Communications to the Editor

On the Self-Consistency of the Hoffman–Miller Theory of Polymer Crystallization[1]

In the Hoffman–Lauritzen (HL) theory, the crystallization of a polymer lamella occurs by initiation and growth of nuclei on substrates of constant length L, which are parts of the edge of the lamella (Figure 1). Hoffman and Miller (HM)[1] analyze growth rate data of polyethylene (PE) crystals measured by Hoffman et al.[2] and by a sophisticated development and conclude a new value for $L \simeq 21$ nm. They claim that "it removes an objection made by Point et al.[3] who noted that if L was actually as large as some of the earlier estimates,[4] nonlineal growth should be readily observed". Our point in this short communication is that, if $L = 21$ nm, it is smaller than the width of a stable secondary nucleus (as calculated by the HM formalism). Therefore, the HL theory is not self-consistent.

In the HM and HL theory, a secondary nucleus is made of ν adjacent stems (Figure 1a) having a width a, a thickness b, and a length l, and the equation

$$\Delta\phi = 2bl\sigma + \nu(2ab\sigma_e) - abl\Delta G = 0 \qquad (1)$$

expresses that the excess free energy $\Delta\phi$ of a just stable nucleus is equal to zero. In the surface term of $\Delta\phi$, σ is the lateral surface free energy, σ_e is the fold surface free energy, and in the volume term $\Delta G = \Delta h_m \Delta T / T_m$. Here, Δh_m is the heat of fusion, T is the isothermal crystallization temperature, T_m is the melting temperature, and $\Delta T = T_m - T$ is the undercooling.

If, for instance, the values of the various involved parameters are chosen as in the numerical example given by HM[5], the width L_t of a stable nucleus is found to be 51 nm and therefore

$$L_t > L(1) \qquad (2)$$

The same inequality holds for each PE fraction and each crystallization temperature experimented by Hoffman et al.[2] and used by HM in their theoretical development.[1] The same result is also obtained if the expression of $\Delta\phi$ given by HM[6] is used to estimate L_t.

The inequality (2) means that, in the completely hypothetical regime I, the growth of a nucleus stops before it is stable (Figure 1b). This cannot be accepted. A fortiori it is not possible to envisage in the polynucleation regime, the development of several nuclei on the same substrate length L. It appears, that the claim of Hoffman and Miller that L is 21 nm makes their theory not self-consistent, a result which might be anticipated from our previous paper on the subject.[7] The just-given development is the original version of this note. Because one of the reviewer suggests a more explicit discussion, we make additional direct comments[8] on our previously[7] expounded position.

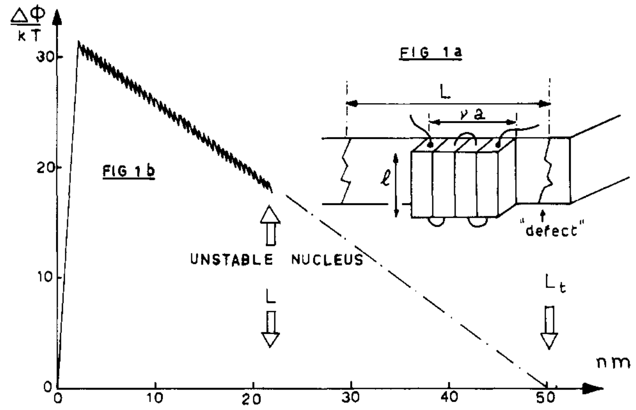

Figure 1. Hoffman–Miller model: (a) Secondary nucleus on the edge of a lamella divided in segments of length L. The surface free energy is σ along the lateral surfaces of area $2bl$ and σ_e along the fold surfaces of area $2\nu ab$. The volume of the nucleus is νabl. (b) Free energy of a surface path. If the width of the nucleus is L, its development stops despite the fact it is unstable (for clarity, the width of the first stem is enlarged).

We note that the calculated value of L_t is too large[7a] in view of the observations made by neutron diffraction[9] on crystals grown from the melt.[10] Because L_t is crucially dependent upon the magnitude of δ, a reviewer suggests to revise the numerical value of δ, which was calculated by Hoffman[2] on the assumption, presently denied by HM[1], that the growth of a nucleus could continue indefinitely along the substrate. But it may be inferred from a detailed calculation given by one of us[7a] that the value of δ does not depend on the assumption of an indefinitely large substrate. Moreover, and this is perhaps more important, the magnitude of δ does not depend critically on detailed assumptions but solely of the invalid approximation,[11] which visualizes the attachment of a full stem as a single stage in the nucleation process. This was pointed out in various circumstances by one of us and by D. Sadler.[12] Therefore in the framework of even revised versions of the Hoffman theory, it is impossible to change significantly the value of L_t. On the other hand, the value of L results from the HM analysis of data, which are accepted[2,13] as giving the proof of the existence of the hypothetical persistence length and of the occurrence of various regimes.

