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ORIGINAL CONTRIBUTION

T. Y. Cho
B. Heck
G. Strobl

Equations describing lamellar structure parameters and melting points of polyethylene-*co*-(butene/octene)s

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B. Heck · G. Strobl
Physikalisches Institut,
Albert-Ludwigs-Universität,
79104 Freiburg, Germany

T. Y. Cho (✉)
School of Chemistry,
Seoul National University,
Seoul, Korea
E-mail: tai-yon@psl.snu.ac.kr

Abstract Time- and temperature-dependent SAXS-experiments were used to determine the effect of octene and butene co-units on the lamellar structure and the melting properties of polyethylene. As expected, melting points decrease with increasing co-unit content, but crystal thicknesses are not affected and depend on the crystallization temperature only. Results can be cast into some simple equations which describe the dependence:

1. Of the melting point T_f on the crystal thickness d_c and the co-unit content x_B
2. Of the equilibrium melting point T_f^∞ on x_B
3. Of d_c on the crystallization temperature T_c
4. Of the long spacing L on T_c, x_B and the molar mass
5. Of T_f on T_c.

Keywords Equations · Lamellar structure parameters · Melting points · Octene · Butene · Polyethylene-*co*-(butene/octene)s

Introduction

The introduction of co-units into a crystallizable stereoregular polymer chain generally reduces the crystallinity. The question arises how this occurs as a consequence of changes in the lamellar thickness d_c and in the packing density of the lamellae as described by the long spacing L. Conventional wisdom relates d_c with the supercooling below the equilibrium melting point of the copolymer. Since the equilibrium melting point surely decreases when the fraction x_B of co-units increases one expected for a fixed crystallization temperature T_c for increasing x_B a growth in the crystal thickness and—considering the decreasing crystallinity—an even larger growth of the long spacing. Surprising for many, this view turned out as being incorrect. A comprehensive investigation carried out by small-angle X-ray scattering (SAXS) for a syndiotactic polypropylene (sPP) and related octene copolymers showed that the crystallite thickness at a fixed T_c is x_B-invariant [1]. The drop in the crystallinity with increasing x_B is therefore a result of a growth of L only. We also investigated polyethylene (PE)-derived copolymers, but for two samples only. The result was qualitatively similar to the sPP-system: at a fixed T_c we found—if any—only a minor difference in d_c [2].

Recently, we obtained a larger series of poly(ethylene-*co*-octene)s (P(E *co*O)) together with several poly(ethylene-*co*-butene)s (P(E *co*B)). All samples have similar molar masses, so that the co-unit content is the only varying property. We have now checked and further extended our previous limited studies on PE. The results are reported in the following. They lead us to the formulation of equations which describe the parameters of the lamellar structure and the related melting points in dependence on the crystallization temperature and the co-unit content.

Experimental

Samples The experiments were carried out for a series of P(E *co*O)s and P(E *co*B)s which were kindly made available to us by Prof. Leo Mandelkern (Tallahassee, USA). Included in the studies was also a sample of linear polyethylene supplied by LG Chemicals, Daejeon, Korea. All samples are specified with their properties in Table 1.

The samples were crystallized isothermally at preset T_cs after a cooling from the melt at 150 °C. The kinetics of crystallization was analyzed by time-dependent SAXS experiments. After completion of the crystallization process samples were—in a second part of the experiment—heated up stepwise until complete melting. The structure variations during the heating were again followed by SAXS.

SAXS The SAXS experiments were carried out with the aid of a Kratky-camera attached to a conventional Cu-K_α X-ray source, employing a temperature controlled sample-holder. Using a position-sensitive metal wire detector, scattering curves were usually registered within a few minutes counting time. The slit-smeared data obtained were deconvoluted by application of an algorithm developed in our group [3]. Desmeared scattering curves were obtained in absolute values, as differential cross sections per unit volume, $\Sigma(q)$. With a knowledge of $\Sigma(q)$ the one-dimensional electron density auto correlation function $K(z)$ and its second derivative $K''(z)$, which gives the interface distance distribution function (IDF) [4, 5], can be directly calculated by applying the Fourier relations

$$K(z) = \frac{1}{r_e^2}\frac{1}{(2\pi)^3}\int_0^\infty \cos qz \cdot 4\pi q^2 \Sigma(q)\mathrm{d}q \qquad (1)$$

and

$$K''(z) = \frac{2}{r_e^2(2\pi)^2}\int_0^\infty \left[\lim_{q\to\infty} q^4\Sigma(q) - q^4\Sigma(q)\right]\cos qz\mathrm{d}q \qquad (2)$$

Here, q denotes the scattering vector $q = 4\pi sin\theta_B/\lambda$ (θ_B: Bragg scattering angle); r_e is the classical electron radius.

