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Microphase Separation Transition of Weakly Charged Copolymers in Solution

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ABSTRACT: The microphase separation transition for neutral and weakly charged diblock copolymers in solution is investigated. The critical parameter for microphase transition is calculated as a function of the numbers of charges and the polymer and the salt concentrations. It is found that χ_m increases substantially either when one block is charged and the other neutral or when both blocks carry charges of opposite signs. Cases of symmetric and nonsymmetric diblocks are considered.

Introduction and General Equations

The microphase separation transition (MST) in bulk of neutral copolymers is a well-documented subject in the literature.[1-6] The case of copolymers in the presence of a low molecular weight solvent has received only modest attention. Few attempts were made to understand the behavior of these systems in the disordered one-phase region,[7-9] and others focused on the effects of preferential solvatation of one block leading to the formation of micelles.[10,11] Recently, Rabin and Marko[12] published a note on the MST of a diblock copolymer made of a neutral block and a weakly charged block in the absence of solvent. Their description uses a generalization of the Flory-Huggins[13] model which was already applied by others[14,15] to study the phase behavior of mixtures of homopolymers containing weakly charged species. Here, we examine the problem of stability and MST of weakly charged copolymers in the presence of a low molecular weight solvent. The scattering properties of this system in the disordered one-phase region were studied elsewhere,[16] and the present work is an attempt to extend this study to the problem of stability near the conditions of MST. The matrix formalism presented below can be applied to linear or branched copolymers but only linear diblock copolymers will be considered here. The starting equation gives the inverse total structure matrix in the interacting system $\mathbf{S}^{-1}(q)$ as a sum of the inverse bare structure matrix in the noninteracting system $\mathbf{S}_o^{-1}(q)$ and the interaction matrix. For neutral polymers, the latter quantity is the usual excluded volume matrix ϑ and for weakly charged systems, it is the sum of ϑ and $\alpha(q)\mathbf{F}$ such that

$$\mathbf{S}^{-1}(q) = \mathbf{S}_o^{-1}(q) + \vartheta + \alpha(q)\mathbf{F} \tag{1}$$

For diblock copolymers, the bare structure matrix $\mathbf{S}_0(q)$ is

$$S_o(q) = \phi N \begin{bmatrix} x^2 P_1(q) & x(1-x)P_{12}(q) \\ x(1-x)P_{12}(q) & (1-x)^2 P_2(q) \end{bmatrix} \tag{2}$$

where q is the amplitude of the scattering wave vector, $q = 4\pi/\lambda \sin(\Theta/2)$ (λ the wavelength of the incident radiation, and Θ the scattering angle), ϕ is the total polymer concentration, N is the total degree of polymerization, x is the composition of monomers 1 per chain, $P_1(q)$ and $P_2(q)$ are the form factors of blocks 1 and 2, $P_{12}(q)$ is the intramolecular interference term, and $P_T(q)$ is the total form factor:

$$P_T(q) = x^2 P_1(q) + (1-x)^2 P_2(q) + 2x(1-x)P_{12}(q) \tag{3}$$

The excluded volume parameters ϑ_{ii} are expressed in terms of the solvent concentration ϕ_s and the Flory-Huggins interaction parameters χ_{ij} as follows:

$$\vartheta_{ii} = 1/\phi_s - 2\chi_{is} \tag{4a}$$

$$\vartheta_{ij} = 1/\phi_s - \chi_{is} - \chi_{js} + \chi_{ij}\ (i \neq j) \tag{4b}$$

Here, we have assumed that the molar volumes of the monomers, $\tilde{\vartheta}_i$ and $\tilde{\vartheta}_j$, and of the solvent molecules, $\tilde{\vartheta}_s$, are equal to unity; a similar approximation is usually made in the Flory-Huggins lattice model by taking $\tilde{\vartheta}_i = \tilde{\vartheta}_j = \tilde{\vartheta}_s$ = volume of a lattice site. The short-range excluded volume interactions are supplemented as shown by eq 1 with long-range q-dependent electrostatic terms. The latter are modeled using the Debye-Hückel approximation in such a way that

$$\alpha(q) = \frac{4\pi l}{q^2 + K^2} \tag{5a}$$

$$K^2 = 4\pi l\{[xf_1 + (1-x)f_2]\phi + \phi_{\text{salt}}\} \tag{5b}$$

where l is the Bjerrum length (i.e. $l = e^2/\epsilon kT$, e is the electron charge, ϵ the dielectric constant, k the Boltzmann constant, and T the absolute temperature), $l = 7$ Å for water at 25 °C, ϕ_{salt} is the concentration of added salt, and K^{-1} is the Debye-Hückel screening length. We should point out that the concentrations are denoted by the symbol ϕ regardless of their units (g/cm^3, number of particles/cm^3, or volume fractions) and particular care is required in numerical applications. The elements of the matrix $\mathbf{F}$ are defined by

$$F_{ii} = f_i^2\ (i = 1, 2) \tag{6a}$$

$$F_{12} = \epsilon f_1 f_2 \tag{6b}$$

$\epsilon = +1$ if the charges on monomers 1 and 2 have the same sign and -1 otherwise. The first term on the right-hand side (rhs) of eq 5b represents the concentration of counterions emitted by block 1, the second corresponds to those of block 2, and the concentration of added salt ϕ_{salt} should not be confused with the solvent concentration ϕ_s. The expression of the screening length in eq 5b is written by using the electroneutrality condition; $f_1 e$ and $f_2 e$ are the charges carried by monomers 1 and 2 respectively; since

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we are dealing with weakly charged polymers, $f_i \ll 1$ (i = 1, 2), and f_i^{-1} may also be defined as the number of monomers between two successive charges. This model was used to investigate the scattering properties of diblock copolymers in solution as a function of the wave vector q, the polymer concentration ϕ, and the salt concentration ϕ_{salt} in various conditions of charge distribution. Here, we would like to focus our attention on the properties of the system near the MST. We shall pay particular attention to the critical parameter for MST χ_m at which the scattering intensity diverges at the wave vector q_m. There are two important differences between weakly charged copolymers and the corresponding mixtures of weakly charged homopolymers. The first is the absence of phase transition at $q = 0$ for copolymers since the two blocks are chemically bound, and in such a limit ($q = 0$) the copolymer nature of the chain becomes irrelevant. The second difference is that the MST can take place in the neutral copolymer system whereas, for homopolymers, the emergence of a peak and the possibility of MST is conditioned by the presence of electrostatic interactions. Because of these distinctions it would be useful to start with a brief discussion of the neutral diblock copolymer system.

