Microphase Separation in Correlated Random Copolymers

Henk Angerman and Gerrit ten Brinke*

Department of Polymer Chemistry and Materials Science Centre, University of Groningen Nijenborgh 4, 9747 AG Groningen, The Netherlands

Igor Erukhimovich

Department of Physics, Moscow State University, Moscow 117234, Russia

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ABSTRACT: In the Leibler description of copolymer systems containing only two kinds of monomers, the state of the system is described by one order parameter, $\psi(r)$, representing the deviation of the local composition from the space-averaged value. The Landau free energy is expanded up to fourth order in powers of $\psi(r)$ and subsequently minimized with respect to the symmetry, the amplitude, and the period of the microstructure. However, if the system contains some kind of polydispersity, so that the copolymers are no longer all identical, the description in terms of only one order parameter is an oversimplification. Recently, Erukhimovich and Dobrynin refined the theory by introducing separate order parameters for each type of molecule (Erukhimovich, I.; Dobrynin, A. V. *Macromol. Symp.* **1994**, *81*, 253). Their procedure eventually leads to a Leibler-like free energy, with various additional terms. One of these terms, called the nonlocal term, is of great importance for the system under consideration, since it is responsible for microphase separation instead of the macrophase separation predicted by previous theories. In our article, the results of the application of this theory to a random copolymer, containing two types of monomers A and B, are presented. The resulting microstructure will be given for various values of the χ-parameter and the A-monomer fraction.

1. Introduction

Recently, there has been much interest in phase transitions in systems with a quenched disorder. In particular, the behavior of random and polydisperse copolymer melts consisting of random[1] or correlated[2−6] sequences of A and B monomers has been investigated. It was shown, in the mean field approximation, that below a critical temperature T_c such systems undergo a phase transition to a microstructure. Until recently it was assumed that in the limit of infinitely many blocks per chain the free energy is degenerate with respect to the symmetry of the microstructure, leading to the prediction of a so-called disordered microphase (see, e.g., ref 5). However, as first demonstrated in ref 6 and confirmed by our calculation, this assumption is not right, and a microstructure with a definite symmetry is predicted. It was also shown in ref 6 that there exists a critical fraction f separating first- and third-order transitions from the homogeneous state. Further investigations, using a modified Brazovskii (Hartree) approximation developed for copolymer systems in refs 7−10, showed that fluctuation corrections might be very important. In particular, for the degenerated case of an uncorrelated random copolymer melt, large fluctuations might result in destruction of the ordered phase,[9] which is related to a special degeneracy of such a system. In the general case of copolymer melts consisting of more or less correlated sequences of monomers, the existence of ordered phases is not excluded. Therefore, both theoretical and experimental studies of possible phase diagrams for copolymer melts with a considerable structural disorder seem to be of great importance. In this paper we present for a realistic model of a correlated copolymer melt a mean field phase diagram, the effect of fluctuations being postponed to a future publication. This phase diagram gives the thermodynamically stable state of the system as a function of composition and temperature. In this paper

nothing will be said about the problems concerning the kinetics of the transition. The interested reader is referred to refs 11 and 12.

2. Model

We consider a melt of linear random copolymers with two kinds of monomer, denoted by A and B. The polymer is polydisperse in chain length as well as in chemical composition. The monomer sequence distribution can be described in the following way. Assign to each monomer of type $\alpha = $ A or B a weight Z_α and to each bond between a monomer of type α and β a weight $k_{\alpha\beta}$, then the "weight" of a specific molecule type is defined as the product of the weights of all monomers and all bonds present in the molecule. The number of molecules of a given type is now taken to be proportional to this weight. In this way all possible sequences of A and B have a non-zero probability.

This distribution is characterized by five parameters:

$$Z_A, \quad Z_B, \quad k_{AA}, \quad k_{AB}, \quad k_{BB} \tag{1}$$

However, not all parameters are necessary. First, it is quite obvious that the following set of parameters describes the same distribution for all positive values of c:

$$cZ_A, \quad cZ_B, \quad c^{-1}k_{AA}, \quad c^{-1}k_{AB}, \quad c^{-1}k_{BB} \tag{2}$$

Hence, without loss of generality Z_B can be set equal to 1. In the remainder of this article, we will also set Z_A equal to unity. However, allowing for other values of Z_A does not lead to additional complications, and all formulas and results can easily be adapted.

If the values of the parameters are known, the properties of interest like the average chain length, the average A-monomer fraction, etc. can be calculated by

partial differentiation of the generating function F, which is defined by

$$F = \sum_s \rho_s = \sum_{\alpha,\beta} Z_\alpha (1 - kZ)_{\alpha\beta}^{-1} \qquad (3)$$

where the following notation has been adopted:

s a molecule type, i.e. a finite, ordered sequence of A's and B's

ρ_s the "weight" of molecule type s, which is proportional to the number of these molecules per unit volume

kZ the matrix with components $(kZ)_{\alpha\beta} = k_{\alpha\beta} Z_\beta$

α, β monomer types (A or B)

