Soft Matter

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Soft Matter

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ROYAL SOCIETY OF CHEMISTRY

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Synergistic effects of ion pairs on the dielectric properties of diblock copolymer melts

Issei Nakamura[1, *]

[1] *State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,*
Chinese Academy of Sciences, Changchun, Jilin 130022, China
(Dated: October 8, 2014)

We study the solvation of ion pairs in diblock copolymer melts. Our theory accounts for the size of the ions, the permanent dipole moment and the molecular polarizability of the monomers, the Kuhn length, the compressibility of the liquid mixtures, and the degrees of polymerization. We demonstrate that the electrostatic field near an ion pair causes marked, synergistic effects on the volume fractions of the two blocks and hence the dielectric function. In particular, we illustrate the oscillatory behavior of the dielectric function near an ion pair and the disparity of the dielectric functions between like and unlike charges. These results depend significantly on the chain length and Kuhn length of the diblock copolymers on the nanometer scales.

The nature of the reorganization of solvent dipoles under electrostatic fields has been a focus of research over the past century [1–3]. As a modern molecular theory, Debye's early studies of polar molecules highlighted the spatial variation in the dielectric function caused by saturated dipoles in proximity to ions [1]. Although current computational and experimental techniques yield a vast array of insights into the electrostatic response of molecules on both the atomic and molecular scales, further fundamental questions and challenges have emerged in the context of solvated ions with the advent of recently developed ion-containing polymers [4]. Specifically, understanding the dielectric properties of polymer electrolytes and hence ushering in a paradigm shift in the deign of the electrochemical devices is considered to be an urgent task in the energy arena [5, 6], but more coherent and intensive studies incorporating theoretical, computer-simulation-based, and experimental approaches would seem to be critically necessary to address the complexity of the electrostatic interactions that relate angstrom-scale and nanometer-scale effects in polymer electrolytes [7].

Of particular importance is the degree of polymerization. Experimentally, the bulk dielectric constants of the salt-free, low-molecular-weight poly(ethylene glycol)s exhibit a notable dependence on the molecular weight of the polymer [8]. In the case of ionic liquids, the bulk dielectric constant decreases as the chain length of the alkyl residues of the cations increases [9, 10]. Although the theories of Onsager [2] and Kirkwood [3] are often invoked to evaluate the bulk dielectric constants, their theories do not account for the polymerized degrees of freedom, the chain connectivity, or polymer architecture. However, it can be intuitively expected that these features may be correlated with the orientational organization of the dipoles, as suggested by early theories of polar polymers [11, 12]. Specifically, if the system consists of a binary component, then the effects of the spatial inhomogeneity of the compositional fraction should also participate in

the correlation. Indeed, recent observations of the static dielectric constants of (polymerized) ionic liquids have revealed notable differences from the Onsager/Kirkwood equation [13, 14]. Given this situation, we need to develop novel theoretical frameworks for ion solvation in polymer mixtures.

Although dielectric continuum theories capture many universal features of dielectric media, the discrete nature of solvent dipoles is the key to accounting for ion solvation [15]. The reorientation of dipoles caused by the strong electrostatic fields near ions leads to spatial variation in the dielectric function. Because the effect of this altered dielectric value is not addressed in the Born solvation energy at the level of the linear dielectric continuum, the theoretical solvation energies of ions in simple liquid mixtures [16] and simple liquids [17] significantly deviate from the experimental values. One theoretically predicted explanation for this discrepancy is that ions are preferentially solvated by higher-dielectric components [16]. However, further complexities of ion solvation in polymer mixtures are substantially beyond the scope of the theory for simple liquids. Our recent theoretical study of ion-containing polymer blends and block copolymer melts, among others, has suggested that ion solvation depends significantly on chain length and chain connectivity [18].