A useful parameter in kinetic measurements and also the analysis of the continuous melting on heating is the Porod coefficient P. It generally describes for two-phase systems the asymptotic behavior of the scattering curve as

$$\lim_{q\to\infty}\Sigma(q) = r_e^2\frac{P}{(q/2\pi)^4} \qquad (3)$$

The Porod coefficient is directly related to the interface area per unit volume, O_{ac}, by

$$P = \frac{1}{8\pi^3}O_{ac}\left(\rho_{e,c} - \rho_{e,a}\right)^2 \qquad (4)$$

whereby $\rho_{e,c}$ and $\rho_{e,a}$ denote the electron densities of the crystals and the fluid phase respectively. This relation is generally valid, for homogeneous as well as heterogeneous structures and therefore, for example, also if spherulites fill a sample only partially.

Results

Figure 1 presents as one example for P(E *co*B(2.8%)) the IDFs derived from the SAXS curves measured both during an isothermal crystallization ($T_c = 106$ °C) and a subsequent melting. The peak relates to the crystals, and its location gives their thickness, $d_c = 6.2$ nm. The adjacent minimum yields the long spacing; alternatively L can also be derived from the location of the maximum of the Lorentz-corrected scattering intensity distribution Iq^2. One observes during the crystallization a fixed value of d_c, i.e., there is no crystal thickening. The temperature dependence of the Porod coefficient during the heating shown in the insert demonstrates that melting begins immediately above T_c and then continuously accelerates in rate. We derive the melting point, denoted T_f, in the same way as in a DSC-experiment, i.e., we associate it with the temperature where the rate of melting is at the maximum. This corresponds here to the temperature with the maximum slope in the curve $P(T)$. Note that the crystal thickness is also constant during the heating. The lower stability of the early-melting crystallites is therefore *not* due to a reduced thickness but to other factors, like the inner degree of order and the surroundings.

Quite different results are obtained for the LPE sample, as is shown in Fig. 2. The IDF here exhibits two peaks. The one at the lower value of z reflects the amorphous layers with a thickness $d_a = 11$ nm, the other one, being located at the beginning of crystallization at $z = 21$ nm, relates to the crystal thickness. d_c is obviously

Table 1 Linear polyethylene, poly(ethylene-*co*-butene)s and poly(ethylene-*co*-octene)s used in the study

Sample	Linear PE	Ethylene-Butene		Ethylene-Octene			
Mw×10^3	60	100	101	105	71	85	92
Mw/Mn	2.9	2.0	2.0	2.0	2.1	2.2	2.3
Comonomer (mol%)	0.0	1.5	2.8	4.6	0.7	3.0	5.0

