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Microphase Separation of Charged Diblock Copolymers: Melts and Solutions

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ABSTRACT: The microphase-segregation properties of diblock copolymers composed of a neutral polymer joined to a polyelectrolyte are described. For weakly charged diblocks under melt conditions, a theory for weak concentration fluctuations is constructed in order to determine the limit of stability of the mixed phase. We present a scaling analysis of the ordered phase and find that the osmotic pressure of the counterion gas tends to disorder the strongly segregated system. We also consider the behavior of the diblocks in a solvent that is poor for the neutral block but which dissolves the charged block; we carry out a mean-field study of the formation of micelles and their properties.

I. Introduction

Diblock copolymers composed of a neutral block joined to a polyelectrolyte combine the celebrated microphase-segregation properties of uncharged diblocks[1] with those of charged polymers. Experiments on such diblocks are now in progress.[2] While we are unaware of any theoretical work besides ours on this subject, the related problem of blends of neutral and polyelectrolyte chains has recently been studied by Khokhlov and co-workers.[3,4] These authors studied the dependence of the free energy on concentration fluctuations, systematically accounting for translational entropy of the polymers and counterions, interfacial tension, and the electrostatic interactions between the charged species. Their study showed that increasing the charge of the polyelectrolyte (a) stabilizes the mixed phase, moving the spinodal point to lower temperatures, and (b) changes the character of the transition from macro- to microphase separation at a characteristic length that is dependent on the polyion charge and the amount of added salt. The former effect is due to counterion entropy, while the latter results from the new length scale introduced by the electrostatic interactions, the Debye screening length. Similar effects have been noted by Joanny and Leibler in a theoretical study of weak segregation of polyelectrolytes in poor solvents.[5]

Our previous paper on this topic[6] presented the results for the onset of phase separation of diblock copolymers composed of connected neutral and weakly charged blocks, in the presence of arbitrary amounts of added salt. We thus obtained a quantitative theory for the instability of the mixed phase, which is *always* toward microphase separation due to the chemical binding of the immiscible components. The electrostatic effects allow one to tune the critical wavelength using the competition between interfacial tension and Coulomb repulsion. In section IIa, we present a more detailed derivation of these results, and we also discuss the effects of asymmetry of the diblock on the phase separation; we find that, as the charged block is made shorter, there is a stronger dependence of the instability wavelength on charging. In the following sections, we present new results for these diblocks under a variety of conditions.

In section IIb, we present a scaling analysis of the well-ordered diblock melt. Assuming a lamellar structure, we consider the competition of chain stretching with interfacial tension, electrostatic interactions, and counterion entropy. Interestingly, the main effect of the electrostatic interactions is to confine the counterions to the charged-polymer region; for weak charging, the dependence of lamellar spacing h on chain size N is the familiar result $h \approx N^{2/3}$. However, for more than $n \approx (\chi N)^{1/3}$ charges per diblock, the strongly segregated structure ceases to be stable; the counterion pressure is large enough compared to the mixing energy to broaden the interface. For large χN, this threshold is very far from the charging required to stabilize the mixed phase (calculated in section IIa), which is $n \propto \chi N$. This novel result suggests a rather large range of weak segregation.

Our interest in this system was in part due to experiments on similar molecules,[2] which to date have focused on grafted polymer layers and solutions. In section III, we consider the behavior of charged-neutral diblocks dispersed at low concentration in a solvent that is poor for the neutral block but which dissolves the charged block. Due to the large energy cost of neutral-solvent contacts, it is favorable for the chains to aggregate; however, Coulomb repulsion sets a preferred size for these aggregates, which take the form of spherical micelles. We apply the mean-field approach of Joanny and Leibler[5] (who studied dilute polyelectrolyte solutions) to the problem of micelle formation in charged-neutral diblocks. We calculate the critical micelle concentration and critical micelle size and aggregation number in the long-chain limit. In section IIIa, we discuss the weak-charging case where there is no charge condensation either for isolated chains or for the micelles. In section IIIb, we analyze the case of highly charged diblocks and consider the possibility that the counterions condense on the micelles to reduce their Coulomb energy.

II. Phase Stability under Melt Conditions

Charged-neutral diblock copolymers are made by attaching a charged polymer A of length fNa to a neutral polymer B of length $(1-f)Na$, where N is the total chemical length, a is the monomer size, and f is the fraction of monomers in the polyelectrolyte block. Each A chain contains n charged ions; the weak-charging limit considered in this section demands $n \ll fN$. For simplicity, we assume that all ions are monovalent of charge e each (e is the electron charge): the generalization to polyvalent ions is straightforward. In this section we consider melt conditions where the system is incompressible; the volume

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fraction of the small counterions and salt ions is negligible, and therefore the volume fractions of the A and B components add to unity. Finally, we note that the n counterions per chain are assumed to be dissociated from the diblocks.

(a) Weak-Segregation Limit. In order to study concentration fluctuations in the charged block copolymer system, we expand the free energy F about its value $\bar{F}$ in the uniform phase, up to second order in deviations from the mean concentrations of the monomers and the mobile ions:

$$F = \bar{F} + \delta F_0 + \delta F_1 \tag{1}$$

The term δF_0 represents the neutral polymer contribution to the free energy, while δF_1 includes the free ion entropies and electrostatic interactions.

