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Calculation of Lamellar Thickness in a Diblock Copolymer, One of Whose Components Is Crystalline

E. A. DiMarzio,* C. M. Guttman, and J. D. Hoffman

National Bureau of Standards, Washington, D.C. 20234. *Received February 8, 1980*

ABSTRACT: We treat a diblock copolymer of lamellar morphology where one of the blocks is amorphous and one is crystalline (amphiphilic copolymer). The proposed models allow for the stretching of polymer chains, the change in packing entropy arising from changes in orientation of bonds, and the space-filling properties of the chains. Formulas are given for the thickness of the amorphous and crystalline lamellae, l_a and l_c, as functions of the lengths of the blocks, r_a and r_c, the surface and fold free energies, σ_s and σ_f, the temperature T, the amount of solvent in the amorphous phase $v_0 = 1 - v_x$, and the densities ρ_a and ρ_c ($\rho_a = v_x\rho_0$). We have $l_a = r_a^{2/3}(\sigma_s + \sigma_f\rho_c)^{1/3}/(3kT\rho_a)^{1/3}$ and $l_c = r_c\rho_a^{2/3}(\sigma_s + \sigma_f\rho_c)^{1/3}/\rho_c r_a^{1/3}(3kT)^{1/3}$.

I. Introduction

In this paper we suggest that there exists a chain-folded system as a condition of *equilibrium*.[1] Specifically, we suggest that diblock copolymers (and also triblock copolymers) form chain-folded systems as a condition of thermodynamic equilibrium when the following conditions are simultaneously fulfilled. (1) One of the components is crystallizable and the other is not (an example is poly(ethylene oxide) copolymerized with atactic polystyrene). (2) The two components are incompatible (do not mix). (3) The system exists in a lamellar morphology. Condition 3 has been included because certain combinations of molecular weights for the two components of the diblock will result in systems that do not form a lamellar morphology. A complete statistical mechanical treatment would predict the type of crystals and morphologies that form over the whole composition range of the diblock components.[2] However, we will assume the lamellar morphology and limit ourselves to a calculation of the equilibrium thickness of the amorphous and crystalline lamellae.

The system we are discussing here has annealing properties which are completely different from those of homopolymers. In homopolymers chain folding is metastable and annealing reduces the amount of chain folding;[3] in the limit of infinite annealing times we would obtain extended chain crystals.[4] The diblock copolymers would anneal to an equilibrium thickness. Further by adding solvent which is imbibed by the amorphous phase we can speed up the annealing process.[5]

It is the purpose of this introductory section to establish that the model of Figure 1 on which we shall make our calculation not only is consistent with the experimental data but actually is unambiguously demanded by the experimental data. It is known from the extensive studies of Lotz, Kovacs, Bassett, and Keller[6] that poly(ethylene oxide)–polystyrene diblock copolymers exist in the lamellar morphology and that the chain stems of the crystalline portions are perpendicular to the planes of the lamellae. If we can show also that the two diblock components are incompatible, then the model of Figure 1 must result. However, many studies have shown the general incompatibility of components.[7] The few exceptions that exist[8] will not be the subject of this paper. Actually there is another model which is consistent with the data[6] and it is identical with that of Figure 1 except that each crystalline lamella is replaced by a pair of lamellae. However, it will become apparent from the theory developed here that such a model has a high free energy.

We shall then restrict ourselves to the prediction of the thermodynamic properties of such a system. The primary variables are r_a and r_c, the molecular weights of the amorphous- and crystalline-forming portions of each molecule, and v_0, the volume fraction of solvent that we assume exists in the amorphous region. We shall be interested in calculating the thickness of the amorphous lamella, l_a, and that of the crystalline lamella, l_c, as a function of these three variables and temperature. The amount of chain folding is given simply as r_c/l_c.

