Macromolecules **1990**, *23*, 3339–3346 **3339**

(15) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* **1988**, *5*, 413.
(16) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1988**, *21*, 2610.
(17) Milner, S. T.; Wang, Z.-G.; Witten, T. A. *Macromolecules* **1989**, *22*, 489.
(18) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* **1989**, *22*, 853.
(19) Milner, S. T. *Europhys. Lett.* **1989**, *7*, 695.
(20) Whitmore, M. D.; Noolandi, J. APS March Meeting, Las Vegas, 1986; APS March Meeting, New York, 1987.
(21) Hong, K. M.; Noolandi, J. *Macromolecules* **1981**, *14*, 727.
(22) Hong, K. M.; Noolandi, J. *Macromolecules* **1983**, *16*, 1083.
(23) Noolandi, J.; Hong, K. M. *Polym. Bull.* **1982**, *7*, 561.
(24) Edwards, S. F. *Proc. Phys. Soc. London* **1965**, *85*, 613.
(25) Dolan, A. K.; Edwards, S. F. *Proc. R. Soc. London* **1975**, *A343*, 427.
(26) Helfand, E. *Macromolecules* **1975**, *8*, 552.
(27) Helfand, E.; Wasserman, Z. R. *Macromolecules* **1976**, *6*, 879.
(28) Helfand, E.; Wasserman, Z. R. In *Developments in Block Copolymers*; Goodman, I., Ed.; Elsevier: New York, 1982; Vol. 1.
(29) Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F.; Scheutjens, J. M. H. M. *Macromolecules* **1987**, *20*, 1692.
(30) Muthukumar, M.; Ho, J.-S. *Macromolecules* **1989**, *22*, 965.
(31) Murat, M.; Grest, G. *Phys. Rev. Lett.* **1989**, *63*, 1074.
(32) Marques, C.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(33) Marques, C. M.; Joanny, J. F. *Macromolecules* **1989**, *22*, 1454.
(34) Munch, M. R.; Gast, A. P. *Macromolecules* **1988**, *21*, 1366.
(35) Theodorou, D. N. *Macromolecules* **1988**, *21*, 1411; *Macromolecules* **1988**, *21*, 1422.
(36) Schaefer, D. W.; Joanny, J. F.; Pincus, P. *Macromolecules* **1980**, *13*, 1280.
(37) Fleer, G. J.; Scheutjens, J. M. H. M.; Cohen Stuart, M. A. *Colloids Surf.* **1988**, *13*, 1.
(38) Deryaguin, B. V. *Kolloid Zh.* **1934**, *69*, 155.
(39) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1988**, *21*, 1485.
(40) Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1979**, *83*, 1619.
(41) Brandrup, J.; Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed.; Interscience: New York, 1975.
(42) Richardson, M. J.; Savill, N. G. *Polymer* **1977**, *18*, 3.
(43) See, for example: Scheutjens, J. M. H. M.; Fleer, G. J. *J. Phys. Chem.* **1980**, *84*, 178; *Adv. Colloid Interface Sci.* **1982**, *16*, 341.
(44) Birkoff, G.; Rota, G. C. *Ordinary Differential Equations*, 2nd ed.; John Wiley and Sons: New York, 1966; pp 288–296.
(45) Hille, E. *Lectures on Ordinary Differential Equations*; Addison-Wesley: London, 1969; pp 394–402.

Polydispersity Effects on the Microphase-Separation Transition in Block Copolymers

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ABSTRACT: The influence of polydispersity on the transitions occurring in the weak segregation regime and on the scattering functions of the disordered phase in diblock copolymers is studied for one-component and multicomponent systems including mixtures with homopolymers. Application of the fluctuation corrections given by Fredrickson and Helfand[9] leads to the determination of the transition windows as a function of degree of polymerization N, polydispersity U, and composition f. The applicability of the fluctuation corrections appears to be extended to lower N and f with increasing U. The prediction of transitions is facilitated by the concept of a reduced phase diagram.

1. Introduction

The capability of block copolymers to form microdomain structures is well-known and widely used to produce a variety of polymer materials with outstanding properties. Understanding the basic principles of the microphase separation thus not only is of interest from a purely scientific point of view but is expected to show new ways to improved polymer materials.

Using methods based on the mean-field theory, Helfand and co-workers,[1] Ohta and Kawasaki,[2] and Semenov[3] have been able to make quantitative predictions on the ranges of stability of the one-, two-, and three-dimensionally periodic structures appearing in the strong segregation limit. New developments are expected in this field since recent studies by Thomas and co-workers[4–6] and Hashimoto and co-workers[7] have shown that the shapes of the domains are not restricted to spheres, cylinders, and lamellae.

The transition from the ordered phase-separated structure to the homogeneous melt and the phase diagram in the weak segregation limit is another feature of general interest. According to the theory of Leibler,[8] this phase diagram is, for diblock copolymers, completely defined by the composition f and the product χN, where χ is the Flory–Huggins interaction parameter and N the total number of statistical segments per molecule. A particularity of Leibler's theory is the prediction that, except for $f = 0.5$, there is no direct transition to ordered structures other than the bcc macrolattice.

Recently, Fredrickson and Helfand[9] have extended Leibler's theory to include the effect of composition fluctuations using a method established by Brazovskii.[10] They find that Leibler's theory is only valid in the limit $N \to \infty$ and that direct transitions from the homogeneous melt

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to the hexagonal and the lamellar phase occur in well-defined ranges of f ("windows") for finite N. Furthermore, the microphase-separation transition (MST) depends on three variables, f, χN, and N, and occurs, for finite N, at larger χN values than the spinodal $(\chi N)_s$ computed according to Leibler's theory.

In the theoretical treatments used by Leibler[8] and by Fredrickson and Helfand,[9] it is assumed that the samples are monodisperse. Calculations of Leibler and Benoit[11] and Hong and Noolandi[12] have shown that polydispersity has a marked effect on the scattering curves of the homogeneous melts of block copolymers. It produces a decrease of the position of the maximum and an increase of the intensity at the maximum, which is related to a decrease of $(\chi N)_s$. This effect cannot be neglected in the evaluation of scattering data of block copolymer melts.[13-15] The aim of the present work is to extend the treatment used by Hong and Noolandi[12] to include the fluctuation corrections so that the results of Fredrickson and Helfand[9] can be applied to samples with nonzero polydispersity.

2. Averaging Procedure

We consider the polydispersity of diblock copolymers to be given by the normalized distribution $n(N_A,N_B)$ of the number of statistical segments N_A and N_B of types A and B. For a sample synthesized in the usual two-step polymerization process, the variance of N_A is, in general, independent of the variance of N_B so that

$$n(N_A,N_B) = n_A(N_A)\, n_B(N_B) \qquad (1)$$

for a given sample (one-component system). An easy way to vary the polydispersity for experimental purposes is a mixture of such samples (mutlicomponent systems). For a mixture of m samples with the number fractions z_i we obtain

$$n(N_A,N_B) = \sum_{i=1}^{m} z_i\, n_{A_i}(N_{A_i})\, n_{B_i}(N_{B_i}) \qquad (2)$$

Following Leibler and Benoit[11] and Hong and Noolandi,[12] we use distribution functions of the type

$$n(N) = kN^{\nu} \exp(-aN) \qquad (3)$$

generally referred to as Schulz–Zimm distributions, to facilitate the calculations. If $\langle N\rangle_n$ is the number average, $\langle N\rangle_w$ the weight average, and $U = (\langle N\rangle_w/\langle N\rangle_n) - 1$ the polydispersity parameter, the constants in eq 3 are given by

$$a = 1/(\langle N\rangle_n U), \quad \nu = (1/U) - 1, \quad k = a^{\nu+1}/\Gamma(\nu + 1)$$

Assuming the variances of N_A and N_B to be independent results in the relationship

$$U = \bar{f}_A^{\,2} U_A + \bar{f}_B^{\,2} U_B \qquad (4)$$

where U, U_A, and U_B are the polydispersities of N $(=N_A + N_B)$, N_A, and N_B, respectively, and $\bar{f}_K = \langle N_K\rangle_n/\langle N\rangle_n$ (K = A or B).

