A New Class of Systems Exhibiting Microphase Separation: Polymer Blends with a Nonlocal Entropy of Mixing

Alexei R. Khokhlov*

Physics Department, Moscow State University, Moscow 117234, Russia

Igor Ya. Erukhimovich

Enterprise "Sitesoft", 32 Korneychuka Street, #3, Moscow 127357, Russia

Received March 15, 1993; Revised Manuscript Received August 20, 1993[⊗]

ABSTRACT: The stability of a binary polymer blend with respect to macro- and microphase separation is considered. It is shown that the loss of stability of the spatially homogeneous state of the blend via microphase separation resulting in formation of an equilibrium microdomain nanoheterogeneous structure is possible. The conditions for this effect are (i) a significant negative entropic contribution to the Flory–Huggins χ parameter, i.e., an entropic contribution to miscibility, and (ii) the nonlocal character of this contribution with a high value of the nonlocality radius. Both these conditions can be met for miscible polymer blends somewhat above their glass transition temperature. It is argued that the nanoheterogeneity recently observed in polystyrene–poly(vinyl methyl ether) blends can be explained by this effect.

1. Introduction

The phenomenon of microphase separation (or of the formation of a microdomain structure) has been known in polymer science for a long time. However, up to recent years the only polymer systems for which this phenomenon was studied in detail were the melts and solutions of poly(A)–poly(B) block copolymers with immiscible blocks.[1–5] For this case the separation into macroscopic A-rich and B-rich phases is impossible due to the fact that the blocks are linked into one chain by valency chemical bonds. Thus, the microdomain structure with alternating A-rich and B-rich domains is formed on the scale of the spatial size of individual blocks (i.e., the microphase separation occurs).

Recently it has been discovered that block copolymers are not unique in forming a microdomain structure, and intensive attention has been paid to other systems exhibiting microphase separation. Among the examples are random copolymers,[6–9] interpenetrating polymer networks,[10,11] weakly charged polyelectrolytes in poor solvents and mixtures of weakly charged polyelectrolytes,[12–16] and ionomers.[17] Thus, the concept of microphase separation has a much wider application in polymer physics than was previously thought. The microdomain structure formation is a typical way to resolve the contradiction between the tendency toward immiscibility of components on a microscopic scale and an opposite stabilizing tendency acting on a somewhat larger scale which prevents the complete demixing of the system under consideration. This latter tendency may be due to the chain connectivity (for copolymers, ionomers, or interpenetrating networks) or to the contribution of mobile counterions to the entropy of mixing (for weakly charged polyelectrolytes).

In this context it is natural to raise the following question: Is it possible to have a microdomain structure in a usual blend of two neutral linear homopolymers [poly(A) and poly(B)]? In this case the components are not linked into one chain; there are no counterions or specific interactions in the system. The answer to this question is affirmative, and that is just what we are going to prove in the present paper.

We will show that the formation of a microdomain structure should be quite common for the cases when A and B links tend to demix for energetic reasons and tend to compatibilize for entropic reasons (e.g., due to steric factors, internal rotations in A and B chains are more free in the presence of both components than in pure A and B phases; thus, the set of possible conformations in the mixed state is more rich). This sort of entropic contribution to the compatibility (to the entropy of mixing) is always nonlocal (the freedom of internal rotation in a dense system largely depends on a rather extended surrounding of a given link), and we will see that this nonlocality plays a key role in the stabilization of the microdomain structure.

It should be generally expected that the nonlocal character of the entropy becomes more pronounced as the glass transition temperature for the blend, T_g, is approached (see below). Therefore, in predicting microphase separation in the polymer blend, we have in mind primarily the phenomenon which may occur somewhat above T_g. However, the analysis of sections 3 and 4 remains valid independently of the physical reason for the nonlocality of entropy, and thus, it can be applied for other physical situations.

We will see that for the characteristic values of the parameters of a polymer blend the spatial scale of the emerging microdomain structure turns out to be on the order of several nanometers. In other words, the microphase separation in the blends under consideration leads to the formation of nanoheterogeneity.

One of the motivations of the present study was ref 18, in which microheterogeneity in the 50:50 weight percent blend of polystyrene (PS) and poly(vinyl methyl ether) (PVME) was discovered by means of two-dimensional wide-line separation NMR. Glass trnasition temperatures T_g of pure PS and pure PVME are 373 and 245 K, respectively (this correlates with the fact that PS links are more bulky and thus there are more restrictions on internal rotations in PS melts). Blends of PS and PVME (50:50) are compatible from a macroscopic point of view, and the glass transition for these blends is at 260 K. The experiments of ref 18 were carried out at 320 K (60 K above T_g), and a clear indication of nanoheterogeneity of the characteristic size 3.5 ± 1.5 nm was obtained. In the heterogeneous state PVME links were shown to be relatively mobile, while for PS links the mobility is very

---

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

restricted. We think that the formation of this microheterogeneous structure can be explained by microphase separation of the type described above. We will consider this point further.

In the next section we will discuss qualitatively the reason for the formation of a microdomain structure. Section 3 is devoted to the formulation of the model for quantitative calculations. A general mathematical analysis of the conditions ensuring formation of a microdomain structure is carried out in section 4. In section 5 we present and discuss numerical results that illustrate some peculiarities of the microphase separation in the system under consideration. In section 6 some concluding remarks and generalizations are made.

2. Microphase Separation in Polymer Blends: A Qualitative Discussion

The easiest although somewhat oversimplified way to explain why the microdomain structure may be formed in a blend of two neutral linear homopolymers [poly(A) and poly(B)] is the following. Suppose that the glass transition temperatures for pure poly(A) and poly(B) are T_g^A and T_g^B ($T_g^A > T_g^B$) and that these polymers are miscible at high temperatures (cf. the example of the PS–PVME blend described above).

In general, the miscibility of two polymers can have either energetic or entropic origin. In the former case A and B links simply attract to each other; in the latter situation (which we assume to be the case for the present study) A and B links like to be in the neighborhood of each other because in this way the greater freedom for internal rotations in the chains is achieved. This may be, e.g., due to steric reasons: if A links are more bulky than B links, their separation with the formation of the pure A phase may restrict the set of possible conformations of A chains that are otherwise realized in the presence of some fraction of B chains.