Under incompressible melt conditions, the A and B blocks are presumed to fill space ($\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$) while the counterions are presumed to occupy negligible volume. In the uniform state, $\phi_A = f$, while $\phi_B = 1 - f$; the order parameter for segregation is thus $\Psi(\mathbf{r}) = \phi_A(\mathbf{r}) - f = 1 - f - \phi_B(\mathbf{r})$. The neutral polymer contribution to the free energy is

$$\frac{\delta F_0}{kT} = \frac{1}{2}\int \frac{d^3q}{(2\pi a)^3} |\Psi(\mathbf{q})|^2 S_0^{-1}(q) \tag{2}$$

where k is Boltzmann's constant and T is the temperature and where the inverse structure factor takes the form computed by Leibler using the random-phase approximation:[1]

$$NS_0^{-1}(q) = \frac{g(1,x)}{g(f,x)\, g(1-f,x) - [g(1,x) - g(f,x) - g(1-f,x)]^2/4} - 2\chi N \tag{3}$$

Here $g(f,x) = 2(fx + e^{-fx} - 1)/x^2$, $x = q^2R^2$, $R = (Na^2/6)^{1/2}$ is the radius of gyration of an ideal chain of N monomers, and χ is the Flory–Huggins binary interaction parameter.

We now derive the interaction between monomer concentration fluctuations induced by fluctuation of the free ions and electrostatic interactions between the polyions and the free ions. Our approach is essentially the same as that of Khokhlov[3,4] and of Joanny and Leibler.[5] The average charge density due to the charged polymer is just $en/(Na^3)$; the excess charge density due to monomer concentration fluctuations is $en\Psi/(fNa^3)$. The counterion density may be written in terms of fluctuations Φ around the average value $c = n/(Na^3)$ as $\phi_I(\mathbf{r}) = c + \Phi(\mathbf{r})$. The charge density due to these ions is $-e\phi_I$. Additional salt dissolved in the mixture at a concentration c_s may be taken into account with fields $\phi_+(\mathbf{r}) = c_s + \Phi_+(\mathbf{r})$ and $\phi_-(\mathbf{r}) = c_s + \Phi_-(\mathbf{r})$. The charge density due to these ions is $e(\phi_+ - \phi_-)$.

The total charge density is thus

$$\rho(\mathbf{r}) = \frac{en}{fNa^3}\Psi(\mathbf{r}) + e[\Phi_+(\mathbf{r}) - \Phi_-(\mathbf{r}) - \Phi(\mathbf{r})] \tag{4}$$

The average charge densities have all canceled, as they must for the system to have an overall electroneutrality. We introduce Fourier transforms

$$\rho(\mathbf{q}) = \int d^3 r\, e^{i\mathbf{q}\cdot\mathbf{r}} \rho(\mathbf{r}) \tag{5}$$

and write the electrostatic energy of the charge fluctuations:

$$\frac{E_{el}}{kT} = \frac{1}{2}\int \frac{d^3q}{(2\pi)^3} \frac{4\pi|\rho(\mathbf{q})|^2}{\epsilon kTq^2} \tag{6}$$

In addition to electrostatic energy, we must consider the ideal-gas free energy (entropy) due to the ion concentration fluctuations:

$$\frac{F_{id}}{kT} = \text{constant} + \int d^3r\, [\phi_I(\mathbf{r}) \log \phi_I(\mathbf{r}) + \phi_+(\mathbf{r}) \log \phi_+(\mathbf{r}) + \phi_-(\mathbf{r}) \log \phi_-(\mathbf{r})] \tag{7}$$

Expansion of this expression in powers of Φ/c, Φ_+/c_s, and Φ_-/c_s gives

$$\frac{F_{id}}{kT} = \text{constant} + \frac{1}{2}\int d^3r \left[\frac{\Phi(\mathbf{r})^2}{c} + \frac{\Phi_+(\mathbf{r})^2}{c_s} + \frac{\Phi_-(\mathbf{r})^2}{c_s}\right] + \mathcal{O}(\Phi^3) \tag{8}$$

The Debye–Hückel approximation is made by ignoring the cubic terms; this is valid only if the fluctuating part of the concentration fields is much smaller than the average value.

Ignoring the constant reflecting the free energy of the uniform state and all terms beyond quadratic order in the ion densities, we may write the effective free energy for the counterions coupled to the polymer charge fluctuations:

$$\frac{F_{ion}}{kT} = \frac{1}{2}\int \frac{d^3q}{(2\pi)^3} \left[\frac{4\pi|\rho(\mathbf{q})|^2}{\epsilon kTq^2} + \frac{|\Phi(\mathbf{q})|^2}{c} + \frac{|\Phi_+(\mathbf{q})|^2}{c_s} + \frac{|\Phi_-(\mathbf{q})|^2}{c_s}\right] \tag{9}$$

We may now integrate over the ion field fluctuations, as they do not appear elsewhere in the system Hamiltonian. This gives rise to an effective interaction between the monomer density degrees of freedom

$$\int \mathcal{D}\Phi\mathcal{D}\Phi_+\mathcal{D}\Phi_- e^{-F_{ion}/kT} = \exp\left[\text{constant} - \frac{1}{2}\int \frac{d^3q}{(2\pi a)^3} |\Psi(\mathbf{q})|^2 S_1^{-1}(q)\right] \tag{10}$$

where the effective interaction S_1^{-1} is

$$S_1^{-1}(q) = \frac{1}{N}\frac{un^2/f^2}{u(n + n_s) + q^2R^2} \tag{11}$$

The constant $u = 4\pi e^2/6\epsilon akT$ is essentially the ratio of the Bjerrum length $l = e^2/\epsilon kT$ to the monomer size a and is of order unity for materials with high dielectric constants (e.g., for water at 300 K with $\epsilon \approx 80$, the Bjerrum length is about 7 Å). We assume $u = 8$ in this section. The radius of gyration of an ideal N monomer chain is $R = (Na^2/6)^{1/2}$, and $n_s = 2Nc_sa^3$ is the dimensionless salt concentration.