Before entering into the actual quantitative calculations we show on physical grounds that there is indeed an equilibrium value for l_c and l_a and therefore an equilibrium amount of chain folding. Consider the covalent links between the amorphous and crystalline portions of each chain and assume for simplicity that they lie on the planes separating the lamellae (see Figure 2). Let the average minimum separations (along the plane) between these links be λ. We seek to estimate the expected value of λ. Since each chain fold costs energy, the extended-chain crystal is the favored state for the crystalline region. Thus the crystalline lamellae will tend to force λ to be small (in the limit of $r_a = 0$ the extended-chain crystal would give $\lambda = 1$). However, if all of the crystalline chains were to be fully extended then the amorphous chains would also have to be fully extended since they otherwise would result in an amorphous density greater than 1. But fully extended amorphous chains are clearly not compatible with the entropy that these chains can gain by achieving at least partially the random coil state. The opposing tendencies of aligned amorphous-forming molecules to increase λ and of the crystalline portions to decrease λ results in an equilibrium value of λ. We now proceed to calculate this value.

II. Theory

We shall assume that the amorphous region is of constant density. This assumption is consistent with the

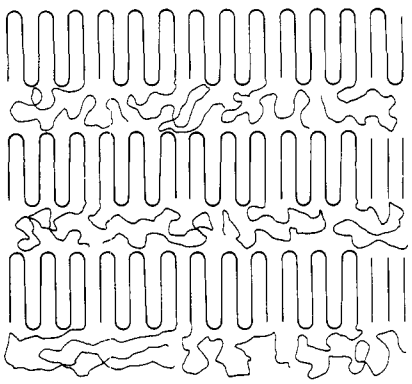

Figure 1. The strict alternation of crystalline and amorphous layers which occurs in a poly(ethylene oxide)–polystyrene diblock copolymer arises from the basic incompatibility of the two species. The value of lamellar thickness results from two opposing tendencies: the energetics of the crystalline regions drives the system toward extended chains with minimal folding, but this tendency is resisted by the amorphous region which favors randomlike chains for the polystyrene portions. (For a lamellar morphology, packing considerations would force the polystyrene portions into an extended form if poly(ethylene oxide) portions were extended.) The result is that an *equilibrium* amount of chain folding exists in the crystalline portion. This paper calculates the equilibrium amount of chain folding and the two lamellar thicknesses l_a and l_c.

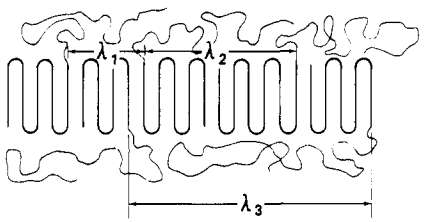

Figure 2. The free energy of an amorphous lamella formed by cilia is a function of λ, the average minimum separation between the cilia tie points in the plane separating the crystal from the amorphous regions. λ is chosen to minimize the total free energy.

small-angle X-ray results of Hashimoto, Todo, Itoi, and Kawai[9] which show that the transition region is very small in systems whose periodicity is large (about 600–700 Å). The transition region is on the order of 15 Å.[10] We have

$$\rho_a = r_a/(\lambda^2 l_a) \tag{1}$$

where ρ_a is the density of amorphous segments, l_a the thickness of the amorphous region, and λ the average separation between nearest-neighbor cilia. r_a is the number of monomer units comprising a cilium. If we allow solvent to also occupy the lamellar region then the density is given by

$$\rho_a = v_x \rho_0 \tag{2}$$

where ρ_0 is the density of pure amorphous polymer and $v_x = 1 - v_0$ is the volume fraction of polymer (v_0 is the volume fraction of solvent). We shall assume an incompressible system.

We now calculate the entropic contribution to the free energy. We shall do this on three models.

