Thermodynamics of Ion-Containing Polymer Blends and Block Copolymers

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We develop a theory for the thermodynamics of ion-containing polymer blends and diblock copolymers, taking polyethylene oxide (PEO), polystyrene and lithium salts as an example. We account for the tight binding of Li^+ ions to the PEO, the preferential solvation energy of anions in the PEO domain, the translational entropy of anions, and the ion-pair equilibrium between EO-complexed Li^+ and anion. Our theory is able to predict many features observed in experiments, particularly the systematic dependence in the effective χ parameter on the size of the anions. Furthermore, comparison with the observed linear dependence in the effective χ on salt concentration yields an upper limit for the binding constant of the ion pair.

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There is much current interest in ion-containing polymers as materials for energy applications [1]. Of particular interest for rechargeable battery applications are block copolymers [2–4] of an ion-dissolving block, typically polyethylene oxide (PEO), and a nonconducting block such as polystyrene (PS), doped with lithium salts. The lithium ions are complexed with EO groups [5], and together with their counterions, provide the charge carriers [6]. The nonconducting block can be tuned to confer other functions, such as mechanical robustness [3,4,6].

Experimentally, the addition of lithium salts has been shown to have significant effects on the order-order and order-disorder transitions in block copolymers [3,7,8]. Among other effects, it is found that the effective χ parameter characterizing the immiscibility of the two blocks *increases* linearly with salt concentration [9,10],

$$\chi_{\mathrm{eff}} = \chi + mr, \tag{1}$$

where χ is the intrinsic Flory-Huggins parameter for the salt-free system, r is the molar ratio of Li^+ ions to EO monomers, and the slope m depends on the anion type. Wanakule *et al.* [10] found that m decreases with increasing anion radius a. No existing theory describes this behavior. Since the Li^+ ions are strongly bound to the EO groups [11], one may consider the PEO with its bound Li^+ ions as an effective polyelectrolyte, with the anions acting as the counterions. However, existing theories for diblock copolymers with a charged block and a neutral block [12,13] predict enhanced miscibility between the blocks relative to the uncharged system, opposite to experimental observations; there is also no dependence on the radius of the counterions.

The strong binding of Li^+ to the EO groups clearly will affect the thermodynamics of PEO-PS diblock copolymers. However, as suggested in Ref. [10] and demonstrated here, a key effect in these ion-containing polymers is the solvation energy of the anions, which has been ignored in all existing theories of ion-containing polymers. An earlier theory developed by one of us [14], taking into account the effects of ion solvation, predicted that adding salts to *binary polymer blends* can decrease the miscibility between the two polymers. However, that theory assumed the salt ions to be fully dissociated and free (i.e., no ion pairs), and did not consider the complexation of the ions with the polymer. A naive application of the theory to the lithium salt doped PEO-PS (by simply ignoring the contributions of the tightly bound Li^+ ions) captured the qualitative trend in the dependence of m on the anion radius, but the predicted values were 5 to 8 times larger than the observed values [10].

In this Letter, we present a new theory for ion-containing polymer blends and block copolymers that accounts for (i) the tight complexation of the Li^+ with the EO groups, (ii) the preferential solvation energy of the anions for the PEO domain, and (iii) the ion-pair formation between the anion and the EO-complexing Li^+. Since the binding energy between Li^+ and oxygen is very large [15], Li^+ ions are predominantly complexed with the EO groups [11,16]. We therefore assume that all Li^+ ions reside on the PEO chains. We treat the EO groups on the PEO chain as binding sites for Li^+; the Li^+ ions are distributed among all the binding sites, subject to an average occupation of r per site. This effectively makes the PEO chain a polyelectrolyte, *with variable and mobile charges* on the backbone. The anions can either be bound with a EO-Li^+ in the form of an ion-pair, with a binding energy $-E_b$ or they can be free. The model is shown schematically in Fig. 1. For a free anion, we ascribe a composition dependent Born energy $V_{\mathrm{Born}} = e^2/(8\pi a \varepsilon_0 \varepsilon_r)$, where a is the radius of the ion, e is the elementary charge, ε_0 is electric permeability of vacuum and ε_r is the local dielectric constant [17]. We assume ε_r to be given by a simple volume-fraction-weighted average, $\varepsilon_r(\vec{r}) = \varepsilon_{\mathrm{PEO}}\phi_A(\vec{r}) + \varepsilon_{\mathrm{PS}}\phi_B(\vec{r})$, where $\phi_A(\vec{r})$ and $\phi_B(\vec{r})$ are the volume fractions of the A and B polymer

