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References and Notes

(1) Tadokoro, H. "Structure of Crystalline Polymers"; Wiley: New York, 1979.
(2) Fraser, R. D. B.; MacRae, T. P. "Conformation in Fibrous Proteins"; Academic Press: New York and London, 1973.
(3) Crick, F. H. C.; Rich, A. *Nature (London)* **1955**, *176,* 780.
(4) Fernândez-Santin, J. M.; Aymami, J.; Rodriguez-Galân, A.; Muñoz-Guerra, S.; Subirana, J. A. *Nature (London)* **1984**, *311,* 53.
(5) Van Slyke, D. D.; Abderhalden, E. 1925. In "Handbuck der Biologishen Arbeitsmethodem"; Urban Schwarzenberg: Wien, 1925; Abt. I, Teil 7, S.263.
(6) Garmon, R. G.; Gibson, M. E. *Anal. Chem.* **1965**, *37* (11), 1309.
(7) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19,* 1837.
(8) Wittmann, J. C.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19,* 1853.
(9) Wittmann, J. C.; Hodge, A. M.; Lotz, B. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21,* 2495.
(10) Cowan, P. M.; McGavin, S. *Nature (London)* **1955**, *176,* 501.
(11) Sasisekharan, V. *Acta Crystallogr.* **1959**, *12,* 903.
(12) Lotz, B.; Keith, H. D. *J. Mol. Biol.* **1971**, *63,* 195.
(13) Rich, A.; Crick, F. H. C. *J. Mol. Biol.* **1961**, *3,* 483.
(14) Ramachandran, G. N.; Kartha, G. *Nature (London)* **1955**, *176,* 593.
(15) Lotz, B. *J. Mol. Biol.* **1974**, *87,* 169.
(16) Arnott, S.; Dover, S. D.; Elliott, A. *J. Mol. Biol.* **1967**, *30,* 201.
(17) Muñoz-Guerra, S.; Fernândez-Santin, J. M.; Rodriguez-Galan, A.; Subirana, J. A. *J. Polym. Sci.* **1985**, *23,* 733.
(18) Masamoto, J.; Sasaguri, K.; Ohizumi, Ch.; Kobayashi, H. *J. Polym. Sci., Part A-2* **1970**, *8,* 1703.
(19) Bunn, C. W.; Garner, W. V. *Proc. R. Soc. London, A* **1947**, *No. A189,* 39.

Onset of Chain Folding in Low Molecular Weight Poly(ethylene oxide) Fractions Crystallized from the Melt

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ABSTRACT: The nucleation theory approach to chain folding is herein extended to the case of short chains and employed to predict the undercooling at which a chain of specified length will exhibit f folds per molecule, where $f = 1, 2, 3, ...$ The extensive data of Kovacs and co-workers on low molecular weight poly(ethylene oxide) fractions, which clearly exhibit once-, twice-, three-times-, and four-times-folded ($f = 1$ through $f = 4$) crystals, are successfully interpreted in terms of the treatment. It would thus appear for this system that the frequently posed question of which factors control the onset of chain folding with increasing molecular weight and undercooling has been answered.

It is known that many high polymers consisting of flexible chains with sufficiently regular chemical chain units crystallize from the melt and dilute solution in the form of lamellar structures where each lamella (or single crystal) exhibits chain folding.[1-4] In a number of respects, our understanding of this phenomenon is in a relatively satisfactory state. For example, kinetic nucleation theory[4,5] predicts the initial lamellar thickness $l_g{}^*$ as a function of undercooling ΔT for high molecular weight polymers, including fractions. This holds for single crystals formed from dilute solution,[4] and recent synchrotron experiments that eliminate the effects of isothermal thickening have shown that it applies equally well to polyethylene when crystallized from the melt.[6] Progress has also been made on the basis of the same theoretical framework in understanding the kinetic processes by which chain folds are incorporated into the crystals as they are being formed, including a description of the overall kinetics of growth[4,7,8] as a function of ΔT. This state of affairs was attained in part because of the recognition of three regimes of crystallization (commonly denoted I, II, and III)[4,7-9] and also because of the introduction of the concept of reptation.[10,11] The latter allows one to understand not only the molecular weight dependence of the growth rate[11] but also how portions of the long molecules in a relatively high molecular weight fraction can be reeled from the entangled melt onto the substrate, allowing the formation of chain-folded clusters.[7,8,10,11] Further, one knows from the "Gambler's Ruin"[12,13] and related calculations[14] that there are definite topological constraints on nonadjacent reentry in high molecular weight polymers that require (for vertical stems) close to two-thirds "tight" folds, i.e., a lamellar surface with two-thirds adjacent or very near adjacent reentry type folds that have no amorphous character in the traverse between the stems. However, there does not appear up to now to be a treatment of the onset of chain folding in low molecular weight fractions. It is the purpose of this paper to outline such a treatment and apply it to the extensive and carefully executed data of Kovacs and co-workers on poly(ethylene oxide) (PEO) fractions crystallized as single crystals from the melt.[15-20] It will emerge that the data yield to a straightforward treatment that provides a clear insight into the physics of the onset of chain folding at low molecular weights. Specifically, we shall herein successfully predict the number of folds per molecule f that will appear in PEO lamellae crystallized from the melt at a specified undercooling ΔT^* for samples consisting of short molecules of length l_0.