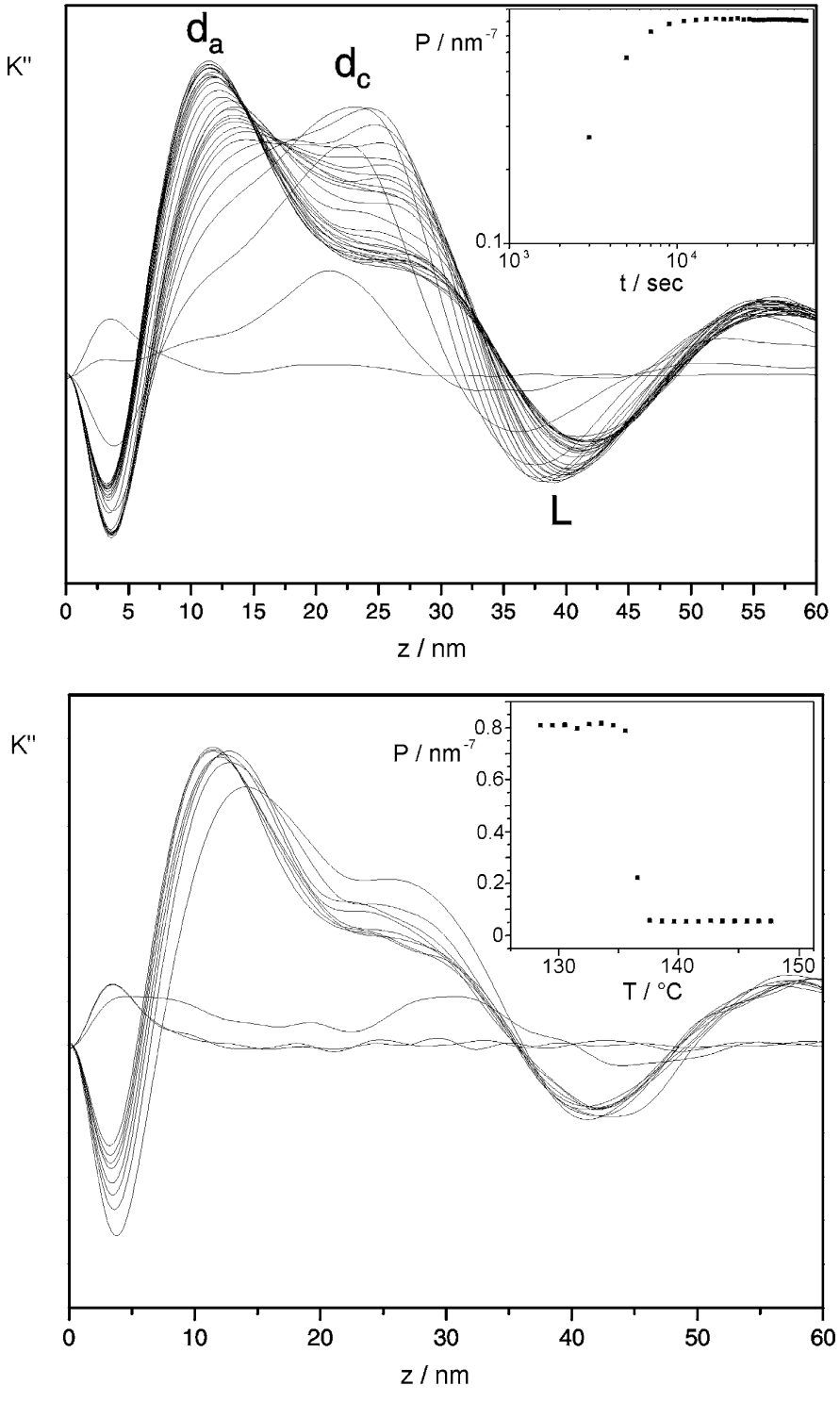

Fig. 1 P(E*co*B(2.8%)): IDFs and Porod-coefficients derived from SAXS-curves obtained at different times during a crystallization at $T_c = 106$ °C (*top*) and at different temperatures during a subsequent heating up to the melt state (*bottom*). *Inserts* show the respective time- and temperature-dependent changes of the Porod-coefficient

not constant during the isothermal crystallization but increases with time.

As a third example, Fig. 3 depicts the results obtained for a copolymer with a low co-unit content, P(E *co*O(0.7%)). We observe again some change in d_c during the isothermal crystallization, but it is smaller than for LPE.

The experiments provide for each chosen T_c the values of the crystal thickness d_c and the long spacing L. For the copolymers with $x_B > 2\%$ these values are

