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Effects of Ion Solvation on the Miscibility of Binary Polymer Blends[†]

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We study the effects of adding salt ions on the miscibility of a binary blend of polymers having different dielectric constants. The competition between the preference of the ions to be solvated by the component of the higher dielectric constant and the entropic tendency for the ions to be distributed uniformly results in nontrivial effects on the miscibility. We first study the thermodynamics of the polymer blend–ion mixture using a simple Born model in a uniform dielectric medium of the average composition of the polymer blend. We then study the effect of local enrichment of the higher dielectric constant polymer near the ion. We find that when the dielectric constants of the polymers are both low, adding salt decreases the miscibility, while when the dielectric constants of the polymers are both high, the addition of salt enhances the miscibility. When the blend consists of a high dielectric constant polymer and a low dielectric constant polymer, miscibility is decreased if the low dielectric constant component is the majority and is increased if the high dielectric constant component is the majority. The effect becomes significant at ion concentrations corresponding to an order of one ion per polymer chain. The quantitative change in the effective χ parameter depends on the functional form of the composition dependence of the dielectric constant of the mixture. We also illustrate the difference between fixed ion concentration and fixed chemical potential of the ions.

1. Introduction

Adding another component to a binary polymer blend or block copolymer is a common means of altering the miscibility of the polymer components or the blocks.¹ Upon addition of another species, some of the pair contacts in the original polymers are replaced by new contacts between the added component and each of the polymers or blocks. This change in the number and type of pair interactions is often the main factor that affects the miscibility of the polymer components. In the case of solvent that is neutral to the two polymers, for example, dilution of the original pair interactions leads to a weakening of the effective interaction between the polymer components.^{2,3}

The argument given in the preceding paragraph can obscure another mechanism for changing the miscibility of the polymers. For even when the amount of the added component does not significantly alter the number of pair interactions in the original polymer mixture or block copolymer, preferential solubility of this component by one of the polymers or blocks can lead to a thermodynamic driving force that affects the miscibility of the polymers or blocks. In this work, we examine a particular example of this mechanism, namely a binary uncharged homopolymer blend with a small amount of added salt ions.

Besides the academic curiosity, the study of this problem is motivated by practical interests in several ion-containing polymeric systems. These include block copolymers containing an ion-dissolving block, such as poly(ethylene oxide), for novel battery applications,^{4–7} ordered inorganic particle synthesis in microphase-separated block copolymer matrices,^{8–10} polymer–ionic liquid mixtures,^{11,12} and electrochemically controlled organometallic block copolymers.¹³ A

basic question for these systems is how the addition of salt ions affects the miscibility of the polymer components or blocks. Several studies^{14–19} have shown, for example, that the addition of a small amount of salt ions to block copolymers containing ion-dissolving blocks such as poly(ethylene oxide) or poly(methyl methacrylate) leads to a dramatic increase in the order–disorder transition temperature, change in the morphology of the ordered phase, and change in the orientation in ordered block copolymer films. The change in the effective Flory–Huggins χ parameter for poly(styrene-*b*-methyl methacrylate) has recently been quantified by Russell and co-workers²⁰ using small-angle neutron scattering. Our goal is ultimately to study the effects of salt ions on the microphase transition and the ion distribution in block copolymers. However, in this current study, we focus on the more modest task of the effects of salt ions on the miscibility of binary polymer blends.

The interaction between small salt ions and polymers can be quite complicated and usually involves consideration of atomic details of the moieties. However, a common and significant part of the interaction is the polarization of the molecular liquid by the ion charge: the free energy of an ion dissolved in a more polarizable medium is lower than the free energy of the same ion dissolved in a less polarizable medium. This effect can be captured qualitatively at the level of continuum electrostatics where the solvent is treated as a dielectric medium with some dielectric constant. The simplest model that treats this effect is the Born model in which an ion is taken as a spherical cavity having radius a with a point charge q placed in the center. The free energy change upon transferring the ion from vacuum to a dielectric medium having uniform dielectric constant (relative permittivity) ϵ is the well-known Born solvation free energy²¹

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$$\Delta f = \frac{q^2}{8\pi\epsilon_0 a} \left(\frac{1}{\epsilon} - 1 \right) \quad (1)$$

where ϵ_0 is the vacuum permittivity. Ignoring the inconsequential vacuum term, we may define the Born energy of the ion in the medium as

$$f_{\text{Born}} = \frac{q^2}{8\pi\epsilon\epsilon_0 a} \quad (2)$$

In this work, we will refer to the energy given by eq 2 as the Born energy and use the more general term solvation energy to include contributions due to local composition change; the Born energy is the leading approximation for the solvation energy. From eq 2, the Born energy is lower in a medium with higher dielectric constant, implying a higher solubility. Since two polymers in general have different dielectric constants, the solubility of an ion will be different in the two polymers. The energetic tendency for the ion to be preferentially solvated by the component with the higher dielectric constant creates a thermodynamic driving force that favors phase separation of the two polymer components. This energetic tendency is countered by the translation entropy of the ions, which favors the mixed, single phase state. When the composition dependence of the solvation energy is known, we can make a thermodynamic model for the phase behavior of the system. This will be the approach adopted in our work.

The rest of the paper is organized as follows. In the next section, we provide a general analysis of the thermodynamics of the salt–polymer blend system by combining the solvation energy of the ions with the Flory–Huggins free energy of mixing for the polymers. By examining the second derivative of the combined free energy with respect to the polymer composition, we obtain a simple expression for the effective Flory–Huggins χ parameter, with a correction due to ion solvation. In section III, we construct a crude mean-field theory using the Born energy in a uniform dielectric medium having a dielectric constant that is the simple volume average of the two polymers. When the dielectric constant is low (to be quantified in the relevant part of that section) for both polymers, the addition of salt ions makes the blend less miscible, as manifested by a positive correction to the χ parameter, while when the dielectric constant is high for both polymers, the addition of salt ions actually enhances the miscibility. When one polymer has high dielectric constant and the other has low dielectric constant, adding ions increases miscibility if the high-dielectric-constant polymer is the majority component and decreases the miscibility if the low-dielectric-constant polymer is the majority component. These effects are significant for ion concentrations as low as one ion per polymer chain. In section IV, we discuss the leading order correction to the effective χ parameter due to local composition change around the solvated ion. The effect is an additional term that decreases the effective χ . The conformation property of the polymers plays an important role in this effect through the packing length. Section V closes with a brief summary and some concluding remarks. Two appendices contain some useful but nonessential details or supplemental materials: the derivation of the solvation free energy allowing for local composition change is given in Appendix A, and results from using a different mixing rule for the dielectric constant of the blend is given in Appendix B.