In the case of the entropic miscibility the Flory–Huggins parameter χ^{19} has the structure

$$\chi = \chi_\epsilon + \chi_s = \epsilon/kT - s \tag{1}$$

where k is the Boltzmann constant, T is the temperature, ϵ is the characteristic energy associated with the direct interaction of links A and B (for most of the cases $\epsilon > 0$), and $s > 0$ is the characteristic entropy gain from the fact that A and B links are in the neighborhood of each other. It follows from eq 1 that at high temperatures $\chi < 0$ and the polymers are miscible, but with decreasing temperature the trend toward immiscibility becomes more and more pronounced, and we finally reach the region where $\chi > 0$ and the phase separation may occur.

Suppose that for a given composition of the blend poly(A)–poly(B) the phase separation begins at a certain temperature T_c located in the interval $T_g^B < T_c < T_g^A$. It is clear that in this case the process of the separation into macroscopic phases cannot be completed: as soon as large enough domains of the A-rich phase appear, they become glassy by virtue of the inequality $T_c < T_g^A$ and the process stops. As a final result some sort of microdomain structure will appear.

The presented explanation of the possibility of realization of a microdomain structure in polymer blends was simplified intentionally and may be somewhat misleading, as regards the effect under consideration in the present paper. The microdomain structure described above is frozen-in; therefore, one may think that it is formed due to kinetic but not thermodynamic reasons. Microheterogeneities of this type are indeed experimentally observed when the system is rapidly brought below the spinodal of macroscopic phase separation, and one of the emerging phases corresponds to the glassy state (see, for example, ref 27; for the theoretical description of these processes, see refs 28 and 29).

However, it will be shown below that in many cases the microphase separation need not be related to the occurrence of the frozen-in structure that appears as a result of glass transition in one of the microphases. As a matter of fact, in the system under consideration the microdomain structure is formed at somewhat higher temperatures and can be described in purely thermodynamic terms (cf. with the case of PS–PVME blends where the microstructures are observed at the temperatures which are 60 K above T_g[18]). Thus, the fact that there is a glass transition at low temperatures plays only an indirect role in the explanation of the microphase separation at these higher temperatures. The more important things are (i) the structure (1) of the χ parameter and the entropically-driven miscibility at high temperatures and (ii) the nonlocal character of the entropic contribution to χ (i.e., the dependence of the freedom for internal rotation of a given link on its extended surroundings).

To be definite, assume that the entropy associated with the internal rotation of a given bulky A link depends on the number of small B links in some sphere of radius R around this A link in such a way that the greater is this number the more rich is the set of possible conformations and hence the larger is the corresponding contribution to the entropy of the system. Let us compare for this case three qualitatively different possibilities: the homogeneous state, macroscopic separation into A-rich and B-rich phases, and microdomain structure. At relatively low temperatures the homogeneous phase cannot be stable due to the energetic repulsion of components described by the term ϵ/kT in eq 1; thus, some sort of demixing is to be expected at these temperatures. However, if the separation into macroscopic phases occurs, then most of the bulky A links will be surrounded by the same type of links in the A-rich phase, and they will lose some entropy associated with the internal rotation degrees of freedom. If this entropy loss is large enough, one can expect that at certain intermediate temperatures the realization of the third possibility, namely, of the microdomain structure formation, is most advantageous for purely thermodynamic reasons. Indeed, let the size L of the domains and the microscopic scale l characterizing short-range segregating interaction satisfy the inequality $l \ll L \leq R$. In this case one may expect that the free energy of the blend is really minimized for such a microheterogeneous structure. Indeed, the fraction of B links within the sphere of radius R around each A link is practically constant, so that the internal rotation entropy loss is small, as opposed to the considerable energy gain due to the reduction of A–B contacts for the spatially modulated structure. On the other hand, for L on the order of the microscopic size l of one link the free energy cost from the formation of numerous interfaces is obviously the dominating factor.

We see that the decisive role in the presented description of the appearance of a microdomain structure in a polymer blend belongs to the conjecture of nonlocal character of entropy and its qualitative implementation in terms of the sphere of radius R around a given A link: the fraction of B links within this sphere defines the entropy per one internal rotation in the A chains.

It is clear that in more exact terms the radius R is the spatial scale connected with the nonlocality of the entropy of internal rotations of A links. Thus, we conclude that

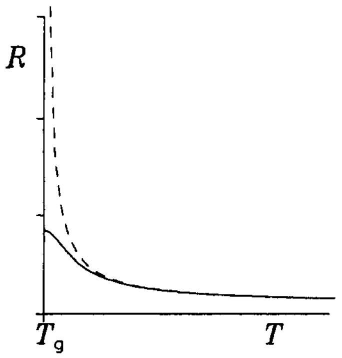

Figure 1. Qualitative dependencies of the nonlocality radius R on the temperature T in the case of a genuine thermodynamic phase transition (dashed line) and in the case of a relaxational transition (solid line).

the microdomain structure in a miscible polymer blend can be expected if the miscibility is caused by a nonlocal entropy contribution to the free energy with R significantly larger than l.

Now it is worthwhile to ask the following question: for which cases is the entropy of internal rotations highly nonlocal, so that R is larger than the microscopic size l? It is at this stage that the possibility of a glass transition at somewhat lower temperatures comes into play. At high temperatures the surroundings cannot restrict the internal rotation of A links, so that the corresponding entropy is local. The surroundings begin to be important, and hence, the nonlocality appears at somewhat lower temperatures (Figure 1). It becomes more and more pronounced as the glass transition temperature is approached. Indeed, if the transition of a blend to a glassy state were a thermodynamic phase transition, the nonlocality radius R would become infinite at $T = T_g$ (Figure 1, dashed line): the introduction of one additional A link at any given point would cause the freezing of the whole system. Even though the transition to a glassy state is regarded as a kinetic phenomenon rather than a genuine phase transition,[20] the significant increase of R as the temperature T_g is approached should still be valid (Figure 1, solid line).

It can be seen from Figure 1 that already at the temperatures much larger than T_g the value of R can exceed significantly the size of one link, so that the conditions for microphase separation discussed above may be met. Thus, the microdomain structure will appear for purely thermodynamic reasons without any direct connection with the freezing of kinetic relaxation processes which occurs at lower temperatures (at $T \approx T_g$). The glass transition at $T = T_g$ will simply fix the microheterogeneous structure formed at $T > T_g$.

