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Catalytic Polymerization of Ethylene in Aqueous Emulsion with a Simple in Situ Catalyst[†]

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ABSTRACT: Catalytic polymerization of ethylene in aqueous emulsion by in situ catalysts based entirely on compounds commercially available from standard chemicals suppliers, namely a chlorinated derivative of 1,4-benzoquinone, triphenylphosphine, and bis(1,5-cyclooctadiene)nickel, is reported. Using miniemulsions of catalyst solutions in a small amount of hydrocarbon solvent for polymerization, stable dispersions of linear semicrystalline polyethylene are obtained. With 2,3,5,6-tetrachloro-1,4-benzoquinone as the quinone component, polyethylenes with molecular weights (M_n up to 3×10^3 g mol^{-1}) clearly exceeding the entanglement limit are accessible. The catalyst is stable in water for hours with productivities of up to 2×10^3 mol(ethylene) mol(Ni)$^{-1}$ h^{-1}. Productivities and molecular weights are in the same range for conventional polymerization in organic solvents. Polyethylene dispersions with solids contents of up to 28% are obtained. Aqueous dispersions of ethylene/1-butene copolymers with comonomer incorporations of up to 3 mol % (6 wt %) were prepared.

Introduction

Emulsion polymerization of olefinic monomers, yielding polymer latexes, is carried out on a vast scale.[1] The use of water as a dispersing medium offers a unique combination of features, such as effective transfer of the heat of reaction, effective stabilization of polymer particles by surfactants, and environmental friendliness. By contrast to polymerization in solution or in the bulk, in emulsion polymerization a large portion of polymer can be generated in a given volume of reaction mixture without a strong increase in viscosity. The nontoxicity and nonflammability of water are also advantageous with regard to applications of latexes: often film formation upon evaporation of the dispersing medium is a key step. To date, emulsion polymerization is carried out industrially by free radical processes exclusively. However, the preparation of polymer latexes by catalytic polymerization of simple olefinic monomers has also received increasing interest recently.[2−8] Such reactions offer access to polymer latexes inaccessible by other techniques.

We[5] and others[6] have recently reported on catalytic polymerization of ethylene in aqueous emulsion. With nickel(II) phosphinoenolate complexes, low-molecular-weight linear polyethylene was obtained in aqueous systems.[5a,b,6] Employing phosphinoenolate complexes bearing electron-withdrawing groups, Claverie and Spitz et al. observed high catalytic activities of up to 10^5 mol(ethylene) mol(Ni)$^{-1}$ h^{-1}.[6b] Low-molecular-weight polymer with typically M_n 1.3×10^3 g mol^{-1} and M_w/M_n 3.1−3.5 was obtained, which is in the range of the entanglement limit (10^3 g mol^{-1}) of polyethylene.[9]

To obtain polymer latexes in catalytic emulsion polymerization, water-soluble complexes can be employed in analogy to traditional free-radical polymerization,[5a,b] or as an alternative concept aqueous miniemulsions of a solution of a lipophilic catalyst precursor in a small amount of hydrocarbon can be utilized (cf. Scheme 3). The latter approach enables the use of the generally more common lipophilic catalysts,[6b] and in addition somewhat water-sensitive catalysts can also be employed.[5c]

An approach to catalytic emulsion polymerization of ethylene that obviates the need for preparing special ligands and complexes is highly desirable for industrial applications and, no less, for fundamental studies of latex properties, e.g., in laboratories equipped for emulsion polymerization but not for organic synthesis.