II. General Considerations

We consider an incompressible binary polymer blend consisting of polymers A and B, with dielectric constant ϵ_A and ϵ_B , respectively. Without loss of generality, we take A to be the component with the higher dielectric constant and use its volume fraction, simply designated as ϕ , to denote the composition of the blend.

To this polymer blend, we now add a small amount of salt. We consider the concentration of the salt to be sufficiently low so that ion–ion interactions can be ignored. Although there is no difficulty in treating the more general case where ions are multivalent, for simplicity of presentation, we consider monovalent cations and anions with unit charge e ; this is in any case the most common situation for salts dissolved in neutral polymers.

The free energy of the system consists of a Flory–Huggins term accounting for the mixing of the two polymers, the solvation energy for the ions, and the translational entropy of the ions. The form of the solvation energy for ions in a polymer mixture will be specified in later sections. For the present purpose, we merely require that the solvation energy for each ion be unaffected by the presence of other ions in the system and depends only on the overall composition of the polymer blend. This point is not as obvious as it might first seem, even though we have assumed the ions to be noninteracting. As we will see in section IV, the local composition change around an ion from the average composition results in an effective coupling between the ions when the solvation energy is expressed in terms of the average composition. However, this is a higher order effect that we can ignore. With this proviso, the free energy density for our system is

$$g = kT \left[\frac{\phi}{N_A v_A} \ln \phi + \frac{1-\phi}{N_B v_B} \ln(1-\phi) + \chi \phi(1-\phi) \right] + c_+ f_+ + c_- f_- + kT [c_+ \ln(c_+/c_+^R) - c_+ + c_- \ln(c_-/c_-^R) - c_-] \quad (3)$$

In this equation, N_A and N_B are respectively the degree of polymerization for polymers A and B, v_A and v_B are their monomer volume, χ is the usual Flory–Huggins parameter characterizing the interaction between the two polymer species, f_+ and f_- are respectively the solvation energy of the cation and anion, and c_+ and c_- are their respective number concentration, with c_+^R and c_-^R some reference concentration. Due to charge neutrality, we have obviously $c_- = c_+$.

In our free energy expression, we have ignored the volume taken by the salt ions. This can be justified on two considerations. First, the partial molar volume of salts in a salt solution is usually quite small and can indeed be negative because the volume increase caused by the addition of the ions themselves is countered by the volume-decreasing effect of electrostriction.²² Second, even if we include the volume change due to the volume of the ions, the change in the free energy is minor in comparison with the solvation energy for most systems.

Note that in our discussion here and in the rest of the paper the concentration of ions refer only to that of free ions. Similarly, when we speak of the concentration of salt, the term should be understood to mean the concentration of salt that has completely dissociated into free ions. Bound ion pairs can affect the miscibility of polymer blend through the strong dipole an ion pair possesses which has its own solvation energy and can also contribute to the dielectric constant of the medium. We will

not consider their effects in this work. We note, however, if we take the concentration of the free ions as the independent variable and only focus on the effects due to the free ions, the presence of ion pairs is irrelevant. Thus, our model does not exclude ion-pair formation per se; we just do not treat their effects on the blend miscibility.

The free energy given by eq 3 applies to a closed system having a fixed polymer composition and salt concentration. For the purpose of determining the phase behavior, it is more convenient to introduce a free energy corresponding to a semiclosed system where the ions are open to a reservoir with chemical potentials μ_+ and μ_- , respectively. This is accomplished by constructing a new thermodynamic potential

$$w = g - c_+\mu_+ - c_-\mu_- \quad (4)$$

and minimizing it over the ion concentration variables c_+ and c_- . Accounting for the charge neutrality with a Lagrange multiplier λ , we obtain

$$c_+ = c_+^R \exp(\beta\mu_+ - \beta f_+ - \lambda) \quad (5)$$

and

$$c_- = c_-^R \exp(\beta\mu_- - \beta f_- + \lambda) \quad (6)$$

Invoking the charge neutrality by equating eq 5 with eq 6, we find the Lagrange multiplier to be

$$\lambda = \frac{1}{2}[\beta\mu_+ - \beta\mu_- + \beta f_- - \beta f_+ + \ln(c_+^R/c_-^R)] \quad (7)$$

Without any loss of generality, we may set $c_+^R = c_-^R = c^R$ —the ratio c_+^R/c_-^R can always be absorbed into the definition of the chemical potentials. Thus, eqs 5 and 6 become

$$c_+ = c_- = c = c^R \exp\left[\frac{1}{2}(\beta\mu_+ + \beta\mu_- - \beta f_+ - \beta f_-)\right] \quad (8)$$

Since the chemical potential of the cation and anion always appear in the combination $\mu_- + \mu_+$, and the same is true for the solvation energy, it is natural to define the chemical potential and solvation energy of the salt

$$\mu_s = \frac{1}{2}(\mu_+ + \mu_-) \quad (9)$$

$$f_s = \frac{1}{2}(f_+ + f_-) \quad (10)$$

as usually done in the physical chemistry of electrolyte solutions.²³ In terms of these quantities, the concentration for the cation and anion becomes

$$c_+ = c_- = c = c^R \exp(\beta\mu_s - \beta f_s) \quad (11)$$

The final free energy is then

$$\begin{aligned} w &= kT \left[\frac{\phi}{N_A v_A} \ln \phi + \frac{1-\phi}{N_B v_B} \ln(1-\phi) + \right. \\ &\quad \left. \chi\phi(1-\phi) - c_+ - c_- \right] \\ &= kT \left[\frac{\phi}{N_A v_A} \ln \phi + \frac{1-\phi}{N_B v_B} \ln(1-\phi) + \chi\phi(1-\phi) - \right. \\ &\quad \left. 2c^R \exp(\beta\mu_s - \beta f_s) \right] \end{aligned} \quad (12)$$

Note that the last term is nothing but the negative of the osmotic pressure of the ions.

As the solvation energy depends on the composition of the polymer blend through the dielectric constant, the presence of the last term alters the thermodynamics of the blend. In particular, the second derivative of the free energy with respect to composition (at fixed chemical potential of the salt) now becomes

$$\begin{aligned} \beta \frac{\partial^2 w}{\partial \phi^2} &= \frac{1}{N_A v_A \phi} + \frac{1}{N_B v_B (1-\phi)} - 2\chi - 2c^R \times \\ &\quad \exp(\beta\mu_s - \beta f_s) [(\beta f_s')^2 - \beta f_s''] \\ &= \frac{1}{N_A v_A \phi} + \frac{1}{N_B v_B (1-\phi)} - 2\chi - 2c [(\beta f_s')^2 - \beta f_s''] \end{aligned} \quad (13)$$

Since the vanishing of this derivative defines the spinodal, the addition of salt ions leads to a shift the location of the spinodal.