It is worthwhile to recall here that the glass transition is manifested in two ways. The first characteristic feature of this transition is the slowing of large-scale kinetic processes as $T \rightarrow T_g$. Second, in the glass transition region the thermodynamic behavior has some peculiarities; in particular, the compressibility of the system varies very rapidly. From what is said above it is clear that it is this latter feature that is important for the occurrence of microphase separation.

One should emphasize that the glass transition is the most transparent but, probably, not the only reason for the entropy nonlocality. The quantitative analysis of sections 3 and 4 and the prediction of the appearance of a microdomain structure remain valid if the entropy nonlocality takes place due to some other physical reasons (not connected with the glass transition) as well.

The arguments presented above are qualitative; thus, they do not prove that the microphase separation is indeed possible. To do this, it is necessary to write the exact expression for the free energy of the blend and to analyze what the conditions are that ensure the existence of the thermodynamically advantageous microheterogeneous structure. This is done in the following sections.

3. Model

Let us now formulate the model of a polymer blend which will enable us to analyze the microphase separation described above in more detail. We will assume that we have a binary polymer blend of poly(A) chains of N_A monomer links and poly(B) chains of N_B links. To be definite, we will use the Gaussian approximation for chain statistics. This approximation is not crucial for the phenomena studied below; any other assumption for the local chain statistics will lead to the same qualitative conclusions.

In order to analyze the stability of the spatially homogeneous state of the blend with respect to macro- and microphase separation, we need an explicit expression for the free energy of this blend as a function of possible nonhomogeneous (and, generally, nonequilibrium) distributions of the A and B link volume fractions $\phi_A(r)$ and $\phi_B(r)$ (cf. refs 3, 4, and 12–14). The random-phase approximation applied for the polymer blend of Gaussian chains in the usual case where there is no nonlocal entropy of mixing gives the following expression for the free energy F_1:[21,22]

$$F/kT = (V/v)((\bar{\phi}_A/N_A)\ln\bar{\phi}_A + (\bar{\phi}_B/N_B)\ln\bar{\phi}_B + \chi_\epsilon\bar{\phi}_A\bar{\phi}_B) + \int\frac{d^3q}{(2\pi)^3}\left\{\frac{1}{N_A\bar{\phi}_A f_D(x_A)} + \frac{1}{N_B\bar{\phi}_B f_D(x_B)} - 2\chi_\epsilon\right\}\frac{|\phi_A(\vec{q})|^2}{2v} \quad (2)$$

where V is the volume of the system, $\bar{\phi}_A$ and $\bar{\phi}_B$ are the average volume fractions of A and B links in the blend, χ_ϵ is the energetic contribution to the Flory–Huggins parameter (cf. eq 1), v is the excluded volume assumed to be the same for both types of links, $x_i \equiv q^2R_i^2/6$ (i = A or B), $R_i^2 = l_i^2N_i$ is the characteristic size of the chains consisting of links of the ith type (l_A and l_B being the Kuhn segment lengths for A and B chains, respectively), $f_D(x)$ is the so-called Debye function defined as $f_D(x) = 2(\exp(-x) - 1 + x)/x^2$, and

$$\phi_A(\vec{q}) = \int d^3r\,(\phi_A(\vec{r}) - \bar{\phi}_A)\exp(i\vec{q}\vec{r}) \quad (3)$$

is the Fourier transformation of the deviation of the actual nonhomogeneous distribution of $\phi_A(\vec{r})$ from its average value $\bar{\phi}_A$. The free energy of the blend can be written in the form of eq 2 if the incompressibility condition

$$\phi_A(\vec{r}) + \phi_B(\vec{r}) = 1 \quad (4)$$

is valid; this will be assumed through the present paper.

The advantage of writing expression 2 for the free energy in terms of Fourier transformations is that in these terms this expression assumes a compact form which is exact for Gaussian chains within the framework of the random-phase (i.e., mean field) approximation. In the usual coordinate space such an exact compact expression does not exist. The approximate form that however clarifies the origin of some terms in expression 2 can be written as follows (cf. refs. 14 and 16):

$$F/kT = \int \mathrm{d}^3r\,\{(\phi_A(\vec r)/N_A)\ln\phi_A(\vec r) + (\phi_B(\vec r)/N_B)\ln\phi_B(\vec r) + \chi_\epsilon\phi_A(\vec r)\,\phi_B(\vec r) + (1/6)(l_A{}^2(\vec\nabla(\phi_A)^{1/2})^2 + l_B{}^2(\vec\nabla(\phi_B)^{1/2})^2)\}/v \tag{2a}$$

The first two terms in the integrand of eq 2a represent the entropy related to the translational degrees of freedom of the chains, the third term is connected with the energy of the short-range A–B interaction, and the last two terms are the contributions describing the entropy loss due to deveiations of the actual nonhomogeneous distribution of $\phi_A(\vec r)$ and $\phi_B(\vec r)$ from the average values $\bar\phi_A$ and $\bar\phi_B$ (the so-called Lifshitz entropy (see refs 23 and 24)).

Expressions 2 and 2a practically coincide if the characteristic scale of inhomogeneities in the system $L = 2\pi/q$ is much smaller than the smallest of two macromolecular sizes R_A and R_B and much larger than the microscopic scale l. On the other hand, they give the same result for F for the homogeneous state ($\phi_A(\vec r) = \phi_A$, $\phi_B(\vec r) = \phi_B$). From this point of view eq 2a can be regarded as the interpolation formula from which the origin of different terms in eq 2 can be elucidated.

In the subsequent calculations we will mainly use the exact expression 2 that is valid in the random-phase approximation, i.e., if the effects of interaction of fluctuations are neglected. The use of eq 2a leads to the same type of results.

In order to take into account the nonlocal entropy of mixing associated with the internal rotation entropy per A link (see the discussion in section 2), we have to add a new term ΔF_s to the conventional expression 2. It is this new term that may cause the microphase separation in the systems under consideration. The expression for ΔF_s can be written from the following considerations.

The conformational entropy of a polymer blend is given by the logarithm of the number of possible conformations of polymer chains. Chains can change their conformations by some internal rotations, leading to the redistribution of trans and gauche isomers, small vibrations of the angles of internal rotation near their equilibrium values, etc. Assume for simplicity that an angle of internal rotation is attributed to each link of polymer chains. In a zeroth approximation each of the angles gives a certain contribution to the conformational entropy (σ_0^A per A link and σ_0^B per B link); thus, the conformational entropy associated with internal rotations is given by

$$S_0 = \sigma_0^A N_A + \sigma_0^B N_B \tag{5}$$

Taken in the zero-order form (5), the entropic contribution to the free energy is trivial and does not lead to any physical effects.