The effective interaction between the polymer volume fraction fluctuations has the form of a screened Coulomb interaction, where the screening length $r_D = Ru^{-1/2}(n + n_s)^{-1/2}$ is due to the fluctuating counterion and salt concentrations. It may easily be shown[3,4] that the condition required to expand the logarithms in powers of Φ/c is the usual condition for the validity of the Debye–Hückel approximation: $c_T r_D^3 \gg 1$, where $c_T = n/(Na^3) + 2c_s$ is the total number density of the counterions and salt ions.

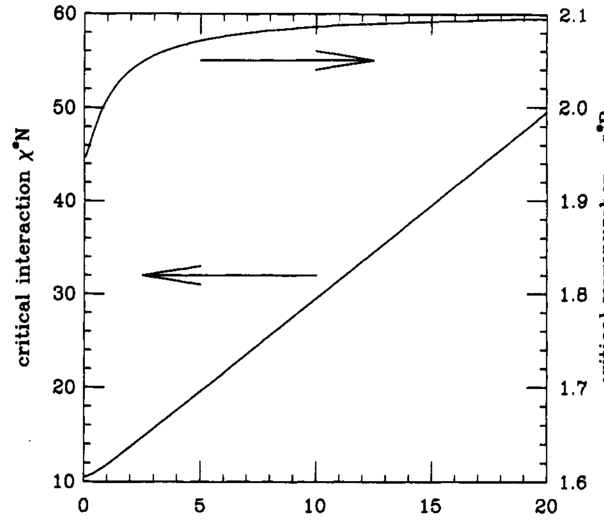

Figure 1. Critical interaction parameter χ^*N (lower curve) and wavenumber q^*R (upper curve) as a function of the number of charges per diblock n, for $f = {}^1/_2$ and $n_s = 0$.

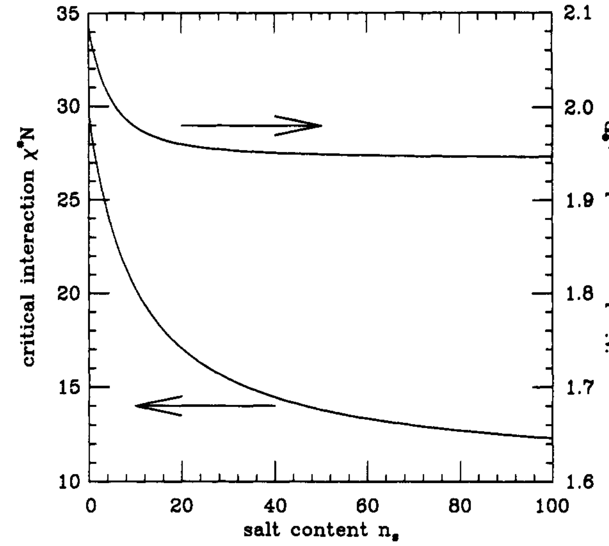

Figure 2. Critical interaction χ^*N (lower curve) and wavenumber q^*R (upper curve) as a function of the salt parameter n_s, with $f = {}^1/_2$ and $n = 10$ charges/diblock.

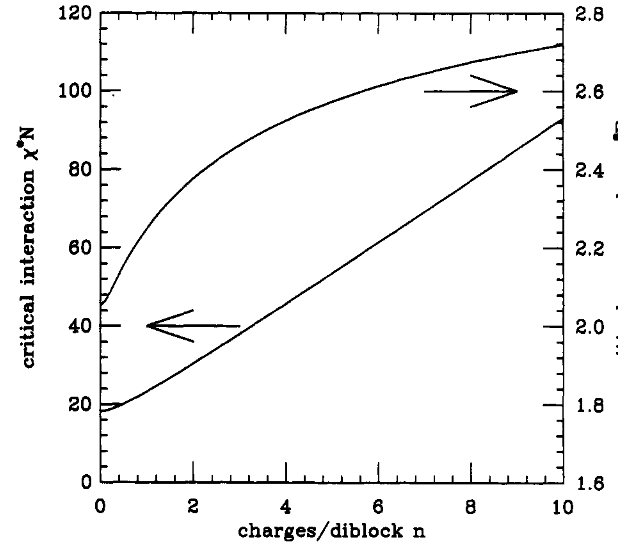

Figure 3. Critical interaction χ^*N (lower curve) and wavenumber q^*R (upper curve) as a function of charging n, for $f = {}^1/_4$ and $n_s = 0$. Note the larger shift in wavenumber than achieved for $f = {}^1/_2$ (see Figure 2).

The fluctuating part of the free energy, $\delta F = \delta F_0 + \delta F_1$, is thus

$$\delta F/kT = \frac{1}{2}\int \frac{d^3q}{(2\pi a)^3} S^{-1}(q)|\Psi(\mathbf{q})|^2 \qquad (12)$$

where the total inverse structure factor is the sum of the neutral and ion contributions discussed above: $S^{-1}(q) = S_0^{-1}(q) + S_1^{-1}(q)$. We focus on the location of the spinodal point where $S(q)$ diverges and calculate the dependence of the critical interaction χ^*N and the critical wavevector q^*R on the number of counterions per chain n and the amount n_s of salt added.