Results and Discussion

Catalyst Synthesis and Proposed Structure. In situ catalysts based entirely on commercially available compounds, namely chlorinated derivatives of 1,4-benzoquinone, triphenylphosphine, and bis(1,5-cyclooctadiene)nickel as a source of Ni^0 (Scheme 1), were investigated (cf. succeeding section on polymerization).[10]

For 2,6-dichloro-1,4-benzoquinone (DCBQ) and 2,3,5-trichlorobenzoquinone (TriCBQ), formation of a P∧O-chelated nickel(II) complex as the active species can be assumed on the basis of the known reaction of 1,4-benzoquinone with triphenylphosphine and of the resulting phosphorane with nickel(0) compounds (Scheme 1).[11] This is also in accordance with the observed selectivity in the C−C linkage of ethylene for formation of *linear* polymer (vide infra), typical for P∧O-chelated nickel(II) complexes.[11d,e]

For 2,3,5,6-tetrachloro-1,4-benzoquinone (TetraCBQ), a strictly analogous reaction is not possible due to the lack of hydrogen atoms. Reaction between the different components of the in situ system is evidenced by pronounced color changes (Figure 1): addition of a toluene solution of PPh_3 (colorless) to TetraCBQ (yellow) affords a rust-red slurry. After addition of methanol a clear red solution forms, which turns orange over ca.

[†] Dedicated to Dr. Dieter Distler on the occasion of his 60th birthday.

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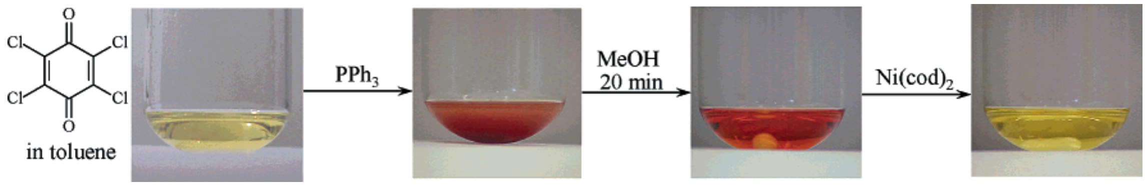
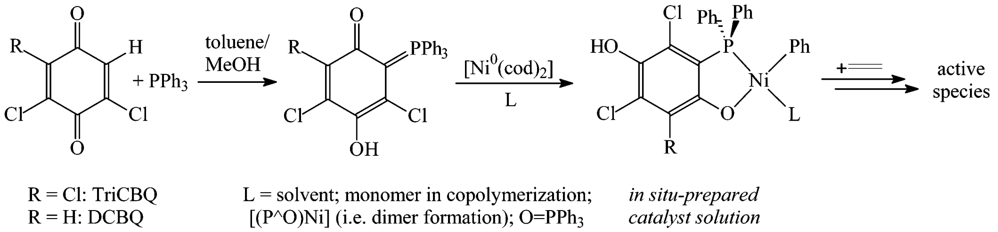
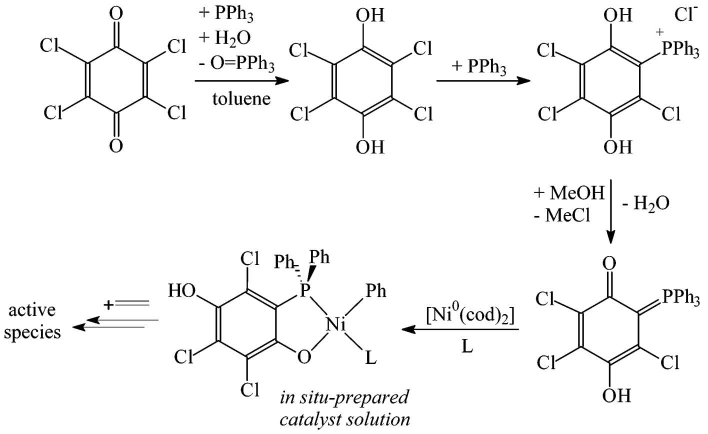


Figure 1. In situ catalyst preparation with tetrachlorobenzoquinone.