However, the situation changes if we take into account the assumed dependence of σ^A and σ^B on the microenvironment of A and B links and thus on $\vec r$ in the inhomogeneous state. To be definite, let us assume (as we did in the qualitative discussion of section 2) that the A links are much more bulky than B links. In this case it is natural to expect that the entropy related to the internal rotation of B links does not depend on their microenvironment and is always equal to σ_0^B while the entropy of the internal rotation of an A link takes the maximum value if this A link is surrounded by small B links and decreases considerably for steric reasons with the increase of the fraction of other bulky A links in the microenvironment.

In this case the expression for the nonlocal entropy of internal rotations, S_{nl}, should be written as follows:

$$\Delta F_s/kT = -S_{nl} = -\sigma_0^B N_B - \int \sigma^A(\vec r)\,\phi_A(\vec r)\,\mathrm{d}^3r/v \tag{6}$$

where $\sigma^A(\vec r)$ is the entropic contribution stemming from the internal rotation of an A link situated at a point $\vec r$. As follows from the considerations presented above, the value of $\sigma^A(\vec r)$ itself is a function of the distribution of A links around the point $\vec r$. In the first approximation

$$\sigma^A(\vec r) = \sigma_0^A - \int \Delta s(\vec r - \vec r\,')\,\phi_A(\vec r\,')\,\mathrm{d}^3r'/v \tag{7}$$

where the kernel $\Delta s(\vec r - \vec r\,')$ is a positive function of its argument tending to zero at $|\vec r - \vec r\,'| \to \infty$. Equation 7 reflects the fact that the appearance of an A link at any finite distance $|r - r'|$ from the test A link can do no more than reduce the set of internal rotations available for the latter and, by doing so, diminish the value of $\sigma^A(r)$ by $\Delta s(r-r')$.

Even though the exact form of the function $\Delta s(\vec r - \vec r\,')$ can be derived from the detailed microscopic considerations only, the reader can think of this function for the moment as a simple exponential form:

$$\Delta s(\vec r - \vec r\,') = s\,\exp(-|\vec r - \vec r\,'|/R)/(4\pi R^3) \tag{8}$$

Although later we will use a somewhat different expression for $\Delta s(\vec r - \vec r\,')$, the two main parameters of the function $\Delta s(\vec r - \vec r\,')$ that determine the occurrence of the microdomain structure are apparent already from eqs 7 and 8: the integral magnitude of the effect

$$s = \int \Delta s(\vec r - \vec r\,')\,\mathrm{d}^3r'/v \tag{9}$$

that turns out to be just the parameter s involved in definition 1 and the radius R of nonlocality of the entropy defined as

$$R = [\int |\vec r - \vec r\,'|^2 \Delta s(\vec r - \vec r\,')\,\mathrm{d}^3r']/[\int \Delta s(\vec r - \vec r\,')\,\mathrm{d}^3r'] \tag{10}$$

Thus, we get finally the following expression for the nonlocal entropy of mixing and the total free energy of the system under consideration:

$$F = F_1 - kTS_{nl} \tag{11}$$

$$S_{nl} = \sigma_0^A N_A + \sigma_0^B N_B - \int \phi_A(r)\,\Delta s(\vec r - \vec r\,')\,\phi_A(r')\,\mathrm{d}^3r\,\mathrm{d}^3r'/v \tag{12}$$

where the quantity F_1 designates the conventional free energy described by formula 2 and the nonlocal contribution into eq 12 is the mathematical implementation of the qualitative idea about nonlocal entropy of mixing that is the main novelty of the presented approach.

4. Conditions of the Stability of a Homogeneous Blend

Now we are able to determine what the nonlocality of the entropy of mixing should be, i.e., what the parameters s and R of the kernel $\Delta s(\vec r - \vec r\,')$ (see eqs 9 and 10) should be that will ensure the formation of a microdomain structure in the system under consideration. To that end we will first carry out the analysis of the stability of the homogeneous state of the blend with respect to infinitesimal density fluctuations assuming the most general form of the kernel $\Delta s(\vec r - \vec r\,')$. Then, after calculating the spinodals of the system with respect to both macro- and microphase separation in this way, we will see what the essential characteristics of the kernel are that influence the locations of these spinodals.

As consistent with refs 3 and 4, the procedure of determining the stability conditions for the homogeneous state in the system under consideration is the following. Combining eqs 2, 11, and 12, taking into account the incompressibility condition (3), and performing the Fourier transformations of all the functions of coordinates involved in the resulting expression for the free energy, we get

$$F = F_0 + \Delta_2 F + ... \tag{13}$$

where $F_0(T,\bar\phi_A,\bar\phi_B)$ is the free energy of the homogeneous state and $\Delta_2 F$ is the quadratic (with respect to the deviations $\phi_A(r) - \bar\phi_A$) change of the free energy.

For F_0 we obtain

$$\frac{F_0}{kT} = \frac{V}{v}\left(\frac{\bar\phi_A}{N_A}\ln\bar\phi_A + \frac{\bar\phi_B}{N_B}\ln\bar\phi_B + \chi\bar\phi_A\bar\phi_B\right) \tag{14}$$

where the effective Flory–Huggins parameter χ has the structure of eq 1, i.e., $\chi = \chi_\epsilon - s$ with s given by eq 9.

The expression for the term F_2 turns out to be the following:

$$\frac{\Delta_2 F}{kT} = \frac{1}{2}\int G^{-1}(q)|\phi_A(q)|^2 \frac{d^3q}{(2\pi)^3} \tag{15}$$

where

$$G^{-1}(q) = \frac{1}{N_A\bar\phi_A f_D(x_A)} + \frac{1}{N_B\bar\phi_B f_D(x_B)} + 2(\Delta s(q) - \chi_\epsilon) \tag{16}$$

In eq 16

$$\Delta s(q) = \int \Delta s(\vec r - \vec r') \exp(i\vec q\vec r')\, d^3r'/v \tag{17}$$

is the Fourier transformation of the kernel $\Delta s(\vec r - \vec r')$. Because of the isotropy of the homogeneous state of the blend, the function $\Delta s(q)$ is actually the function of q^2. Thus, it can be expanded in powers of q^2 as follows:

$$\Delta s(q) = s(1 - q^2R^2/6 + ...) \tag{18}$$

where we made use of definitions 9 and 10.