The last term can obviously be interpreted as a change in the effective Flory–Huggins χ parameter, i.e.

$$\Delta\chi = c[(\beta f_s')^2 - \beta f_s''] \quad (14)$$

In the next two sections, we derive explicit expressions using specific forms for f_s .

III. A Crude Mean-Field Theory

As a crude approximation, we assume that the solvation energy of an ion is given by the Born energy eq 2, with the dielectric constant that of the uniform mixture. The dielectric constant of a mixture depends in a complicated manner on the details of the polarization mechanism of the atomic groups and their local structure and in general does not admit of a simple expression in terms of the dielectric constants of the components. However, empirically, the dielectric constant of many binary molecular mixtures can be fitted to a simple linear function of the composition.²⁴ Therefore, for the sake of simplicity, following a number of authors in modeling the dielectric property of polymer mixtures,^{25–27} in the main body of this paper we assume that the dielectric constant of the mixture is a simple volume fraction weighted average, i.e.

$$\epsilon = \epsilon_A \phi + \epsilon_B (1-\phi) \quad (15)$$

The result of assuming a different mixing rule for the dielectric constant based on the Clausius–Mossotti relation is given in Appendix B.

To highlight the main effects while avoiding the cumbersome of having many parameters, we present results for

the case of equal degree of polymerization and monomer volume for the two polymers, i.e., $N_A = N_B = N$, $v_A = v_B = v$, as well as equal radius for the cation and anion, i.e., $a_+ = a_- = a$.

Since the phase behavior of a binary polymer blend is governed by the combination $Nv\chi$ ($Nv\chi = 2$ defines the critical point), we consider the change in χ multiplied by Nv . From eq 14 with the use of eq 15, we obtain

$$Nv\Delta\chi = Nvc \frac{\beta e^2}{8\pi\epsilon\epsilon_0 a} \left(\frac{\beta e^2}{8\pi\epsilon\epsilon_0 a} - 2 \right) \left(\frac{\Delta\epsilon}{\epsilon} \right)^2 \quad (16)$$

Equation 16 captures the main effect of adding salt on the miscibility of a binary blend. It predicts a correction to $Nv\chi$ [or equivalently a shift in the spinodal value $(Nv\chi)_s$] that is proportional to the square of the difference of the dielectric constants of the two polymers; this is to be expected since it does not matter which component has the higher dielectric constant. In most cases (with small ion sizes and/or low dielectric constant), the Born energy is more than 10 times the thermal energy kT , so the correction is positive, which means decreased compatibility between the two polymers. However, the correction can change sign when $\beta e^2/(8\pi\epsilon\epsilon_0 a) = 2$, i.e., when $e^2/(8\pi\epsilon\epsilon_0 a) = 2kT$. For $\beta e^2/(8\pi\epsilon\epsilon_0 a) < 2$ (larger ion radius, high temperature, and/or high dielectric constant), eq 16 predicts a negative shift in the effective χ . This somewhat surprising result comes about because the energy difference for the ions to be partitioned into two media depends not only on the difference in the dielectric constant but also on the dielectric constant itself. For high dielectric constant, the energetic difference is not sufficient to overcome the entropic tendency to have the ions distributed evenly in the mixture. Finally, we observe that the correction is significant when $Nvc \sim O(1)$, which corresponds to a concentration of just one ion per polymer, quite achievable even for relatively low dielectric constant polymers.

Equation 16 can be written in a more convenient form by introducing the Bjerrum length in vacuum

$$l_0 = \frac{\beta e^2}{4\pi\epsilon_0} \quad (17)$$

which is the separation at which the interaction between two unit charges equals the thermal energy kT . For $T = 400$ K, $l_0 = 42$ nm.

In terms of the Bjerrum length, eq 16 can be written as

$$Nv\Delta\chi = \frac{1}{4} Nvc \frac{l_0}{a\epsilon} \left(\frac{l_0}{a\epsilon} - 4 \right) \left(\frac{\Delta\epsilon}{\epsilon} \right)^2 \quad (18)$$

As an order of magnitude estimate of the effect, take $T = 400$ K, $a = 0.25$ nm, $v = 0.1$ nm³, $c = 1$ mM, $N = 3000$, and assume $\epsilon_A = 11.5$, $\epsilon_B = 8.5$, and equal volume fraction for the two polymers. We find $Nv\Delta\chi = 0.87$. The change is quite significant considering that the critical value of $Nv\chi$ is 2.

Equation 18 or more generally eq 14 is most naturally interpreted as the change in the effective Flory–Huggins parameter at a given concentration of the salt ions. It thus gives this change as a function of the composition of the polymer blend for a given ion concentration. But the expression can equally be considered an expression for the change in the effective Flory–Huggins parameter at a given chemical potential of the salt ions. Experimentally, a fixed chemical potential can

be accomplished by having an excess amount of undissolved salt or by having the system in contact with an aqueous salt solution. In this case, as the composition of the blend changes, the actual salt concentration in the polymer blend will also change, according to eq 11, as a result of the composition dependence in the solvation energy. This results in additional composition dependence in the change in the effective Flory–Huggins parameter. In particular, it enhances the effect at higher volume fractions of the higher dielectric constant polymer because of increased salt concentration.

IV. Effects of Local Composition Change around the Ion

In the previous section, we used an ion solvation free energy that treats the medium as having a uniform dielectric constant corresponding to the bulk composition of the blend. However, in the vicinity of the ion, the component with the higher dielectric constant will be enriched while the component with the lower dielectric constant will be depleted. Thus, the local composition around the ions will be different from the global composition. The effect of this local composition change is a decreased tendency for phase separation since the ions can partially satisfy their need to be surrounded by the higher dielectric constant polymer. In the following, we study the solvation of the ion by taking into account such composition change and calculate the change in the free energy. The resulting solvation free energy is then used to construct the total free energy of the polymer blend.