In this Communication, we study the solvation of ion pairs in block copolymer melts. We develop a dipolar self-consistent field theory for an ion pair immersed in a block copolymer melt, accounting for the key parameters of the ions and polymers: the size of the ions, the reorganization of the permanent and induced dipoles, the degrees of polymerization, the Kuhn length, and the compressibility of the components. Although the compressible nature of the liquid mixtures caused by the electrostriction near ions is an important factor that affects the dielectric function [18, 19], we use the value that corresponds to a nearly incompressible state to concisely highlight the essential features of our theory. Our prediction of a marked disparity between the dielectric functions for like and unlike charges may be intuitively considered to be an analog to that between the screening functions for like and unlike

*nakamura@ciac.ac.cn

charges in simple liquids [20]; however, the synergistic effects of the electrostatic field near an ion pair in a block copolymer melt are strikingly novel phenomena inherent to ion-containing polymers.

We consider two monovalent ions of radius a that are immersed in n_c A-B diblock copolymers with a total degree of polymerization N_c. Each ions is modeled as a cavity with a point charge e in the center. The degrees of polymerization for block A and block B are N_A and N_B, respectively. The volumes of monomer A and monomer B are v_A and v_B, respectively. We thus write the volume fractions of block A and block B as $\phi_A = N_A n_c v_A / V$ and $\phi_B = N_B n_c v_B / V$, respectively, where V is the volume of the system. The position of the t-th monomer of the i-th block P is denoted by $\vec{R}_{it}^p$, and its dipole moment is denoted by $\vec{p}_{it}^{\,p}$. By referring to the dipolar self-consistent field theory for polymer mixtures presented in Ref. [18], we write the grand canonical partition function of the fixed ions at the positions $\vec{r}_1$ and $\vec{r}_2$ in the block copolymer melt as follows:

$$Z_{\mathrm{BC}} = \sum_{n_c} \frac{\lambda_c^{n_c}}{n_c!} \int \prod_{i=1}^{n_c} \prod_{p=A,B} \mathcal{D}\vec{R}_{it}^p d\vec{p}_{it}^{\,p} \, \delta\left[\vec{R}_{iN_A}^A - \vec{R}_{i0}^B \right]$$

$$\times \exp\Bigg[-\sum_{i=1}^{n_c} \sum_{p=A,B} \sum_{t=1}^{N_p} \frac{3}{2b_p^2} (\vec{R}_{it}^p - \vec{R}_{it-1}^p)^2$$

$$- \frac{1}{2} \int d^3r d^3r' \, \widehat{\rho}(\vec{r}) v(\vec{r} - \vec{r}') \widehat{\rho}(\vec{r}')$$

$$- V_H - V_{\mathrm{hp}} \Bigg], \tag{1}$$

where $v(\vec{r} - \vec{r}') = e^2/(4\pi\epsilon_0|\vec{r} - \vec{r}'|)$ is the Coulomb potential in vacuum, b_p is the Kuhn length for block P, and λ_c is the fugacity of the dipolar block copolymer. We express all energies in units of $k_B T$. The δ function in Eq. (1) enforces the chain connectivity between the two blocks, where $\widehat{n}_p(\vec{r}) = \sum_{i=1}^{n_c} \sum_{t=1}^{N_p} \delta[\vec{r} - \vec{R}_{it}^p]$ is the number density for the monomer P. The total charge density $\widehat{\rho}(\vec{r})$ is given by $\widehat{\rho}(\vec{r}) = \sum_{i=1,2} z_i \delta(\vec{r} - \vec{r}_i) + \sum_{p=A,B} \widehat{\rho}_p(\vec{r})$ and $\widehat{\rho}_p(\vec{r}) = -\sum_{i=1}^{n_c} \sum_{t=1}^{N_p} \vec{p}_{it}^{\,p} \cdot \nabla\delta(\vec{r} - \vec{R}_{it}^p)$, where $\widehat{\rho}_p(\vec{r})$ is the charge density resulting from the dipoles and z_i is the ion valency of the i-th ion. The dipoles on the monomers consist of an intrinsic (permanent) contribution $\overline{p}_p$ and a contribution that is induced by the electric field.

