Submicron Polyethylene Particles from Catalytic Emulsion Polymerization

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Abstract: Particles of linear polyethylene ($M_n = (2-3) \times 10^3$ g mol^{-1}; $M_w/M_n = 2-4$) obtained by catalytic emulsion polymerization of ethylene possess a nonspherical, lentil-like shape with an average aspect ratio of ca. 10 and diameters from 30 to >300 nm, as determined by TEM and AFM. The particle structure results from a stacking of the lamellae along the one shorter axis of the lentils (i.e., their height, by contrast to the diameter). In addition to these multilamellae particles, remarkably, a considerable number of the particles consist of only a single lamella. The thickness of the lamellae (spacing) as determined by TEM is only 9−11 nm, depending on the polymerization temperature during the synthesis of the dispersions. Crystallization in the dispersions during emulsion polymerization differs dramatically from the usual heterogeneous nucleation of bulk polyethylene samples. Each submicron droplet crystallizes individually, independently from the other droplets, resulting in large supercoolings of around 55 °C.

Aqueous dispersions of submicron polymer particles, so-called polymer latexes, are produced on a large scale by emulsion polymerization. They find numerous applications, such as environmentally benign paints and coatings of all kinds.[1]

To date, polymer dispersions are produced by free-radical polymerization exclusively. This limits the range of accessible polymer microstructures, and correspondingly the attainable materials properties. For example, the synthesis of dispersions of saturated UV-stable polymers, which at the same time do not bear functional groups subject to slow hydrolysis in applications, is a challenge.[1b] The synthesis of dispersions from simple olefins directly obtained from cracking of hydrocarbon feedstocks, without the need for further energy and raw material consuming conversion to other monomers (such as acrylates or vinyl-acetate), is desirable. Catalytic polymerization enables the synthesis of a variety of polymers inaccessible by free-radical techniques. However, the catalysts employed are usually highly water sensitive.[2] Only recently, the synthesis of polymer dispersions by catalytic emulsion polymerization has drawn increased interest.[3−9]

To date, the structure of the dispersed polymer particles and its formation remains unknown. We now report on the morphology and properties of submicron particles of linear polyethylene prepared by catalytic emulsion polymerization.

Aqueous polyethylene dispersions were prepared by nickel-(II)-catalyzed emulsion polymerization (cf., Supporting Information).[6d] The dispersions are composed of linear polyethylene with M_n in the range from 2×10^3 to 3×10^3 g mol^{-1}; M_w/M_n = 2−5. Polymer crystallinities determined by DSC are in the range from 72% to 80%.

An overview transmission electron microscopy (TEM) image of the particles is shown in Figure 1. Observation of single particles at different tilt angles in the electron microscope (Figure 2) reveals that the particles are not spherical but have a shorter extension along the *z*-direction; that is, they can be described as lentil-like. This finding is also supported by AFM investigations (vide infra). Such a structure with approximately equal extensions in two dimensions (*x* and *y* direction, i.e., diameter) and a shorter extension along the third axis (*z*-direction, i.e., height; Scheme 1) is due to the propensity of polyethylene to crystallize in lamellae, an individual lamella growing only in

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(2) (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169−204. (b) Mecking, S. *Coord. Chem. Rev.* **2000**, *203*, 325−51. (c) Mecking, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 534−40. (d) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29. (e) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283−316.
(3) Review on catalytic polymerization in aqueous systems: (a) Mecking, S.; Held, A.; Bauers, F. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 544−61. (b) Mecking, S.; Claverie, J. In *Late Transition Metal Polymerization Catalysis*; Rieger, B., Baugh, L. S., Kacker, S., Striegler, S., Eds.; Wiley-VCH: Weinheim, 2003; pp 231−278.
(4) Early work on butadiene dispersions: (a) Henderson, J. N.; Donbar, K. W.; Barbour, J. J.; Bell, A. J. (Goodyear) U.S. Patent 4429085, 1984. (b) Ono, H.; Kato, T. *J. Polym. Sci., Part A* **2000**, *38*, 1083−1089.
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(8) Held, A.; Kolb, L.; Zuideveld, M. A.; Thomann, R.; Mecking, S.; Schmid, M.; Pietruschka, R.; Lindner, E.; Sunjuk, M.; Khanfar, M. *Macromolecules* **2002**, *35*, 3342−7.
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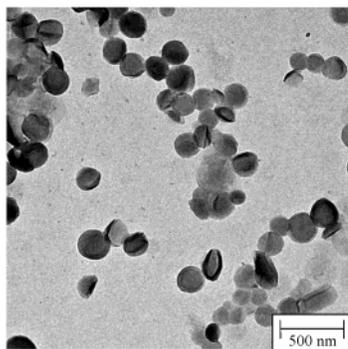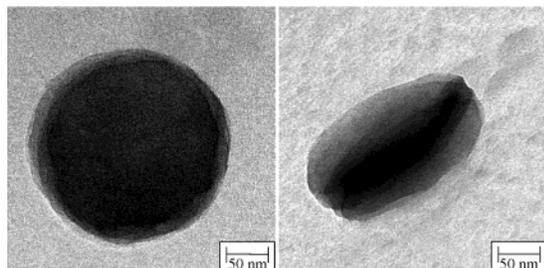
Figure 1. TEM image of polymer particles, overview.

