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Notes

Observation of the Early Stages of Crystallization in Polyethylene by Time-Dependent SAXS: Transition from Individual Crystals to Stacks of Lamellae

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Introduction

The basic feature in polymer crystallization is the formation of thin lamellar crystals. These lamellae are arranged in stacks, with layers of amorphous material being inserted between the crystalline lamellae. Crystallites form by a lateral attachment of stretched chain sequences. Although polymer crystal growth thus is basically a two-dimensional process, crystal thicknesses are not constant but may increase as a result of subsequent reorganization processes. In order to discriminate the primary two-dimensional growth mechanisms from the secondary reorganization processes, it is necessary to observe the initial stages of crystallization in time-dependent experiments. Barham and Keller[1] were able to observe early stages of the crystallization of polyethylene by SAXS, using synchrotron radiation and a self-nucleation method. A stepwise process of lamellar thickening was detected, taking place within the already formed stacks of lamellae. We have recently performed a time-dependent SAXS experiment on polyethylene, starting from the quiescent melt, and observed the growth kinetics during an even earlier stage of crystallization. We could follow in detail the transition from the occurrence of single lamellae at the very beginning of crystallization to the formation of stacks at later stages. Schultz and Hendricks[2] already reported scattering curves indicative for single lamellae, showing up at the beginning of crystallization, but the analysis of the curves was incomplete, due to a total neglect of all interlamellar interferences between different crystallites.

We employed in our analysis direct space methods based on the determination of the correlation function and the interface distribution function.[3,4] These methods can be used in particular to analyze states intermediate between single lamellae and the final stack.

Theory

Assuming that the scattering particles are thin, laterally extended lamellae, the scattering intensity $I(s)$ can be related to the one-dimensional electron density correlation function $K(z)$ defined as[4]

$$K(z) = \langle \delta\rho(z')\delta\rho(z' + z)\rangle_{z'} \tag{1}$$

Here $\delta\rho$ denotes the deviation of the density from the mean value

$$\delta\rho(z) = \rho(z) - \langle\rho\rangle \tag{2}$$

and z is the coordinate in the direction perpendicular to the surfaces of the lamellae. From the scattering intensity $I(s)$ the correlation function $K(z)$ can be calculated by

$$K(z) = 2\int_0^\infty 2\pi s^2 I(s)\cos(2\pi sz)\,\mathrm{d}s \qquad \text{with } s = \frac{2}{\lambda}\sin\frac{\theta}{2} \tag{3}$$

The second derivative of the correlation function, $K''(z)$, shows the distribution of distances between interfaces[3]

$$K''(z) = \frac{O_s}{2}\Delta\rho^2[h_\mathrm{a}(z) + h_\mathrm{c}(z) - 2h_\mathrm{ac}(z) + h_\mathrm{aca}(z) + h_\mathrm{acc}(z)...] \tag{4}$$

The expression between the brackets is set up of a series of distribution functions, the subscripts indicating which phases (amorphous and crystalline) are to be traversed while going from one interface to the other. Of practical importance are only the first three contributions to $K''(z)$. They give the distributions of the thickness of the amorphous and the crystalline layers (h_a and h_c) and of the sum of both resulting in the long period L (h_ac). If the system possesses sharp phase boundaries, the asymptotic behavior of the I(s) is described by Porod's law

$$\lim_{s\to\infty} I(s) = \frac{P}{s^4} \qquad \text{with} \qquad P = \frac{O_s\Delta\rho^2}{8\pi^3} \tag{5}$$

$K''(z)$ then follows from the scattering intensity $I(s)$ as

$$K''(z) = 16\pi^3\int_0^\infty \mathrm{d}s\,[\lim_{s\to\infty} I(s)s^4 - I(s)s^4]\cos(2\pi sz) \tag{6}$$

Before applying eq 6 to experimental data, the superposed background scattering caused by the density fluctuations within the individual phases has to be subtracted. This contribution can be separated by fitting the data in the region of high scattering vectors by a superposition of the Porod scattering and a constant contribution. In addition, the short-range order in the amorphous phase is taken into account as usual by a quadratic term. A smoothing of the data is required in order to reduce the effect of noise.

It is instructive to look at the functions $K(z)$ and $K''(z)$ obtained for a numerical example, shown in Figure 1. The effects of the contributions h_c, h_a, and h_ac to the total interface distribution function $\sim K''(z)$ are obvious. In the case of a dilute system of single lamellae, this reduces to the contribution h_c and it is evident how $K(z)$ then changes. There remains only the linear part of $K(z)$ beginning at the origin—the "self-correlation triangle". All interferences between different lamellae, which are portrayed in the maximum of $K(z)$ at higher values of z, disappear.