One can make sure by straightforward calculations that the function $G(q)$ is connected with the correlation functions (cf. refs 3, 4, 21, and 22):

$$\int \phi_A(r)\, \phi_A(0) \exp(iqr)\, d^3r/v = \int \phi_B(r)\, \phi_B(0) \exp(iqr)\, d^3r/v = -\int \phi_B(r)\, \phi_A(0) \exp(iqr)\, d^3r/v = G(q) \tag{19}$$

As follows from eq 15, $\Delta_2 F$ is a positive definite quadratic form if the function $G^{-1}(q)$ is positive everywhere over the region $0 \le q < \infty$. In this case the increase of the amplitudes $\phi_A(\vec q)$ with any value of $|\vec q|$ will increase the free energy of the system. This is thermodynamically disadvantageous, and thus, the homogeneous blend is stable.

In the opposite case, when there exists some interval $q_1 \le q \le q_2$ in which the function $G^{-1}(q)$ is negative, the increase of the amplitudes $\phi_A(\vec q)$ with values of $|\vec q|$ lying in this interval will lead to the decrease of the free energy of the system. Thus, the deviations from the homogeneous distribution corresponding to these wavenumbers will amplify; the homogeneous state is unstable, and the spinodal decomposition or microphase separation takes place.

Summing up, we get the following equation for the spinodals, i.e., the boundaries of stability of a homogeneous blend:

$$\min G^{-1}(q) = 0 \tag{20}$$

where the minimum is sought in the range $0 \le q < \infty$ at given values of T and $\bar\phi_A$. Thereby two variants are possible (cf. refs 4 and 12–14): (i) the value of q satisfying eq 20 is equal to zero in which case the system undergoes the separation into two macroscopic phases and (ii) the value of q satisfying eq 20 is equal to a finite quantity q_0 in which case microphase separation occurs and the microdomain structure with the spatial period $\lambda = 2\pi/q_0$ appears.

The expression for $G^{-1}(q)$ is given by eq 16; thus, the stability analysis using eq 20 is straightforward. However, to perform this analysis, it is necessary to define the exact form of the function $\Delta s(q)$ which will be used in the calculations.

If the function $\Delta s(\vec r - \vec r')$ is given by eq 8, we obtain from eq 17

$$\Delta s(q) = \frac{s}{(1 + q^2R^2/12)^2} \tag{21}$$

The main shortcoming of eq 8 (and, hence, of eq 21) is a rather slow decrease of $\Delta s(\vec r)$ in the interval $l < r = |\vec r| < R$: at $r \ll R$ the value of $\Delta s(\vec r)$ is constant, although it is clear that the mutual influence of A and B links should become stronger with the decrease of r in the region $r \ll R$ as well.

The Ornstein–Zernicke kernel

$$\Delta s(\vec r - \vec r') = \frac{3s}{2\pi R^2}\frac{\exp(-6^{1/2}|\vec r - \vec r'|/R)}{|\vec r - \vec r'|} \tag{22}$$

is free of this shortcoming: it decreases in a reasonable way in the interval $l < |\vec r - r'| < R$. Moreover, eq 22 is natural from the point of view of the parallels with the theory of phase transitions (see ref 25), and its singularity at $|\vec r - \vec r'| \rightarrow 0$ is integrable and has no influence on the final physical results. Therefore, in section 5 we will present the results for this form of the function $\Delta s(\vec r - \vec r')$, which yields

$$\Delta s(q) = \frac{s}{1 + q^2R^2/6} \tag{23}$$

However, two points should be emphasized here. (i) Equation 22 is a reasonable phenomenological expression; the exact form of this kernel can be derived only from microscopic considerations or computer simulations. (ii) The exact form of the function $\Delta s(\vec r)$ is important only for the details of the effect described. For example, the conditions for the instability of the homogeneous state with respect to microphase separation depend on the values of the parameters s and R (see eqs 9 and 10) but not on the exact form of $\Delta s(\vec r)$ (see below).

Taking into account eqs 16 and 23, the function $G^{-1}(q)$ can be written in the form

$$G^{-1}(q) = \frac{1}{N_A\bar\phi_A f_D(x_A)} + \frac{1}{N_B\bar\phi_B f_D(x_B)} - 2\chi_\epsilon + \frac{2s}{1 + q^2R^2/6} \tag{24}$$

It is worthwhile to recall now the corresponding expression for the correlation function in the mixture of weakly charged polyelectrolytes (cf. refs 12–15):

$$G^{-1}(q) = \frac{1}{N_A\bar\phi_A f_D(x_A)} + \frac{1}{N_B\bar\phi_B f_D(x_B)} - 2\chi_\epsilon + \frac{2I}{r_{DH}^{-2} + q^2} \tag{25}$$

where I is the ionic strength of the solution and r_{DH} is the

Debye–Huckel radius of the screening of electrostatic interactions.

We see that expressions 24 and 25 are identical if the substitutions $r_{DH}^2 \leftrightarrow R^2/6$ and $I \leftrightarrow 6s/R^2$ are made. Thus, it is evident that the phenomenon of microphase separation in the mixtures of weakly charged polyelectrolytes and polymer blends with a nonlocal entropy of mixing can be described in an analogous way if eq 23 is used for the function $\Delta s(q)$. (Note, however, that this analogy is not complete since, generally speaking, the dependencies $r_{DH}(T,\phi_A)$ and $I(T,\phi_A)$ are not the same as $R(T,\phi_A)$ and $s(T,\phi_A)$.) The possibility to use this analogy to enrich our understanding of the effect under consideration is one more reason for the choice of eq 23 for the function $\Delta s(q)$.