Figure 2. TEM image of an individual polymer particle (left), and of the same particle tilted by 60° (right).
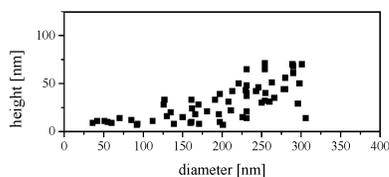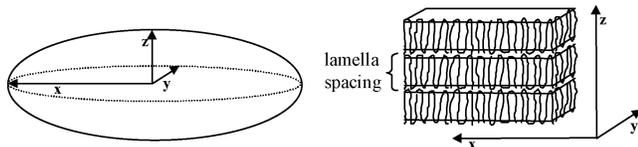

Figure 3. Particle dimensions determined from AFM section analyses.

Scheme 1. Schematic Representation of the Orientation of Lamellae in the Particles[19]

two directions.[10] In the particle, the lamellae separated by amorphous regions are stacked along the *z*-direction. Accordingly, a discontinuous, stepwise loss of the thickness is observed at the edge of the particles (Figure 2, left image), which are composed of lamellae of different diameter or of imperfectly stacked lamellae.

It should be noted that independently of our work Claverie et al. have envisioned that the latex particles obtained by catalytic emulsion polymerization of ethylene will have a unique morphology due to the specifics of polyethylene crystallization.[11]

AFM phase mode images of individual particles again show stacked lamellae (Supporting Information). The dimensions of the particles were quantified by section analyses of a larger number of particles (Figure 3). A broad size distribution with respect to both particle height and diameter is observed. For a
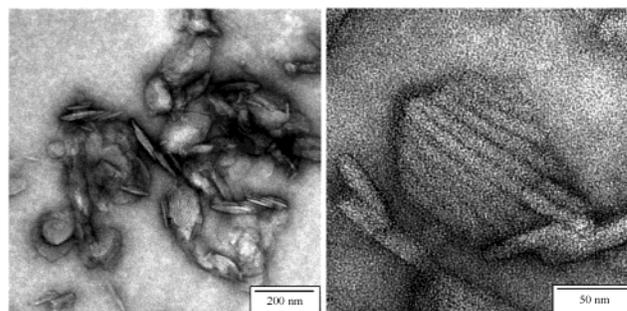

Figure 4. TEM micrographs of microtome cuts of latex particles.

typical sample, an average diameter of 200 nm and a height of 30 nm were found. This finding of a height much lower than the diameter of the particles is in accordance with the non-spherical, lentil-like structure observed by TEM (vide supra).

To avoid any conceivable misassignments, TEM and AFM images of the same position of the sample were taken (Supporting Information). The results confirm that objects of only a relatively low contrast in TEM are identical to the very thin particles (consisting of one or only few lamellae) found by AFM.

Particle sizes of dispersions are measured routinely by dynamic light scattering (DLS). It is of interest to compare results of this rapid routine method with the above TEM and AFM studies; also, DLS can provide evidence of any conceivable aggregation in dispersion.[12] For the particular sample shown in Figure 3, an average particle size of 118 nm was determined by DLS, assuming a spherical particle structure. The diffusion coefficient of an oblate ellipsoid of dimensions $2a = 200$ nm and $2b = 30$ nm corresponds to a sphere with a diameter $2R_h = 74$ nm.[13] In view of the broad distribution of particle size as well as aspect ratios, the DLS and AFM data are in reasonable agreement with one another. The data do not provide evidence for formation of conceivable aggregates in dispersion.

