (doublet of doublet) has the 2 fold intensity as expected for the naturally abundant $^{13}\text{CH}_3$.

Branching. The branch content of the samples obtained after 30 sec is higher than the branch content of a typical sample obtained after 30 min polymerization time. Besides individual methyl branches the samples also contain some minor amount of ethyl branches, 1,4- and 1,5-methyl branches which is due to the unstable pressure conditions in the first seconds of the polymerization (Figure S11). The formation of the 1,4-branches can be explained by the chain walking mechanism, the formation of 1,5-branches is unclear. One possible mechanism could be the insertion of a higher olefinic species than ethylene. Samples obtained after 2 min polymerization are similar to typical samples obtained after 30 min polymerization in branch content and branch pattern. The methyl branch pattern of the labeled $^{13}\text{CH}_3$ -groups also requires special attention and can be observed in the ^1H NMR (Figure S17 and S19). The main doublet at δ 0.93 (d, $J = 6.6$ Hz, 100 H) ppm represents methyl branches. Its $^{13}\text{CH}_3$ analogs, a doublet of a doublet at δ 0.93 (dd, $J = 124.2, 6.4$ Hz, 2 H) ppm has an area which is double as large as expected for the $^{13}\text{CH}_3$ -satellite of the main peak (natural abundance of ^{13}C is 1.1 %). Some error is certainly due the peak broadening of the main peak and the resulting baseline error, however, also in the ^{13}C -NMR spectra (Figure S16 and S21) B^* signals have a slightly smaller area than the 1B_1 -signals, which might be due to the incorporation of the ^{13}C -label in the methyl branch, as a result of the chain walking mechanism. In this case the question arises, whether the ^{13}C -label is also incorporated within the main chain. Unfortunately the labeled $^{13}\text{CH}_2$ -groups within the chain cannot be distinguished from the unlabeled ones via NMR spectroscopy.

Influence of the pressure and temperature on catalytic aqueous ethylene polymerization

Table S3. Influence of temperature and pressure on aqueous ethylene polymerization using **1-TPPTS** as catalyst precursor.

entry ^a	T [°C]	p [bar]	polymer [%] ^b	TON ^c	d _{Part} [nm] ^d	T _m [°C] (crystallinity [%]) ^e	M _n [10 ⁵ g mol ⁻¹] (M _w /M _n)	chains per Ni/ chain transfer per Ni
S3-1	15	40	1.37	9747	8	137 (75)	0.9 (2.1)	3/2
S3-2	10	40	0.89	6547	11	138 (79)	2.3 (1.6)	0.78/n.a.
S3-3	20	40	0.85	7068	7	136 (74)	2.0 (1.6)	0.85/n.a.
S3-4	30	40	0.30	2207	8	131 (80)	0.8 (1.7)	0.75/n.a.
S3-5	15	30	1.15	8460	7	134 (72)	1.1 (2.1)	2.1/1.1
S3-6	15	20	1.22	8623	10	135 (75)	1.6 (1.6)	1.5/0.5
S3-7	15	10	0.82	5717	10	131 (73)	1.8 (1.5)	0.9/n.a.

^a Reaction conditions: 10 μmol **1-TPPTS**, 200 mL water, 26 mmol L⁻¹ SDS, 60 min. ^b Determined by precipitation. ^c [mol ethylene mol cat.⁻¹]. ^d Particle diameter determined by DLS. ^e Determined by DSC.

Temperature. Among all the polymerization conditions presented in Table S3 at 10 °C and 40 bar the longest catalyst life time of ~ 60 min was observed at 10 °C and 40 bar. However, at this temperature the reaction can be easily perturbed by the formation of ethylene hydrate as indicated by spontaneous high ethylene consumption (Figure S23, red dotted curve). Ethylene hydrate formation is probably promoted either by formation of PE nanocrystals or by formation of hydrated SDS crystals as the solubility of SDS strongly decreases below the Krafft point ($T_{\text{KrSDS}} = 15$ °C)⁵ (Figure S30).

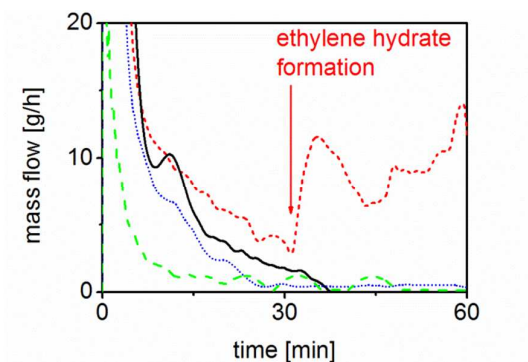


Figure S23. Influence of the reaction temperature on the polymerization rate (---) 10 °C, (—) 15 °C, (···) 20 °C, (— —) 30 °C at 40 bar ethylene.

Polymerization at higher temperature would be more favorable in terms of the solubility of the surfactant, however, polymerization at 30 °C results in a very short catalyst life time. The catalyst is deactivated completely within 20 minutes. Strong catalyst deactivation in water at 50 °C was already reported by Korthals et al.^{2a}

Pressure. The polymerization rate and yields decrease at low pressure (Figure S24 and Table S3) due to the pronounced β -H elimination, indicated by the high amount of unsaturated end groups (cf. Figure S25, top)

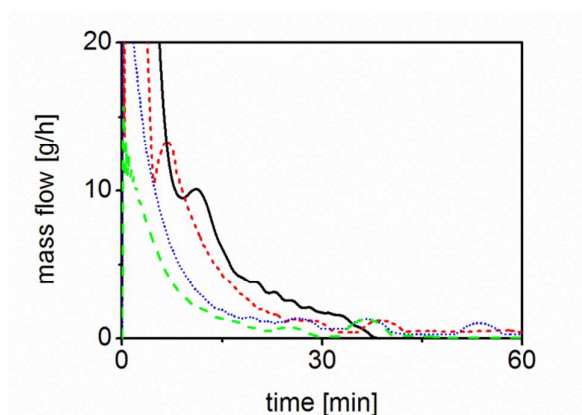


Figure S24. Influence of the ethylene pressure on the polymerization rate (—) 40 bar, (---) 30 bar, (···) 20 bar, (- -) 10 bar at 15 °C.

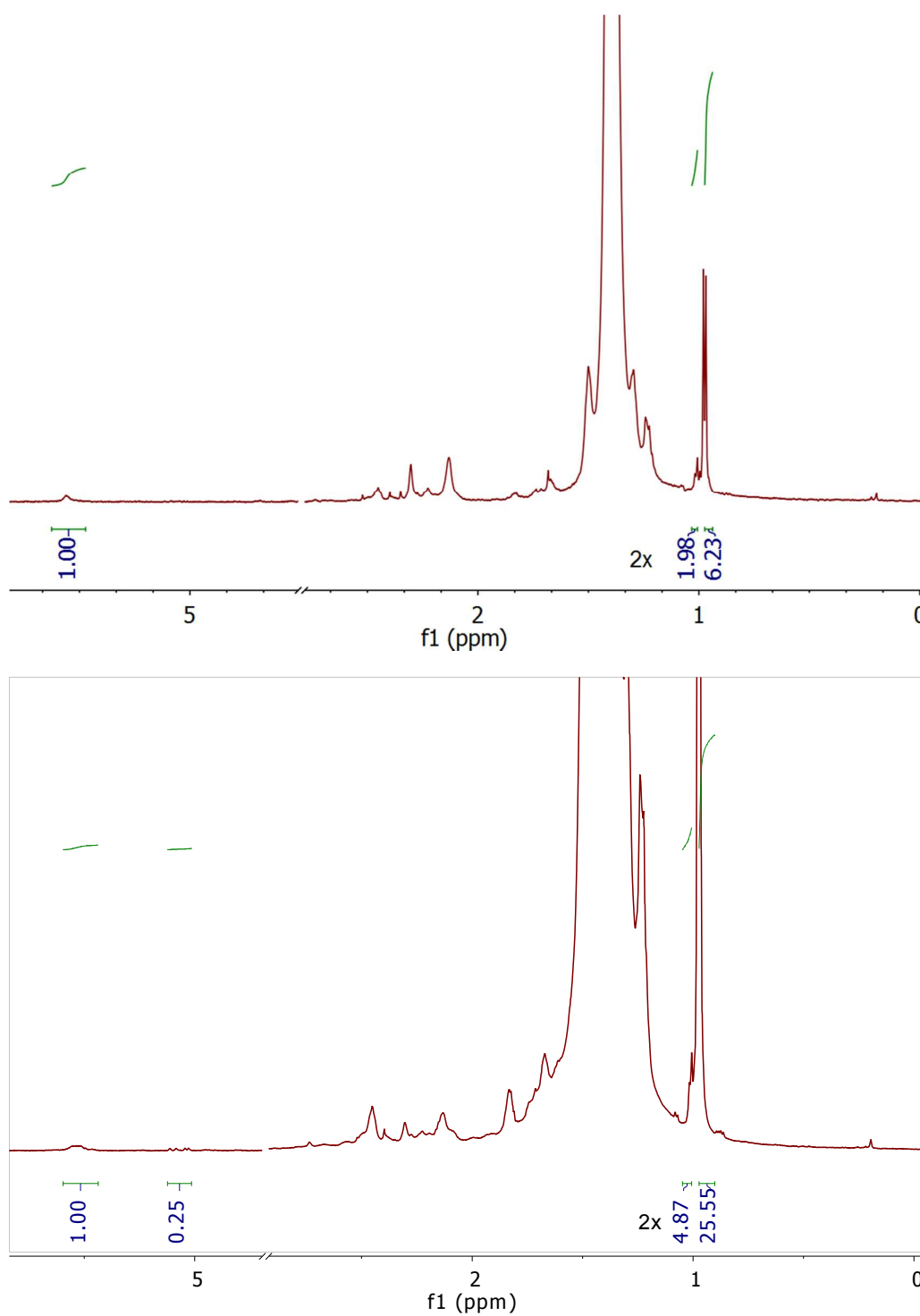


Figure S25. ^1H NMR spectrum (403 K in $\text{C}_2\text{D}_2\text{Cl}_2$) of the polyethylene sample obtained after 60 min polymerization time using **1-TPPTS** at 10 bar (top) or 40 bar (bottom) (entry S3-7 and S3-1, respectively, Table S3).

Polyethylene analysis

Table S4. Analysis of selected polyethylene samples

entry	reaction conditions	reaction time [min]	catalyst precursor [$\mu\text{mol L}^{-1}$]	yield [g]	$M_n^{\text{GPC(1H NMR/13C NMR)}}$ $10^3 [\text{g mol}^{-1}]$	chains ⁱ [μmol]	olef / aliph ^c	olef / Me ^d	$^{13}\text{C} / ^{12}\text{C}$ aliph ^e	d ^f [nm]	V _{particle} ^g [10^{-25} m^3]	particle ^h [μmol]
S4-1	-	60	50	2.740	95	28.94	n.e.	0.04		8	2,7	17.87
S4-2	-	1	50	0.628	7.3 (n.e / 7.1)	n.e.	0.15	0.05		10	5.2	2.10
S4-3	-	0.5	50	0.085	n.e (19 / 16)	5.25	0.33	0.07		(5)	5.2	4.44
S4-4	1-¹³C-TPPTS	0.5	50	0.014	6.7 (20 / 7.6)	2.09	0.10	0.02	0.19	(4)	5.2	0.73
S4-5	1-¹³C-TPPTS	0.5	100	0.052	11 (18 / 12)	4.68	0.08	0.02	0.18	(4)	5.2	2.71
S4-6	1-¹³C-TPPTS	2	100	0.192	21 (19 / 19)	9.19	0.11	0.02	0.10	(5)	5.2	2.96
S4-7	1-¹³C-TPPTS , DMF ^a	2	100	0.039	10 (44 / 7.2)	5.42	0.04	0.01	0.34	(5)	5.2	10.02
S4-8	in D ₂ O	0.5	100	0.032	5.7	5.52	n.e.	0.02		(4)	1.1 ^d	1.64
S4-9	10 bar	60	50	1.640	180 (50 / n.e)	9.11	0.75	0.13		10	5.2	5.48
S4-10	30 °C	60	50	0.600	80 (72 / n.e)	7.50	0.45	0.04		8	2.7	3.91
S4-11	no SDS	60	50	1.050	10	105.00	n.e.	0.08		n.e.	n.e.	n.e.
S4-12	DMF ^a	180	n.e.	8.640	160	54.00	0.41	0.72		10	5.2	28.86
S4-13	DMF ^b	300	n.e.	8.380	300	27.93	n.e.	0.51		17	2.6	5.70
S4-14	100 μmol TPPTS	60	50	4.540	n.e.	n.e.	n.e.	0.18		10	5.2	15.16

Reaction conditions: 40 bar, 15 °C, 200 mL water, 26 mmol L⁻¹ SDS. ^a 0.13 mol L⁻¹. ^b 0.32 mol L⁻¹. ^c Number of olefinic endgroups was determined from the integral of the peak 5.56 ppm (I_{olef}). Number of saturated endgroups was calculated from the triplet at 1.06 ppm in ¹H NMR spectra (I_{aliph}). It was assumed, that all the double bonds were isomerized to internal double bonds, which is reasonable, because almost no peaks corresponding to terminal double bonds were observed around 5.1 ppm.