Neutral Diblock Copolymer

Let us first examine the case of a symmetric diblock with the composition $x = {}^1/_2$. Only two form factors are needed to characterize the static structure properties of the solution since $P_1(q) = P_2(q) = P_{1/2}(q)$. Combining eq 1 with (6) and letting $f_1 = f_2 = 0$ yields

$$\frac{4S_{11}(q)}{\phi N} = \frac{P_{1/2}(q) + \vartheta\phi N P_T(q)(P_{1/2}(q) - P_T(q))}{\left[1 + \left(\vartheta + \frac{\chi}{2}\right)\phi N P_T(q)\right]\left\{1 - \frac{\chi}{2}\phi N[P_{1/2} - P_T(q)]\right\}} \tag{7}$$

where, for simplicity but without loss of generality, it was assumed that the polymer–solvent interaction parameters χ_{1S} and χ_{2S} are equal to χ_{PS}, and the polymer–polymer Flory–Huggins interaction parameter is denoted by χ. This yields

$$\vartheta_{11} = \vartheta_{22} = \vartheta = 1/\phi_s - 2\chi_{PS} \tag{8a}$$

$$\vartheta_{12} = \vartheta + \chi = 1/\phi_s - 2\chi_{PS} + \chi \tag{8b}$$

It is interesting to write eq 7 as follows:

$$\frac{4S_{11}(q)}{\phi N} = \frac{S_T(q)}{\phi N} + \frac{4S_I(q)}{\phi N} \tag{9}$$

where $S_T(q)$ is the structure factor one would obtain if the indices of refraction or scattering lengths of the two blocks are equal:

$$S_T(q) = \frac{\phi N P_T(q)}{1 + \left(\vartheta + \frac{\chi}{2}\right)\phi N P_T(q)} \tag{10a}$$

This quantity represents the spatial correlation of the total concentration fluctuations

$$S_T(q) = \langle \rho_T(q)\rho_T(-q)\rangle \tag{10b}$$

$\rho_T(q)$ being the total polymer concentration

$$\rho_T(q) = \rho_1(q) + \rho_2(q) \tag{10c}$$

and the symbol $\langle ...\rangle$ denotes the ensemble average. The second term on the rhs of eq 9 is the structure factor one would measure if the increments of the refractive indices of the two blocks are equal but have opposite signs.[8,16] In this so-called optical θ condition or zero average contrast condition, one has

$$\frac{4S_I(q)}{\phi N} = \frac{P_{1/2}(q) - P(q)}{1 - \frac{\chi}{2}\phi N[P_{1/2}(q) - P_T(q)]} \tag{11a}$$

$S_I(q)$ represents the static correlations of composition fluctuations, namely if $\rho_I(q)$ is the quantity

$$\rho_I(q) = \left[\frac{\rho_1(q)}{1-x} - \frac{\rho_2(q)}{x}\right] = 2[\rho_1(q) - \rho_2(q)] \tag{11b}$$

then $S_I(q)$ is defined as

$$S_I(q) = \langle \rho_I(q)\rho_I(-q)\rangle \tag{11c}$$

The result in eq 9 shows that the scattering signal $S_{11}(q)$ is the sum of the signals due to concentration and composition fluctuations and that there is no coupling between these two variables. This decoupling seems to be a general property of symmetrical systems. The composition fluctuations as expressed by eq 11a represent the result one would obtain in a pure copolymer system (bulk state) with a reduced apparent interaction parameter $\chi\phi$. The bulk limit of eq 9, which can be obtained by letting $\vartheta \rightarrow \infty$ and $\phi \rightarrow 1$, yields

$$S(q) = S_{11}(q) = S_I(q) \quad \text{and} \quad S_T(q) = 0 \text{ (bulk)} \tag{12}$$

$S(q)$ has a maximum at $q_m \approx 2/R_g$ where R_g represents the total radius of gyration whereas the maximum of $S_{11}(q)$ depends on the concentration ϕ. Equations 9 and 11a show that $S_{11}(q)$ and $S_I(q)$ diverge if the parameter χ reaches the limiting value χ_m which is given by

$$\chi_m = \frac{2}{\phi N[P_{1/2}(q_m) - P_T(q_m)]} \tag{13}$$

$N\chi_m$ is approximately equal to 10 in the bulk limit (ϕ = 1) and $10/\phi$ in solution at the total volume fraction ϕ. To understand the importance of labeling on the phase behavior, one notes that if the two blocks have approximately the same index of refraction, one measures $S_T(q)$ which reflects the behavior of a neutral homopolymer and hence has no possibility of showing an MST. If the index of refraction of solvent is intermediate between those of the two polymers in such a way that their increments of the refractive indices are equal but have opposite signs, one observes a maximum at all concentrations including the infinite dilute limit (single chain). The interaction parameter has a threshold value χ_m beyond which the structure factor becomes negative and the system undergoes an MST. The onset of this transition takes place at χ_m which is inversely proportional to the concentration ϕ, as shown by eq 13. For an infinitely dilute solution, this value is out of reach (infinite) and, although $S_{11}(q)$ presents a well-defined peak, its amplitude remains finite. When the concentration increases, χ_m decreases and reaches its smallest value in the bulk where $\chi_m = 2/N(P_{1/2} - P_T)_m \approx 10/N$. In this limit, a slight incompatibility between the two blocks is sufficient to induce an MST. If one of the blocks (say block 2) is isorefractive with the solvent, one observes that the signal $S_{11}(q)$ has a less pronounced peak because of the contribution of the total polymer concentration fluctuations given by the first term on the rhs of eq 9. The plots of $S_{11}(q)$ versus q are given elsewhere.[16] They show that the peak becomes more pronounced and its position q_m shifts to higher values when the concentration increases. The contribution of $S_T(q)$ tends to dominate the q dependence of $S_{11}(q)$, as shown by eq 9. Hence the critical parameter for MST is approximately defined by eq 13. These observations are, of course, not specific to symmetric copolymers. Similar observations can be made for nonsymmetrical diblocks. Since the variations of $S_{11}(q)$ were studied elsewhere[16] for arbitrary values of x, we content ourselves here with giving the bulk limit which is obtained by letting $\phi_s \to 0$ or $\vartheta \to \infty$ and $\phi = 1$: The result reads $S_{11}(q) = S_I(q) = S(q)$ and $S_T(q) = 0$ with

$$S(q) = \frac{x^2(1-x)^2 N[P_1(q)P_2(q) - P_{12}{}^2(q)]}{P_T(q) - 2\chi N x^2(1-x)^2[P_1(q)P_2(q) - P_{12}{}^2(q)]} \qquad (14)$$

