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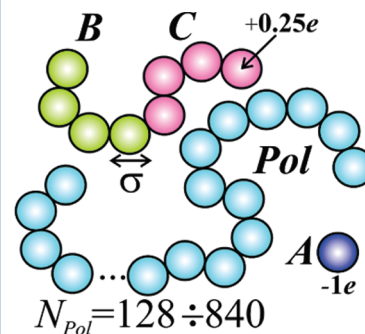
Long-Range Correlations in Polymer-Containing Ionic Liquids: The Case of Good Solubility

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ABSTRACT Ionic liquids containing macromolecules as solutes are of considerable interest for polymer materials science. However, these systems are at an early stage of investigation. In this study, the structural features of ionic liquids containing flexible polymer chains under good solubility conditions are investigated on the basis of the polymer integral equation method. The structural properties of the system are analyzed in reciprocal space by using partial structure factors. In the presence of attractive interaction between the polymer chains and polar cationic groups, there is a range of polymer concentrations at which the long-range correlations of polymer chains are observed. When these correlations are pronounced and the polymer chain size is much larger than the correlation length of pure ionic liquid, the decrease of the characteristic scale of the long-range polymer ordering with increasing polymer concentration fits the power dependence. The effect of such an increase on the ordering of the ions of the solvent is also considered.

SECTION Macromolecules, Soft Matter



Ionic liquids (ILs) have many unique physicochemical properties.^{1–6} The important peculiarity of the ILs is that they have the ability to dissolve a range of inorganic, organic, and polymeric materials at very high concentrations.^{6–9} Furthermore, various pairs of cations and anions forming an IL can be chosen, and thus the physicochemical properties of ILs may be tuned by choosing a specific combination of ions among numerous possibilities. Due to the enormous potential of ILs for industrial applications,^{10–12} these organic salts have been the subject of many experimental and theoretical investigations over the past decade. Polymer-containing ILs have generated considerable interest since the combinations of polymer molecules with ILs can lead to new opportunities in developing polymer-based materials.^{6,13–16} ILs may be used as a medium in which polymerizations take place or into which a polymer may be dissolved or dispersed.^{6,13} The major reports on ILs and polymers have dealt with the use of ILs for polymerization solvents.¹⁷ IL functionality may also be incorporated into the polymer itself.⁶

There have been a few studies that refer to the phase behavior of polymers in ILs.^{18–21} However, to the best of our knowledge, there have been no theoretical works that are focused specifically on the structural properties of ILs containing macromolecules as a solute. For the case of ILs as additives, IL concentration, temperature, and the alkyl-chain length effects on equilibrium structure of polymer electrolytes have been studied.¹⁶ ILs are good solvents for a wide range of polymer molecules. For this reason, it seems to be very important to study the structural behavior of polymer-containing ILs for the case of good polymer solubility in ILs. The factors responsible for polymer solubility in ILs are complex and not

readily predicted.⁶ In the present paper, we will not focus on the problems of polymer solubility in ILs. Our special interest here is how the structural properties of polymer-containing ILs depend on the polymer concentration and polymer chain length when the IL is a good solvent for polymer. The study of the ordering of macromolecules in ILs is useful in the understanding of polymer-containing systems where the ILs are used as a medium.

In the present work, the structural properties of polymer-containing ILs are investigated on the basis of the polymer integral equation or PRISM (polymer interaction site model) theory of Curro and Schweizer,²² which is an extension of the RISM theory of Chandler and Andersen.²³ This approach is believed to be well-suited for describing the equilibrium structure of polymer solutions including polyelectrolytes.^{24–27} As to ILs, both one-dimensional RISM theory^{28–30} and three-dimensional generalization (3D-RISM)³¹ were applied to imidazolium-based ILs. RISM theory was shown to adequately describe the liquid structure^{28,30} and solvation properties^{29,31} of ILs. ILs containing polymer additives or polymer materials containing IL as one of the components have not yet been studied on the basis of integral equation theory. In this work, we pioneer the application of the PRISM theory to polymer-containing ILs. However, this method can be successfully applied to ILs containing macromolecules only by sacrificing a large degree of accuracy in intramolecular structure. Nevertheless, the simple model of ILs we use here has been

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shown to adequately describe the structural properties of pure ILs.³⁰