Model A. Entropy Calculation on a Model of Flory[11] and of Motomura and Matuura.[12] In this model the chains never take backward steps, but rather always press forward. Of the N_c cilia comprising a lamella we can have any fraction, f, starting from one plane and the remainder, $1 - f$, starting from the other. We stipulate, however, that they continue till their last segment touches the other side. The evaluation of the entropy does not depend on the value of f. An individual chain with l_a vertical steps (perpendicular to the planes defining the lamella) and $r_a - l_a$ horizontal steps has

$$W = \frac{r_a![s(1-a)]^{r_a - l_a}}{(r_a - l_a)! l_a!}(sa/2)^{l_a} \tag{3}$$

possible configurations, where s is the coordination number of the lattice on which the molecules walk in the amorphous region, $1 - a$ is the fraction that lies in the horizontal direction, and $a/2$ is the fraction that steps up (or down). We will use a cubic lattice with $a = {}^1/_3$. Equation 3 is from the paper of Motomura and Matuura.[12] The total number of configurations W_c and the entropy S_c are

$$W_c = W^{N_c} \tag{4a}$$

$$S_c = k \ln W_c \tag{4b}$$

where N_c is the total number of cilia.

We must now account for the packing of the chains. Motomura and Maturra use a simple volume fraction (Flory fraction) but because the chains can order we will use the correction of DiMarzio.[13] The fraction of bonds in the perpendicular and parallel directions is

$$\alpha_1 = l_a/r_a \tag{5a}$$

$$\alpha_2 = (r_a - l_a)/r_a \tag{5b}$$

If it is realized that the bonds laying parallel to the plane are in two orientations then we have for the packing entropy[13]

$$\frac{S_p}{k(N_0 + r_a N_a)} = -v_0 \ln v_0 - \frac{v_x}{r_a}\ln\left(\frac{v_x}{r_a}\right) + \left(1 - \frac{(r_a - 1)v_x\alpha_1}{r_a}\right)\ln\left(1 - \frac{(r_a - 1)v_x\alpha_1}{r_a}\right) + 2\left(1 - \frac{(r_a - 1)v_x\alpha_2}{2r_a}\right)\ln\left(1 - \frac{(r_a - 1)v_x\alpha_2}{2r_a}\right) \tag{6}$$

The total entropic contribution of the amorphous layer is

$$S_a = S_p + S_c \tag{7}$$

By virtue of eq 1 and 5 both S_p and S_c are seen to be λ dependent.

To obtain the free energy of the amorphous region we must consider the energetics. For the simplest approximation, we have

$$E_a = kTN_0 v_x \chi_1 \tag{8}$$

where N_0 is the total number of solvent molecules and χ_1 is the χ parameter. The total free energy of the amorphous region is

$$F_a = E_a - TS_a \tag{9}$$

The interfacial free energy will be approximated by

$$E_s = \sigma_s \lambda^2 N_a \tag{10}$$

where N_a is the number of amorphous chains. The meaning of σ_s will be discussed later.

Finally we have the free energy of the crystalline region

$$E_c = N_c r_c \Delta H + \sigma_f r_c N_c / l_c = N_c r_c \Delta H + \sigma_f \lambda^2 \rho_c N_c \tag{11}$$

where N_c is the number of crystalline chains ($N_c = N_a$), r_c is the number of c-type monomers in each chain, ΔH is the bulk free energy per monomer unit, σ_f is the fold free energy, and l_c is the thickness of the crystalline lamella. The λ dependence of the second term of eq 11 is, of course, the same as that of eq 10. We have an equation analogous to eq 1 for the crystal

$$\rho_c = r_c/(\lambda^2 l_c) \tag{12}$$

The equilibrium value of λ can now be determined by using eq 1 and 12 to eliminate l_a and l_c and eq 5 to eliminate α_2 and α_1. We obtain as the condition of equilibrium

$$\partial(F_a + E_s + E_c)/\partial\lambda = 0 \tag{13}$$

λ is a function of v_0, r_a, r_c, ρ_c, ρ_a, σ_f, σ_s, and ΔH. The equilibrium values of l_a, l_c and α_1, α_2 are given by eq 2, 12, and 5 and the equilibrium amount of chain folding n is