Figure 1 (upper diagram) shows schematically how in the experiments of Kovacs and co-workers the growth rate G of a PEO fraction of fixed length l_0 varies with the undercooling ΔT. We choose to measure the undercooling for a given fraction consisting of molecules of length l_0 from the extended-chain melting point T_m appropriate to that fraction. Curves of the type shown define experimentally for each l_0 the undercooling $\Delta T^*{}_f$ where, with increasing undercooling, the onset of lamellae with f chain folds per molecule without conspicuous initial ciliation occurs. Once-folding ($f = 1$) obtains at the lowest undercooling $\Delta T^*{}_1$; this is then followed at the larger undercooling $\Delta T^*{}_2$

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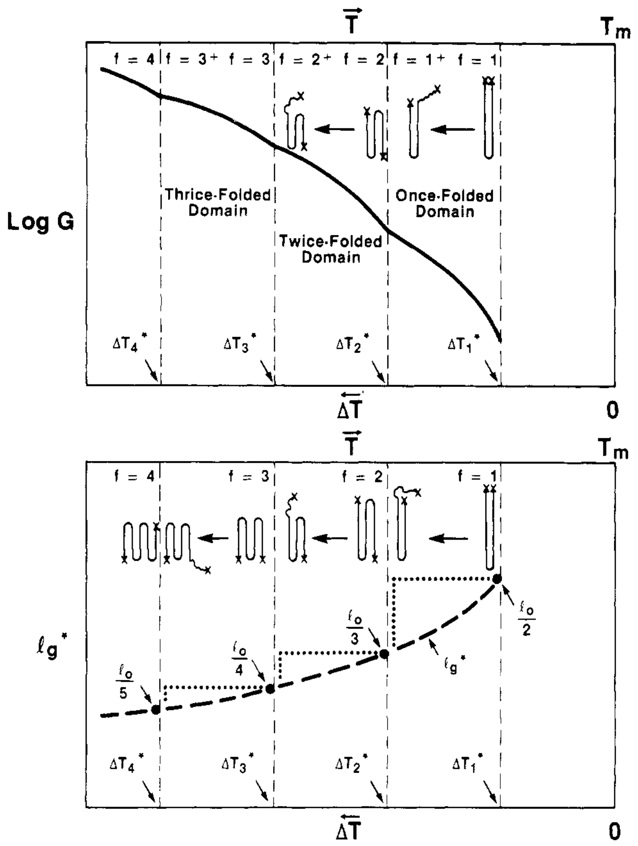

Figure 1. Variation of growth rate G and initial lamellar thickness l_g^* as a function of temperature and undercooling ΔT for a short-chain polymer of fixed length l_0 (schematic). Heavy dots (lower diagram) show undercooling where l_g^* is identical with $l_0/(1 + f)$. (Lightly dotted lines in lower diagram show effect of isothermal thickening on observed lamellar thickness; see footnote 21. The growth rate at the onset of each domain corresponding to ΔT^*_f is denoted G_f^*.

by twice-folding and so on up to ΔT^*_4 ($f = 4$) for some of the specimens. In the case of the samples with the larger l_0, the curves are compressed toward the $\Delta T = 0$ side of the diagram. Observe that the definition of the undercooling at which a given number of folds per molecule appears is determined on a kinetic basis. Accordingly, the treatment to be given below will deal with the problem in terms of the kinetic theory of chain folding.