The critical parameter for MST is immediately deduced from this expression as

$$\chi_m = \frac{P_T(q_m)}{2Nx^2(1-x)^2[P_1(q_m)P_2(q_m) - P_{12}{}^2(q_m)]} \qquad (15)$$

The location of the maximum q_m can be obtained as a function of x by differentiating eq 14 with respect to q and finding q_m, for which the derivative is zero. One can also read the maximum and its location q_m from the plots of $S(q)$ versus q. Furthermore, the zero scattering angle limit, which will be referred to hereafter as the thermodynamic limit, of $S_{11}(q{=}0)$ for nonsymmetrical copolymers has the following form:

$$S_{11}(q{=}0) = \frac{\phi N}{4\left[1 + \left(\vartheta + \frac{\chi}{2}\right)\phi N\right]} \qquad (16)$$

In good solvent conditions $S_{11}(q{=}0)$ is always positive and $S_I(q{=}0)$ is always zero in such a way that the copolymer nature is completely lost. The chains behave as identical pointlike particles in a good solvent, and this behavior constitutes one of the essential differences between copolymers and mixtures of homopolymers. In particular, it shows that no phase separation can take place in copolymer solutions in the thermodynamic limit ($q = 0$).

Partially Charged Diblock Copolymers

The MST in partially charged diblock copolymers has been adressed by Rabin and Marko[12] by using the Flory–Huggins lattice model and considering the case of pure copolymers in the absence of solvent. Here, we examine a similar problem in the presence of a low molecular weight solvent, using the formalism described in the first part of this paper. The presence of solvent introduces additional properties which do not arise in the bulk state. These new properties are either of a thermodynamic nature, such as the excluded volume parameter $\vartheta = 1/\phi_s - 2\chi_{PS}$ and the reduced apparent interaction parameter $\chi\phi$, or of a structural nature since one can define several structure factors such as $S_{11}(q)$, $S_{22}(q)$, $S_T(q)$, and $S_I(q)$. All these structure factors are directly accessible by scattering techniques with appropriate choices of the solvent. Let us first consider the case of a symmetric diblock copolymer, where block 1 is charged and block 2 is neutral. The partial structure factor corresponding to the charged block $S_{11}(q)$ is known as[16]

$$\frac{4S_{11}(q)}{\phi N} = \frac{P_{1/2}(q) + \vartheta\phi N P_T(q)[P_{1/2}(q) - P_T(q)]}{D(q)} \qquad (17a)$$

where the denominator $D(q)$ is

$$D(q) = D_{\text{neutral}}(q) + \alpha(q) f_1{}^2 \frac{\phi N}{4}\{P_{1/2}(q) + \vartheta\phi N P_T(q)[P_{1/2}(q) - P_T(q)]\} \qquad (17b)$$

$$D_{\text{neutral}}(q) = \left[1 + \left(\vartheta + \frac{\chi}{2}\right)\phi N P_T(q)\right] \times \left\{1 - \frac{\chi}{2}\phi N[P_{1/2}(q) - P_T(q)]\right\} \qquad (17c)$$

$\alpha(q)$ is defined by eq 5a and the Debye–Hückel screening length is given by

$$K^2 = 2\pi l\left(\frac{1}{2}\phi f_1 + \phi_{\text{salt}}\right) \qquad (17d)$$

One notes that the decoupling between concentration and composition fluctuations is lost since eq 17a cannot be written as a sum of $S_T(q)$ and $S_I(q)$ as in the neutral limit (see eq 9) and the symmetry is broken by the charging procedure. Equation 17a can be written in the reciprocal form as follows:

$$\frac{\phi N}{4S_{11}(q)} = \left[\frac{\phi N}{4S_{11}(q)}\right]_{\text{neutral}} + \frac{1}{4}\alpha(q) f_1{}^2 \phi N \qquad (18)$$

The first contribution in the rhs of this equation can be obtained from eq 9. The variations of $S_{11}(q)$ versus q for several values of f_1[16] show a trend similar to that in ordinary polyelectrolyte solutions. The position of the peak q_m shifts to higher values when the polymer concentration ϕ increases and to smaller values when the salt concentration ϕ_{salt} increases. This behavior was also observed in single polyion systems both theoretically[17,18] and experimentally[19–21] and therefore it is not necessary to develop a detailed discussion about this subject. We only mention that the charge distribution along the chain does not seem to play a crucial role as long as these charges are of the same sign and the condition of weakly charged polyelectrolytes expressed by $f_1 \ll 1$ is fulfilled. In the thermodynamic limit (i.e. $q = 0$) one obtains

$$\frac{4S_{11}(q{=}0)}{\phi N} = D^{-1}(q{=}0) \qquad (19a)$$

with

$$D(q{=}0) = 1 + \left[\vartheta + \frac{\chi}{2} + \frac{f_1{}^2}{2(f_1\phi + 2\phi_{\text{salt}})}\right]\phi N \qquad (19b)$$

and in the bulk limit $D^{-1}(q{=}0)$ is zero. This means that in good solvent conditions the scattering at zero angle is small and cannot diverge, ruling out the possibility of a phase transition. A similar conclusion was reached in the neutral limit and makes clear the important difference with the mixtures of homopolymers. The variations of q_m with ϕ_s and f_1 are consistent with the results of Rabin and Marko[12] but with much slower rates for solutions and for smaller polymer concentrations. The presence of a low molecular weight solvent reduces the loss of entropy of counterions which seems to be the major source of the MST, as explained by Rabin and Marko for copolymers[12] and Khokhlov and Nyrkova for homopolymers.[14] The solvent provides a large medium where counterions can escape, producing a relative excess of entropy which does not exist in the bulk state. The bulk limit can easily be obtained from eq 17a by letting $\vartheta \to \infty$ and $\phi = 1$:

$$\frac{4S(q)}{N} = \frac{P_{1/2} - P_T}{1 - \frac{1}{2}\left[\chi - \frac{\alpha(q)}{2} f_1{}^2\right] N(P_{1/2} - P_T)} \qquad (20a)$$