$$n = r_c/l_c \tag{14}$$

Equation 13 reads explicity

$$\frac{kT2r_a}{\rho_a}\left[\ln\left(\frac{2l_a(1-a)}{a(r_a-l_a)}\right) + \frac{r_a-1}{r_a}\ln\left(\frac{1-\dfrac{(r_a-1)v_x\alpha_2}{2r_a}}{1-\dfrac{(r_a-1)v_x\alpha_1}{r_a}}\right)\right] + 2\lambda^4(\sigma_s + \sigma_f\rho_c) = 0 \tag{15}$$

One notices that the bulk energy contributions in eq 9 and 11 do not contribute to a determination of λ.

Model B. Entropy Calculation When Reversals Are Allowed. In this model we allow the chains to walk randomly in the amorphous region. We retain the notion that the chains pack with a constant amorphous density so that eq 1 remains valid. Also we retain the idea that the total amorphous entropy is a sum of two parts: as in eq 7, where S_p is given again as in eq 6 and S_c is to be calculated. The only difference between models A and B is in the calculation of S_c and the minimization procedure. In model A there was only one independent variable, λ, but in model B α_1 is also an independent variable. Equations 5a,b, which connect α_1 to λ, are not valid for model B. Accordingly, in model B we must minimize the total free energy with respect to both the λ and the α_1 variables simultaneously.

The calculation of S_c involves certain implicit assumptions which we make explicit by discussion. We assume that each chain has the properties of an average chain. This means that (1) each chain has an average segment density which is constant as a function of distance into the layer and (2) the fraction of bonds in each of the orientations is given by α_1 and α_2 for each chain. A better appreciation of these assumptions is obtained after our calculation of S_c. Formulas 4a,b are again used and we need only calculate the number of configurations W for an isolated chain of length r_a (r_a steps) given that $\alpha_1 r_a$ of them are steps in the perpendicular orientation and $\alpha_2 r_a = (1 - \alpha_1)r_a$ steps are divided in the two orientations parallel to the planes. We also stipulate that the average segment density is constant.

To solve the isolated chain with constant density we recall that the work of DiMarzio and Rubin[14] on an isolated polymer between two plates shows that there exists a critical value of energy of attraction of surface for segments, ϵ_c, for which the segment density is indeed a constant. Use of this critical value of energy is equivalent to the use of a reflecting boundary near the surface.[15] These statements are valid when the chain length is large compared to the plate separation or when the chains are free or floating. However, if the chain length r_a were comparable to the plate separation l_a, then we would not have constant density for the special case of one end tied to a plate, the other end free, which is the case of interest here. To avoid this difficulty we solve the problem as a chain that begins on one plate and ends on the other. This specification does more nearly result in constant density. Note that we do not tie the end points of the chain to a particular point of each plane but only stipulate that it terminate in *any* point of the plane. (The end point need not be vertically above the starting point.)

The above stipulation on the end points gives the exact result for $l_a = r_a$ for then the chain can just bridge the amorphous region. However, for the case of $r_a > l_a$ the calculation underestimates the number of configurations since in the real system the end point is free to terminate in any of the layers rather than in the last layer only. But we can show that this is not a serious error. We write

$$W = \sum_{j=1}^{l_a} W_{1j} \tag{16}$$

where W_{1j} is the number of configurations of a chain that begins in layer 1 and ends in layer j. We can rewrite eq 16 as

$$W = l_a\langle W_{1l_a}\rangle \tag{17}$$

where $\langle W_{1l_a}\rangle$ is the average value of W_{1j}. Because of the factorial terms contained in $\langle W_{1l_a}\rangle$ ln W is insensibly different from ln $\langle W_{1l_a}\rangle$ so that the only approximation made is the replacement of the average value of W_{1j} by W_{1l_a}. Thus the pinning of the end points is not a serious error.