We consider a single ion of radius a and charge q placed in a binary polymer blend of volume V . Again to simplify notation, we consider the case of equal degree of polymerization $N_A = N_B = N$, equal monomer volume $v_A = v_B = v$, and equal statistical segment length $b_A = b_B = b$ for the polymer as well as equal charge and radius for the cation and anion; extension to the more general case is straightforward. We seek to calculate the excess free energy due to the presence of a single ion—the free energy change upon adding the ion while keeping the same overall composition, which for the present purpose will be denoted by ϕ . Our approach is similar to that of Onuki and Kitamura²⁸ in their treatment of ion solvation by a critical fluid mixture. The free energy of the polymer blend with the ion present consists of an electrostatic contribution and the inhomogeneous free energy for the polymer blend. For the electrostatic part, we write a variational free energy functional in terms of the (variational) electrostatic potential²⁹

$$f_e = \int d\mathbf{r} \left[\rho\psi - \frac{1}{2} \epsilon(\phi) \epsilon_0 (\nabla\psi)^2 \right] \quad (19)$$

where ρ is the charge distribution, ψ is the electrostatic potential, and $\epsilon(\phi)$ is the local composition-dependent dielectric constant assumed to have the same *local* composition dependence as eq 15. For the inhomogeneous free energy of the polymer blend, we use the Flory–Huggins–de Gennes square-gradient free energy functional³⁰

$$F_{\text{FHdG}} = \int d\mathbf{r} \left[f_{\text{FH}}(\phi) + \frac{1}{2} \kappa(\phi) (\nabla\phi)^2 \right] \quad (20)$$

where f_{FH} is the usual Flory–Huggins free energy of mixing per unit volume (the first line of eq 3) and $\kappa(\phi) = kTb^2/[18v\phi(1 - \phi)]$.

The total free energy is

$$F = \int d\mathbf{r} \left[\rho\psi - \frac{1}{2}\epsilon(\phi)\epsilon_0(\nabla\psi)^2 + f_{\text{FH}}(\phi) + \frac{1}{2}\kappa(\phi)(\nabla\phi)^2 \right] \quad (21)$$

The electrostatic potential and composition profile are obtained from extremization of the free energy, with the following resulting equations:

$$\epsilon_0 \nabla \cdot (\epsilon \nabla \psi) = -\rho \quad (22)$$

and

$$-\frac{\epsilon_0}{2} \frac{\partial \epsilon}{\partial \phi} (\nabla \psi)^2 + \frac{\partial f_{\text{FH}}}{\partial \phi} - \nabla \cdot (\kappa \nabla \phi) = \mu \quad (23)$$

where μ is a Lagrange multiplier introduced to enforce the constancy of the overall composition

$$\int d\mathbf{r} (\phi - \bar{\phi}) = 0 \quad (24)$$

We note that μ plays the role of a chemical potential coupled to the composition variable ϕ .

Equations 22 and 23 are to be solved with appropriate boundary conditions. Obviously, eq 22 is simply the Poisson equation in a dielectric medium with spatially varying dielectric constant. Far away from the ion, eq 23 reduces to

$$\frac{\partial f_{\text{FH}}(\phi_0)}{\partial \phi_0} = \mu \quad (25)$$

which in essence defines the chemical potential in terms of the composition ϕ_0 at the boundary. For an infinitely large system, the local composition at the boundary is the same as the overall composition, i.e., $\phi_0 = \bar{\phi}$. For a finite system, the composition change induced by the ion in general results in $\phi_0 \neq \bar{\phi}$.

The set of coupled, nonlinear differential equations generally require numerical solutions. In this work, we aim to obtain an analytical expression for the free energy of a binary polymer blend in the presence of ions. We see from the previous section that the effects of ions on the spinodal is reflected in a term of the order $(\Delta\epsilon/\epsilon)^2$. To this order, an analytical expression for the free energy change due to local composition change around the ion can be obtained using a perturbation expansion around the uniform composition ϕ_0 and the electrostatic potential corresponding to this uniform composition; details are to be found in the Appendix A. The excess free energy due to ion solvation is obtained by taking the difference between the free energy eq 21 and the free energy of the uniform state with composition $\bar{\phi}$; the result is

$$f_s = V[f_{\text{FH}}(\phi_0) - f_{\text{FH}}(\bar{\phi}) - \mu(\phi_0 - \bar{\phi})] + f_{\text{Born}}(\phi_0) - \frac{9kT\phi_0(1 - \phi_0)}{4\pi^3} \left(\frac{l_0^2 \lambda_p}{\epsilon^2 a^3} \right) \left(\frac{\Delta\epsilon}{\epsilon} \right)^2 \quad (26)$$

λ_p in the second line of the equation is the packing length of the polymer defined as $\lambda_p = v/b^2$. The first line arises from the difference between the overall composition $\bar{\phi}$ and the composition at the boundary of the volume ϕ_0 . We now discuss the origin of this difference and the choice of the volume.

Writing the spatially dependent composition as $\phi = \phi_0 + \delta\phi$, we see from the constancy of the overall composition, eq 24, that

$$\bar{\phi} - \phi_0 = \frac{1}{V} \int d\mathbf{r} \delta\phi \quad (27)$$

i.e., the decrease in the local composition variable from its global value is due to the enhancement near the ion. The amount of the total (integral) enhancement is independent of volume; the expression is given in Appendix A. Therefore, $\bar{\phi} - \phi_0 \sim V^{-1}$. Expanding $\bar{\phi}$ around ϕ_0 in the first line of eq 26, and noting the definition of the chemical potential eq 25, we find that the terms in the bracket reduce to $(1/2)f''_{\text{FH}}(\phi_0)(\bar{\phi} - \phi_0)^2$ to leading order. The first line therefore is of order V^{-1} . By the same argument, replacing ϕ_0 in the last two terms of eq 26 results in corrections also of this order.

How do we choose V ? Since our system consists of a total concentration of $2c$ ions, the volume per ion is simply $(2c)^{-1}$. Thus, the order V^{-1} terms are just the order c terms. Because the solvation free energy per ion, eq 26, is multiplied by c to get the free energy per unit volume (cf. eq 3), the first line in eq 26 is of order c^2 in the total free energy density. While this is an interesting effect—that an effective interaction emerges from ions assumed to be noninteracting due to the change in composition around the ions—for consistency we have to consider other effects due to the Coulomb interactions between the ions if we want to include this effect. Since we are working at low salt concentration and ignoring ion–ion interactions, we will not account for this higher order effect. To leading order, therefore, the solvation free energy is simply

$$f_s = f_{\text{Born}}(\phi) - \frac{9kT\phi(1 - \phi)}{4\pi^3} \left(\frac{l_0^2 \lambda_p}{\epsilon^2 a^3} \right) \left(\frac{\Delta\epsilon}{\epsilon} \right)^2 \\ = f_{\text{Born}}(\phi) \left[1 - \frac{9\phi(1 - \phi)}{2\pi^3} \left(\frac{l_0^2 \lambda_p}{\epsilon a^2} \right) \left(\frac{\Delta\epsilon}{\epsilon} \right)^2 \right] \quad (28)$$

where for notation simplicity we have restored our use of ϕ for the overall composition.

As expected, the allowance of local composition change leads to a decrease in the solvation energy. That the magnitude of this decrease goes up with the increasing packing length is also to be expected, since the larger the packing length, the smaller the free energy penalty for creating composition inhomogeneity and hence the easier it is for the high dielectric constant component to accumulate near the ion.

