polymer concentrations and why the effect should be independent of the chain length of the added polymer. At this stage, more is to be gained by a candid expression of our lack of understanding than by the proposal of an interpretation which may fit only part of the data.

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Theory of Copolymer Crystallization

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ABSTRACT: A theory of the crystallization of copolymers of A and B reveals that they do not achieve an equilibrium composition. Rather, the fraction of B is determined by kinetic considerations. The kinetic theory employed is that of Lauritzen, DiMarzio, and Passaglia. Specific attention is devoted to the case where B is in low concentration, and there are positive free-energy terms associated with the incorporation of B into the lattice. Qualitatively one finds that as conditions and parameters are varied, the faster the crystal growth, relative to the equilibration processes, the greater is the inclusion of excess B. A few numerical results have been worked out with results which vary from a fewfold to manyfold excess of B concentration over equilibrium predictions.

I. Introduction

The nature of polymer crystals can be profoundly affected by rather small amounts of coconstituents (in the form of comonomers, stereoisomers, branches, chain ends, etc.). In this paper we shall consider copolymer crystals, and demonstrate that their composition is kinetically controlled. The role of kinetics in determining the properties of polymer crystals is amply attested to by previous experimental and theoretical studies. Furthermore, we now have faith in the ability of a fairly simple mathematical model to simulate the observed behavior.[2a,b]

By "kinetic control" of properties we mean that various states of the crystal are not found in equilibrium concentration. Rather, they are present in proportions which reflect the rates at which these states are added to the crystal, detach from the crystal, and eventually are trapped in the crystal. Specifically, consider a sequential growth process; *i.e.*, growth of a sequence by addition and detachment of elements only at the end of the line. An example is the case of interest: lamellar crystal growth by addition onto a substrate of a portion of a polymer chain, followed by a fold, addition of another portion, etc. These portions of polymer chains added to the crystal are called stems. The developing sequence of stems forms a strip of crystal which we call the growth strip. Eventually this strip will serve as a substrate for deposition of the next strip of stems, and thus is built up the lamellar polymer crystal.

Consider that each growth element (the stem) can be in one of several states (here, the comonomer content of the stem). When a stem is added, the initial probability distribution function for its states will be a reflection of the forward rate constants. The faster the rate constant for addition of a stem in a given state, the more likely that state is to appear. Now a process begins which brings the population toward equilibrium. The stem just added may dissociate, and the states which dissociate most rapidly have a decreased representation in the distribution. The gist of the law of detailed balance is that the ratio of forward to backward rate constants must be such as to ensure that infinite repetition of the addition–dissociation process leads to an equilibrium probability distribution. If, however, the process is interrupted, equilibrium concentrations will not be achieved. In the present case of sequential growth this interruption will occur if the stem in the end position, upon which we have been focusing attention, is covered. Maybe the cover will detach and allow the equilibration to proceed, but eventually the cover will be covered, and so on. Then the distribution of states for this stem is fixed, short of equilibrium. Thus the role of forward and reverse rate constants, as well as time available for equilibration (as reflected in growth rates), is clarified.

A quantitative theory of kinetically controlled, sequential processes was devised by Lauritzen, DiMarzio, and Passaglia (LDP).[2b] Their technique, outlined in section III, is general enough to handle the features which appear necessary in a description of copolymer crystallization. An innovation is that we treat the equations in a self-consistent, rather than explicit, manner, in order to account, in what we believe to be good approximation, for the effect of the substrate's state on the growth rate.

To apply the LDP theory, rate constants for the crystal growth and dissolution processes must be provided. The physics of the crystal growth model is translated into these rate constants in section IV.

For the present study we envision the process of copolymer crystal growth as follows. The basic model is the familiar one employed in the homopolymer theory. Stems, *i.e.*, portions of chains, each n monomer units long, are added sequentially onto a substrate to build up a lamella. After each stem of n units is completed, the macromolecule folds back and attaches another stem of n. The fold free energy, Q_f, includes contributions dependent on the energy of making the fold, the distribution of loop sizes, and the composition. Its determination is a problem separate from that being considered here.

To treat the A–B copolymer problem, within the context of the present model, we must specify the number of B units in each stem. (A more complete and accurate theory can be constructed if one specifies the location of each B in the stem, but such a theory is numerically intrac-

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†The order of the authors was settled in a poker game.

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(2) (a) J. I. Lauritzen, Jr., and J. D. Hoffman, *J. Res. Nat. Bur. Stand.*, **64**, 73 (1960). (b) J. I. Lauritzen, Jr., E. A. DiMarzio, and E. Passaglia, *J. Chem. Phys.*, **45**, 4444 (1966). This is referred to as LDP.

table.) As each monomer unit enters the crystal the free energy is lowered by an amount ΔF_0. However the inclusion of a B unit, instead of an A, costs a free energy ϵ, generally much greater than ΔF_0. The B's not only modify the thermodynamic properties, but also profoundly effect the kinetic barriers to crystal growth and decay. A realistic picture should recognize that the free-energy price, ϵ, is paid in several parts. We will assume a three-installment model. The first energy, ϵ_1, is collected immediately upon addition of the B unit in the crystal growth niche. When the next stem attempts to pass the position of this B a toll ϵ_2 is exacted. Finally, this B becomes part of the substrate, and when a new stem of the growth strip is placed on top the cover charge is ϵ_3. (We will not bother to divide ϵ_3 into two parts for hexagonal crystals.)

Some pictures will help to clarify the situation. Figure 1 is a schematic of the growing crystal with locations of B's in the substrate and growth strip indicated. Figure 2 depicts part of the free energy of the system as stems are deposited. The first section represents the large nucleation barrier to initiation of a new growth strip by addition of the first stem onto the substrate. The barrier is largely due to the new lateral surface this stem exposed. Subsequent stems, on average, lower the free energy. If the polymer contained no B's the free energy on adding the second stem would follow the dotted curve. Owing to addition of B's, as well as covering of previous inclusions, the free-energy well does not sink as deeply. If follows that the barrier to back-reaction (*i.e.*, detachment of the stem) is lower when more B is included and covered. Also indicated in the diagram are the barriers to addition of stems due to the fold free energy.