In the reciprocal form, which is perhaps more appealing, one has

$$\frac{1}{4S_{11}(q)} = \frac{1}{N(P_{1/2} - P_{\mathrm{T}})} - \frac{\chi}{2} + \frac{1}{4}\alpha(q){f_1}^2 \qquad (20b)$$

This result is identical with the one reported by Rabin and Marko,[12] but the notations are quite different. The critical parameter for MST can be obtained from the generalized spinodale equation:

$$D(q{=}q_{\mathrm{m}}) = 0 \qquad (21)$$

which defines the border line between the zone of unstability $D(q{=}q_{\mathrm{m}}) < 0$ and the zone of stability $D(q{=}q_{\mathrm{m}}) > 0$. We consider the scattering at the particular wave vector q_{m} because the intensity is maximum at this point and hence the fluctuations are at their strongest. This is the mode that governs the transition from stable to unstable conditions. We assume, of course, that all modes with a wave vector different from q_{m} are stable and decay much faster than the time during which the variation of $S(q)$ versus q is observed. In the bulk limit, one obtains immediately from eq 20a

$$\chi_{\mathrm{m}} = \chi_{\mathrm{m}}(\mathrm{neutral}) + \frac{1}{2}\alpha(q_{\mathrm{m}}){f_1}^2 \qquad (22a)$$

with

$$\chi_{\mathrm{m}}(\mathrm{neutral}) = \frac{2}{N[P_{1/2}(q_{\mathrm{m}}) - P_{\mathrm{T}}(q_{\mathrm{m}})]} \qquad (22b)$$

$$\alpha(q_{\mathrm{m}}) = \frac{1}{{q_{\mathrm{m}}}^2 + K^2} \qquad (22c)$$

This result shows the important increase of the critical parameter at which an MST can take place. It denotes a substantial enhancement of compatibility between the two species similar to the one observed in mixtures of charged and neutral homopolymers.[14] The χ_{m} for solutions is somewhat more involved and should be calculated from the stability condition requiring that $D(q)$ defined by eq 17b is positive or zero. The latter condition yields at $q = q_{\mathrm{m}}$

$$D(q{=}q_{\mathrm{m}}) = \left[1 - \frac{\chi_{\mathrm{m}}}{2}\phi N(P_{1/2\mathrm{m}} - P_{\mathrm{Tm}})\right] \times \left[1 + \left(\vartheta + \frac{\chi_{\mathrm{m}}}{2}\right)\phi N P_{\mathrm{Tm}}\right] + \alpha_{\mathrm{m}}{f_1}^2\frac{\phi N}{4}[P_{1/2\mathrm{m}} + \vartheta\phi N P_{\mathrm{Tm}}(P_{1/2\mathrm{m}} - P_{\mathrm{Tm}})] = 0 \qquad (23)$$

where the subscript m means that the quantity is evaluated at $q = q_{\mathrm{m}}$. The critical parameter χ_{m} can be deduced immediately from this equation as follows:

$$\chi_{\mathrm{m}} = \left[\frac{P_{1/2\mathrm{m}}}{\phi N P_{\mathrm{Tm}}(P_{1/2} - P_{\mathrm{Tm}})} + \vartheta + \alpha_{\mathrm{m}}{f_1}^2\right]^{1/2} \times \left[\frac{P_{1/2\mathrm{m}}}{\phi N P_{\mathrm{Tm}}(P_{1/2} - P_{\mathrm{Tm}})} + \vartheta\right]^{1/2} + \frac{2P_{\mathrm{Tm}} - P_{1/2\mathrm{m}}}{\phi N P_{\mathrm{Tm}}(P_{1/2} - P_{\mathrm{Tm}})} - \vartheta \qquad (24)$$

In the high-concentration regime where $\vartheta\phi N P_{\mathrm{Tm}}$ is very large as compared to 1, one can get an approximate form of the parameter χ_{m}, which is relatively simple:

$$\chi_{\mathrm{m}} = \frac{2}{\phi N(P_{1/2\mathrm{m}} - P_{\mathrm{Tm}})} + \frac{\alpha_{\mathrm{m}}{f_1}^2}{2} \qquad (25)$$

This result reproduces the bulk limit by simply putting $\phi = 1$. Let us now examine the total structure factor

$$S_{\mathrm{T}}(q) = S_{11}(q) + S_{22}(q) + 2S_{12}(q)$$

An important difference with the corresponding mixture of charged and neutral homopolymers is the strong screening of electrostatic interactions by the neutral homopolymers. A small amount of neutral polymer is sufficient to screen out almost totally the Coulomb forces and to remove the peak of $S_{\mathrm{T}}(q)$. In the copolymer case, the peak of $S_{\mathrm{T}}(q)$ appears even for small values of f_1. $S_{\mathrm{T}}(q)$ could be measured directly by starting from a homopolymer (e.g. polystyrene) and by assuming that only half of the chain is sulfonated (e.g. NaPSS–PSS). One also assumes that the charging procedure (sulfonation) does not change the scattering properties (scattering length or index of refraction) significantly. The expression of $S_{\mathrm{T}}(q)$, including a thermodynamic incompatibility to account also for the case of copolymers built with different monomers, is

$$\frac{S_{\mathrm{T}}(q)}{\phi N} = \frac{P_{\mathrm{T}}(q)\left\{1 - \frac{1}{2}\left[\chi - \frac{\alpha(q){f_1}^2}{2}\right]\phi N[P_{1/2}(q) - P_{\mathrm{T}}(q)]\right\}}{D(q)} \qquad (26)$$

where $D(q)$ is given by eq 17c. First, one notes that $S_{\mathrm{T}}(q{=}0) = 4S_{11}(q{=}0)$ as it can be shown from eqs 17a and 26:

$$4S_{11}(q{=}0) = S_{\mathrm{T}}(q{=}0) = \frac{\phi N}{1 + \left[\vartheta + \frac{\chi}{2} + \frac{{f_1}^2}{2(\phi f_1 + 2\phi_{\mathrm{salt}})}\right]\phi N} \qquad (27)$$