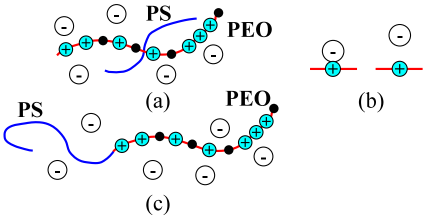

FIG. 1 (color online). Schematic descriptions for our model systems. The black filled circles denote binding sites of Li$^+$ ions, i.e., EO monomers. (a) PEO and PS blend system. (b) Binding and unbinding of an anion to EO-Li$^+$. (c) PEO-b-PS block copolymer system.

(block), respectively. We do not explicitly consider the solvation energy of the Li$^+$ ion, as the primary solvation is by the oxygen groups, whose treatment will require quantum chemistry calculations. Its effects are accounted for phenomenologically through the ion-pair binding energy E_b and the monomer interaction parameters χ_1 and χ_2 introduced below. We consider low salt concentration and treat the ions as volumeless particles.

We start with binary polymer blends since most of the salient features of our theory are more easily explained for this simpler system. We note that the same field-theoretical techniques as we use later for diblock copolymers can be used to derive the theory for the polymer blends. However, here we follow a more intuitive thermodynamic approach that more easily shows the different physical components in the theory. Consider an incompressible polymer blend consisting of n_A high-dielectric polymers A (PEO) of N_A segments with monomer volume v_A, n_B low dielectric polymers B (PS) of N_B segments with monomer volume v_B, n_0 monovalent cations (Li$^+$), and n_0 monovalent anions (X^-) in a volume, V (Fig. 1). Let n_b be the number of bound anions (in ion pairs), the free energy, in units of kT, for the bound ions is $F_b = n_b \ln(n_b/n_0) + (n_0 - n_b) \times \ln(1 - n_b/n_0) - n_b E_b$, where the first two terms arise from the number of ways of selecting n_b out of the total n_0 anions to pair with the EO-Li$^+$. The free energy of the $n_f = n_0 - n_b$ free anions consists of the translational free energy of the ions and their Born energy, $F_f = n_f \ln(n_f/V\xi) - n_f + n_f V_{\mathrm{Born}}$, where ξ is the internal partition function of the anions, which has the dimension of volume^{-1}. The total free energy density is then the sum of the standard Flory-Huggins free energy for a binary polymer mixture and the free energy of the anions $[f_{\mathrm{anion}}(\phi) \equiv F_b/V + F_f/V]$,

$$f_{\mathrm{tot}} = \frac{\phi}{v_A N_A} \ln\phi + \frac{(1-\phi)}{v_B N_B} \ln(1-\phi) + f_{\mathrm{anion}}(\phi) + [\chi + \chi_1 r(1-x) + \chi_2 r x]\phi(1-\phi), \tag{2}$$

where $\phi = n_A N_A v_A / V$ is the volume fraction of PEO, $x = n_b/n_0$ is the fraction of Li$^+$ or X^- in ion pairs, and $r = n_0/(n_A N_A)$ is the molar ratio of Li$^+$ ions to PEO repeating units. The Born energy depends on the polymer composition through the ϕ dependence in the dielectric constant. In general, the χ parameter for the interaction between empty EO and styrene monomers can be altered by the complexation of Li$^+$ ions, and further binding by the anions. The parameters χ_1 and χ_2 in Eq. (2) are introduced to reflect the shifts in the original χ due to the altered monomer identity in the EO-Li$^+$ and EO-Li$^+$-X^- monomers, respectively. χ_1 depends on the identity of the cations, whereas χ_2 depends on the identity of both the cations and anions. Minimizing the free energy Eq. (2) with respect to x leads to the ion-pair equilibrium condition, $x/(1-x)^2 = (\alpha r\phi/v_A)\exp(V_{\mathrm{Born}})$, where α is the ion-pair binding constant [18].