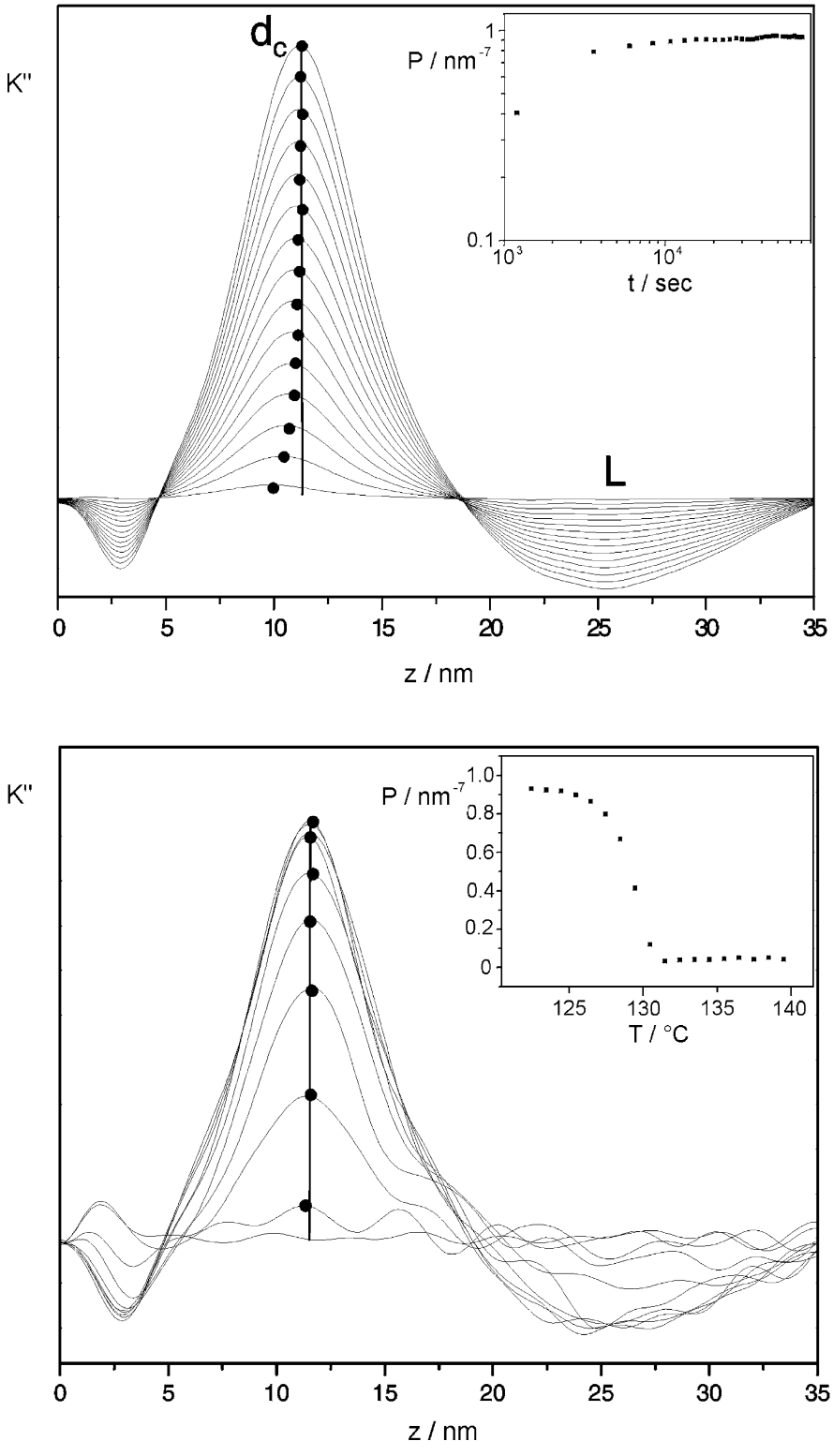

Fig. 2 LPE: IDFs derived from SAXS-curves obtained at different times during a crystallization at $T_c = 129$ °C (*top*) and at different temperatures during a subsequent heating up to the melt state (*bottom*). The assignments of the peaks to d_a, d_c, and L (thicknesses of amorphous layers and of crystallites, long spacing) are indicated

well-defined since thickening processes are absent. For the samples with lower co-unit content and LPE this is no longer the case. As a second result we can derive for all samples the melting points together with the crystal thicknesses at T_f. The results thus obtained for all samples are presented together in Fig. 4. As suggested by the Gibbs-Thomson equation, the inverse thickness d_c^{-1} rather than d_c and, correspond-