The preceeding discussion enables us to rewrite eq 24 in the form

$$G^{-1}(q) = \frac{1}{N_A\bar{\phi}_A}\frac{((1/6)q^2l_A{}^2N_A)^2/2}{\exp(-(1/6)q^2l_A{}^2N_A) - 1 + (1/6)q^2l_A{}^2N_A} + \frac{1}{N_B\bar{\phi}_B}\frac{((1/6)q^2l_B{}^2N_B)^2/2}{\exp(-(1/6)q^2l_B{}^2N_B) - 1 + (1/6)q^2l_B{}^2N_B} - 2\chi - \frac{2sq^2R^2/6}{1 + q^2R^2/6} \qquad (26)$$

where $\chi = \chi_\epsilon - s$ is the Flory–Huggins parameter with both energetic and entropic contributions (see eq 1). Expression 26 allows one to see in the explicit form what the main parameters involved in most of the specific calculations related to the problem under consideration are. These are the volume fraction $\bar{\phi}_A$ ($\bar{\phi}_B = 1 - \bar{\phi}_A$), Kuhn segment lengths l_A and l_B, polymerization degrees N_A and N_B, Flory–Huggins parameter χ and entropic contribution to this parameter s, and, finally, the range of nonlocality R. Instead of R we will use the following dimensionless combination of these parameters:

$$\Sigma = 2sR^2/l^2 \qquad (27)$$

where $l^2 = l_A{}^2 + l_B{}^2$.

It is the value of the parameter Σ that determines the possibility of the existence of a microdomain structure. To prove this, let us determine the spatial period λ of the appearing microdomain structure. As follows from eq 20, the value of the wavenumber corresponding to this period can be determined from the minimization of the function $G^{-1}(q)$. For example, in the most interesting limit, $q^2l_A{}^2N_A \gg 1$, $q^2l_B{}^2N_B \gg 1$ (scale of microheterogeneties smaller then the size of both A and B blocks), the following asymptotic of expression 26 is valid:

$$G^{-1}(q) = \frac{1}{N_A\bar{\phi}_A} + \frac{1}{N_B\bar{\phi}_B} - 2\chi + \frac{q^2l_A{}^2}{12\bar{\phi}_A} + \frac{q^2l_B{}^2}{12\bar{\phi}_B} - \frac{2sq^2R^2/6}{1 + q^2R^2/6} \qquad (28)$$

(Note that the asymptotic form (28) corresponds to the approximation 2a for the free energy.) By minimizing this expression, we obtain from eq 20

$$q_0{}^2 = \frac{(12s)^{1/2}}{Rl\,\mathrm{d}(\phi_A)} - (6/R^2) \qquad (29)$$

where we have introduced the notation

$$\mathrm{d}^2(\phi_A) = \frac{l_A{}^2/l^2}{12\bar{\phi}_A} + \frac{l_B{}^2/l^2}{12\bar{\phi}_B} \qquad (30)$$

As follows from eqs 20, 29, and 30, the microdomain structure is formed provided the following inequalities are valid:

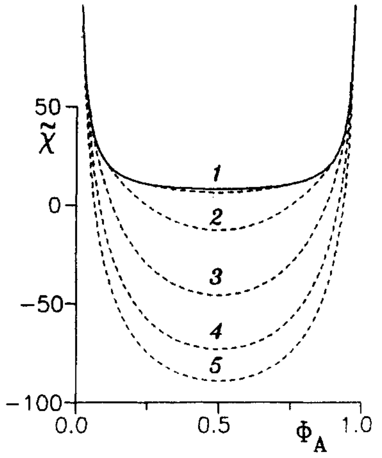

Figure 2. Spinodals of the spatially homogeneous state of the symmetric blend with $l_A = l_B$, $N_A = N_B$, and $s = 2$ in variables reduced Flory–Huggins parameter $\tilde{\chi} = 2\chi(N_A + N_B)$–volume fraction $\bar{\phi}_A$ of A links. Here and in the rest of the figures, spinodals with respect to macro- and microphase separation are shown by solid and dashed lines, respectively. Curves 1–5 correspond to the values of Σ equal to 1, 2, 4, 7, and 10, respectively.

$$G^{-1}(q_0) < 0; \quad q_0{}^2 > 0 \qquad (31)$$

The latter of these inequalities leads to the condition

$$\Sigma > \Sigma_{cr}{}^{\circ} = 6\,\mathrm{d}^2(\phi_A) \qquad (32)$$

Actually, inequality 32 is not exact since it was obtained using asymptotic expression 28 that is not valid at $q^2 \to 0$. The exact calculation using expression 26 gives the condition

$$\Sigma > \Sigma_{cr} = 4\,\mathrm{d}^2(\phi_A) \qquad (33)$$

instead of eq 32. We see that the exact and approximate formulas, eqs 32 and 33, differ in the numerical factor only.

5. Results and Discussion

The results of the stability analysis with eq 26 for $G^{-1}(q)$ for the symmetric blend ($l_A{}^2 = l_B{}^2 = l^2/2$ and $N_A = N_B = N$) are shown in Figure 2 where the spinodals of macro- and microphase separation are plotted in the variables reduced Flory–Huggins parameter $\tilde{\chi} = 2\chi(N_A + N_B)$–volume fraction of A links ϕ_A for different values of the parameter Σ at a fixed value of the parameter s. (For simplicity the values of Σ and s were supposed to be independent of both $\bar{\phi}_A$ and χ.) The full line is the conventional spinodal with respect to macrophase separation:

$$(N_A\bar{\phi}_A)^{-1} + (N_B\bar{\phi}_B)^{-1} = 2\chi \qquad (34)$$

and the dashed lines are the spinodals corresponding to the microphase separation. The critical value of the parameter Σ at which the equilibrium microdomain structure begins to be observed in the symmetric blend is $\Sigma_{cr} = 2/3$. From Figure 2 it is possible to see that the region of microphase separation (between the full and the corresponding dashed line) broadens with the increase of Σ, i.e., of the nonlocality radius, as it should be.

In Figure 3 the values of the quantity $x = q_0{}^2l_A{}^2$ are plotted as a function of $\bar{\phi}_A$ along the dashed curves of Figure 2 for $N = N_A + N_B = 10^2$. One can see that $\lambda = 2\pi/q_0$ is normally on the order of several times l which corresponds to 20–50 Å, i.e., to nanoheterogeneity. However, near the points where dashed curves in Figure 2 cross

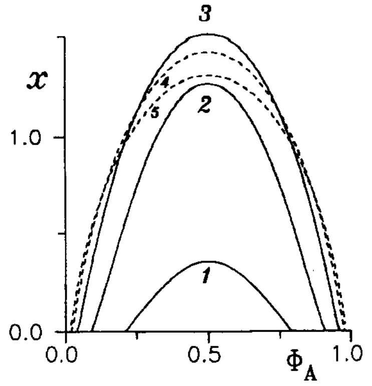

Figure 3. Dependencies of the value of $x = q_0^2 l_A^2$ corresponding to the characteristic size of the microdomain structure along curves 1–5 of Figure 2.