The system will be studied in the limit where the average number of monomers per block is large (high correlation along the chain). This can be accomplished by taking

$$k_{AA} = 1 - \frac{e_{AA}}{n}; \qquad k_{AB} = \frac{e_{AB}}{n}; \qquad k_{BB} = 1 - \frac{e_{BB}}{n} \qquad (4)$$

where n is large and e_{AA}, e_{AB}, and e_{BB} are positive constants with the restriction

$$e_{AB}^2 < e_{AA} e_{BB} \qquad (5)$$

which is required to keep the sum of the weights of all molecule types finite. Since a common factor can be absorbed in n, only the ratio between e_{AA}, e_{AB}, and e_{BB} is of interest, so e_{AB} can be set equal to unity. When n increases (for fixed values of the parameters e_{AA} and e_{BB}), the average number of monomers per block increases as well, while the average number of blocks per molecule remains constant. Also, the fraction f of A monomers is independent of n. From now on, the model will be studied for large values of n; i.e. contributions to the free energy which are of order n^{-2} will be neglected (the main contribution to the free energy is proportional to n^{-1}). Moreover, we will restrict ourselves to the case where the average number of blocks per molecule, $\langle N_b \rangle$, is infinite. The implication of the last assumption for the parameters e_{AA} and e_{BB} follows from the expression for $\langle N_b \rangle$:

$$\langle N_b \rangle - 1 = g_{AB} \frac{\partial \ln F}{\partial g_{AB}} =$$
$$\frac{2 e_{AB}(e_{AA} + e_{AB})(e_{AB} + e_{BB})}{(e_{AA} + 2 e_{AB} + e_{BB})(e_{AA} e_{BB} - e_{AB}^2)} \qquad (6)$$

which demonstrates that the limit $\langle N_b \rangle \rightarrow \infty$ corresponds to the limit

$$e_{AA} e_{BB} \downarrow e_{AB}^2 \qquad (7)$$

By now, only one independent parameter is left, which will be denoted by e:

$$e_{AA} = e; \qquad e_{AB} = 1; \qquad e_{BB} = 1/e \qquad (8)$$

The value of the parameter n will have no influence on

the final results, since it appears only as a prefactor for the free energy, if the condition $n \gg 1$ is fulfilled.

With the use of the generating function F defined in eq 3 it is possible to express various properties of interest in terms of e and n; for example the average A-monomer fraction f, the average length of an A-block $\langle N_A \rangle$, the average length of a B-block $\langle N_B \rangle$, and the conditional probabilities $p_{\alpha\beta}$ that a monomer of type α is followed by a monomer of type β are given by

$$f = \frac{Z_A \dfrac{\partial F}{\partial Z_A}}{Z_A \dfrac{\partial F}{\partial Z_A} + Z_B \dfrac{\partial F}{\partial Z_B}} = \frac{1}{1 + e^2}$$

$$p_{AA} = 1 - \frac{e}{n}; \qquad p_{AB} = \frac{e}{n}; \qquad p_{BB} = 1 - \frac{1}{ne};$$
$$p_{BA} = \frac{1}{ne} \qquad (9)$$

$$\langle N_A \rangle = \frac{n}{e}; \qquad \langle N_B \rangle = ne$$

In the case of a monodisperse diblock, the relevant parameter describing the segregation is not the Flory–Huggins parameter χ itself, but rather the rescaled parameter $\tilde{\chi} = N\chi$, where N is the sum of the lengths of an A-block and a B-block.[13] In our model, this rescaled χ-parameter has the form (see also eq 9)

$$\tilde{\chi} = (\langle N_A \rangle + \langle N_B \rangle)\chi = n\chi \frac{e}{1 + e^2} \qquad (10)$$

In the phase diagram presented further on, this parameter is put along the vertical axis.

In ref 5, Fredrickson and co-workers introduced an alternative model for correlated random copolymers. This model was also considered in ref 6. Their starting point is a melt of random copolymers consisting of segments A and B. Each segment is assumed to consist of M monomers (much like prepolymers). The system is monodisperse in chain length, and the number of segments per molecule is denoted by Q. The sequence distribution of the segments is described in terms of two parameters f and λ. The latter is defined by

$$\lambda = p_{AA} + p_{BB} - 1 \qquad (11)$$

where p_{AA} and p_{BB} are the conditional probabilities that during the reaction A reacts with A and B reacts with B. Since our model is by definition polydisperse, it differs in an essential way from the model of Fredrickson et al. However, setting $M = 1$ and taking the limits $Q \rightarrow \infty$ followed by $\lambda \uparrow 1$, both models give the same phase diagram under the correspondence

$$p_{AA} = 1 - \frac{e}{n}; \qquad p_{BB} = 1 - \frac{1}{en} \qquad (12)$$

hence

$$\lambda = 1 - \frac{e}{n} - \frac{1}{en} \qquad (13)$$

The equivalence of both models in the indicated limit is due to the fact that then the average chain length is

much larger than the average block length, whereas both models have the same block length distribution. If the chain lengths are much larger than the block lengths, the distribution of the total chain length has no influence on the phase diagram. The above equations will be used further on to demonstrate the equality of the spinodal expressions of both models.

3. Method

We have studied our model in the weak segregation limit advanced first by Leibler[13] in his classic paper dealing with microphase separation in molten (monodisperse) diblock copolymers. The procedure developed by Erukhimovich and Dobrynin[14] to extend the theory to polydisperse copolymers has been used. We will start by giving a short summary of these theories.

