Conformations of Molten Diblock Copolymer Macromolecules near the Point of Microphase Separation Transition

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ABSTRACT: Some conformational characteristics of molten diblock copolymer A_nB_m individual macromolecules are calculated near the point of microphase separation as functions of reduced Flory parameter $\tilde{\chi} = \chi N$, χ being the conventional Flory parameter and $N = n + m$—the total degree of polymerization. To carry out these calculations, Edwards' perturbative approach was generalized, "screened" monomer–monomer interaction energy being obtained by taking into account fluctuation effects beyond the random-phase approximation. Presented results verify the basic assumption of the weak segregation theory of microphase separation as to "almost Gaussian" conformational behavior of molten diblock copolymer macromolecules and indicate the significance of fluctuation effects.

Introduction. Recently Leibler's theory of microphase separation of molten diblock copolymers[1] was tested by Monte Carlo simulation.[2] In particular, it was found that the size of the diblock copolymer macromolecule as a whole increases as the system approaches the point of microphase-separation transition (MST) from the side of the liquid (disordered) phase. This interesting effect was not predicted by any direct theoretical calculation. In this paper we give the theoretical description of this phenomenon.

Calculation of Average Conformational Diblock Copolymer Macromolecule Characteristics. The general idea of our calculation was first presented by Edwards[3,4] and developed by de Gennes[5,6] and one of us[7,8] and in more recent works.[9,10] Assume that deviations of conformational sets of all macromolecules from ideal Gaussian ones are small. It follows that all corrections to characteristics of any individual macromolecule averaged over all its conformations can be easily calculated using perturbation theory given an effective monomer–monomer interaction energy $U^{\mathrm{ef}}(r)$, r being the distance between monomers pertaining to the macromolecule. The problem to be resolved is to account for a "screening" of an initial interaction of these monomers due to their interaction with monomers of all other macromolecules. The assumption as to "nearly Gaussian" macromolecule behavior turns out to correspond to the well-known random-phase approximation (RPA) enabling the calculation of $U^{\mathrm{ef}}(r)$ explicitly. Thus, having calculated the swelling (contraction) of all macromolecules, one can verify this approach. For example, to calculate the swelling ratio $\alpha^2 = \langle H^2\rangle/\langle H^2\rangle_0$ ($\langle H^2\rangle$ and $\langle H^2\rangle_0$ being mean-square distances between the ends of a homopolymer chain perturbed due to self-interaction and of an ideal one, respectively), the following expression was presented:[4]

$$\alpha^2 - 1 = \frac{a^2}{18N}\int q^2 U^{\mathrm{ef}}(q)\Psi(q)\frac{\mathrm{d}^3q}{(2\pi)^3} \qquad (1)$$

Here $U^{\mathrm{ef}}(\vec{q}) = \int \mathrm{d}V\, U^{\mathrm{ef}}(r)\exp(i\vec{q}\vec{r})$, a and N are the Kuhn segment and the polymerization index of the chain, respectively, and

$$\Psi(q) = \sum_{l=1}^{l=N} \nu(l)\, l^2 \exp\left(-\frac{q^2a^2l}{6}\right)$$

where $\nu(l) = N - l$ is the number of all monomer pairs on the chain separated by l bonds.

Consider now the molten diblock copolymer A_nB_m. Note that a diblock copolymer is characterized by both the swelling ratios of each block and one of the macromolecules as a whole and the mean cosine of the angle of the vectors $\vec{h}_A$ and $\vec{h}_B$ drawn from the block junction to the end of the block:

$$\alpha_{\mathrm{total}}{}^2 = \langle H^2\rangle/\langle H^2\rangle_0;\quad \alpha_A{}^2 = \langle h_A{}^2\rangle/\langle h_A{}^2\rangle_0; \quad \alpha_B{}^2 = \langle h_B{}^2\rangle/\langle h_B{}^2\rangle_0$$

$$\langle\cos\varphi\rangle = \langle \vec{h}_A\vec{h}_B\rangle/(\langle h_B{}^2\rangle\langle h_A{}^2\rangle)^{1/2}$$

$$\langle H^2\rangle = \langle(\vec{h}_A - \vec{h}_B)^2\rangle = \langle h_A{}^2\rangle + \langle h_B{}^2\rangle - 2\langle\vec{h}_A\vec{h}_B\rangle \qquad (2)$$

The brackets $\langle\ \rangle$ and $\langle\ \rangle_0$ denote averaging over all perturbed and unperturbed diblock copolymer macromolecule conformations.