We describe the deformation energy of induced dipoles as follows [21]: $V_H = \sum_{i=1}^{n_c} \sum_{p=A,B} \sum_{t=1}^{N_p} \frac{1}{2\alpha_p} (|\vec{p}_{it}^{\,p}| - \overline{p}_p)^2$, where α_p is the molecular polarizability of the monomer P. We also write the non-bonded interactions in terms of a harmonic penalty: $V_{\mathrm{hp}} = \int d\vec{r} \frac{1}{2\kappa} [\sum_{p=A,B} v_p \widehat{n}_p(\vec{r}) - 1]^2$, where κ denotes the compressibility of the A-B block copolymer. This energy accounts for the deviation in the density from that in the incompressible state with $\sum_{p=A,B} v_p \widehat{n}_p(\vec{r}) = 1$, which is primarily attributable to the electrostriction near an ion in the current system.

Using the mean-field approximation implemented via self-consistent field formulations [18], we obtain the mean-field equation as follows:

$$\nabla \cdot \left[\varepsilon(\vec{r}) \nabla \psi(\vec{r}) \right] = -4\pi l_0 [z_1 \delta(\vec{r} - \vec{r}_1) + z_2 \delta(\vec{r} - \vec{r}_2)]. \tag{2}$$

Here, $\psi(\vec{r})$ is the electrostatic potential scaled by the elementary charge e. $\varepsilon(\vec{r})$ represents the local dielectric function,

$$\varepsilon(\vec{r}) = 1 + 4\pi l_0 \lambda_c \sum_{p=A,B} I_p(\vec{r})^{-1} \int_0^{N_p} dt \, q_p(\vec{r}, N_p - t)$$

$$\times q_p^+(\vec{r}, t) \int d\vec{p}_p \, e^{-\frac{1}{2\alpha_p}(|\vec{p}_p| - \overline{p}_p^2)} p_p^2 F(p_p|\nabla\psi(\vec{r})|)$$

$$n_p(\vec{r}) = \lambda_c \int_0^{N_p} dt \, q_p(\vec{r}, N_p - t) q_p^+(\vec{r}, t)$$

$$\omega_p(\vec{r}) = \frac{v_p}{\kappa} \left[\sum_{p=A,B} v_p n_p(\vec{r}) - 1 \right]. \tag{3}$$

F_p is related to the Langevin function, $\mathcal{L}(x) = 1/\tanh x - 1/x$, as follows: $F = \mathcal{L}(x) \sinh x/x^2$. $\omega_p^{\mathrm{eff}} = \omega_p[\vec{R}^p(t)] - \ln I_p[\vec{R}^p(t)]$, where the function $I_p(\vec{r})$ is given by

$$I_p(\vec{r}) = \int d\vec{p}_p \, e^{-\frac{1}{2\alpha_p}(|\vec{p}_p| - \overline{p}_p^2)} \frac{\sinh[p_p|\nabla\psi(\vec{r})|]}{p_p|\nabla\psi(\vec{r})|}. \tag{4}$$

q_p^+ is obtained by solving the modified diffusion equation, $\partial q_p^+(\vec{r}, t)/\partial t = \frac{b_p^2}{6}\nabla^2 q_p^+(\vec{r}, t) - \omega_p^{\mathrm{eff}}(\vec{r}, t) q_p^+(\vec{r}, t)$ with the initial conditions $q_A^+(\vec{r}, 0) = q_B(\vec{r}, N_B)$ and $q_B^+(\vec{r}, 0) = q_A(\vec{r}, N_A)$. A similar equation holds for $q_p(\vec{r}, t)$, with the initial condition $q_p(\vec{r}, 0) = 1$. From Eq. (2), we can identify the electric field and the electric displacement field as $\vec{E}(\vec{r}) \equiv -\nabla\psi(\vec{r})$ and $\vec{D}(\vec{r}) \equiv \varepsilon(\vec{r})\vec{E}(\vec{r})$, respectively. The solvation energy for the transference of an ion from vacuum into a dielectric medium can then be calculated as follows: $\Delta G = \frac{1}{2} \int d\vec{r} [\vec{D}(\vec{r}) \cdot \vec{E}(\vec{r}) - \vec{D}_0(\vec{r}) \cdot \vec{E}_0(\vec{r})]$, where the subscript 0 denotes the vacuum state. It is important to note that the change in the dielectric function $\varepsilon(\vec{r})$ changes the solvation energy ΔG.