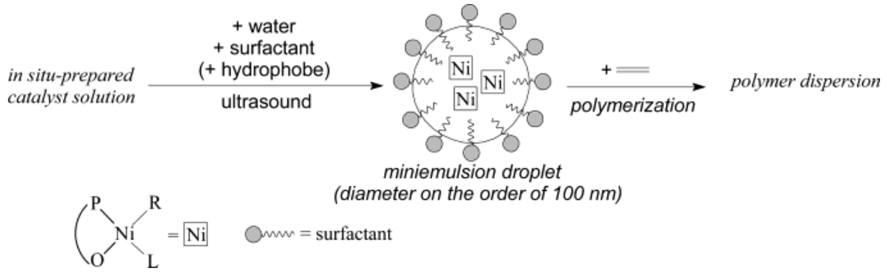
Scheme 1. Proposed Formation of the Catalyst Precursor with Di- and Trichlorobenzoquinone



Scheme 2. Proposed Formation of the Catalyst Precursor with Tetrachlorobenzoquinone



Scheme 3. Miniemulsification of the Catalyst Solution



20 min. This reacts with a toluene solution of [Ni(cod)$_2$] to a clear yellow solution, which is active for ethylene polymerization.

As for the nature of the active species, the reaction of TetraCBQ with triphenylphosphine and 1 equiv of water has been reported to afford triphenylphosphine oxide and 2,3,5,6-tetrachlorohydroquinone, based on IR and UV analysis.[11b] In agreement with this finding, for the in situ catalyst system, that is for a 1:1 mixture of TetraCBQ and triphenylphosphine in toluene/methanol, the formation of triphenylphosphine oxide was observed by ^{31}P NMR ($\delta = 32.3$ ppm, assignment confirmed by enrichment with a genuine sample of $Ph_3P{=}O$). An additional peak at $\delta = 17.6$ ppm, integrating for approximately 20% of the $Ph_3P{=}O$-peak, is observed (Figure 2). This is similar to the resonance of the adduct of triphenylphosphine with 1,4-benzoquinone[11] ($\delta = 22$ ppm; CD_3OD) and with TriCBQ ($\delta = 18$ ppm; toluene-d_8/CD_3OD). Tetrachlorohydroquinone and also $Ph_3P{=}O$ were identified in the reaction mixture by thin-layer chromatography (4:1 toluene/methanol) by comparison to genuine samples of the compounds. As expected, the clear yellow solution obtained by combining 1 equiv of triphenylphosphine oxide with [Ni(cod)$_2$] was entirely catalytically inactive, in the absence as well as the presence of added 2,3,5,6-tetrachlorohydroquinone or TetraCBQ.

On the basis of the aforementioned findings, the reaction sequence given in Scheme 2 is proposed as a possible pathway to the active species.

Polymerization. For emulsion polymerization, the catalyst solution was miniemulsified by means of high shear generated by ultrasound (Scheme 3).[5c,6b] The resulting catalyst miniemulsion was transferred to a pressure reactor and exposed to a constant ethylene pressure.

Polymerization with the TetraCBQ-based catalyst was investigated in detail (Table 1). The catalyst is stable in the aqueous system, as evidenced by a linear

Table 1. Polymerization with a TetraCBQ-Based Catalyst[a]