As we shall see, there is an important entropic factor which enters into the expression for the forward rate constant for crystal growth. This is associated with the probability distribution for the number of B's contained in the stem which presents itself for addition. Its effect is not included in the schematic.

The section of the free-energy curve (Figure 2) which pertains to the fourth stem illustrates one of the complications which may occur. Here the fold free energy is not the top of the barrier. We also see in this section that the end of the stem need not be the bottom of the well. The net result is to make the beginnings and ends of the stems conform more closely to equilibrium statistics. These effects can be included in the kinetic equations, but the computations become overwhelming. We are considering an approximate way of treating this situation. For now, we prefer not to introduce a major complication which will probably lead to only a minor correction.

In section V the crystal growth equations are solved analytically in the limit of total exclusion of B. Some of the features of copolymer crystallization are insensitive to this specialization, so much is learned.

In section V one finds the numerical results of calculations when B can be included, but at a free-energy price. Typical values for the parameters are employed, and attention is restricted to rather low concentration of B in the amorphous phase, 1 or 2%.

Qualitative features which emerge are the following. (1) The concentration of B in the crystal is significantly greater than is predicted by equilibrium theory, commonly many times larger. As a consequence, the crystals may be expected to melt at a lower temperature than predicted by equilibrium melting point depression theory, even accounting for the effect of finite lamella thickness.

(2) Such changes in parameters that tend to speed up the growth process relative to the equilibration process (*i.e.*, increase the crystallization driving force) lead to larger excess inclusion of B.

(3) The temperature influences the process in two ways. First, all energies and barriers are divided by kT. An even more significant effect is the temperature dependence of ΔF_0, which we take as that appropriate near the melting point

$$\Delta F_0 = (\Delta H_f / T_m{}^\circ)(T_m{}^\circ - T) \qquad (1.1)$$

Here $T_m{}^\circ$ and ΔH_f are the melting point and heat of fusion of the pure crystal, respectively. Decreasing temperature increases nonequilibrium inclusion of B.

(4) The copolymer lamellae must be thicker than pure ones, the extra thickness being necessary to compensate for the free-energy increment associated with the impurities. A major consequence is that the overall crystal growth rate is much slower for copolymer crystals.

These descriptive conclusions are based on a presupposed negligible change in the surface free energy with varying temperature and composition, and would need modification should this not be the case.

An example of a system for which the present theory seems appropriate is lightly chlorinated polyethylene. Crystals of such a material have been investigated recently by Roe, Cole, Morrow, and Gieniewski.[3] Another interesting case is polyisoprene, studied by Andrews, Owen, and Singh.[4] Trans isomers are the impurities in the predominantly cis polymer.

II. Equilibrium Theory

We have indicated that if crystal growth is slow enough, equilibrium concentrations of copolymer units will be achieved. What these equilibrium concentrations are will be determined in this section.

Actually, the most naive argument produces the correct result. Consider a polymer with a fraction x of B units, and a fraction $(1 - x)$ of A. The free-energy change upon incorporating an A into the crystal is $-\Delta F_0$, while that of incorporating a B is $-\Delta F_0 + \epsilon$. According to equilibrium statistical mechanics the ratio of B to A in the crystal is

$$xe^{-\beta\epsilon}/(1 - x)$$

where

$$\beta = 1/kT$$

Then the fraction, c^{eq}, of B in the crystal is

$$c^{\text{eq}} = \frac{xe^{-\beta\epsilon}}{(1-x) + xe^{-\beta\epsilon}} \qquad (2.1)$$

The connectivity of the chain, the thickness of the lamella, and the crystal growth model do not influence the result. Nevertheless, it is instructive to derive the formula from an argument which recognizes the polymer crystal picture.

Consider an n-monomer stem of random copolymer. The probability that m units are B's is given by the binomial distribution

$$\mu(m) = [n!/m!(n-m)!]x^m(1-x)^{n-m} \qquad (2.2)$$

(We do not explicitly display in the notation the n or x dependences of $\mu(m)$, nor of many other functions in this paper.) When incorporated in the crystal the energy of this stem, relative to the amorphous phase, is

$$-n\Delta F_0 + m\varepsilon + Q_f$$

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(3) R.-J. Roe, H. F. Cole, and D. R. Morrow in "Advances in Polymer Science and Engineering," K. D. Pae, D. R. Morrow, and Y. Chen, Ed., Plenum Press, New York, N. Y., 1972. R.-J. Roe and C. Gieniewski, *Macromolecules*, to be published.

(4) E. H. Andrews, P. J. Owen, and A. Singh, *Proc. Roy. Soc., Ser. A*, **324**, 79 (1971).

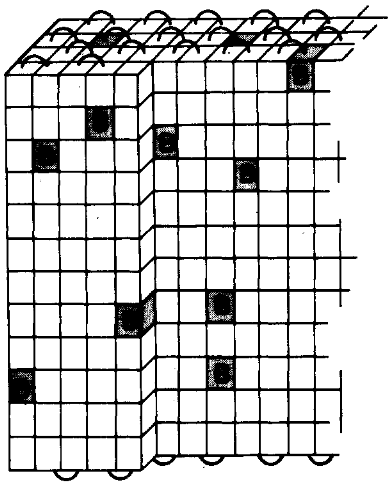

Figure 1. Schematic diagram of the polymer crystal, showing the deposit of growth-strip stems on a substrate.

with $\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3$. Therefore the probability of a stem in the crystal having m impurities is

$$\psi^{\mathrm{eq}}(m) = (1/Z)\mu(m) \exp[-\beta(Q_{\mathrm{f}} - n\Delta F_0 + m\epsilon)] \quad (2.3)$$

The partition function, Z, is

$$\begin{aligned} Z &= \exp[-\beta(Q_{\mathrm{f}} - n\Delta F_0)] \sum_{m=0}^{n} \mu(m) e^{\beta m\epsilon} \\ &= \exp[-\beta(Q_{\mathrm{f}} - n\Delta F_0)](1 - x + xe^{-\beta\epsilon})^n \end{aligned} \quad (2.4)$$

Equation 2.1 for the crystal fraction of B follows from

$$c^{\mathrm{eq}} = (1/n) \sum_{m=0}^{n} m\psi^{\mathrm{eq}}(m) \quad (2.5)$$

Since the result is independent of n, no average over lamella thickness need be taken.

