Block Formation during Polymer Crystallization

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Introduction

The lamellae which are formed when a polymer crystallizes have a granular substructure. Evidence is provided by the widths of the Bragg reflections in wide-angle X-ray scattering patterns. For polymers they are much broader than in the case of low molar mass crystals and generally indicate lateral coherence lengths of the order of several to some tens of nanometers. This is the same order of magnitude as the lamellar thickness. There are cases in which the block structure also shows up directly in images, for example, in TEM images, when the staining agent can enter into the boundaries within the lamellae[1] or in favorable cases also in AFM tapping mode images, for both flat-on and edge-on oriented lamellae.[2,3] In a recent work of Goderis et al.[4] block sizes in AFM images and coherence lengths derived from reflections half-widths were compared, and the agreement was satisfactory. The blocky substructure is fundamental for the deformation properties of semicrystalline polymers.[5,6] A main yielding mechanism is block sliding, and this sets in cooperatively at the yield point. The strain-controlled, comparatively simple deformation properties of semicrystalline polymers are mainly based on the many degrees of freedoms offered by block sliding—internally stiff crystal layers would cause a quite different, much more complex deformation behavior.

The granular substructure thus represents a basic structural property of semicrystalline polymers, even if it remains unconsidered in many discussions. However, knowledge about it is limited. There exist, of course, many measurements of reflection line widths, carried out for different reasons, but we are not aware of studies that would have systematically analyzed the variation of the lateral block size with the crystallization temperature or, in chemically nonregular polymers, the effect of counits or stereodefects. In recent years we had carried out comprehensive SAXS investigations to determine the temperature dependence of crystal thicknesses. As it was generally found, crystal thicknesses vary inversely with the supercooling below a temperature T_c^∞, which is always located many degrees above the equilibrium melting point.[7,8] We now selected three of the investigated systems, polyethylene with octene copolymers, *s*-polypropylene with octene copolymers, and *i*-polystyrene, and determined in addition in WAXS studies the variations in the lateral coherence lengths. The results are briefly reported in this paper.

Experimental Section

Polyethylenes (PE) with 2, 7, and 14 wt % of octene counits (PEcO2, PEcO7, PEcO14) were supplied by Dow Chemicals Europe. The (weight-average) molar masses are all roughly 3 $\times$ 10^4 Da.

Three samples of *s*-polypropylene (sPP) were synthesized in the group of Prof. Mühlhaupt in the Institute of Macromolecular Chemistry of our university. One of them is a homopolymer with 3% meso diades; the two other samples include 15% and 20 wt % of octene counits (sPP, sP(P-*co*-O)-15, sP(P-*co*-O)20). Weight-averaged molar masses are in the range 6 $\times$ 10^4−10^5 Da. In addition, a commercial sample supplied by Fina Oil, Brussels, was investigated. It has 83% syndiotactic pentades and a molar mass of 6 $\times$ 10^4 Da.

The *i*-polystyrene (iPS) of the study was purchased from Scientific Polymer Products, Inc. The tacticity amounts to 90%, and the molar mass is 4 $\times$ 10^5 Da.

Wide-angle X-ray scattering patterns $I(\theta)$ (θ: Bragg angle) were registered either using the diffractometer Siemens D500 or with the aid of a SWAXS twin camera produced by Hecus-Braun Co., Graz, Austria. The latter allows a simultaneous recording of small-angle X-ray scattering curves.

Line widths were measured for each system for one selected convenient reflection, one with a high intensity and a good separability from other reflections and the halo. We chose the following ones:

PE: 110 ($\theta = 10.4°$)

sPP: 200 ($\theta = 6.05°$)

iPS: 200 ($\theta = 10.3°$)

To determine the coherence length D_{hkl} associated with the reflection at angle θ_{hkl}, a Gaussian function

$$I(\Delta\theta) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(\Delta\theta)^2}{2\sigma^2}\right) \tag{1}$$

was adjusted to the profile of the reflection after its separation from the background ($\Delta\theta = \theta - \theta_{hkl}$). D_{hkl} then follows from the Scherrer equation[9] as

$$D_{hkl} = \frac{\lambda}{2\cos\theta\sqrt{2\pi}\sigma} \tag{2}$$

$\sqrt{2\pi}\sigma$ is the integral width of the reflection.

Results

Samples were always crystallized isothermally at a series of temperature T_c at which crystallization was completed within a time between 10 min and several

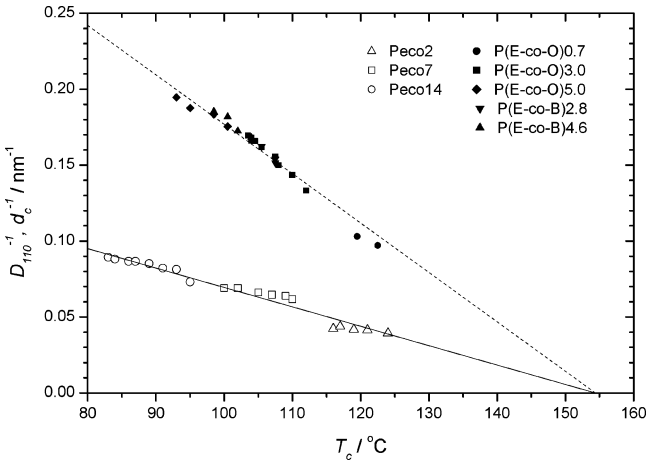

Figure 1. Different samples PEc(O/B)*x* crystallized at various temperatures T_c: crystallization line d_c^{-1} vs T_c determined by SAXS (from ref 10) and lateral coherence lengths D_{110} derived from the line width of the 110 reflection (open symbols).