To avoid unnecessary redefinitions of symbols, we adopt widely the notation used by Leibler[8] and by Fredrickson and Helfand[9] throughout this paper.

In order to calculate the scattering function of the melt, we need the first-order correlation functions

$$S_{ij}(\vec{q}) = c_0^{-1} \int \mathrm{d}^3r\, \exp(-i\vec{q}\vec{r})\, \tilde{S}_{ij}(\vec{r}) \qquad i, j = 1, 2 \qquad (5)$$

for a block copolymer system without any interaction between the polymer chains (i.e., for an ideal system). Here

$$\tilde{S}_{ij}(\vec{r}) = \langle [c_i(0) - \bar{c}_i][c_j(\vec{r}) - \bar{c}_j] \rangle$$

$c_1(\vec{r})$ and $c_2(\vec{r})$ are the local concentration of segments of type A and B, respectively, and c_0 is the mean total concentration of segments. The conformations of different chains are not correlated in an ideal system; therefore, the calculation of the function $\tilde{S}_{ij}$ is essentially a one-chain problem. For a monodisperse system of N_A and N_B copolymers the function $\tilde{S}_{ij}$ can obviously be represented as

$$\tilde{S}_{ij}(\vec{r};N_A,N_B) = N_i \rho_0\, K_{ij}(\vec{r};N_A,N_B) \qquad (6)$$

where $\rho_0 \equiv c_0/N$ is the concentration of chains $(N = N_A + N_B)$, $N_i\rho_0$ is the concentration of segments i (i.e., A for $i = 1$ and B for $i = 2$), and $K_{ij}(\vec{r})\, \mathrm{d}^3r$ is the conditional probability that a segment of type j is within the small volume d^3r around the point $\vec{r}$ if a segment of the type i of the *same* chain is at $\vec{r} = 0$.

Similarly, for the general polydisperse case we have

$$\tilde{S}_{ij}(\vec{r}) = \int \mathrm{d}N_A\, \mathrm{d}N_B\, N_i\, \rho(N_A,N_B)\, K_{ij}(\vec{r};N_A,N_B) \qquad (7)$$

where

$$\rho(N_A,N_B)\, \mathrm{d}N_A\, \mathrm{d}N_B = [c_0/\langle N\rangle_n]\, n(N_A,N_B)\, \mathrm{d}N_A\, \mathrm{d}N_B \qquad (8)$$

is the concentration of the chains with N_A and N_B within small intervals $\mathrm{d}N_A$ and $\mathrm{d}N_B$. Combining eqs 5–8, we get

$$S_{ij}(\vec{q}) = \int \mathrm{d}N_A\, \mathrm{d}N_B\, [N\, n(N_A,N_B)/\langle N\rangle_n]\, S_{ij}(\vec{q};N_A,N_B) \qquad (9)$$

where $S_{ij}(\vec{q};N_A,N_B)$ corresponds to the monodisperse function $\tilde{S}_{ij}(\vec{r};N_A,N_B)$ via eq 5.

Therefore, the correct averages of the first-order "ideal" correlation functions S_{ij} are the weight averages (see also Hong and Noolandi[12]). This statement also holds for the higher order correlation functions G_{ijk} and G_{ijkl} defined in Leibler's work. The proof can be obtained in exactly the same manner as above via the corresponding cumulants

$$\tilde{S}_{ijk}(\vec{r}_1,\vec{r}_2) = \langle c_i(0)\, c_j(\vec{r}_1)\, c_k(\vec{r}_2) \rangle_c$$

and

$$\tilde{S}_{ijkl}(\vec{r}_1,\vec{r}_2,\vec{r}_3) = \langle c_i(0)\, c_j(\vec{r}_1)\, c_k(\vec{r}_2)\, c_l(\vec{r}_3) \rangle_c$$

3. Scattering of the Homogeneous Melt

The scattering function of the homogeneous melt is given by

$$S(q) = N/[F(f,x) - \alpha]$$

where $\alpha = 2\chi N$ according to Leibler[8] and $\alpha = 2(\chi N)_s - \epsilon$ according to Fredrickson and Helfand[9]

$$F(f,x) = N(S_{11} + S_{22} + 2S_{12})/(S_{11}S_{22} - S_{12}^{\,2}) = \frac{g_1(1,x)}{g_1(f,x)\, g_1(1-f,x) - {}^1\!/_4[g_1(1,x) - g_1(f,x) - g_1(1-f,x)]^2}$$

$$g_1(f,x) = 2[fx - 1 + \exp(-fx)]/x^2$$

$$x = q^2R^2 = q^2Nb^2/6$$

with q denoting the absolute value of the scattering vector, R the radius of gyration of an ideal chain, and b the length of a statistical segment. The weight averages of S_{ij} correspond to averages of the type $\langle N\, g_1(f,x)\rangle_w$, which

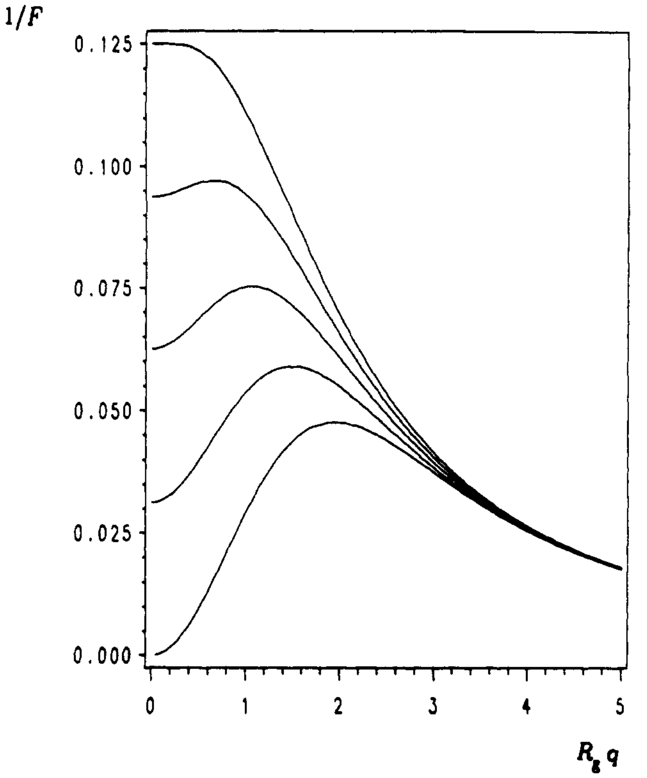

Figure 1. Scattering function $1/F$ plotted versus $\bar{x}^{1/2} = \langle R^2\rangle_n^{1/2}q$ for a one-component system, U_K varying from 0 (lower curve) to 1 (upper curve) in steps of 0.25, $f = 0.5$, independent variances of N_K, $U_A = U_B$.

