Emulsion Polymerization

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Aqueous Dispersions of Nonspherical Polyethylene Nanoparticles from Free-Radical Polymerization under Mild Conditions**

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Polyethylene, the top manufactured polymer by volume, is usually synthesized from low-pressure and -temperature catalytic processes[1,2] or from a high-temperature (above 200 °C) and -pressure (greater than 1000 bar), highly energy-consuming free-radical polymerization process.[3–5] In the latter case a branched, low-density, polyethylene is produced (LDPE), in contrast to Ziegler–Natta catalysis, which enables the synthesis of high-density polyethylene (HDPE) that exhibits higher crystallinities and melting temperatures. These well-established polymerization processes require improvement: reduction of energy consumption and of the use of volatile organic compounds (VOCs) are important targets. The VOC issue has been largely solved for low-pressure catalytic Ziegler–Natta polymerizations by using solvent-free gas-phase processes. For slurry polymerization, new catalysts compatible with "green" diluents such as supercritical CO_2[6,7] or water[8–11] have been developed.

Recently we successfully produced polyethylene (PE) by a radical pathway under less energy-consuming conditions: medium pressure below 250 bar and a low temperature of 70 °C using organic solvents (toluene or THF).[12] PE was synthesized in high yields and exhibited intermediate melting points and crystallinities in comparison to HDPE and LDPE ($115 < T_m < 119$ °C; crystallinity of 55–70 %). However, polymer molecular weights remained low (number-average molecular weight $M_n < 5000\,\mathrm{g\,mol^{-1}}$, polydispersity index PDI ≈ 2) because of frequent transfer reactions to the solvent.

Transposition to an emulsion polymerization in aqueous dispersed medium (benefiting from the compartmentalization of radicals and from the low transfer ability of water) should be useful to increase both molecular weight and yield and at the same time to solve the VOC issue.

Only a few studies of free-radical polymerization (FRP) of ethylene in aqueous dispersed media have been reported,[13–17] and these use relatively high pressures ($P >$ 300 bar) and a wide range of temperatures. The interpretation of the results in these early works (1945–1975) is difficult because of the lack of analytical tools available at the time to study colloidal properties of the obtained polymer dispersions.

Note that the emulsion process for ethylene polymerization cannot be a classical one. Ethylene is introduced as a supercritical gas, and consequently no ethylene droplets exist during the polymerization and no unreacted liquid monomer can remain in the latex. Furthermore, PE is a crystalline material, in contrast to most conventional polymers produced by FRP.

Herein, FRP of ethylene in emulsion under mild conditions has been investigated, representing an innovative, low-energy, "green", efficient way to produce PE by a free-radical mechanism. The transposition of the ethylene polymerization process to aqueous medium has been achieved by using a cationic water-soluble initiator, 2,2-azobis(2-amidinopropane)dihydrochloride (AIBA). FRP of ethylene was performed in water at 70 °C with and without a standard cationic surfactant (CTAB, cetyltrimethylammonium bromide) to assist nucleation and particle stabilization. In all cases, ethylene was polymerized with significant yields, and stable dispersions of PE particles were obtained for ethylene pressure up to 250 bar (Figure 1). Interestingly, PE can be synthesized by this FRP process down to a pressure of 50 bar.

In the surfactant-free system, yield is lower than that obtained using the same amount of initiator in THF but is

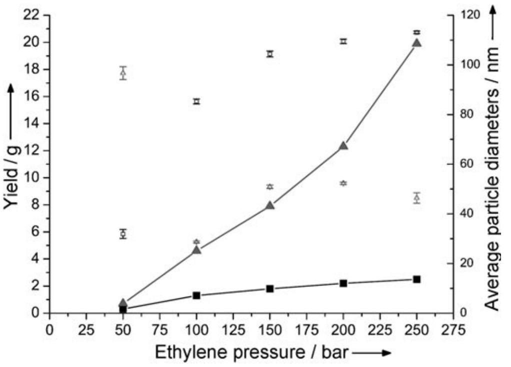

Figure 1. Free-radical polymerization of ethylene in aqueous dispersed medium: ■ yield and □ average particle diameter versus ethylene pressure (80 mg AIBA, 50 mL water, 4 h at 70 °C under ethylene pressure); ▲ yield and △ average particle diameter versus ethylene pressure (80 mg AIBA, 50 mL water with 1 g L^{-1} CTAB, 4 h at 70 °C under ethylene pressure). Average particle diameter determined by DLS.

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higher than in toluene.[12] The stabilization of PE particles is assumed to result from the cationic fragments of the initiator attached at the chain end, which induce electrostatic repulsion. Average particle diameters (D_p) measured by DLS (dynamic light scattering) increase with the ethylene pressure (and consequently with the yield) from 30 to 110 nm. Polydispersity indexes of the particle size distribution remain very low (PI ≈ 0.05), thus indicating the monodisperse character of particle size distribution. Furthermore, the yield/D_p^3 ratio, standing for the number of particles, remains constant whatever the ethylene pressure.