^d Olef/aliph corresponds therefore to $(6 \times I_{\text{olef}})/(2 \times I_{\text{aliph}})$, number of methyl groups was calculated from the doublet at 0.85 ppm in ¹H-NMR (I_{Me}). Olef/Me corresponds to $(3 \times I_{\text{olef}})/(2 \times I_{\text{aliph}})$. ^e ¹³C / ¹²C aliph was calculated from the ¹³C spectra using 1S and 2S integral according to $1S_{\text{labeled}}/1S_{\text{unlabeled}}$. ^f Measured by DLS, values in brackets are estimated from TEM, V_{particles}. ^g $V = 4/3\pi r_{\text{part}}^3$ with $r_{\text{part}} = 0.5 \text{ d}$. ^h Assuming spherical particles with diameter d, $N_{\text{part}} = V/V_{\text{part}}$. ⁱ Calculated according $N_{\text{chain}} = M_n/28 \text{ g/mol}$.

Polymerization in deuterium oxide

Table S5. Ethylene polymerization in deuterium oxide.

entry	reaction time [min]	Catalyst [$\mu\text{mol L}^{-1}$]	SDS [mmol L^{-1}]	Yield polymer [g]	M_n^f [10^5g mol^{-1}] (M_w/M_n)	T_m [$^{\circ}\text{C}$] / cryst. [%]	Particle size [nm] ^g
S5-1 ^b	0,5	50	26	0.003	n.m.	n.e.	n.e.
S5-2 ^b	0,5	100	26	0.032	0.05 (2.4)	n.e.	n.e.
S5-3 ^b	5	50	26	0.082	0.42 (1.3)	n.e.	7, 49 (50%)
S5-4	30	50	26	4.6	2.6 (1.6)	135 (83)	45
S5-5	300	50	78	21.3	2.0 (2.5)	137 (85)	11
S5-6 ^a	300	50	78	20.5	3.3 (1.8)	138 (78)	16
S5-7	600	100	208	27.6	6.2 (1.4)	137 (77)	15
S5-8 ^c	120	50	52	6.8	1.6 (1.2)	132 (81)	13
S5-9	24 h	100	208	52.0 ^d	1.9 (4.6)	136 (71)	20
S5-10	24 h	25	208	8.7	5.1 (1.3)	139 (77)	27

reaction conditions: **1-TPPTS**, SDS, 200 mL water, 15 $^{\circ}\text{C}$, 40 bar. ^a 0.13 mol L⁻¹ DMF. ^b Immediate depressurizing-. ^c 1.46×10^{-3} mol L⁻¹ CsOH, pH 10. ^d + 3 g coagulates. ^e According to DLS. ^f Measured by GPC vs. linear PE standards. ^g according to DLS.

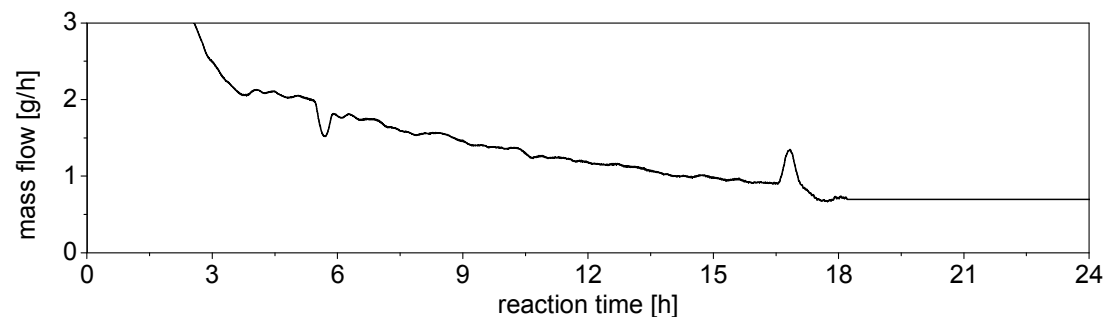


Figure S26. Ethylene consumption during polymerization in deuterium oxide at 15 $^{\circ}\text{C}$ and 40 bar ethylene using catalyst precursor **1-TPPTS** (from entry S5-10, Table S5).

Influence of pH on catalytic aqueous ethylene polymerization

Table S6. Ethylene polymerization at different pH.

entry	CsOH [mol · L ⁻¹]	pH	polymer [%]	M _n ^{GPC} [10 ⁵ g mol ⁻¹] (M _w /M _n)	T _m [°C] / cryst. [%]	particle size [nm] ^g
S6-1	1.1 × 10 ⁻⁴	9	1.61	5.8 (1.5)	139	24
S6-2	1.5 × 10 ⁻³	11	4.08	5.3 (1.6)	138	18
S6-3	3.2 × 10 ⁻³	11.5	5.44	4.6 (1.4)	139	15
S6-4	1.4 × 10 ⁻²	12.1	5.60	6.1 (1.3)	137	14
S6-5	3.4 × 10 ⁻²	12.5	6.97	7.2 (1.2)	139	15
S6-6	1.7 × 10 ⁻¹	13.2	1.29	2.8 (1.2)	136 (77)	18
S6-7 ^b	1.5 × 10 ⁻³	11	0.67	2.2 (1.5)	139	18
S6-8 ^{c,f}	1.5 × 10 ⁻³	10	0.34	1.6 (1.2)	132 (81)	13
S6-9 ^d	1.7 × 10 ⁻¹	13.2	0.25 ^e	n.e.	133 (64)	181
H ₂ SO ₄ conc. [mL]						
S6-10	4.9 × 10 ⁻³	2.3	-	n.e.	n.e.	n.e.
S6-11	4.9 × 10 ⁻⁸	6.0	4.5 × 10 ⁻⁵	n.e.	n.e.	n.e.
S6-12	9 × 10 ⁻¹¹	6.7	2 × 10 ⁻⁴	n.e.	n.e.	n.e.
NaOH [g]						
S6-12	3.5 × 10 ⁻²	12.5	4.97	4.3 (1.5)	137 (83)	19
S6-13 ^f	1.8 × 10 ⁻²	13.2	4.12	3.9 (1.5)	140 (85)	21
KOH [g]						
S6-14	3.4 × 10 ⁻²	12.5	4.96 + ~1g coagg.	3.2 (1.6)	137 (84)	70

Reaction conditions: 50 μmol L⁻¹ **1-TPPTS**, 52 mmol L⁻¹ SDS, 200 mL water, 15 °C, 40 bar, reaction time 1 h.

^a 26 mmol L⁻¹ SDS. ^b 0.13 mol L⁻¹ DMF. ^c In D₂O. ^d No SDS. ^e Coagulates as product. ^f Reaction time 2 h. ^g According to DLS.

Ethylene polymerization was performed at different pH using inorganic alkali hydroxides for the pH adjustment (**Table S6**). At pH of 12.5 dispersions with 7 wt.-% polyethylene can be accessed at 15 °C and 40 bar using 50 μmol L⁻¹ **1-TPPTS**. The overall activity is increased at high pH (**Figure S27**). Accounting for the molecular weight, at pH 12.5 polyethylene with narrow MWD M_w/M_n = 1.3 and molecular weight of up to 7.2 × 10⁵ g mol⁻¹ were obtained. At pH 13.2 the catalyst productivity drops due to the increasing viscosity of the reaction mixture (honey-like liquid) which is caused by the formation of the cesium dodecyl sulfate (CsDS).

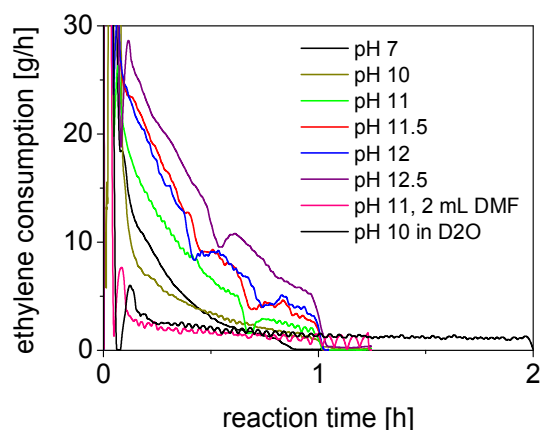


Figure S27. Ethylene consumption in aqueous ethylene polymerization in presence of CsOH at 15 °C, 40 bar ethylene using 50 $\mu\text{mol L}^{-1}$ **1-TPPTS** and SDS as surfactant.

Sampling experiments (for details cf. *Sampling*) were performed in presence of CsOH at pH 12.5 and 13.2 (**Figure 28**). In both cases the polymerization ceases after ~ 60 min. Higher yields and molecular weight were obtained at pH 12.5 than at pH 13.2 due to the higher viscosity of the reaction mixture in the second case. The melting point and the crystallinity of the obtained PE are also higher when the polymerization is performed at pH 12.5. The monolamellar structure of the particles does not change in presence of CsOH (**Figure 29**, left). The polymerization at pH 13.2 was also performed without SDS. The catalyst productivity is similar to the reaction in neutral conditions, however in alkaline conditions the polymer is completely precipitated (compare entry S2-2 from **Table S2** and entry S6-9 from **Table S6**). The polymerization at high pH was also studied in presence of DMF. No significant change comparing to the polymerization at pH 7 was observed. In this case the DMF-coordination is more dominant than the pH effect.

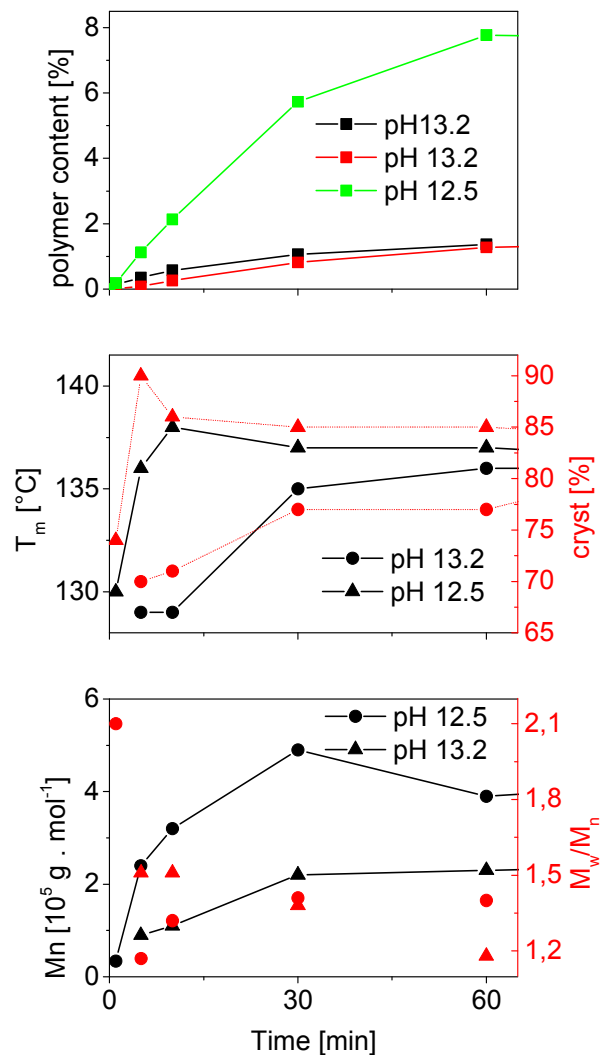


Figure S28. Ethylene polymerization at different pH at 40 bar and 15 °C using CsOH and $50 \mu\text{mol L}^{-1}$ **1-TPPTS**. (top) yield (center) melting temperature and crystallinity (bottom) molecular weight and MWD of the obtained polymers dependent on the reaction time.

Also potassium hydroxide and sodium hydroxide were used for the pH control (Table S6, entries S6-12 – S6-14). Addition of the potassium hydroxide to the reaction mixture results in the immediate precipitation of potassium dodecyl sulfate (KDS) (**Figure S30, a**). Krafft point of potassium dodecyl sulfate is $T_{K_r, \text{CsDS}} = 33 \text{ }^{\circ}\text{C}$ which is far above the reaction temperature of $T = 15 \text{ }^{\circ}\text{C}$. Addition of pH neutral potassium salts like potassium bromide results as well in the immediate precipitation of KDS (Figure S30, b). In this case, finely dispersed KDS

crystals act as nucleation sites and lead to formation of large, multilamellar polyethylene particles (Figure S29, center). Polymerization in presence of sodium hydroxide results in stable dispersions with small monolamellar polyethylene particles (Figure 29, right). However, the catalyst productivity is low compared to reactions in presence of cesium hydroxide, meaning, that also the counter ion, namely, cesium plays an important role. Some influence may have the formation of CsDS where the cesium ion is stronger bounded to the dodecyl sulfate moiety than its sodium analog.⁶ Increase of the pH to 13.2 using sodium hydroxide does not lead to a strong productivity change like it was observed in the case of the cesium hydroxide, confirming that the productivity drop in the latter case is due to the viscosity change.