(see also eq 19). The variations of $S_{\mathrm{T}}(q)$ versus q was given before[16] for several values of f_1. The behavior of $S_{11}(q)$ and $S_{\mathrm{T}}(q)$ with the parameters f_1, ϕ, and ϕ_{salt} are found to be qualitatively similar. The position of the maximum q_{m} first increases with f_1 and levels off quickly to a constant value. The critical parameter for MST has the same expression as in eqs 24 and 25 but one should keep in mind that this expression involves the value of q_{m} which depends on the structure factor under consideration. This means that the MST could be observed in one case and not in the others. Such a distinction is not possible in the bulk limit where there is only one structure facor $S(q)$. In the solution problem, one can also introduce the structure factor for composition fluctuations $S_{\mathrm{I}}(q)$, which in general presents trends similar to those of the bulk structure factor for reasons that are clear since in the bulk limit we have only composition fluctuations. Since one block is charged and the other neutral, $S_{11}(q) \neq S_{22}(q)$ and $S_{\mathrm{I}}(q)$ is given by

$$S_{\mathrm{I}}(q) = 4[S_{11}(q) + S_{22}(q) - 2S_{12}(q)] \qquad (28)$$

One finds[16]

$$\frac{4S_{\mathrm{I}}(q)}{\phi N} = \frac{[P_{1/2}(q) - P_{\mathrm{T}}(q)]\left\{1 + \left[\vartheta + \frac{\chi}{2} + \frac{\alpha(q)}{4}{f_1}^2\right]\phi N P_{\mathrm{T}}(q)\right\}}{D(q)} \qquad (29)$$

where the denominator is given by eq 17c. It was observed[16] that q_{m} first increases and then decreases when the charges parameter f_1 increases. This unusual behavior should be taken into account when one examines the MST in the conditions where $S_{\mathrm{I}}(q)$ is observed. The latter structure factor is a particularly convenient quantity for studying the MST when one is interested in the composition fluctuations for concentrations ranging from infinitely dilute to the bulk limit. The correct value of q_m should be substituted into eq 24a or 25 to obtain the critical parameter for MST. Another interesting observation can be made concerning the coupling between concentration and composition fluctuations. By comparing eqs 17a, 26, and 29, one observes that $S_{11}(q)$ cannot be written as a sum of contributions from $S_T(q)$ and $S_I(q)$ independently, as was the case for neutral symmetric copolymers. This implies that the symmetry is broken and there is a strong complex between the fluctuation in total concentration and in composition.

Nonsymmetrical Partially Charged Copolymer

Here, the charged block has a composition of monomers which is not necessarily $^1/_2$. One needs three form factors $P_1(q), P_2(q)$, and $P_T(q)$ to describe the structural properties of the system. The partial structure factor $S_{11}(q)$ is found as[16]

$$\frac{S_{11}(q)}{x^2\phi N} = \frac{P_1(q) + \vartheta(1-x)^2\phi N[P_1(q)P_2(q) - P_{12}{}^2(q)]}{D(q)} \qquad \text{(30a)}$$

where the denominator $D(q)$ is

$$D(q) = D_{\text{neutral}}(q) + \alpha(q)f_1{}^2x^2\phi N\{P_1(q) + \vartheta\phi N(1-x)^2[P_1(q)P_2(q) - P_{12}{}^2(q)]\} \qquad \text{(30b)}$$

and $D_{\text{neutral}}(q)$ is given by

$$D_{\text{neutral}}(q) = 1 + \vartheta\phi NP_T(q) + 2\chi x(1-x)\phi NP_{12}(q) - \chi(\chi + 2\vartheta)x^2(1-x)^2\phi^2N^2[P_1(q)P_2(q) - P_{12}{}^2(q)] \qquad \text{(30c)}$$

In this case, the screening length K^{-1} is given by

$$K^2 = 4\pi l(xf_1\phi + \phi_{\text{salt}}) \qquad \text{(30d)}$$

The variation of $S_{11}(q)$ with the wave vector q and the composition x was given in ref 16. It shows that the peak of $S_{11}(q)$ shifts to higher values when x increases from 0.1 to 0.9. This behavior is expected since when $x \rightarrow 1$, one must recover the single polyion limit for which $q_m{}^{-1}$ should be the smallest as compared to partially charged polyelectrolytes. The condition of stability requires that the denominator $D(q)$ remains positive. The critical parameter for MST is obtained from the generalized spinodal at $q = q_m$, which yields the following solution:

$$\chi_m = \left[\frac{P_{1m}}{\phi N(1-x)^2\Delta P_m} + \vartheta\right]^{1/2} \times \left(\frac{P_{2m}}{\phi Nx^2\Delta P_m} + \vartheta + \alpha_m f_1{}^2\right)^{1/2} + \frac{P_{12m}}{\phi Nx(1-x)\Delta P_m} - \vartheta \qquad \text{(31)}$$

where we have introduced the quantity $\Delta P_m = P_{1m}P_{2m} - P_{12m}{}^2$ for convenience. The high-concentration limit of eq 31a yields the approximate result

$$\chi_m \approx \frac{P_{Tm}}{2x^2(1-x)^2\phi N(P_{1m}P_{2m} - P_{12m}{}^2)} + \frac{\alpha_m f_1{}^2}{2} \qquad \text{(32)}$$

In the symmetric case where $x = {}^1/_2$, one finds $P_{1m}P_{2m} - P_{12m}{}^2 = 4P_{Tm}(P_{1/2m} - P_{Tm})$ and eq 25 is recovered. Taking the bulk limit of eq 30a yields

$$S(q) = \frac{x^2(1-x)^2N[P_1(q)P_2(q) - P_{12}{}^2(q)]}{P_T(q) - 2\left[\chi - \frac{1}{2}\alpha(q)f_1{}^2\right]x^2(1-x)^2N[P_1(q)P_2(q) - P_{12}{}^2(q)]} \qquad \text{(33)}$$