To calculate corresponding corrections to the unperturbed values of these quantities, we derived the following generalization of expression 1:

$$\alpha_{\mathrm{total}}{}^2 - 1 = \frac{a^2}{18N}\int q^2 U_{ij}^{\mathrm{ef}}(q)\,\Psi_{ij}(q)\frac{\mathrm{d}^3q}{(2\pi)^3} \qquad (3)$$

$$\Psi_{ij}(q) = \sum_l \nu_{ij}(l)\, l^2 \exp\left(-\frac{q^2a^2l}{6}\right)$$

$$\alpha_A{}^2 - 1 = \frac{a^2}{18n}\int q^2 U_{ij}^{\mathrm{ef}}(q)\,\Phi_{ij}^{A}(q)\frac{\mathrm{d}^3q}{(2\pi)^3} \qquad (4)$$

$$\Phi_{AA}^{A}(q) = \Psi_{AA}(q),\quad \Phi_{AB}^{A} = \sum_{l=1}^{l=n}\sum_{k=1}^{k=m} l^2 \exp\left(-\frac{q^2a^2(l+k)}{6}\right)$$

$$\alpha_B{}^2 - 1 = \frac{a^2}{18m}\int q^2 U_{ij}^{\mathrm{ef}}(q)\,\Phi_{ij}^{B}(q)\frac{\mathrm{d}^3q}{(2\pi)^3} \qquad (5)$$

$$\Phi_{BB}^{A}(q) = \Psi_{BB}(q),\quad \Phi_{AB}^{B} = \sum_{l=1}^{l=n}\sum_{k=1}^{k=m} k^2 \exp\left(-\frac{q^2a^2(l+k)}{6}\right)$$

Here a is the Kuhn segment supposed to be the same for bonds A–A and B–B, $N = n + m$ is the total polymerization index, and $\nu_{ij}(l)$ is the number of all monomer pairs of the ith and jth type situated on the macromolecule

A_nB_m separated by l bonds. In formulas 3–5 the summation is carried out over all values of repeated indices (i, j = A, B).

The final expression for the Fourier transformation $U^{\text{ef}}(q)$ of the matrix of molten diblock copolymer effective pair potentials calculated within the framework of the random-phase approximation taking into account the effect of the redistribution of monomers pertaining to all other macromolecules is[10]

$$U_{ij}^{\text{ef}}(x) = -v f_{ij}(x)\, G(x)/N \tag{6}$$

where the following designations are introduced:

$$f_{11}(x) = 1 - 2\tilde{\chi} g_{22}(x);\quad f_{22}(x) = 1 - 2\tilde{\chi} g_{11}(x)$$

$$f_{12}(x) = 1 + 2\tilde{\chi} g_{12}(x);\quad x = q^2a^2N/6$$

$$G^{-1}(x) = g_{11}^{-1}(x) + g_{22}^{-1}(x) - 2g_{12}^{-1}(x) - 2\tilde{\chi} \tag{7}$$

$\tilde{\chi} = \chi N$, χ is the conventional Flory parameter characterizing A–B interaction,[11] and v is the excluded volume supposed to be the same for both monomers A and B. *Note that functions $g_{ij}(x)$ and $G(x)$ are structural correlators of the block copolymer and the scattering function of the melt.*[1,12,13]

One should note that the function $G(x)$ in eq 4 has the following form near the spinodal:[1,13]

$$G(q) = \{C((|q| - q_0)^2) + \tau\}^{-1} \tag{8}$$

q_0 is the value of the wave number characterizing the most dangerous (as to microphase-separation instability) density fluctuations; the constant C and variable τ (the reduced distance from the spinodal restricting the region of the spatially homogeneous state stability) are defined as follows:

$$C = \partial^2(g_{11}^{-1}(q) + g_{22}^{-1} - 2g_{12}^{-1}(q))/\partial q^2|_{q=q_0}/2 \tag{9}$$

$$\tau = g_{11}^{-1}(q_0) + g_{22}^{-1}(q_0) - 2g_{12}^{-1}(q_0) - 2\tilde{\chi} \tag{10}$$

