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Microphase Separation in Charged Diblock Copolymers: The Weak Segregation Limit

The theory of blends of neutral and weakly charged polymers was recently studied by Khokhlov and coworkers.[1,2] A Flory–Huggins-type free-energy functional was constructed, which accounts for the translational entropy of the polymers and the small ions, the interfacial tension, and the electrostatic interaction between the charged species. A mean-field study of concentration fluctuations in this system shows that increasing the polyelectrolyte charge (i) moves the spinodal to lower temperatures (stabilizes the homogeneous phase) and (ii) changes the character of the transition from macro- to microphase separation with a characteristic length scale $1/q^*$ that depends on the amount of charge and the concentration of added salt. The first effect is a consequence of the translational entropy of the counterions while the second arises from the appearance of a new length scale, i.e., the Debye screening length.

In this work we study the onset of phase separation in diblock copolymers made of neutral and weakly charged blocks, in the presence of arbitrary amounts of added salt. The difference between the block copolymer and the polymer blend problems is that, in the former case, there is chemical binding of the components. Consequently, macrophase separation cannot take place even in the absence of charge, and in the limit of weak segregation the system undergoes microphase separation with a domain size determined by the unperturbed dimensions of the polymers. When one of the chains is charged, one expects to see an interesting competition between interfacial tension and electrostatic effects in determining the length scale of the microphase-separation pattern.

A diblock copolymer is 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 number of monomers, a is the monomer size, and f is the fraction of monomers in the polyelectrolyte block. Each A chain contains n charged ions, and since in this work we only consider weakly charged polyelectrolytes, we assume $n \ll fN$. For simplicity, we assume that all ions are monovalent of charge e (e is the electron charge): the generalization of our results to the polyvalent case is straightforward. Furthermore, we assume that the system is incompressible and that the volume fraction of the small counterions and salt ions is negligible and therefore that the volume fractions of the A and the B components add to unity.

In order to study the concentration fluctuations in the charged block copolymer system, we expand the free-energy functional F about its value $\bar{F}$, in the homogeneous phase, up to second order in the deviations from the mean concentrations of the monomers and the small ions. This gives

$$F/kT = (\bar{F} + \delta F_0 + \delta F_1)/kT \qquad (1)$$

where k is the Boltzmann constant and T is the temperature. The second term on the right-hand side of (1) represents the neutral polymer contribution to the free energy, and the third term includes the small-ion entropies and the electrostatic interaction energies. One can now minimize the free energy with respect to the small-ion concentration fluctuations and use the electroneutrality condition to relate the above fluctuations to those of the charged polymer. The fluctuating part of the free energy, $\delta F = \delta F_0 + \delta F_1$, can be written as

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

where $\Psi(\vec{q})$ is the Fourier transform of the deviation of the volume fraction of the charged component (A) from its mean value f and where the inverse static structure factor $S^{-1}(q)$ is the sum of neutral (S_0^{-1}) and electrostatic (S_1^{-1}) contributions.

The structure factor of neutral block copolymers, $S_0(q)$, was calculated in the random-phase approximation by Leibler,[3] who obtained

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

where $g(f,x) = 2(fx + e^{-fx} - 1)/x^2$, $x = q^2Na^2/6 = q^2R^2$ (R is the radius of gyration of an ideal chain of N monomers), and χ is the Flory–Huggins binary interaction parameter. The electrostatic and the small-ion translational free-energy contributions to the inverse structure factor can be calculated in the same way as for the neutral-charged polymer blend case,[2] yielding

