(10) Weiss, G. H.; Rubin, R. J. *Adv. Chem. Phys.* **1983**, *52*, 363.
(11) Weiss, G. H.; DiMarzio, E. A.; Gaylord, R. J. *J. Stat. Phys.*, in press.
(12) Carslaw, H. S.; Jaeger, J. C. "Conduction of Heat in Solids", 2nd ed.; Clarendon Press: Oxford, 1959; p 360.
(13) Gaylord, R. J. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1985**, *26* (2), 41 and ref 6 have also obtained these $\phi(t)$, $G''(\omega)$ relations using a different approach in which $\phi(t)$ is given by the probability function $[\int_t^\infty F(t)\,dt]$ where $F(t)$is the first-passage time probability density for a CTRW.

Communications to the Editor

Simple Criterion of the Applicability of the Hoffman–Lauritzen Theory of Crystal Growth: A Comment on Hoffman's Paper (*Macromolecules* 1985, *18*, 772)

Five years ago, in a paper with Kovacs[1] on the kinetics of growth of extended-chain and folded-chain crystals of poly(ethylene oxide) fractions, we showed that one cannot consider the deposition of the first stem of a secondary nucleus as a single stage. There are major objections[2] to such a postulate; the large free energy barrier pertaining to the deposition of a full first stem, well illustrated in Figure 1 of Hoffman's paper,[3] leads to an overestimate of both the kinetic length[4] $(2g/i)^{1/2}$ and the substrate completion rate g.

In his paper,[3] Hoffman makes the suggestion of the "presence in poly(ethylene oxide) of a mode of growth very different from that which occurs in the corresponding hydrocarbons", and in his analysis of the data of Leung, Manley, and Panaras[5a] for polyethylene fractions he reaches conclusions quite different from the above, despite the fact that, for the samples studied, molecular weight and polydispersity of both the poly(ethylene oxide) fractions and the polyethylene fractions were quite similar.

In contradistinction, on the basis of a comprehensive analysis of the data of Leung et al., we maintain the need to postulate a surface nucleation model where the surface nucleus builds up piecemeal by successive addition of parts of stems of molecules. Such models have been described previously.[9,10]

We suggest here a definitive scheme of coordinate experiments and calculations to decide in any circumstance the applicability of the Hoffman–Lauritzen (H–L) theory, and we illustrate this option in a new analysis of the data of Leung et al.[5a] When extended-chain growth rate data are considered, Hoffman[3] bases his conclusion solely on a numerical agreement between predicted and experimental values of G. In contradistinction, we propose to calculate also the initiation rate i, the rate of lateral spreading of a secondary nucleus g, the kinetic length $L_k = (2g/i)^{1/2}$, and the area A_n of the nucleation site for a full stem. Then we recall that not only G but also the kinetic length $L_k = (2g/i)^{1/2}$ may be measured[8] (or at least bounded) by a study of the dependence of the growth rate on the size of the involved facet. Finally we propose to compare the theoretical estimates of G and L_k with the experimental vallues (or bounds) for these quantities and in addition to discuss if both the values of g (see also Simon et al.[11]) and A_n are reasonable or unrealistic. The most innovative part of our proposal is a critical comparison of the experimental value of L_k (or of experimental bounds for this quantity) with its theoretical estimate. The way to measure L_k is fully discussed elsewhere[8] and a way to bound it is given below. Clearly, an efficiently decisive criterion for the validity of the theory is obtained when data pertaining to different chain lengths are available, as shown in our paper with Kovacs.[1]

We apply now our procedure to an analysis of the data of Leung et al.[5a] on a polyethylene fraction (denoted 3100) whose number-average molar mass, 2.9×10^3, corresponds to C-207 and where $M_w/M_n = 1.07$. Our analysis is in fact an extension of that given by Hoffman[3] but includes the calculation and examination of the values obtained for L_k, g, and A_n. The calculation of L_k is made from eq 42.c and 13 of Hoffman's paper

$$iL_p^2/4g = C_0ns^2/4[A_0/A]$$

$$L_p = n_sa_0$$

from the expressions for A_0 and A (footnote 11 of the same paper), and from the following figures: $C_0 = 10^4$, $\sigma'_1 = 0$, $\sigma = 76$ erg/cm^2, $l_x = 2.629 \times 10^{-6}$ cm, $\sigma(1 - \gamma) = 10.52$ errg/cm^2, and $T_0 = 86.6$ °C. From the inequality $\psi\gamma W\Delta T > 0$, we obtain for $T_c = 81$ °C

$$L_k = (2g/i)^{1/2} > [2a_0^2/C_0\{\exp(-2a_0b_0\sigma'/kT)\} \times \exp(2b\sigma(1-\gamma)l_x/kT)]^{1/2} = 0.55 \text{ cm} \quad (1)$$