A basic concept that we shall use here is that at the onset of a given fold domain, i.e., for lamellae of a given f, the fold period l_{fold} will closely correspond to the stem length l_g^* predicted by nucleation theory (see heavy dots, Figure 1, lower diagram). Thus at the onset temperature where ciliation is minimal, we let

$$l_{\mathrm{fold}} = l_0/(f + 1) = l_g^* \tag{1}$$

Hence for once-folded chains ($f = 1$) l_{fold} is $l_0/2$, and this will be equal to the more or less smoothly varying function l_g^* only at one specific undercooling ΔT^*_1 for a given l_0. For $f = 2$ l_{fold} is $l_0/3$, and the undercooling where l_g^* is the same as $l_0/3$ is ΔT^*_2 and so on. Within a given fold domain, say $f = 1$, increasing undercooling causes l_g^* to diminish so that increasing initial ciliation results (see $f = 1 \rightarrow f = 1^+$, etc., in Figure 1). This has interesting consequences,[21] but here we confine our interest to predicting ΔT^*_f at the onset temperature where initial ciliation is minimal.

For the variation of l_g^* with temperature and undercooling at each onset temperature we use the kinetically derived expression for the initial lamellar thickness[4,5]

$$l_g^* = (2\bar{\sigma}_e/\Delta G) + \delta = (2\bar{\sigma}_e T_m/(\Delta h_f)(\Delta T)) + \delta \tag{2a}$$

where

$$\bar{\sigma}_e = \sigma_{e(\infty)}[f/(f + 1)] \tag{2b}$$

In eq 2a we have used the simplified expression $\Delta G = \Delta h_f(\Delta T/T_m)$ to describe the driving force for crystallization. This will prove to be an adequate approximation in the present application. In the above, Δh_f is the heat of fusion in units of energy per unit volume. The quantity δ is approximately $kT/b_0\sigma$ in the simplest approximation[4,5] (k is Boltzmann's constant, b_0 is the layer thickness, and σ is the lateral surface free energy); in the more elaborate and more accurate approximations that permit fluctuations of fold period,[22] δ is roughly 1.5 times larger than $kT/b_0\sigma$, but this causes no difficulty in the present treatment. The value of δ, though small compared to l_g^*, must be greater than zero, since otherwise the lamella would melt at its crystallization temperature.[4,5,8] The quantity $\bar{\sigma}_e$ is the mean value of the "fold" surface free energy associated with a substrate of designated f. Equation 2b, which we have suggested before,[23] seems a suitable approximation for this average; $\sigma_{e(\infty)}$ is the surface free energy of a fully folded surface. In a lamellar system where the chain ends do not protrude from the fold surface as cilia, which is the case at ΔT^*_f, there is neither a chain-end term involving $\sigma_{\text{chain end}}$ nor a cilium free energy in the eq 2b when T_m(extended chain) is used as the basis for obtaining ΔT. Equation 2b implies the presence of a high degree of adjacent or very near adjacent reentry in the substrate completion process; we find the "switchboard" analogy particularly inappropriate in this case where the growth rate is known experimentally to be "quantized" $f = 1$ through $f = 4$. Equations 2a and 2b define an l_g^* for a specified l_0 that falls with increasing ΔT, as depicted schematically in Figure 1 (heavy dashed lines, lower diagram). This line superficially resembles, but is not equivalent to, the shape of the l_g^* vs. ΔT plot that is obtained with a constant σ_e.

From the above one readily finds the desired relationship between the undercooling ΔT^*_f corresponding to the onset of a specified number of folds per molecule f and the overall length of the chain l_0. This is

$$\Delta T^*_f = \frac{2\sigma_{e(\infty)}T_m}{\Delta h_f}\left(\frac{f}{f + 1}\right)\Big/\left[\left(\frac{l_0}{f + 1}\right) - \delta\right] \tag{3}$$

Since eq 2a is independent of the regime of crystallization, the same is therefore true of eq 3. The reader is reminded that eq 3 is fundamentally of *kinetic* origin. There are no tenable equilibrium theories of chain folding.