The critical parameter for MST in the pure copolymer system, where one block is charged, is immediately obtained from this equation. It has the same form as eq 32, but ϕ should be replaced by 1 because of the incompressibility assumption. The second term in the rhs of eq 32 describes the enhancement of compatibility due to charge interactions. It represents a significant contribution which would stabilize the system against the formation of micellar complexes. The total structure factor $S_T(q)$ is obtained as follows:[16]

$$\frac{S_T(q)}{\phi N} = \frac{\left\{P_T(q) - 2\left[\chi - \frac{\alpha(q)}{2}f_1{}^2\right]x^2(1-x)^2\phi N[P_1(q)P_2(q) - P_{12}{}^2(q)]\right\}}{D(q)} \qquad \text{(34)}$$

Where $D(q)$ is given by eq 30. $S_T(q)$ reflects the properties of the chain as a whole in spite of the fact that the diblock is strongly assymetric. The qualitative variation of $S_T(q)$ versus q is similar to the case of a single polyion system. However, one expects that when $x \rightarrow 0$, the position of the maximum q_m moves quickly to zero. Furthermore, one can consider the structure factor for composition fluctuations $S_I(q)$ which is defined by

$$S_I(q) = \frac{S_{11}(q)}{x^2} + \frac{S_{22}(q)}{(1-x)^2} - \frac{2S_{12}(q)}{x(1-x)}$$

This function has a maximum at q_m, which is quite sensitive to x. This sensitivity of the scattering function with q_m must be taken into account to calculate the critical parameter for MST as given by eq 31 or 32.

Diblock Copolymers Having Charges of Opposite Signs

Let us consider a symmetric diblock copolymer where block 1 has few positive charges and block 2 has few negative charges (or vice versa). We first assume that the structural and thermodynamic properties remain the same as before and in particular $P_1(q) = P_2(q) = P_{1/2}(q)$ and $\vartheta_{11} = \vartheta_{22} = \vartheta_{12} - \chi = \vartheta$. To preserve the symmetry, we also let $f_1 = f_2 = f$. The number of charges on the chain is assumed to be small and not enough to induce micelles or aggregates. It was shown[16] that the structure factors for this system have the same expressions as in the neutral case with modified interaction parameters. The excluded volume parameters ϑ and the Flory–Huggins parameter χ should both be modified to incorporate the effect of long-range electrostatic interactions. These interactions are repulsive for similar blocks and attractive for different blocks. The modifications are introduced via the effective parameters $\vartheta_{\text{eff}}(q)$ and $\chi_{\text{eff}}(q)$ which are given by

$$\vartheta_{\text{eff}}(q) = \vartheta + \alpha(q)f^2 \qquad \text{(35)}$$

$$\chi_{\text{eff}}(q) = \chi - 2\alpha(q)f^2 \qquad \text{(36)}$$

where $\alpha(q)$ is defined in eq 5a and the Debye–Hückel screening length K^{-1} is

$$K^2 = 4\pi l(f\phi + \phi_{\text{salt}}) \tag{37}$$

Recalling the result in the neutral limit (see eq 9), one can immediately write the partial structure factor $S_{11}(q)$ as

$$\frac{4S_{11}(q)}{\phi N} = \frac{4S_{\text{I}}(q)}{\phi N} + \frac{S_{\text{T}}(q)}{\phi N} \tag{38a}$$

with

$$\frac{4S_{\text{I}}(q)}{\phi N} = \frac{P_{1/2}(q) - P_{\text{T}}(q)}{1 - \frac{1}{2}\chi_{\text{eff}}(q)\phi N[P_{1/2}(q) - P_{\text{T}}(q)]} \tag{38b}$$

$$\frac{S_{\text{T}}(q)}{\phi N} = \frac{P_{\text{T}}(q)}{1 + \left(\vartheta + \frac{\chi}{2}\right)\phi N P_{\text{T}}(q)} \tag{38c}$$

One observes that the decoupling between concentration fluctuations whose space correlations are expressed by $S_{\text{T}}(q)$ and composition fluctuations giving rise to the correlation function $S_{\text{I}}(q)$ is still valid in this case in spite of the fact that the charges on both blocks have different signs. The second observation is that the correlation function $S_{\text{I}}(q)$ is extremely sensitive to the electrostatic attraction between the two blocks and shows a substantial enhancement of compatibility. This property may be useful for the stabilization of micellar forming systems which are encountered for example in systems made of copolymers in selective solvents. Another interesting observation is that the total structure factor $S_{\text{T}}(q)$ does not depend on the electrostatic interactions because of a subtle compensation between excluded volume repulsion and interspecies attraction since $\vartheta + \chi / 2 \equiv \vartheta_{\text{eff}}(q) + 1 / 2\chi_{\text{eff}}(q)$. This means that if one could measure $S_{\text{T}}(q)$ directly, one would obtain a result which is characteristic of a neutral system. This is perhaps reasonable as long as the total charge per chain adds up to zero. In the thermodynamic limit ($q = 0$), the first term in eq 38a, which reflects the copolymer nature, is exactly zero and one obtains a result which is independent of electrostatic interactions:

$$S_{11}(q{=}0) = \frac{\phi N}{4[1 + (\vartheta + \chi/2)\phi N]} \tag{38d}$$

For symmetrical neutral diblock copolymers ($f = 0$), the variation of $S_{11}(q)$ versus q shows a peak at a wave vector q_{m}. If one distributes few charges on the chain in such a way that there is a charge $+fe$ per monomer of type 1 and $-fe$ per monomer of type 2, with $f \ll 1$, the overall charge per chain adds up to zero but, nevertheless, a completely different variation of $S_{11}(q)$ from the neutral limit ($f = 0$) is obtained. The peak disappears and the variation of $S_{11}(q)$ is dominated by the contribution of $S_{\text{T}}(q)$ as if the system were made of homopolymers. The physical reason of this behavior originates from the enhancement of compatibility between the two blocks which compensates not only for the thermodynamic repulsion due to the thermodynamic parameter χ but seems to eliminate the structural properties of the copolymer as well. In the bulk limit, we let $\vartheta \rightarrow \infty$ and $\phi = 1$ and obtain immediately from eqs 38 $S_{11}(q) = S_{\text{I}}(q) = S(q)$ with

$$S(q) = \frac{N}{4}\,\frac{P_{1/2}(q) - P_{\text{T}}(q)}{1 - \left[\frac{\chi}{2} - \alpha(q)f^2\right]N[P_{1/2}(q) - P_{\text{T}}(q)]} \tag{39}$$

This function admits a maximum which can diverge and even become negative if the condition of stability is not fulfilled. The generalized spinodal defines the parameter χ_{m} at which the MST takes place:

$$\chi_{\text{m}} = \frac{2}{N(P_{1/2\text{m}} - P_{\text{Tm}})} + 2\alpha_{\text{m}}f^2 \tag{40}$$

where the subscript m means that the quantity should be evaluated at the wave vector q_{m} where $S(q)$ is maximum. This result shows that χ_{m} is substantially increased in the presence of electrostatic interactions.