When polymerizations were performed in the presence of a standard cationic surfactant (CTAB) at $1\,\mathrm{g\,L^{-1}}$ (above the critical micelle concentration of $0.2\,\mathrm{g\,L^{-1}}$ at 25 °C), much higher activities were found (Figure 1). This emulsion system is even more efficient than the polymerization in THF.[12] In these non-optimized conditions, up to 40 % solid content is obtained (after degassing the 250 bar ethylene). Average particle diameters seem to reach a plateau at 50 nm with increasing ethylene pressure. This result indicates that the number of particles increases with the yield. Surprisingly, polydispersity indexes measured by DLS remain higher (PI ≈ 0.5) than for the surfactant-free process.

The produced PE exhibits a low melting point (T_m ≈ 100 °C) and low crystallinity (30–40 %). Highest values were obtained in the case of the surfactant-free polymerization process (see the Supporting Information, Table S1). As expected, high molecular weights PE ($M_n = 10^4$–$10^5\,\mathrm{g\,mol^{-1}}$) were produced. The number of PE chains synthesized is greater with CTAB, thus indicating a possible transfer to surfactant (see the Supporting Information, Figure S1). The PE obtained is moderately branched under both conditions (Figure S1: 30 branches per 1000 carbons without surfactant and 37 branches per 1000 carbons with CTAB) as determined by ^{13}C NMR spectroscopy,[18] which is in agreement with the crystallinities and melting temperatures measured. This higher branching level in water than in an organic solvent (THF: 9 branches per 1000 carbons or toluene: 7 branches per 1000 carbons)[12] can be explained by the compartmentalization of the growing PE chains, which increases transfer reactions to the polymer. The proportion of short chain branches is lower in emulsion (25 vs. 35 % in organic solvent) owing to favored intermolecular over intramolecular transfer reactions in a confined environment.

To link solvent and emulsion processes, the influence of the addition of organic solvents to water (water-miscible THF or immiscible toluene) was investigated. PE molecular weights dropped in the presence of solvents (see the Supporting Information, Table S2). The M_n value dropped from $50\,500\,\mathrm{g\,mol^{-1}}$ in water to 8300 and $2350\,\mathrm{g\,mol^{-1}}$ for toluene/H_2O (1:4) and THF/H_2O mixtures, respectively, in the presence of CTAB. This decrease can be attributed to an increased frequency of transfer reactions to solvent (contrary to water, THF and toluene exhibit high transfer abilities),[12] which has been confirmed by NMR spectroscopy (see the Supporting Information, Figure S2). With THF, the transfer reaction should take place in the continuous aqueous phase or at the particle surface and not in the particles, because THF is not an efficient swelling agent for amorphous PE (the same D_p is observed before and after removal of THF by partial reduced-pressure evaporation). For toluene, the D_p drops by about 10 nm after removal of the organic solvent (toluene is a swelling solvent for PE), so transfer could additionally take place inside the particles.

Surfactant-free and classical emulsion polymerization processes were compared by investigating the reaction profile at 70 °C under 100 bar ethylene (Figure 2). For the surfactant-free system, particle diameters increase with yield and the yield/D_p^3 ratio remains constant, thus no renucleation or aggregation takes place during the polymerization.

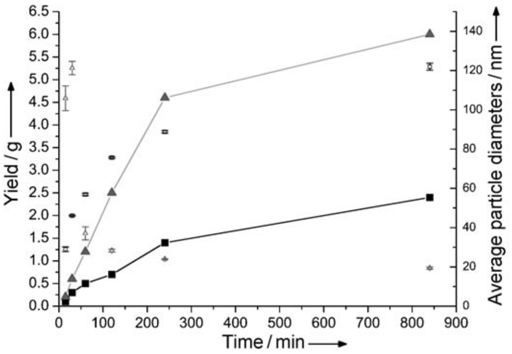

Figure 2. Reaction profile for free-radical polymerization of ethylene in aqueous dispersed medium: ■ yield and □ average particle diameter versus time (80 mg AIBA, 50 mL water at 70 °C under 100 bar); ▲ yield and △ average particle diameter versus time (80 mg AIBA, 50 mL water with $1\,\mathrm{g\,L^{-1}}$ CTAB at 70 °C under 100 bar). Average particle diameter determined by DLS.

In the presence of CTAB the behavior is quite different. Initially, particles with large diameters are formed, which seem to disappear with time to generate only small particles (D_p ≈ 30 nm) after 2 h. The mechanism for the extinction of large particles to generate very small particles still remains unknown, but preliminary experimental results suggest a crucial role of the surfactant itself. For example, if $1\,\mathrm{g\,L^{-1}}$ CTAB is added to surfactant-free PE latex, after stirring at 70 °C small particles are recovered (see the Supporting Information, Figure S3).

The PE latexes were also characterized using TEM analysis (Figure 3). In the surfactant-free process, quasi-spherical particles were observed. The rigid lamellas of semicrystalline PE prevent the formation of spheres (as already observed for latex prepared by catalytic emulsion polymerization).[19] Nevertheless, particles show relatively homogeneous diameters, in agreement with DLS measurements (low PI).