We conclude, as Hoffman did, that his theory implies that crystallization occurs definitively in regime I. The calculation of i and g is performed from the experimental value[5] for the growth rate at 81 °C ($G = 1.25 \times 10^{-7}$ cm/s) and from Hoffman's estimate of the persistence length L_p:

$$i = G/bL_p = 3 \times 10^4 \text{ cm}^{-1} \text{ s}^{-1} \quad (2)$$

$$g = iL_k^2/2 > 4.58 \times 10^3 \text{ cm/s} \quad (3)$$

The value of A_n area of a nucleation site for a full stem comes from the C_0 value:

$$A_n = a_0l_x/C_0 = 1.2 \times 10^{-17} \text{ cm}^2$$

The experimental bounds for L_k and L_p are obtained from the following consideration. As widely recognized[6] and discussed extensively elsewhere,[8] the growth rate of crystals smaller than both the persistence length and the kinetic length cannot be a constant. But Leung et al.[5] find for crystal size smaller than 1000 nm a *decrease* of the growth rate. We are, thus, forced to conclude that either $L_k \ll 10^{-4}$ cm or $L_p \ll 10^{-4}$ cm or both. Hoffman's analysis performed on the basis of the H–L theory leads to $G_{calcd} = G_{exptl}$, $L_p = 10^{-4}$ cm, $L_k = 0.55$ cm, $g > 4.58\ 10^3$ cm/s, and $A_n = 1.2 \times 10^{-17}$ cm^2; then L_p or L_k or both are too large. The value of A_n is much too small and the value of g is far too large to be credible.[7] Let us consider this last point in some detail. According to Hoffman, when crystallization at 81 °C from the 0.001 wt % solution is considered, coverage of the hypothetical persistence length by *attachment* of 2200 molecules would occur in 0.14 μs. But in this time interval, even *in a gas phase* (with the same number of molecules per unit volume) only 82 molecules *hit* the concerned part of the surface of the crystal. This

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is an overestimate, since adsorption occurs when the molecules strike the surface. (Such an adsorption would imply a partial exhaustion of the solution in the vicinity of the crystal and a decrease of the flux of molecules incident to the growth facet.) Moreover, the calculation is for the number of molecules that hit the surface and not for the number of molecules that are adsorbed and diffused to the growth step in a very short time. The apparent agreement claimed by Hoffman between the predicted and experimental values of G relies on the introduction of various arbitrary parameters in the expression of G. More particularly, one may notice C_0 and the empirical concentration factor $c^{0.4}$, which cannot have physical meaning because it depends on the units in which c is expressed. For the sake of completeness, we observe with Hoffman[3] that origin and estimation of C_0 are challenges that still confront his theory, and we examine thus the effect of other choices for C_0 and L_p.

In the picture given by Hoffman the area of a nucleation site for a full stem is very small (1.2×10^{-17} cm^2). Accordingly, Hoffman accepts that C_0 may have lower values. But the effect of choosing $C_0 < 10^4$ is to increase the value of g (eq 1 and 3). Similarly, choice of a lower value of L_p leads to an increase of calculated value for g (eq 2 and 3). As an example, if we choose $C_0 = 10^2$, $\sigma(1 - \gamma) = 9.42$ erg/cm^2, and $L_p \leq 10^{-4}$ cm, we get $G_{calcd} \leq G_{exptl}$, $L_k > 0.47$ cm, $g > 3.32 \times 10^3$ cm/s, and $A_n = 1.2 \times 10^{-15}$ cm^2. The values of g and A_n are again too large and too small, respectively.

We examine now the origin and significance of these incorrect predictions. The incoherence comes from overestimation of $(2g/i)^{1/2}$, which is a direct consequence of the occurrence of the factor $\exp(2b\sigma(1-\gamma)l_x/kT)$ on the right-hand side of eq 1. This factor represents the effect of the large free energy barrier associated with the deposition of a full first stem. As shown in our paper with Kovacs,[1] the barrier may be lowered *fictitiously* by assuming *formally* low values of σ, but far too low to be credible. The way to escape this paradox has previously been given:[9,10] the nucleus must be assumed to build up piecemeal by successive addition of parts of the first stem. In this way we get a free energy barrier expressed by $2b\sigma\Delta l$, in which Δl is much smaller than $l_x(1 - \gamma)$. From my point of view[1,2,8] the same basic objection may be formulated as a concern in the application of the H–L theory to growth of folded-chain crystals.