The number of ways to place $r_a\alpha_1$ perpendicular bonds and $r_a\alpha_2$ parallel bonds on a cubic lattice is

$$W = [2^{\alpha_1 r_a} p_{1,l_a\pm1}^{(\alpha_1 r_a)}]\left[\frac{4^{\alpha_2 r_a} r_a!}{(\alpha_1 r_a)!(\alpha_2 r_a)!}\right] \tag{18}$$

where the first bracketed term gives the number of ways to place $\alpha_1 r_a$ bonds on a one-dimensional line segment with reflecting boundary conditions and the second bracketed term gives the number of ways to decorate these $\alpha_1 r_a$ bonds with $\alpha_2 r_a$ bonds in the parallel orientation. Note that the decoration process does not affect the density profile. $p_{i,k}^{(n)}$ is the probability of stepping from level i to level k in n steps on a line segment which is l_a steps long. The problem of evaluation of $p_{i,k}^{(n)}$ for reflecting boundary conditions has been solved by Takacs.[16] The result is

$$p_{1,l_a\pm1}^{(\alpha_1 r_a)} = \frac{1}{l_a+1} - \sum_{j=1}^{l_a} \frac{\cos^{\alpha_1 r_a}\left(\dfrac{\pi j}{l_a+1}\right)\sin\left(\dfrac{\pi j}{l_a+1}\right)\sin\left(\dfrac{\pi j l_a}{l_a+1}\right)}{(l_a+1)\left[1-\cos\left(\dfrac{\pi j}{l_a+1}\right)\right]} \tag{19}$$

The minimization procedure for model B is straightforward. All the expressions for entropy and energy are the same in models A and B except that eq 18 is used in place of eq 3 for W. Also as was mentioned before, eq 5 can no longer be used to eliminate α_1 and α_2 so that the two independent minimization variables for model B are λ and α_1 rather than just λ as in model A.

Model C. An Approximation to Model B. Model B has the disadvantage of being difficult to implement. For this reason we seek to replace the difficult part of this model, $p_{1,l_a\pm1}^{(\alpha_1 r_a)}$ of eq 18, by something simpler. If we let the number of steps in each direction be limited by the two constraints

$$n_+ + n_- = \alpha_1 r_a \tag{20a}$$

$$n_+ - n_- = l_a \tag{20b}$$

then the first bracketed term of eq 18 can be replaced by

$$[2^{\alpha_1 r_a} p_{l_a, l_a \pm 1}^{(\alpha_1 r_a)}] \rightarrow \frac{(\alpha_1 r_a)!}{n_+! n_-!} = \frac{(\alpha_1 r_a)!}{\left(\frac{\alpha_1 r_a + l_a}{2}\right)! \left(\frac{\alpha_1 r_a - l_a}{2}\right)!} \tag{21}$$

Model C then is model B with the replacement afforded by eq 21. Equation 21 allows the bonds to spill over outside of the two planes. Thus the shape of the individual chain implied by (21) is not realistic. However, the entropy calculated may not be much different from the more exact result. In this regard, notice that the value of α_1 which maximizes eq 18 with the substitution afforded by eq 21 is

$$\alpha_1 = \frac{-1 + (1 + 3[(2l_a/r_a)^2 + 1])^{1/2}}{2} \tag{22}$$

and this has the values $\alpha_1 = {}^1/_3$ for $l_a = 0$ and $\alpha_1 = 1$ for $l_a/r_a = 1$. Thus the behavior of S_c as a function of α_1 and l_a is about what we expect qualitatively.