For the symmetric case $f = {}^1/_2$ with no added salt, the critical parameters are displayed as a function of n in Figure 1. Even a small number of charges has a dramatic effect on the spinodal, increasing the critical interaction far above the corresponding neutral block copolymer value. In the limit $n \gg 1$, a linear dependence of χ^*N on n is observed, in accordance with the fact that, in this limit, the free energy is dominated by the electrostatic interaction and counterion entropy contributions of (11). The electrostatic stabilization of the homogeneous phase is very effective since phase separation involves an entropy loss of order kT per counterion. We also observe (Figure 1) that, as one adds more charges to the polymers, q^*R increases; i.e., microphase separation is taking place on progressively shorter length scales. This mechanism was discussed in ref 3 for the case of a neutral–charged *blend*: polymer concentration fluctuations reduce the counterion entropy by forcing rearrangement of the counterions. This entropy loss increases with the length scale of the fluctuations and saturates at length scales that are larger than the dimensions of the counterion "cloud" ($r_D \propto n^{-1/2}$). Notice that the weak-segregation assumption implies that polymers maintain their Gaussian random-coil configurations and that we cannot consider large values of n for which $1/q^*$ is much smaller than R.

Figure 2 shows the added-salt concentration dependence of the critical parameters for the case of a symmetric diblock copolymer with 10 charges/chain. The addition of salt reduces the electrostatic interactions, and the critical interaction parameter approaches the neutral chain limit. The decay of the critical wavenumbers q^* with salt concentration appears to be nearly exponential with a half-width on the order of n, consistent with the expectation that since both the added salt and the counterions contribute to the screening of the electrostatic interactions, salt effects become dominant when the salt concentration exceeds that of the counterions. The decay of the critical interaction χ^* to the neutral chain value predicted by Leibler[1] is slower, in agreement with the observation that the electrostatic contribution to the free energy remains significant as long as $n^2/(f^2 n_s) \gg 1$ (see eq 11).

Figures 3 and 4 show the critical parameters as a function of charging n with no added salt for $f = 0.25$ and $f = 0.75$, respectively. We note that, for $n = 0$, the critical wavelength and interaction for $f = 0.25$ and $f = 0.75$ are the same because the cases differ only by the labeling of the blocks. However, adding charge to the A blocks breaks the A–B interchange symmetry, and thus the dependence of the critical parameters on charging differs for the two cases (we note that the lack of A–B symmetry for charged diblocks with $f = {}^1/_2$ forces the phase transition to be first order even in mean-field theory). For $f = 0.25$, both q^* and χ^* are shifted more strongly by the addition of charge than are blocks with $f = 0.75$. This is due to the f^{-2} dependence of the ion contribution to the inverse structure

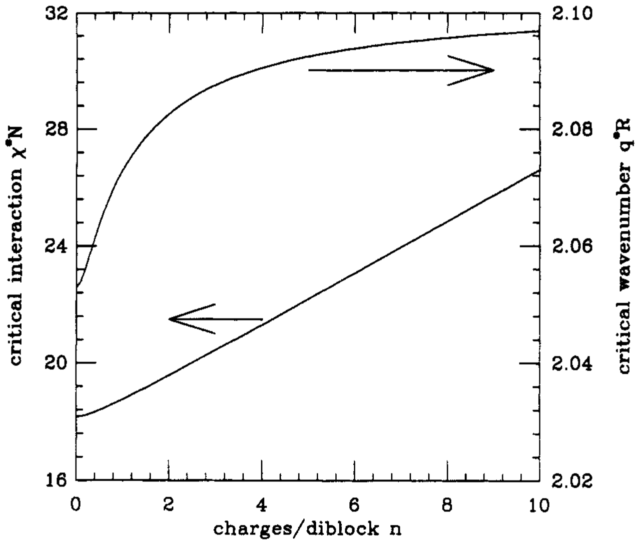

Figure 4. Critical interaction χ^*N (lower curve) and wavenumber q^*R (upper curve) as a function of charging n, for $f = {}^3/_4$ and $n_s = 0$.

factor S_1^{-1}. We note that the dielectric constant ϵ can also be used to change the critical wavelength; larger ϵ causes phase separation at shorter length scales.

(b) Strong-Segregation Limit. When the quantity χN becomes much larger than χ^*N, the A–B interface becomes well-defined, and the system is said to be in the "strongly segregated limit" (SSL). For the uncharged system, it is known[7–10] that, for the symmetric, lamellae-forming case, the scaling form of the free energy density of a lamellar sample with wavelength h is

$$\frac{f}{kT} = \frac{h^2}{N^2 a^5} + \frac{\gamma}{h} \tag{13}$$

where the first term is the Gaussian stretching energy and the second term is the A–B interface energy due to the demixing interactions. The surface tension is $\gamma = \chi^{1/2}/a^2$. Minimization of this free energy gives the familiar scaling laws for the wavelength, $h \approx a\chi^{1/6}N^{2/3}$, and for the free energy density, $f/kT \approx a^{-3}\chi^{1/3}N^{-2/3}$.

We now ask how this picture is affected by the addition of charge to the A blocks, with no added salt. As we see in Figure 1, the spinodal line for $f = {}^1/_2$ with no added salt is roughly $\chi^*N = 2n$; exactly this scaling behavior may be easily derived from the structure factor of the previous section for the limit $n \to \infty$. If χN is large enough, then we expect strong segregation of the form described above, with $h \approx N^{2/3}$. We note that the Debye length is of order $a(N/un)^{1/2}$ and is thus much shorter than the lamellar spacing. This indicates that the counterions must be confined to the (otherwise charged) A domains; the counterions form a uniform ideal gas of density n/Na^3. Since the volume occupied by A is fixed and since the free enery of this uniform counterion gas depends only on the volume of the A region, we find that the presence of the counterions cannot change the lamellar wavelength in the strongly segregated case. Addition of salt to the melt will further reduce the screening length and will accentuate this effect.