are equivalent to the number averages $\langle N^2\, g_1(f,x)\rangle_n/\langle N\rangle_n$. Due to the form of $F(f,x)$, the averaging procedure results in replacing the functions $g_1(f,x)$ by

$$\bar{g}_1(\bar{f}_K,\bar{x}) = \langle N^2\, g_1(f_K,x)\rangle_n/\langle N\rangle_n^{\,2} = 2[\bar{f}_K\bar{x} - 1 + \langle \exp(-f_Kx)\rangle_n]/\bar{x}^2$$

and

$$\bar{g}_1(1,\bar{x}) = 2[\bar{x} - 1 + \langle \exp(-x)\rangle_n]/\bar{x}^2$$

where

$$\bar{x} = \langle N\rangle_n b^2q^2/6$$

Using a Schulz–Zimm distribution, we obtain

$$\langle \exp(-f_Kx)\rangle_n = (1 + U_K\bar{f}_K\bar{x})^{-1/U_K}$$

for a one-component system and

$$\langle \exp(-f_Kx)\rangle_n = \sum_{i=1}^{m} z_i\langle \exp(-f_{K_i}x_i)\rangle_n = \sum_{i=1}^{m} z_i(1 + U_{K_i}\bar{f}_{K_i}p_i\bar{x})^{-1/U_{K_i}}$$

for a multicomponent system, where $x_i = q^2N_ib^2/6$, $\bar{f}_{K_i} = \langle N_{K_i}\rangle_n/\langle N_i\rangle_n$, $p_i = \langle N_i\rangle_n/\langle N\rangle_n$, and $\bar{x}_i = p_i\bar{x}$. Furthermore, $\bar{f}_K = \sum_i z_ip_i\bar{f}_{K_i}$.

Due to the independence of U_A and U_B, we find

$$\langle \exp(-x)\rangle_n = \langle \exp(-f_Ax)\rangle_n\langle \exp(-f_Bx)\rangle_n$$

for a one-component system and, accordingly

$$\langle \exp(-x)\rangle_n = \sum_{i=1}^{m} z_i\langle \exp(-f_{A_i}x_i)\rangle_n\langle \exp(-f_{B_i}x_i)\rangle_n$$

for a multicomponent system.

Figure 1 shows plots of $1/F$ versus $\bar{x}^{1/2} = \langle R^2\rangle_n^{1/2}\, q$ for a one-component system, U_K varying from 0 to 1, $f = 0.5$, and independent variances of N_K as given by eq 4, but taking $U_A = U_B$. These curves are proportional to the scattering intensity of diblock copolymer melts with $\alpha = 0$; i.e., $\chi = 0$ in Leibler's approach.

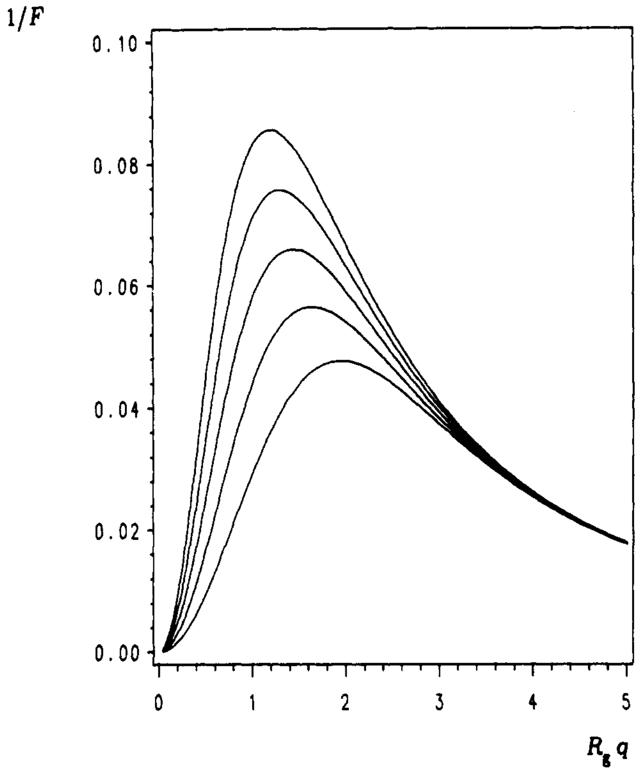

Figure 2. Scattering function $1/F$ plotted versus $\bar{x}^{1/2} = \langle R^2\rangle_n^{1/2}q$ for a one-component system, U_K varying from 0 (lower curve) to 1 (upper curve) in steps of 0.25, $U = U_A = U_B$.

Figure 2 shows similar plots corresponding to calculations taking $U = U_K$ as proposed by Hong and Noolandi.[12] The latter assume that only the size but not the composition of the molecules is affected by the polydispersity. One observes a much less pronounced effect of the polydispersity and, in particular, due to the invariance of the composition, a vanishing intensity for $q \to 0$ independent of the magnitude of the polydispersity. This approximation is, however, inadequate since in all cases of practical interest both the composition and the size of the molecules are affected by the polydispersity.

Figures 3 and 4 show plots of x^*, the position of the maximum in the scattering intensity, and of the ratio $(\chi N)_s/(\chi N)_s{}^0 = F(U,f,x^*)/F(0,f,x^*)$, as a function of the polydispersity U_K for various values of f assuming independent variances of N_K. We see that x^* tends toward 0 for finite values of U_K; e.g., $U_K = 1$ for $f = 0.5$. This means that above these limiting values of U_K, the scattering curves show a maximum at $q = 0$ comparable to that observed in homopolymer melts. The value of $(\chi N)_s$ decreases considerably with increasing polydispersity and falls below the $(\chi N)_s$ values for the corresponding mixture of (monodisperse) homopolymers.[13]

Figure 5 shows the upper limits of U_K for nonzero x^* as a function of f.

It is of interest to note that the equations developed for multicomponent systems also hold for mixtures of block copolymers with homopolymers (and, in principle, also for homopolymer mixtures).

Figures 6 and 7 show x^* and $(\chi N)_s$ curves, respectively, as a function of U_K for a two-component mixture of a homopolymer with a diblock copolymer. The composition of the diblock copolymer is $f = 0.5$, the number fraction of homopolymer molecules is $z_1 = 0.5$, the poly-

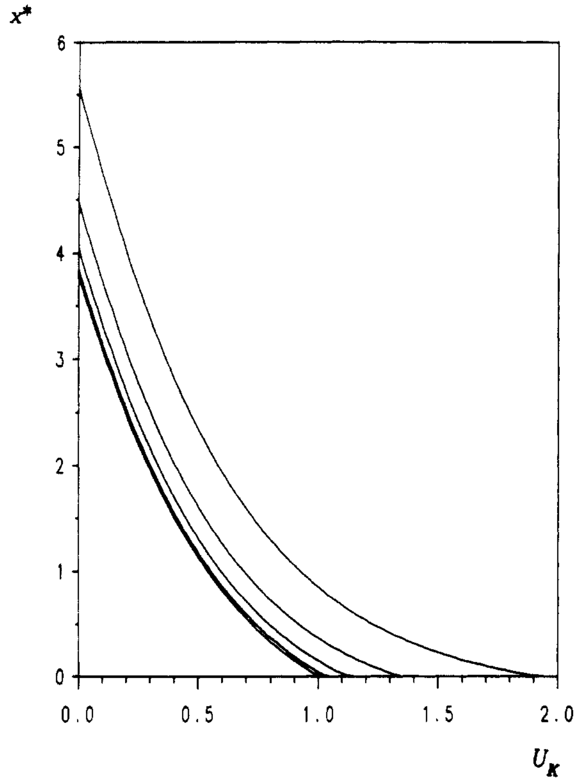

Figure 3. Position of the maximum x^* in the scattering function for a one-component system plotted versus U_K, values of f varying from 0.1 (upper curve) to 0.5 (lower curve) in steps of 0.1, independent variances of N_K, $U_A = U_B$.