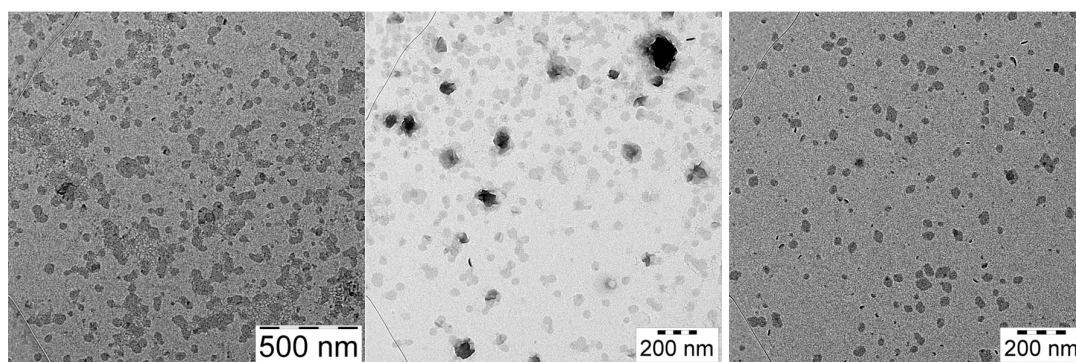


Figure S29. TEM micrographs of dialyzed polyethylene dispersions obtained in presence of (left) CsOH, (center) KOH (right) NaOH at pH 12.5 from Table S6, entries 6-5, 6-14 and 6-12.

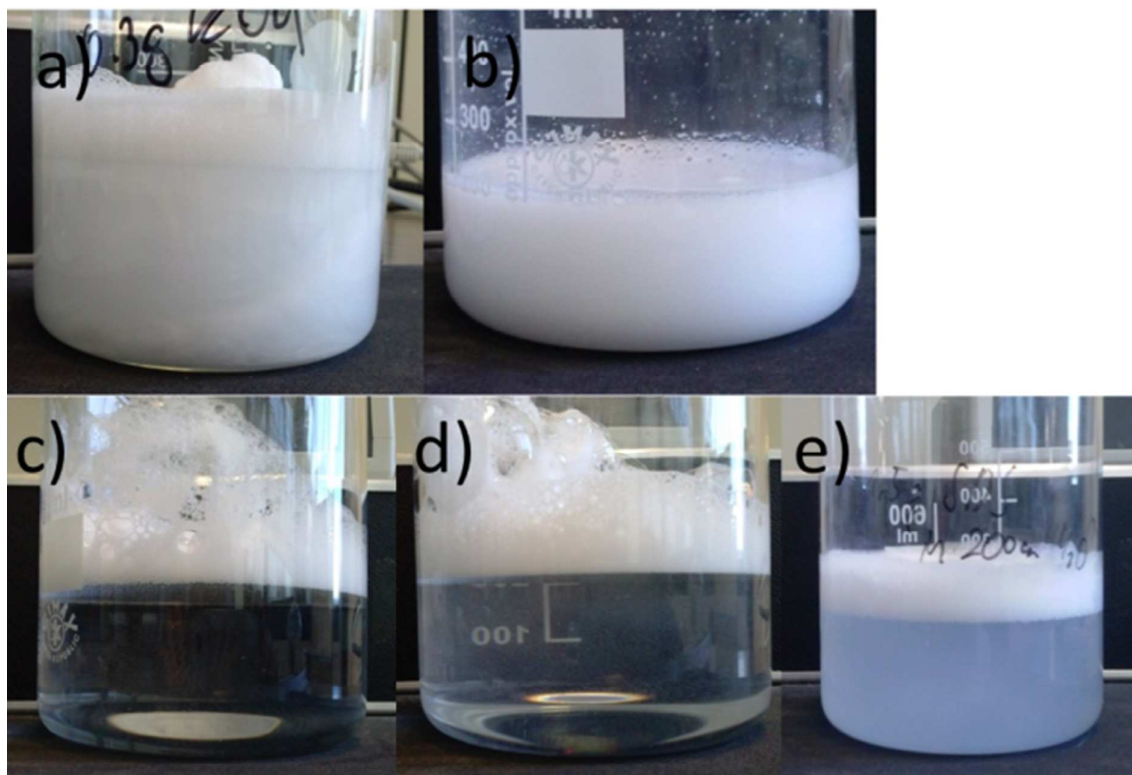


Figure S30. (a) Mixture of 5.2 mmol L^{-1} SDS and $2.9 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ KOH in water, (b) mixture of 5.2 mmol L^{-1} SDS and $3.3 \times 10^{-2} \text{ mol L}^{-1}$ KBr in water. (c-e) Solubility of 5.2 mmol L^{-1} SDS in water at (left) room temperature, (center) 13°C , (right) 5°C .

Aqueous ethylene polymerization ceases immediately in acidic conditions (Table S6). At pH 2 no polymer could be obtained and at pH 6.7 only polymer traces were isolated.

Catalyst-Stabilizing additives

A number of potentially coordinating water soluble additives were tested regarding their stabilizing ability of catalyst in aqueous ethylene polymerization. Amides like *N,N*-Dimethylformamide (DMF) or *N*-formylpiperidine as well as O-donor compounds like THF were studied. The catalyst ($[\mathbf{1-TPPTS}] = 50 \text{ } \mu\text{mol L}^{-1}$) can be stabilized for 1 h using 65 mmol L^{-1} DMF at 15°C and 40 bar ethylene (Table S7). Higher DMF concentration leads to a longer catalyst life time (Figure S30, left, (●) and (■)) at the expense of catalyst activity

(Figure S31, left (○) and (□) and Figure 32, a)). At 0.32 mol L⁻¹ DMF the catalyst activity is almost constant for at least 5 hours (Figure 32 top, black dashed line).

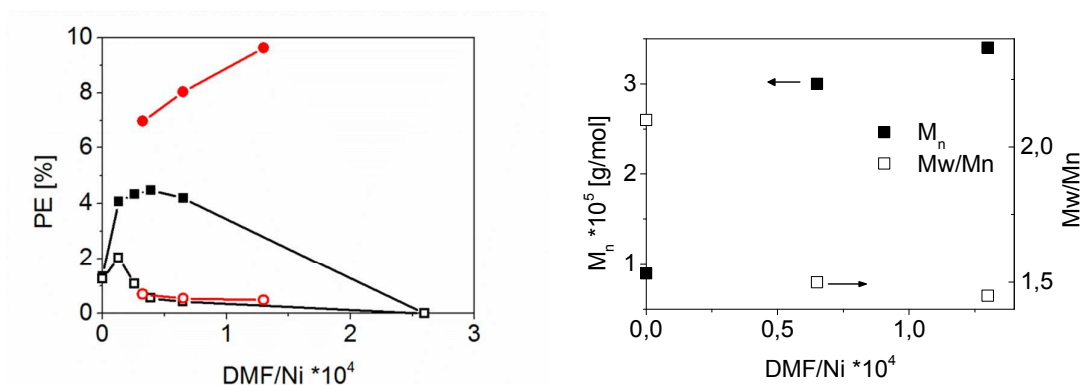


Figure S31. (left) Polymerization activity **1-TPPTS** in presence of DMF. (□) 50 μmol L⁻¹ and (○) 100 μmol L⁻¹ **1-TPPTS**, 0.5 h; (■) 50 μmol L⁻¹ and (●) 100 μmol · L⁻¹ **1-TPPTS**, 10 h. (right) Molecular weight and M_w/M_n of PE depending of DMF concentration used. Reaction was performed at 15 °C and 40 bar ethylene.

Table S7. Influence of DMF on the ethylene polymerization in water.

entry ^a	time [h]	DMF [mol L ⁻¹]	polymer ^b [%]	TOF ^c	TON ^d	particle size [nm] ^e	T _m [°C] (crystallinity [%]) ^f	M _n ^{GPC} [10 ⁵ g · mol ⁻¹] (M _w /M _n)
S7-1	1	0.07 ^{g,j}	4.07	28581	28581	9	135 (80)	
S7-2	0.5	0.13 ^{g,i}	2.06	28379	14189	35 (0.4%), 10	134 (73)	1.4 (1.9)
S7-3	2	0.13 ^{g,j}	4.32	14784	29568	10	137 (86)	
S7-4	4	0.19 ^{g,j}	4.48	8057	32227	52 (0.2 %), 13	136 (70)	1.6 (1.6)
S7-5	5	0.32 ^{g,j}	4.19	5847	29233	17	136 (69)	3.0 (1.5)
S7-6	2	1.3 ^{g,k}	-	-	-	-	-	
S7-7	5	0.32 ^{h,j}	6.55	4786	23930	8	135 (77)	1.1 (2.0)
S7-8	5	0.32 ^{h,k}	6.98	4747	23737	9	135 (77)	1.1 (2.3)
S7-9	7	0.65 ^{h,k}	8.04	4211	29474	10	138 (77)	2.4 (1.6)
S7-10 ^l	20	1.30 ^{h,k}	9.63	1771	35422	10	137 (75)	3.4 (1.5)

^a Reaction conditions: 200 mL water, 15 °C, 40 bar. ^b Determined by precipitation. ^c [mol ethylene mol cat.⁻¹ h⁻¹]. ^d [mol ethylene mol cat.⁻¹]. ^e Determined by DLS. ^f Determined by DSC. ^g 50 µmol L⁻¹ **1-TPPTS**. ^h 100 µmol L⁻¹ **1-TPPTS**. ⁱ 26 mmol · L⁻¹ SDS. ^j 52 mmol L⁻¹ g SDS. ^k 78 mmol L⁻¹ SDS. ^l After 10 h no constant pressure because of the closed PE bottle, pressure drop to 38 bar after additional 10 h.

At 1.3 mol L^{-1} DMF no more polymer is formed but even after 5 hours no catalyst decomposition occurs, indicated by the orange-red color of the final mixture in contrast to the pale yellow color of the decomposed catalyst in aqueous solution. The equilibrium between the active and the DMF coordinated dormant species is shifted to the side of the dormant species which is inactive in ethylene polymerization.

Higher catalyst concentration ($100 \text{ } \mu\text{mol L}^{-1}$) requires higher DMF concentration for the catalyst stabilization. Nearly constant catalyst activities over prolonged period of time were achieved at 1.30 mol L^{-1} DMF resulting in catalyst life time > 10 hours at 40 bar ethylene and $15 \text{ }^{\circ}\text{C}$. Stable polyethylene dispersions with particle size of $\sim 10 \text{ nm}$ and polymer content of up to 9.6 wt.-% polyethylene were obtained.