Leibler Theory. In Leibler's theory,[13] the state of a polymer system is described by the order parameter $\psi(x)$, which is defined as the deviation of the A-monomer density $\rho_A(x)$ from its space-averaged value $\langle \rho_A \rangle$:

$$\psi(x) = \rho_A(x) - \langle \rho_A \rangle \qquad (14)$$

The Landau free energy is developed in a power series up to fourth order in ψ

$$F = \sum_{n=2}^{4} \frac{1}{n!} \sum_{q_1 \ldots q_n} \Gamma^{(n)}(q_1, \ldots, q_n)\, \psi(q_1) \ldots \psi(q_n) \qquad (15)$$

In the vicinity of the critical point, in which the third-order term in (15) vanishes due to the symmetry of the system, it suffices to keep only the terms up to fourth order, and this is just the region of validity of the weak segregation (weak crystallization) approach. The coefficients $\Gamma^{(n)}$ in this expansion are related to the intramolecular correlation functions, which can easily be determined due to the fact that macromolecules obey Gaussian statistics in the homogeneous (and almost homogeneous) melt.[15,16] The interaction is taken into account in the usual way by including the Flory–Huggins χ-parameter in the second-order term. This second-order term plays an important role in determining the period of the microstructure. If its Fourier transform attains its minimum at some positive q value, then Leibler's theory predicts microphase separation, and the periodicity is inversely proportional to this q value. This period is assumed to be constant in the weak segregation regime (allowing for its actual dependence on temperature goes beyond the accuracy of the weak segregation theory). The next step consists of calculating the free energy of various microstructures and choosing the one that gives the minimum. To this end, the order parameter is written as a sum of plane waves. All these waves have the same period, which is given by the position of the minimum of the second-order vertex function. The directions of these waves are such that they form the first coordination sphere of the reciprocal of the symmetry lattice under consideration. The free energy must be minimized with respect to both the amplitudes and the phases of these waves. Symmetry arguments show, that all amplitudes are equal when the free energy reaches its minimum. So, after proper minimization with respect to the phases,[13] the expression for the free energy has been reduced to a fourth-order polynomial in the amplitude, which can easily be minimized. This procedure can be extended in several ways.

Higher Harmonics. In the original weak crystallization theory approach, the order parameter is written as a sum of plane waves, whose momenta are given by the vectors belonging only to the first coordination sphere of the studied reciprocal lattice. It is assumed thereby that contributions of plane waves associated with other vectors in the reciprocal lattice can be neglected. However, it is just these contributions which result in a transition from the weak to the strong segregation regime. The first attempts to allow for these so-called higher harmonics were presented in papers by Olvera de la Cruz et al.[17] and Cates and Marques.[18] The main problem here is related to the question of how many higher harmonics should be taken into account. It was shown in ref 14 that within the accuracy of the weak crystallization theory the only higher harmonics to be taken into account are those which can be written as the sum of two vectors belonging to the first coordination sphere.

Detailed Densities (Multiple Order Parameters). Although the system under consideration contains many different molecule types, in the extension of the Leibler approach to polydisperse AB-copolymer systems first presented by Burger, Ruland, and Semenov[19] its state is still described by only one order parameter. This is an oversimplification; relevant thermodynamic degrees of freedom contributing essentially to the free energy may be missed this way. To account for this, Erukhimovich and Dobrynin[14] introduced two order parameters for *each* molecule type involved, one describing the A-monomer concentration, the other describing the B-monomer concentration. These order parameters are called detailed densities. The free energy must be minimized with respect to all these order parameters. In the case of the long polydisperse (random) copolymer one should, therefore, introduce infinitely many order parameters. Minimization of the free energy seems an enormous task; it is, however, simplified by the following observation. At the spinodal, the system becomes critical with respect to one particular linear combination of order parameters. This linear combination is called the strongly fluctuating field $\tilde{E}_\alpha^s$. It can be found by inspection of the second-order vertex function. In the disordered state (below the spinodal with respect to the χ-parameter), all eigenvalues of this matrix are positive, for all q values. At the spinodal, for a particular q value $q = q_0$ one of these eigenvalues becomes zero. The corresponding eigenvector is the strongly fluctuating field $\tilde{E}_\alpha^s$ given by (see ref 14)

$$\tilde{E}_\alpha^s = \sum_\beta g_{\alpha\beta}^s (q_0)\, z_\beta^0(q_0)$$

$$z_\beta^0(q) = \langle g^s(q) \rangle_{\beta A}^{-1} - \langle g^s(q) \rangle_{\beta B}^{-1} \qquad (16)$$