We can define a free energy for inclusion of an average monomer in the crystal as

$$\Delta F(x) = \Delta F_0 + kT \ln (1 - x + xe^{-\beta\epsilon}) \quad (2.6)$$

and the free energy of the strip and fold relative to the amorphous phase is

$$-n\Delta F(x) + Q_{\mathrm{f}}$$

Stability demands that this free energy be negative, so that the lamellae must have thickness $n \geq n^*$, where

$$n^* = Q_{\mathrm{f}}/\Delta F(x) \quad (2.7)$$

On the other hand, the solution of the equation

$$n = n^*(T) \quad (2.8)$$

gives the highest temperature for which a lamella of thickness n is stable. The thermodynamic melting point, T_{m}, the melting point of an infinitely thick equilibrium crystal, is given by a standard melting point depression formula

$$\Delta H_{\mathrm{f}} \left(\frac{1}{T_{\mathrm{m}}} - \frac{1}{T_{\mathrm{m}}^{\circ}}\right) = -k \ln [1 - x + x \exp(-\epsilon/kT_{\mathrm{m}})] \quad (2.9)$$

III. Summary of the Lauritzen–DiMarzio–Passaglia Theory

The LDP theory[2b] deals with the general process of growth of a sequence made up of elements of various types, labeled i. In the present case of copolymer crystallization, where the development process depends on the state of the stems in the growth strip and the substrate, we allow the index i to stand for a pair of numbers. One is the number of B impurities in a stem of the growth strip, g_i; the other is the number of B's in the corresponding stem of the substrate, s_i. Thus $i \equiv (g_i, s_i)$.

The basic parameters in the LDP theory are rate constants. The rate of addition of an element of state j (a stem with g_j impurities on a substrate stem with s_j impurities) to a sequence ending in state i is called $\alpha(ij)$. The reverse "reaction" is detachment of an element j from a sequence ending i,j. The rate is $\beta(i,j)$.

Consider an ensemble of sequences of elements (stems) formed according to these kinetic laws, and containing a representative population of sequences ν elements long, $\nu = 1, 2, 3, \ldots$. LDP develop equations to calculate the steady-state value of the following quantities. (1) $N_\nu(j)$ is the number of sequences in the ensemble which are ν elements long, with the final element being in the state j. (2) $P_\nu(ij)$ is the number of sequences ν elements long, with the last element in state j and the penultimate element in state i. (3) $S_\nu(j)$ is the steady-state flux of sequences from $\nu - 1$ to ν elements in length, the νth element being in state j. We may also define $S_{2,\nu}(ij)$ as the flux of sequences from a $(\nu - 1)$st element which is in state i to a νth in state j. These two fluxes are related by

$$S_\nu(j) = \sum_i S_{2,\nu}(ij) \quad (3.1)$$

$S_{2,\nu}(ij)$ may be written as a difference between a forward and a reverse flux, related to the rate constants and population by

$$S_{2,\nu}(ij) = \alpha(ij)N_{\nu-1}(i) - \beta(ij)P_\nu(ij) \quad (3.2)$$

(5) The total flux, S_{T}, is given by

$$S_{\mathrm{T}} = \sum_j S_\nu(j) \quad (3.3)$$

In the steady state it is shown not to be a function of ν.

A proof is presented in LDP that at steady state the ratio of flux to occupation number is dependent only on terminal state (not on ν, or earlier states)

$$\frac{S_\nu(j)}{N_\nu(j)} = \frac{S_{2,\nu}(ij)}{P_\nu(ij)} = \lambda(j) \quad (3.4)$$

Consequently the $\lambda(j)$ satisfy

$$\lambda(i) = \sum_j \frac{\alpha(ij)\lambda(j)}{\beta(ij) + \lambda(j)} \quad (3.5)$$

The occupation numbers of sequences of length $\nu - 1$ and ν are related by

$$N_\nu(j) = \sum_i N_{\nu-1}(i) \frac{\alpha(ij)}{\beta(ij) + \lambda(j)} \quad (3.6)$$

an equation to be used in two ways. In the asymptotic limit, *i.e.*, large ν, $N_\nu(j) \rightarrow N(j)$ independent of ν; so

$$N(j) = \sum_i N(i) \frac{\alpha(ij)}{\beta(ij) + \lambda(j)} \quad (3.7)$$

Another statement of eq 3.7 is that $N(j)$ is a left eigenvector of the matrix

$$Y(ij) = \alpha(ij)/[\beta(ij) + \lambda(j)] \quad (3.8)$$

having the eigenvalue unity. The corresponding right eigenvector is $\lambda(j)$, according to eq 3.5. It is convenient to define a vector $C(j)$ proportional to $N(j)$, and normalized so that

$$\sum_j C(j)\lambda(j) = 1 \qquad (3.9)$$

i.e.