In the frame of the PRISM method, we treat a polymer-containing IL as a “four-component” system consisting of anions, cationic polar head groups, cationic nonpolar tails and polymer chains. Cations are considered as being constructed from four charged and four neutral spherical sites, arranged in a linear manner, with diameter σ and bond length σ . Anions are spherical interaction sites with diameter σ . The species diameter σ is used to set the length scale. An anion carries the unit negative charge e . Every polar cationic site carries the positive charge $0.25e$. The linear polymer molecule contains N_{pol} spherical sites with diameter σ and bond length σ . Both cations and polymer chains are considered as Gaussian chains. The total number density is $0.54\sigma^{-3}$. We adapt the relatively low number density of $0.54\sigma^{-3}$ to obtain the liquid-like state of our model polymer-containing ILs. One needs to notice that the features of long-range correlations in our model system are not sensitive to moderate changes in the total number density, as our PRISM calculations in the appropriate ranges of energetic parameters have shown. The temperature is equal to 350 K. The main parameters of the calculations are the polymer concentration ρ_{pol} and chain length N_{pol} .

We rely on the fact that in ILs containing short to medium length cationic tails, the dominant interaction is electrostatic. In the present model, dispersion interactions are not taken into account. The interaction potential between any two species of IL α and β separated by the distance r is given by

$$u_{\alpha\beta}(r) = \begin{cases} +\infty, & r \leq \sigma \\ \frac{q_{\alpha}q_{\beta}}{4\pi\epsilon_0 r} + \epsilon^{\text{rep}}\left(\frac{\sigma}{r}\right)^{12}, & r > \sigma \end{cases} \quad (1)$$

where ϵ^{rep} is a parameter of the repulsive part of the Lennard-Jones potential, and q_{α} and q_{β} are the charges on the interaction sites α and β , respectively. The solubility can be controlled by both the solute–cation and solute–anion interactions, which can be dominated, for instance, by hydrogen bonding. We have chosen the case where polymer chains interact strongly with the cations. In order to provide good polymer solubility, we assume that the interaction between polymer sites and polar cationic sites is attractive and described by a Yukawa-type potential

$$u^{\text{attr}}(r) = \begin{cases} 0, & r > 6\sigma \\ -\frac{\epsilon^{\text{attr}}\sigma}{r} \exp(-(r-\sigma)/\sigma), & \sigma < r \leq 6\sigma \end{cases} \quad (2)$$

The reason for using a Yukawa-type potential for the solute–solvent interaction is that the Yukawa solute–solvent interaction offers more flexibility than the Lennard-Jones, particularly in the case of large solute molecules. That is a very important point in our studies on polymer-containing ILs because our forthcoming publications will include the effect of both the strength and the range of the solute–solvent interaction on structural behavior. One has to mention that a Yukawa-type potential model has been widely used to describe a broad range of fluids in liquid state physics.

The polymer–polymer interaction is a hard-core repulsion. The interactions between polymer chain and IL species are described by the repulsive part of the Lennard-Jones potential. The values of the parameters ϵ^{rep} and ϵ^{attr} are set $0.3k_{\text{B}}T$ and $0.35k_{\text{B}}T$, respectively, except when the effect of changing the value of ϵ^{attr} on the polymer structural characteristics is investigated. The results of the last-named calculations described below determine the selected value of ϵ^{attr} .

The matrix PRISM equation is written as^{21,22}

$$\mathbf{H} = \mathbf{W} \times \mathbf{C} \times (\mathbf{W} + \mathbf{D}\mathbf{H}) \quad (3)$$

where the asterisks denote convolution integrals, and matrices \mathbf{H} , \mathbf{C} , \mathbf{W} , and \mathbf{D} consist of the site–site total correlation functions, $h_{\alpha\beta}(r)$, the site–site direct correlation functions, $c_{\alpha\beta}(r)$, the intramolecular correlation functions, $w_{\alpha\beta}(r)$, and reduced densities of each component. Matrices \mathbf{W} and \mathbf{D} are given, whereas \mathbf{H} and \mathbf{C} are calculated. The matrix eq 3 is solved numerically with RLWC closure relation^{32,33}

$$\begin{aligned} h_{\alpha\beta}(r) &= -1, \quad r \leq \sigma_{\alpha\beta} \\ [\mathbf{W} \times \mathbf{C} \times \mathbf{W}]_{\alpha\beta} &= [\mathbf{W} \times (\mathbf{C}^{(\text{ref})} - \mathbf{P}) \times \mathbf{W}]_{\alpha\beta} \\ &+ h_{\alpha\beta}(r) - h_{\alpha\beta}^{(\text{ref})}(r) - \ln \frac{g_{\alpha\beta}(r)}{g_{\alpha\beta}^{(\text{ref})}(r)}, \quad r > \sigma_{\alpha\beta} \end{aligned} \quad (4)$$

where $g(r) = h(r) + 1$ is the pair correlation function, matrix \mathbf{P} is defined as $\mathbf{P} = \parallel u_{\alpha\beta}(r)/k_{\text{B}}T \parallel$. In eq 4, the superscript “ref” refers to correlation functions evaluated at the same density as the system under consideration but in the hard-core limit. The reference correlation functions are calculated by solving the PRISM equation with the standard Percus–Yevick closure for hard spheres

$$\begin{aligned} h_{\alpha\beta}^{(\text{ref})}(r) &= -1, \quad r \leq \sigma_{\alpha\beta} \\ c_{\alpha\beta}^{(\text{ref})}(r) &= 0, \quad r > \sigma_{\alpha\beta} \end{aligned}$$