Because eq 28 is obtained as a perturbation expansion, the correction term in the bracket should be less than one. Indeed, we expect the solvation free energy to be strictly positive (recall that we have discarded the uninteresting vacuum term). To guarantee the positivity, we write eq 28 in the following “resummed” form

$$f_s = f_{\text{Born}}(\phi) \left[1 + \frac{9\phi(1 - \phi)}{2\pi^3} \left(\frac{l_0^2 \lambda_p}{\epsilon a^2} \right) \left(\frac{\Delta\epsilon}{\epsilon} \right)^2 \right]^{-1} \quad (29)$$

If we further realize that f_s should never be lower than the Born energy in the medium of the pure polymer with the higher dielectric constant, we obtain the following condition for the validity of our perturbation expansion

$$\frac{9}{2\pi^3} \phi \left(\frac{l_0 \lambda_p}{\epsilon a^2} \right) \left(\frac{\Delta\epsilon}{\epsilon} \right) < 1 \quad (30)$$

which is more stringent than the requirement that the correction term in the bracket in eq 28 be less than 1. The resulting solvation free energy eq 29 is shown in Figure 1 and compared with the Born energy.

Using eq 29 and following similar development as in the last section, we find a correction for the Flory–Huggins parameter to leading order in $\Delta\epsilon/\epsilon$

$$N\nu\Delta\chi = \frac{1}{4} N\nu c \frac{l_0}{a\epsilon} \left(\frac{l_0}{a\epsilon} - 4 - \frac{18\lambda_p l_0}{\pi^3 \epsilon a^2} \right) \left(\frac{\Delta\epsilon}{\epsilon} \right)^2 \quad (31)$$

Equation 31 predicts a positive shift in the χ parameter if

$$\frac{l_0}{a} \left(1 - \frac{18\lambda_p}{\pi^3 a} \right) > 4\epsilon \quad (32)$$

and a negative shift if the inequality is reversed. As in eq 18, we see that the polymers are more miscible when the dielectric constant is high and less miscible when the dielectric constant is low, but the threshold depends on the chain conformation through the packing length. Here, too, it is possible to have $N\nu\Delta\chi$ change sign as a function of the composition for the same polymer pairs—the blend is more miscible if the high dielectric constant component is the majority and less miscible if the low dielectric constant component is the majority. For sufficiently large packing length corresponding to bulky monomers and very flexible chains such that

$$\frac{l_0}{a} \left(1 - \frac{18\lambda_p}{\pi^3 a} \right) < 4 \quad (33)$$

Equation 31 predicts only enhanced miscibility regardless of the value of the dielectric constant (note that the dielectric constant cannot be less than one).

To see the effect of the local composition change around the ion, we calculate $N\nu\Delta\chi$ using eq 31 for the same set of parameters as used in our estimate in the last section below eq 18. If we assume a packing length $\lambda_p = 0.25$ nm, we find $N\nu\Delta\chi = 0.21$, which is much reduced from the estimate using the crude mean-field expression eq 18, but still quite significant. If the Flory–Huggins parameter is primarily enthalpic, and assuming a critical temperature of 400 K in the absence of ions, the shift in the critical temperature is 42 K.

With $\lambda_p = 0.25$ nm, $l_0 = 42$ nm, and $a = 0.25$ nm, the value of the dielectric constant at which $N\nu\Delta\chi$ switches sign is 17. For this set of parameters, qualitatively different behavior is predicted depending on whether the dielectric constant of the polymer is greater or less than 17. The experiments in refs 14–19 all involve polymers with dielectric constant much less than this value. For these systems, therefore, adding salts always makes the blocks less miscible.

To summarize the behavior predicted by eq 31, we plot in Figure 2 the three different scenarios for the shift in the effective χ at fixed ion concentration. All calculations assume $N\nu c = 1$ corresponding to two ions per chain. Other parameters are $\lambda_p = 0.25$ nm, $a = 0.25$ nm, and $l_0 = 42$ nm (corresponding to $T = 400$ K). Curve (a) is for $\epsilon_A = 16$ and $\epsilon_B = 12$; it shows

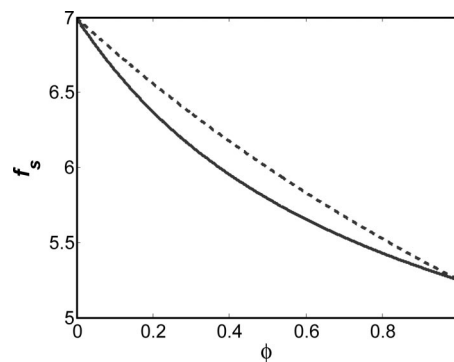


Figure 1. Solvation free energy in units of kT as a function of the blend composition. The dashed line is the Born energy, and the solid line is the free energy given by eq 29. The parameters are $\lambda_p = 0.25$ nm, $l_0 = 42$ nm, $a = 0.25$ nm, $\epsilon_A = 16$, and $\epsilon_B = 12$.

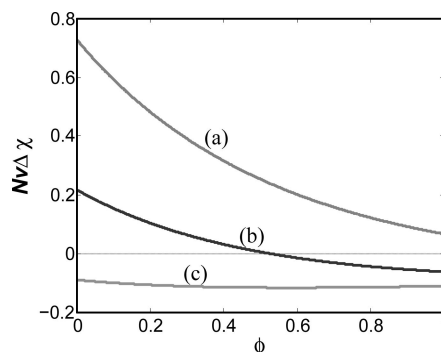


Figure 2. Three different scenarios for the change in the scaled effective Flory–Huggins parameter as a function of the blend composition at fixed ion concentration. (a) $\epsilon_A = 16$, $\epsilon_B = 12$; (b) $\epsilon_A = 20$, $\epsilon_B = 15$; (c) $\epsilon_A = 26$, $\epsilon_B = 20$. Other parameters are $N\nu c = 1$, $\lambda_p = 0.25$ nm, $a = 0.25$ nm, and $l_0 = 42$ nm (corresponding to $T = 400$ K).

strictly positive change in the effective Flory–Huggins parameter, making the blend less miscible. Curve (b) corresponds to $\epsilon_A = 20$ and $\epsilon_B = 15$, and the behavior is decreased miscibility for low volume fraction of the higher dielectric constant polymer and enhanced miscibility for high volume fraction of this component. Finally, curve (c), which is for $\epsilon_A = 26$ and $\epsilon_B = 20$, predicts enhanced miscibility at all compositions.