$$C(j) = N(j) / \sum_i N(i)\lambda(i) \qquad (3.10)$$

The statistical properties of this kinetically formed ensemble are determined by the fact that the fraction of type j elements present, $f(j)$, is proportional to the flux of j

$$f(j) = S(j)/S_{\mathrm{T}} \qquad (3.11)$$

By eq 3.3, 3.4, and 3.10 this can be reexpressed as

$$f(j) = C(j)\lambda(j) \qquad (3.12)$$

In LDP it is shown that the probability distribution of pairs is

$$f(ij) \equiv S(ij)/S_{\mathrm{T}} \qquad (3.13)$$

$$= C(i)\frac{\alpha(ij)}{\beta(ij) + \lambda(j)}\lambda(j) \qquad (3.14)$$

To complete the picture we must discuss the procedure for calculating the total flux, S_{T}. Since S_{T} is independent of ν, its value is set by the initiation process for new sequences. Here it may be necessary to supply more information, such as rate constants $\alpha_1(j)$ for the formation of new sequences by deposition of element j, and $\beta_1(j)$ for the return of this first element back to the pool. Also needed are the numbers $N_0(j)$ describing the population from which the elements are drawn. Then S_{T} is

$$S_{\mathrm{T}} = \sum_j S_1(j)$$

$$= \sum_j N_1(j)\lambda(j) \qquad (3.15)$$

the latter by eq 3.4. For $N_1(j)$ there is a form of eq 3.6 appropriate to $\nu = 1$; so

$$S_{\mathrm{T}} = \sum_i N_0(j)\alpha_1(j)\lambda(j)/[\beta_1(j) + \lambda(j)] \qquad (3.16)$$

In section IV we will show that it is possible and easier to apply eq 3.15 directly to calculate S_{T}.

This summary of LDP is all too brief, but the meaning of the terms should become clearer as we discuss them in the context of the copolymer crystallization problem.

IV. Copolymer Crystallization

In the Introduction the model of crystal growth by stem addition was described. The energies involved in incorporating in the crystal monomers units of A or B, in covering B's, and in forming folds were defined. It was stated that all quantities would have to be indexed with integers representing the number of impurities in the growth-strip stem, g_j, and in the substrate stem, s_j. Actually, another required index is n, the number of monomer units in a stem, *i.e.*, the lamella "thickness." Since we will consider n to be a constant throughout the growth process of a single lamella we may leave it implicit, carry out all calculations for each fixed n, and average, in appropriate fashion, as a last step.

Now we must translate the copolymer crystal model into expressions for the required rate constants. The forward rate $\alpha(ij)$ for going from state g_is_i to g_js_j is composed of several factors

(1) The first is the binomial distribution, $\mu(g_j)$, which express the probability that the stem presenting itself has g_j impurities (*cf.* eq 2.2).

(2) The second is the probability $p(s_j|s_i)$ that the substrate, where the stem is to be added, has s_j impurities, given that there were s_i in the previous substrate stem. A self-consistent equation for $p(s_j|s_i)$, eq 4.13, will be developed, as a good approximate means of handling the two-dimensional statistical aspect of crystal growth.

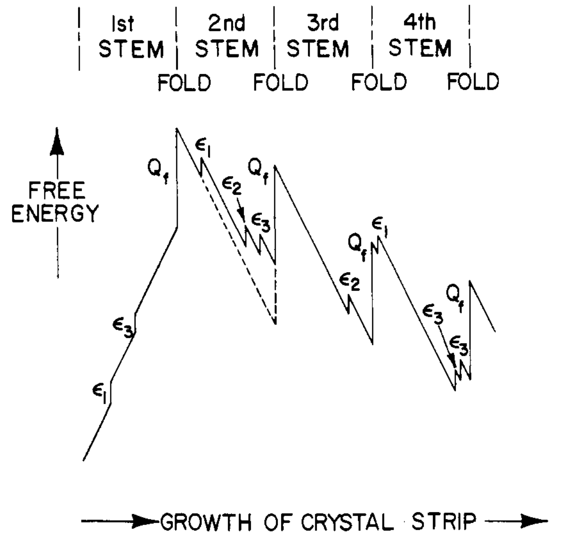

Figure 2. Schematic diagram of the free energy as monomer units are added to the crystal's growth strip.

(3) The energy barrier to the process of depositing a new stem is the fold free energy, Q_f. Thus there is a factor of $\exp(-\beta Q_f)$.

(4) Finally there is a basic rate constant, α_0, which reflects the fundamental rate of the molecular processes involved in fold formation. It's value establishes the time scale, but does not enter into the final expression for the composition.

Collecting these factors, the forward rate constant is

$$\alpha(g_is_i, g_js_j) = \alpha_0\mu(g_j)p(s_j|s_i)\exp(-\beta Q_f) \qquad (4.1)$$

The rate constant for detachment of a stem with g_j impurities from a substrate stem with s_j impurities, when the previous state is g_is_i, also contains the basic rate parameter α_0. The activation barrier in the absence of impurities would be $n\Delta F_0$, the crystal stabilization energy. However, the impurities raise the depth of the well, *i.e.*, decreases this barrier, by $g_j\epsilon_1 + g_i\epsilon_2 + s_j\epsilon_3$. The backward rate constant is thus

$$\beta(g_is_i, g_js_j) = \alpha_0 \exp[-\beta(n\Delta F_0 - g_j\varepsilon_1 - g_i\varepsilon_2 - s_j\varepsilon_3)] \qquad (4.2)$$

We can write the LDP eq 3.5 for the λ's of the present model as

$$\lambda(g_is_i) = \sum_{g_js_j} Y(g_is_i, g_js_j)\lambda(g_js_j) \qquad (4.3)$$

$$Y(g_is_i, g_js_j) = \frac{\alpha_0\mu(g_j)p(s_j|s_i)\exp(-\beta Q_f)}{\alpha_0\exp[-\beta(n\Delta F_0 - g_j\epsilon_1 - g_i\epsilon_2 - s_j\epsilon_3)] + \lambda(g_js_j)} \qquad (4.4)$$