We consider now independently determined values of $\sigma_{e(\infty)}$ for use in eq 3. From an analysis of the melting point data on once-folded PEO chains using the thermodynamic expression

$$T_m - T_f' = \frac{2\bar{\sigma}_e T_m}{\Delta h_f[l_0/(f + 1)]} = \frac{2\sigma_{e(\infty)} f T_m}{\Delta h_f l_0} \tag{4}$$

where $T_f' = T_1'$ is the observed melting point of the once-folded lamellae[19] and $\Delta h_f = 2.4 \times 10^9$ erg cm^{-3}, we find that $\sigma_{e(\infty)}$ is roughly 45 erg cm^{-2} for PEO. From a detailed analysis of the kinetics of crystallization we have found that the best fit is obtained with $\sigma_{e(\infty)} \cong 42.2$ erg cm^{-2} and $\sigma \cong 10.6$ erg cm^{-2} (see later). Also, the empirical relation[4] $\sigma \simeq 0.1(\Delta h_f)(a_0 b_0)^{1/2}$ gives $\sigma \simeq 11.1$ erg cm^{-2}. Accordingly, we see no major contradictions with regard to the input data.

The solid lines in Figure 2 show ΔT^*_f vs. l_0 for $f = 1$ through $f = 5$, as calculated with eq 3 for the case $\sigma_{e(\infty)} =$

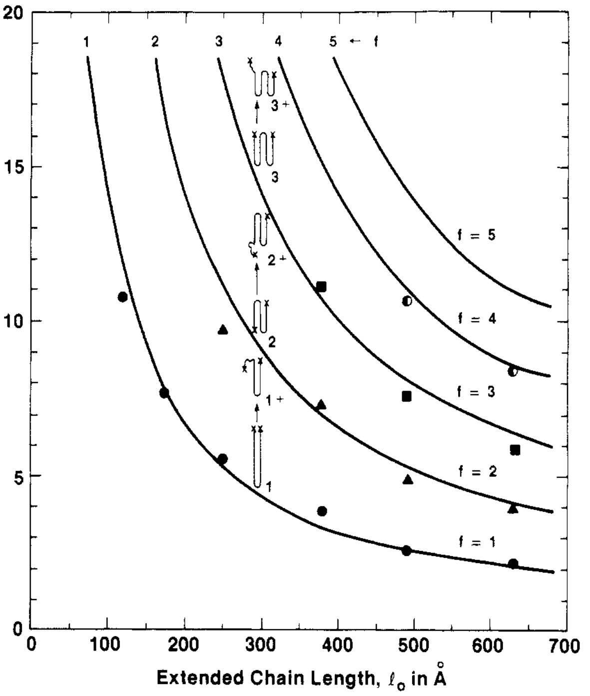

Figure 2. Comparison of theoretical chain-folding onset undercooling ΔT^*_f as a function of extended-chain length l_0 for various f values (solid lines) with experiment for PEO fractions. Experimental points given by Kovacs:[20] once-folded (f = 1), ●; twice-folded (f = 2), ▲; three times-folded (f = 3), ■; four-times-folded (f = 4), ◐.

42.2 erg cm^{-2}, $\Delta h_f = 2.4 \times 10^9$ erg cm^{-3}, and $\delta = 12 \times 10^{-8}$ cm or 12 Å. (The value of δ used here is in accord with the expectations of fluctuation theory; the δ calculated from the simple approximation $kT/b_0\sigma$ with σ = 10.6 erg cm^{-2} and $b_0 = 4.63 \times 10^{-8}$ cm is ~9.3 Å.) These lines were calculated by using the measured values of T_m for each l_0 (see below). If an average value of T_m equal to T_m = 60.6 °C = 333.8 K had been employed in eq 3, the resultant ΔT^*_f values would never have differed more than 2.5% from those plotted as solid lines in Figure 2.