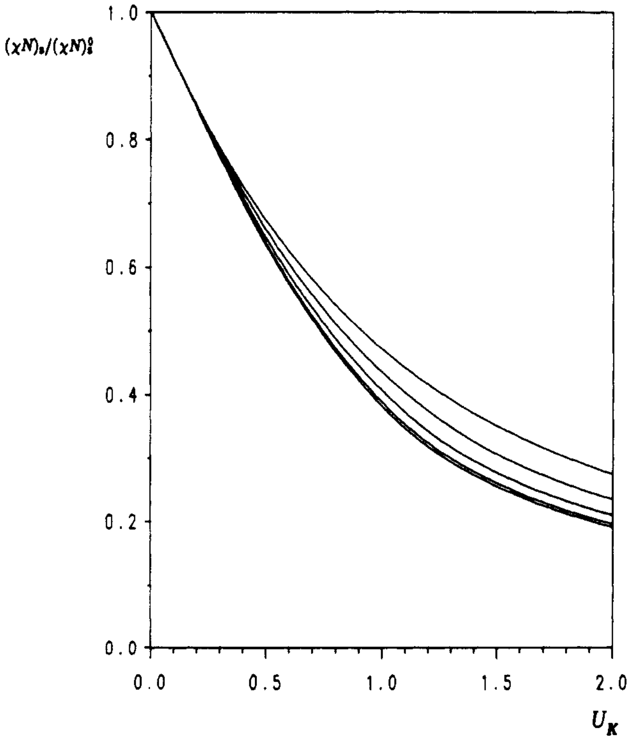

Figure 4. Plot of the ratio $(\chi N)_s/(\chi N)_s^0$ for a one-component system as a function of U_K, values of f varying from 0.1 (upper curve) to 0.5 (lower curve) in steps of 0.1, independent variances of N_K, $U_A = U_B$.

dispersities of the homopolymer and the copolymer blocks are assumed to be equal, and N is the same for both components.

To include the fluctuation correction into the computation of the scattering curve of the homogeneous melt, the coefficient ϵ has to be calculated. According to Fre-

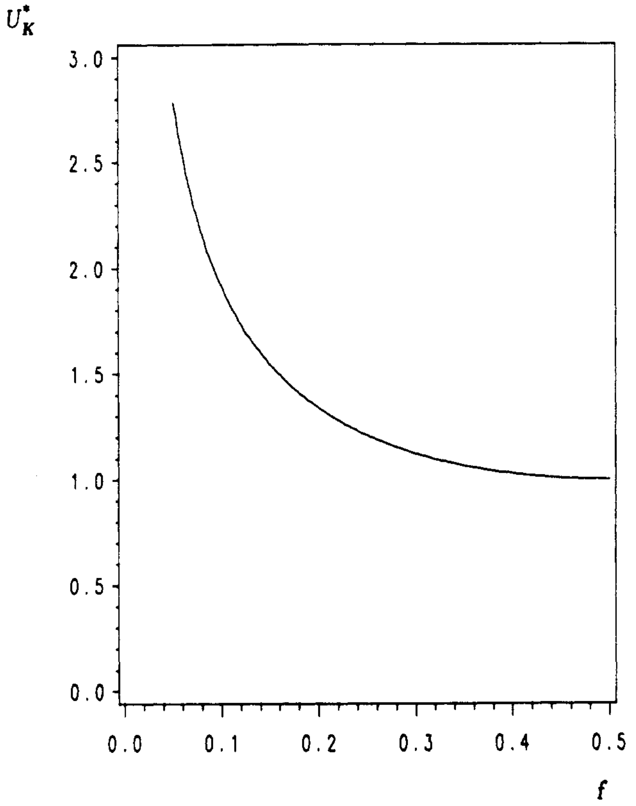

Figure 5. Plot of U_K^*, the upper limit of U_K for nonzero x^*, versus the composition f, independent variances of N_K, $U_A = U_B$.

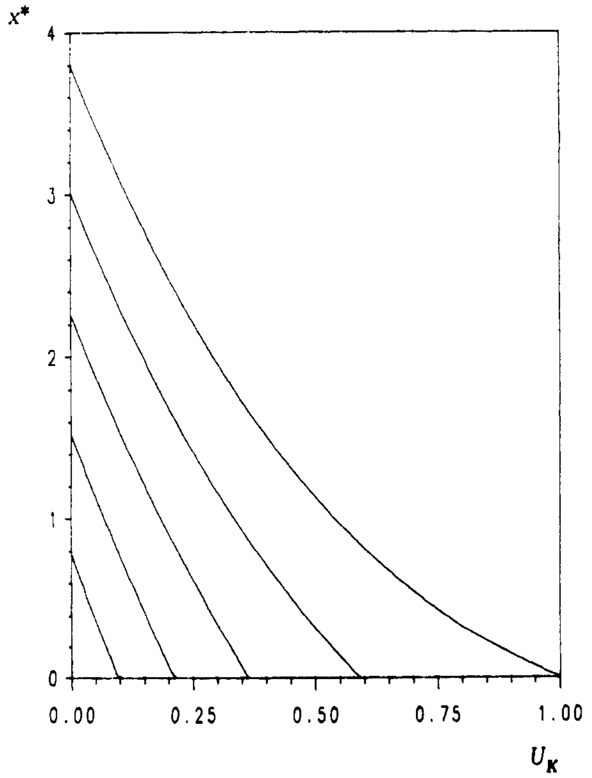

Figure 6. Position of the maximum x^* in the scattering function for a two-component mixture plotted versus U_K; component 1 is a homopolymer ($f_1 = 0$), component 2 is a block copolymer ($f_2 = 0.5$), equal degree of polymerization of the components, number fraction of component 1, z_1, varying from 0 (upper curve) to 0.4 (lower curve) in steps of 0.1, independent variances of N_K and $U_A = U_B$ for the block copolymer. Polydispersity of the homopolymer equal to U_K of the block copolymer.