To further investigate the internal particle structure, the polymer particles were embedded in a solid matrix and cut into thin sections with a microtome. In addition to particles composed of stacked lamellae, TEM (Figure 4) also reveals isolated single lamellae. In agreement herewith, in the aforementioned AFM section analysis diagram of the polymer particles (Figure 3), a considerable portion of particles with a height of only ca. 8 nm which corresponds to only one lamella is observed (length up to 200 nm). Apparently, during the catalytic polymerization in a considerable portion of submicron droplets colloidally stable particles consists of only a single lamella. This is remarkable, as usually single isolated lamella are only obtained by careful crystallization in model systems.[14]

The lamella spacing (from TEM) decreases only slightly with decreasing polymerization temperature during latex preparation from 11 nm (70 °C) to 9 nm (30 °C).[15,16] The spacing of the 70 °C sample compares with the lowest fold length reported to

(10) Strobl, G. R. *The Physics of Polymers*, 2nd ed.; Springer: Berlin, 1997; pp 143−190.

(11) Claverie et al. suggested[7c] that the particle shape should be related to the known ability (Organ, S. J.; Keller, A. *J. Mater. Sci.* **1985**, *20*, 1571−1585) of polyethylene single crystals to form curved faces. This differs somewhat from our findings.

(12) For much larger disk-shaped particles also more uniform with respect to diameter and aspect ratio, a stacking into rodlike columnar aggregates in dispersion has been observed by optical microscopy: Mason, T. G. *Phys. Rev. E* **2002**, *66*, 060402.

(13) Tanford, C. *Physical Chemistry of Macromolecules*; Wiley: New York, 1961; p 327.

(14) Blundell, D. J.; Keller, A. *J. Macromol. Sci., Phys.* **1968**, *B2*, 301−36.

(15) Lamella thickening is negligible at these polymerization temperatures, such that the lamellae are indeed observed as formed during polymerization. Chivers, R. A.; Barham, P. J.; Martinez-Salazar, J.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1717−1732.
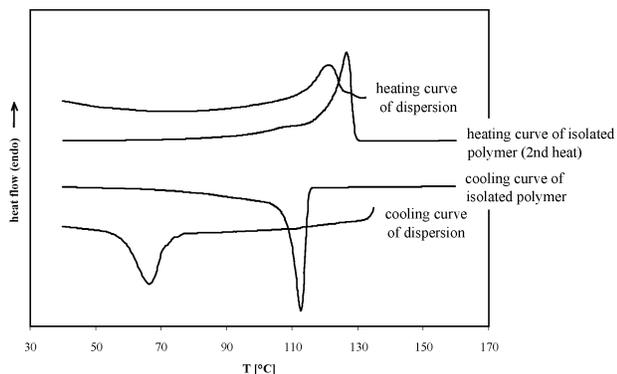
Figure 5. DSC traces of a polymer dispersion and of isolated bulk polymer.

date for melt or solution crystallized polyethylene at high super-coolings.[17−19]

Differential scanning calorimetry (DSC) measurements were carried out on the dispersions (Figure 5). As expected, by comparison to the isolated bulk polymers, there is no large difference with respect to the melting point T_m. A somewhat lower $T_m^{emul} = 120$ °C of the dispersed polymers by comparison to $T_m^{bulk} = 127$ °C can be related to impurities of toluene and hexadecane in the dispersion from latex synthesis.[20]

The crystallization temperature of the dispersed polymers is lowered dramatically, however. By comparison to the isolated bulk polymer samples ($T_c^{bulk} = 113$ °C), the crystallization temperature is lowered by about $\Delta T = 45$ °C to $T_c^{emul} = 66-70$ °C.[21] In several consecutive heating/cooling cycles, the observed T_c^{emul} values are not significantly altered. A sample

was cooled to 90 °C and held at 90 °C for 12 h. Upon further cooling again, crystallization occurred at 70 °C, demonstrating the stability of the polymer latexes under the conditions of DSC measurements. An increase of the cooling rate from the usual 10 K min^{-1} to 20 K min^{-1} or a decrease to 5 K min^{-1} causes only a slight decrease or increase, respectively, of the observed T_c^{emul} of about 2 °C.