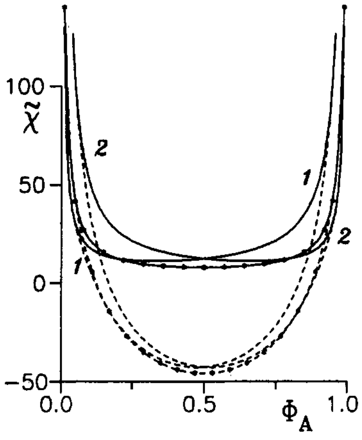

Figure 4. Spinodals of the spatially homogeneous state of the blends asymmetric in N (with $l_A = l_B$) in variables $\tilde{\chi}$–$\bar{\phi}_A$. For all curves $s = 1$ and $\Sigma = 4$. Curves 1 correspond to $N_A/N_B = 4$ and curves 2 to $N_A/N_B = 0.25$. The curves corresponding to the symmetric case ($N_A = N_B$) are labeled with asterisks.

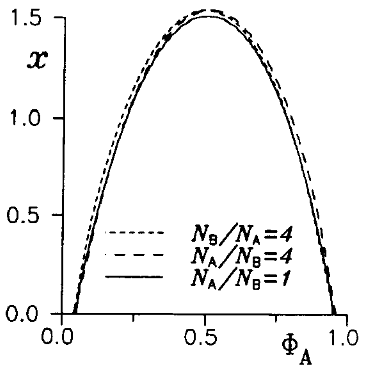

Figure 5. Dependencies of the value of $x = q_0^2 l_A^2$ corresponding to the characteristic size of the microdomain structure along the curves of Figure 4. The designations are given in the legend.

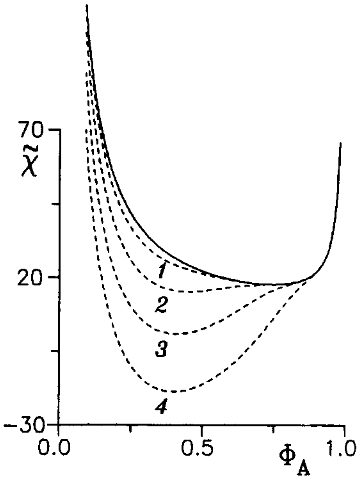

Figure 6. Spinodals of the spatially homogeneous state of the blends asymmetric in both N and l ($l_A^2/l_B^2 = 1/9$, $N_A/N_B = 1/9$, $s = 1$) in variables $\tilde{\chi}$–$\bar{\phi}_A$. Curves 1–4 correspond to the values of Σ equal to 0.5, 0.7, 1, and 1.5, respectively.

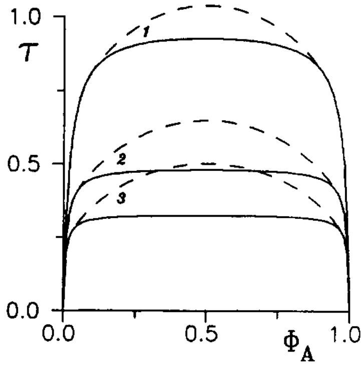

Figure 7. Spinodals of the spatially homogeneous state of the symmetric blend ($l_A = l_B$, $N_A = N_B$, $\Sigma = 4s$) in variables $\tau = (2\chi_\epsilon)^{-1}$–$\bar{\phi}_A$. Curves 1–3 correspond to the values of s equal to 0.5, 1, and 1.5, respectively.

the solid curve, $q_0 \rightarrow 0$ and $\lambda \rightarrow \infty$; thus, in this region a rather large-scale microstructure can emerge. It follows from eqs 26 and 29 that the value of $q_0(\phi_A)$ increases (and the spatial period λ decreases) with the increase of Σ in the interval from 2/3 to 4 (cf. Figure 3, curves 1–3). This behavior is mainly due to the fact that the dashed curves in Figure 2 for higher values of Σ are more remote from the spinodals of macrophase separation; therefore, the corresponding characteristic scale (so-called Cahn wavelength[26]) decreases. With a further increase of Σ the trend changes to the opposite (cf. Figure 3, curves 4 and 5). This is consistent with eq 30, according to which at $\Sigma \gg \Sigma_{cr}^\circ$ the spatial period λ is described by the following asymptotic expression:

$$\lambda = 2\pi(d^2(\phi_A)/(12s))^{1/4}(Rl)^{1/2} \qquad (35)$$

In other words, the spatial period is proportional to the geometric mean of the microscopic size l and the nonlocality radius R.

The role of the possible asymmetry in the degree of polymerization of A and B chains (at $l_A = l_B$) is illustrated in Figures 4 and 5. One can see that for these asymmetric cases the area of microphase separation is changed less than the conventional spinodal for macrophase separation. In the situations with high asymmetry both in N and l (Figure 6) the phase diagram can be very asymmetric as well with the whole region of microdomain structure situated at $\chi > \chi_{cr}$, where χ_{cr} is the critical point of separation into macroscopic phases (Figure 6, curve 1). However, such a situation takes place only at values of Σ close to Σ_{cr}. With an increase of Σ, the region of the microdomain structure becomes more symmetric (Figure 6, curves 2–4).

It is slightly more complicated to analyze the role of the parameter s, i.e., of the integral magnitude of the effect (see eq 9). The problem is that the value of χ itself depends on s according to eq 1. Therefore, in Figure 7, where the spinodals for macro- and microphase separation are plotted for different values of s, the variables chosen are a reduced temperature $\tau = (2\chi_\epsilon)^{-1} = kT/2\epsilon$ (see eq 1) and $\bar{\phi}_A$. Since $\Sigma = sR^2/l^2$ is proportional to s, its value is also adjusted in order to see explicitly what the effect is of variation of s alone with other parameters fixed. It can be seen that the spinodals for macroscopic phase separation are shifted to lower temperatures as the value of s increases. This is

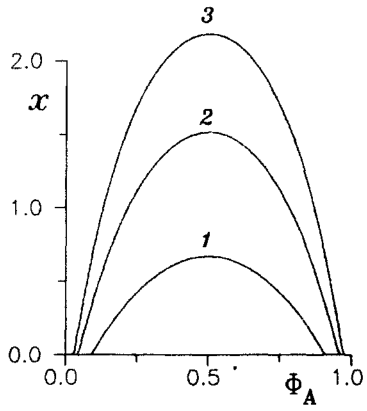

Figure 8. Dependencies of the value of $x = q_0{}^2 l_A{}^2$ corresponding to the characteristic size of the microdomain structure along curves 1–3 of Figure 7.

understandable, since the negative entropic contribution to χ becomes higher. Simultaneously, the region of the instability of the homogeneous state with respect to microphase separation also becomes slightly broader. The spatial period of the appearing microstructures generally decreases with the increase of s (see Figure 8).