Nonsymmetric Diblock Copolymer

We shall assume that the composition of the diblock is not necessarily $^1/_2$, $f_1 = f_2 = f$, and the charges on the two blocks have different signs. In this case, in spite of the fact that the copolymer is not symmetric and the charges on both blocks do not add up to zero, one finds that the results of the neutral limit remain still valid and one needs only to change ϑ and χ to $\vartheta_{\text{eff}}(q)$ and $\chi_{\text{eff}}(q)$ as indicated in eqs 35 and 36. Therefore, $S_{11}(q)$ can be written as

$$\frac{S_{11}(q)}{x^2\phi N} = \frac{P_1(q) + \vartheta_{\text{eff}}(q)(1-x)^2\phi N[P_1(q)P_2(q) - P_{12}{}^2(q)]}{D(q)} \tag{41}$$

where the denominator $D(q)$ is given by

$$D(q) = 1 + \vartheta_{\text{eff}}(q)\phi N P_{\text{T}}(q) + 2\chi_{\text{eff}}(q)x(1-x)\phi N P_{12}(q) - \chi_{\text{eff}}(q)(\chi + 2\vartheta)x^2(1-x)^2\phi^2N^2[P_1(q)P_2(q) - P_{12}{}^2(q)] \tag{42}$$

This is a somewhat more complicated results than in the symmetrical case, and in particular, it cannot be put in the form of a sum of $S_{\text{T}}(q)$ and $S_{\text{I}}(q)$ since the concentration and composition fluctuations are coupled. The total structure factor $S_{\text{T}}(q)$ can also be written immediately from the neutral limit as

$$\frac{S_{\text{T}}(q)}{\phi N} = \frac{P_{\text{T}}(q) - 2\chi_{\text{eff}}(q)\phi N x^2(1-x)^2[P_1(q)P_2(q) - P_{12}{}^2(q)]}{D(q)} \tag{43}$$

as well as the correlation function for composition fluctuations $S_{\text{I}}(q)$:

$$\frac{S_{\text{I}}(q)}{\phi N} = \frac{P_{\text{I}}(q) + [\vartheta_{\text{eff}}(q) + 2\chi_{\text{eff}}x(1-x)]\phi N[P_1(q)P_2(q) - P_{12}{}^2(q)]}{D(q)} \tag{44a}$$

where $P_{\text{I}}(q)$ is defined by

$$P_{\text{I}}(q) = P_1(q) + P_2(q) - 2P_{12}(q) \tag{44b}$$

The stability condition is common to these three structure factors and is expressed by the inequality $D(q) > 0$. The generalized spinodal line defines the critical parameter χ_{m} for MST. It has the following equation:

$$D(q{=}q_{\text{m}}) = 0 \tag{45a}$$

or

$$-\chi^2{}_{\text{eff}}(q)x^2(1-x)^2\phi^2N^2\Delta P_{\text{m}} + 2\chi_{\text{eff}}(q)x(1-x)\phi N[P_{12\text{m}} - \vartheta_{\text{eff}}(q)x(1-x)\phi N\Delta P_{\text{m}}] + 1 + \vartheta_{\text{eff}}(q)\phi N P_{\text{Tm}}(q) = 0 \tag{45b}$$

where ΔP_{m} has been defined previously. The explicit solution of this equation is trivial but lengthy. We reproduce only its limit for high concentration corresponding to $\vartheta\phi NP_{\mathrm{Tm}} \gg 1$:

$$\chi_{\mathrm{m}} = \frac{P_{\mathrm{Tm}}}{2x^2(1-x)^2\phi N(P_{1\mathrm{m}}P_{2\mathrm{m}} - P_{12\mathrm{m}}{}^2)} + 2\alpha_{\mathrm{m}}f^2 \qquad (46)$$

This result illustrates clearly the large increase of χ_{m} due to the long-range electrostatic attraction between the two species. The bulk limits of the above structure factor are immediately obtained by letting $\vartheta \to \infty$ and $\phi = 1$. As expected, one finds that $S_{\mathrm{T}} \to 0$ and $S_{11}(q) = S_{\mathrm{I}}(q) = S(q)$ such that

$$S(q) = \frac{x^2(1-x)^2N[P_1(q)P_2(q) - P_{12}{}^2(q)]}{P_{\mathrm{T}} - 2\chi_{\mathrm{eff}}(q)x^2(1-x)^2N[P_1(q)P_2(q) - P_{12}{}^2(q)]} \qquad (47\mathrm{a})$$

In the reciprocal form one has the standard equation:[17,22,23]

$$\frac{1}{S(q)} = \frac{P_{\mathrm{T}}(q)}{Nx^2(1-x)^2[P_1(q)P_2(q) - P_{12}{}^2(q)]} - 2\chi_{\mathrm{eff}}(q) \qquad (47\mathrm{b})$$

The critical parameter for MST is the same as in eq 46 with $\phi = 1$, since the solvent is absent from this system.