Two very simple criteria have been used throughout this work and are of general applicability: (i) If the growth rate does not increase with the crystal size, L_p, L_k, or both are smaller than the crystal size. In most cases this leads to the conclusion that only the polynucleation regime is plausible. (ii) The estimation of the order of magnitude of both g and A_n is very illuminating. Often this simple calculation rules out the applicability of the H–L kinetic theory of crystal growth unless the nucleation term is modified as explained above. If this modification is made, the limitation of the thickness of folded-chain crystals does not result from a free energy balance pertaining to a full fold length.[9]

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References and Notes

(1) Point, J. J.; Kovacs, A. J. *Macromolecules* **1980**, *13*, 399.
(2) Point, J. J. *Discuss. Faraday Soc.* **1979**, *68*, 167.
(3) Hoffman, J. D. *Macromolecules* **1985**, *18*, 772.
(4) Frank, F. C. *J. Cryst. Growth* **1971**, *22*, 233.
(5) (a) Leung, W. M.; Manley, R. St. J.; Panaras, A. R. *Macromolecules* **1985**, *18*, 760. (b) Manley, R. St. J., personal communication.
(6) Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I., Jr. In "Treatise on Solid State Chemistry"; Hannay, N. B., Ed.; Plenum Press, New York.
(7) When crystallization occurs from the melt, a large value of g may be plausible according to Hoffman (private communication).
(8) Point, J. J.; Colet, M. C.; Dosiere, M. *J. Polym. Sci.*, submitted.
(9) Point, J. J. *Macromolecules* **1979**, *12*, 770.
(10) DiMarzio, E. A.; Guttman, C. M. *J. Appl. Phys.* **1982**, *53*, 6581.
(11) Simon, B.; Grassi, A.; Boistelle, R. *J. Cryst. Growth* **1974**, *26*, 77.

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CP/MAS ^{13}C NMR Spectroscopy of Hydrated Amyloses Using a Magic-Angle Spinning Rotor with an O-Ring Seal

Many kinds of synthetic and naturally occurring polymers have been examined by cross-polarization/magic-angle sample spinning (CP/MAS) ^{13}C NMR spectroscopy. However, most of these measurements have been performed in the dry state and only a few reports[1-3] have been published on polymers containing some water. A major obstacle in the application of this form of spectroscopy to such hydrated polymers is that the large centrifugal force produced by rapid spinning readily removes water from samples packed in a conventional MAS rotor. We have recently developed a new rotor with an O-ring seal by modifying a commercial bullet-type rotor. This type of rotor can be steadily rotated at a rate of 3–4 kHz without practical loss of water for samples with any water content. Its high performance is sufficiently good, even for 1-week measurements, that ^{13}C spin–lattice relaxation times, T_1, which are normally of the order of 10–1000 s for crystalline components of polymers, can also be obtained.

In this communication we report CP/MAS ^{13}C NMR studies of corn and potato starches with different water contents. These two samples have different crystalline forms defined as A- and B-amyloses, respectively, which are assumed to be identical in molecular conformation but to differ with respect to the packing of the helical chains.[4,5] In addition, water molecules are arranged in different ways for the two forms. Therefore, CP/MAS ^{13}C NMR measurements in hydrated forms are essential for those samples to characterize the detailed molecular conformation and chain dynamics.

The MAS rotor shown in Figure 1 was machined from poly(chlorotrifluoroethylene), Daifuron (Daikin Co. Ltd.), which was annealed in advance at temperatures above 195 °C. This sort of annealing was necessary to improve the long-term stability of the spinning. An O-ring made of nitrile rubber with carbon black was used, since there was no appreciable contribution from this material in the spectra. CP/MAS ^{13}C NMR measurements were carried out with a JEOL JNM-FX200 spectrometer equipped with a CP/MAS unit operating under a static magnetic field of 4.7 T. The spinning rate was 3.2–3.5 kHz for both dry and hydrated samples. ^{1}H and ^{13}C radiofrequency field strengths $\gamma B_1/2\pi$ were 69 kHz for the CP process, while the ^{1}H dipolar decoupling field was set to 54 kHz. The contact time was 2.0 ms throughout this work. The chemical shifts relative to tetramethylsilane (Me$_4$Si) were

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