

Submicron Polyethylene Particles from Catalytic Emulsion Polymerization

F. M. Bauers, R. Thomann, S. Mecking*

Supporting Information

General methods and materials

DSC was performed on a Perkin Elmer DSC 7 instrument or on a Pyris 1 DSC at a heating and cooling rate of 10 K min^{-1} . Samples were heated from room temperature to $140 \text{ }^\circ\text{C}$, and kept at this temperature for 1 min before cooling to room temperature. Optionally the cycle was repeated several times. DSC traces of polymer dispersions were obtained on 20 to 30 mg of dispersion with ca. 5 % by weight polymer content. Optionally, stability can also be improved by addition of SDS surfactant or of ethylene glycol as a viscosity enhancer. Standard crimped sample pans proved to be reliably tight and stable up to $140 \text{ }^\circ\text{C}$. T_m data reported are local maxima of the second heats.¹

TEM investigations were carried out on a LEO 912 Omega apparatus using an acceleration voltage of 120 kV. Samples were prepared by applying a drop of the latex to a carbon coated grid. Samples were not stained, except for the microtome cuts (stained with RuO_4). For microtome cutting, the latex particles were embedded in nanoplast[®] (a hydrophilic melamine resin). Microtome cuts of ca. 50 nm thickness were prepared with a Reichert & Jung Ultracut E microtome equipped with a 45° diamond knife supplied by Diatome.

AFM experiments were performed with a Nanoscope III scanning probe microscope. The height and phase images were obtained simultaneously while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers which was typically around 180 kHz. Typical scan speeds during recording were 0.3-1 line/s using scan heads with a maximum range of $16 \times 16 \text{ } \mu\text{m}$. The phase images represent the variations of relative phase shifts (i. e. the phase angle of the interacting cantilever relative to the phase angle of the freely oscillating cantilever at the resonance frequency) and are thus able to distinguish materials by their material properties (e.g. amorphous and crystalline polymers).

Polyethylene latexes were prepared according to [2]. Ethylene was polymerized in aqueous emulsion with SDS as a surfactant (0.2 % to 1 % by weight) at 30 to $70 \text{ }^\circ\text{C}$ (usually $50 \text{ }^\circ\text{C}$) employing an *in situ* catalyst formed from 2,3,5,6-tetrachloroquinone, triphenylphosphine and *bis*(1,5-cyclooctadiene)nickel. The hydrophobic catalyst was added as a solution in toluene/hexadecane droplets (2 mL) which were miniemulsified³ in the aqueous phase (100 mL). Latexes of 5 to 20 wt-% polymer content were obtained.

- (1) *UserCom 2000*, 1, 1-7 (Mettler Toledo, Schwerzenbach).
- (2) Bauers, F. M.; Chowdhry, M.; Mecking, S. manuscript in preparation.
- (3) Bauers, F. M.; Mecking, S. *Angew. Chem.* **2001**, 113, 3112-5; *Angew. Chem Int. Ed.* **2001**, 40, 3020-2.