Substituting eqs 6–8 into eqs 3–5, one can arrive at the following final expressions for the swelling ratios:

$$\alpha_{\text{total}}^{\ 2} = 1 - \frac{6^{1/2}x_*^{\ 2}/\bar{N}^{1/2}}{2(\tau C)^{1/2}\pi}\Psi_{ij}(x_*)\, f_{ij}(x_*) \tag{11}$$

$$\alpha_{\text{A,B}}^{\ 2} = 1 - \frac{6^{1/2}x_*^{\ 2}/\bar{N}^{1/2}}{2(\tau C)^{1/2}\pi}\Phi_{ij}^{\text{A,B}}(x_*)\, f_{ij}(x_*)/f_{\text{A,B}} \tag{12}$$

Here $x_* = q_0^2a^2N/6$, $\bar{N} = N/(v/a^3)^{1/2}$ and $f_A = 1 - f_B = n/N$ is the compound of block copolymer. One can calculate the quantities 2 now (see dashed lines on Figure 1a). One can see that in the vicinity of the spinodal ($\tau \Rightarrow 0$) the deformation of the diblock copolymer tends to infinity. However, this effect is a result of an extrapolation of expressions 11 and 12 obtained within the framework of the mean-field approximation into the fluctuation region where this approximation is not valid. Thus, in the vicinity of the spinodal we have to take into account fluctuation effects. The proper consideration of this subject[14–16] was carried out by us[17] and in the paper of Barrat and Fredrickson.[18] The general line of consideration and the main result of refs 17 and 18 are essentially identical: in the case of the liquid (disordered) phase, the structure of the correct expression for effective pair potentials $U_{ij}^{\text{ef}}(x)$ calculated taking into account fluctuation effects is the same as the one of expression 4, if one substitutes for quantities $G(x)$ and $f_{ij}(x)$ their renormalized values. In particular, in formulas 6, 9, and 10 one should substitute *for τ the quantity r which characterizes the correlation* radius of the system under investigation and is determined from[14–16]

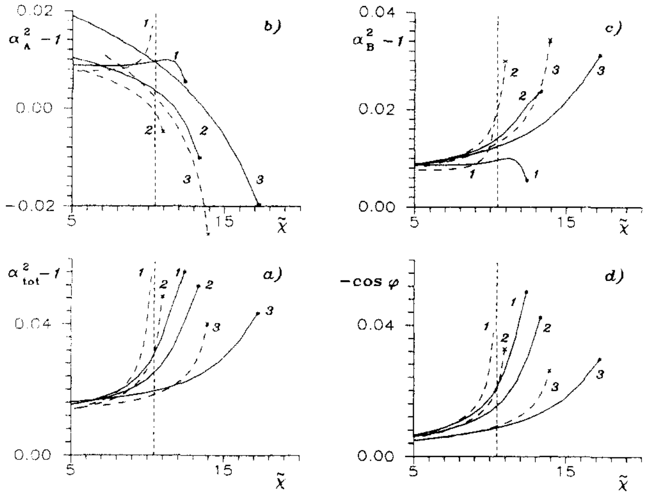

Figure 1. Conformational characteristics of diblock copolymers as functions of the reduced Flory parameter χ (inverse temperature). Curves labeled by numbers 1–3 correspond to molten diblock copolymers with f_A = 0.5, 0.4, and 0.3, respectively. (- - -) Results calculated within the framework of the random-phase approximation.[10] (—) Results calculated within the framework of the BFH approximation[14,16] for $\bar{N} = 10^4$. (a) The total swelling ratio $\alpha_{\text{total}}^2(\chi)$. (b) The partial swelling ratio of a shorter block $\alpha_A^2(\chi)$. (c) The partial swelling ratio of a longer block $\alpha_B^2(\chi)$. (d) The angle interblock correlation characteristic $\langle\cos\varphi\rangle$.

$$r - zs\xi/2r^{1/2} = \tau \tag{13}$$

Here the following designations are introduced: $s = x_*/(2\pi C^{1/2})$ and $\xi = \int_0^4\gamma^{(4)}(h,0)\,dh/4$, the function $\gamma^{(4)}(h,0)$ being defined in ref 1.