Discussions and Conclusions

In this paper, we have discussed some properties of MST and the stability of weakly charged copolymers in solution and in bulk. These properties are discussed in several conditions of charge distributions, ionic strength, and polymer concentration and composition. The importance of the contrast conditions, which determine the scattering functions under consideration and to some extent the type of MST, was underlined. For symmetrical diblock copolymers, simple equations were derived and, in the cases where the symmetry is conserved, a total decoupling between concentration and composition fluctuations is observed. This was the case in the neutral limit and for copolymers having charges of opposite signs. If the symmetry is broken, a strong coupling between composition and concentration fluctuations takes place and the formulas are somewhat more involved. In particular, one cannot write the scattering function $S_{11}(q)$ as a sum of contributions from $S_{\mathrm{T}}(q)$ and $S_{\mathrm{I}}(q)$. However, in the high-concentration regime, it was possible to derive simple expressions for the critical parameter χ_{m} above which an MST can take place. These expressions can be summarized as follows:

$$\chi_{\mathrm{m}} = \chi_{\mathrm{m}}(\mathrm{neutral}) + \frac{\alpha_{\mathrm{m}}}{2}(f_1 - \epsilon f_2)^2 \qquad (48\mathrm{a})$$

where

$$\alpha_{\mathrm{m}} = \frac{1}{q_{\mathrm{m}}{}^2 + K^2} \qquad (48\mathrm{b})$$

$$K^2 = 4\pi l\{[xf_1 + (1-x)f_2]\phi + \phi_{\mathrm{salt}}\} \qquad (48\mathrm{c})$$

The neutral critical parameter χ_{m} (neutral) is

$$\chi_{\mathrm{m}}(\mathrm{neutral}) = \frac{P_{\mathrm{Tm}}}{2x^2(1-x)^2\phi N(P_{1\mathrm{m}}P_{2\mathrm{m}} - P_{12\mathrm{m}}{}^2)} \qquad (48\mathrm{d})$$

ϵ is the sign parameter of the charges on the two blocks. For partially charged copolymers, where block 2 is neutral ($f_2 = 0$), one has

$$\chi_{\mathrm{m}} = \chi_{\mathrm{m}}(\mathrm{neutral}) + \frac{\alpha_{\mathrm{m}}}{2}f_1{}^2 \qquad (49)$$

These results show a substantial increase of χ_{m} because of the electrostatic interactions and, hence the MST should be delayed because of enhanced compatibility of the two species. For blocks carrying charges of opposite signs, this enhancement is further increased by a factor 4 and one finds

$$\chi_{\mathrm{m}} = \chi_{\mathrm{m}}(\mathrm{neutral}) + 2\alpha_{\mathrm{m}}f^2 \qquad (50)$$

where we have let $f_1 = f_2 = f$. If the numbers of charges are high, one may observe a phase transition of a different nature related with the formation of micellar complexes. We have not considered here the case where charges on both blocks have the same sign $\epsilon = +1$. One notes from eq 48a that the increase of χ_{m} is small and vanishes if $f_1 = f_2$. In this case, the interaction between the two species is controlled entirely by the thermodynamic parameter χ, which in turn controls the MST at it does in the neutral limit. Another example of weakly charged copolymers, which may show interesting properties, is obtained when charges are distributed randomly along the chains. One may consider several possibilities: (i) a real statistical copolymer where monomers 1 and 2 carrying charges f_1e and f_2e are randomly distributed (This case can be described approximately by assuming a single polyion system in solution where each monomer unit carries an effective charge $\frac{1}{2}(f_1 + \epsilon f_2)e$. This encompasses all possible cases where monomer 2 is neutral ($f_2 = 0$) or where monomers 1 and 2 carry charges either of the same sign ($\epsilon = +1$) or opposite signs ($\epsilon = -1$)); (ii) a diblock copolymer made of two monomer species with a finite χ parameter and different indices of refraction, assuming that the charges are distributed randomly along the chain (This system should structurally, optically, and thermodynamically be considered as an ordinary copolymer. Electrostatically, however, the system behaves as an ordinary polyelectrolyte and the above formalism can certainly accommodate this situation as well. We have not attached a larger attention to the thermodynamic limit at $q = 0$ because the chains behave as scattering points and lose their copolymer nature completely. In this limit, the system is essentially sensitive to the quality of solvent and the only phase separation possible is the trivial polymer solvent phase separation which is not of interest here).

The validity of these results relies on two approximations: (i) The mean field approximation or, more precisely, the random phase approximation may break down if the system undergoes strong fluctuations. In this respect it is worth noting that when eq 1 is applied to mixtures of homopolymers in solution, one finds in the $q = 0$ limit the result which was obtained a long time ago by Stockmayer[24] from a pure statistical mechanical approach. This result was the basis for describing the phase behavior of polymer mixtures using different techniques and, in particular, the light-scattering method. Its extension to a finite value of q was made relatively recently.[25] It is true that the addition of a low molecular weight solvent enhances the effects of local concentration fluctuations and a legitimate question concerning the validity of this model may be raised. Extensive data for several ternary mixtures obtained by light scattering.[26,27] have revealed that this model remains valid in a wide range of concentrations, except in the immediate vicinity of the critical point where deviations are observed. Furthermore, this model predicts that the effects of local demixing interactions are strongly reduced in the presence of solvent as a result of a substantial increase of the entropy of mixing. This point is made clear in our discussions since the critical parameter for microphase separation, which in the high-concentration and neutral limits is denoted χ_{m}(neutral), is found to be inversely proportional to the polymer volume fraction ϕ. (ii) The Debye–Hückel approximation for the electrostatic interactions between charged monomers is valid if the fluctuations due to these interactions are negligible and if a substantial screening phenomenon takes place. This means that the number of charges within the screening volume K^{-3} should be much larger than one even when no salt is added. Such a condition is met in the semidilute and concentrated polymer regimes where the counterions due to the ionization of the polymer exist in a large number because of the electroneutrality requirement.

The conditions of validity of the mean field approximation and the Debye–Hückel approximation for weakly charged polyelectrolytes in solution are discussed in ref 14, where the authors apply the Flory–Huggins lattice model to derive the condition of stability for homopolymers. In particular, it is shown that the quantity K^2 in the definition of $\alpha(q)$ (see eq 5a of this paper), which describes the effect of electrostatic screening, comes directly from the entropy contribution of small free ions, both from the polyelectrolyte itself and from the added salt, as shown by eq 5b. Preliminary tests of these approximations are encouraging,[14,28] since data reported on zinc sulfonated polystyrene/poly(ethylacrylate-*co*-4-vinylpyridine)/tetrahydrofuran seem to fit quite well into a model based on these approximations. Because our investigation is limited to weakly charged polyelectrolytes, it should be possible to find appropriate mixtures with an organic solvent having a sufficiently high dielectric constant (such as THF) which can dissolve both the neutral and the charged components.

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