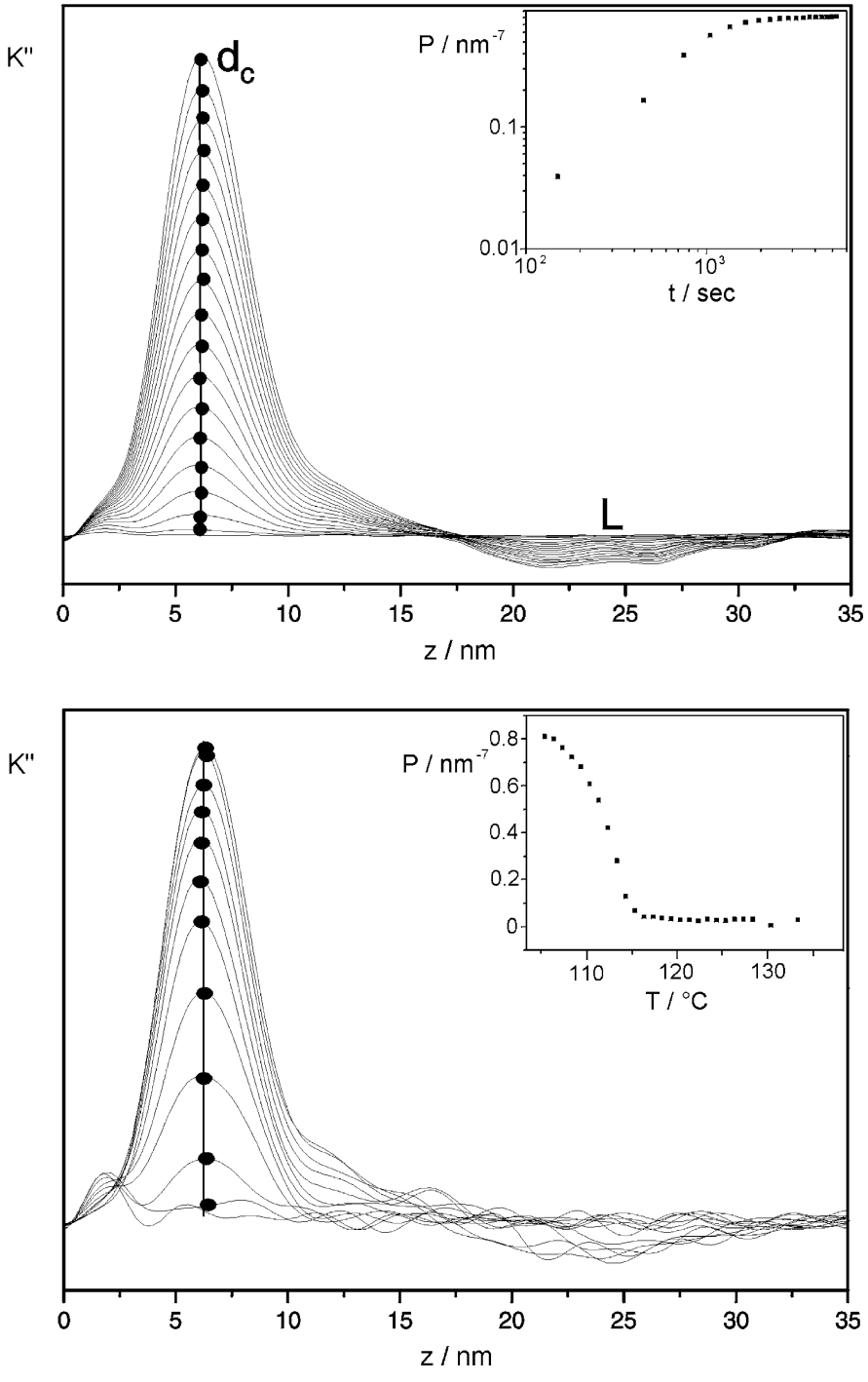

Fig. 3 P(E *co*O(0.7%)): IDFs and Porod-coefficients obtained during a crystallization at $T_c = 123$ °C (*top*) and a subsequent heating into the melt state (*bottom*)

ingly, L^{-1} rather than L are chosen as variables. It can be seen that all the melting points can be allocated on a series of parallel "melting lines" with a downward shift for increasing x_B. In view of the limited accuracy no discrimination is made between LPE and P(E *co*O(0.7%)) or between P(E *co*O(2.8%)) and P(E *co*O(3%)); they are assembled on one common line respectively. The melting line for LPE extrapolates for an infinite crystal thickness to 141 °C. This indeed is nearly identical with the equilibrium melting point of polyethylene, $T_f^{\infty}(x_B = 0) = 141.4$ °C, as determined by Wunderlich in measurements on extended chain samples [6].

Different from the melting lines which vary with x_B one finds for the dependence $d_c^{-1}(T_c)$ for all copolymers, both of the octene- and butene-type, for co-unit contents

above 2% a common, unique line. Deviations towards larger thickness values are only observed for a lower co-unit content and LPE, i.e., those samples which show a thickening during isothermal crystallization. When the "crystallization line" is linearly extrapolated to $d_c^{-1} = 0$ it starts from the temperature $T_c^{\infty} = 154\ ^{\circ}C$, i.e., clearly not from $T_f^{\infty}(0)$.