Because of the superposition principle of the electric displacement field and the spherical symmetry of the electric displacement field that arises from each ion, integrating Eq. (2) once with respect to the radial distance r reduces the equation to

$$|\vec{D}(\vec{r})| = |\vec{D}_1(\vec{r}) + \vec{D}_2(\vec{r})|$$

$$= \sqrt{|\vec{D}_1|^2 + |\vec{D}_2|^2 + 2|\vec{D}_1||\vec{D}_2|cos\varphi_\pm}. \tag{5}$$

Here, φ_+ for like charges ($z_1 = z_2$) and φ_- for unlike charges ($z_1 = -z_2$) denote the angles between $\vec{D}_1$ and $\vec{D}_2$. $|\vec{D}_i(\vec{r})| = z_i e/(4\pi\varepsilon_0|\vec{r} - \vec{r}_i|^2)$ corresponds to the electric displacement field arising from the i-th ion. Through a geometric analysis, we obtain $\varphi_- = \pi - \varphi_+$. Thus, Eqs. (2)-(5) must be solved in a self-consistent manner.

Our previous theoretical study suggested that both the degree of polymerization and the chain connectivity

significantly affect the spatial variation in the dielectric function $\varepsilon_r(r)$ near an ion on the nanometer scale [18]. Thus, it appears that the effect of the superposition of the electrostatic fields in Eq. (5) should give rise to strong nonlinearity in the dielectric function $\varepsilon_r(r)$ through the correlation of the polymerized degrees of freedom. Furthermore, the dielectric function $\varepsilon_r(r)$ near an ion must exhibit some disparity in value between like and unlike charges, subject to φ_+ and φ_-.

We first present our striking results for unlike charges. To facilitate comparison with previous studies of a single ion [16, 18], we use the same model parameters as those used for the solvation of an Ag$^+$ ion ($a = 1.15$ [Å]) with $(\overline{p}_A, \alpha_A, v_A, b_A, \overline{\phi}_A) = (1.70$ [D], 3.29×10^{-24} [cm^3], 67.3 [Å^3], 5 [Å], 0.8), $(\overline{p}_B, \alpha_B, v_B, b_B, \overline{\phi}_B) = (3.84$ [D], 4.4×10^{-24} [cm^3], 87.7 [Å^3], 5 [Å], 0.2), and $\kappa = 2.77 \times 10^{-13}$ [Pa^{-1}] for a nearly incompressible mixture. With these parameters, block A and block B become the lower- and higher-dielectric components, respectively. If there is no ion, the mixture of the block copolymer becomes disordered. In Fig. 1 (a), we demonstrate that the volume fractions of block A and block B vary significantly on the nanometer scale, despite the nanometer-scale separation between the two charges, which is greater than the radius of gyration $R_g = b_A\sqrt{N_c/6} = 9.13$ [Å]. Note that the solvation of ions by a higher-dielectric component is energetically favorable [16, 22]. This preferential solvation leads to the local enrichment of the higher-dielectric block B near ions, leading to the unconventional lamellar-like structure of the spatial variations in the volume fractions. This lamellar-like structure tends to be weakened as a total degree of polymerization N_c is increased.
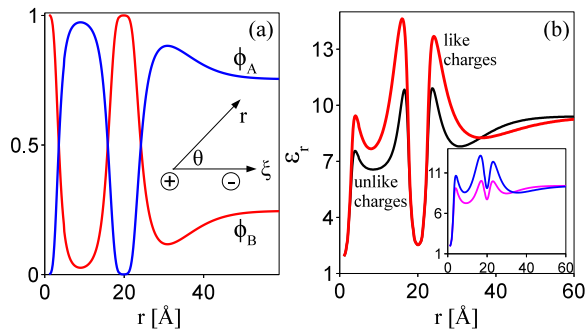
of polymer mixtures. We therefore plotted the dielectric functions $\varepsilon_r(r)$ in Fig. 1 (b), which clearly illustrates the substantial disparity between the dielectric functions $\varepsilon_r(r)$ for unlike and like charges. It is important to note that this result reflects the highly complicated nature of the solvation energies of ions in polymer mixtures. Previous studies at the level of the Born solvation energy have suggested that the solvation energy of an ion is an important factor that can cause a qualitative shift in the phase boundary of a salt-doped block copolymer [4]. Although several theoretical predictions such as the nonlinear effective Flory-Huggins χ parameter [23] and the salt-induced phase coexistence between the lamellar and the disordered phases [24] have been investigated in recent experimental studies, our current results imply additional non-intuitive phenomena in polymer electrolytes.