Polymerization experiments using the ^1H - ^{13}C -TPPTS were also performed in presence of 0.13 mol L^{-1} DMF (Table 1, entries 1-8 and 1-9). After 0.5 min polymerization minor polymer traces and after 2 min 39 mg of the polymer could be isolated. The branch content of the obtained polyethylene is significantly lower than in samples obtained without DMF (about 3 branches per chain). The microstructure of the polymer isolated from the 20 h experiments using unlabeled **1-TPPTS** is linear, with 2 branches per 1000 carbon atoms (**Figure S33**). According to GPC molecular weights of $> 3 \times 10^5 \text{ g mol}^{-1}$ were obtained, which is 3 fold as high as the typical molecular weight of the polymers obtained without DMF at $15 \text{ }^{\circ}\text{C}$ with M_n of $\sim 0.9 \times 10^5 \text{ g mol}^{-1}$ (Figure S31, right). The polymerization rate in presence of DMF is significantly slower than without an additive, as expected, when DMF coordination is present. The coordination of DMF probably takes place via the carbonyl oxygen and not via the nitrogen, similar to the previously reported nickel(II) DMF complexes.⁷

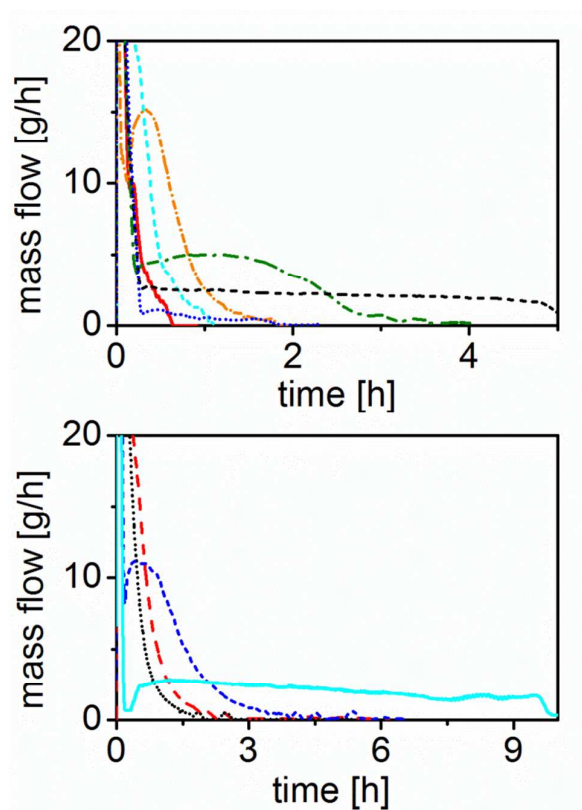


Figure S32. Mass flow traces for ethylene polymerization in presence of DMF; (top) 50 $\mu\text{mol L}^{-1}$ **1-TPPTS**, 52 mmol L^{-1} SDS, (—) 0 mol L^{-1} DMF, (---) 0.065 mol L^{-1} DMF, (- · -) 0.13 mol L^{-1} DMF, (- · · -) 0.19 mol L^{-1} DMF, (- - -) 0.32 mol L^{-1} DMF, (···) 1.3 mol L^{-1} DMF, (bottom) 100 $\mu\text{mol L}^{-1}$ complex **1**, (---) 0.32 mol L^{-1} DMF, 52 mmol L^{-1} SDS, (···) 0.32 mol L^{-1} DMF, 78 mol L^{-1} SDS, (---) 0.65 mol L^{-1} DMF, 78 mmol L^{-1} SDS, (—) 1.3 mol L^{-1} DMF, 78 mmol L^{-1} SDS.

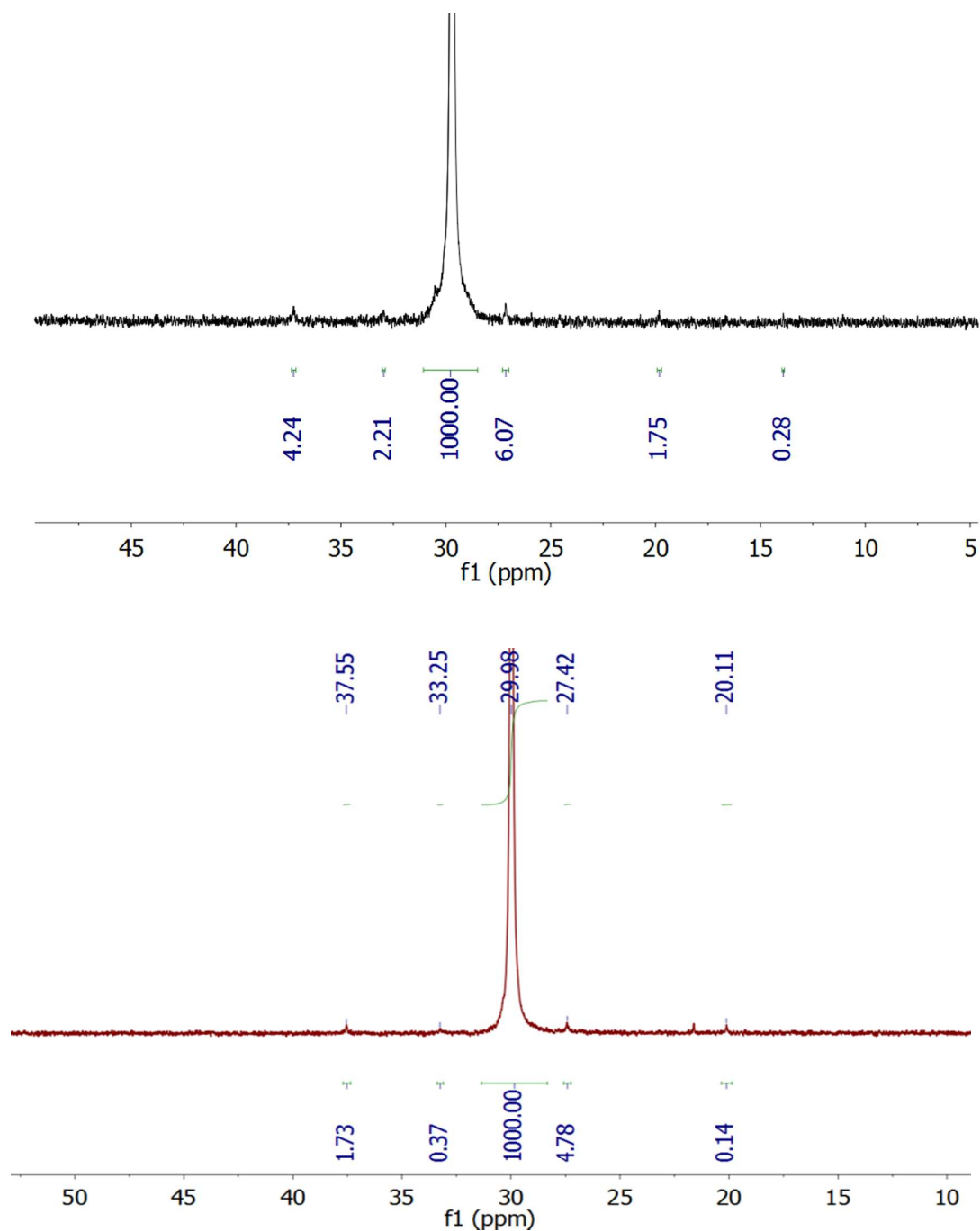


Figure S33. (top) ^{13}C NMR of polymer synthesized in presence of DMF. Recorded at 150 MHz Bruker Avance DRX 600 NMR device with relaxation time of 6 sec and 10240 scans at 388 K in 1,1,2,2-tetrachloroethane- d_2 . Sample obtained in presence of DMF from entry 7-5, Table S7. (bottom) sample obtained at pH 12.5 using CsOH, from entry S6-5, Table S6.

Other coordinating additives were studied (Table S8). The catalyst precursor concentration of $50 \mu\text{mol L}^{-1}$ was chosen. For comparison reasons additive concentration of 130 mmol L^{-1} was chosen as standard condition.

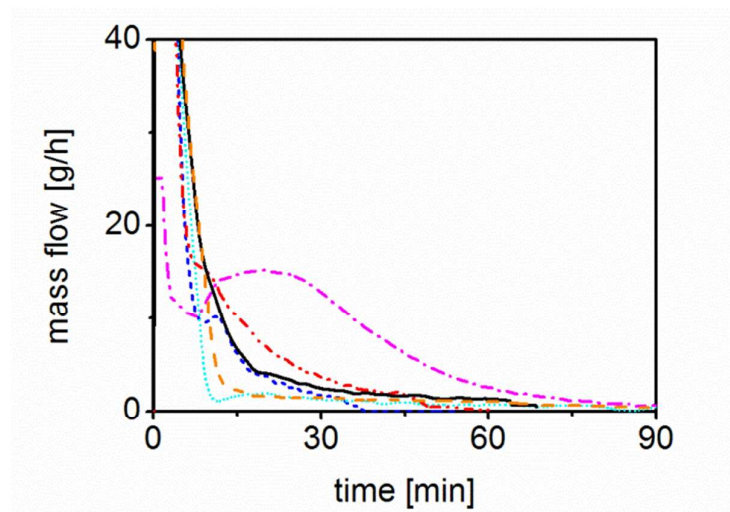
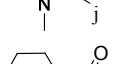
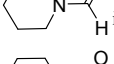
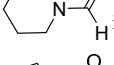
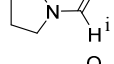
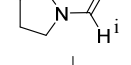
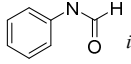
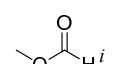


Figure S34. Mass flow traces for ethylene polymerization in presence of coordinating additives, (— · —) DMF, (— · —) THF, (—) DMA, (— —) *N*-methylformamide, (····) *N*-formylpiperidine, (---) no additives. 130 mmol of the additive at 15 °C and 40 bar using $50 \mu\text{mol L}^{-1}$ **1-TPPTS**.

N-methylformamide does not stabilize the reaction; the catalyst is quickly deactivated (Figure S34, dashed orange line) and its productivity is even lower in comparison to the reaction without an additive. *N*-methylformamide contains an amide proton which may promote the catalyst deactivation. Addition of *N,N*-dimethylacetamide (DMA), a compound having similar coordination strength like DMF, leads only to a moderate increase of the catalyst life time and productivity compared to the reaction without an additive. In contrast to DMF, higher DMA concentration leads to a lower yield without increasing the catalyst life time. This can be attributed to a slightly higher acidity of DMA compared to DMF.

Table S8. Influence of coordinating substrates on the ethylene polymerization in water.

entry ^a	time [h]	additives	polymer ^b [%]	TOF ^c	particle size [nm] ^d	T _m [°C] (crystallinity [%]) ^e
S8-1	2		0.76	2617	10	nd
S8-2	1		0.71	4860	9	131 (67)
S8-3	2		0.78	2721	13	nd
S8-4	1		2.29	15977	11	134 (80)
S8-5	1		1.18	8451	10	136 (76)
S8-6	2		0.04	143	10	126 (62)
S8-7 ^f	1		0.04	296	12	126 (63)
S8-8	1		0.02	134	8	114 (51)
S8-9 ^g	1		0.08	551	20	131 (61)
S8-10	2		-	-	-	-
S8-11	1		-	-	-	-
S8-12	1		0.15	1081	11	131 (68)
S8-13	2		-	-	-	-
S8-14	1	dmso ⁱ	0.70	5047	13	132 (67)
S8-15	1	THF ⁱ	2.04	14142	11	134 (74)
S8-16	1	diglyme ⁱ	0.41	2956	12	137 (68)

^a Reaction conditions: 200 mL water, 15 °C, 40 bar, 10 μmol **1-TPPTS**. ^b Determined by precipitation. ^c [mol ethylene · mol cat.⁻¹ · h⁻¹]. ^d Determined by DLS. ^e Determined by DSC. ^f 20 °C. ^g 50 °C. ^h 130 mmol L⁻¹. ⁱ 260 mmol L⁻¹. ^j 520 mmol L⁻¹.

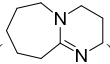
Using stronger coordinating ligands like *N*-formylpiperidine or *N*-formylpyrrolidine only low catalyst activity is observed even at 50 °C and very low polymer yields are obtained (Figure S34 and Table S8). Other stronger coordinating ligands like dmso decrease the catalyst productivity compared to the reaction without an additive. Aromatic compounds like

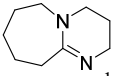
N-methylformanilide or halogenated compounds like 2-chloro-*N,N*-dimethylacetamide decompose the catalyst completely (Figure S35, left). Final dispersions had a pH of 4 and 2 respectively. No polymer was obtained in both cases (Table S8). Addition of methyl formate leads to a strongly decreased catalytic activity compared to the polymerization without an additive. Being a quite unstable compound it can produce trace amounts of formic acid which deactivate the catalyst. Addition of THF, which is a much weaker coordinating ligand than DMF, increases the catalyst life time to up to 1 h. Multisite coordinating ethers like diglyme decrease the catalyst activity compared to the reaction without an additive.



Figure S35. Polymerization mixture after 1 month from Table S8 (left) 2-chloro-*N,N*-dimethyl acetamide as additive, pH 2 entry S8-13, (right) DMA, pH 7 entry S8-5. The black color indicates the formation of Ni black as the result of the catalyst decomposition.

Addition of weakly coordinating tertiary amines like 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) leads to the catalyst stabilization similarly to DMF, however much lower DBU concentrations are necessary ($\sim 0.7 \text{ mmol L}^{-1}$, **Table S9**). Having a $\text{pK}_{\text{a,H}_2\text{O}} \sim 12$ DBU is not a simple coordinating agent, but also influences the pH of the reaction mixture making it basic. An even weaker coordinating tertiary amine, 1,4-diazabicyclo[2.2.2]octane (DABCO), $\text{pK}_{\text{a,H}_2\text{O}} = 2.97, 8.82$ respectively, increase the catalyst productivity when used at higher concentrations. Polymer contents of $\sim 6 \text{ wt.-%}$ are accessible with $50 \text{ } \mu\text{mol L}^{-1}$ complex after polymerization for 1 h at $15 \text{ } ^\circ\text{C}$ and 40 bar ethylene (**Table S10**). DABCO is probably acting similarly to a “buffer” and not as coordinating agent.