	reaction conditions					results						
entry no.	n(cat.)/ μmol	ethylene press./ bar	c(sds)/ [mmol L^{-1}]	reacn time/ h	reacn temp/ °C	solids content/ %	productivity/ (mol(ethylene) × mol (cat.)$^{-1}$)	av activity/ (mol (ethylene) × mol (cat.)$^{-1}$ h^{-1})	M_n/(g × mol^{-1})	M_w/ M_n[b]	av size of particles/ nm[14]	T_m/ °C
						Aqueous Emulsion						
1	258	40	34.7	2.0	70	17.7	2440	1220	2.6×10^3	3.2	92 (0.24)	127
2	62	40	34.7	2.0	60	5.6	3230	1615	3.0×10^3	2.1	*c*	129
3	69	40	34.7	2.0	50	6.9	3550	1775	3.1×10^3	4.1	95 (0.22)	127
4	66	40	34.7	2.0	40	1.7	930	465	3.2×10^3	7.5	*c*	129
5	66	40	34.7	2.0	30	0.5	290	145	*c*	*c*	72 (0.17)	*c*
6	165	40	52.0	0.5	50	4.0	870	1740	*c*	*c*	108 (0.14)	*c*
7	165	40	52.0	1.0	50	7.8	1680	1680	2.6×10^3	5.2	130 (0.25)	*c*
8	165	40	52.0	1.5	50	10.4	2250	1500	*c*	*c*	98 (0.20)	130
9	66	30	34.7	2.0	50	4.6	2480	1240	*c*	*c*	91 (0.15)	*c*
10	66	20	34.7	2.0	50	2.8	1510	755	*c*	*c*	78 (0.16)	127
11	66	10	34.7	2.0	50	2.2	1170	585	1.7×10^3	5.3	74 (0.14)	*c*
						Nonaqueous						
12	66	40		2.0	70	2.8[d]	1480	740	*c*	*c*	-	126
13	66	30		2.0	70	4.5[d]	2410	1205	*c*	*c*	-	127
14	66	20		2.0	70	2.7[d]	1430	715	*c*	*c*	-	124
15	66	10		2.0	70	1.4[d]	780	390	*c*	*c*	-	123

[a] Reaction conditions: entries 1−11: 95 mL of water, 1 mL of methanol, 5 mL of toluene, 0.3 mL of hexadecane; entries 12−15: 90 mL of toluene, 10 mL of methanol. [b] Bi- or multimodal distributions. [c] Not determined. [d] Polymer yield in g.

Table 2. Polymerization Results with Catalysts Based on Different 1,4-Benzoquinones[a]

entry no.	quinone employed	n(cat.)/ μmol	solids content/%	productivity/ (mol(ethylene)× mol(cat.)$^{-1}$)	av activity/ (mol(ethylene)× mol(cat.)$^{-1}$ h^{-1})	M_n/ (g mol^{-1})	M_w/M_n	T_m/°C
1	TetraCBQ	69	6.9	3550	1775	3.1×10^3	4.1	127
2	TriCBQ	66	5.2	2810	1405	*b*	*b*	125
3	DCBQ	66	28.0	15120	6050[c]	8.3×10^2	2.9	118
4	1,4-benzoquinone	66	1.9	750	375	3.3×10^2	3.8	109

[a] Reaction conditions: 50 °C reaction temperature; 2 h reaction time; 40 bar ethylene pressure; 95 mL of water, 1 mL of methanol, 5 mL of toluene, 0.3 mL of hexadecane; $c(SDS) = 34.7$ mmol/L. [b] Not determined. [c] 2.5 h reaction time.

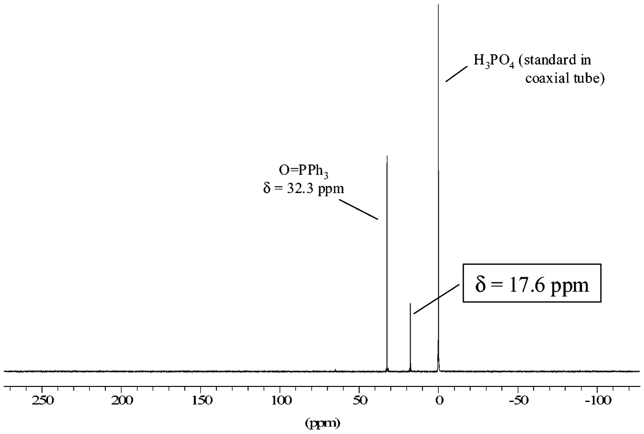


Figure 2. ^{31}P NMR spectrum of the reaction mixture of triphenylphosphine with 2,3,5,6-tetrachloro-1,4-benzoquinone (solvent: toluene-d_8/CH_3OH 4:1 v/v).