Dominant fluctuations of the detailed densities $\psi_\alpha^s(\bar{q})$ will have the form

$$\psi_\alpha^s(\bar{q}) = \delta(\bar{q} - \bar{p})\tilde{E}_\alpha^s \qquad (17)$$

for some vector $\bar{p}$ having length q_0. (n.b. $g_{\alpha\beta}^s$ is the second-order correlation function of a molecule of type

s). All other eigenvectors belonging to the same *q* value, are called weakly fluctuating fields. Because of the higher harmonics, some values of *q* bigger than q_0 are also relevant. The corresponding eigenvectors also belong to the weakly fluctuating fields. Let ψ denote the amplitude of the strongly fluctuating field, and φ the amplitude of some weakly fluctuating field. The procedure is to expand the free energy to fourth order in ψ and to such an order in φ and their products with ψ that the resulting contribution would be no more than fourth order in ψ (after expressing φ in terms of ψ by minimization with respect to φ). Then the only relevant coupling term proves to be $\int \psi^2 \varphi \, dV$ (it is instructive to compare it with a similar procedure used in the paper by Fredrickson and Leibler[20]), which results immediately in explicit expressions for the weakly fluctuating fields in terms of ψ. Inserting these expressions leads to a free energy functional depending only on one order parameter ψ, and from that point the minimization can be performed along the same lines as in Leibler's theory. The second- and the third-order vertex functions of the free energy thus obtained coincide with those of the free energy functional presented in ref 19. The fourth-order vertex function, however, has some additional terms. The complete free energy reads (see ref 14):

$$F = F_{\text{BRS}} + F_{\text{hh}} + F_{\text{nl}} + \Delta F \qquad (18)$$

F_{BRS} is the contribution already derived in ref 19. The term F_{nl} is the so-called nonlocal term, which was first derived by Shakhnovich and Gutin[1] (for the particular case of randomly distributed monomers) and by Panyukov and Kuchanov in the most general form.[2,4] For the case of random multiblock copolymers it was also presented by Fredrickson, Milner, and Leibler.[5] It is this term which prevents macrophase separation in the random copolymer, by assigning a high free energy to microstructures with a long wavelength. In the multiple order parameter theory[14] its appearance is due to the fact, that the free energy is expanded in powers of the amplitude of the strongly fluctuating field rather than in powers of the amplitude of the conventional order parameter.

The term F_{hh} accounts for the higher harmonics and is a consequence of the minimization with respect to the weakly fluctuating fields associated with *q* values bigger than q_0.

The contribution ΔF, obtained only in ref 14, allows for those degrees of freedom which are related to the adjusting of different macromolecules to the same lattice. This term is a consequence of the minimization with respect to the weakly fluctuating fields associated with q_0. For the sake of simplicity the consequences of the terms arising from the weakly fluctuating fields will not be considered here.

A few words must be said about the way of averaging. In the systems under consideration three different time scales are present:

1. the time for an individual polymer coil to go through all possible conformations

2. the experimental time scale on which the average concentration profile is measured

3. the time scale on which chemical bonds are broken and re-formed

Normally, it is assumed that the time scale increases from 1 to 3. In these cases, instead of the usual (so-called annealed) averaging of the partition function, one must first take the logarithm, and only then average over the different molecule species. This is called a quenched average. It can be performed with the replica trick, but in polymer systems this can often be circumvented.[5] It is instructive to note that the expression for the nonlocal term was first derived in refs 1, 2, and 4 using the replica trick, but that the same result was obtained by Erukhimovich and Dobrynin[14] straightforwardly averaging the conventional partition function (annealed average) with due regard for the aforementioned "hidden" thermodynamic degrees of freedom (detailed densities). One can expect generally that an annealed average using detailed densities should give the same results as a quenched average. (These two procedures can give different results only if a sort of replica symmetry breaking occurs.) In the calculations performed in this article, the partition function has been averaged without taking the logarithm, but with due regard for the detailed densities. So, it corresponds to the usual situation where the time scale increases from 1 to 3.

4. Results and Discussion

Application of the theory described in section 3 to the model described in section 2 leads to an expression for the free energy of the form

$$F = \frac{\tau(f,q_0,\chi)A^2 + \alpha(f,q_0)A^3 + \beta(f,q_0)A^4}{n} \qquad (19)$$

In this formula, *A* is proportional to the amplitude of the microstructure and the vertex functions τ, α and β depend on the microstructure, the average A-monomer fraction *f*, the dominant wave vector q_0, and the interaction parameter χ (only τ depends on χ). Expressions for these vertex functions are presented in the Appendix. They have been written in terms of the parameters *e*, *y*, and $\tilde{\chi}$ instead of, respectively, *f*, q_0, and χ. The relations between these parameters are (see also eqs 9 and 10)

$$f = \frac{1}{1 + e^2}; \qquad \tilde{\chi} = n\chi \frac{e}{1 + e^2}; \qquad y = \frac{1}{6} na^2 q_0^{\ 2} \qquad (20)$$

From eq A2 for the second-order vertex function it is clear that it attains its minimum for $y = 0$ ($q_0 = 0$). The spinodal is found by setting this minimum equal to zero. The result is

$$\tilde{\chi}_c = \frac{1}{4f^2(1-f)^2} \qquad (21)$$

This expression needs to be compared with the spinodal found by Fredrickson and co-workers[5] (see also section 2), which is

$$M\chi_c = \frac{1-\lambda}{2f(1-f)(1+\lambda)} \qquad (22)$$

For $M = 1$, (21) and (22) are equivalent (use (13) and (20)).