The corresponding left eigenvector of Y satisfies the equations

$$C(g_js_j) = \sum_{g_is_i} C(g_is_i)Y(g_is_i, g_js_j) \qquad (4.5)$$

$$\sum_{gs} C(gs)\lambda(gs) = 1 \qquad (4.6)$$

Once the C's and λ's are known the probability for s impurities in the substrate stem and g in the growth-strip stem is

$$f(gs) = C(gs)\lambda(gs) \tag{4.7}$$

while the probability of an adjacent pair (g_is_i,g_js_j) is

$$f(g_is_i,g_js_j) = C(g_is_i)Y(g_is_i,g_js_j)\lambda(g_js_j) \tag{4.8}$$

We will be interested in the probability distributions of impurities in the substrate, which we can determine by summing over the growth-strip variable. Thus, the probability of a stem with s impurities in the substrate is

$$f_s(s) = \sum_g f(gs) \tag{4.9}$$

Similarly, the probability of a stem with g impurities in the growth strip is

$$f_g(g) = \sum_s f(gs) \tag{4.10}$$

and the probability of adjacent stems in the growth strip with g_ig_j is

$$f_g(g_i,g_j) = \sum_{s_is_j} f(g_is_i,g_js_j) \tag{4.11}$$

The theory still contains the undetermined function $p(s_j|s_i)$, the conditional probability that the stem to be added to the growth strip encounters a substrate stem with s_j impurities, given that the previous stem of the substrate had s_i impurities. It must be recognized that the substrate stem with s_j impurities about which we are speaking is uncovered at the time we need its probability distribution, so that its statistics are those characteristic of a growth strip. The conditional distribution, p, is determined as

$$p(g_j|g_i) \equiv f_g(g_i,g_j)/f_g(g_i) \tag{4.12}$$

$$= \frac{\sum\limits_{s_is_j} C(g_is_i)Y(g_is_i,g_js_j)\lambda(g_js_j)}{\sum\limits_{s_i} C(g_is_i)\lambda(g_is_i)} \tag{4.13}$$

(an implicit set of equations, since Y is linear in p), with normalization

$$\sum_{gj} p(g_j|g_i) = 1 \tag{4.14}$$

Equations 4.3–4.6 and 4.13 form the deterministic set of equations for the λ's, C's, and p's. We have had to solve them iteratively on the computer. (For conditions such that the fluxes are small, the λ's are small, p is near to its equilibrium value, and an explicit, first-order solution can be written.)

Once the equations are solved, the impurity statistics are known, but all this is only for one lamellar thickness n. The next task is to determine the fraction of the crystals which grow with a given n. According to the principle of kinetic control this fraction, $\varphi(n)$, is proportional to the flux for growth of lamella of thickness n

$$\varphi(n) = S_{\mathrm{T}n}/S_{\mathrm{T}} \tag{4.15}$$

$$S_{\mathrm{T}} = \sum_n S_{\mathrm{T}n} \tag{4.16}$$

We must return to the LDP theory to determine the fluxes. As indicated in section III that is done by considering the nucleation process for new strips on crystals of thickness n.

The first stem that is laid down on a substrate creates two new lateral surfaces, with associated surface free energy, σ, per unit area. If each monomer unit has length Δl, and width b, this unit, upon crystallization in the pure case, changes the free energy by an amount $-\Delta F_0 + \Omega$, where

$$\Omega = 2b\Delta l\sigma \tag{4.17}$$

When impurities, B, are present we must include the energy involved in incorporating and covering them, which we take to be the same in the first stem as in later ones.

Let us proceed by assuming that the first stem is in equilibrium with the mother liquor. Then the number of first stems of length n containing g impurities on substrate stems containing s impurities is

$$N_1(gs) = N_0\mu(g)f_g(s)\exp[-\beta(n\Omega - n\Delta F_0 + g\epsilon_1 + s\epsilon_3)] \tag{4.18}$$

N_0 is a parameter which sets the size of the ensemble, and does not effect the composition or statistical distribution. Second stems are added to these first stems in accord with the kinetic laws used earlier for processes further into the layer. Thus the flux of states gs begins as

$$S_1(gs) = N_1(gs)\lambda(gs) \tag{4.19}$$

and the total (conserved) flux for lamellar crystals of thickness n is

$$S_{\mathrm{T}n} = \sum_{gs} N_1(gs)\lambda(gs) \tag{4.20}$$

An assumption is involved in using an equilibrium distribution for the first stem, but it is usually correct. The assumption is that the time required to surmount any obstacle to the beginning of crystallization of this stem (such as diffusional limitations) is small compared with the time required to make a fold. More complex initiation can be handled in the standard manner of LDP, but that does not seem to be necessary here.

We now have formulas for the statistical characterization of impurity levels, so interesting averages can be calculated. For a given n one can determine the average fraction of impurities in the bulk of the crystal. Since no change in distribution occurs once substrate is covered, $f_s(m)$ is the probability of m impurities in an interior stem. The average number of B's in a stem of the crystal of thickness n is

$$\langle m\rangle_n = \sum_{m=0}^{n} mf_s(m) \tag{4.21}$$

The next step is to average over crystal thicknesses, which are distributed according to $\varphi(n) = S_{\mathrm{T}n}/S_{\mathrm{T}}$. The average lamella thickness is (in repeat units)

$$\bar{n} = \sum_n n\varphi(n) \tag{4.22}$$

Note, however, that a fraction $(n/\bar{n})\varphi(n)$ of the material is contained in lamellae of thickness n. It follows that the fractional B content of the crystal, c, is

$$c = \sum_n \langle m\rangle_n\varphi(n)/\bar{n} \tag{4.23}$$

V. A Special Case: Exclusion of B Units from the Crystal

The special case in which B units are noncrystallizable corresponds to the limit of ϵ_1, ϵ_2, ϵ_3 becoming infinite. Aspects of such a model have been treated Flory,[5] by Andrews, Owen, and Singh,[4] and by others. The solution of our equations, which can be obtained analytically, illus-

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(5) P. J. Flory, *Trans Faraday Soc.*, **51**, 848 (1955).

trates the dependences of the flux and mean thickness on parameters other than ϵ. This will provide insight into the phenomenon of excess impurity inclusion discussed in the next section.