The configurational entropy derived from eq 18 and 21 is

$$\frac{S_c}{N_c} = -\alpha_2 r_a \ln \alpha_2 - (\alpha_1 + r)\frac{r_a}{2} \ln (\alpha_1 + r) - (\alpha_1 - r)\frac{r_a}{2} \ln (\alpha_1 - r) + r_a \ln 2 + \alpha_2 r_a \ln 2 \tag{23}$$

$$r = l_a/r_a$$

The minimization of the total free energy can be done in two steps. First we maximize $S_p + S_c$ with respect to α_1. This is equivalent to minimization of free energy with respect to α_1 because E_i and E_c do not depend to α_1. We obtain

$$r_a \ln \left[\frac{\alpha_2(\alpha_1^2 - r^2)^{-1/2}}{2}\right] + (r_a - 1) \ln \left[\frac{1 - \frac{(r_a - 1)v_x\alpha_2}{2r_a}}{1 - \frac{r_a - 1}{r_a}v_x\alpha_1}\right] = 0 \tag{24}$$

The minimization with respect to λ results in eq 25.

$$-\left(\frac{kTr_a}{\rho_a}\right) \ln \left(\frac{\alpha_1 + r}{\alpha_1 - r}\right) + 2\lambda^4(\sigma_s + \rho_c\sigma_f) = 0 \tag{25}$$

III. Discussion of Results

Equation 24 can be simplified considerably when $r_a \gg 1$. We obtain

$$\frac{\alpha_2(1 - v_x\alpha_2/2)}{2(\alpha_1^2 - r^2)^{1/2}(1 - v_x\alpha_1)} = 1 \tag{26}$$

Equation 26 reduces to eq 22 for $v_x = 0$; for $v_x = 1$ we obtain

$$\alpha_1 = 1 + [1 + 15(16r^2 + 1)]^{1/2}/15 \qquad v_x = 1 \tag{27}$$

The expansions of eq 27 and 22 for small r are

$$\alpha_1 = {}^1/_3 + r^2 \qquad v_x = 0 \tag{22'}$$

$$\alpha_1 = {}^1/_3 + 2r^2 \qquad v_x = 1 \tag{27'}$$

The factor of 2 in the coefficient of the r^2 term results in a contribution to the elastic force due to packing which is twice for $v_x = 1$ what it is for $v_x = 0$. An identical factor of 2 occurs in the liquid-like theory of rubber elasticity developed by Tanaka and Allen[17] compared to the original estimate of DiMarzio.[13] Also eq 27' leads to a stress optical coefficient which is twice as large as that obtainable from eq 22'. This effect has been observed by Fukuda, Wilkes, and Stein.[18]

For $r = 0$ eq 26 reduces to

$$\alpha_1 = {}^1/_3 \qquad r = 0 \tag{28}$$

for all v_x. Because α_1 is quadratic in r for small r eq 25 can be solved to linear order in r by simply using $\alpha_1 = {}^1/_3$. The result is

$$\lambda^4 = \frac{3kTl_a}{\rho_a(\sigma_s + \sigma_f\rho_c)} \tag{29}$$

which when combined with eq 1 gives

$$l_a = \frac{r_a^{2/3}(\sigma_s + \sigma_f\rho_c)^{1/3}}{(3kT\rho_a)^{1/3}} \tag{30}$$

This is a very interesting result. The crystalline lamellar thickness is

$$l_c = \frac{r_c\rho_a^{2/3}(\sigma_s + \sigma_f\rho_c)^{1/3}}{\rho_c(3kT)^{1/3}r_a^{1/3}} \tag{31}$$

which immediately determines the amount of chain folding via eq 14.