As we show in the supplementary material [18], the presence of ion pairs results in a nonlinear dependence of χ_{eff} on the salt loading r. Experimentally, very good linearity is observed in all cases. By comparing the theoretical predictions with experiments, and by an independent simple estimate, we estimate an upper limit for α to be $\sim 5 \times 10^{-6}$ $[M^{-1}]$, and the fraction of ions pairs x to be at most 0.068 for salt loading up to $r = 0.1$. The effects of such a small fraction of ion pairs are insignificant for the thermodynamics of the ion-containing polymers, so we ignore ion pairs in subsequent discussions. For $x = 0$, the only relevant contributions from the free energy of the anions are the Born energy and the translational entropy of the ions in the form of $(r\phi/v_A)[\ln(r\phi/v_A) - 1]$. Neglecting the inconsequential linear term in ϕ, we can recast Eq. (2) into $f_{\mathrm{tot}} = (\phi/v_A N_A^R)\ln\phi + [(1-\phi)/v_B N_B]\ln(1-\phi) + (\chi + \chi_1 r)\phi(1-\phi) + l_0 r\phi/[2 v_A a \varepsilon_r(\phi)]$, where $N_A^R \equiv N_A/(1 + rN_A)$ may be considered as a renormalized degree of polymerization for PEO [19] due to the dissociated anions. We have introduced the vacuum Bjerrum length $l_0 = e^2/(4\pi\varepsilon_0)$ in the Born energy. Because $N_A^R < N_A$, this renormalization effect alone would lead to enhanced miscibility of PEO and PS.

The vanishing of the second derivative of the free energy defines the spinodal. Therefore, the additional terms in the free energy to the Flory-Huggins expression lead to a shift in the spinodal, which can be interpreted as a change in the χ parameter [14]. Thus, $\Delta\chi = \chi_1 r - (1/2)\partial^2 f_{\mathrm{anion}}/\partial\phi^2 \equiv \chi_1 r + \Delta\chi_{\mathrm{entropy}} + \Delta\chi_{\mathrm{Born}}$, where $\Delta\chi_{\mathrm{entropy}}$ and $\Delta\chi_{\mathrm{Born}}$ are the contributions of the entropy and the Born energy of anions. We then obtain

$$\begin{aligned} \Delta\chi_{\mathrm{entropy}} &= -\frac{r}{2v_A\phi} < 0, \\ \Delta\chi_{\mathrm{Born}} &= -\frac{1}{2}\frac{\partial^2}{\partial\phi^2}\left(\frac{l_0 r\phi}{2v_A a\varepsilon_r(\phi)}\right) = \frac{l_0\varepsilon_{\mathrm{PS}}\Delta\varepsilon r}{2v_A a\varepsilon_r^3(\phi)}, \end{aligned} \tag{3}$$

where $\Delta\varepsilon = \varepsilon_{\mathrm{PEO}} - \varepsilon_{\mathrm{PS}}$. For $\varepsilon_{\mathrm{PEO}} > \varepsilon_{\mathrm{PS}}$, $\Delta\chi_{\mathrm{Born}} > 0$, so the Born energy term decreases the miscibility between PEO and PS. We note that the dependence on the dielectric constants in $\Delta\chi_{\mathrm{Born}}$ differs from that in the theory in

Ref. [14]. This is a result of the locking of the anion concentration with the polymer composition due to stoichiometry constraint imposed by charge neutrality and fixed total number of Li^+ ions on the PEO backbones.

We now consider the case of the PEO-PS diblock copolymer system consisting of n_c chains of N_A segments of PEO (block A), N_B segments of PS (block B), n_0 Li^+ ions and n_0 anions. For the model parameters, the Kuhn lengths, $b_{\mathrm{PEO}} = 0.56$ [nm] and $b_{\mathrm{PS}} = 0.68$ [nm], $v_0\chi = -0.007\,05 + 21.3/T$ [20], $v_A = 0.069$ [nm^3], and $v_B = 0.179$ [nm^3] are used. In contrast to the case of polymer blends, where we only need to consider homogeneous states, here we must deal with spatial inhomogeneity associated with microphase separation, which leads to two effects not present in the case of the homogeneous system. First, Li^+ ions can be unevenly distributed along the PEO backbone (for example, enriched towards the free end and depleted near the PEO-PS junction) and second, charge neutrality in general does not hold locally. Therefore, we must explicitly treat the distribution of Li^+ ions on PEO. This is accomplished by introducing an Ising-like binding variable for the EO-Li^+ sites [21]. We must also confront the electrostatics in an inhomogeneous medium with spatially varying dielectric constant and hence spatially varying Born energy [17]. The details of the calculation will be presented in a future publication; here we give a brief outline. Using standard field-theoretical techniques [22], we first integrate over the degree of freedom of the polymers and ions (for cations, this includes summing over the Ising-like binding variable), to write the free energy of the system in terms of field variables,