$$NS_1^{-1}(q) = \frac{un^2/f^2}{q^2R^2 + u(n + n_S)} \qquad (4)$$

where n_S is a parameter that depends on the added-salt concentration c_S and on the polymer molecular weight: $n_S = 2c_Sa^3N$. The constant u, defined as $u = 4\pi e^2/6\epsilon akT$, is essentially the ratio of the Bjerrum length ($e^2/\epsilon kT$) to the monomer size a, which 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). Since the experiments that we are considering involve melts of weakly charged carbohydrate polymers, we expect the dielectric constant to be much lower, and in order to achieve ionization of the charges on the chains, one may have to dilute the diblock copolymer melt in a high-ϵ solvent. In this paper, we assume $T = 300$ K, $\epsilon = 20$, and $a = 7$ Å, which yields $u = 8$. Notice that while the above derivation involves neglecting the spatial variation of the Debye screening length r_D, corrections to this approximation are of order $e^2/\epsilon kTr_D$ (ϵ being the average dielectric constant) and therefore are beyond the scope of the Debye–Hückel approximation assumed in this work.

We now study the spinodal point at which $S(q)$ diverges and consider the dependence of the critical interaction χ^*N and the critical wavevector q^*R on the number of counterions per chain n and on the added-salt parameter n_S. Taking a symmetric ($f = {}^1/_2$) diblock copolymer and no added salt, we plot the above critical parameters as a function of n, in Figure 1. The addition of even a relatively small number of charges has a dramatic effect on the spinodal and increases the critical interaction parameter far above the corresponding neutral block copolymer value. In the limit $n \gg 1$, a linear variation of χ^*N with n is observed, in agreement with the expectation that in this limit the free energy of the system is dominated by the electrostatic interaction and counterion entropy contributions of (4). The electrostatic stabilization of the homogeneous phase is very effective since phase separation involves a loss of entropy 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. The

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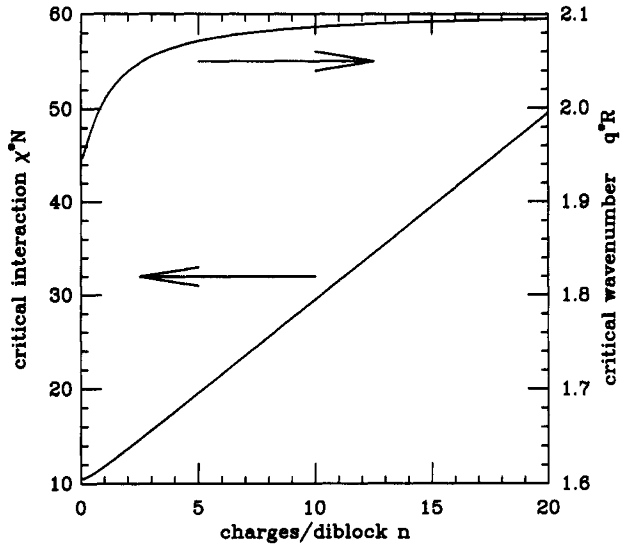

Figure 1. Critical interaction parameter χ^*N (lower curve) and wavenumber q^*R (upper curve) as a function of the number of charges per diblock n, for $f = {}^1/_2$ and $n_S = 0$.

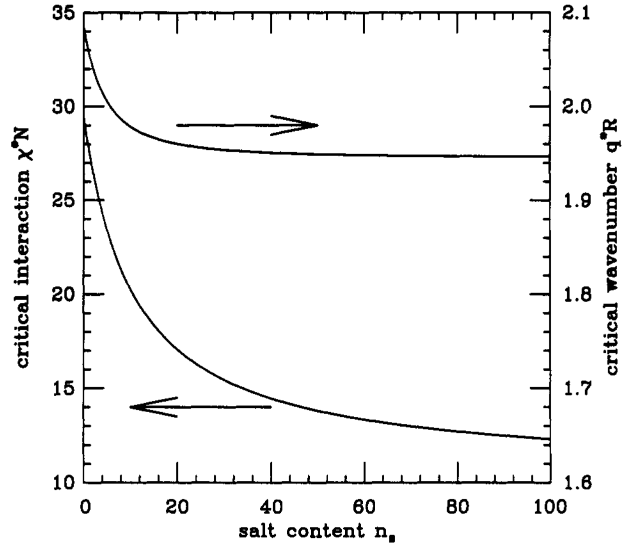

Figure 2. Critical interaction χ^*N (lower curve) and wavenumber q^*R (upper curve) as a function of the salt parameter n_S, with $f = {}^1/_2$ and $n = 10$ charges/diblock.