Discussion

The results as presented in Fig. 4 confirm our first studies on PE and perfectly agree in the scenario with a general scheme first found for sPP and its copolymers. The invariance of d_c for samples with different co-unit content implies that the crystal thickness is *not* controlled by the supercooling below the respective melting point. Melting points decrease with increasing x_B, as is again demonstrated by the experiments, but the crystal thicknesses remain constant. Considering the appearance of the "crystallization line" T_c vs d_c^{-1}, it can be stated that d_c is indeed also determined by a supercooling, but one which refers to another specific temperature, $T_c^{\infty} = 154\ ^{\circ}C$, which is located 13 K above the equilibrium melting point of PE.

In discussions of the melting point reduction by co-units often a simple result of Flory's equilibrium theory is used. It states that the melting point reduction agrees with that introduced by a diluent with the same molar fraction, and is therefore also to be described by Raoult's law, in the form

$$T_f^{\infty}(0) - T_f^{\infty}(x_B) = \frac{R\left[T_f^{\infty}(0)\right]^2}{\Delta h} x_B \qquad (5)$$

where Δh denotes the heat of melting per mole of C_2H_4-groups. The results in Fig. 4 enable a check to be carried out. Figure 5 depicts the equilibrium melting points $T_f^{\infty}(x_B)$ as given for the different samples by the limiting values of the Gibbs-Thomson lines for $d_c^{-1} \to 0$, in a comparison with Eq. (5). Non-negligible deviations are observed which increase with x_B. Such differences had already been found for the other investigated system, sPP and its copolymers, where they were even larger. Hence, treating copolymer systems by equilibrium thermodynamics does not seem to be of much value.

Figure 4 includes also values found for the long spacing. They are allocated on four different lines, one commonly for the copolymers with 4.6 and 5.0 mol% of co-units, one for 2.8 and 3.0 mol% of co-units, and the other two for 1.5 mol% and 0.7 mol% respectively. In the figure all lines start from T_c^{∞} as the "crystallization line". This choice implies that the linear crystallinity $\phi_1 = d_c/L$ does not change with the crystallization temperature.

Such an invariance is, however, not found for the global crystallinity ϕ as derived from the heat of fusion. For example, while the linear crystallinity of P(E *co*B(2.8%)) is always $\phi_1 = 0.22 \pm 0.01$ the global crystallinity is $\phi = 0.19$, 0.16, 0.06 for $T_c = 104\ ^{\circ}C$, 106 °C, and 109 °C respectively. ϕ is always smaller than ϕ_1 and decreases with increasing T_c. Where does this difference come from? ϕ_1 represents a geometric property, related to the short-range ordering of the crystal lamellae. If laterally extended lamellae would completely fill the sample volume one expects agreement between ϕ_1 and the global crystallinity ϕ. This changes if the lateral extension is limited and distances arise between laterally adjacent lamellae. This seems to be the case here. The