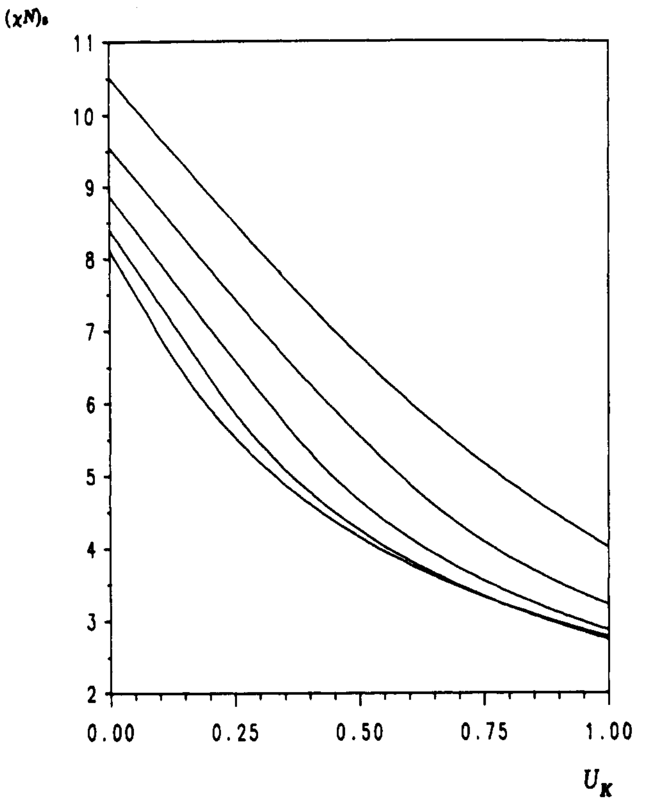

Figure 7. Plot of $(\chi N)_s$ as a function of U_K for a two-component mixture: component 1 is a homopolymer ($f_1 = 0$), component 2 is a block copolymer ($f_2 = 0.5$), equal degree of polymerization of the components, number fraction of component 1, z_1, varying from 0 (upper curve) to 0.4 (lower curve) in steps of 0.1, independent variances of N_K and $U_A = U_B$ for the block copolymer. Polydispersity of the homopolymer equal to U_K of the block copolymer.

drickson and Helfand,[9] ϵ is given by

$$\epsilon = c^2\tau + c^3 d\lambda/(\epsilon N)^{1/2} \tag{10}$$

where

$$\tau = [F(x^*,f) - 2\chi N]/c^2$$

$$c = [x^* F''(x^*,f)/3]^{1/2}$$

$$d = 3x^*/2\pi$$

and

$$\lambda = N\Gamma_4(0,0)/c^4$$

If we define reduced coefficients $\hat{\epsilon}$ and $\hat{\tau}$ by

$$\hat{\epsilon} = \epsilon c^{-2}(d\lambda)^{-2/3}N^{1/3}$$

and

$$\hat{\tau} = \tau(d\lambda)^{-2/3}N^{1/3}$$

eq 10 becomes

$$\hat{\tau} = \hat{\epsilon} - \hat{\epsilon}^{-1/2} \tag{11}$$

Figure 8 shows a plot of $\hat{\epsilon}$ versus $-\hat{\tau}$. If the temperature dependence of χ can be approximated by $\chi = a + b/T$, this represents the general features of a plot $1/S(x^*)$ versus $1/T$. Such plots have been used to determine T_s, the temperature at the spinodal, by linear extrapolation toward $1/S(x^*) = 0$ from low values of $1/T$, i.e., high values of $1/S(x^*)$.[14-20] Inspection of Figure 8 shows clearly that such an extrapolation, although possible in principle, leads for finite values of N to an underestimation of the value of T_s since the correct value of T_s corresponds to $\hat{\tau} = 0$.

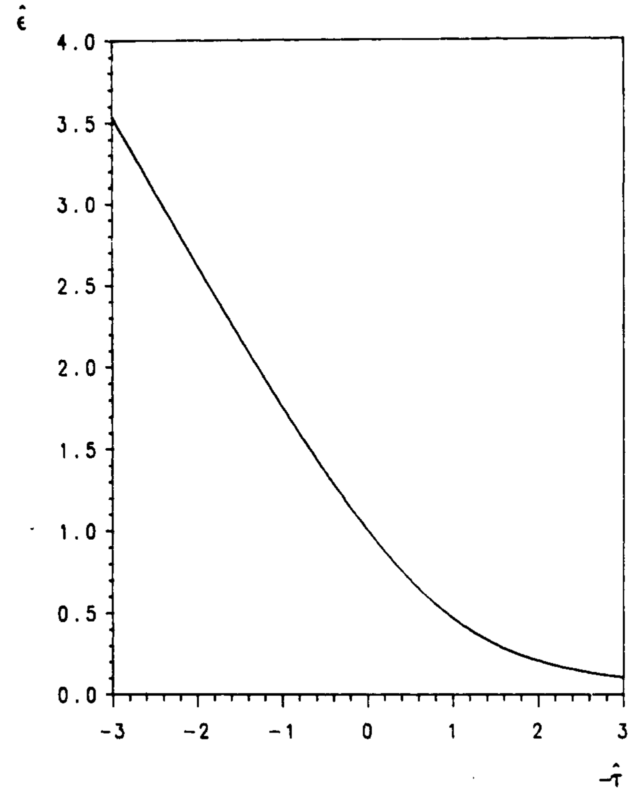

Figure 8. Coefficient $\hat{\epsilon}$ as a function of $-\hat{\tau}$. $\hat{\epsilon}$ is proportional to $1/S(x^*)$; $-\hat{\tau}$ is proportional to $1/T - 1/T_s$, if $\chi(T) = a + b/T$.

4. Coefficients at the MST

To calculate the exact value of ϵ, we have to compute the coefficient $\Gamma_4(0,0)$ for finite values of the polydispersity. To obtain the values at the MST, ϵ_t and $(\chi N)_t$, and the ranges in f corresponding to the direct transitions from the homogeneous melt to the cubic, hexagonal, and lamellar phase, we need the corresponding coefficient Γ_3 as well. This involves the application of the averaging procedures discussed in section 2 to the higher order correlation functions G_{ijk} and G_{ijkl} given in Appendix C of Leibler's[8] work. If eq 1 is valid and Schulz–Zimm distributions are used, one obtains analytical expressions for these functions. In the Appendix of this paper, the averaging procedure is demonstrated on some examples.

In Figures 9 and 10, the ratios Γ_3/Γ_3^0 and $\Gamma_4(0,0)/\Gamma_4^0(0,0)$, respectively, are plotted as functions of the polydispersity parameter U_K of the blocks for various values of the composition f (Γ_i^0 corresponds to $U_K = 0$). Γ_3/Γ_3^0 changes only slightly with f but strongly with U_K, whereas both U_K and f produce a marked change of $\Gamma_4(0,0)/\Gamma_4^0(0,0)$.

In order to compute the values of ϵ_t and $(\chi N)_t$, we have to find a numerical solution for the set of eqs 3.10–3.21 and 4.1 given by Fredrickson and Helfand in their paper.[9] This is facilitated by the use of reduced coefficients

$$\tau^* = \tau_t(d\lambda)^{-2/3}N^{1/3} = \hat{\tau}_t$$

$$\mu^* = \mu\lambda^{-5/6}d^{-1/3}N^{1/6}$$

where τ_t, μ, and λ are defined according to Fredrickson and Helfand.[9] It can be shown that, for a given type of transition, τ^* is a function of μ^* only. For the transition to the lamellar phase ($n = 1$), τ^* is constant (= −2.0308). For the transition to the hexagonal phase ($n = 3$) and the cubic phase ($n = 6$), τ^* is increasing with increasing

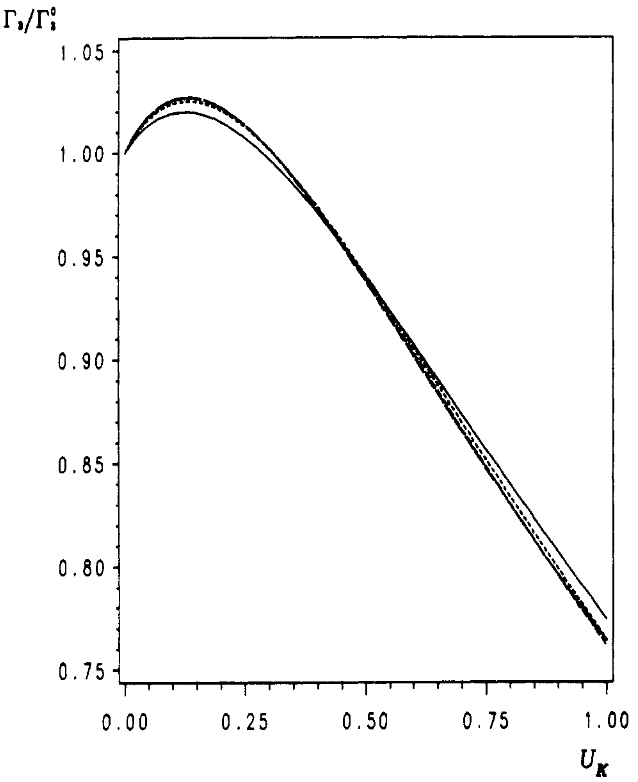

Figure 9. Plot of the ratio $\Gamma_3/\Gamma_3{}^0$ for a one-component system as a function of U_K, values of f varying from 0.1 (lower curve at $U_K = 0.2$) to 0.4 (upper curve at $U_K = 0.2$) in steps of 0.1, independent variances of N_K, $U_A = U_B$.