Effective Vertices. The free energy (19) should be minimized with respect to q_0 and to *A*. Suppose we minimize first with respect to q_0. This will give q_0 as a

function of A. Inserting this into the equation for F, and taking into account only contributions up to fourth order in A, will lead to (see also ref 6)

$$nF = \tau'(f,\chi)A^2 + \alpha'(f)A^3 + \beta'(f)A^4 \qquad (23)$$

That part of the original fourth-order vertex $\beta(f,q_0)$ which is proportional to $1/q_0^2$ (originating from the nonlocal term) will give a positive contribution to $\alpha'(f)$. Therefore although in the original series (19) the third-order coefficient $\alpha(f,q_0)$ is never positive, this is not true any more for the renormalized vertex $\alpha'(f)$. As pointed out in ref 6, this results in the existence of a critical fraction $f_c < 0.5$ with the following property:

$$\alpha'(f) > 0 \quad \text{for} \quad f_c < f < 1 - f_c$$

$$\alpha'(f) < 0 \quad \text{for} \quad 0 < f < f_c \ \text{ or } \ 1 - f_c < f < 1 \quad (24)$$

Because of this, the transition from the disordered state to the ordered state (for $f \neq 0.5$ this will be the body-centered cubic (bcc) phase) will be continuous (third order) for values of f satisfying $f_c < f < 1 - f_c$ and discontinuous (first order) for values of f outside this interval.

The effective vertices can be calculated in the following way. First the free energy has to be differentiated with respect to y. (The expression for the free energy can be found in the Appendix: eqs A1−A3 and A12−A16.) For the bcc phase this leads to the minimization condition

$$\frac{\partial nF_{bcc}}{\partial y} = \frac{(1 + e^2)^2}{2e^2} A^2 \pm \frac{(e^2 - 1)(1 + e^2)^3}{e^4 \sqrt{6}} A^3 +$$

$$\frac{(1 + e^2)^4(...)}{4e^6 y^2 (1 + e^2 + 2ey)^2} A^4 = 0 \quad (25)$$

The upper (plus) sign is valid for $e < 1 \leftrightarrow f > 0.5$, while the lower (minus) sign is valid for $e > 1 \leftrightarrow f < 0.5$. We look for a solution of the form

$$y = \sum a_n A^n \qquad (26)$$

Equation 25 can only be satisfied if $a_0 = 0$. In order to get the free energy up to fourth order in A, it is sufficient to determine only the coefficients a_1 and a_2. The result is

$$y^*_{bcc} = \frac{(1 + e^2)^2}{e^2 \sqrt{2}} A \pm \frac{(1 - e^2)(1 + e^2)^3}{2e^4 \sqrt{3}} A^2 \qquad (27)$$

The final expression for the free energy of the bcc phase in terms of e and A will be

$$nF_{bcc} = \left(-\frac{2e\chi'}{1 + e^2} + \frac{(1 + e^2)^3}{2e^3}\right)A^2 +$$

$$\frac{(1 + e^2)^4(e\sqrt{3} \pm (e^2 - 1))}{e^5 \sqrt{6}}A^3 +$$

$$\frac{(1 + e^2)^5(261 \pm 32e(e^2 - 1)\sqrt{3} - 294e^2 + 261e^4)}{192e^7}A^4$$

$$(28)$$
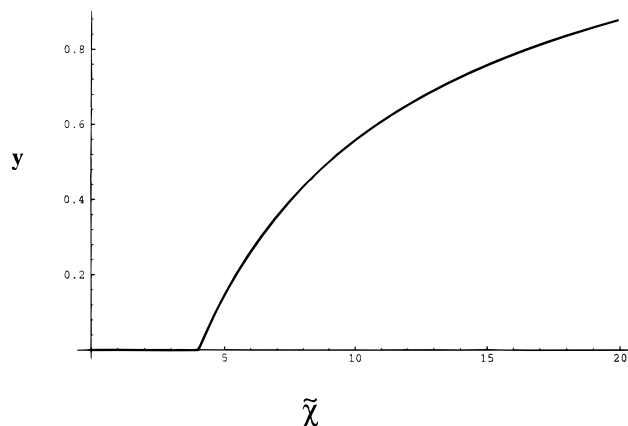
Figure 1. Value of $y = {}^1/_6 n a^2 q_0^2$ as a function of $\tilde{\chi}$ for $f = 0.5$.

Similar procedures can be followed for the cylindrical and lamellar phases. The result reads

$$y^*_{cyl} = \frac{(1 + e^2)^2}{e^2 \sqrt{2}} A \pm \frac{(1 - e^2)(1 + e^2)^3}{2e^4 \sqrt{6}} A^2 \qquad (29)$$

$$y^*_{lam} = \frac{(1 + e^2)^2}{e^2 \sqrt{2}} A \qquad (30)$$

$$nF_{cyl} = \left(-\frac{2e\tilde{\chi}}{1 + e^2} + \frac{(1 + e^2)^3}{2e^3}\right)A^2 +$$

$$\frac{(1 + e^2)^4(e\sqrt{6} \pm (e^2 - 1))}{2e^5 \sqrt{3}}A^3 +$$

$$\frac{(1 + e^2)^5(93 \pm 8\sqrt{6}e(e^2 - 1) - 102e^2 + 93e^4)}{96e^7} A^4 \quad (31)$$

$$nF_{lam} = \left(-\frac{2e\tilde{\chi}}{1 + e^2} + \frac{(1 + e^2)^3}{2e^3}\right)A^2 + \frac{(1 + e^2)^4}{e^4\sqrt{2}}A^3 +$$