Further details of the marked variations in the dielectric function are presented in Fig. 2 (a): The changes in the dielectric function are remarkably non-monotonic near the two ions. This highly oscillatory behavior in the dielectric function $\varepsilon_r(r)$ must be primarily caused by the chain connectivity because simple liquid mixtures do not exhibit such a feature [18]. From Fig. 2 (b), it is also evident that the non-monotonic variation in the dielectric function $\varepsilon_r(r)$ in the inner region between the charges changes from a convex to a concave structure, as the charge separation decreases from 2 [nm] to 1 [nm]. Thus, ion pairing in a block copolymer melt causes the drastic changes in the dielectric function $\varepsilon_r(r)$ on the scale of a few nanometers.
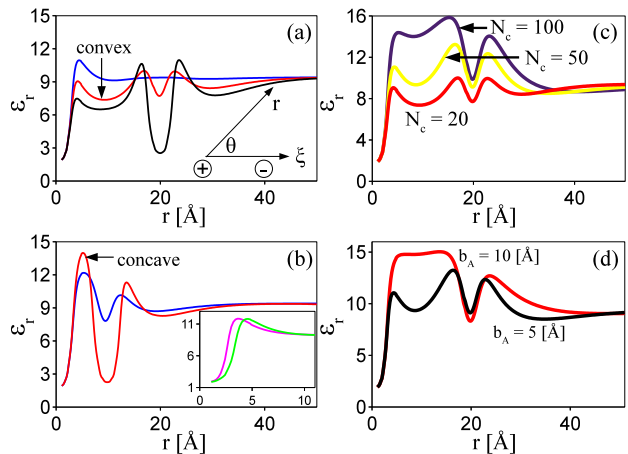

FIG. 1. (a) Volume fractions of block A (blue) and block B (red) with $N_c = 20$ on the r axis for unlike charges separated by 2 [nm]. r is the distance from the left-hand ion. The angle of elevation is $\theta = 5°$. (b) Dielectric functions $\varepsilon_r(r)$ for $N_c = 50$ on the r axis for unlike and like charges. The charge separation is 2 [nm]. $\theta = 5°$ (black for unlike charges and red for like charges) and $\theta = 9°$ (purple for unlike charges and blue for like charges).

FIG. 2. The dielectric function $\varepsilon_r(r)$ on the r axis for unlike charges separated by L. r is the distance from the left-hand ion. In (a) and (b), the colors of the lines correspond to different angles of elevation: $\theta = 5°$(black), $\theta = 9°$(red), $\theta = 18°$(blue), $\theta = 78°$(green), and $\theta = 85°$(purple). The chain length is $N_c = 20$. (a) $L = 2$ [nm]. (b) $L = 1$ [nm]. The inset presents $\varepsilon_r(r)$ for contacting unlike charges separated by the ionic diameter, $2a = 2.3$ Å. (c) $L = 2$ [nm] and $\theta = 9°$ with various chain lengths. (d) $L = 2$ [nm], $N_c = 50$, and $\theta = 9°$ with various Kuhn lengths.

Another theoretical prediction is that the reorganization of solvent dipoles is responsible for the significant difference between the screening functions for unlike and like charges [20]. In view of this fact and Eq. (5), it is also conceivable that similar effects should occur in the case

Of further interest is the reorganization of monomer dipoles in proximity to nearly contacting ions. Note that

the substantial change in the dielectric function near the ion pair (see the inset in Fig. 2 (b)) exists as a consequence of dielectric saturation. By contrast, in theoretical modeling, it is common for an ion pair that contains one positive and one negative charge to be treated as a charge-neutral species or a dipolar species that affects the bulk dielectric constant at the linear-dielectric level [25]. However, our present result suggests that the dielectric saturation near an ion pair and hence the ion-pair solvation energy should also be of considerable importance.