increase of polymer yield with reaction time over 90 min (entries 6−8). The rate of polymerization is dependent to some extent on ethylene pressure in aqueous emulsion as well as in comparative nonaqueous polymerizations in neat toluene (entries 3 and 9−15). For nickel(II) phosphinoenolate complexes such as $Na^+[\{\kappa^2P,O\text{-}Ph_2P{-}C(SO_3^-){=}C(-O)\text{-}4\text{-}MeC_6H_4)\}NiPh(PPh_3)]$ (abstraction of PPh_3 by phosphine scavengers for polymerization), the rate of polymerization is highly dependent on monomer concentration. In polymerization in aqueous emulsion, low monomer concentrations at the active sites related to restricted mass transfer can strongly reduce polymerization activities. By comparison, the influence of ethylene pressure is moderate for the in situ system subject to this work. Accordingly, no strong differences in rate between polymerization in emulsion and nonaqueous polymerization are observed. Polymerization occurs only sluggishly at room temperature; for an efficient polymerization temperatures of 50−70 °C are required (entries 1−5). With anionic surfactants sodium dodecyl sulfate (SDS) or Dowfax2A1 (sodium salt of disulfonated, alkyl-substituted diphenyl ether), stable polyethylene dispersions with reasonably high solid contents were obtained at surfactant concentrations of down to 0.2 wt %.

Comparing differently substituted quinones, of the compounds investigated DCBQ was found to be the most active with an average activity of 6×10^3 mol(ethylene) mol(Ni)$^{-1}$ h^{-1} (Table 2). However, product molecular weights are relatively low. In accordance with the above considerations regarding formation of the active species (Schemes 1 and 2), which should result in the same active species employing TriCBQ and TetraCBQ, a similar polymer melting point is observed with both quinones (Table 2, entries 1 and 2). All chlorinated quinones investigated were found to result in significantly more active catalysts than the parent unsubstituted 1,4-benzoquinone (entry 4).

With respect to film formation from latexes, a control of polymer crystallinity is of interest. Copolymerization with 1-butene and 1-octene was investigated. Butene as a comonomer is of special interest as it is not only very cheap, but also its volatility allows for a facile removal and recycling of unreacted monomer from dispersions. Carrying out a polymerization under the conditions of entry 3, Table 1 (40 bar of ethylene; 75

mL of water), in the presence of 20 mL of 1-butene, an incorporation of 3 mol % (6 wt %) was determined by ^{13}C NMR on the polymer isolated from the dispersion obtained. The productivity is lowered to 7×10^2 TO by comparison to the 3.6×10^3 TO observed in ethylene homopolymerization. Similar results were obtained with 1-octene (3 mL of 1-octene added; incorporation 0.4 mol % = 1.6 wt %, 1.3×10^3 TO). Nonaqueous butene copolymerization was studied for comparison, as in this initially homogeneous single-phase system monomer concentrations are known by contrast to the multiphase aqueous systems. At 10 bar ethylene pressure and 70 °C reaction temperature with a reaction solution containing 50 mL of 1-butene comonomer, 10 mL of methanol, and 40 mL of toluene the incorporation is 3 mol %. With $[\text{butene}] = 6$ mol L^{-1} and $[\text{ethylene}] \approx 2$ mol L^{-1}, this corresponds to a relative incorporation on the order of ethylene:butene = 100:1 at equal monomer concentrations.[12] Neutral nickel(II) catalysts are known to generally possess a high selectivity for ethylene by comparison to incorporation of 1-olefin,[6c,11d] and the catalyst system investigated is apparently no exception. Nonewithstanding, dispersions of copolymers with a certain degree of comonomer incorporation can be obtained. The lowered activities by comparison to ethylene homopolymerization can be ascribed to a slower chain growth upon insertion of comonomer.

