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Single Lamella Crystals of Polyethylene Accessible by Catalytic Emulsion-polymerization

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INTRODUCTION

Since many decades, polyethylene (PE) is one of the commodity polymers which has become ubiquitous because of its low price and good mechanical properties.[1] Hence, the number of applications of the material is huge and many millions of tons are produced worldwide annually. However, PE has hardly played any role in the emerging field of nanotechnology so far. This is due to the problem that PE is either produced by free radical polymerization under high pressure and temperature or with metal-organic catalysts working exclusively under strictly water-free conditions. Polymer nanoparticles and their composites with inorganic compounds, however, are very often produced in aqueous systems.[2]

Recently, it was demonstrated that ethylene can be polymerized in aqueous systems in a catalytic fashion by Ni(II) complexes.[3] By virtue of this novel synthesis, long chains of polyethylene can be generated in a well-controlled environment and at ambient temperature. Thus, it could be shown that aqueous PE-dispersions can be produced. Up to now, the particles synthesized in this way were semicrystalline and consisted of stacks of many crystalline lamellae.[3]

Here we demonstrate that well-defined polyethylene particles consisting of a single lamella can be generated in this way selectively. The analysis presented here employs a combination of cryogenic transmission electron microscopy (cryo-TEM[4]) and small-angle X-ray scattering (SAXS[5,6]). While cryo-TEM allows us to study the shape of the particles in a shock-frozen solution, the analysis by SAXS leads to the in situ determination of the internal structure of the particles.

EXPERIMENTAL

The system was prepared by catalytic polymerization as delineated previously.[7] The original dispersion as obtained only contains PE (3.6 wt.%) and just enough of the surfactant sodium dodecylsulfate (SDS) to stabilize the particles against coagulation. The molecular weight of the resulting polymer is $2 \cdot 10^5$g/Mol and the polydispersity is 2. This finding points to a well-defined process of polymerization.

Specimens for cryogenic transmission electron microscopy (cryo-TEM) were prepared by vitrification of a thin liquid film of the diluted dispersion supported by a copper grid in liquid ethane. Examinations were carried out at temperatures around 90 K (for details of the general procedure cf. reference[4]).

RESULTS AND DISCUSSION

Figure 1 displays a micrograph of the particles in dilute aqueous solution as obtained by cryo-TEM. Evidently, the dispersion consists of circular discs with a rather narrow size distribution. The different grey scales for different particles can be easily rationalized by different viewing angles: If the disc-like particles are nearly parallel to the electron beam, the length of the optical path through the particles is much longer than for perpendicular arrangement. From cryo-TEM images we determined a diameter of 25.4 ± 4.3 nm and a

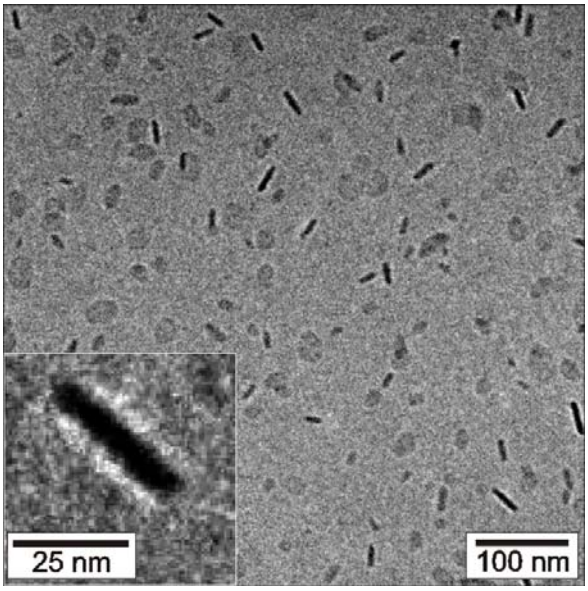

Figure 1. Cryo-TEM micrograph of the polyethylene particles in aqueous dispersion. The weight concentration of the particles was 0.4 wt.%. The grey background is the low-density amorphous ice in which the particles are dispersed. Disc-like particles parallel to the electron beam appear as rods. Perpendicular orientation results in a circular appearance. The inset shows one nearly parallel particle in magnification.