It is important to note that the molecular parameters are also of essential importance to the dielectric function near an ion pair in a block copolymer melt. Figures 2 (c) and (d) indicate that the chain length N_c and the Kuhn length b_A give rise to striking changes in the dielectric function $\varepsilon_r(r)$ near unlike charges. It should also be noted that in linear dielectric theories, the equilibrium constant for a bound ion pair in a liquid can be written in the form $4\pi(1/T^*)^3 \int_{T^*}^{1} dx \ x^2 \exp[1/x]$ [25], where T^* is the dimensionless temperature $2a\overline{\varepsilon}_r/l_0$ defined in terms of the ionic radius a and the bulk dielectric constant $\overline{\varepsilon}_r$. Thus, our current results also suggest that in the case of ion-containing polymer mixtures, modification of the linear-dielectric expression will be required to account for the effects of the chain length, the Kuhn length, and the chain connectivity, and hence the local dielectric function.

In summary, we studied like- and unlike-charged ion pairs immersed in diblock copolymer melts using a dipolar self-consistent field theory for polymer mixtures [18]. Our theory accounts for the size of the ions, the permanent and induced dipole moments of the monomers, the Kuhn length, the compressibility of the liquids mixtures, and the degrees of polymerization. Our current results indicate that the correlation between the chain connectivity of polymers and the dielectric response can be substantially striking in the study of ion solvation. In Fig. 1 (a), we present the lamellar-like structure of the volume fractions of the two blocks near an ion pair, which arises from the preferential solvation of the ions by the higher-dielectric component. As a consequence of this local enrichment, the dielectric function $\varepsilon_r(r)$ becomes oscillatory near the ion pair. Our conceptually novel finding is the substantial disparity between the dielectric functions $\varepsilon_r(r)$ for like and unlike charges [Fig. 1 (b)]. Remark-ably, the dielectric function $\varepsilon_r(r)$ near an ion pair changes on the nanometer scale in a significantly non-monotonic manner, despite the large distance between the charges (for example, 2 [nm]) [Fig. 2 (a)]. We note that this synergistic effect of the ion pair is caused by the fact that the superimposed electrostatic fields that arise from the ion pair give rise to strong nonlinearity through the chain propagators in the dielectric function $\varepsilon_r(r)$ in Eq. (3). When the distance between the two ions is decreased from 2 [nm] to 1[nm], the primary curvature of the dielectric function $\varepsilon_r(r)$ in the region between the two ions is qualitatively altered [Fig. 2 (b)]. Moreover, the molecular parameters, such as the chain length and the Kuhn length, are of essential importance to the dielectric function $\varepsilon_r(r)$ near an ion pair [Fig. 2 (c)]. Recent theoretical studies have suggested that the reorganization of solvent dipoles is responsible for the observed decrease in the dielectric value of the ionic solution as the ionic concentration increases [26, 27]. Therefore, we anticipate that the bulk dielectric constants of polymer mixtures at high ionic concentrations may also be qualitatively altered by the effects of both ion pairing and the nature of polymers. In this context, further in-depth studies of the dielectric function for (polymerized) ionic liquids would be intriguing. In such a system, it is very likely that modification of the Onsager/Kirkwood formula will be required. Our theory is at the level of a mean-field approximation and draws upon the Gaussian chain; therefore, the present predictions yet require quantitative validation based on molecular dynamics simulations.

Finally, we suggest that the present results should motivate further focus on the synergistic effects of neighboring ions on polymer mixtures that drive strongly correlating molecular interactions from the angstrom scale to nanometer scale [7, 28, 29]. Along the same lines, the fluctuation effects arising from both the chain length and electrostatic interactions are well-known to cause qualitative and quantitative changes in the phase behavior of polymers. Thus, the nature of the correlations in the molecular interactions is likely to give rise to additional non-conventional features of ion-containing polymers, particularly under external electrostatic fields [30].

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