In the presence of CTAB, TEM pictures show a low contrast for the surface of particles, which could be an indication of flat particles. This morphology has been confirmed by tilting the sample: disks were observed at 0° and ellipses at 60°. Note that no significant changes were observed when the PE latex obtained from surfactant-free polymerization was tilted. From the hypothesis of cylinder-like particles, the dimensions of these objects were estimated

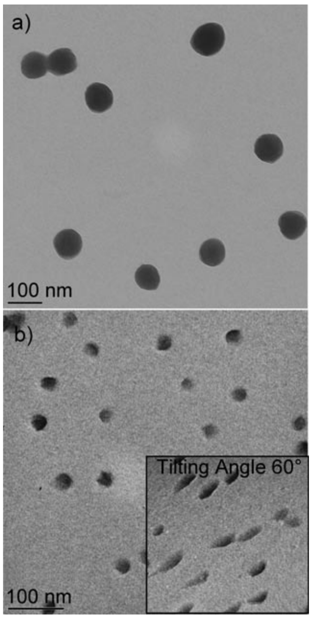

Figure 3. TEM pictures of PE latex: a) Standard particles without CTAB, 100 bar, 4 h at 70 °C. b) Standard particles with 1 g L^{-1} CTAB (inset: tilting angle of 60°), 100 bar, 4 h at 70 °C.

(average disks diameters about 35 nm and thickness about 3–4 nm). From these findings we can better explain the high values of PI (ca. 0.5) obtained by DLS (the autocorrelation function of DLS is calculated for a size distribution of spherical particles), which were not in agreement with the apparent homogeneity in the diameters of particle sizes observed by TEM.[20]

In summary, compartmentalization in water from emulsion processes (with or without surfactant) is a very promising way to produce high-molecular-weight polyethylenes in the low to very low density range by FRP under mild conditions from a water-soluble cationic initiator. PE yields are higher than for the solvent processes previously developed. From a colloidal point of view, FRP in emulsion exhibits unexpected original behavior. In the presence of surfactant, very small cylindrical PE particles are generated, while larger quasi-spherical particles were formed in the surfactant-free process. The coating properties of these attractive PE nanoparticles are currently being investigated.

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[1] R. Mülhaupt, *Macromol. Chem. Phys.* **2003**, *204*, 289–327.
[2] D. L. Beach, Y. V. Kissin in *Encyclopedia of Polymer Science and Engineering*, *Vol. 6*, 2nd ed. (Eds.: H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges), Wiley Interscience, New York, **1985**, pp. 454–489.
[3] K. W. Doak in *Encyclopedia of Polymer Science and Engineering*, *Vol. 6*, 2nd ed. (Eds.: H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges), Wiley Interscience, New York, **1985**, pp. 386–428.
[4] S. L. Aggarwal, O. J. Sweeting, *Chem. Rev.* **1957**, *57*, 665–742.
[5] S. P. Ehrlich, G. A. Mortimer, *Adv. Polym. Sci.* **1970**, *7*, 386–448.
[6] M. Kemmere, T. de Vries, M. Vorstman, J. Keurentjes, *Chem. Eng. Sci.* **2001**, *56*, 4197–4204.
[7] A. Bastero, G. Francio, W. Leitner, S. Mecking, *Chem. Eur. J.* **2006**, *12*, 6110–6116.
[8] L. Kolb, V. Monteil, R. Thomann, S. Mecking, *Angew. Chem.* **2005**, *117*, 433–436; *Angew. Chem. Int. Ed.* **2005**, *44*, 429–432.
[9] A. Held, F. M. Bauers, S. Mecking, *Chem. Commun.* **2000**, 301–302.
[10] R. Soula, C. Novat, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* **2001**, *34*, 2022–2026.
[11] S. Mecking, *Colloid Polym. Sci.* **2007**, *285*, 605–619.
[12] E. Grau, J. P. Broyer, C. Boisson, R. Spitz, V. Monteil, *Macromolecules* **2009**, *42*, 7279–7281.
[13] H. Hopff, R. Kern, *Modern Plastics* **1946**, 153–220.
[14] A. F. Helin, H. K. Stryker, G. J. Mantell, *J. Appl. Polym. Sci.* **1965**, *9*, 1797–1805.
[15] A. F. Helin, H. K. Stryker, G. J. Mantell, *J. Appl. Polym. Sci.* **1965**, *9*, 1807–1822.
[16] T. Suwa, H. Nakajima, M. Takehisa, S. Machi, *Polym. Lett. Ed.* **1975**, *13*, 369–375.
[17] H. K. Stryker, G. J. Mantell, *J. Polym. Sci. Part C* **1969**, *27*, 35–48.
[18] G. B. Galland, R. F. de Souza, R. S. Mauler, F. F. Nunes, *Macromolecules* **1999**, *32*, 1620–1625.
[19] F. M. Bauers, R. Thomann, S. Mecking, *J. Am. Chem. Soc.* **2003**, *125*, 8838–8840.
[20] High PI can also be partially due to a wide distribution in cylinder thickness.