We now justify ignoring any electrostatic contribution to the A–B interface energy. We expect the charge interface to have a thickness of order $r_D = a(N/un)^{1/2}$. The energy cost per unit area of forming this charge interface is on the order of the counterion gas free energy density (in units of kT) n/Na^3 times r_D, or $\gamma_{el} = (n/Nu)^{1/2}a^{-2}$. For this to be comparable to the A–B demixing surface tension we require $n \approx u\chi N$. Since this condition holds only near the spinodal line, we may ignore the electrostatic contribution to the surface tension in the strong-segregation limit (where $n \ll \chi N$).

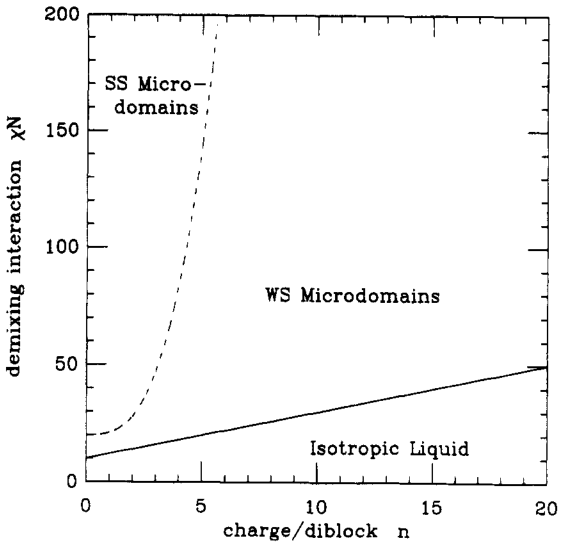

Figure 5. Schematic phase diagram for the diblock melt with $f = {}^1/_2$ as a function of demixing interaction χN and charge per diblock n. The solid line ($\chi N \propto n$) represents first-order phase transitions and separates the disordered phase from the weakly segregated (WS) ordered phase. The dashed line ($\chi N \propto n^3$) roughly indicates the boundary of the sharp-interface (strongly segregated or SS) region of the ordered phase; it is not a phase boundary.

If, under the strong-segregation conditions described above, the charge n is increased, the free energy density of the counterion gas will increase as $f/kT = n/Na^3$. When this free energy becomes larger than the interfacial contribution γ/h, the interface must broaden in order to reduce the counterion gas pressure. This condition is $\chi N = n^3$; for charging larger than $n \approx (\chi N)^{1/3}$ charges per chain, there *cannot* be strong segregation. However, as we argued in section IIa, the melt is microphase-separated for charging up to $n \approx \chi N$. For long chains, there is thus a large regime of weak segregation where the diblock melt is ordered, but with "thick" A–B interfaces. These regimes are schematically illustrated in Figure 5.

III. Micelle Formation in a Solvent

In this section we discuss the behavior of polyelectrolytes in a solvent that is poor for the neutral B blocks but which will dissolve the A blocks. We also assume that the solvent effectively screens the A–B incompatibility; χ is set to zero in this section. We focus instead on the formation of micelles comprised of a B core and a charged A corona (see Figure 6); the micelle properties are determined by the balance of the B–solvent interface energy (minimized for large micelles) with Coulomb repulsion (minimized for isolated chains). Our notation for the description of the chains is the same as that used in section II. The parameter ϕ used in this section is the polymer volume fraction of the solution. In this section, we only briefly discuss the effects of added salt.

(a) Weak-Charge Limit. In the weak-charging limit (small n/N), we assume that the n counterions per chain are always dissociated and form an ideal gas whose free energy is *independent* of the arrangement of the polymers. We presume that the B block is collapsed, and we measure temperature in terms of the Θ temperature of the B block using the variable $\tau = (\Theta - T)/\Theta$. If the A block also

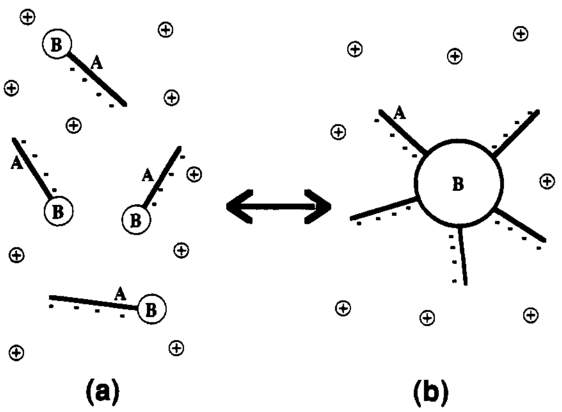

Figure 6. Micelle formation in solvent. (a) Isolated chains have collapsed neutral B blocks and extended charged A blocks; the positive counterions form a homogeneous ideal gas. (b) Micelle formed by aggregation of the collapsed neutral blocks; the corona is composed of the charged A blocks.

collapses, then the problem of micelle formation reduces to that of charged chains treated by Joanny and Leibler,[5] with the exception that the charged block forms a dense coat around a neutral core to minimize Coulomb energy.