$$\frac{(1 + e^2)^5(21 - 22e^2 + 21e^4)}{32e^7}A^4 \quad (32)$$

From eq 28 the critical fraction f_c can be obtained by solving the equation $\alpha'(f) = 0$. The result is (using eq 20)

$$f_c = \frac{1}{2} - \frac{\sqrt{21}}{14} \cong 0.173 \qquad (33)$$

which coincides with the value given in ref 6. In the region $f_c < f < 1 - f_c$ the effective third-order vertex α' is positive. As a result, the binodal will coincide with the spinodal and close to the spinodal in the phase-separated area the quantities A, y, and $-\tau$ are proportional to each other. Hence

$$F \propto \tau^3 \qquad (34)$$

and the phase transition is third order. The proportionality between q_0^2 and $-\tau$ for random copolymers was first noticed by Panyukov and Kuchanov.[4] In Figure 1 the value of $y = {}^1/_6 n a^2 q_0^2$ has been plotted versus the rescaled χ-parameter $\tilde{\chi}$ for the symmetric case $f = 0.5$. If $(\tilde{\chi} - \tilde{\chi}_c)$ is small, then y increases linearly, but for large values of this parameter it approaches the limit $y \rightarrow \sqrt{2}$. This can qualitatively be understood in the following way. Near the spinodal, the segregation is so small that only the large blocks contribute to the phase
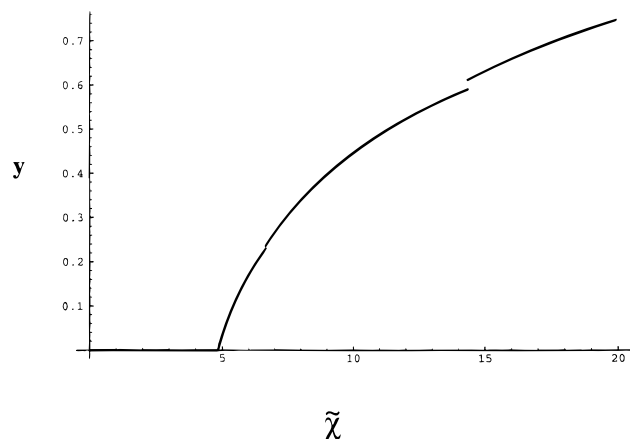
Figure 2. Value of $y = \frac{1}{6}na^2q_0^2$ as a function of $\tilde{\chi}$ for $f = 0.65$.
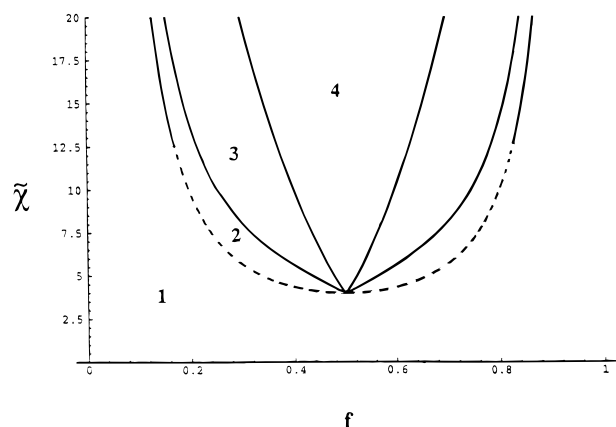

Figure 3. Phase diagram of the random copolymer: (dashed line) third-order transition; (solid line) first-order transition; (1) disordered phase; (2) bcc phase; (3) hexagonal phase; (4) lamellar phase.

separation, and consequently, the wave vector is small. Going away from the spinodal, the segregation increases and smaller blocks join in the separation. If the segregation is high, all blocks contribute, and the resulting wave vector $y = \sqrt{2}$ is determined by the average block length. For A-monomer fractions different from 0.5, the graph looks similar, the only difference being that at the phase transitions to other structures, small jumps to somewhat higher y values occur (Figure 2).

To construct the phase diagram the free energies of the lamellar, cylindrical, bcc, face-centered cubic (fcc), and the quasi crystal morphology have been compared. (The quasi crystal phase is a quasi periodic structure with a 5-fold symmetry. The vectors in the first coordination sphere of the reciprocal lattice form the edges of an isocahedron.) Although the fcc and the quasi crystal morphology do not appear in the phase diagram, for completeness we have given the expressions for their vertex functions in the Appendix.

The phase diagram is shown in Figure 3. Although for extreme values of f (i.e. $f < .173$ or $f > .827$) the binodal and the spinodal do not coincide, the difference is so small that it cannot be displayed in the scale of Figure 3. For $f = 0.1$ and $f = 0.9$ this difference is less than 1% of the spinodal value, and it increases up to almost 6% for $f \to 0$ or 1.