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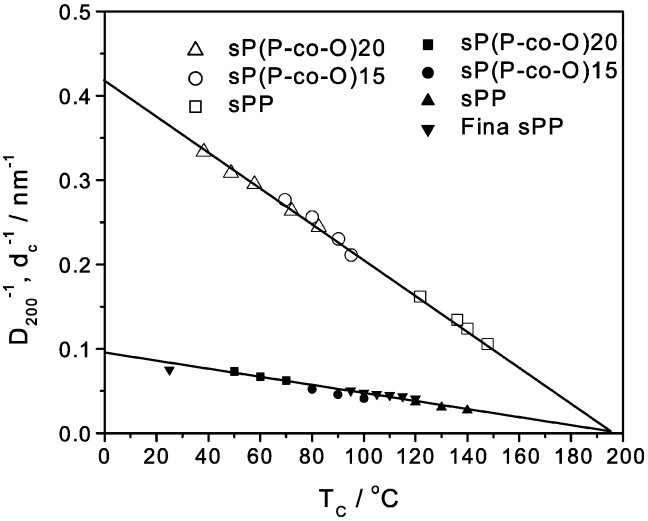

Figure 2. Different samples of sPP (sPP, sP(P-*co*-O)*x*, and the commercial Fina sPP) crystallized at various temperatures T_c: crystallization line d_c^{-1} vs T_c determined by SAXS (from ref 7) and lateral coherence lengths D_{200} derived from the line width of the 200 reflection (filled symbols).

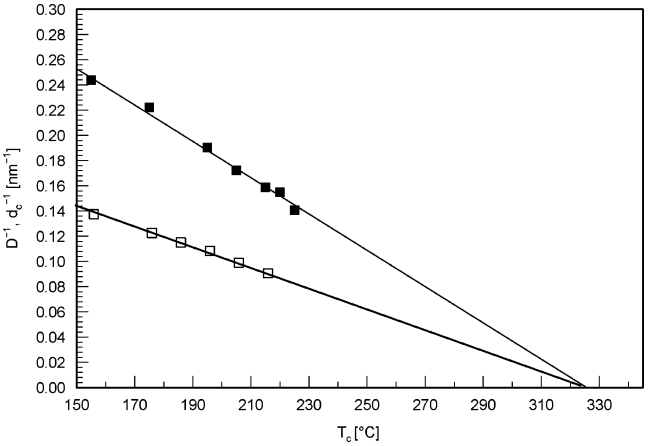

Figure 3. iPS crystallized at various temperatures T_c: crystallization line d_c^{-1} vs T_c determined by SAXS (from ref 8) and lateral coherence lengths D_{200} derived from the line width of the 200 reflection (open circles).

hours. The PEs were rapidly cooled from the melt (above 160 °C) to T_c, iPS was quickly heated from the amorphous glassy state, and the sPPs were both cooled from the melt and heated from the glass to T_c. Temperature equilibrium was established within several minutes.

Figures 1, 2, and 3 present the results obtained for the PEs, sPPs, and iPS, respectively. The coherence lengths are always plotted in the form D_{hkl}^{-1} vs T_c and for all three systems together with the respective "crystallization line" d_c^{-1} vs T_c.

The findings are very clear: D_{hkl} and d_c are strictly correlated for all three systems under study. We had previously found that d_c decreases inversely with the supercooling below a certain temperature T_c^∞, i.e.

$$d_c \propto \frac{1}{T_c^\infty - T_c} \tag{3}$$

and observe now that D_{hkl} obeys the same law:

$$D_{hkl} \propto \frac{1}{T_c^\infty - T_c} \tag{4}$$

For the copolymers d_c is independent of the counit content, and the same invariance is now found for D_{hkl}.

For us these results are not surprising. On the basis of a variety of observations from other workers and ourselves, we are convinced that polymer crystallization uses a multistage route via an intermediate mesomorphic phase.[7,11] We have introduced a corresponding model, at first on a qualitative basis and then also embedded in a thermodynamic scheme.[12] The scheme identifies T_c^∞ with the (virtual) transition temperature T_{mc}^∞ between the mesomorphic phase—for polyethylene identical with the "hexagonal" phase—and the crystalline state. The model assumes as one step in the development of growing polymer lamellae the formation of crystal blocks out of the mesomorphic phase. The findings reported in this paper suggest that such a block formation is indeed an elementary step and thus support our views.

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