Samples

We chose a linear polyethylene with low molecular weight, $M_\mathrm{w} \approx 17\,000$, as our sample. As electron microscopy indicates,

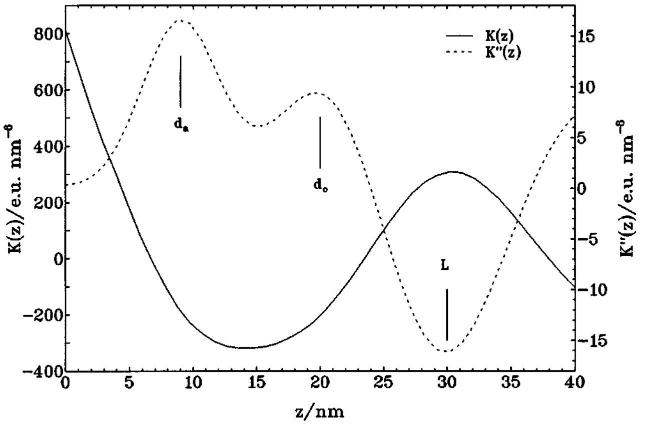

Figure 1. Numerical example of the functions $K(z)$ and $K''(z)$.

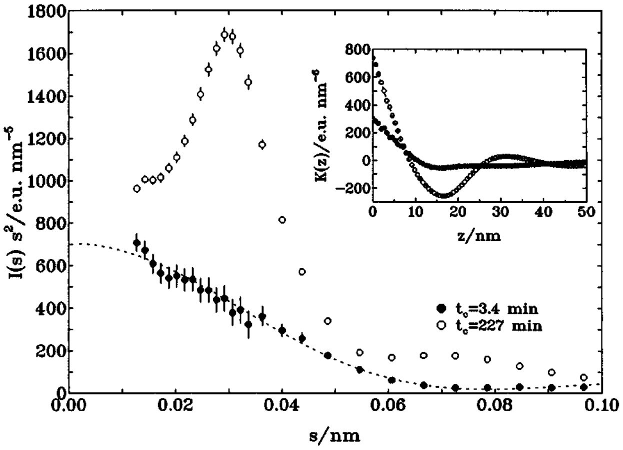

Figure 2. Desmeared scattering intensity $I(s)s^2$ measured at the beginning and during the final stage of the isothermal crystallization after subtraction of the background intensity. The broken line shows an adjusted calculated structure factor for a single lamella. The corresponding correlation functions $K(z)$ are shown in the inset.

polyethylenes with low molecular weights form more perfect lamellar structures than those with higher M_w's.[5] The material was synthesized with a metallocene catalyst.[6] The molecular weight was determined by viscosity measurements.

Experiments

SAXS experiments were carried out with a conventional X-ray tube and a Kratky compact camera equipped with a temperature-controlled sample holder. Intensities were measured with the aid of a position-sensitive metal wire detector. Values of sufficient accuracy were obtained within a few minutes' counting time. As the camera is equipped with a slit focus, data had to be deconvoluted. This was achieved by applying the desmearing algorithm by Strobl.[7]

Before crystallization, samples were heated up to 160 °C and subsequently cooled as fast as possible to the crystallization temperature. The data shown here were obtained from a sample crystallized at a temperature T_c = 121 °C. By observation of the scattering intensity, it was made sure that crystallization did not start before isothermal conditions were reached.

Results

To illustrate the qualitative change in the form of the scattering curve from the initial to a final stage during the process of crystallization, two measurements in plots of the desmeared intensity $I(s)s^2$ versus s are shown in Figure 2. The broken line depicts an adjusted calculated structure factor of a single lamella. The calculation provides a satisfactory representation of the first measurement. The second measurement, taken later, shows a strong peak, corresponding to a long period $L = 1/s_{max} \approx 33$ nm in the stack of lamellae. The correlation functions $K(z)$ calculated from these data are shown in the same figure. A change from the behavior of single lamellae, as indicated by the appearance of the self-correlation triangle" only, to the form expected for lamellar stacks is observed. Measured curves agreed asymptotically with Porod's law. Therefore, the calculation of the interface distribution functions was straightforward. The gradual formation of stacks during crystallization can be seen in Figure 3, which shows the functions $K''(z)$ obtained for a whole series of measurements. At the beginning, only the crystalline contribution is found, being indicative for isolated lamellae. During further development, the contributions associated with the amorphous layers and the long period emerge simultaneously and grow in amplitude, thus indicating that the space between the lamellae formed at first is filled up by newly grown crystallites. Throughout the development, an isothermal thickening can be observed, becoming apparent in the shift of the crystalline contribution in $K''(z)$ to larger values of z. Figure 4 demonstrates this change in a comparison of two measurements, one carried out at the beginning of crystallization and the other in a final stage. The growing number of crystallites during this process is reflected in the increase of the Porod constant P, as