corresponding width of the discs of 6.3 ± 0.8 nm (image analysis of 67 particles with approximately perpendicular orientation to the electron beam). We interpret the observed discs as single lamellae of polyethylene with a thickness L_c of 6.3 nm. The crystalline lamellae visible in Fig. 1 are expected to be covered by an amorphous layer. However, it is not possible to detect this by cryo-TEM. This is due to the fact that the electron density of amorphous PE is virtually the same as the one of the low density amorphous ice. Hence, there is not a sufficient contrast between a possible amorphous layer and the surrounding medium.Fig. 1 also demonstrates that the particles are well-dispersed in the aqueous medium, virtually no aggregates are found.

In the following we describe the analysis of the particles by small-angle X-ray scattering. The intensity *I(q)* as the function of the magnitude *q* of the scattering vector ($q = (4\pi/\lambda)\sin(\theta/2)$; λ: wavelength of radiation; θ : scattering angle) is sensitive towards the difference between the electron density of the particle and the electron density ρ_m the surrounding medium. Contrast variation in SAXS is achieved by varying the electron density of the medium by adding an adequate contrast agent. SAXS data are then recorded for different values of the adjusted contrast. The scattering intensity *I(q)* of *N* particles per volume *V* can be rendered as follows:

$$I(q) = \frac{N}{V} I_0(q)\, S(q) = \phi(\Delta\rho)^2 V_p P(q) S(q) \qquad (1)$$

where V_p denotes the volume of the solute particle. Eq. (1) hence suggests to normalize the intensity to ϕ , the volume fraction of the dispersed particles. The quantity $\Delta\rho$ is the contrast of the dissolved particles given by the difference of averaged scattering length density of the particle $\overline{\rho}$ and of the scattering length density of the solvent ρ_m. *P(q)* is the form factor describing the shape and the structure of a single particle. The structure factor *S(q)* includes the scattering contributions due to interparticle interactions (cf. Ref.[8] for further details).

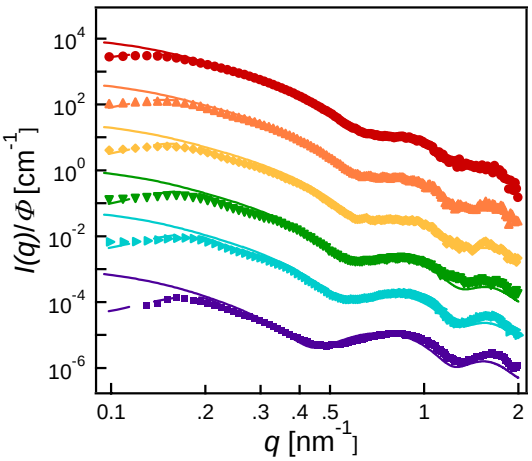

Figure 2. Cryo Measured scattering intensity I(q)/ϕ of polyethylene nanoparticles as a function of the magnitude of the scattering vector q (symbols). All intensities have been normalized to the volume fraction ϕ of the particles in the dispersion. The volume fraction of the added sucrose increases from bottom to top (0, 6.2, 10.3, 18.0, 25.4, 37.8 vol.%) while the volume fraction ϕ of the nanoparticles decreases from bottom to top (1.73, 1.56, 1.44, 1.23, 1.02, 0.68 vol.%). For reasons of clarity, the five lowermost intensities are shifted down by a factor of 10, 100, 1000, 10000, 10000, respectively. The solid lines represent the result of the modelling of the SAXS-data (see Fig. 3) assuming a dispersion of non-interacting polydisperse discs according to Eqs. (1) and (2) (S(q) = 1). The short dashed lines (q < 0.25 nm-1) represent the scattering intensity calculated for a dispersion of interacting discs as obtained from the PRISM integral equation theory.[8] The differences between the dotted and solid lines reflect the intermolecular interaction between the nanoparticles.[8]