According to eq 2.6 the free-energy change per inclusion of a monomer unit is

$$\begin{aligned} -\Delta F(x) &= -\Delta F_0 - kT\ln(1-x) \\ &= -\Delta H_f + T[(\Delta H_f/T_m^\circ) - k\ln(1-x)] \end{aligned} \tag{5.1}$$

Thus the entropy of fusion is increased by exclusion of B units from the crystal. The melting point, in the limit of infinite thickness, is depressed to

$$T_m = T_m^\circ\,[1 - (kT_m^\circ/\Delta H_f)\ln(1-x)] \tag{5.2}$$

Since no B units may be incorporated in the crystal, all $\lambda(gs)$ vanish except $\lambda(0,0)$, which by eq 4.3-4 is

$$\lambda(0,0) = \alpha_0\exp(-\beta n\Delta F_0)\{\exp(\beta[n\Delta F(x) - Q_f]) - 1\} \tag{5.3}$$

The result is only valid for positive growth rate which occurs when

$$n\Delta F(x) - Q_f > 0$$

or $n > n^*$, where

$$n^* = Q_f/\Delta F(x) \tag{2.7}$$

For the total flux of thickness n crystals we obtain

$$S_{Tn} = N_0\alpha_0(1-x)^n e^{-\beta n\Omega}\{\exp(\beta[n\Delta F(x) - Q_f]) - 1\} \tag{5.4}$$

The term within braces monotonically increases with n, while the prefactor decreases monotonically. For small or moderate undercoolings, S_{Tn} increases as n increases above n^*, goes through a maximum, and decreases.

The total flux proportional to crystal growth rate, is obtained by summing over all $n \geq n_m$; where n_m is the least-integer thickness which is stable

$$n_m = [n^*] + 1 \tag{5.5}$$

For this model the steady-state flux is

$$S_T = N_0\alpha_0(1-x)^{n_m}\exp(-\beta n_m\Omega) \times \left(\frac{\exp\{\beta[n_m\Delta F(x) - Q_f]\}}{1-(1-x)\exp\{\beta[\Delta F(x) - \Omega]\}} - \frac{1}{1-(1-x)\exp(-\beta\Omega)}\right) \tag{5.6}$$

For small and moderate undercoolings, where n_m varies essentially as $1/\Delta F(x)$, the factor $\exp(-\beta n_m\Omega)$ is the most important one, indicating that the flux is nucleation controlled.

In Figure 3, log S_T is shown plotted against $[T_m(x) - T]^{-1}$. The parameters have been chosen close to those appropriate for polyethylene

$$\begin{aligned} T_m &= 420^\circ\mathrm{K} \\ \Delta H_f/k &= 510^\circ\mathrm{K}\ (\Delta H_f = 1.0\ \mathrm{kcal/mol}) \\ \Omega/k &= 80^\circ\mathrm{K}\ \ (\Omega = 0.16\ \mathrm{kcal/mol}) \\ Q_f/k &= 2800^\circ\mathrm{K}\ (Q_f = 5.6\ \mathrm{kcal/mol}) \end{aligned} \tag{5.7}$$

The concentration of B units in the amorphous phase is taken as $x = 0.01$. For comparison the flux of pure polymer A at the same undercooling is pictured, too.

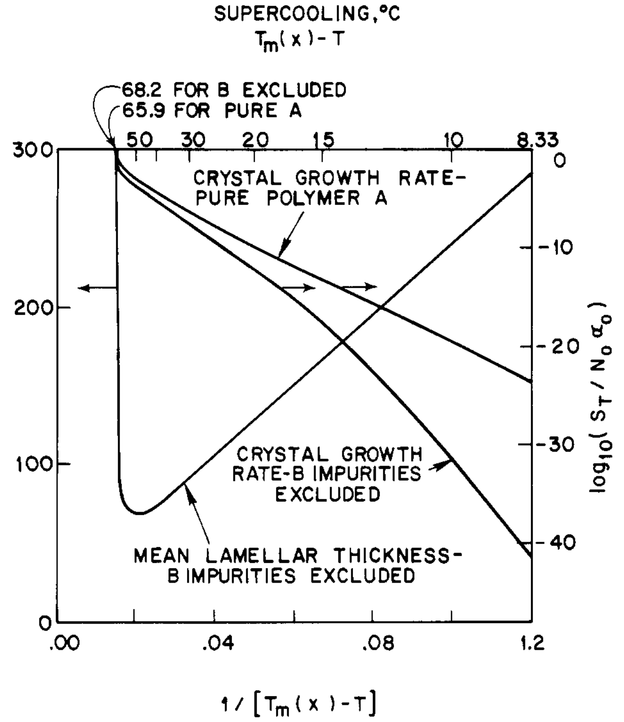

Figure 3. The variation with undercooling of mean crystal thickness and crystal growth rate in the case of total B exclusion. Also illustrated is the corresponding growth rate for pure polymer A crystals at the same undercooling (therefore not the same temperature).

The mean crystal thickness, $\bar{n}$, has been calculated, by eq 4.25. It is plotted *vs.* $[T_m(x) - T]^{-1}$ in Figure 3. Let us think of $\bar{n}$ as

$$\bar{n} = n^* + \delta n \tag{5.8}$$

At small supercooling $\bar{n}$ is very large, reflecting the large n^* required for stability; while δn is fairly small and relatively insensitive to temperature.

At high supercoolings the predicted behavior is quite different, but the forecast of the model is not verified experimentally.[6] As the supercooling increases the calculated $\bar{n}$ falls until it reaches a minimum. With further supercooling $\bar{n}$ rises until it blows up at a finite supercooling (for the given parameters, 348.35°K). At the same temperature the total flux in eq 5.6 diverges. This behavior the authors believe to be spurious. The rate constants and model are more appropriate for smaller undercooling. Nevertheless, most kinetic theories of crystallization exhibit this blowup.[2a,7-9]

The general dependence of S_T and $\bar{n}$ on the parameters x, Q_f, and Ω is not greatly changed when ϵ_1, ϵ_2, and ϵ_3 are finite.