Here we treat the cases where either (a) the A backbone is soluble in the solvent or (b) although the solvent is poor for the backbone the charged groups make the A block soluble. In either case, we ignore any excluded-volume effects in favor of considering Coulomb repulsions. In view of the approximate nature of the analysis, we shall take $u = 1$ and suppress all numerical factors. We follow the method of ref 5 and write the chemical potential of a single isolated diblock:

$$\mu/kT = \log \phi + E_B + E_A \quad (14)$$

The first term in the chemical potential is simply the translational entropy of the diblocks. We do not include the counterion entropy contribution since we assume that, in the weak-charging limit, micellization does not affect the number of uncondensed counterions. Therefore, counterion entropy terms cancel in the calculation of the grand potential of the micelle (eq 16). This assumption differs from the one in ref 5; notice, however, that in order to account for counterion condensation on the micelle, the Coulomb energy contribution to the micelle free energy (eq 16) must be adjusted. We will consider this effect in section IIIb.

The second term in eq 14, $E_B = \tau^{4/3}N_B^{2/3}$, is the surface energy of the collapsed B block.[5] The final term E_A, the energy of the A block, is computed by considering the competition between electrostatic repulsion and Gaussian stretching using the free energy:[11]

$$E_A = \frac{R_A^2}{N_A a^2} + \frac{n^2 a}{R_A} \quad (15)$$

The A block assumes an extended conformation of size $R_A = an^{2/3}N_A^{1/3}$ which gives an energy of $E_A = n^{4/3}N_A^{-1/3}$; the neglect of excluded-volume effects in favor of Coulomb repulsion is justified for $R_A \gg aN_A^{3/5}$ or for $n \gg N_A^{2/5}$. An important observation is that, for long, very weakly charged chains, the surface energy E_B will dominate over the electrostatic energy E_A. However, if the A charge fraction n/N_A and N_A/N_B are held fixed while N is taken to infinity at the same rate as N_B, E_A eventually will dominate over E_B. This is in opposition to the case of self-repulsion due to excluded-volume effects, where $E_A \approx N_A^{1/5}$ scales much slower than E_B with N.

Now we compute the free energy of a p-chain micelle which has a dense core composed of p B blocks. The core radius is $R_C = a(pN_B)^{1/3}\tau^{-1/3}$. The surface energy of the core is $kT\tau^{4/3}(pN_B)^{2/3}$. The corona of the micelle is composed of p blocks of A type extended a typical distance of the micelle size R_M (here we consider the case $R_M \gg R_C$ in which the micelle size is determined by the corona); the stretch energy is thus $pkTR_M^2/(a^2N_A)$. The charge of the corona contributes repulsion energy $kTa(pn)^2/R_M$. Neglecting excluded-volume energy and counterion entropy terms, the grand potential of the micelle is thus

$$\frac{\Omega}{kT} = \tau^{4/3}(pN_B)^{2/3} + \frac{pR_M^2}{a^2N_A} + \frac{(pn)^2a}{R_M} - \frac{p\mu}{kT} \quad (16)$$

We note that there are some restrictions that arise in order to guarantee the validity of the B–solvent surface energy of the micelle. The first requirement is that the temperature be far enough below the coil–globule collapse transition[12] so that the number of monomers per blob in the core is much smaller than N_B: this is true when $\tau \gg N_B^{-1/2}$. The second requirement is that the distance between chains at the micelle surface $(R_C/p^{1/2})$ must be much larger than the monomer size, in order not to screen the B–solvent interaction. This condition reduces to $p \ll (N_B/\tau)^2$.

At the micelle formation threshold, we have $\Omega = d\Omega/dp = d\Omega/dR_M = 0$. Simultaneously solving the equations $\Omega - p\,d\Omega/dp = 0$ and $d\Omega/dR_M = 0$ leads to the transition properties

$$p^* \approx (\tau^4 N_A N_B^2/n^4)^{1/3} \quad (17a)$$

and

$$R_M^* \approx a(\tau^2 n N_A^2 N_B)^{2/9} \quad (17b)$$

The requirement that the micelle size be much larger than the core radius leads to the condition

$$n \gg (N_B/\tau N_A)^{1/2} \quad (18)$$

We may compute the critical micelle concentration (cmc) ϕ^* using

$$0 = \frac{\Omega}{kT} = (p^*N_B)^{2/3}\tau^{4/3} + p^*[-\log \phi^* - \tau^{4/3}N_B^{2/3} - E_A] \quad (19)$$

If $p^* \gg 1$, micelle formation can occur since the surface energy cost of the micelle (the first term) is smaller than the surface energy of p^* isolated chains. We may thus identify two regimes for micelle formation, depending on whether E_A is smaller or larger than E_B. In the former case where $n^{4/3}N_A^{-1/3} \ll \tau^{4/3}N_B^{2/3}$ (achieved in the weak-charging limit where n is fixed and N is taken to infinity), we have micelle formation at a concentration

$$-\log \phi^* \approx \tau^{4/3}N_B^{2/3} \quad (20)$$

which is an arbitrarily low concentration for large N. Notice that replacing N_B by N gives the cmc for the formation of micelles of uniformily charged, collapsed polyelectrolytes.[13]

In the latter case where the inequality is reversed, $n^{4/3}N_A^{-1/3} \gg \tau^{4/3}N_B^{2/3}$, micelles form at a concentration of

$$-\log \phi^* \approx n^{4/3}N_A^{-1/3} \quad (21)$$

This latter concentration becomes arbitrarily low in the limit where n/N_A and N_A/N_B are held fixed and N is taken to infinity or when the B blocks are sufficiently short for the above inequality to hold. We emphasize that, for our estimates to be valid, the critical micelle concentration must be low enough that the individual chains be isolated; namely, $\phi^* \ll N(a/R_A)^3$.