In bulk polyethylene samples, heterogeneous nucleation occurs exclusively, and a few nuclei are sufficient to induce crystallization of a relatively large sample. However, in the polymer dispersion, the submicron droplets crystallize independently from one another. The large supercoolings observed match with the highest supercoolings reported to date for model systems with ≥ 1 μm polyethylene compartments.[18,22,23] The results indicate that, at polymerization temperatures $\geq$ca. 80 °C or a decrease of the crystallization temperature by introduction of branches, a colloidally stable supercooled dispersed polymer melt may be obtained initially in catalytic emulsion polymerization of ethylene.

In summary, submicron latex particles prepared by catalytic polymerization of ethylene in emulsion possess a unique structure, as a result of the crystallization in a confined space. The dispersions contain a large portion of single lamella particles, which do not aggregate. In the dispersions, each submicron droplet crystallizes individually and independently from the other droplets.

Supporting Information Available: General methods and materials; various AFM and TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(16) It is an interesting question whether polymerization occurs more rapid than crystallization (a), such that crystallization resembles that of preformed polymers from the melt as in most model studies on crystallization, or whether crystallization occurs more rapid than polymerization (b), such that the polymer chain is directly incorporated into a growing lamella as it is formed at the catalytically active center. While this question currently remains open, it can be noted that the low temperature dependence of lamella thickness found by no means necessarily implies the latter mechanism (b). Rather, the previous studies,[17,18] which were carried out at temperatures as low as 80 °C, show that the usual stronger temperature dependence on lamella thickness levels off in the lower temperature regime.
(17) Barham, P. J.; Chivers, R. A.; Keller, A.; Martinez-Salazar, J.; Organ, S. J. *J. Mater. Sci.* **1985**, *20*, 1625−30.
(18) Barham, P. J.; Jarvis, D. A.; Keller, A. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1733−1748.
(19) The onset of chain folding occurs at $M = 2 \times 10^3$ g mol^{-1}. Ungar, G.; Stejny, J.; Keller, A.; Bidd, I.; Whiting, M. C. *Science* **1985**, *229*, 386−389. Thus, for the polymer dispersions investigated ($M_w \geq 6 \times 10^3$ g mol^{-1}), the large majority of chains will be folded as indicated in Scheme 1.
(20) The Flory equation predicts a maximum decrease of 12 °C. Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, 1953; pp 568−71. Calculated with $T_m° = 400$ K, $\Delta H_{mu} = 3.3$ kJ unit^{-1}, $\chi_1 = 0.39$, $v_u = 17.3$ cm^3 mol^{-1}, $v_1 = 115$ cm^3 mol^{-1}, $\nu_1 = 0.22$.
(21) A significant effect of residual toluene and hexadecane on the T_c can be excluded on the basis of the considerations concerning T_m.[20] Also, in some DSC measurements on latexes with insufficient colloidal stability during DSC, crystallization of a part of the sample at $T_c = 109$ °C was observed, which differs only slightly from $T_c^{bulk} = 113$ °C.

(22) (a) Cormia, R. L.; Price, F. P.; Turnbull, D. *J. Chem. Phys.* **1962**, *37*, 1333−40. Also cf.: (c) Hoffman, J. D. *Polymer* **1983**, *24*, 3−26. (d) Clausse, D. *J. Therm. Anal.* **1998**, *51*, 191−201. (e) Arnal, M. L.; Müller, A. J. *Macromol. Chem. Phys.* **1999**, *200*, 2559−2576. (f) Montenegro, R.; Antonietti, M.; Mastai, Y.; Landfester, K. *J. Phys. Chem. B* **2003**, *107*, 5088−5094.
(23) Supercoolings $\Delta T = T_m - T_c^{compartimented}$ up to 60 °C have been reported for high-molecular-weight polyethylene ($T_c^{comp.} = 75$ °C).[18] Supercooling is known to decrease with molecular weight. For $M_w = 2.1 \times 10^3$ g mol^{-1} (M_w/M_n 1.15), a supercooling of 50 °C was reported (Kraack, H.; Sirota, E. B.; Deutsch, M. *Polymer* **2001**, *42*, 8225−8233). Thus, the supercoolings observed for our dispersions correspond reasonably with the above studies on model systems.