As alluded to near the end of the last section, the composition dependence for $N\nu\Delta\chi$ is different when the chemical potential instead of the concentration of the salt is fixed. For comparison, in Figure 3 we show $N\nu\Delta\chi$ for the same set of dielectric constants as in Figure 2, but with a fixed chemical potential of the salt. We choose a chemical potential such that $N\nu c^R \exp(\beta\mu_s) = 500$. The actual concentration will vary with the polymer composition according to eq 11, with the solvation free energy given by eq 29. With $N = 3000$ and $\nu = 0.1$ nm³, this gives $c^R \exp(\beta\mu_s) = 2.77$ M, which can be interpreted as the concentration of an ideal solution in a medium of infinite dielectric constant. The equivalent concentration in a medium of dielectric constant 80 would be 0.97 M.

The same qualitative trend is observed for the curves in Figure 3 as those in Figure 2. However, the shapes of these curves differ quite substantially from their counterparts in Figure 2. In particular, the effects for higher dielectric constant pairs are magnified, and for the same polymer pairs the effects are magnified as the volume fraction of the higher dielectric constant component increases. This is due to the increased ion concentration in a higher dielectric constant medium.

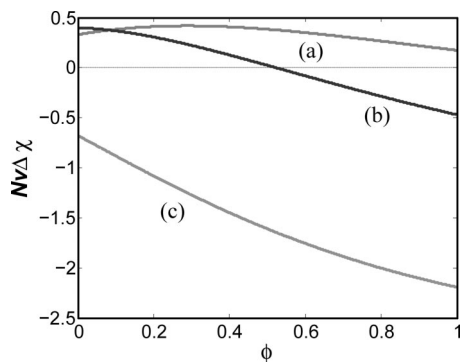


Figure 3. Three different scenarios for the change in the scaled effective Flory–Huggins parameter as a function of the blend composition at fixed chemical potential of the ions. (a) $\epsilon_A = 16$, $\epsilon_B = 12$; (b) $\epsilon_A = 20$, $\epsilon_B = 15$; (c) $\epsilon_A = 26$, $\epsilon_B = 20$. Other parameters are $Nv\epsilon^R \exp(\beta\mu_s) = 500$, $\lambda_p = 0.25$ nm, $a = 0.25$ nm, and $l_0 = 42$ nm (corresponding to $T = 400$ K).

V. Summary and Conclusion

In this work, we have examined the effects of adding salt ions to a binary blend of uncharged polymers on the miscibility of the two polymers. We find that even a small amount of ions—corresponding roughly to one ion per polymer chain—can have a significant effect on the miscibility. The resulting effect on the miscibility, manifested in the change of the dimensionless interaction parameter $Nv\Delta\chi$, reflects a combination of several physical effects: the tendency for an ion to be preferentially solvated by the high dielectric constant component, the translational entropy of the ions which favors uniform distribution in the single phase, and the ability of the polymer blend to adjust its local composition near the ion. The first factor provides the driving force for decreased miscibility, while the other two factors both favor the single phase state.

The packing length of the polymer blend, which controls the ease of composition fluctuation, is found to play an important role in determining the magnitude and indeed the sign of $Nv\Delta\chi$. For packing lengths less than or comparable to the ion radius, which is the case for most polymer ion systems, our theory predicts decreased miscibility when the dielectric constants for both polymers are low (<17). For sufficiently large packing lengths (corresponding to bulky but flexible polymers), the facility of the blend to adjust its local composition in response to the electric field of the ion sufficiently satisfies the need for the ions to be preferentially solvated by the high-dielectric-constant component and thus has a stabilizing effect on the single phase mixture. We also find that in some range of parameter space it is possible to get enhanced miscibility when the blend is rich in the high dielectric constant polymer and decreased miscibility when the blend is rich in the low dielectric constant component.

The theory involves several assumptions and approximations. At the level of the model, we have ignored the interaction between the ions, so our theory is only applicable for low salt concentrations. We have ignored the volume taken by the ions in the thermodynamic treatment of the ion–polymer blend mixture; thus, our theory is not directly applicable to systems involving bulky ions, such as ionic liquid–polymer mixtures. We also have not accounted for the presence of ion pairs that inevitably form for salts dissolved in relatively low dielectric constant media. While the contributions on the blend miscibility due to free ions remain unchanged since our equations use the concentration of the free ions as the independent variables, the solvation of ion pairs gives rise to additional contributions that

affect the blend miscibility. In our attempt to formulate our theory in analytical closed forms, we have resorted to a number of approximations in deriving the final results, including the low-order perturbation expansion, the use of a square-gradient free energy to treat the composition inhomogeneity, and the neglect of critical fluctuations. These approximations to some degree compromise the quantitative accuracy of the results. However, the most serious assumption and approximation is treating the ion solvation within a coarse-grained continuum framework, which ignores any effects due to specific interactions between the ions and the atomic groups in the molecules. Because of this and the other assumptions and approximations, our theory can only be considered as a first attempt at capturing some qualitative features of the problem. Nevertheless, we hope that the current theory can provide a simple useful guide for interpreting experimental data and motivating future experiments as well as serve a stepping stone for developing improved theories.

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Appendix A. Solvation Free Energy Due to Local Composition Change

In this appendix, we provide the details of our derivation for the solvation free energy due to local composition change around the ion.

1. A Modified Model for the Ion. While the cavity model with a point charge in the center of a spherical cavity is the most natural and most widely used model for studying ion solvation, the presence of a cavity in a liquid mixture and the point charge distribution introduce some undesirable features in a continuum model calculation for the binary liquid mixtures. Since we only consider ions in small concentration, thus ignoring the interaction between ions, we choose a surrogate model for the ion that has a continuous charge distribution and does not occupy volume, but reproduces the same Born solvation energy. As the electric field for a spherical ion must behave as

$$E = \frac{q}{4\pi\epsilon\epsilon_0 r^2} \quad (\text{A1})$$

at sufficiently large r , we construct a model which captures this far-field behavior. It is easily seen that the electric field given by

$$E = \frac{q}{4\pi\epsilon\epsilon_0} \frac{1}{(r^2 + \pi^2 a^2/16)} \quad (\text{A2})$$

meets this criterion and yields an electrostatic energy

$$\begin{aligned} f_e &= \frac{1}{2}\epsilon\epsilon_0 \int d\mathbf{r} E^2 \\ &= \frac{q^2}{8\pi\epsilon\epsilon_0} \int_0^\infty dr \frac{r^2}{(r^2 + \pi^2 a^2/16)^2} \\ &= \frac{q^2}{8\pi\epsilon\epsilon_0 a} \end{aligned} \quad (\text{A3})$$

which is just the Born energy.

The electric field given by eq A2 corresponds to a charge distribution of

$$\rho(r) = \frac{q\pi a^2}{32r(r^2 + \pi^2 a^2/16)^2} \quad (\text{A4})$$

by the Poisson equation. While such an ion model is quite different than the cavity model, a priori there is no reason why the cavity model is any more preferable. Since our interest lies in the macroscopic behavior and the model for the polymer is already coarse-grained, we expect the microscopic details of the ion model to have little bearing on the phenomenon of interest.