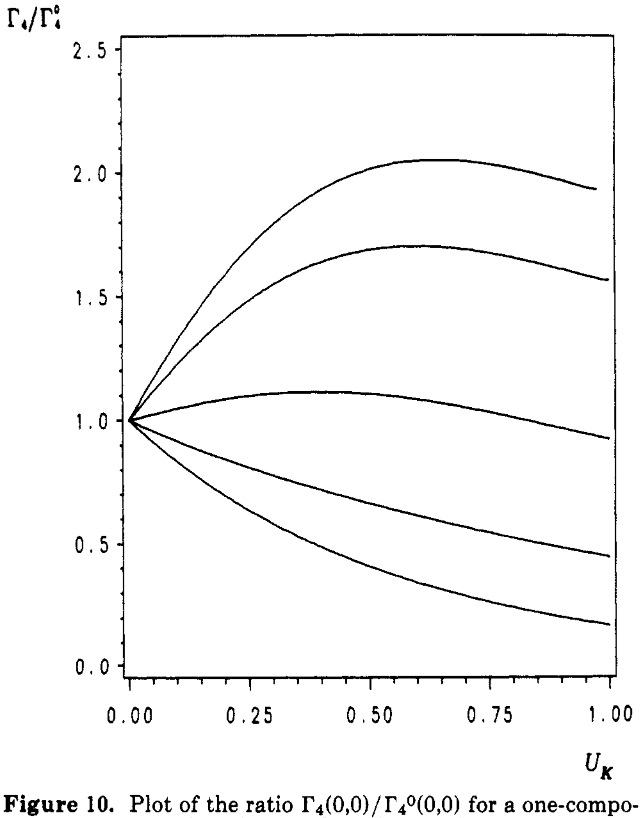

Figure 10. Plot of the ratio $\Gamma_4(0,0)/\Gamma_4{}^0(0,0)$ for a one-component system as a function of U_K, values of f varying from 0.1 (lower curve) to 0.5 (upper curve) in steps of 0.1, independent variances of N_K, $U_A = U_B$.

$|\mu^*|$. The points of intersection (triple points) are located at

$$\mu^*_1 = -0.5641, \quad \tau^*_1 = -2.0308 \qquad \text{for } n = 1 \text{ and } n = 3$$

$$\mu^*_2 = -1.4089, \quad \tau^*_2 = -1.1298 \qquad \text{for } n = 3 \text{ and } n = 6$$

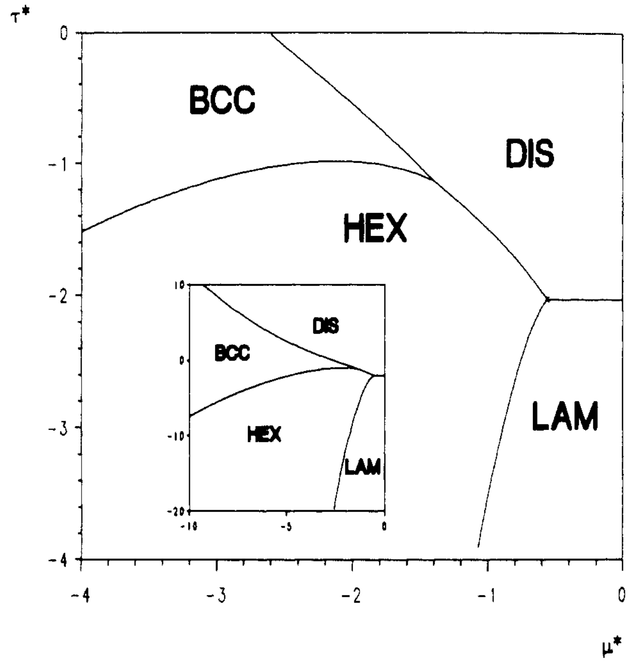

Figure 11. Reduced phase diagram for diblock copolymers in a plot of τ^* versus μ^*.

Hence, for $0 < |\mu^*| < 0.5641$, the MST is to the lamellar phase, for $0.5641 < |\mu^*| < 1.4089$ to the hexagonal phase, and for $|\mu^*| > 1.4089$ to the cubic phase. For $|\mu^*| > 2.6197$, τ^* is positive, which means that $(\chi N)_s > (\chi N)_t$.

Figure 11 shows a plot of τ^* as a function of μ^* for the MST as well as for the transitions within the ordered phase. The latter have been obtained by numerical solution of eqs 4.7 and 4.8 given in Fredrickson and Helfand's[9] paper. The plot is a reduced phase diagram in which μ^*_1 and μ^*_2 represent triple points.

The value of ϵ_t is obtained from τ^* using eqs 10 and 11. The value of $(\chi N)_t$ is given by

$$(\chi N)_t = (\chi N)_s - KN^{-1/3}$$

where

$$K = \tau^* c^2 (d\lambda)^{2/3}/2$$

For the transition to the lamellar phase, K is a function of f and U_K only, since τ^* is a constant. For the transition to the hexagonal and to the cubic phase, K is a function of N as well so that the variation of $(\chi N)_s - (\chi N)_t$ with N becomes more complicated. For example, τ^* varies approximately linear with μ^* in the range $1.7 < |\mu^*| < 3.0$. If this relationship is given by $\tau^* = a_0 + a_1\mu^*$, we get

$$(\chi N)_t = (\chi N)_s - AN^{-1/3} - BN^{-1/6}$$

where $A = a_0 c^2 (d\lambda)^{2/3}/2$ and $B = a_1 c^2 d^{1/3} \lambda^{-1/6}/2$.

Knowing μ^*_1 and μ^*_2, we can calculate the relationship between N, U_K, and the limits of the transition windows in f. For a given value of U_K, we obtain the functions $N_1(f)$ and $N_2(f)$ from the relationship

$$N_i = (\mu^*_i/\mu)^6 \lambda^5 d^2$$

where i is 1 or 2.