$$F = -n_0 \ln\left[\frac{Q_-(\omega_-)}{n_0}\right] - n_0 - n_c \ln\left[\frac{Q_c(\omega_p, \omega_+)}{n_c}\right] - n_c + \int d\vec{r}\Big[-\frac{\varepsilon_r}{8\pi l_0}|\nabla\psi|^2 + \psi(c_+ - c_-) + c_- V_{\mathrm{Born}} + (\chi\phi_A + \chi_1 v_A c_+)\phi_B - \sum_{p=A,B}\omega_p\phi_p - \sum_{I=+,-}\omega_I c_I\Big]. \tag{4}$$

In this equation, ϕ_p and c_I denote the density fields of polymer P and ion I, ω_s is the conjugate field for the s-th species, and ψ is the electrostatic potential. Q_c, and Q_- are the single molecular partition functions of the block copolymer and anion, respectively. The appearance of the field ω_+ in Q_c is a result of summing over the Ising-like binding variable, which couples ω_+ to ω_A. All these position-dependent fields are to be obtained by solving the set of self-consistent field equations, which result from extremization of the above free energy functional with respect to the field variables.

To study the effects of salt doping on the miscibility of the two blocks, we examine the shift in the spinodal of the homogeneous (disordered) phase with respect to microphase separation. This is done by expanding the free energy change around the disordered phase, ΔF, to quadratic order in the field variables [22]. Integrating first over the field variables other than the polymer density [19], we can cast ΔF into the form, $\Delta F = \frac{1}{2(2\pi)^3}\int d\vec{k}\,\delta\tilde{\phi}_A(\vec{k})S^{-1}(\vec{k})\delta\tilde{\phi}_A(-\vec{k})$, where $\delta\tilde{\phi}_A(\vec{k})$ denotes the fluctuation of the volume fraction of PEO around the average value in Fourier space. The inverse of the structure factor, $S^{-1}(\vec{k}) = S_0^{-1} + S_{\mathrm{ions}}^{-1}$ where S_0^{-1} is that for the salt-free system and S_{ions}^{-1} arises from the coupled effects of all the interactions due to the ions. As in the case of uncharged diblock copolymers, $S(\vec{k})$ is peaked at some finite wave number k^*, corresponding to the size of the microphase separated domains. However, unlike the salt-free systems for which k^* is independent of χ in the disordered phase, here k^* changes slightly with temperature [3] and salt concentration; the changes in k^* with the salt ions are primarily due to the Born energy. More importantly, in the absence of the Born energy effect, the peak value $S(k^*)$ would decrease upon the addition of salt, relative to the salt-free system [13], implying enhanced miscibility between the two blocks. Without the solvation energy effect, the translational entropy of the anions always makes the two blocks more miscible, consistent with our analysis of the entropic contribution for the case of the binary blend.

The vanishing of $S(k^*)$ defines the spinodal of the disordered phase. Again, the shift in the χ parameter at the spinodal from its value for the salt-free system defines the change in the χ parameter, $\Delta\chi$. In Fig. 2, we plot $m = v_0\Delta\chi/r$ using the reference volume, $v_0 = 0.1$ [nm^3], $\phi_A = \phi_B = 0.5$, and $l_0 = 43.6$ [nm] at 110 °C. We take $\varepsilon_{\mathrm{PEO}} = 7.5$, which is the accepted value for the dielectric constant of PEO [23]. We take $\varepsilon_{\mathrm{PS}} = 4$; the value reported in literature ranges from 2.6 to 4 [24] but we find the higher value fits the data better. Because we want to compare

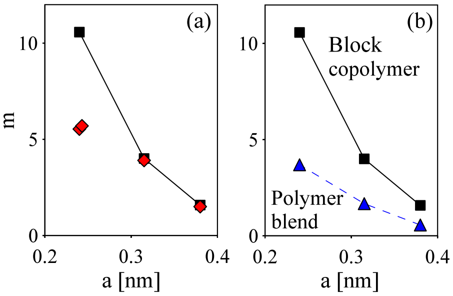

FIG. 2 (color online). (a) Theoretical (black squares) and experimental values (red diamonds) [9,10] of m for lithium salts of different anions. $a = 0.240$ [nm] ($\mathrm{ClO_4^-}$), $a = 0.243$ [nm] ($\mathrm{AsF_6^-}$), 0.315 [nm] ($\mathrm{CFSO_4^-}$), and 0.381 [nm] ($\mathrm{TFSI^-}$) are used for the radius of anions. (b) Comparison between theoretical results for the blend (blue triangles) and block copolymer (black squares).