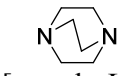
Table S9. Ethylene polymerization in presence of DBU ()

entry	reaction time [h]	 [mmol L ⁻¹]	pH	polymer [%]	M _n ^{GPC} [10 ⁵ g · mol ⁻¹] (M _w /M _n)	T _m [°C] / cryst. [%]	particle size [nm] ^b
S9-1	1	0.17	7,1	4.8	5.5 (1.3)	135 (83)	13, 50 (0.2 %)
S9-2 ^a	5	0.67	7,5	2.25	3.5 (1.5)	137 (86)	14
S9-3	1	1.67	9,2	1.99	3.3 (1.5)	138 (79)	12
S9-4	1	3.34	10	1.38	2.6 (1.4)	140 (85)	12

Reaction conditions: cat. 50 μmol L⁻¹ **1-TPPTS**, 52 mmol L⁻¹ SDS, 200 mL water, 15 °C, 40 bar

^a26 mmol L⁻¹ SDS. ^bParticle size by DLS

Table S10. Ethylene polymerization in presence of DABCO ()

entry	reaction time [h]	 [mmol · L ⁻¹]	pH	polymer [%]	M _n ^{GPC} [10 ⁵ g mol ⁻¹] (M _w /M _n)	T _m [°C] / cryst. [%]	Particle size [nm] ^a
S10-1	1	1.56	8	4.62	3.6 (1.6)	137 (81)	59
S10-2	1	4.27	8	4.37	4.6 (1.5)	136 (83)	17
S10-3	1	44.3	8	5.65	5.3 (1.4)	137 (83)	12

Reaction conditions: cat. 50 μmol L⁻¹ **1-TPPTS**, 52 mmol L⁻¹ SDS, 200 mL water, 15 °C, 40 bar.

^aParticle size by DLS.

To sum up, stronger ligands than DMF (i.e. dmso, *N*-formylpiperidin, *N*-formylpyrrolidine) lead to a lower catalyst activity, compared to the polymerization without an additive, by blocking the coordination site. The same accounts for more sterically hindered additives. Weaker coordinating compounds like THF increase the catalyst productivity. However, they cannot increase the catalyst life time significantly. Polar or activated compounds destroy the catalyst (methyl formate, *N*-methylformanilide, chloro-*N,N*-dimethylacetamide). Bases like DBU or DABCO stabilize the system similarly to the base + DMF combinations.

Sampling system

In order to monitor a reaction two general routes can be pursued. The classical sample drawing is a widely spread technique which allows to follow the progress of the reaction. The sample can be immediately quenched and further characterized by all available analysis methods. Prior purification steps can be easily performed. However, sample drawing can lead to modification of the analyzed sample. Another approach, called on-line monitoring, implies the analysis of the reaction mixture directly in the reaction vessel. On-line monitoring of emulsion or dispersion polymerization reactions has been reported by various groups.⁸ The most important disadvantages of these on-line techniques are their sensitivity to the increase of the solid content, turbidity change and formation of precipitates. Reactions at high pressure are usually not available for the analysis techniques like microscopy or X-ray scattering.

Sample drawing followed by off-line analysis was chosen to monitor the ethylene polymerization in water. The drawn samples were characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), dynamic light scattering (DLS), analytical ultracentrifugation (AUZ), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), surface tension measurement (STM) and conductivity measurement (CM).

Sampling chamber. Sampling of strongly foaming liquids like the polyethylene dispersions under pressure is very challenging. A pressure drop results in the formation of the dense foam and possibly in creaming of the dispersion and clogging of the valves. To avoid these inconveniences a special sampling chamber was constructed which enables sampling at pressures such as 40 bar (Figure S36).

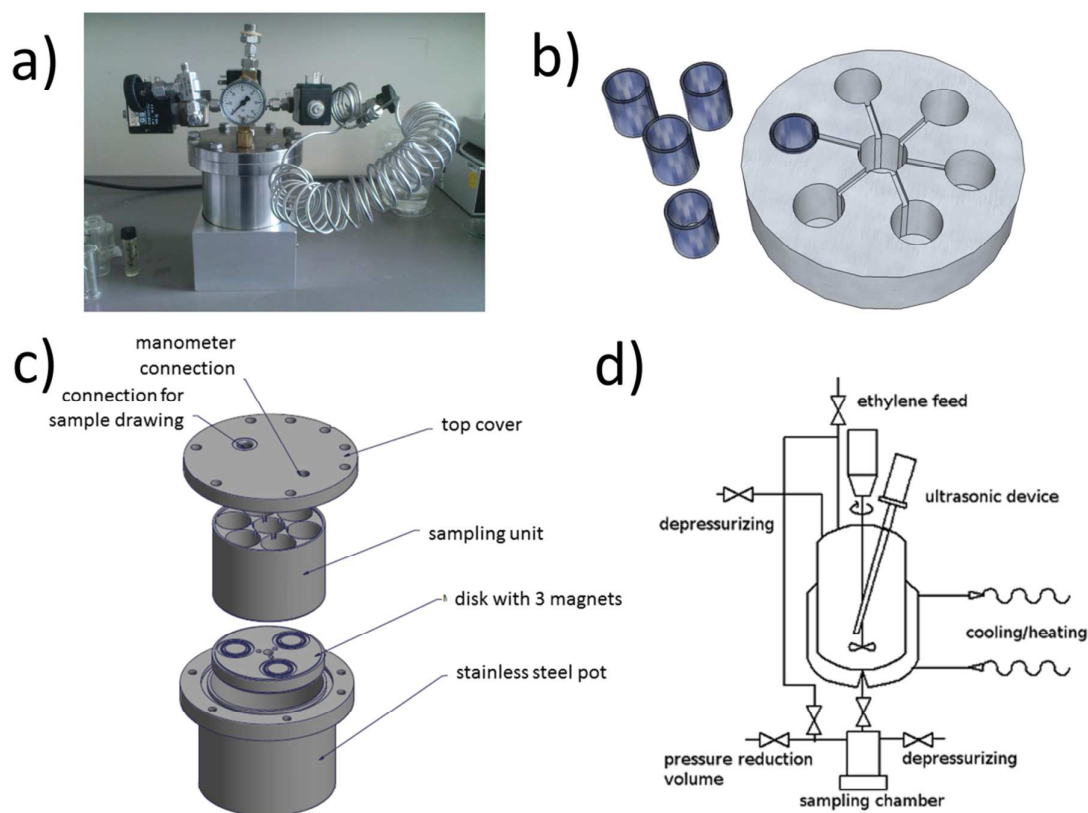


Figure S36. (a) Sampling chamber with the pressure control mechanism, (b) sampling unit with sampling vessels (model), (c) sampling chamber and rotating sampling unit (sketch) and (d) sketch of the reactor system and the sampling chamber.

The sampling chamber is a pressurizable stainless steel vessel which is connected to the reactor and the gas feed via solenoid valves (Figure S36). It contains an exchangeable polypropylene sampling unit that can be precisely rotated via an electromagnetic clutch. The whole process is fully automated and can be operated using the LabVision Automation Software (HitechZang). The number of samples which can be drawn during the reaction depends only on the geometry of the polypropylene sampling unit, for example, in our case 6×10 mL sampling vessels were used.

Sampling procedure. During the polymerization reaction the sampling chamber is set under exactly the same pressure as the reactor. To draw a sample a small additional volume is

connected to the sampling chamber (Figure S36). The pressure inside the sampling chamber drops slightly, thus the pressure difference between the reactor and the sampling chamber is high enough to transfer a small amount of the reaction mixture from the reactor into the sampling vessel. The valve between the reactor and the sampling chamber is closed and the sampling chamber is set again at the exactly the same pressure as the reactor. Using sampling intervals of ≥ 30 s at 40 bar, the temperature and the pressure inside the reactor can be kept almost constant (Figure S37). Higher sampling frequencies result in inconstant temperature and overall pressure drop inside the reactor. When all samples are drawn the sampling chamber is slowly depressurized via a pulsed solenoid valve. The depressurizing takes 1.5 – 2 h, to ensure that all samples remain stable and no foaming occurs inside the sampling vessel (cf. Supporting Information Figure S38).

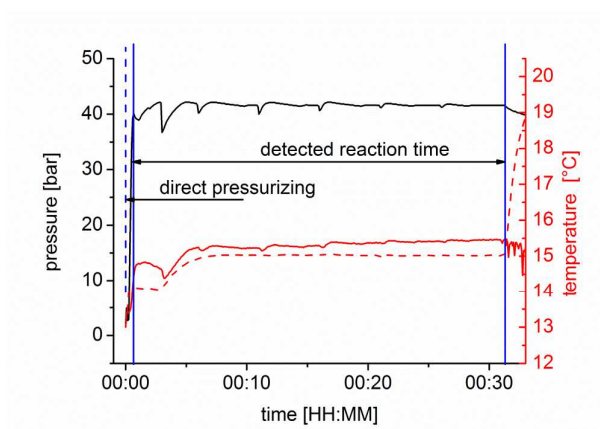


Figure S37. Pressure and temperature during polymerization with sampling. Reaction with high ethylene conversion; spikes of the pressure curve are attributed to the pressure decrease during sampling. (—) pressure; (---) temperature outflow thermostat; (—) temperature inside the reactor.

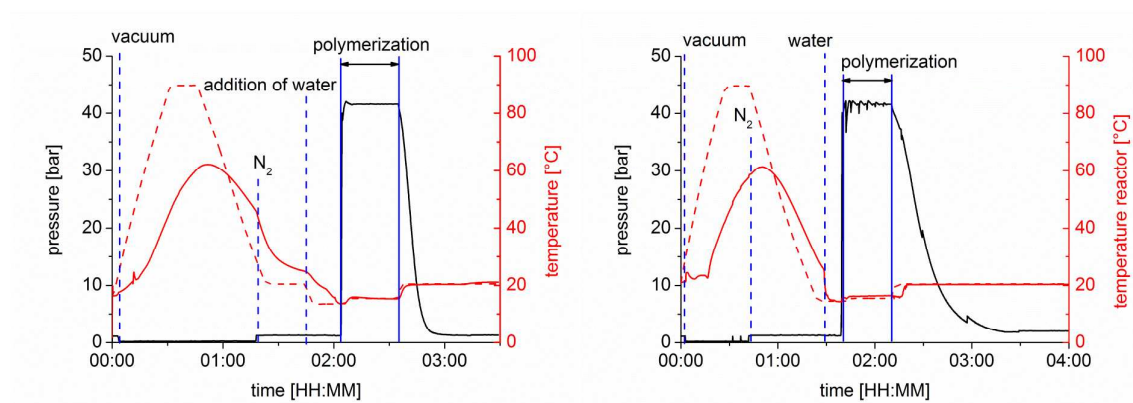


Figure S38. Pressure and temperature during the setting of the reactor and polymerization; (—) pressure; (---) temperature outflow thermostat; (—) temperature inside the reactor (left) without sampling (right) with sampling.

Validation of the sampling system

In order to validate the sampling procedure, first, the stability of the dispersion after the sample drawing was proven. Fully characterized polyethylene dispersion was filled into the reactor, pressurized with 40 bar ethylene under stirring. Samples were drawn and characterized by DLS, tensiometry and conductivity. The polymer content of the drawn sample was estimated by precipitation of the dispersion in methanol. No deviation between the characteristics of the initial dispersion and the drawn sample could be observed (**Table S11**).

Table S11. Analysis of the preformed ethylene dispersion before and after sample drawing.

	before	after
	sample drawing	
Polymer content [%]	1.92	1.99
Particle size [nm]	11	10
Conductivity [mS cm ⁻¹]	0.369	0.373
Surface tension [mN m ⁻¹]	58.5	58.3

Additionally, it had to be proven that after sample drawing no further polymerization occurs inside the pressurized sampling chamber. The sample inside the sampling chamber is not

cooled and not stirred. The ethylene solubility in water is low ($\sim 0.14 \text{ mol L}^{-1}$ at 35°C and 40 bar⁹), thus the efficiency of the polymerization also depends on the sufficient ethylene transport. When the reactor was charged with 200 mL water, 26 mmol L^{-1} SDS, and $75 \text{ }\mu\text{mol L}^{-1}$ catalyst precursor **1-TPPTS** and pressurized with 40 bar ethylene at 15°C for 30 min without stirring no ethylene consumption was detected and no polymer could be isolated from the reaction mixture. Thus, the ethylene transport by diffusion is too slow to enable significant ethylene polymerization without stirring. Additionally, the catalyst used rapidly deactivates at higher temperature.¹⁰ Further, to prevent the polymerization after sample drawing a quencher can be added to the sampling vessel. The catalyst precursor applied can be easily decomposed by acids or oxidizing agents.¹⁰ Two drops of a 30 %-hydrogen peroxide solution were added into the sampling vessel before the polymerization procedure. No difference in particle size, surface tension and polymer content could be observed between the quenched samples and the samples without H_2O_2 (Figure S39). Based on these results we assumed that no further polymerization occurs inside the sampling chamber. All further reactions were performed without addition of hydrogen peroxide as quencher.