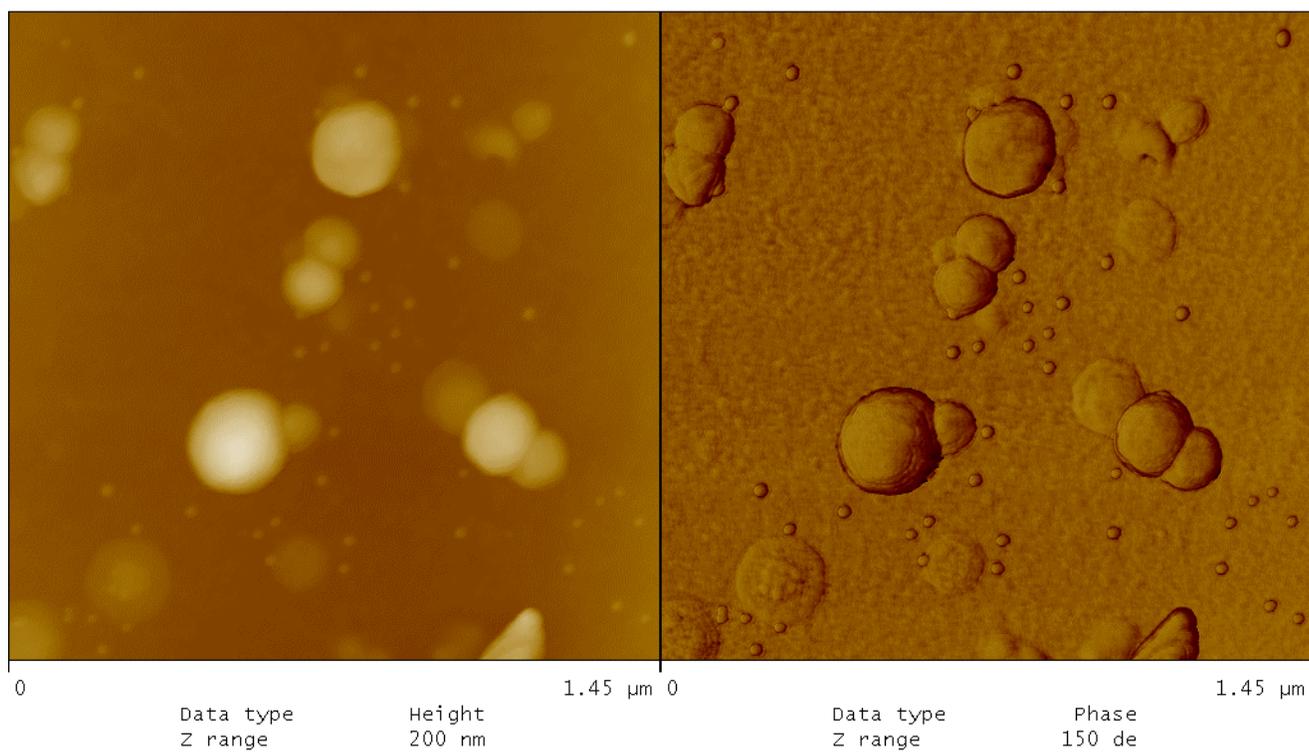


Figure S1. AFM images of particles (left: height mode, right: phase mode). Note the apparently concentric, discontinuous structure particularly well visible for the larger particle slightly offset to the lower left of the middle of the image.

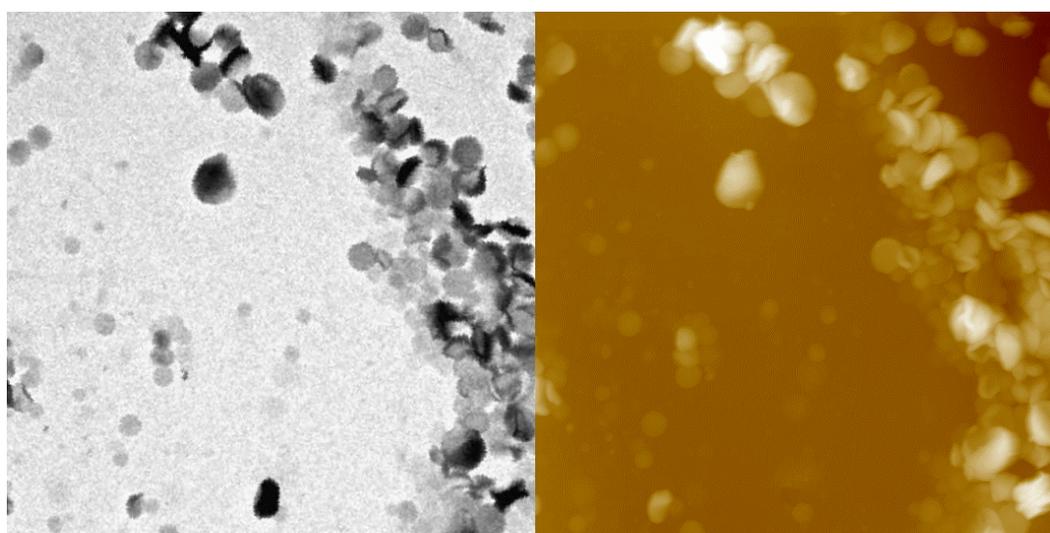


Figure S2. TEM (left) and AFM (right; height mode) micrograph of polymer particles in the same area ($4 \times 4 \mu\text{m}$ cut-out).

Table S1. Dependence of average lamella spacing (from TEM of microtome cuts on multi-lamellae particles) on polymerization temperature during latex synthesis.

polymerization temp. / °C	30	50	70
lamella spacing / nm	9	10	11