6. Conclusions

In the present paper we have demonstrated that in the ordinary polymer blends with nonlocal entropy of mixing the microphase separation may occur, with equilibrium nanoheterogeneous structures emerging as a result of this process. From the qualitative discussion of section 2 it is clear that the microheterogeneous structure observed in ref 18 may be just due to this effect.

From the curves of Figure 2 it can be seen that the region of stability of the microdomain structure exists if the parameter $\Sigma = sR^2/l^2$ is large enough. This is the case if (i) there is a negative entropic contribution to the χ parameter (entropic miscibility) and this contribution is not small and (ii) this contribution is of nonlocal character, the radius of nonlocality being significantly larger than the microscopic size. In section 2 we explained that a high value of the radius of entropy nonlocality can be achieved somewhat above the glass transition temperature T_g (see Figure 1). However, this line is not pursued quantitatively in the present paper. In fact, if the trend of Figure 1 is taken into account, the values of R and s themselves become temperature- and composition-dependent, this fact leading to many new effects in the phase diagrams for both macro- and microphase separation. However, the quantitative study of these effects requires deepening into the microscopic theory of glass transition in polymers, and this is what we try to avoid in the present paper. The corresponding consideration will be the subject of a subsequent publication.

Another generalization of the present approach is the calculation of the full phase diagrams, not only spinodals of the homogeneous state. Taking into account the analogy with the case of the mixtures of weakly charged polyelectrolytes mentioned above, we expect diagrams similar to that calculated in refs 15 and 16 for this latter case. However, this problem requires additional quantitative consideration.

References and Notes

(1) *Developments in Block Copolymers*; Goodman, I., Ed.; Applied Science: New York, 1982; Vol. 1; 1985; Vol. 2.
(2) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(3) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(4) Erukhimovich, I. Ya. *Vysokomol. Soedin.* **1982**, *A24*, 1942; *Polym. Sci. USSR (Engl. Transl.)* **1983**, *24*, 2223.
(5) Semenov, A. N. *Sov. Phys.—JETP (Engl. Transl.)* **1985**, *61*, 733.
(6) Shakhnovich, E. I.; Gutin, A. M. *J. Phys. (Paris)* **1989**, *50*, 1843.
(7) Panyukov, S. V.; Kuchanov, S. I. *Zh. Eksp. Teor. Fiz.* **1991**, *99*, 659; *Sov. Phys.—JETP (Engl. Transl.)* **1991**, *72*.
(8) Dobrynin, A. V.; Erukhimovich, I. Ya. *JETP Lett. (Engl. Transl.)* **1991**, *53*, 570.
(9) Fredrickson, G. H.; Millner, S. T. *Phys. Rev. Lett.* **1991**, *67*, 835.
(10) Binder, K.; Frisch, H. *J. Chem. Phys.* **1984**, *81*, 2126.
(11) Frisch, H.; Grosberg, A. *Macromol. Chem. Theory Simul.* **1993**, *2*, 517.
(12) (a) Borue, V. Yu.; Erukhimovich, I. Ya. *Sov. Phys.—Dokl. (Engl. Transl.)* **1986**, *31*, 146. (b) Borue, V. Yu.; Erukhimovich, I. Ya. *Macromolecules* **1988**, *21*, 3240.
(13) Joanny, J. F.; Leibler, L. *J. Phys. (Paris)* **1990**, *51*, 545.
(14) (a) Nyrkova, I. A.; Khokhlov, A. R.; Kramarenko, E. Yu *Vysokomol. Soedin.* **1990**, *A32*, 918. (b) Khokhlov, A. R.; Nyrkova, I. A. *Macromolecules* **1992**, *25*, 1493.
(15) Dobrynin, A. V.; Erukhimovich, I. Ya. *Zh. Eksp. Teor. Fiz.* **1991**, *99*, 1344; *Sov. Phys.—JETP (Engl. Transl.)* **1991**, *72*, 751.
(16) Nyrkova, I. A.; Doi, M.; Khokhlov, A. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 926.
(17) Nyrkova, I. A.; Khokhlov, A. R.; Doi, M. *Macromolecules* **1993**, *26*, 3601.
(18) Schmidt-Rohr, K.; Clauss, J.; Spiess, H. W. *Macromolecules* **1992**, *25*, 3273.
(19) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(20) Sanditov, D. S.; Bartenev, G. M. *Physical Properties of Disordered Structures*; Nauka Publishers: Novosibirsk, 1982.
(21) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, and London, 1979.
(22) Erukhimovich, I. Ya. *Vysokomol. Soedin.* **1979**, *A21*, 427; *Polym. Sci. USSR (Engl. Transl.)* **1980**, *21*, 470.
(23) Lifshitz, I. M.; Grosberg, A. Yu.; Khokhlov, A. R. *Rev. Mod. Phys.* **1978**, *50*, 683.
(24) Grosberg, A. Yu.; Khokhlov, A. R. *Statistical Physics of Macromolecules*; Nauka Publishers: Moscow, 1989.
(25) Landau, L. D.; Lifshitz, E. M. *Statistical Physics*; Nauka Publishers: Moscow, 1976; Part I.
(26) (a) Cahn, J. W.; Hilliard, J. E. *J. Chem. Phys.* **1959**, *31*, 68. (b) de Gennes, P. G. *J. Chem. Phys.* **1980**, *72*, 4756. (c) Pincus, P. *J. Chem. Phys.* **1981**, *75*, 1996.
(27) Callister, S.; Keller, A.; Hikmet, R. M. *Makromol. Chem., Macromol. Symp.* **1990**, *39*, 19.
(28) Mitlin, V. S.; Manevich, L. I. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1.
(29) Kotnis, M. A.; Muthukumar, M. *Macromolecules* **1992**, *25*, 1716.