In Figure 4 the lower curve represents the value of y directly after the transition, while the upper curve represents its value for large segregation. From this figure it can be deduced that for extreme asymmetric
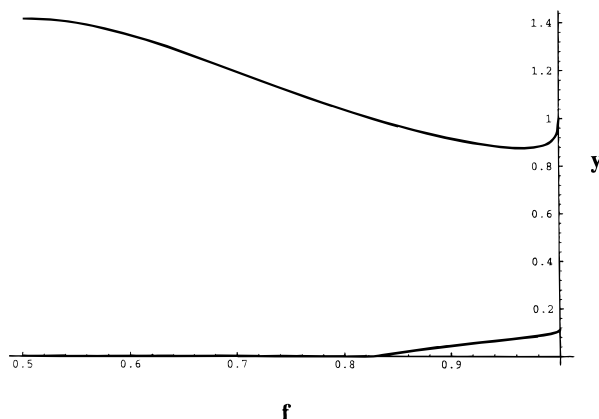
Figure 4. Lower curve: value of y directly after the transition. Upper curve: value of y in the highly segregated region.

random copolymers (say for $f > 0.95$) the wavelength of the microstructure directly after the transition is around 3 times bigger than the wavelength in the highly segregated region.

In the phase diagram displayed in Figure 3, the line separating the lamellar region from the cylindrical region, as well as the line separating the cylindrical region from the bcc region has a discontinuous derivative at $f = 0.5$. To see why this happens, we have (after minimization with respect to the amplitude A), expanded the free energy of the various phases near $f = 0.5$ in powers of the parameters

$$h = \tilde{\chi} - 4$$

$$\epsilon = 1 - e \qquad (35)$$

The equality of the free energies of two different phases is expected to occur for values of h which scale linearly with ϵ. The leading term in the expansion is of third order. Since all morphologies have the same free energy up to this order, one should make the expansion till fourth order. The result is (for $e < 1 \Leftrightarrow f > 0.5$):

$$F_{\text{lam}} = -\frac{h^3}{864} + \frac{5h^4}{20736} + \frac{h^2 e^2}{36} \qquad (36)$$

$$F_{\text{cyl}} = -\frac{h^3}{864} + \frac{7h^4}{20736} + \frac{h^2 e^2}{36} - \frac{h^3 e}{216\sqrt{6}} \qquad (37)$$

$$F_{\text{bcc}} = -\frac{h^3}{864} + \frac{19h^4}{41472} + \frac{h^2 e^2}{36} - \frac{h^3 e}{216\sqrt{3}} \qquad (38)$$

From these expressions, the slope of the line separating two phases can be found by equating the corresponding free energies:

$$\frac{d\chi}{de} = \frac{h}{\epsilon} = 8\sqrt{6}$$

for the lamellar/cylindrical border line (39)

$$\frac{d\chi}{de} = \frac{h}{\epsilon} = (2 - \sqrt{2})\frac{32\sqrt{3}}{5}$$

for the cylindrical/bcc border line (40)

The reason for these discontinuities lies in the third-order vertex function. It has to be negative for all f values and contains a factor $|1 - e|$. (The vertical lines denote an absolute value.)

5. Concluding Remarks

The analysis in this paper can be extended in several ways. E.g., the influence of the weakly fluctuating

fields, quantified by F_{hh} and ΔF (eq 18), can be investigated. To get an idea about the influence these terms might have on the phase diagram, and to what extent the present analysis is valid, we have calculated the effect of the higher harmonics and found that they do not change the phase diagram quantitatively in the region $0.48 < f < 0.52$ and not qualitatively in the region $0.42 < f < 0.58$. Beyond $f = 0.58$, the higher harmonics favor the fcc phase rather than the hexagonal phase, and the region of the bcc phase broadens. However, to account for the weakly fluctuating fields, the term ΔF has to be taken into account as well, and this will be addressed in a forthcoming publication. Another improvement would be to consider the possibility of two-phase regions, where two or more ordered states coexist. Also the calculation of the fluctuation effects is of interest, since in the case of a random copolymer without correlations between the monomers, they have been shown to be responsible for the complete elimination of the microstructure predicted by the mean field theory.[9]

6. Appendix

In this Appendix, the coefficients of the Landau expansion for the various possible microstructures are presented. As a function of the amplitude A, the free energy can be written as

$$nF = \tau A^2 + \alpha A^3 + \beta A^4 \qquad \text{(A1)}$$

The coefficients τ, α, and β depend on the parameters e and y and on the type of microstructure considered. The second-order coefficient τ, which also depends on the rescaled χ-parameter $\tilde{\chi}$, is the same for all structures and given by

$$\tau = \frac{(1 + e^2)^2(1 + e^2 + ey)}{2e^3} - \frac{2e\tilde{\chi}}{1 + e^2} \qquad \text{(A2)}$$

The third-order vertex functions for the various microstructures differ only by a multiplication factor (see, e.g., ref 14)

$$\alpha_{\text{lamellar}} = 0 \qquad \alpha_{\text{fcc}} = 0$$

$$\alpha_{\text{hexagonal}} = -\frac{2\gamma_0}{3\sqrt{3}} \qquad \alpha_{\text{quasi crystal}} = -\frac{4\gamma_0}{3\sqrt{15}} \qquad \text{(A3)}$$

$$\alpha_{\text{bcc}} = -\frac{4\gamma_0}{3\sqrt{6}}$$

$$\gamma_0 = \pm\frac{3(1 - e^2)(1 + e^2)^3(1 + e^2 + ey)}{4e^5} \qquad \text{(A4)}$$