2. Perturbation Expansion of the Free Energy. We write the local volume fraction and electrostatic potential as

$$\phi = \phi_0 + \delta\phi \quad (\text{A5})$$

and

$$\psi = \psi_0 + \delta\psi \quad (\text{A6})$$

where ϕ_0 is the composition at the boundary and ψ_0 is the electrostatic potential generated by the ion in a uniform dielectric medium having composition ϕ_0 . Assuming that the linear volume fraction average for the dielectric constant applies locally, we can write

$$\epsilon = \epsilon(\phi_0) + \Delta\epsilon\delta\phi \quad (\text{A7})$$

For other mixing rules, we merely need to replace $\Delta\epsilon$ by $\partial\epsilon/\partial\phi$.

We treat $\Delta\epsilon$ as a smallness parameter and perform a systematic expansion in powers of this parameter. Substituting eqs A5, A6, and A7 into the variational condition eqs 22 and 23, we obtain

$$\nabla^2\delta\psi + \Delta\epsilon\nabla\cdot(\delta\phi\nabla\psi_0 + \delta\phi\nabla\delta\psi) = 0 \quad (\text{A8})$$

and

$$-\frac{1}{2}\epsilon_0\Delta\epsilon(\nabla\psi_0 + \nabla\delta\psi)^2 + f''_{\text{FH}}(\phi_0)\delta\phi + O[(\delta\phi)^2] - \kappa(\phi_0)\nabla^2\delta\phi = 0 \quad (\text{A9})$$

We see from the eq A9 that $\delta\phi \sim O(\Delta\epsilon)$, and hence, using eq A8, we have $\delta\psi \sim O[(\Delta\epsilon)^2]$. Thus, to order $O[(\Delta\epsilon)]^2$, we only need to keep the free energy expansion to order $(\delta\phi)^2$ and order $(\delta\psi)^0$. The free energy to this order is

$$F = V f_{\text{FH}}(\phi_0) + \int d\mathbf{r} \left[\mu\delta\phi + \rho\psi_0 - \frac{1}{2}\epsilon\epsilon_0(\nabla\psi_0)^2 - \frac{1}{2}\epsilon_0\Delta\epsilon\delta\phi(\nabla\psi_0)^2 + \frac{1}{2}f''_{\text{FH}}(\phi_0)(\delta\phi)^2 + \frac{1}{2}\kappa(\phi_0)(\nabla\delta\phi)^2 \right] \quad (\text{A10})$$

The $\mu\delta\phi$ term in the integral comes from the variation condition, eq 23. Using eq 24 in conjunction with (A5), the integral over this term gives simply $V\mu(\bar{\phi} - \phi_0)$. The next two terms in the integral yield the Born self-energy of the ion in a uniform

dielectric medium of dielectric constant $\epsilon(\phi_0)$. $\delta\phi$ is calculated from the expansion of eq A9 at order $\delta\phi$ and $(\delta\psi)^0$. The equation is most conveniently solved in Fourier space

$$\delta\phi(\mathbf{k}) = \frac{1}{2}\Delta\epsilon S(k)E_0^2(\mathbf{k}) \quad (\text{A11})$$

where

$$S(k) = \frac{1}{f''_{\text{FH}}(\phi_0) + \kappa(\phi_0)k^2} \quad (\text{A12})$$

is the structure factor and

$$E_0^2(\mathbf{k}) = \int d\mathbf{r} E_0^2(\mathbf{r})e^{-i\mathbf{k}\cdot\mathbf{r}} \quad (\text{A13})$$

is the Fourier transform of the square of the electric field, *not be confused with the square of the Fourier transform of the electric field*.

Substituting the solution into the free energy, we obtain

$$F = V[f_{\text{FH}}(\phi_0) + \mu(\bar{\phi} - \phi_0)] + f_{\text{Born}}(\phi_0) - \frac{1}{8}\epsilon_0^2(\Delta\epsilon)^2 \frac{1}{(2\pi)^3} \int d\mathbf{k} S(k)E_0^2(\mathbf{k})E_0^2(-\mathbf{k}) \quad (\text{A14})$$

With the electric field given by eq A2, the Fourier transform of its square is found to be

$$E_0^2(\mathbf{k}) = \frac{q^2}{4\pi\epsilon_0^2\epsilon^2a} e^{-\pi a k/4} \quad (\text{A15})$$

The Fourier integral in the last term in eq A14 becomes

$$\begin{aligned} I &= \frac{\epsilon_0^2(\Delta\epsilon)^2}{16\pi^2} \int_0^\infty dk \frac{k^2}{f''_{\text{FH}}(\phi_0) + \kappa(\phi_0)k^2} \left(\frac{q^2}{4\pi\epsilon_0^2\epsilon^2a} \right)^2 e^{-\pi a k/2} \\ &= \frac{\epsilon_0^2(\Delta\epsilon)^2}{16\pi^2} \frac{q^4}{(4\pi\epsilon_0^2\epsilon^2a)^2\kappa} \left[\int_0^\infty dk e^{-\pi a k/2} - \frac{f''_{\text{FH}}}{f''_{\text{FH}} + \kappa k^2} \int_0^\infty dk \frac{e^{-\pi a k/2}}{f''_{\text{FH}} + \kappa k^2} \right] \\ &= \frac{\epsilon_0^2(\Delta\epsilon)^2}{16\pi^2} \frac{q^4}{(4\pi\epsilon_0^2\epsilon^2a)^2\kappa} \left[\frac{2}{\pi a} - \frac{1}{\xi} \int_0^\infty dy \frac{e^{-\pi y a/(2\xi)}}{1 + y^2} \right] \end{aligned} \quad (\text{A16})$$

where $\xi = (\kappa/f''_{\text{FH}})^{1/2}$ is the correlation length of the polymer blend.

The second term in the bracket of the last equation arises from long-range correlations due to proximity to spinodal. The term itself vanishes at the spinodal but, upon taking the derivative with respect to the volume fraction, generates divergence at the spinodal. However, at any given distance to the spinodal, this term can always be made to vanish by taking the $N \rightarrow \infty$ limit (the mean-field limit). Since we are interested in developing a mean-field theory, we shall ignore this term

and any terms generated from it. Introducing the packing length for the polymer $\lambda_p = v/b^2$ and using our definition of the vacuum Bjerrum length, eq 17, we get

$$I = \frac{9kT\phi(1-\phi)\left(\frac{l_0^2\lambda_p}{\epsilon^2a^3}\right)\left(\frac{\Delta\epsilon}{\epsilon}\right)^2}{4\pi^3} \quad (\text{A17})$$

Putting this expression in eq A14 and taking the difference of the free energy with the uniform state at global composition $\bar{\phi}$, we obtain the final expression for the excess free energy eq 26.