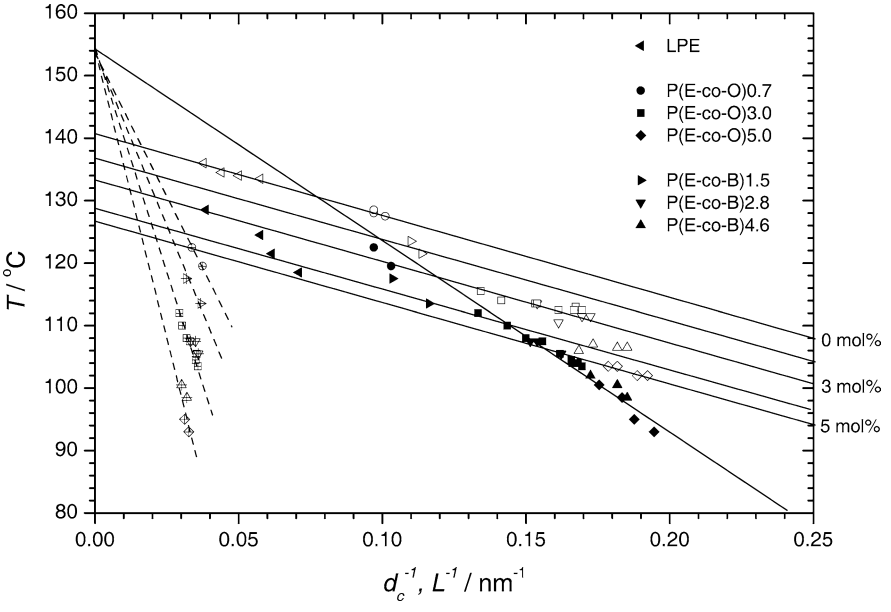

Fig. 4 Results of SAXS experiments on LPE, P(E *co*O)s and P(E *co*B)s. Crystal thicknesses and long spacings at the end of crystallizations at different temperatures, plotted as d_c^{-1} and L^{-1} vs T_c (*filled and crossed symbols*). Melting temperatures T_f and crystal thicknesses at T_f (*open symbols*). Representation of results using Gibbs-Thomson lines, one "crystallization line" for d_c^{-1} and four lines for L^{-1}

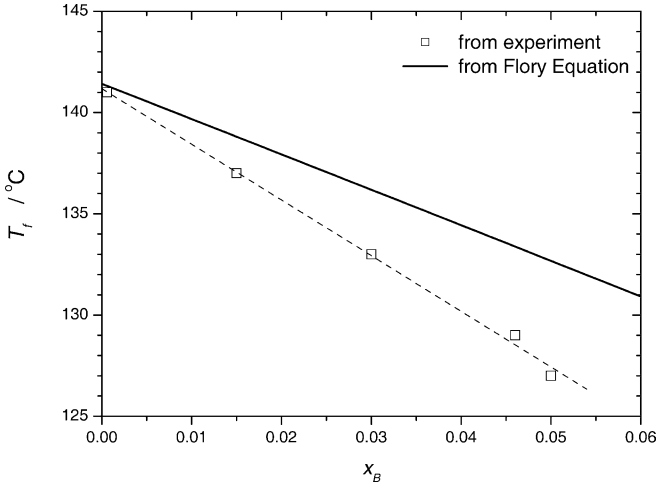

Fig. 5 LPE, P(E *co*O)s, and P(E *co*B)s. Equilibrium melting points d_c^{-1} in dependence on the co-unit content, derived from the Gibbs-Thomson lines in Fig. 4. Comparison with Flory's equation (Eq. 5)

higher the crystallization temperature, the larger are these distances. For a higher T_c and correspondingly a higher d_c the growing lamellae become more selective with regard to the attachment of chain sequences between co-units. As it appears, the too short sequences, which cannot be included into the crystal and are therefore rejected, are not only placed in the interlamellar amorphous layers between the fold surfaces but increasingly also between adjacent lateral surfaces.

Derived relationships

The results as given in Fig. 4 can be expressed by a number of equations. A first one is the specification of the Gibbs-Thomson relation for the investigated system. The melting lines in the figure relate the melting points of crystals in a copolymer melt to their thickness as

$$\begin{array}{lcl} T_f & = & T_f^\infty(x_B) - \frac{C_1}{d_c} \\ \text{with } C_1 & = & 132\text{K nm} \end{array} \qquad (6)$$

where C_1 denotes the slope which is common to all the melting lines. $T_f^\infty(x_B)$ is the limiting value of T_f for $d_c^{-1} \to 0$, where a macroscopic, co-unit free crystal is in equilibrium with the copolymer melt. $T_f^\infty(x_B)$ thus represents the equilibrium crystallization/melting temperature of a copolymer with a volume fraction x_B of co-units. The Gibbs-Thomson relation gives for C_1 the expression

$$C_1 = \frac{2\sigma_e T_f^\infty(0)\Delta z}{\Delta h} \qquad (7)$$

Application of Eq. (7) yields for the surface free energy per endgroup, σ_e, the value 5.0 kJ mol^{-1}, choosing for the molar heat of fusion per C_2H_4-group, Δh, the value 293×28 J mol^{-1} = 8.2 kJ mol^{-1}; Δz is the length of a C_2H_4-unit in chain direction, equal to 0.254 nm.

The x_B-dependence of the equilibrium crystallization/melting temperature $T_f^\infty(x_B)$ which is shown in Fig. 5 can be empirically described by the expression

$$\begin{array}{lcl} T_f^\infty(x_B) & = & T_f^\infty(0) - \alpha_1 x_B \\ \text{with } T_f^\infty(0) & = & 141.2\ ^\circ\text{C} \\ \alpha 1 & = & 2.75 \times 10^2\text{K} \end{array} \qquad (8)$$

Here we use the exact value of the equilibrium crystallization/melting temperature of PE.