If a monovalent salt is added at a concentration c_s, we expect the micelles to be unaffected unless so much salt is added that the screening length $r_D \approx (c_s a)^{-1/2}$ is smaller than the micelle size R_M.[5] The condition for this to occur is $c_s a^3 > (\tau^2 n N_A^2 N_B)^{-4/9}$; if this holds, in the absence of excluded-volume interactions favoring micellization, we expect bulk phase separation of the diblocks from the solvent since the Coulomb repulsion will no longer limit the micelle size.

(b) Strong-Charge Limit. In the previous section we ignored the possibility that the counterions might condense on the micelles to lower the Coulomb energy. In this section, we attempt to estimate under what conditions the majority of the counterions are confined to the micelles at the cmc. We find that the counterion entropy (i.e., counterion osmotic pressure inside the micelles), which opposes confinement, is strong enough under most circumstances to prevent strong condensation of charge onto the micelles and consequently stabilizes the dilute solution of polyions against micelle formation.

We consider the case where $n \approx N_A$, with $u = 1$. Since, at present, there is no reliable theory of salt-free polyelectrolyte solutions, we feel free to introduce simplifying assumptions to the description of the isolated polyions. Neglecting counterion condensation for isolated chains, i.e., assuming that for isolated chains all counterions are free, we find that the A blocks of isolated chains have a size $R_A \approx aN_A$ and are thus fully extended. The single-chain chemical potential is

$$\mu/kT = (1 + N_A) \log \phi + \tau^{4/3} N_B^{2/3} + E_A \tag{22}$$

where $E_A = N_A$ for the extended A block. We note that, in opposition to the previous section, we now take explicit account of the entropy of each free counterion of the isolated chains (the term $N_A \log \phi$).

If we consider the possibility of condensation of $N_A - n^*$ counterions per chain, the free energy of a p-chain micelle contains contributions from two distinct regions of quite different counterion density: the dilute gas outside the micelles and the dense gas of counterions inside the micelles. The total charge of a micelle of radius R_M is given by the uncondensed charge pn^*. We thus write the grand potential for a p-chain micelle:

$$\frac{\Omega}{kT} = pn^* \log \frac{n^*\phi}{N} + \tau^{4/3}(pN_B)^{2/3} + \frac{pR_M^{\,2}}{a^2 N_A} + \frac{(pn^*)^2 a}{R_M} + p(N_A - n^*) \log \frac{a^3 p(N_A - n^*)}{R_M^{\,3}} - \frac{p\mu}{kT} \tag{23}$$

The first term accounts for the ideal-gas entropy of the pn^* free ions of the micelle which have a volume fraction of $n^*\phi/N$. The second term is the B-solvent contact energy, and the third term is the stretching energy of the A chains in the micelle corona. The fourth term is the Coulomb energy due to uncondensed charge. The fifth term is the ideal gas entropy of the $p(N_A - n^*)$ counterions confined to a volume R_M^3. The final term accounts for the free energy of the p isolated chains.

We are interested in determining when $n^* \ll N_A$ or when there is strong condensation of the counterions. Computing $d\Omega/dn^* = 0$ leads to the equation

$$n^* = \frac{R_M}{2ap} \log \left[\frac{a^3 pN}{R_M^{\,3}\phi}\left(\frac{N_A}{n^*} - 1\right) \right] \tag{24}$$

Minimizing the grand potential with respect to the micelle size, $d\Omega/dR_M = 0$, gives us

$$0 = \frac{pR_M}{a^2 N_A} - \frac{(pn^*)^2 a}{R_M^{\,2}} - \frac{3p(N_A - n^*)}{R_M} \tag{25}$$

where we have contributions from chain stretching, Coulomb repulsion, and counterion pressure, respectively. Since $n^* \approx R_M/pa$, the Coulomb contribution to (25) is of order $1/a$. The counterion pressure contribution to (25) is of order pN_A/R_M if there is strong condensation. Thus, we expect it to dominate over the Coulomb term for large p (R_M is restricted to values less than aN_A). Notice that, even if we ignore the Coulomb term, eq 25 indicates that in fact the chains in the corona are fully stretched by the counterion pressure:[14]

$$R_M = aN_A \tag{26}$$

Our requirement that $n^* \ll N_A$ therefore reduces to the (reasonable) requirement that $p \gg 1$. This is consistent with our assumption that the counterions are not condensed for isolated chains ($p = 1$).

Now we must calculate the aggregation number at the micelle formation threshold. Since $\Omega = 0$ and $d\Omega/dp = 0$ at this threshold, we may compute $p\,d\Omega/dp - \Omega = 0$; this gives us

$$0 = -\tau^{4/3}(pN_B)^{2/3} + \frac{(pn^*)^2 a}{R_M} + N_A p \tag{27}$$

The first term is the micelle surface energy, the second is Coulomb repulsion, and the last is due to counterion entropy. Again, we may eliminate the Coulomb term (of order $R_M/a \approx N_A$) in favor of the entropy term for large p. We thus find the aggregation number at the micelle formation threshold:

$$p^* = \frac{\tau^4 N_B^{\,2}}{N_A^{\,3}} \tag{28}$$

For this calculation to be consistent, p^* must be large; we see that this can only be so for $N_B \gg N_A^{3/2}/\tau^2$ or for very short A blocks attached to long B blocks. Under these conditions, the critical micelle concentration ϕ^* is found by setting $\Omega = 0$:

$$0 = -p^*[(1 + N_A) \log \phi^* + \tau^{4/3} N_B^{2/3} + N_A] \tag{29}$$

Under the conditions $N_B \gg N_A^{3/2}/\tau^2$, we obtain the result

$$-\log \phi^* = \frac{\tau^{4/3} N_B^{\,2/3}}{N_A} = p^{*1/3} \tag{30}$$

Clearly p^* must be very large for ϕ^* to be a low concentration consistent with the assumption of nonoverlap of the isolated chains.