The surface tension due to the amorphous phase is

$$\tau_a = -\frac{\partial F_a}{\partial A} = -\frac{\partial F_a}{\partial(\lambda^2 N_a)} = -\sigma_s + \left(\frac{kTr_a}{2\rho_a\lambda^4}\right) \ln \left(\frac{\alpha_1 + r}{\alpha_1 - r}\right) \tag{32}$$

where the equilibrium value of α_1 determined from eq 24 is to be used. This force is an elastic restoring force. Notice that one does not need to have both ends of a polymer chain tied to a network in order to have a restoring force. This is in accord with the observations of Gaylord, who has shown that chains that are tied to the network at one end only and free chains contribute to the elastic force in a rubber.[19] The σ_s of eq 32 covers a multitude of sins. What we have done is place all our ignorance and unsolved parts of the problem into this variable. The works of Helfand,[20] Meier,[21] and others[22] are useful to further understand the meanings of σ_s. For the present paper we shall treat it as a parameter. It is obvious that eventually an integrated theory which allows for both orientation, which has been done, and density variation, which has not been done, is required. This paper should be viewed as a preliminary step to this more comprehensive theory.

Equations 30 and 31 show several interesting features. At first sight l_a might be thought to vary with $r_a^{1/2}$. It is clear that the packing effect (excluded volume but not self-excluded volume) results in a ${}^2/_3$ dependence. Thus, model C (and model B) has some of the character of model A which would be expected to result in an r_a dependence. The intermediate character of ${}^1/_2 < {}^2/_3 < 1$ is pleasing. The r_c dependence of l_c is easy to understand. For a given amount of folds per chain, increasing the length of the chain does not affect the force balance. Thus everything would remain the same as we increase r_c except l_c, which would vary linearly with r_c. An interesting feature of the solvent dependence is that adding solvent simultaneously increases l_a and decreases l_c. Reversible changes of l_a and l_c with changes of solvent should provide an interesting test of the idea that an equilibrium amount of chain folding

exists. de Gennes has given a treatment of amphiphilic copolymers which assumes that l_c remains constant.[23] His formula for l_a, which is different from ours, reflects this fact.

IV. Some Related Problems

The methods used in this paper allow us to solve several interesting problems.

First, the model of Lotz, Kovacs, Basset, and Keller,[6] which allowed an alteration of amorphous layers with crystal bilayers rather than a crystal monolayer, is easily solved. If one calls the bilayer thickness l_c, then the equations are identical with those of this paper except that we use $2\sigma_f$ instead of σ_f, there being twice as many folds. Another modification is to add the fold–fold surface free energy, σ_{ff}, to σ_s. The free energy of the bilayer system is larger than that of the monolayer system and stability is not to be expected.

Second, one can treat a triblock system by a simple modification of eq 11 and 12. If the center block is the crystallizable one, we have

$$\rho_c = r_c/(2\lambda^2 l_c) \tag{33}$$

$$E_c = N_c r_c \Delta H + \sigma_f r_c N_c / l_c = N_c r_c \Delta H + 2\sigma_f \lambda^2 \rho_c N_c \tag{34}$$

$$N_a = 2N_c \tag{35}$$

The resultant equations are identical with eq 30 and 31 except that eq 31 has a factor $^1/_2$ multiplying the right-hand side.

The case of the center block being the amorphous component is not so easily treated because the crystal then serves to pin the two ends and this is different from the case of one pinned end. Nevertheless this problem can be easily solved by replacement of the second term on the right-hand side of eq 18 by a product of two terms each of which is similar in form to the right-hand side of eq 21.

Third, we can give structure to the solvent. One, for example, can treat the addition of plasticizer molecules of various types. Because of the ordering effects of the amorphous block, one must resort to the methods of Alben, Ågren, Cotter, Dowell, and Martire[24] et al. to solve this problem.

Fourth, one can treat a normal compressive force whose effect would be to thin the lamellae.

Fifth, one can predict the actual phase transition temperature, the temperature at which the system spontaneously self-assembles, by simply equating the total free energy expression to that of the melt.[25]

The above problems are all now solvable by simple modification of the methods of this paper. Two problems require new methods not yet developed for crystallizable block copolymer: (1) There is the question of morphology. When do we go from lamellar morphology to other morphologies? This problem is at least as difficult as the corresponding problem for noncrystallizable block copolymers. (2) The simultaneous treatment of spatial density changes and orientation changes remains an intractable problem.

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