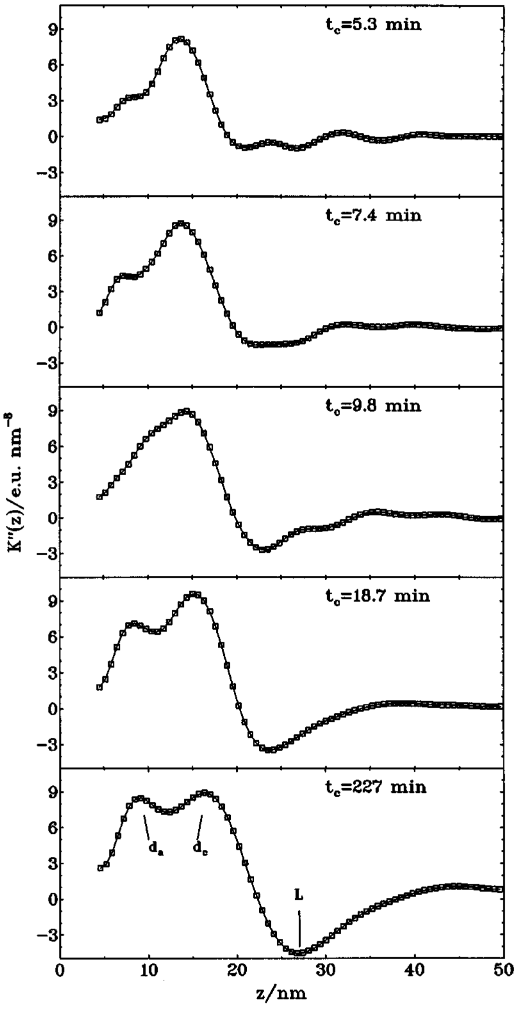

Figure 3. Gradual formation of stacks in the early stages of isothermal crystallization as reflected in the interface distribution function. Functions $K''(z)$ are calculated from a series of measurements taken during isothermal crystallization.

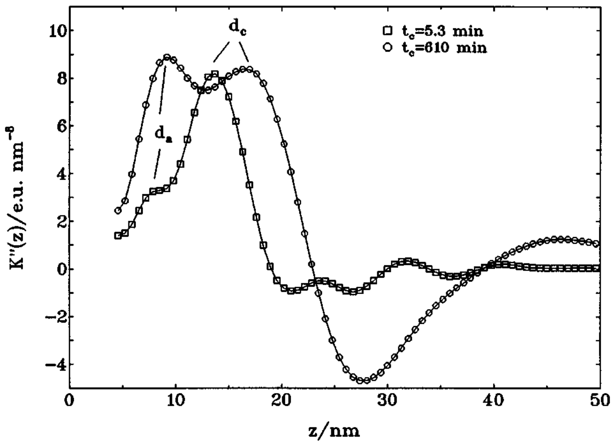

Figure 4. Function $K''(z)$ at the beginning and at a final stage of isothermal crystallization. The shift of the contribution due to the crystallite thickness indicates isothermal thickening.

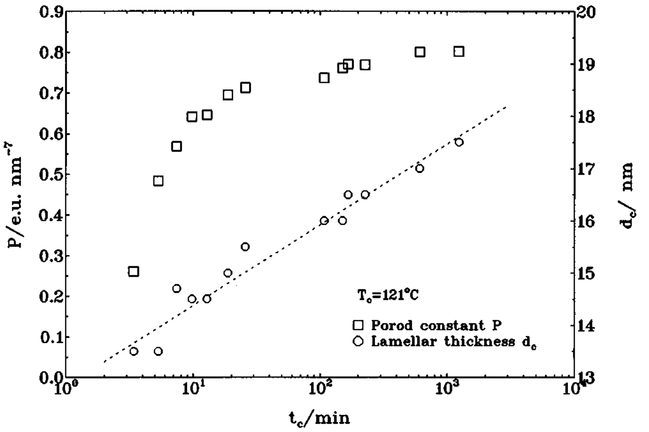

Figure 5. Crystal growth and lamellar thickening during isothermal crystallization. Porod constant P as determined from the scattering data and the lamellar thickness d_c as a function of crystallization time. The values of d_c are derived from the maxima in the functions $K''(z)$.

shown in Figure 5. The thickness of the crystallites as derived from the maxima of the corresponding contribution in $K''(z)$ is depicted in the same figure. We find a logarithmic time dependence $dd_c \sim d \ln t$ for the increase of d_c, and for $T_c \approx 121$ °C an initial value $d_c \approx 13$ nm. Experiments performed at different crystallization temperatures and on samples with higher molecular weight show analogous effects.

Conclusions

Crystallization of polyethylene in its early stages was studied by time-resolved SAXS. Data evaluation on the basis of directly calculated correlation functions enables a detailed analysis of the occurring processes. In particular, a determination of the lamellar thickness is possible, through all stages of the crystallization. The value obtained for the initial lamellar thickness agrees up to experimental errors with the values obtained by Barham et al.^{8}

Starting from the initial stage with single lamellae, a gradual formation of stacks of lamellae is observed. This is accompanied by a continuous growth of the crystallite thickness obeying a logarithmic time dependence. There were no indications for a stepwise thickening process, as observed by Barham and Keller for fractionated materials. As they report, it appears that the latter process is a peculiarity only found in fractionated materials.

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