What we have found with this calculation is that micelle formation, accompanied by counterion condensation, can only take place when the charged A blocks are very short compared to the B blocks. Under these conditions, we have "crew-cut" micelles, with short, extended A "hairs" sticking out of a relatively large core[15] (the core radius is $R_C = a\tau N_B/N_A$). The assumption that R_M is the micelle size is thus not valid; however, going back and using R_C (which is much larger than R_M in this limit) as the micelle size gives a new estimate for n^*:

$$n^* = \frac{R_C}{2ap} \log \left[\frac{a^3 pN}{R_M R_C^2 \phi} \left(\frac{N_A}{n^*} - 1 \right) \right] \tag{31}$$

We find that $n^* \approx N_A^2/(\tau^3 N_B)$, and thus we require $N_A/(\tau^3 N_B) \ll 1$ for $n^*/N_A \ll 1$ to hold; again the A block must be very short. The estimates for R_M, p^*, and ϕ^* are unaltered: in particular, we still require $\tau^4 N_B^2/N_A^3 \gg 1$ to achieve $p^* \gg 1$. This condition is exactly the condition $p^* \gg 1$ derived from eq 17a in section IIIa with $n = N_A$; we conclude that, for strongly charged diblocks, micelle formation is always accompanied by strong counterion condensation.

Added salt at concentration c_s cannot affect these condensed-counterion micelles until c_s is comparable to the (high) counterion density in the A corona.[14] The corona counterion density is $p^* N_A/(a N_A R_C^2)$, so we expect added salt to become important when $c_s a^3 \approx \tau^2/N_A$. At salt concentrations beyond this threshold, the diblocks will behave as if they are uncharged, and in the absence of excluded-volume effects favoring micellization, they will bulk phase separate from the solvent.

We must remember that, for sufficiently large charging, there will be condensation of counterions onto the isolated chains.[16] One possibility in this case is that the isolated polymers, each carrying some *effective* charge n, will combine into micelles without affecting the number of counterions that are condensed along their contour: in this case, we expect the theory presented in this section to be applicable. However, one cannot rule out the possibility that the number of counterions bound to isolated chains will differ from the number bound to chains in a micelle. This problem, and the problem of micelle formation in a solution of overlapping chains, are as yet unsolved.

IV. Discussion

In this paper we have considered the formation of microphases of charged diblock copolymers, under a variety of conditions. In the first section, weak segregation of a melt was considered in the weak-charging limit. We stress that, in order to achieve the dissociation of the counterions from the charged chains, an experiment will have to use polymers whose backbones will dissolve the counterions. Typically, these will be polymers with fairly large dielectric constants ($\epsilon \approx 20$) such as polynitriles or polymers with side-chain alcohols. An alternative possibility is to dilute the chains in a high-ϵ solvent; obviously too much dilution may result in screening of the A–B demixing interaction or even in bulk phase separation of the chains from the solvent.

The result of section IIb is that, in the microphase-separated state, for chargings n in the range $(\chi N)^{1/3} < n < \chi N$, there cannot be strong segregation because of the large entropy cost of confining the counterions to the charged regions of the microphase pattern. The consequence is a large region in the χN–n phase diagram where there is strong order but thick A–B interfaces. Our calculations are suggestive, and it would be of interest to carry out a more complete study of the structure of this state using a self-consistent mean-field treatment of the polymer conformations[7-10] and the charge distributions.

It would also be of interest to show, using the weak-segregation limit theory, that the A–B interface is broad in this new regime. Unfortunately, this requires a treatment of the charge fluctuations beyond the Debye–Hückel approximation used in section IIa; higher order terms in the counterion entropy must be studied in the case that their distribution becomes strongly inhomogeneous. In this same vein, extension of either the weak-segregation or strong-segregation theories to determine the relative stability of various ordered structures (e.g., lamellae, rods, spheres, etc.) would be desirable. One must keep in mind that, in experiments carried out on shorter chains, the lamellar spacing may be comparable to the electrostatic screening length in the strongly segregated regime; this circumstance is really not covered in section IIb, which is intended to apply to the $N \to \infty$ limit.

The results of section III may be relevant to current experiments being carried out on charged diblocks in solution.[2] We have developed a theory for micelle formation in dilute solutions of these molecules along lines similar to that for collapsed polyelectrolyte chains.[5] However, in our treatment, only the *uncharged* chains are collapsed, while the polyelectrolyte blocks stretch to form a charged corona.

In our study of strongly charged diblocks (section IIIb), we found that strong condensation of the counterions onto the micelles occurs only when the B blocks are very long compared to the charged A blocks. When strong condensation occurs, the osmotic pressure of the confined counterion gas strongly stretches the polyelectrolyte chains in the corona. The strong asymmetry condition ($N_A \ll \tau^3 N_B$) indicates that highly charged diblocks will not form stable micelles under most circumstances and that micelle formation will predominantly occur in dilute solutions of weakly charged diblocks.

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