A reviewer suggests too that a metastable patch firstly limited in one persistence length may be later on stabilized by completion on an adjacent length, but this cannot be accepted because the premise of the model is that, in regime I, one nucleus develops in a single persistence length.

It must be underlined that the inequality (2) is a consequence not of adjustable sophisticated developments (involving reptation process or arguments based on statistical mechanics...) but from the fact that δ is calculated in an elementary way to be small. It is small because the attachment of a full stem is considered as a single stage of the nucleation process. In this respect, note that the usual procedure of deriving, from the dependence of the growth rate G versus the crystallization temperature T, the value of the product $\sigma\sigma_e$ of the co-called lateral and fold surface free energies is definitely an evaluation of the free energy barrier, which opposes the deposition of the first of these full stems and thus relies on an invalid oversimplification. The fact that this procedure was previously used is not by itself a proof of its validity. Finally, we seriously question the existence of regime transitions. We note, according to Lovinger et al.,[14] that regime I → II transitions have been reported only for polyethylene and poly(L-lactic acid), and polymers such as poly(oxyethylene), poly(tetramethyl-p-silphenylene siloxane), for whose extensive ranges of growth rates at high temperatures are available, do not show discernible regime I → II breaks.

0024-9297/89/2222-3501$01.50/0

References and Notes

(1) Hoffman, J. D., Miller, R. L. *Macromolecules* **1988**, *21*, 3038.

(2) Hoffman, J. D.; Frolen, L. J.; Ross, G. S.; Lauritzen, J. I., Jr. *J. Res. Natl. Bur. Stand.* **1975**, *A79*, 671.

(3) Point, J. J.; Colet, M. C.; Dosière, M. *J. Polym. Sci., Polym. Phys Ed.* **1986**, *24*, 357.

(4) Hoffman, J. D. *Polymer* **1985**, *26*, 803.

(5) This example concerns a PE fraction with $M_W = 115\,000$ and $n_z = 14\,500$ (ref 1, p 3041) crystallized at $T = 401.7$ K. The values of the parameters are taken as $b = 0.415$ nm, $a = 0.455$ nm, $\sigma = 11.8$ mJ/m^2, $\sigma_e = 90$ mJ/m^2, $\Delta h_m = 2.8\ 10^8$ J/m^3, $T_m = 418.1$ K, $l = 2\sigma_e/\Delta G + kT/2b\sigma$.

(6) We start from the equation

$$\Delta\phi = 2bl\sigma - abl\Delta G + \lambda kT \ln (l_o/x_o) - (\nu - 1)ab(l\Delta G - 2\sigma_e) \tag{3}$$

The condition $\Delta\phi = 0$ with $l = l_g^* = l_c + \delta$ where $l_c = 2\sigma_e/\Delta G$ (6) and $\delta = kT/2b\sigma$ gives

$$L_t > (\sigma/\sigma_e)l_c^2/\delta + (\sigma/\sigma_e)l_c - (a/\delta)l_c \tag{4}$$

The sign ">" occurs because, in the right-hand side of this inequality, we have omitted the third term of the right-hand side of the equation (3) (because the exact values of x_o and λ are not given in ref 1). The lower bounds of L_t for representative PE fractions studied by Hoffman et al.[2] are the following. For the fraction of $M_W = 18\,100$, $n_z = 2000$, it varies from 33.1 to 78.2 nm when the crystallization temperature t goes from 122.5 to 129 °C. For the fraction $M_W = 30\,600$, $n_z = 2740$, it varies from 34.4 to 82.6 nm when t goes from 124 to 130.5 °C. For the fraction $M_W = 74\,400$, $n_z = 6130$, it varies from 25.0 to 75.7 nm when t goes from 122 to 131 °C. Thus the inequality $L_t > L$ is obtained from the HM theory in each experimental condition used by Hoffman et al. in their classical work,[2] which is considered as the foundation of the HL theory. See also: Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I., Jr. In *Treatise on Solid State Chemistry*; Hannay, N. B., Ed.; Plenum: New York, Vol. 3, Chapter 7, or any textbook on polymer physical chemistry.

(7) (a) Point, J. J. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 177. (b) Point, J. J. *Macromolecules* **1986**, *19*, 929.

(8) We have other remarks on the HM paper concerning the use of the reptation concept, the sharpness of the observed "regime transition", and the assumed shape of the molecules in the nuclei. However, we think that it is more appropriate, in this paper, to concentrate our attention on the inequality (2).

(9) (a) Keller A *Faraday Discuss. Chem. soc.* **1979**, *68*, 145. (b) Stamm, M.; Fischer, E. W.; Dettenmaier, M.; Convert, P. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 264.

