Macromolecules **1992,** *25,* 1617–1617 **1617**

Break in the Curve Giving the Thermal Dependence of Crystal Growth Rate as a Signature of Regime Transition? 1

J. J. Point

Université de Mons Hainaut, 20, Avenue Maistriau, Mons, Belgium

Received July 22, 1991
Revised Manuscript Received December 30, 1991

In 1986, I proposed[1] a path in which to discuss the validity of the standard kinetic theory of crystallization. In this letter, I apply these same considerations to the crystallization of poly(ethylene oxide) (PEO) from dilute solutions in toluene.[2]

Let me once again explain the argument. In the framework of the standard nucleation theory, there exist two regimes of crystallization, namely, regimes I and II, in which the crystal growth rates are respectively

$$G_{\mathrm{I}} = bLi \text{ (regime I)} \tag{1}$$

$$G_{\mathrm{II}} = b(2g_0 i)^{1/2} \text{ (regime II)} \tag{2}$$

In these expressions, L is a constant length, i and g_0 are the nucleation and substrate completion rates, and b is the thickness of a crystal stem. Moreover, the ratio of the slopes of a ln G versus $1/T\Delta T$ curve in these two regimes is 2. This implies that, in regime II, g_0 does not depend noticeably on T_c and that the kinetic length, L_k (the mean distance between two nuclei on the substrate), is inversely proportional to G_{II}[3]

$$L_k = (2g_0/i)^{1/2} \approx 1/G_{\mathrm{II}} \tag{3}$$

In a recent paper, I and M. Ch. Colet propose to denote that application of this consideration is to be known as the Point–Colet criterion.[9]

Let us apply eq 3 to the data of Ding and Amis[2] for PEO, M_w 7.7 × 10^5. At the temperature where the growth rate curve presents a break ($T_{\mathrm{I,II}} = T_{0\mathrm{d}} - \Delta T_{\mathrm{I,II}}$) the kinetic length is estimated to be around 50 nm, and the growth rate is reduced by a factor of $10^{2.5}$ of its maximum value of G_{II} (namely, G_{II} at T_c = 289 K). At this last temperature we get from eq 3 L_k = 0.158 nm, clearly a meaningless value. Consider now the crystallization of PEO, M_w 5.63 × 10^4, which is assumed to occur in regime II. The ratio of the extreme values of G being 10^3, it appears that L_k (the maximum value of which is 50 nm) must take values as low as 0.05 nm (a meaningless value).[8]

These values may be changed by increasing the estimated value of L by a factor of (for instance) 20. But this leads to a value of 1 μm for L, a value larger than the size of the seeds. This is clearly not the case because Ding and Amis do not observe that the growth rate depends on the size of the crystals.

It thus appears that the data of Ding and Amis cannot be explained by the standard theory of crystallization. This theory is more explicitly discussed in ref 9.

References and Notes

(1) Point, J. J. *Macromolecules* **1986**, *19*, 929.

(2) Ding, N.; Amis, E. J. *Macromolecules* **1991**, *24*, 3914.

(3) Frank's model of nucleation-controlled growth,[4] which is an ingredient in the standard theory of polymer crystal growth, does not allow us to derive such a result. In Frank's calculation, the rather complicated dependence of G on i and g may be expressed in an elementary formula in two asymptotic cases. If there is only one nucleus at a time on the substrate (mononucleation case) or if many nuclei grow simultaneously on the substrate (polynucleation case), then one arrives at

$$G = bL_s i \tag{4}$$

$$G = b(2gi)^{1/2} \tag{5}$$

respectively. In eq 4 L_s is the length of the substrate and may be thought as the length of the crystal facet; then G depends not only on T_c but also on the size of the crystal (a situation well-documented on experimental grounds[5,6]). In eq 5, because as noted by a reviewer the affinity of deposition of a stem is an increasing function of the supercooling, one may expect, by contradistinction to a major assumption made in the standard theory of polymer crystal growth, that the substrate completion rate g increases with supercooling (a fact well-documented on experimental grounds[6,7]). Note, as did one reviewer, that Ding et al. actually assume that g is (nearly) constant. This reviewer has calculated from ref 2, for the 7.7 × 10^5 PEO fraction, the ratio of nucleation rates $i_{289}/i_{\mathrm{I,II}}$ = 4 × 10^4, while for the completion rates $g_{289}/g_{\mathrm{I,II}}$ = 1.3.

(4) Frank, F. C. *J. Cryst. Growth* **1974**, *22*, 233.

(5) Point, J. J.; Colet, M. C.; Dosiére, M. In *Morphology of Polymers*; Sedlacek, B., Ed.; Walter de Gruyter: Berlin and New York, 1986; p 153.

(6) Toda, A. *J. Polym. Sci., Part B* **1989**, *27*, 1721.

(7) Part 2: Point, J. J.; Damman, P.; Janimak, J. J., submitted to *Macromolecules*.

(8) In view of these values one of the reviewers said that it is possible, although unprecedented for solution growth, that these numbers from the region of maximum growth rate reflect a transition to regime III growth which was not recognized by Ding and Amis. I do not think so, because the thermal dependence of G greatly differs from that assumed when a "transition to regime III" (a rather vague concept scrutinized in the next paper of this series) occurs. From my point of view, the only way to escape the paradox raised in this paper is to recognize that g depends on T_c, despite the fact that this implies a quite dramatic conclusion, that the thermal dependence of G cannot be used to estimate the nucleation barrier and hence the value of $\sigma\sigma_e$ (the so-called surface free energies).

(9) Point, J. J.; Colet, M. Ch. *Ann. Chim. Fr.* **1990**, *15*, 221.

Registry No. PEO, 25322-68-3; PhMe, 108-88-3.

0024-9297/92/2225-1617$03.00/0