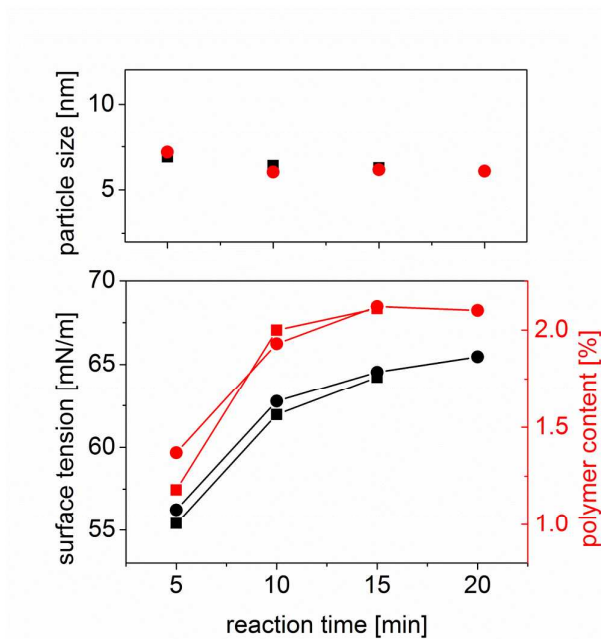


Figure S39. Validation of the sampling chamber. Samples were drawn in a parallel way from the same reaction mixture. (●) no quencher added (■) 2 drops H_2O_2 added in the sampling vial. Reaction conditions: 40 bar, 15 °C, 200 mL water 100 $\mu\text{mol L}^{-1}$ **1-TPPTS**, 26 mmol L^{-1} SDS.

Surface stabilization of the polyethylene particles. Aqueous ethylene polymerization was studied at different reaction times by drawing samples at 40 bar and 15 °C. PE particles are hydrophobic and adsorb the surfactant on their surface. This can be monitored via tensiometry and conductivity measurements (Figure S40, a), b)). The surface tension of the reaction mixture increases and the conductivity of the reaction mixture decreases already in the very first minutes of the polymerization. After ~ 10 min a surface tension of $\gamma \sim 60 \text{ mN m}^{-1}$ and conductivity $\sigma < 0.4 \text{ mS cm}^{-1}$ are reached at polymer contents of ~ 2 wt % PE.

At surfactant concentrations above CMC the maximum surface concentration of the surfactant is reached and additional surfactant molecules are organized in micelles. When the surface tension of a surfactant solution becomes higher than the surface tension at CMC, surfactant micelles are no longer present in the surfactant solution. The initial SDS

concentration used in the polymerization experiment was $[\text{SDS}]_{\text{init}} = 26.0 \text{ mmol L}^{-1}$, the $\text{CMC}_{\text{SDS}} = 8.3 \text{ mmol L}^{-1}$, thus at least 17.7 mmol ($\sim 5 \text{ g}$) of SDS are adsorbed by 1 L of a newly formed polyethylene dispersion when the surfactant concentration drops below CMC. Note, the polymer content of the polyethylene dispersion obtained after 1 min using $50 \mu\text{mol L}^{-1}$ of the catalyst precursor was only $\sim 0.3 \text{ wt } \%$ and the surface tension $\gamma > \gamma_{\text{CMC}}$. According to the tensiometry measurements at polymer contents of 2 wt % virtually all the surfactant is adsorbed on the surface of the particles.

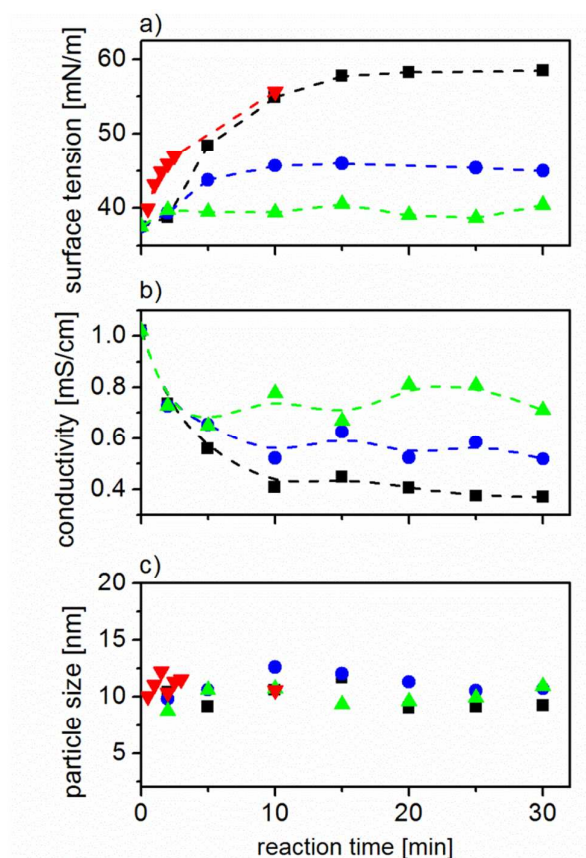


Figure 40. a) Surface tension b) conductivity c) particle size vs. reaction time. Reaction conditions: 40 bar, 15 °C, 200 mL water (■) 100 $\mu\text{mol L}^{-1}$ 1-TPPTS, 26 mmol L^{-1} SDS; (●) 75 $\mu\text{mol L}^{-1}$ cat, 26 mmol L^{-1} SDS; (▲) 50 $\mu\text{mol L}^{-1}$ 1-TPPTS, 26 mmol L^{-1} SDS; (▼) 50 $\mu\text{mol L}^{-1}$ 1-TPPTS, 13 mmol L^{-1} SDS.

Table S12. Aqueous ethylene polymerization using water soluble catalyst precursor **1-TPPTS** without DMF.

entry	Catalyst [μmol]	Reaction time [min]	Polymer content [wt %]	Surface tension [mN/m]	particle diameter [nm] ^{DLS}
S12-1	20	30	1.87	58.5	9
S12-2	15	30	0.67	45.0	11
S12-3	10	30	0.45	40.4	11
S12-4 ^b	10	10	0.62	55.7	11
S12-5 ^c	10	30	1.72	56.5	12
S12-6 ^c	10	120	3.43	50.2	14

^a40 bar ethylene, 30 min, 15 °C, 26 mmol L⁻¹ SDS, 200 mL water,

^b13 mmol L⁻¹ SDS, ^c0.13 mol L⁻¹ DMF.

Sampling experiment using 100 $\mu\text{mol L}^{-1}$ **1-TPPTS** was repeated at shorter sampling period. According to DLS also this time no significant particle growth is observed (Figure S40, red reversed triangles, for PSD Figure S41).

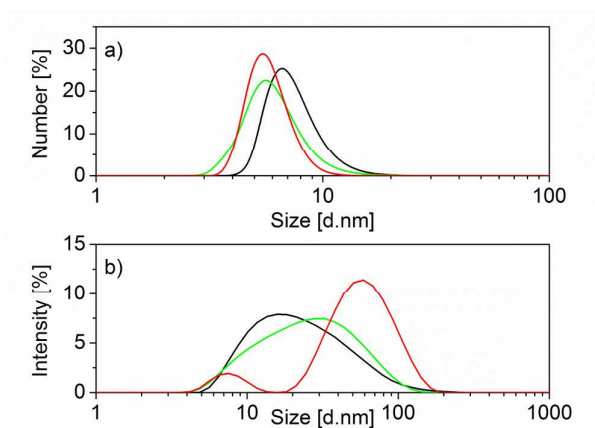


Figure S41. Particle size distribution by a) number^{DLS}, b) intensity^{DLS}. Reaction time: (—) 1.5 min (—) 2.5 min (—) 10 min. The samples were obtained during the polymerization without DMF at 15 °C and 40 bar using **1-TPPTS**.

However, having a look at the initial intensity curves a shift to the larger particle diameters is present. The CONTIN algorithm which is used for the evaluation of the autocorrelation function uses the spherical particle approximation. In our samples the particle are plate-like

(according to TEM). The polydispersity of the sample also implies uncertainties during the analysis.

Analyses of particles obtained with the sampling system by TEM

TEM micrographs of the samples were recorded and analyzed. After 0.5 min the number of observable particles is very low and increases significantly after 10 min. The close-up to the sample drawn after 1.5 min polymerization time reveals small, well dispersed, plate-like particles with an average diameter of ~ 10 nm (**Figure S42, (a)**) and only few larger particles in accordance with the results reported earlier.³ Sample drawn after 10 min contains significantly larger particles with an average diameter of ~ 20 nm (**Figure S42, (c)**). In order to quantify these observations, particles of a micrograph were counted and characterized by their average, maximum and minimum diameter (**Figure S42, (b), (d)** the particles are sorted according to their size, each size class is highlighted by different color). The number of the analyzed particles and the average particle size with the standard deviation (analySIS software by Soft Imaging System GmbH) is shown in **Table S13**).

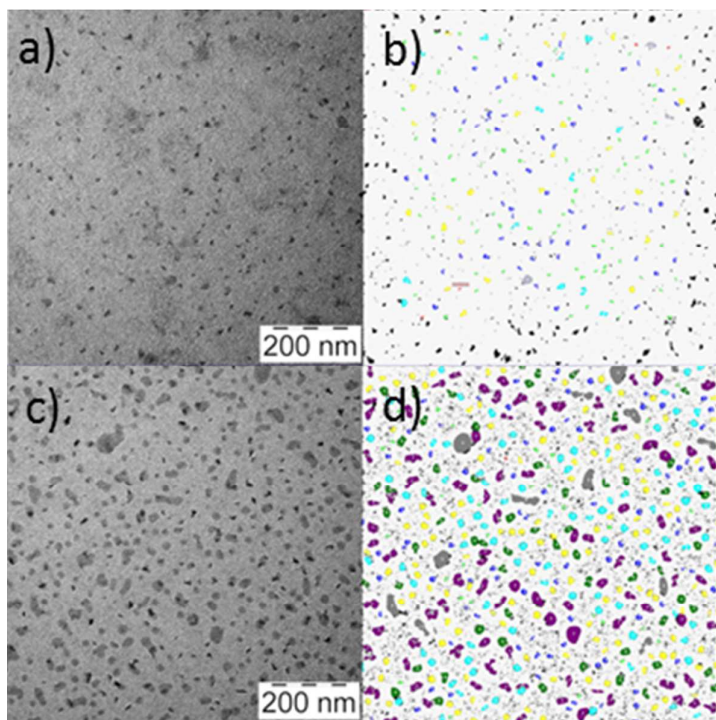


Figure S42. (a) sample drawn after 1.5 min polymerization time; original TEM micrograph; (b) particles sorted according to their maximum diameter; (c) residual reaction mixture after 10 min polymerization time; original TEM micrograph (d) particles sorted according to their maximum diameter.

Table S13. Particle statistics estimated from the TEM micrographs, the polymerization reaction was carried out without DMF at 15 °C and 40 bar using **1-TPPTS**.

Entry	Reaction time [min]	Nb. of particles analysed	Average size [nm]	standard deviation [nm]
S13-1	1.5	284	10.11	3.48
S13-2	2.5	570	19.15	8.65
S13-3	10	519	19.13	9.30

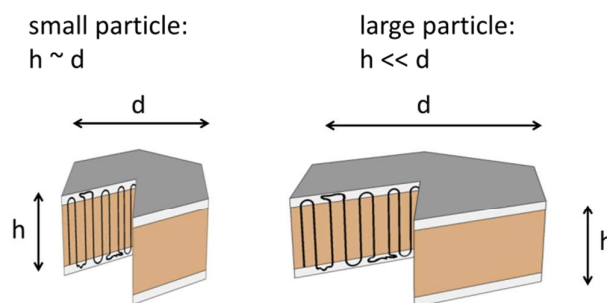


Figure S43. Particle dimensions strongly influence the orientation of the particle on the TEM grid. Small particles orient statistically, large particles orient horizontally.

However, it has also to be taken into account that the orientation of a particle on the TEM grid strongly depends on its size. Small plate-like particles have a similar height h and diameter d (**Figure S43**). Contrarily, h is much smaller than d for large plate-like particles. It must be noted, that TEM samples were prepared by simple evaporation of aqueous polymer dispersion on the copper grid. The large particles will therefore orient horizontally and the small ones will orient rather statistically. This implements an ambiguity into the particle analysis. In the case of small particles the height and the diameter can be analyzed as minimum particle size. In the case of the large particles only the height corresponds to the minimum particle size. Maximum particle size always corresponds to the diameter of the particle independent of its orientation and size.