If x increases, the equilibrium melting temperature, $T_m(x)$, decreases; so for a fixed crystallization temperature the supercooling is reduced. Thus the minimum stable thickness n^* is raised by the decrease in $\Delta F(x)$. The total flux, S_T, is decreased through the layer nucleation-barrier factor, $\exp(-\beta n_m\Omega)$, as well as other terms. Systems with a higher fold free energy, Q_f, likewise have a larger minimum stable thickness, which leads to a decreased flux.

If Ω is increased, S_T decreases through the term

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Table I
Calculated Characteristics of Copolymer Crystals[a]

Changes in Standard Set of Parameters	T	n^*	$\bar{n}$	δn	$S_T/N_0\alpha_0$	c/x (%)	c^{eq}/x (%)	c/c^{eq}
	400	136.8	149.0	12.24	7.45E-13	14.11	4.98	2.81
	393.84	100	113.1	13.13	1.81E-09	19.80	4.80	4.13
	380	62.3	78.5	16.18	7.66E-06	38.60	4.29	8.99
	360	40.4	75.9	35.56	2.68E-03	80.73	3.60	22.41
$Q_f/k = 3080°K$	393.84	110	123.2	13.24	2.21E-10	19.52	4.80	4.07
$\epsilon_1/k = 200°K$, $\epsilon_2/k = \epsilon_3/k = 500°$	393.84	100	113.4	13.36	4.06E-08	20.25	4.80	4.22
$\epsilon_2/k = 200°K$, $\epsilon_1/k = \epsilon_3/k = 500°K$	393.84	100	112.6	12.64	1.66E-09	17.92	4.80	3.65
$\epsilon_3/k = 200°K$, $\epsilon_1/k = \epsilon_2/k = 500°K$	393.84	100	113.5	13.55	1.89E-09	20.69	4.80	4.31
$\Omega/k = 60°K$	393.84	100	120.1	20.10	6.58E-07	28.09	4.80	5.86
$x = 0.02$, $Q_f/k = 2419.4°K$	393.84	100	112.9	12.86	6.31E-10	15.04	4.84	3.11
$x = 0.02$	390.75	100	113.6	13.61	6.93E-10	17.20	4.73	3.64

[a] The standard set of parameters is $T_m = 420°K$, $\Delta H_f/k = 510°K$, $\Omega/k = 80°K$, $Q_f/k = 2800°K$, $\epsilon_1/k = \epsilon_2/k = \epsilon_3/k = 400°K$, $x = 0.01$.

$\exp(-\beta n_m \Omega)$. Although n^* remains the same, $\delta n = \bar{n} - n^*$ decreases, since the effect of $\exp(-\beta n \Omega)$ in S_{Tn} is to kinematically constrain n to be closer to the minimal value.

VI. Inclusion of B in the Crystal

The full version of the theory is needed to determine the degree and consequences of inclusion of B impurities in the crystal. We shall attempt to illuminate these effects by exhibiting the results of several numerical examples. Again we use the parameters of eq 5.7, *i.e.*, parameters appropriate to pure polyethylene (with a bit of rounding of figures). Consider that growth occurs from an amorphous phase which has 1% of randomly copolymerized B units. We will take

$$\epsilon_1/k = \epsilon_2/k = \epsilon_3/k = 400°K$$

($\epsilon_i = 0.8$ kcal/mol). At equilibrium this leads to a melting point depression from 420°K to 416.75°K. We will calculate the characteristics of crystals grown at various temperatures. Then we will observe the changes as the parameters are varied one, or a few, at a time. The features to be examined are: (1) the minimum stable crystal thickness, n^*; (2) the mean crystal thickness, $\bar{n}$; (3) the total growth rate, in reduced units, $S_T/N_0\alpha_0$; and (4) the fractional concentration of B in the crystal, c. The B concentrations in the crystal will be compared with the equilibrium predictions of section II. Results are presented in Table I.

Qualitatively, the behavior of the flux and mean thickness as a function of supercooling is the same as in the case of total exclusion of B. As the temperature is lowered ($S_T/N_0\alpha_0$) increases. The mean thickness decreases due to the fall of n^*, though eventually the predicted $\bar{n}$ will increase as the blowup is approached. The deviation $\delta n = \bar{n} - n^*$ monotonically increases.

The concentration of B units incorporated in the crystal also increases monotonically as the crystallization temperature is decreased. This may be understood in the following way. For small supercoolings the difference $\bar{n} - n^*$ is small, indicating that crystallization is proceeding in crystals of a thickness close to the limit of stability. The λ's, which are essentially rate constants for crystal growth in the various impurity states, are small as a result of the small driving force; *i.e.*, the rates of addition and subtraction of strips are nearly equal. Under these conditions detailed balance has time to operate and bring the concentrations closer to equilibrium. At larger supercoolings δn is greater, so there is a representation of crystals with higher crystallization driving force, hence greater disparity between the rate of addition and detachment. Inclusion of excess B is enhanced.

If the fold free energy, Q_f, is increased the principle effect is the increase of n^*, but the distribution of $n - n^*$ is not greatly modified. For this reason the crystals are thicker and grow more slowly, but the concentration of B units is effected but little.

If the value of ϵ_1, ϵ_2, and ϵ_3 are changed, but $\epsilon_1 + \epsilon_2 + \epsilon_3$ remains constant the supercooling will be unchanged. The crystal thickness remains roughly the same. Changes in the B inclusion are seen to be small, but to the extent they occur they are in the same sense as the changes in δn.

If Ω is decreased the growth rate $S_T/N_0\alpha_0$ is much more rapid. At the same time the reduction of Ω allows a wider variation in $n - n^*$, so a great increase in the concentration of B units in the crystal occurs.