Figure 12 shows plots of log N_1 (lower family of curves) and log N_2 (upper family of curves) versus f for various values of U_K. The minima in these curves obviously indicate that the limits of the applicability of the fluctuation corrections derived by Fredrickson and Helfand[9] do

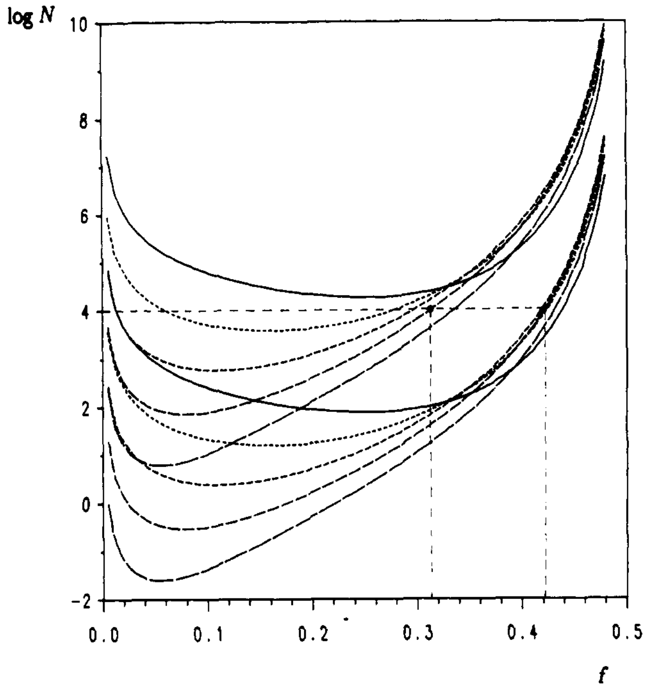

Figure 12. Limits of the transition windows from the disordered phase to the lamellar phase (lower family of curves) and to the hexagonal phase (upper family of curves) as a function of N and f for one-component systems. Within a given family of curves, U_K varies from 0 (upper curve at $f = 0.25$) to 0.8 (lower curve at $f = 0.25$) in steps of 0.2, independent variances of N_K, $U_A = U_B$. Example of evaluation: For $N = 10^4$ and $U_K = 0.6$, the lower limit of the window of the transition from the disordered phase to the lamellar phase is $f = 0.422$; the window of the transition from the disordered phase to the hexagonal phase extends from $f = 0.313$ to $f = 0.422$.

depend not only on N but also on f and U. The position of the minimum in $\log N_2$ for $U = 0$ agrees with the assumption that the lower limit of N is approximately 10^4 as estimated by these authors. The position of this minimum in f indicates a lower limit of approximately 0.25. The curves for nonzero values of U_K show that both limits are shifted toward smaller values with increasing polydispersity, i.e., the range of applicability of the fluctuation corrections is increased in polydisperse systems.

In Figure 13, the effect of polydispersity is demonstrated in a phase diagram for $N = 10^4$. The solid lines mark the transitions expected for $U = 0$, the diagram corresponds to that already published by Fredrickson and Helfand.[9] The dashed lines and the dotted lines are obtained for $U_K = 0.4$ and $U_K = 0.8$, respectively. The effect of polydispersity on the transition from the ordered to the disordered phase as well as on the transition from one ordered phase to another is clearly visible. For a given composition f, the χN values at the transitions are generally decreasing with increasing U_K. For $U = 0$, there is no transition to the bcc phase, which can also be seen in Figure 12. The exact coordinates of the triple points can be calculated using the corresponding fixed coordinates of the triple points in the reduced phase diagram.

5. Summary and Discussion

The results of the present work show that polydispersity has a strong influence on the coefficients characterizing the MST. With the relationships developed it is possible to predict the behavior of samples of practical interest, especially mixtures including homopolymers, in the weak segregation regime. The relationship between the widths of the transition windows, the polydispersity, and the degree of polymerization indicates that the range of validity is extended to values of N lower than 10^4 with increasing polydispersity. Furthermore, this relationship shows clearly that the applicability is also limited in f. Extending the applicability to lower N is of interest for experimental studies of the MST.

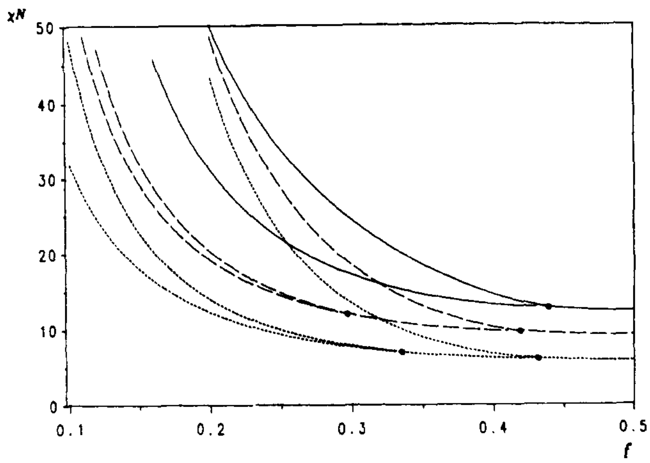

Figure 13. Phase diagrams χN vs f for $N = 10^4$, polydispersities $U = 0$ (solid lines), $U_K = 0.4$ (dashed lines), and $U_K = 0.8$ (dotted lines), independent variances of N_K, $U_A = U_B$. Triple points are marked with circles. The only triple point present for $U = 0$, hex/lam/dis, is located at $f = 0.439$ and $\chi N = 12.85$. The diagrams for $U_K = 0.4$ and $U_K = 0.8$ show two triple points with the coordinates $f = 0.297$, $\chi N = 12.02$, and $f = 0.335$, $\chi N = 6.944$, respectively, for bcc/hex/dis, and $f = 0.419$, $\chi N = 9.669$ and $f = 0.432$, $\chi N = 6.066$, respectively, for hex/lam/dis.

The concept of the reduced phase diagram shown in Figure 11 facilitates the prediction of the transitions for given sample characteristics. This concept has been incorporated in a computer program together with the calculation of all relevant coefficients for the scattering curves of the disordered phase. The program runs on a standard PC.

We hope that the present study will help experimentalists to improve the evaluation of scattering data for block copolymer systems in the weak segregation regime. It should be mentioned, however, that block copolymers and block copolymer/homopolymer systems have subtle energetics and are thus very sensitive to several practical variables that can have a major influence on the behavior of the system. More quantitative experimental studies are needed to check the validity of the assumptions used in the treatment of fluctuations based on the theory of Fredrickson and Helfand.[9] The general concept of polydispersity corrections for correlation functions presented in this paper is, however, expected to be valid also for future improvements of the fluctuation theory.

Acknowledgment. We are indebted to G. H. Fredrickson for sending us his program for the calculation of the MST coefficients. Thanks are also due to Professor A. Khokhlov for stimulating discussions during the stay of W.R. at Moscow University. The support of the work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Appendix

Nonlinear Response Functions of Gaussian Copolymer Chains with Polydispersity. We consider the effect of polydispersity to be given by the weight averages of the response functions $G_{ijk}(h)$ and $G_{ijkl}(h_1,h_2)$. As examples, we carry out the averaging on the functions $G_{121}(h)$ and $G_{1122}(0,0)$.