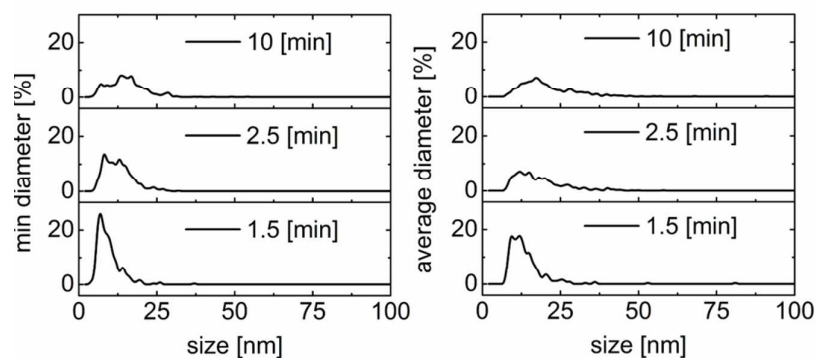


Figure S44. Particle size distributions according to the minimum (left) and average (right) particle diameter. The polymerization procedure was carried out without DMF at 15 °C and 40 bar using **1-TPPTS**.

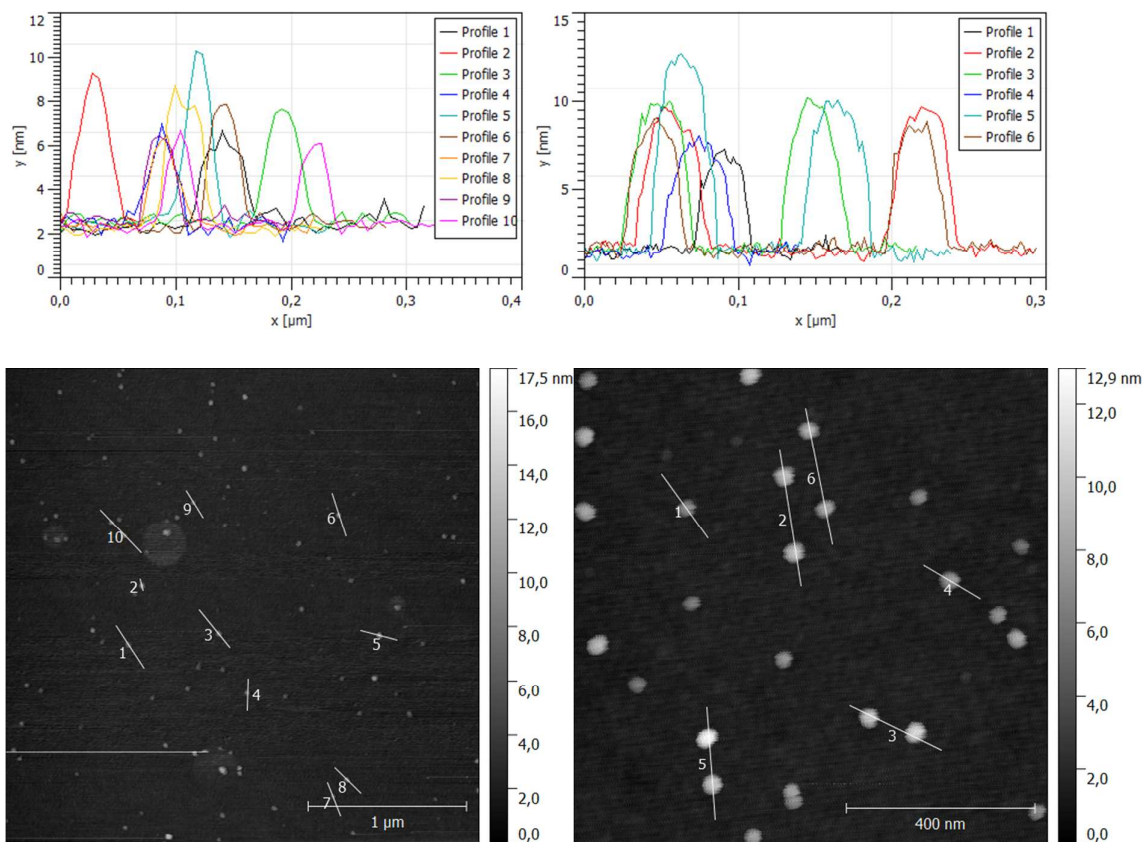


Figure S45. AFM micrograph of the polyethylene dispersion (height image) and cross section of several particles (left) from entry S13-1, Table S13 and (right) entry S13-3, Table S13.

Sampling in presence of DMF. DMF increases the catalyst life time and minimizes the side reactions, thus the sampling procedure was repeated in presence of DMF (Table S14). 0.13 mol L⁻¹ DMF were added to obtain high solids dispersions and to facilitate the sample analytics. The increased catalyst lifetime leads automatically to very high polymer yields on a long term scale, thus higher surfactant concentrations were used in the long term experiment (Table S15) by which the final surface tension was kept below $\gamma < 65 \text{ mN m}^{-1}$ (Figure S46 b), which is prerequisite for a uniform particle growth.

Table S14. Short-time sampling with DMF.

entry	reaction time [min]	average particle size [nm] TEM	standard deviation [nm]	number of particles used for TEM analysis
S14-1	0.5	19	9	670
S14-2	1	17	9	870
S14-3	1.5	20	9	848
S14-4	2.5	21	10	480
S14-5	3	17	7	875
S14-6	30	34	17	460

Reaction conditions: 200 mL water, 26 mmol L⁻¹ SDS, 0.13 mol L⁻¹ DMF, 50 $\mu\text{mol L}^{-1}$ 1-TPPTS, 40 bar ethylene, 15 °C.

Table S15. Long-time sampling with DMF.

entry	reaction time [min]	average particle size [nm] TEM	standard deviation [nm]	number of particles used for TEM analysis
S15-1	3	14	5	672
S15-2	3.5	22	8	1084
S15-3	4	25	12	1934
S15-4	9	28	10	1144
S15-5	30	27	12	437
S15-6	60	30	16	558

Reaction conditions: 200 mL water, 52 mmol L⁻¹ SDS, 0.13 mol L⁻¹ DMF, 50 $\mu\text{mol L}^{-1}$ 1-TPPTS, 40 bar ethylene, 15 °C.

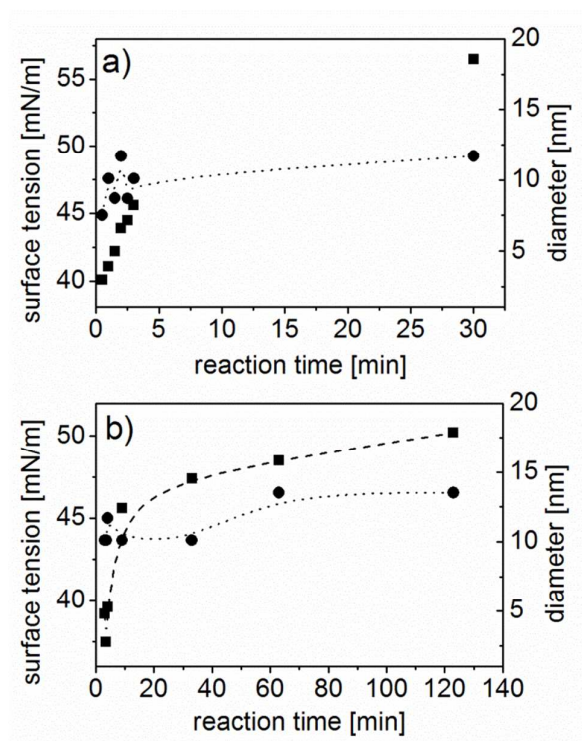


Figure S46. Surface tension and particle size of samples obtained at 40 bar ethylene at 15 °C with 50 $\mu\text{mol L}^{-1}$ **1-TPPTS** in a) short-term experiment (Table S14), 130 mmol L^{-1} SDS; b) long-term experiment (Table S15), 260 mmol L^{-1} SDS; (■) surface tension (●) diameter.

The particle size distributions were additionally evaluated via TEM by the methods presented in the previous section (Table S14, Table S15 and Figures S46 and S47).

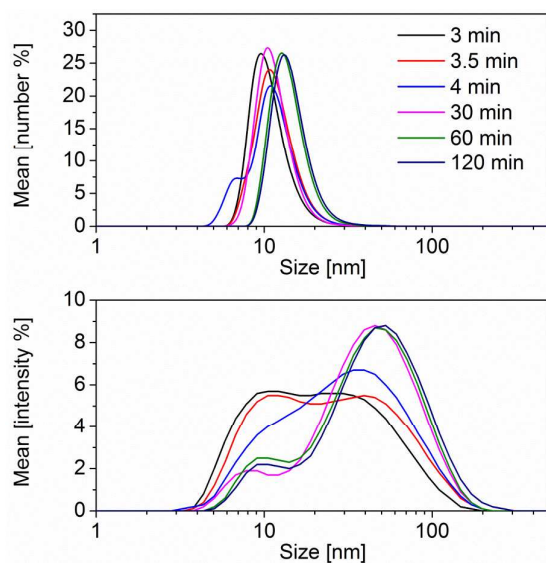


Figure S47. DLS traces of the polymer dispersions obtained in presence of DMF after sampling according to Table S15. Particle size distribution by number (top) and by intensity (bottom)

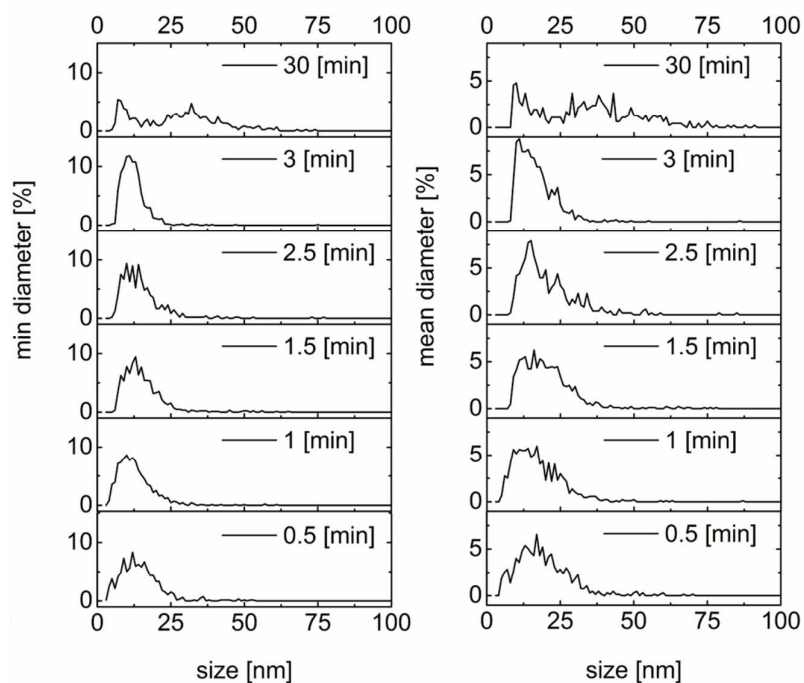


Figure S48. Short term sampling (Table S14) particle size distributions according to (left) minimum and (right) average particle diameter. The reaction was performed in presence of 130 mmol L^{-1} DMF at 15°C and 40 bar using **1-TPPTS**.

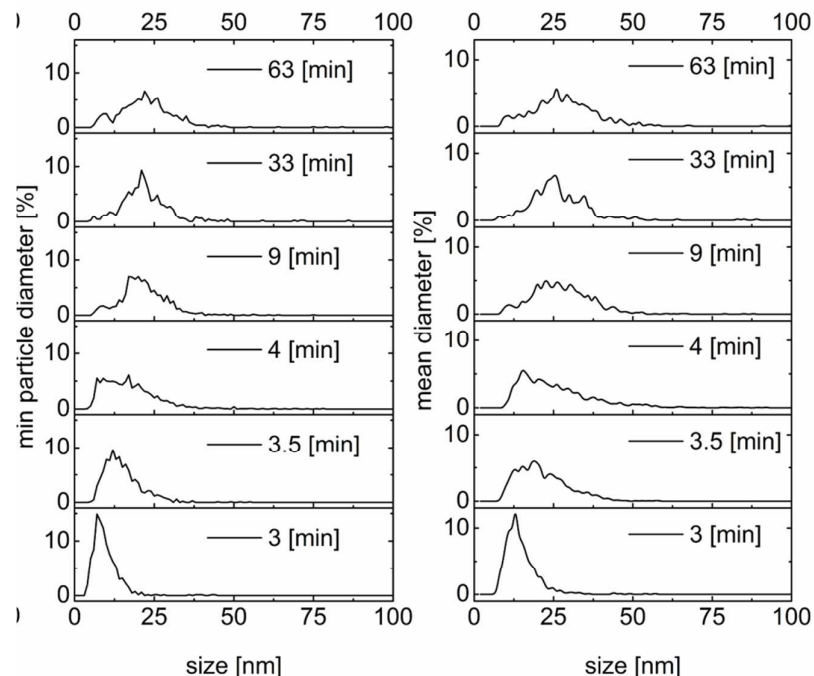


Figure S49. Long term sampling (Table S15) particle size distributions according to (left) minimum and (right) average particle diameter. The reaction was performed in presence of 130 mmol L^{-1} DMF at 15°C and 40 bar using **1-TPPTS**.