The upper sign is valid for $e > 1$; the lower sign is valid for $e < 1$. Finally, the fourth-order contribution to the

free energy has the form[14]

$$\frac{1}{4!}\sum_{\vec{q}_1\vec{q}_2\vec{q}_3\vec{q}_4} \Gamma^{(4)}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4)A^4 \qquad \text{(A5)}$$

where the summation is restricted to vectors $\vec{q}_1 + \vec{q}_2 + \vec{q}_3 + \vec{q}_4 = 0$ belonging to the first coordination sphere of the reciprocal lattice. The function $\Gamma^{(4)}$ is symmetric in its arguments and depends only on the mutual orientation of the four vectors $\vec{q}_1$, $\vec{q}_2$, $\vec{q}_3$, and $\vec{q}_4$. Since all these vectors have the same length q_0, this mutual orientation is completely determined by the parameters h_1, h_2, and h_3 defined by

$$(\vec{q}_1 + \vec{q}_2)^2 = h_1 q_0^2$$

$$(\vec{q}_1 + \vec{q}_4)^2 = h_2 q_0^2 \qquad \text{(A6)}$$

$$(\vec{q}_1 + \vec{q}_3)^2 = h_3 q_0^2$$

These three parameters are not independent; they satisfy the relation

$$h_1 + h_2 + h_3 = 4 \qquad \text{(A7)}$$

The fourth-order vertex defined in eq A5 depends only on the values of h_1, h_2, and h_3 and can therefore be written as

$$\Gamma^{(4)}(\vec{q}_1, \vec{q}_2, \vec{q}_3, \vec{q}_4) = \Gamma^{(4)}(h_1, h_2, h_3) \qquad \text{(A8)}$$

This function $\Gamma^{(4)}(h_1, h_2, h_3)$ is completely symmetric in its arguments. In our model, it is given by

$$\Gamma^{(4)}(h_1, h_2, h_3) = (1 + e^2)^4 (15 - 3e^2 - 3e^4 + 15e^6 + 16ey - 16e^3y + 16e^3y + 16e^5y)/(8e^7) \quad \text{(A9)}$$

of all three numbers h_1, h_2, and h_3 are different from zero;

$$\Gamma^{(4)}(h, 4-h, 0) = (1 + e^2)^4(2e + 6e^3 + 6e^5 + 2e^7 + 9y + 12e^2y + 6e^4y + 12e^6y + 9e^8y + 24ey^2 + 24e^7y^2 + 16e^2y^3 - 16e^4y^3 + 16e^6y^3)/(4e^7y(1 + e^2 + 2ey)) \quad \text{(A10)}$$

if $h \neq 0$ and $h \neq 4$; and finally,

$$\Gamma^{(4)}(4, 0, 0) = (1 + e^2)^4(8e + 24e^3 + 24e^5 + 8e^7 + 21y + 36e^2y + 30e^4y + 36e^6y + 21e^8y + 50ey^2 + 6e^3y^2 + 6e^5y^2 + 50e^7y^2 + 32e^2y^3 - 32e^4y^3 + 32e^6y^3)/(8e^7y(1 + e^2 + 2ey)) \quad \text{(A11)}$$

These expressions give rise to the following fourth-order

coefficients:

$$\beta_{\text{lamellar}} = (1 + e^2)^4(8e + 24e^3 + 24e^5 + 8e^7 + 21y + 36e^2y + 30e^4y + 36e^6y + 21e^8y + 50ey^2 + 6e^3y^2 + 6e^5y^2 + 50e^7y^2 + 32e^2y^3 - 32e^4y^3 + 32e^6y^3)/32e^7y(1 + e^2 + 2ey) \quad (A12)$$

$$\beta_{\text{hexagonal}} = (1 + e^2)^4(24e + 72e^3 + 72e^5 + 24e^7 + 93y + 132e^2y + 78e^4y + 132e^6y + 93e^8y + 242ey^2 + 6e^3y^2 + 6e^5y^2 + 242e^7y^2 + 160e^2y^3 - 160e^4y^3 + 160e^6y^3)/(96e^7y(1 + e^2 + 2ey)) \quad (A13)$$

$$\beta_{\text{bcc}} = (1 + e^2)^4(16e + 48e^3 + 48e^5 + 16e^7 + 87y + 108e^2y + 42e^4y + 108e^6y + 87e^8y + 238ey^2 - 6e^3y^2 - 6e^5y^2 + 238e^7y^2 + 160e^2y^3 - 160e^4y^3 + 160e^6y^3)/(64e^7y(1 + e^2 + 2ey)) \quad (A14)$$

$$\beta_{\text{fcc}} = (1 + e^2)^4(32e + 96e^3 + 96e^5 + 32e^7 + 99y + 156e^2y + 114e^4y + 156e^6y + 99e^8y + 246ey^2 + 18e^3y^2 + 18e^5y^2 + 246e^7y^2 + 160e^2y^3 - 160e^4y^3 + 160e^6y^3)/(128e^7y(1 + e^2 + 2ey)) \quad (A15)$$

$$\beta_{\text{quasicrystal}} = (1 + e^2)^4(120e + 360e^3 + 360e^5 + 120e^7 + 645y + 804e^2y + 318e^4y + 804e^6y + 645e^8y + 1762ey^2 + 42e^3y^2 - 42e^5y^2 + 1762e^7y^2 + 1184e^2y^3 - 1184e^4y^3 + 1184e^6y^3)/(480e^7y(1 + e^2 + 2ey)) \quad (A16)$$

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