(10) It may be that this disagreement does not occur when crystals grown from solution are concerned. Nevertheless, we show elsewhere[15] that the HL theories cannot explain the kinetics of crystallization of LPE single crystals grown from solution.

(11) Point, J.-J. *Macromolecules* **1979**, *12*, 770.

(12) Sadler, D. *Polymer* **1984**, *25*, 1447.

(13) Bassett D. C. In *Principles of Polymer Morphology*; Cambridge University Press: Cambridge, 1981; p 165.

(14) Lovinger, A. J.; Davis, D. D.; Padden, F. J., Jr. *Polymer* **1985**, *26*, 1595.

(15) Point, J.-J.; Colet, M.-Ch.; Dosière, M. *J. Polym. Sci., Polym. Phys. Ed.*, submitted for publication.

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Response to Criticism of Nucleation Theory As Applied to Crystallization of Lamellar Polymers

In the preceding paper, Point and Dosière[1] (hereafter P&D) criticize a widely used body of theory concerning crystallization of lamellar polymers because of a supposed major inconsistency involving the magnitude of the substrate length L and because they apparently do not accept experimental evidence concerning the reality of regime transitions in such polymers. Regarding the latter, they state "Finally, we seriously question the existence of regime transitions". This refers specifically to the regime I → II transition. The theoretical framework they challenge is that commonly termed "LH" or "HL", which is based on the work of Lauritzen and Hoffman[2] as extended to include the prediction of regime I → II transitions[3-5] (involving the introduction of a finite substrate length L), regime II → III transitions,[6,7] the effect of reptation,[8] and recently an improved version of the latter by Hoffman and Miller (HM)[9] that included a rough estimate of L for melt-crystallized polyethylene. It is this estimate of L that constitutes part of their objection. Evidently P&D consider regime I to be "completely hypothetical", which if correct would leave no room for believing in the reality of a I → II transition, let alone the presence of a substrate of length L to explain it. To counter the views of P&D, we first cite experimental results showing that regime transitions do occur and then deal with their criticism of the magnitude of L.

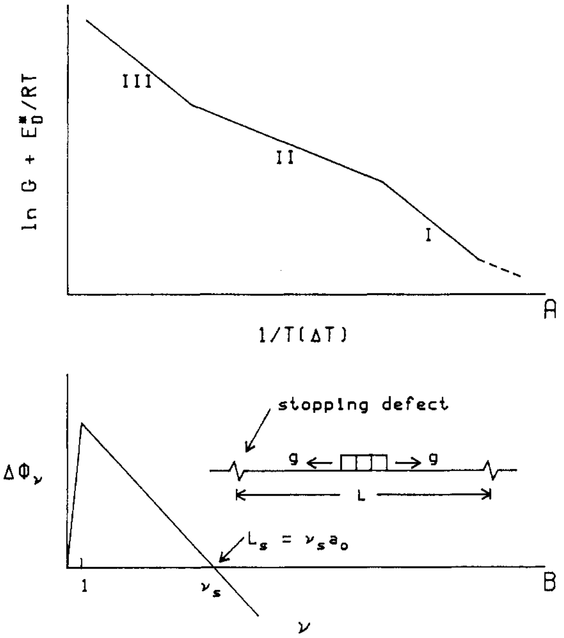

Figure 1. (A) Method of detecting regime transitions. The dashed line indicates a reversion to regime II that may occur at high temperatures (see ref 25). For bulk rate data, ln G is replaced by ln (τ_χ^{-1}). (B) Barrier system for HL–HM models. Inset shows schematic representation of substrate length L. The quantity g is the substrate completion rate.

A. Are Regime Transitions Real? For crystallization of lamellar polymers with chain folding, nucleation theory predicts the presence of three regimes denoted I–III.[3-7,9] To detect them, one commonly plots $\ln G + E_D^*/RT$ vs $1/T(\Delta T)$ as shown schematically in Figure 1A. Here G is the observed lineal growth rate, T the isothermal crystallization temperature, ΔT the undercooling, and E_D^* the activation energy of transport of molecules to the crystal interface.[10] Where the bulk crystallization rates are employed, one plots $\ln (\tau_\chi^{-1}) + E_D^*/RT$ vs $1/T(\Delta T)$ where τ_χ is the time required to attain a fixed degree of crystallization χ. The slope changes in Figure 1A signify the presence of regime transitions. As one goes from regime I to regime II, the slope is predicted to fall by a factor[3-5] of 2, and as one goes from regime II to regime III, the slope is predicted to increase by a factor[6] of 2. Polymer systems showing *experimentally* such slope changes are listed in Table I and discussed more fully below. We quote only those examples where the author(s) stated that the I →