Kovacs and co-workers[15-19] have obtained growth rate data of the general type depicted in Figure 1 on six PEO fractions whose lengths and extended-chain melting points follow: l_0 = 120 Å (T_m = 52.7 °C), 175 Å (T_m = 57.6 °C), 248 Å (T_m = 60.4 °C), 378 Å (T_m = 63.3 °C), 490 Å (T_m = 64.3 °C), and 632 Å (T_m = 65.4 °C). The ΔT^*_f results obtained therefrom are plotted as data points in Figure 2.[20]

The agreement between theory (solid lines) and experiment (f = 1 through f = 4 data points) in Figure 2 appears to be satisfactory. Two key parameters required for the predictions are the heat of fusion and ideal fold surface free energy $\sigma_{e(\infty)}$ or, alternatively, the work of chain folding q as in $\sigma_{e(\infty)} = q/2a_0b_0$, where a_0b_0 is the cross-sectional area of the chain. The value of δ is also important, especially when $l_0/(f + 1)$ is small. For instance, the (clearly incorrect) assumption δ = 0 would have led to ΔT^*_1 = 9.5 °C for f = 1, l_0 = 120 Å, which is in notably poorer agreement with experiment than the ΔT^*_1 shown in Figure 2 calculated by using δ = 12 Å. We note further that the agreement between theory and experiment illustrated in Figure 2 is in no little part a result of the at least approximate validity of the substrate surface free energy averaging law given in eq 2b. This bears the clear implication that $\bar{\sigma}_e$ as given by eq 2b applies rather well to the kinetics of formation of the surface nucleus and the subsequent substrate completion process pertaining to a "fresh" or unannealed single crystal face where no isothermal thickening, multilayering, or other rearrangement has yet taken place.

We observe in passing that eq 2b for $\bar{\sigma}_e$ will likely require modification in cases where annealed multilayered systems with "quantized" f are concerned, since here rather strong interlamellar interactions involving chain folds and remanent cilia can be present. It is for this reason that we have given the thermodynamic $\sigma_{e(\infty)}$ obtained from melting point data with eq 4 above only for f = 1, and then only as a rough approximation; the f = 2 and f = 3 melting points lead to deviations attributable to the aforementioned interactions.[24] However, this does not detract from the validity of eq 2b as applied to surface nucleus formation and the ensuing substrate completion process on the relatively young and "unannealed" growth front of a single crystal to obtain the kinetically determined quantity ΔT^*_f, which application is in any case successful as is shown in Figure 2.

It remains to highlight certain aspects of the growth kinetics as they relate to ΔT^*_f and l_g^*. It is seen that it has not been necessary to know the absolute growth rate G_f^* at the onset of each domain of chain folding (f = 1, 2, 3, etc., as depicted in Figure 1, upper diagram) in order to calculate ΔT^*_f as a function of l_0. It is only necessary to know $\sigma_{e(\infty)}$, Δh_f, and δ in eq 3 to find ΔT^*_f. One of the reasons that eq 3 works so well, as is illustrated in Figure 2, is that the kinetic expression for l_g^* inherent in its derivation, eq 2a, is independent of regime. However, G_f^* may depend on regime. It is instructive to note here that according to chain fold nucleation theory the growth rate G is related to l_g^* by the relation[4,5]

$$G \propto \exp[-jb_0\sigma l_g^*/kT] \tag{5a}$$

where j = 2 for regimes I and III and j = 1 for regime II. This is altogether equivalent to the usual expression[4,5] where G varies as

$$G \propto \exp[-2jb_0\sigma\bar{\sigma}_e T_m/(\Delta h_f)(\Delta T)kT] \tag{5b}$$

Thus G^*_f depends on regime even though l_g^* does not. From eq 5a it is seen qualitatively why the growth rate tends to increase as l_g^* falls, as is shown schematically in Figure 1, and further, from eq 5b why the growth rate increases as ΔT increases. Observe from eq 5 that a change of regime could cause disturbances in the variation of G^*_f with l_g^* (or ΔT). As will be noted shortly, this evidently occurs at the extremum of very short chains with once-folding in PEO fractions. One of the strengths of the present treatment is that ΔT^*_f is calculated in such a way as to avoid the necessity of knowing the regime involved in the crystallization or the absolute crystallization rate G_f^* at ΔT^*_f. Observe also that the present scheme is such that it is not required to deal with extended-chain crystallization rates. This is also an advantage, since in extended-chain crystallization, one might well expect deviations from some of the simple assumptions commonly employed in successfully dealing with the kinetics of chain-folded high polymers. As matters now stand, the approach suggested here for low molecular weight systems gives ΔT^*_f as a function of l_0 for f = 1, 2, 3, ... in a direct manner that avoids unnecessary complications resulting from uncertainty of regime or any peculiarities in the details of extended-chain crystallization. The current treatment converges smoothly toward the customary high-polymer treatment for l_g^* and G and is for practical purposes equivalent to it when f is about 4 or 5 or greater.