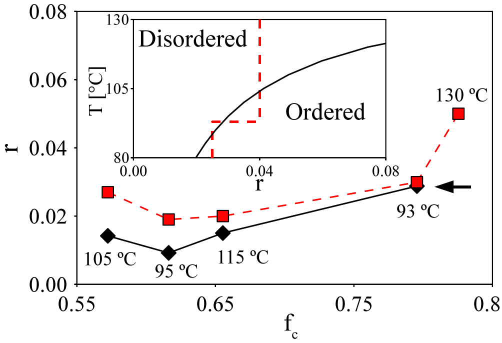

FIG. 3 (color online). Order-disorder transition (ODT) boundary in the salt content r vs block composition $f_c = N_A/(N_A + N_B)$. Red squares: experimental ODT values [10]; black diamonds: spinodal for the disordered phase. The lines are only guide to the eye. Inset: phase diagram in temperature T vs salt content r at the composition indicated by the arrow. Red dashed line: experimental data for ODT [10]; black solid line: spinodal for the disordered phase.

with the phase diagram data from Ref. [10] for the $\mathrm{Li[N(SO_2CF_3)_2]}$ (LiTFSI) system, we perform our fitting using only the data for the $\mathrm{TFSI^-}$ anion (which has a radius $a = 0.381$ [nm]), with $v_0\chi_1$ our only fitting parameter; the fitting yields $v_0\chi_1 = -3.6$. Remarkably, this same parameter value also captures the behavior for the $\mathrm{LiClO_4}$, $\mathrm{LiAsF_6}$, and $\mathrm{LiCFSO_4}$ systems. We emphasize that χ_1 is an essential new parameter necessitated by the change of monomer identity upon $\mathrm{Li^+}$ complexation with the EO. The dependence of m on the anion radius provides a means for estimating this parameter.

The difference in m between diblock copolymers and binary polymer blends is shown in Fig. 2(b). The effect is stronger for the diblocks than for the blends, particularly when the radius of an anion is small; experimental validation of this prediction will be welcome.

We use the same parameter set, $(\varepsilon_{\mathrm{PEO}}, \varepsilon_{\mathrm{PS}}, v_0\chi_1) = (7.5, 4.0, -3.6)$ determined in Fig. 2, to compute the spinodal for the PEO-PS + LiTFSI system studied in Ref. [10]. In Fig. 3, the results are compared with order-disorder transition (ODT) data from the experiment. Notwithstanding experimental error bars and the difference between the spinodal and the ODT boundary, we see good qualitative agreement, further confirming the validity of the essential physics in our theory.

In summary, we have developed a theory for an important class of ion-containing polymers, accounting for the tight complexation of the $\mathrm{Li^+}$ ions to the EO groups, and ion pairing between EO-complexed $\mathrm{Li^+}$ ions and anions, and the preferential solvation of anions by the PEO. Our theory provides a framework for understanding the structure and thermodynamics of ion-containing polymers. Results from the theory are in agreement with a broad range of experimental observations. The theory allows us to estimate an upper bound for the extent of ion-pair formation from the experimentally observed linear increase in the effective χ_{eff} with salt loading. For all the four lithium salts studied, we conclude that ion-pair formation is not significant in the PEO-PS systems for salt loading up to $r = 0.1$. In the absence of ion pairs, the primary effect of the cation is reflected in a change in the monomer identity through the newly introduced parameter χ_1. Importantly, the solvation energy of the anions, which is neglected in the existing literature on ion-containing polymers, is shown to play a key role in the phase behavior of lithium salt doped polymer blends and block copolymers. While the present form of our theory employs a mean-field expression of the solvation energy in the form of a local Born energy based on continuum dielectrics, a more accurate expression can be obtained by explicitly accounting for the polarizability and permanent dipoles of the solvating molecules [25,26].

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