When x is increased the supercooling at a fixed crystallization temperature is changed, and comparisons are more difficult. However, at a fixed undercooling we find that the excess B inclusion is reduced.

Finally, we call attention to the dramatic percentage deviations of the concentrations of B in the crystal from their equilibrium value.

We plan to report on further aspects of this model of copolymer crystals—thermodynamic and statistical characteristics—in a future paper.

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VII. Appendix

In this section we shall investigate the properties of a copolymer crystal model in which the effect of the impurities on the rate processes are different from those used earlier. The model may be considered as more mathematically defined, and less in conformity with the physics of copolymer crystal growth. Still, it is an interesting study because the results are simpler analytically, and because comparison of the two models provides some estimate of the sensitivity of the results to the assumptions.

We will fix the energies for incorporation of impurities at the same values as before. Thus, equilibrium predictions are as before, and the ratios of forward to backward rate constants are unchanged, by detailed balance. However, we now assume that the energies of adding and covering impurities are part of the crystallization reaction barrier; so the forward rates are

$$\alpha(g_is_i, g_js_j) = \alpha_0\mu(g_j)\exp[-\beta(g_j\epsilon_1 + g_i\epsilon_2 + s_j\epsilon_3)]p(s_j|s_i)\exp(-\beta Q_f) \quad (A.1)$$

while the backward rate constants are

$$\beta(g_is_i, g_js_j) = \alpha_0\exp(-\beta n\Delta F_0) \quad (A.2)$$

This model leads to a simpler solution than in the article. If we write the λ's in the form

$$\lambda(g_js_j) = \alpha_0\exp[-\beta(n\Delta F_0 + g_j\epsilon_2)]u \quad (A.3)$$

then the set of eq 4.3 reduces to a single equation for u as a function of n

$$1 = \exp[\beta(n\Delta F_0 - Q_f)]J_n(u,\epsilon_2,\epsilon) \quad (A.4)$$

with

$$J_n(u,x,y) = \sum_{m=0}^{n}\frac{\mu(m)e^{-\beta ym}}{1 + ue^{-\beta xm}} \quad (A.5)$$

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3 \quad (A.6)$$

There is a positive solution for u only when the crystal is thick enough to be stable, $n > n^*$.

We omit the details of the derivation of eq A.4 and subsequent results. A key step is the proof that $p(s_j|s_i)$ is a function of s_j only.

The current, for a fixed n, is found to be

$$S_{Tn} = N_0\alpha_0ue^{-\beta n\Omega}\{1 - x + x\exp[-\beta(\epsilon_1 + \epsilon_2)]\}^n\frac{J_n(u,\epsilon_2,\epsilon)}{J_n(u,\epsilon_2,\epsilon_1 + \epsilon_2} \quad (A.7)$$

This flux turns out to behave in similar ways to the flux in the principle model.

The B content in the crystalline region, for a given n, is

$$\langle m\rangle_n = nxe^{-\beta\epsilon}\frac{J_{n-1}[u\exp(-\beta\epsilon_2),\epsilon_2,\epsilon]}{J_n(u,\epsilon_2,\epsilon)} \quad (A.8)$$

The concentration c may be determined by weighted summing of eq A.8 over n, according to eq 4.26. While this summation cannot be performed analytically, one can show that c is bounded by

$$\frac{x\exp[-\beta(\epsilon_1 + \epsilon_3)]}{1 - x + x\exp[-\beta(\epsilon_1 + \epsilon_3)]} > c > \frac{xe^{-\beta\epsilon}}{1 - x + xe^{-\beta\epsilon}} \quad (A.9)$$

The lower limit is the equilibrium value achieved at small supercoolings in this model, and the main model, when growth is slow. The upper value is that determined by the forward rate constants alone and is achieved when the flux is so rapid as to prevent any detachment. For the previous model the upper limit was the amorphous composition, x. The placement of the concentration between upper and lower limits in both models is effected in similar ways by variation of physical parameters, because in both cases it is a question of the extent of kinetic control *vs.* equilibration.

Nuclear Magnetic Resonance Relaxation Study of Poly(γ-benzyl L-glutamate) Side-Chain Mobility in Helix-Coil Transition[1a]

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ABSTRACT: Nmr spin-lattice relaxation times T_1 of F_3CCOOH proton and the side-chain phenyl protons of poly(γ-benzyl L-glutamate) ($(BzlGlu)_n$) were measured in $(BzlGlu)_n$-F_3CCOOH-$CDCl_3$. T_1 was affected by the solvent-induced helix-coil transition. F_3CCOOH proton T_1 behavior was interpreted by a two-site model, *i.e.*, F_3CCOOH molecules bind to the $(BzlGlu)_n$ or are free in solution. The T_1 values for the phenyl ring terminating the $(BzlGlu)_n$ side-chain increase before the onset of the helix-coil transition. This increase in side-chain mobility is discussed in terms of the effects of polydispersity and the concept of a side-chain secondary structure.

Studies with synthetic polypeptides have provided new insights into the understanding of protein structure. In the last 25 years a major part of the concentrated and sustained investigation of synthetic polypeptides has concerned the helix-random-coil transition in dilute solution. The literature contains numerous mechanisms describing how helix-breaking solvents might induce the helix-coil transition. Explanations of helix disruption by halogenated acids range from protonation of[2a,b] and hydrogen bonding with[3] the polypeptide amide group to less specific acid-polymer interactions involving the periphery of the polypeptide,[4] *e.g.*, solvation of side chains destroying helix-stabilizing side-chain–side-chain interactions.

The importance of the outer portions of polypeptide side chains in determining both the stability and precise conformation of the α helix has been recognized for some time. The concept of side-chain secondary structure has evolved; this term implies a regular arrangement of side chains to promote energetically favorable interactions between neighboring side chains and/or to minimize the occurrence of sterically hindered side-chain conformations.

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