A particularly simple relationship holds for the crystal thickness d_c. In the absence of solid state thickening processes, which is given for not too low co-unit contents, d_c is independent of x_B and varies with T_c as described by the equation

$$\begin{array}{lcl} d_c(T_c) & = & \frac{C_2}{T_c^\infty - T_c} \\ \text{with } T_c^\infty & = & 427\text{K and } C_2 = 308\text{K nm} \end{array} \qquad (9)$$

The question about the origin of this relation is a primary one in the understanding of polymer crystallization. Our repeatedly expressed hypothetical answer [7] is: The "crystallization line" following from Eq. (9) when relating T_c to d_c^{-1} represents in the same manner as the Gibbs-Thomson line the locus of a thickness-dependent phase transition. Since the limiting temperature T_c^∞ definitely differs from the PE-equilibrium melting point $T_c^\infty(0)$, it cannot be a phase transition between the melt and the crystal, but must include an intermediate "mesomorphic" phase. The invariance of the line with regard to x_B would then mean that the co-units are already rejected when this mesomorphic phase forms out of the isotropic melt. There might exist other explanations, maybe quite different ones, but the experimental facts are obvious and speak clearly against a control of the structure formation process by the supercooling below the respective equilibrium melting point.

For the long spacing, we may formulate the equation

$$L(T_c, x_B) = \frac{\alpha_3(x_B)}{T_c^\infty - T_c} \qquad (10)$$

which expresses a dependence on both, the crystallization temperature and the co-unit content. The observed x_B-dependence can be expressed in a linear approximation by

$$\alpha_3(x_B) = \alpha_4(1 + \alpha_5 x_B) \qquad (11)$$

with

$$\alpha_4 = 0.8 \times 10^3\text{K nm and } \alpha_5 = 26 \qquad (12)$$

The long spacing is known to depend on the molar mass. In a work on PEEK Fougnies et al. [8] have found that L

changes with the degree of polymerization N in a way first suggested by Rault [9], namely similar to the radius of gyration as

$$L \sim N^{1/2} \tag{13}$$

The finding indicates that a given chain usually is included in one lamellae only. The simplest expression accounting for this dependence together with the x_B-dependence of Eq. (11) is

$$\alpha_3(x_\mathbf{B}, N) = \alpha_6 N^{1/2}(1 + \alpha_5 x_B) \tag{14}$$

leading for the degree of polymerization of the series of samples, $N \approx 3200$ ($M \approx 90 \times 10^3$ g mol^{-1}), to a parameter value

$$\alpha_6 = 14\text{K nm}$$

Finally, by combining the above equations it is possible to derive a relation between the crystallization temperature T_c and the subsequent melting point T_f, under the assumption of a complete absence of thickening and melting-recrystallization processes. As the SAXS experiments show, this is often the case for copolymers and is generally favored by high heating rates. One obtains

$$T_f(x_B, T_c) = T_f^\infty(x_B) - \frac{C_1}{C_2}\left(T_c^\infty - T_c\right) \tag{15}$$

and for the difference $T_f(x_B,T_c) - T_c$ the expression

$$T_f(x_B, T_c) - T_c = T_f^\infty(x_B) - \frac{C_1}{C_2} T_c^\infty + T_c\left(\frac{C_1}{C_2} - 1\right) \tag{16}$$

Introducing some of the numerical values leads to

$$T_f(x_B, T_c) - T_c = 231\text{K} - 231 x_B - 0.57 T_c \tag{17}$$

Note that the criterion

$$T_f(x_B, T_c) - T_c = 0$$

does *not* yield the equilibrium melting point as assumed in the popular Hoffmann-Weeks plot. The temperature where it is fulfilled, we denote it T_{cf}, represents—in our view—the crossover point from a pathway of polymer crystallization which uses an intermediate phase to a direct crystal formation out of the melt. Above T_{cf} the latter pathway, which requires a much longer time, remains the only available one. According to Fig. 4, T_{cf} varies with the co-unit content and reaches for LPE the highest value, located around 130 °C. Indeed, to our restricted knowledge, all T_c-dependent, isothermal crystallization experiments on LPE which started from a relaxed, quiescent melt end in temperature range 130–131 °C.

We expect the coefficients C_1 and C_2 as well as T_c^∞ to be basically stable whereas all the different coefficients α_i may vary somewhat between different products, as they will depend upon the molar mass distribution and the co-unit distribution in the chains which often does not show an ideal randomness.

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