The scattering intensity of a single particle is given by $I_0(q)$. The SAXS intensities of the polyethylene nanoparticles were measured at six different contrasts starting from a stock solution of $\phi = 0.017$ of the nanoparticles dispersed in pure water (see Fig. 2). The different contrasts are adjusted by adding different amounts of sucrose.[6] The volume fractions of added sucrose ϕ_S increased from $\phi_S = 0.000$ (lowest contrast) to $\phi_S = 0.378$ (highest contrast) while the corresponding volume fraction of the nanoparticles decreased from $\phi = 0.017$ to $\phi = 0.007$ Fig. 2 demonstrates that varying the contrast leads to marked differences in the scattering intensities. In particular, the maxima of the scattering intensities are shifted in a characteristic manner when changing the contrast $\Delta\rho$. All scattering intensities are slightly depressed at lowest q-values. This points immediately to the influence of mutual interaction as expressed through $S(q)$. Previous work has shown, however, that $S(q)$ approaches unity for higher scattering angles.[6,8]

The analysis of the SAXS-intensities for $q > 0.2\text{nm}^{-1}$ can be performed as follows:[6,8] The average scattering length density $\overline{\rho}$ of the solute was calculated to $\overline{\rho} = 330$ electrons per nm^3 from the experimental determined specific volume ($\nu_2 = 1.042$ cm^3/g) and the chemical composition of polyethylene. The quantity $\overline{\rho}$ obtained was used to calculate the contrast $\Delta\rho$ for each intensity shown in Fig. 2. The SAXS-intensities derived from the measurements carried out at different contrasts were modeled in terms of the scheme shown in Fig.

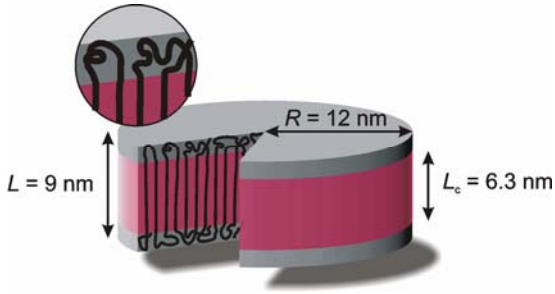

Figure 3. Scheme of the "nano-Hamburger"-model used for description of the structure of the polyethylene nanoparticles. The particles consist of a single lamella with a thickness L_c of 6.3 nm sandwiched between two amorphous sheets resulting in an overall thickness of 9 nm. The overall thickness L comprises both the crystalline lamella as well as the amorphous layers. The particles exhibit a circular shape with a radius R.

3. The scattering intensity of such a "nano-Hamburger" can be calculated from the formfactor of a cylinder.[5] The solid lines in Fig. 2 display the optimal fits thus obtained. The overall dimensions following from this fit are a weight-average radius R_w = 12 nm and a weight-average thickness L_w = 9 nm. The standard deviations of the radius was 6 nm and for the thickness 1 nm. The thickness of the crystalline layer is L_c = 6.3 nm. From these parameters the volume fraction of the crystalline part can be determined to ϕ_{cryst} = 0.70. From the particle volume, the polyethylene density and the chain molecular weight, we estimate each particle is made up from of ca. 14 chains.

CONCLUSION

In conclusion, a full structural analysis can be achieved by the present combination of cryo-TEM and SAXS. The above discussion demonstrates that these techniques supplement each other in a nearly ideal fashion to elucidate the structure of these single lamella nanoparticles depicted in figure 3. Compared with literature studies of bulk PE, the lamellar thickness L_C is very small which is due to the low temperature of synthesis (15°C). The crystallization has thus occurred more than 110°C below the melting point of polyethylene. This extreme supercooling of PE is not accessible by any other method used so far for the crystallization of polyethylene. Further studies of these single lamella particles are under way.

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