It follows from eq 13 that $r(\tau)$ is a monotonic increasing function of τ which tends to 0 when the value of τ tends to minus infinity. This removes the divergence of the macromolecular deformation in the vicinity of $\tau = 0$, which proved to be not a spinodal but a crossover point. In fact, the renormalization of the correlation function G results in the renormalization of both r and q_0 as well as some other parameters characterizing the function G.[18–20] The effect of the q_0 renormalization was observed experimentally[21] and is often interpreted[19–21] as evidence of the chains' stretching near the MST. However, the period $L = 2\pi/q_0$ of the arising lattice is related to the size of chains $\langle H^2\rangle$ in a very indirect manner. Consider, for example, a blend which consists of equal numbers of chains $A_{fN}B_{(1-f)N}$ and $A_{(1-f)N}B_{fN}$. (The limit $f \Rightarrow 0$ corresponds to the blend of homopolymers A and B.) One can ascertain easily that for this system the value of q_0, calculated in the random-phase approximation,[1,13] decreases from the one corresponding to a molten symmetric diblock copolymer to zero when the value of f decreases from 0.5 to $(\sqrt{3} - 1)/(\sqrt{3} + 1)$, notwithstanding the Gaussian (in this approximation) behavior of the chains. Thus, it is only the straightforward calculation along the line presented above which gives the valid information concerning one-chain conformational characteristics. It was carried out in ref 18 for the case of a symmetric diblock copolymer only.[18] In our work we investigated the more general case of an asymmetric diblock copolymer and found that apart from the renormalization of G a renormalization of f_{ij} takes place and results in some quantitative corrections absent in ref 18. For the sake of brevity we omit here the rather cumbersome description of these corrections and present the final results of the numerical calculation of the quantities 2 in Figure 1. (Note, however, that when calculating the function G, we restricted ourselves to allowing for the renormalization of r only, which is a more rough approximation than the one used in ref 18. The proper improvement will be presented elsewhere.)

Discussion. The solid curves in Figure 1a are for $N = 10$.[4] They are in rather good agreement with curves for the dependence of the mean-square gyration radius on $\tilde{\chi}$ calculated both by means of Monte Carlo simulation[2] and analytically in ref 18 for $\bar{N} = 8000$. The new dependencies for the "partial" swelling ratios of block α_A and α_B and the angle correlation characteristics $\langle \cos \varphi \rangle$ lead to the following conclusions: (i) When approaching the MST point, the longer block swells, whereas the shorter one shrinks. The physical reason for the difference in the behavior of short and long blocks is very clear: for an asymmetric copolymer the environment of any individual block consists mainly of long blocks (say, B). Therefore, the α of the surroundings are similar for the longer blocks but dissimilar for the shorter ones. This means that the effective B–B interaction is more or less a screened repulsion similar to the one in the B homopolymer melt. On the contrary, the behavior of the short blocks can be considered roughly as one of a chain placed in conditions corresponding to its coil–globule transition (it is instructive to compare this effect with the contraction of chains in a homopolymer solution near the spinodal of the latter[7,9]). For the symmetrical (and almost symmetrical) diblock copolymer the subtle balance of these two tendencies leads to the nonmonotonic dependence of α_i on $\tilde{\chi}$. (ii) The total swelling of the diblock copolymer increases in the region and is contributed mostly by its stretching due to the presence of the angle correlation between blocks of the same macromolecule. (iii) Macromolecules remain "nearly Gaussian" within the whole region of the disordered phase up to the first-order phase transition. Thus, we verified the basic assumption of the weak segregation theory of microphase separation as the Gaussian conformational behavior of molten diblock copolymers (at least in this region) and indicated the significance of fluctuation effects in the screening of interactions near the point of microphase separation.

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