Since the kinetic effects are of general interest and also have a bearing on the input data employed in this paper, most especially the values $\sigma \cong 10.6$ erg cm^{-2} and $\sigma_{e(\infty)} \cong$

42.2 erg cm^{-2}, it is worthwhile to comment briefly on the results of an analysis of G_f* for $f = 1$ through $f = 4$ as a function of l_0 for the PEO fractions mentioned earlier in this work. Details will be published elsewhere.[24] With expressions of the form of eq 5, it was found for all fractions exhibiting three- and four-times-folding ($f = 3$ and $f = 4$) that with the averaging law for $\bar{\sigma}_e$, eq 2b, the rate data yielded $\sigma \cong 10.6$ erg cm^{-2} and $\sigma_{e(\infty)} \cong 42.2$ erg cm^{-2}. Regime II was indicated. The specimens exhibiting once-folding ($f = 1$) went into regime III when they were short and crystallized rapidly; however, no large deviation of σ and $\sigma_{e(\infty)}$ from the values noted above was required. Up to this point, i.e., for all $f = 3$ and $f = 4$ data and the shorter chain $f = 1$ and $f = 2$ cases, all that was needed to analyze the data sensibly was to use the expressions for the growth rate based on the conventional single-stem surface nucleus model, as expressed in simple form in eq 5, at the same time giving proper attention to the question of regime. Notice that the averaging law for $\bar{\sigma}_e$ was explicitly employed; without this, the treatment would have failed. In the single-stem model,[4,5] the work required to put down the first full ($\nu = 1$) stem is associated with the maximum free energy barrier to surface nucleation; subsequent stems ($\nu > 1$) refer to substrate completion, and their addition involves a progressive increase of stability of the surface patch. However, for the $f = 1$ specimens of higher chain length, a multistem nucleus rather than the conventional single-stem nucleus appeared quite abruptly when the fold period exceeded about 125 Å. This abrupt change in nucleus type in the $f = 1$ case represented a departure from the single-stem model customarily employed in treating polymers,[4,5] but a detailed treatment of the multistem nucleus predicted the abrupt change, and normal surface free energies still obtained for the multistem nucleus. In the multistem model, the maximum in the free energy barrier occurs at $\nu > 1$, and under certain circumstances this maximum can be lower than that associated with the single-stem model at $\nu = 1$. The multistem nucleus did not appear in most $f = 2$ specimens and was completely absent in the $f = 3$ and $f = 4$ cases.

In summary, the analysis of the PEO rate data supports the input values for σ and $\sigma_{e(\infty)}$ employed in this paper. There is no indication that σ is a strong function of chain length, as was implied by an earlier analysis of the same data by Point and Kovacs.[19] The difference is partly a result of our recognition that regime III enters the picture for very short once- and twice-folded chains.[24] It is also partly a result of our use of an appropriate though still approximate averaging law for $\bar{\sigma}_e$. Another difference stems from our finding that an energetically inexpensive multistem nucleus rather than the conventional single-stem nucleus occurs in the extremum of sufficiently long once-folded ($f = 1$) chains. The multistem nucleus does not occur at all for three- and four-times-folded chains and occurs only marginally for long twice-folded ($f = 2$) chains. The result is then that the usual type of single-stem nucleus treatment (with appropriate regime selection and fold surface free energy averaging) is quite adequate for rather closely approximating the behavior of log G^*_f for short chains with $f = 1$ and $f = 2$ and all $f = 3$ and $f = 4$ cases of any chain length. The values of σ and $\sigma_{e(\infty)}$ are in all cases in the normal range. The usual expressions based on the single-stem concept, which have been successfully employed for analysis of the growth rate and initial lamellar thickness of high polymers,[4,5,25] are for practical purposes recovered when f is 4 or 5 or greater.

Though we have not yet completed the analysis of the extended-chain case, it would be reasonable to surmise that a multistem nucleus will occur there for sufficiently long chains and lead to a lower free energy of formation than the corresponding single-stem nucleus. We would remark, however, that such an interesting result would not bespeak a breakdown of the conventional single-stem surface nucleation approach as applied in situations where the molecular length and lamellar thickness were such as to allow about two or three or more folds per molecule, irrespective of whether the system in question was oligomeric or polymeric.