Appendix B. Results Using a Different Mixing Rule of the Dielectric Constant

The Clausius–Mossotti equation relates the dielectric constant of a medium to the molecular polarizability.³¹ If we assume independence of the molecular polarizability of the two polymer species, we get the following mixing rule for the dielectric constant of the mixture

$$\frac{\epsilon - 1}{\epsilon + 2} = \phi \frac{\epsilon_A - 1}{\epsilon_A + 2} + (1 - \phi) \frac{\epsilon_B - 1}{\epsilon_B + 2} \quad (\text{B1})$$

The derivation with this mixing rule is very similar to that with the linear mixing rule, so it will not be repeated here. We merely write the final result for the correction to the effective scaled Flory–Huggins parameter

$$Nv\Delta\chi = Nvc \frac{l_0}{36a} \left(\frac{\epsilon + 2}{\epsilon} \right)^3 \left[\frac{l_0}{a} \left(1 - \frac{18\lambda_p}{\pi^3 a} \right) \left(\frac{\epsilon + 2}{\epsilon} \right) - 8 \right] \times \left(\frac{\epsilon_A - 1}{\epsilon_A + 2} - \frac{\epsilon_B - 1}{\epsilon_B + 2} \right)^2 \quad (\text{B2})$$

In spite of the very different dependence on the dielectric constant, eqs B2 and 31 predict qualitatively similar behaviors. Both equations predict a threshold involving the combination of the vacuum Bjerrum length l_0 , the polymer packing length λ_p , and the ion radius a . If

$$\frac{l_0}{a} \left(1 - \frac{18\lambda_p}{\pi^3 a} \right) > 8 \quad (\text{B3})$$

a positive shift always ensues, with the shift larger for lower dielectric constant mixtures, whereas if

$$\frac{l_0}{a} \left(1 - \frac{18\lambda_p}{\pi^3 a} \right) < \frac{8}{3} \quad (\text{B4})$$

a negative shift is predicted. For the same polymers, it is also possible to have eq B2 change sign with composition within certain range of parameters. In that case, the polymers are more miscible when the high dielectric constant is the majority and less miscible when the low dielectric constant is the majority.

References and Notes

- (1) Hanley, K. J.; Lodge, T. P.; Huang, C. I. *Macromolecules* **2000**, *33*, 5918.
- (2) Lodge, T. P.; Pan, C.; Jin, X.; Liu, Z.; Zhao, J.; Maurer, W. W.; Bates, F. S. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 2289.
- (3) Naughton, J. R.; Matsen, M. W. *Macromolecules* **2002**, *35*, 5688.
- (4) Jannasch, P. *Chem. Mater.* **2002**, *14*, 2718.
- (5) Sadoway, D. R. *J. Power Sources* **2004**, *129*, 1.
- (6) Niitani, T.; Shimada, M.; Kawamura, K.; Kanamura, K. *J. Power Sources* **2005**, *146*, 386.
- (7) Guilherme, L. A.; Borges, R. S.; Moraes, E. M. S.; Silva, G. G.; Pimenta, M. A.; Marletta, A.; Silva, R. A. *Electrochim. Acta* **2007**, *53*, 15503.
- (8) Templin, M.; Franck, A.; DuChesne, A.; Leist, H.; Zhang, Y. M.; Ulrich, R.; Schadler, V.; Wiesner, U. **1997**, *278*, 1795.
- (9) Spatz, J. P.; Herzog, T.; Mossmer, S.; Ziemann, P.; Moller, M. *Adv. Mater.* **1999**, *11*, 149.
- (10) Sohn, B. H.; Yoo, S. I.; Seo, B. W.; Yun, S. H.; Park, S. M. *J. Am. Chem. Soc.* **2001**, *123*, 12734.
- (11) He, Y. Y.; Li, Z. B.; Simone, P.; Lodge, T. P. *J. Am. Chem. Soc.* **2006**, *128*, 2745.
- (12) Ueki, T.; Watanabe, M. *Macromolecules* **2008**, *41*, 3739.
- (13) Eitouni, H. B.; Balsara, N. P. *J. Am. Chem. Soc.* **2004**, *126*, 7446.
- (14) Ruzette, A. V.; Soo, P. P.; Sadoway, D. R.; Mayes, A. M. *J. Electrochem. Soc.* **2001**, *148*, A537.
- (15) Epps, T. H.; Bailey, T. S.; Pham, H. D.; Bates, F. S. *Chem. Mater.* **2002**, *14*, 1706.
- (16) Epps, T. H.; Bailey, T. S.; Waletzko, R.; Bates, F. S. *Macromolecules* **2003**, *36*, 2873.
- (17) Wang, J.-Y.; Leiston-Belanger, J. M.; Sievert, J. D.; Russell, T. P. *Macromolecules* **2006**, *39*, 8487.
- (18) Kim, S. H.; Misner, M. J.; Yang, L.; Gang, O.; Ocko, B. M.; Russell, T. P. *Macromolecules* **2006**, *39*, 8473.
- (19) Wang, J.-Y.; Chen, W.; Roy, C.; Sievert, J. D.; Russell, T. P. *Macromolecules* **2008**, *41*, 963.
- (20) Wang, J.-Y.; Chen, W.; Russell, T. P. *Macromolecules* **2008**, *41*, 4904.
- (21) Born, M. *Z. Phys.* **1920**, *1*, 45.
- (22) Bockris, O'M.; Reddy, A. K. N. *Modern Electrochemistry I. Ionics*; Plenum: New York, 1998.
- (23) Atkins, P.; de Paula, J. *Physical Chemistry*; Freeman: New York, 2006.
- (24) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.
- (25) Onuki, A.; Fukuda, J. *Macromolecules* **1995**, *28*, 8788.
- (26) Wang, Q.; Taniguchi, T.; Fredrickson, G. H. *J. Phys. Chem. B* **2004**, *108*, 6733.
- (27) Lin, C.-Y.; Schick, M.; elman, D. *Macromolecules* **2005**, *38*, 5766.
- (28) Onuki, A.; Kitamura, H. *J. Chem. Phys.* **2004**, *121*, 3143.
- (29) Wang, Z.-G. *J. Theor. Comput. Chem.* **2008**, *7*, 397.
- (30) (a) de Gennes, P. G. *J. Chem. Phys.* **1980**, *72*, 4756. (b) Pincus, P. *J. Chem. Phys.* **1981**, *755*, 1996.
- (31) Blythe, A. R.; Bloor, D. *Electric Properties of Polymers*; Cambridge University Press: New York, 2005.

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