Polymer and Latex Properties. The polyethylene obtained is linear, as high-temperature ^{1}H and ^{13}C NMR demonstrate. In addition to vinyl and corresponding alkyl end groups, a small portion (about 10% relative to the number of vinyl end groups) of internal olefinic resonances is observed in some samples by ^{1}H NMR. High-temperature GPC analyses reveal number-average molecular weights in the range of M_n $1.7 \times 10^3 - 3.1 \times 10^3$ g mol^{-1} for the TetraCBQ-based systems (Table 1). This exceeds the entanglement molecular weight of polyethylene of 10^3 g mol^{-1}; that is, a true polymer is formed.[9] A bimodal molecular weight distribution with an additional mode at roughly 10^5 g mol^{-1} is observed in some cases, indicating the presence of more than one active species. Interestingly, particularly in copolymerization experiments the amount of higher molecular weight fractions can be such that high overall weight-average molecular weight results, e.g., M_w 1.2×10^5 g mol^{-1} for an ethylene/1-octene copolymer (M_w/M_n 40).

It should be noted that the molecular weights of the samples approach the lower limit of accurate GPC detection. However, the number-average molecular weights calculated from the integrals of the end groups in the ^{1}H NMR and the determined T_m values[13] support the GPC data. The molecular weights obtained in nonaqueous polymerizations resemble the ones of the aqueous catalytic polymerizations as confirmed by ^{1}H NMR spectroscopy and also the T_m.

Polymer crystallinities determined by DSC on polymer isolated from aqueous dispersions are in the range 70−80%, as expected for linear polyethylene. By comparison to typical high molecular weight polyethylene ($T_m = 138$ °C), the moderate molecular weights result in a slight lowering and broadening of the melt peak. Incorporation of 3 mol % butene results in a decrease of the melting point to $T_m = 108$ °C and of the crystallinity to ca. 45%.

Polyethylene latexes with up to 28% solids content were prepared (Table 2, entry 3). As expected, upon increasing the surfactant concentration from 0.2 to 1 wt % a reduction in average polymer particle size is observed (e.g., from 118 to 92 nm under the conditions of entry 1, Table 1; particle sizes determined by dynamic light scattering, DLS).[14] At the lowest surfactant concentration, polymerization was frequently accompanied by formation of some coagulate. It should be noted that, by contrast to classical free radical miniemulsion polymerization of liquid monomers, in this catalytic polymerization gaseous ethylene monomer is added continuously during polymerization *after* miniemulsification of a solution of the in situ catalyst in a small amount of liquid organic solvent. Thus, extensive rearrangement of the dispersion during polymerization by comparison to the initial miniemulsion can occur.

A key feature in applications of polymer latexes is film formation. Latices were spread on a glass substrate, the dispersing medium water was evaporated, and the residual polymer was tempered for 20 min at 165 °C in an oven. Films of ca. 0.4 μm thickness were obtained. AFM reveals a continuous film. Polarized light microscopy reveals spherulites in the linear polyethylene (HDPE) film. By comparison, in a film formed from a commercial LDPE latex prepared by traditional high-pressure free radical polymerization the formation of such spherulites is less distinctive and the formed spherulites are smaller (Supporting Information).

Summary and Conclusions

Aqueous dispersions of linear polyethylene can be prepared conveniently with a catalyst prepared in situ from reagents available from standard laboratory chemicals suppliers. Low-molecular-weight linear polyethylene is obtained; however, with tetrachlorobenzoquinone as a catalyst component M_n clearly exceeds the entanglement limit. Polyethylene dispersions of up to 28% solids content can be obtained at rather moderate reaction conditions. A low incorporation of 1-butene is observed in copolymerization experiments; however, the amount incorporated is sufficient to significantly lower polymer crystallinity. In addition to providing a basis for development toward typical polymer latex applications, the present system is also of particular interest as a low-pressure route to wax dispersions.

Experimental Section

Materials and General Considerations. Ethylene (99.9%) and 1-butene (99.6%) supplied by Messer-Griesheim were used without further purification. Triphenylphosphine (Aldrich), TetraCBQ (Aldrich), TriCBQ (Sigma-Aldrich-USA), DCBQ (Sigma), sodium dodecyl sulfate (Fluka), and bis(1,5-cyclooctadiene)nickel (Aldrich or Strem) were used without further purification. Toluene and methanol were distilled from drying agents (toluene: Na; methanol: Mg) under argon. Hexadecane and 1-octene were distilled under argon. Deionized water was degassed prior to use.