We close with the following remarks and conclusions:

(1) A simple treatment based on the kinetic nucleation theory of chain folding has been given that for short chains gives the undercooling at which a specified number of folds per molecule will appear in an isothermal crystallization if kinetics permit. With independently supportable input data, this theory appears successfully to predict the temperature and molecular length domains where once-, twice-, three-, and four-times-folding will occur in low molecular weight PEO fractions. In general, short chains require a significantly higher undercooling to attain a specified number of folds per molecule than do larger ones.

(2) We note further that the theory outlined here has been employed to predict the onset of chain-folding effects in ultralong n-paraffins.[26] A plot similar in general character to Figure 2 is easily constructed for this system, and the results appear to be in the least qualitative accord with recent work[27] on pure n-paraffins $C_{150}H_{302}$ to $C_{390}H_{782}$.

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References and Notes

(1) Keller, A. *Philos. Mag.* **1957**, *2*, 1171.
(2) Fischer, E. W. *Z. Naturforsch., A: Astrophys., Phys. Phys. Chem.* **1957**, *12A*, 753.
(3) See review by: Khoury, F.; Passaglia, E. In *Treatise on Solid State Chemistry*; Hannay, N. B., Ed.; Plenum: New York, 1976; Vol. 3, Chapter 6, pp 335–496.
(4) See also review by: Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I., Jr. *Ibid.* Chapter 7, pp 497–614.
(5) Lauritzen, J. I., Jr.; Hoffman, J. D. *J. Appl. Phys.* **1973**, *44*, 4340.
(6) Barham, P. J.; Chivers, R. A.; Keller, A.; Martinez-Salazar, J.; Organ, S. J. *J. Mater. Sci.* **1985**, *20*, 1925.
(7) Hoffman, J. D. *Polymer* **1983**, *24*, 3.
(8) Hoffman, J. D. *Polymer* **1985**, *26*, 803.
(9) See review by: Hoffman, J. D. In *Polyethylene 1933–1983*, Golden Jubilee Conference, Proceedings of Plastics and Rubber Institute; Plastics and Rubber Institute: London, 1983; pp D3.1–D3.13.
(10) Klein, J.; Ball, R. C. *Discuss. Faraday Soc.* **1979**, *68*, 198.
(11) Hoffman, J. D. *Polymer* **1982**, *23*, 656.
(12) DiMarzio, E. A.; Guttman, C. M.; Hoffman, J. D. *Polymer* **1981**, *22*, 1466.
(13) Guttman, C. M.; DiMarzio, E. A. *Macromolecules* **1982**, *15*, 525.
(14) Mansfield, M. L. *Macromolecules* **1983**, *16*, 914.
(15) Kovacs, A. J.; Gonthier, A.; Straupe, C. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 50*, 283.
(16) Kovacs, A. J.; Straupe, C.; Gonthier, A. *J. Polym. Sci., Polym. Symp.* **1977**, *No. 59*, 31.
(17) Kovacs, A. J.; Straupe, C. *J. Cryst. Growth* **1980**, *48*, 210.
(18) Kovacs, A. J.; Straupe, C. *Discuss. Faraday Soc.* **1979**, *68*, 225.
(19) Point, J. J.; Kovacs, A. J. *Macromolecules* **1980**, *13*, 399.
(20) The author is deeply indebted to Dr. Kovacs for his considerable assistance in supplying and assembling the transition and melting temperature data from the original work and ref 15–19 from which the ΔT^*_f data were deduced, and further thanks him for a number of private communications pertaining thereto.
(21) If isothermal thickening does not occur, which may obtain at low crystallization temperatures, the cilia will remain and lower the degree of crystallinity in the regions 1^+, 2^+, etc. If this situation applies, the observed lamellar thickness will

correspond to l_g^*, which, except for small deviations resulting from the contribution of the cilia to $\bar{\sigma}_e$, will be a smoothly varying function of ΔT (heavy dashed line in Figure 1, lower diagram). If, on the other hand, isothermal thickening takes place subsequent to the establishment of the initial lamellar thickness l_g^*, as is apt to happen at high crystallization temperatures, the observed lamellar thickness will appear to drop in stepwise fashion as $l_0/2 \to l_0/3$ at ΔT^*_2, etc., with increasing ΔT (dotted lines in Figure 1, lower diagram).