mechanism is identical with that discussed by Khokhlov et al.[2] for the case of neutral-charged polymer blends: polymer concentration fluctuations reduce the counterion entropy by forcing rearrangement of the counterions. This entropy loss increases with the length scale of fluctuations and saturates at length scales that are larger than the dimensions of the counterion "cloud" ($r_D \propto (1/n)^{1/2}$). Notice that the weak-segregation assumption implies that polymers maintain their Gaussian random-coil configuration and that we cannot consider very large values of n for which the domain size $1/q^*$ is much smaller than R.

The added-salt concentration dependence of the critical parameters is shown in Figure 2 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 its neutral chain limit. The decay of the critical wavenumber q^* with salt concentration appears to be nearly exponential with a half-width of the order of n, consistent with the expectation that since both the added salt and the counterions contribute to the screening of the electrostatic interaction, salt effects become dominant when the salt concentration exceeds that of the counterions. The decay of the critical interaction parameter χ^* to the neutral chain value predicted by Leibler[3] is slower, in agreement with the observation that the electrostatic contribution to the free energy remains significant as long as $n^2/(f^2n_S) \gg 1$ (see eq 4).

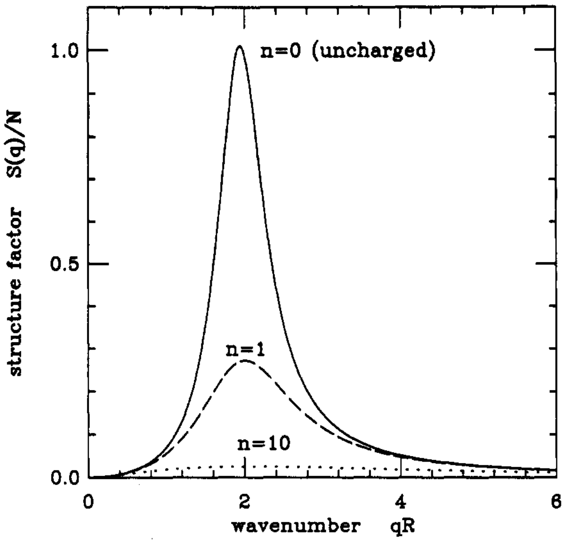

Figure 3. Scattering intensities $S(q)/N$ as a function of wavenumber qR for zero (solid curve), 1 (dashed curve), and 10 (dotted curve) charges/chain, for the symmetric diblock with no added salt ($f = {}^1/_2$, $n_S = 0$) and $\chi N = 10$.

In Figure 3 we plot the static structure factor (proportional to the scattering intensity) for the symmetric diblock copolymer without added salt, for the cases of 0, 1, and 10 charges/chain. The interaction parameter is taken to be $\chi N = 10$, slightly below the critical value for the uncharged case. In agreement with our previous observations, we see that concentration fluctuations are strongly suppressed by the presence of even a relatively small number of charges per chain. The smaller effect of the increase of the wavenumber corresponding to the maximum of the structure factor is also evident. We note that this latter effect becomes much stronger, i.e., phase separation occurs at much shorter length scales, when the dielectric constant ϵ of the polymer is increased.

In this work we have investigated the weak segregation limit for polyelectrolyte-uncharged diblock copolymers. Experiments on such systems are now in progress.[4] The strong dependence of the critical interaction parameter (and hence of the spinodal temperature or the critical chain length) and of the wavelength of microphase separation on the chain charge and on the salt concentrations suggests that the stability and the morphology of the resulting phases can be controlled and fine-tuned by adjusting these parameters. This rather unusual sensitivity is interesting from a fundamental point of view and may lead to important technological applications.

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