NMR spectra were recorded on a Bruker ARX 300 instrument (^{1}H: 300 MHz; ^{13}C: 75 MHz) or on a Bruker AVANCE DPX 200 spectrometer (^{31}P: 81 MHz). ^{1}H NMR chemical shifts were referred to TMS as an internal standard. ^{13}C{^{1}H} NMR chemical shifts were calibrated against the deuterated solvent multiplet and referenced to TMS. ^{31}P{^{1}H} NMR chemical shifts were measured relative to internal 85% H_3PO_4 (coaxial tube) with downfield values being taken as positive. High-temperature NMR measurements were performed in 1,1,2,2-tetrachloroethane-d_2 at 122 °C. The comonomer incorporation was determined by integration of corresponding signals in the ^{13}C NMR (1-octene: $\delta = 34.6$ ppm (3 C, $-CH_2CH(CH_2C_5H_{11})CH_2-$); 1-butene: $\delta = 39.7$ ppm (1 C, $-CH_2CH(C_2H_5)CH_2-$)).[15] Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 or on a Pyris 1 DSC at a heating rate of

10 K/min. Ethylene homopolymers were investigated in the temperature range 25−180 °C; copolymers were studied at −100 to 180 °C. DSC data reported are second heats. Gel permeation chromatography of polyethylene was performed in 1,2,4-trichlorobenzene at 140 °C using a Polymer Laboratories PL-220 instrument equipped with mixed bed PL columns. Data reported were determined vs polystyrene standards and corrected for linear polyethylene (universal calibration: K_α(PS) 1.21×10^{-4} mL g^{-1}, α(PS) 0.707, K_α(PE) 4.06×10^{-4} mL g^{-1}, α(PE) 0.725). Dynamic light scattering on dispersions was performed on a Malvern particle sizer.

Catalyst Preparation. The preparation of catalyst solutions was performed by standard Schlenk techniques under argon. Equal molar amounts of triphenylphosphine and the chlorinated 1,4-benzoquinone were dissolved in a mixture of the given amounts of methanol and toluene. For experiments in aqueous systems, hexadecane was added as a hydrophobe for subsequent miniemulsification (vide supra) of the catalyst solution. After stirring for about 20 min the obtained solution was transferred to a 1.1-fold molar excess of bis(1,5-cyclooctadiene)nickel.

Polymerization Procedure. Polymerization was carried out in a mechanically stirred 250 mL pressure reactor equipped with a heating/cooling jacket, the temperature being controlled automatically by means of a sensor dipping into the reaction mixture. The total volume of the added liquid phase (water and/or organic solvent) amounted to 100 mL. For polymerization in miniemulsion the main part of an aqueous solution of the surfactant was transferred to the reactor while the other part was added to the catalyst solution. The latter biphasic mixure was ultrasonified (Bandelin HD2200 with a KE76 tip, operated at 120 W) to afford a miniemulsion, which was then also transferred to the polymerization reactor via a Teflon cannula. For copolymerization with 1-octene a part of the toluene was replaced by the comonomer. In the case of 1-butene as a comonomer the gaseous 1-olefin first was condensed to a graduated reservoir and then to the cooled reactor followed by addition of the miniemulsified catalyst solution. The reactor was flushed and pressurized with ethylene, while rapidly heating to the specified temperature under vigorous stirring (1000 rpm). After the specified reaction time, the reaction was stopped by cooling and releasing the gas pressure. In experiments yielding precipitated polymers these were isolated, washed with water and methanol, and dried in a vacuum. In experiments yielding a polymer latex, the latter was filtered through a funnel with glass wool prior to further workup and analysis. For determination of the solids content, the latex was added to an excess of methanol. The precipitated polymers were isolated, washed with methanol, and dried in a vacuum.

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Supporting Information Available: AFM and optical microscopy of films formed from polymer dispersions. This material is available free of charge via the Internet at http://pubs.acs.org.

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