(22) Lauritzen, J. I., Jr.; Passaglia, E. *J. Res. Natl. Bur. Stand. Sect. A*: **1967**, *71A*, 261.
(23) Hoffman, J. D.; Frolen, L. J.; Ross, G. S.; Lauritzen, J. I., Jr. *J. Res. Natl. Bur. Stand., Sect. A*: **1975**, *79A*, 671.
(24) Hoffman, J. D., to be submitted.
(25) Hoffman, J. D. *Polymer* **1983**, *24*, 3.
(26) Hoffman, J. D. *Polym. Commun.* **1986**, *27*, 39.
(27) Ungar, G.; Stejny, J.; Keller, A.; Bidd, I.; Whiting, M. C. *Science (Washington, D.C.)* **1985**, *229*, 386.

Freezing/Melting Transition of Polymer Chains on the Diamond Lattice

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ABSTRACT: A Monte Carlo simulation of polymer chains with gauche/trans energy differences was carried out on the diamond lattice. The Flory mean-field lattice theory predicts a first-order phase transition for such a system. However there has been recent speculation that this could be an artifact of the mean-field approximation. In the present calculation the lattice was fully occupied and Mansfield's method for generating allowed moves via bond breaking/reformation was utilized. It was found that a freezing/melting transition does take place. It appears to be clearly first order. The melting point and the conformational composition of the disordered state are in good accord with the predictions of the mean-field lattice theory (in the Huggins occupational probability approximation).

Lattice calculations have long formed a convenient basis for assessing the statistical properties of polymer chains. One of the more interesting applications was a treatment by Flory[1] of conformationally "stiff" chains (e.g., chains possessing conformational energy differences). With the use of a random approximation for site occupational probabilities, it was found that the partition function factors into a term arising from packing on the lattice and a conformational term identical with that of a free chain. It was demonstrated that this model exhibits a first-order melting/freezing transition. This arises because in the lattice representation of the disordered state, the conformation free energy (which increases with decreasing temperature), can no longer offset the positive free energy of packing. The total free energy becomes positive and thus the zero free energy ordered crystalline state becomes more stable. The model, when generalized to include the second-order conformational energy effects, has been used to discuss the role of polymer conformational structure on the thermodynamics of melting.[2,3]

Recently the model has been the subject of renewed interest. New statistical mechanical arguments have been advanced that have led to questioning the existence of such a transition.[4-6] These arguments and the model in general have recently been discussed by Nagle et al.[7] The case for the prediction of a first-order transition has been reiterated by Flory.[8] Monte Carlo simulations have contributed to clarifying the situation. Baumgaertner and Yoon[9] carried out a simulation on the plane square lattice and found a first-order transition. The quantitative results were not in particularly good agreement with the model predictions, and it has been commented[10] that the results (presumably due to finite system size effects) do not satisfy known bounds. Later Yoon and Baumgaertner reported a simulation on the cubic lattice[11] that showed a transition and gave better agreement with the mean-field model predictions.

The Monte Carlo lattice simulations use periodic boundary conditions with a number of elementary unit cells of the lattice filling a super unit cell or "box". The chains to be simulated are placed in the box and the latter is replicated to approximate an infinite system. In the above simulations,[9,11] Baumgaertner and Yoon used reptation as the move and this was allowed by the presence of a small number of vacant lattice sites. The chain lengths chosen were nearly the linear size of the box. Baumgaertner[12] has reported simulations on both the plane square and cubic lattices where the chain size was much smaller that the box size. Here it was found that at low temperature the system orders into domains of parallel extended chains whose boundaries are defined by surfaces composed of chain ends. The orientation of chain direction from domain to domain was disordered. In other words, the system became polycrystalline with crystallite thickness determined by chain length. However, the chain-ordering process was gradual with decreasing temperature; no transition was found. The disordering due to multiple orientations of the domains apparently was sufficient to prevent it. Since there is no energy penalty associated with surface formation it is apparent that domains whose orientations are disordered can easily have lower free energy than a completely ordered system. However, it seems equally apparent that as the chain size is allowed to increase the contribution of the domain-directional disordering to the free energy on a per bead basis would become small compared to that from the internal chain conformations. The transition would reappear in a really large simulation (presently impractical) of long chains and with box size even much larger and in which the bulk free en-

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