According to Leibler,[8] the function $G_{121}(h)$ is given by

$$G_{121}(h) = N^2[g_4(f_A,h) + g_3(f_A,1)]$$

where

$$g_3(f_A,1) = [1 - \exp(-f_B x)][1 - f_A x \exp(-f_A x) - \exp(-f_A x)]/x^3$$

and

$$g_4(f_A,h) = [1 - \exp(-f_B x)][1 + \exp(-h f_A x)/(h-1) - h \exp(-f_A x)/(h-1)]/(h x^3)$$

The weight average is given by

$$\begin{aligned}\langle G_{121}(h)\rangle_w &= \langle N G_{121}(h)\rangle_n / \langle N\rangle_n \\ &= [\langle N^3 g_4(f_A,h)\rangle_n + \langle N^3 g_3(f_A,1)\rangle_n]/\langle N\rangle_n\end{aligned}$$

We define the averaged functions $\bar{g}_i$ (i = 2–4) by

$$\langle N^3 g_i(f_A,h)\rangle_n = \langle N\rangle_n^{\,3}\bar{g}_i(\bar{f}_A,h)$$

If eq 1 is valid, we find for a one-component system

$$\bar{g}_3(\bar{f}_A,1) = [1 - \langle\exp(-f_B x)\rangle_n][1 - \langle f_A x \exp(-f_A x)\rangle_n - \langle\exp(-f_A x)\rangle_n]/\bar{x}^3$$

and

$$\bar{g}_4(\bar{f}_A,h) = [1 - \langle\exp(-f_B x)\rangle_n][1 + \langle\exp(-h f_A x)\rangle_n/(h-1) - h\langle\exp(-f_A x)\rangle_n/(h-1)]/(h\bar{x}^3)$$

where the average $\langle\exp(-f_K x)\rangle_n$ has already been given in section 3 and

$$\begin{aligned}\langle f_K x \exp(-f_K x)\rangle_n &= \bar{f}_K\bar{x}(1 + U_K\bar{f}_K\bar{x})^{-(1+1/U_K)} \\ &= \bar{f}_K\bar{x}\langle\exp(-f_K x)\rangle_n/(1 + U_K\bar{f}_K\bar{x})\end{aligned}$$

if a Schulz–Zimm distribution is used.

For a multicomponent system, the averaging is more tedious since the expressions in square brackets cannot be treated separately. We obtain

$$\bar{g}_3(\bar{f}_A,1) = [1 - \langle f_A x \exp(-f_A x)\rangle_n - \langle\exp(-f_A x)\rangle_n - \langle\exp(-f_B x)\rangle_n + \langle f_A x \exp(-x)\rangle_n + \langle\exp(-x)\rangle_n]/\bar{x}^3$$

and

$$\bar{g}_4(\bar{f}_A,h) = [1 + \langle\exp(-h f_A x)\rangle_n/(h-1) - h\langle\exp(-f_A x)\rangle_n/(h-1) - \langle\exp(-f_B x)\rangle_n - \langle\exp(-h f_A x)\exp(-f_B x)\rangle_n/(h-1) - h\langle\exp(-x)\rangle_n/(h-1)]/(h\bar{x}^3)$$

where the averages $\langle\exp(-f_K x)\rangle_n$ and $\langle\exp(-x)\rangle_n$ have already been given in section 3 and

$$\langle f_K x \exp(-f_K x)\rangle_n = \sum_{i=1}^{m} z_i\langle f_{K_i} x_i \exp(-f_{K_i} x_i)\rangle_n$$

$$\langle f_{K_i} x_i \exp(-f_{K_i} x_i)\rangle_n = \bar{f}_{K_i} p_i\bar{x}(1 + U_{K_i}\bar{f}_{K_i} p_i\bar{x})^{-(1+1/U_{K_i})}$$

$$\langle f_A x \exp(-x)\rangle_n = \sum_{i=1}^{m} z_i\langle f_{A_i} x_i \exp(-f_{A_i} x_i)\rangle_n\,\langle\exp(-f_{B_i} x_i)\rangle_n$$

$$\langle\exp(-h f_A x)\exp(-f_B x)\rangle_n = \sum_{i=1}^{m} z_i\langle\exp(-h f_{A_i} x_i)\rangle_n\langle\exp(-f_{B_i} x_i)\rangle_n$$

The function $G_{1122}(0,0)$ is given by

$$G_{1122}(0,0) = 4N^3 f_3(f_A,0)\, f_3(f_B,0)$$

For the average we get

$$\langle G_{1122}(0,0)\rangle_w = 4\langle N^4 f_3(f_A,0)\, f_3(f_B,0)\rangle_n/\langle N\rangle_n$$

For a one-component system we find

$$\langle G_{1122}(0,0)\rangle_w = 4\langle N\rangle_n^{\,3}\,\bar{f}_3(\bar{f}_A,0)\,\bar{f}_3(\bar{f}_B,0)$$

where

$$\bar{f}_3(\bar{f}_K,0) = \bar{g}_1(\bar{f}_K,\bar{x})/2$$

For a multicomponent system the averaging leads to

$$\langle G_{1122}(0,0)\rangle_w = 4\langle N\rangle_n^{\,3}[\langle f_A f_B x^2\rangle_n + \langle\exp(-x)\rangle_n + 1 + \langle f_B x \exp(-f_A x)\rangle_n + \langle f_A x \exp(-f_B x)\rangle_n - \bar{x} - \langle\exp(-f_A x)\rangle_n - \langle\exp(-f_B x)\rangle_n]/\bar{x}^4$$

where the new averages occurring in this relationship are

$$\langle f_A f_B x^2\rangle_n = \bar{x}^2\sum_{i=1}^{m} z_i p_i^{\,2}\bar{f}_{A_i}\bar{f}_{B_i}$$

and

$$\langle f_B x \exp(-f_A x)\rangle_n = \bar{x}\sum_{i=1}^{m} z_i\bar{f}_{B_i} p_i\langle\exp(-f_{A_i} x_i)\rangle_n$$

References and Notes

(1) Helfand, E.; Wasserman, Z. In *Developments in Blockcopolymers*; Goodman, I., Ed.; Applied Science: New York, 1982; Chapter 4.

(2) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.

(3) Semenov, A. N. *Sov. Phys.-JETP* **1985**, *61*, 733.

(4) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, D. C.; Handlin, D. L.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197.

(5) Herman, D. S.; Kinning, D. J. *Macromolecules* **1987**, *20*, 2940.

(6) Thomas, E. L.; Anderson, D. M.; Henkee, C. S.; Hoffman, D. *Nature* **1988**, *334*, 598.

(7) Hasegawa, H.; Tanaka, K.; Yamasaki, K.; Hashimoto, T. *Macromolecules* **1987**, *20*, 1651.

(8) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(9) Fredrickson, G. H.; Helfand, E. *J. Chem. Phys.* **1987**, *87*, 697.

(10) Brasovskii, S. A. *Sov. Phys.-JETP* **1975**, *41*, 85.

(11) Leibler, L.; Benoit, H. *Polymer* **1981**, *22*, 195.

(12) Hong, K. M.; Noolandi, J. *Polym. Commun.* **1984**, *25*, 265.

(13) For polydisperse systems, N appearing in coefficients like $(\chi N)_s$, $(\chi N)_t$, ϵ, τ, μ, λ, etc., stands for $\langle N\rangle_n$.

(14) Bates, F. S. *Macromolecules* **1985**, *18*, 525.

(15) Bates, F. S.; Hartney, M. A. *Macromolecules* **1985**, *18*, 2478.

(16) Mori, K.; Hasegawa, H.; Hasimoto, T. *Polym. J. Jpn.* **1985**, *17*, 799.

(17) Zin, W.-C.; Roe, R.-J. *Macromolecules* **1984**, *17*, 183.

(18) Hewel, M.; Ruland, W. *Makromol. Chem., Makromol. Symp.* **1986**, *4*, 197.

(19) Nogima, S.; Roe, R.-J. *Macromolecules* **1985**, *18*, 183.

(20) Fischer, E. W.; Jung, W. G. *Makromol. Chem., Makromol. Symp.* **1989**, *26*, 178.