AUZ measurements.

AUZ measurements were performed (Figure S50). No sufficient signal quality could be obtained in the case of the short term experiment (samples were drawn after 0.5 and 1.5 min) due to low polymer concentration. In the case of the long term experiment (samples were drawn after 3.5 and 4 min) a shift to larger particle sizes was observed, confirming the observations by TEM. The quantitative comparison of the particle size observed by TEM and AUZ cannot be performed, as the particles diameters observed by AUZ correspond to the hydrodynamic radius of the apparent sphere, while the analysis by TEM leads to the apparent diameter of the anisotropic plate.

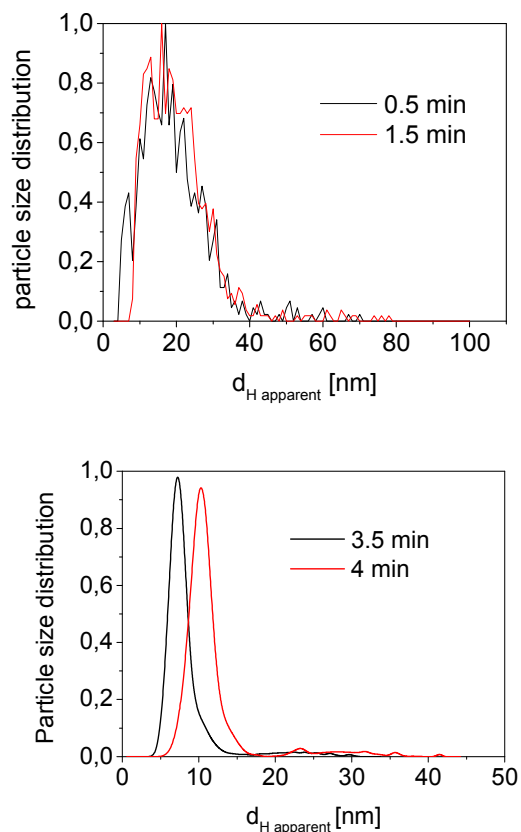


Figure S50. AUZ measurements of the particle size distribution (left) from short term experiment (Table S14), due to very low polymer concentration the distribution is badly resolved (right) particle size distribution from the long term experiment (Table S15), a shift to larger particle diameters can be observed.

Volume of a particle

Usually the particle size is estimated from DLS measurement. However, this estimation, particularly using one-angle DLS measurement, is only reliable for monodisperse spherical particles. Here, we demonstrate the influence of particle shape on its volume.

For selected samples we calculated the mean particle volumes using the particle surfaces areas estimated by TEM, and assuming that the particle thickness is constant at all particle sizes $h = 8$ nm according to Equations (S8)-(S9). We also calculated the particle volumes $V_{\text{mean,sphere}}$ using the hydrodynamic radii R_H of oblate ellipsoids with dimensions $a = \sqrt{(\text{surface$

area^{TEM}/π) and b = 8 nm according to (S10) and (S11). The volumes obtained from DLS and by approximation as oblate ellipsoid are comparable. However, when the particle volume is calculated using the true particle geometry obtained by TEM much higher particle volumes are obtained, particularly in the case of large particles, meaning, that the mistake made assuming the R_H to be directly related to the real particle volume is in the order of magnitude of 10¹.

$$V_i = A_i \cdot h_i \quad (\text{S8})$$

$$V_{\text{mean}} = \frac{\sum V_i x_i}{\sum x_i} \quad (\text{S9})$$

$$R_H = \frac{\sqrt{a^2 - b^2}}{\arctan(\sqrt{a^2 - b^2}/b)} \quad (\text{S10})$$

$$V_{i,\text{sphere}} = 4/3\pi R_H^3 \quad (\text{S11})$$

Table S16. Particle volumes calculated from DLS and TEM data. Samples were obtained at 15 °C and 40 bar.

entry	Particle volume ^{DLS} [10 ⁻²⁵ m ³]	Particle volume ^{oblate approximation} [10 ⁻²⁵ m ³]	Particle volume ^{TEM} according to (S9) [10 ⁻²⁵ m ³]	Reaction time [min]	Yield [g]
S16-1	2.2	3.1	9.0	1.5	
S16-2	1.8	3.0	9.3	5	0.082
S16-3	1.0	3.6	21.2	10	4.38
S16-4	7.0	4.1	30.2	30	4.580
S16-5	42.2	22.1	92.2	240	15.60
S16-6	17.7	16.6	254	600	27.60

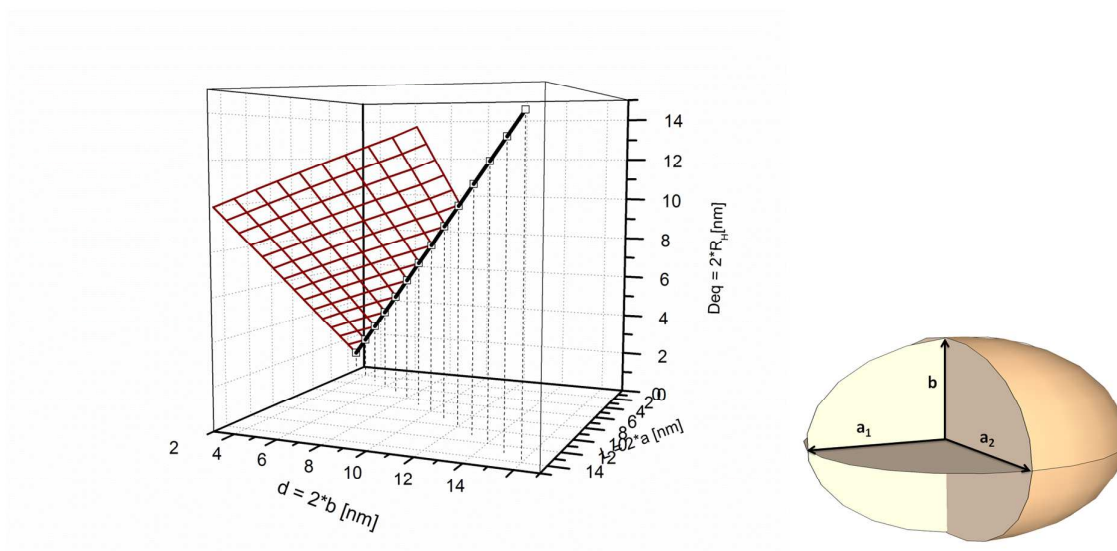


Figure S51. (left) (red grid) Equivalent diameter D_{eq} of an oblate ellipsoid with dimensions a , b ; $a > b$. (black line) sphere with dimensions $a = b$, (right) PE particles can be approximately described as oblate ellipsoids with $a_1 = a_2 > b$.

Particle thickness measurements

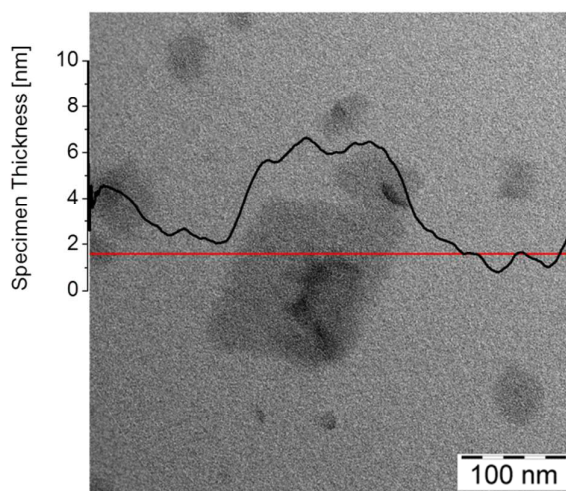
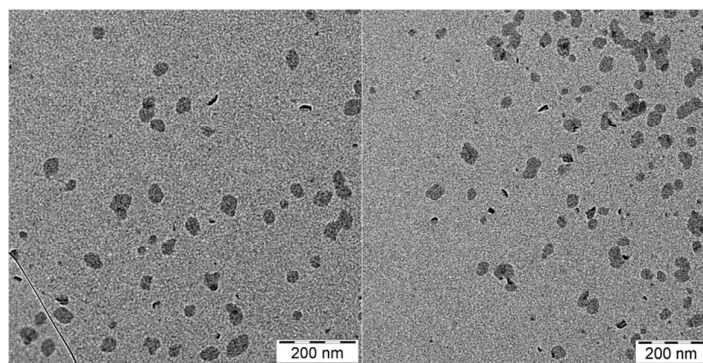


Figure S52. Particle thickness of a lozenge shaped particle obtained after 4 h polymerization using **1-TPPTS** by electron energy loss.



Figures S53. TEM micrographs of a sample obtained after 24 h polymerization in D₂O at 15 °C and 40 bar from entry S5-10 Table S5.

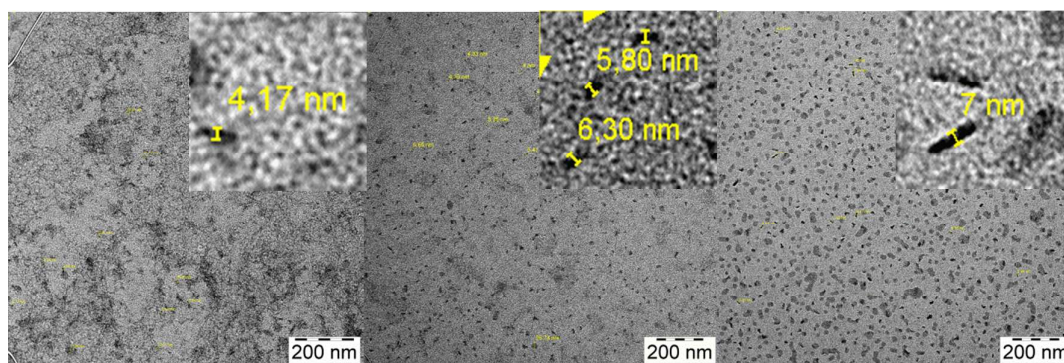


Figure S54. TEM micrographs of dispersions obtained after 0.5, 1.5 and 10 min polymerization time using **1-TPPTS** at 15 °C and 40 bar. The mean particle thicknesses for these samples are 4.1 ± 0.6 nm, 4.5 ± 0.7 nm and 7.1 ± 0.8 nm respectively. Note, the dispersion obtained after 30 s contains very small polymer concentration.

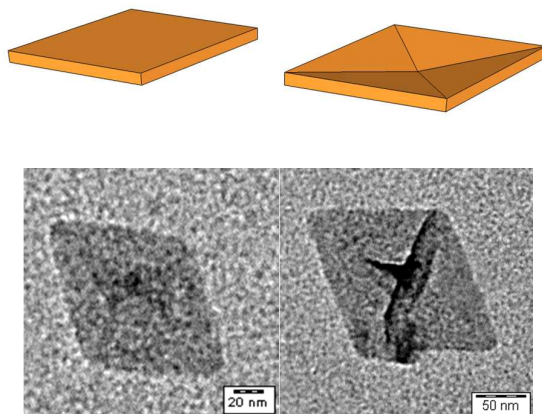


Figure S55. (left) flat lozenge (right) hollow pyramid. (top) Sketch, (bottom) TEM micrographs (from entry S2-8, Tables S2).

Additional TEM micrographs

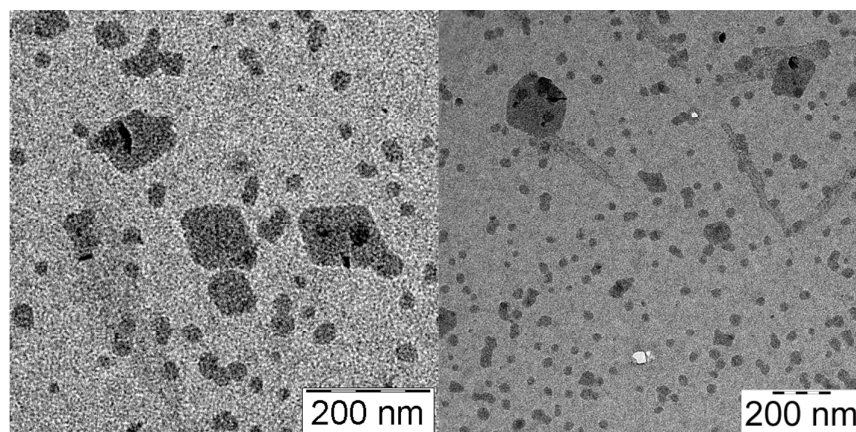


Figure S56. Lozenge shaped polyethylene crystals obtained in presence of DMF and with final surface tensions $\gamma > 65 \text{ mN m}^{-1}$ from entry S7-5, Table S7.

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