In the present paper, the main structural characteristic of the system is the partial structure factor defined as $S_{\alpha\beta}(q) = [\mathbf{E} - \hat{W}(q)\hat{C}(q)]^{-1}\hat{W}_{\alpha\beta}(q)$. Here, \mathbf{E} is the diagonal unity matrix, and $[\dots]^{-1}$ denotes the matrix inverse.

Figure 1 presents the structure factors of polymer chains, $S_{\text{pol}}(q)$, at various polymer concentrations. The appearance of the well-pronounced small-angle peak in the functions $S_{\text{pol}}(q)$ at $\rho_{\text{pol}} > 0.006$ reflects the liquid-like ordering of polymer chains on long length scales in ILs. The characteristic scale of the ordering, $r^* = 2\pi/q^*$ (q^* is the peak position), decreases with increasing polymer density, does not exceed the double size of Gaussian chains, $2N_{\text{pol}}^{1/2}$, and does not take on a value less than half the size of the polymer chains. In the case of liquid-like ordering of polymer chains, a polymer solution could be schematically represented by correlation spheres with diameter r^* , which pack among each other as hard spheres of a simple liquid. Depending on the polymer concentration, each correlation sphere confines either a polymer chain or its fragment. As the ordering of correlation spheres in a polymer solution is similar to that of simple liquids of hard spheres, such a type of polymer ordering is considered to be a liquid-like one. The more chain fragments present among

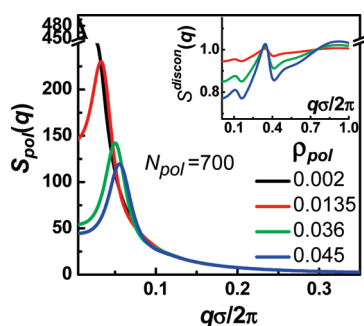


Figure 1. Partial structure factors of the polymer chains, $S_{\text{pol}}(q)$, at various polymer densities ρ_{pol} . Inset: the structure factors, $S^{\text{discon}}(q)$, of disconnected polymer monomers.

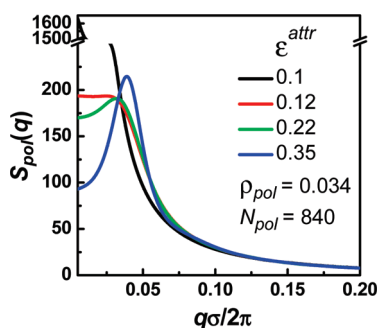


Figure 2. Partial structure factors of the polymer chains, $S_{\text{pol}}(q)$, at various values of the energetic parameter, ϵ^{attr} .

those that can be confined by the correlation spheres, the more prominent the liquid-like ordering of polymer chains.

The inset in Figure 1 shows the structure factors, $S^{\text{discon}}(q)$ of disconnected polymer monomers. An implicit assumption in the standard PRISM calculations is that the probable polymer conformations in a dense, multimolecular system do not change greatly as compared to those observed for a single polymer in an infinitely dilute θ solution. In this case, $w(r)$ satisfies the Gaussian approximation. The lack of taking into account the conformational changes of polymer chains in our calculations needs to be justified. The functions $S^{\text{discon}}(q)$ demonstrate the feebly marked ordering of disconnected monomers. No aggregation or microphase separation of monomers is observed. One can conclude that connected monomers do not also aggregate under the same conditions. Therefore, the conformational changes of the polymer chains cannot be crucial, and the Gaussian approximation for polymer intramolecular correlation function is acceptable.

The long-range correlations of the polymer chains are obviously caused by the presence of the attractive interaction between polymer monomers and polar sites on cations. As can be seen from Figure 2, the low- q peak in polymer structure factors gradually disappears with weakening the attraction and the distribution of polymer becomes uniform. Moreover, further decreasing the energetic parameter ϵ^{attr} leads to a drastic increase of the value of the reduced compressibility, which is defined by the zero- q limit of the structure factor. An increase in this value indicates the tendency of the polymer chains toward macrophase separation.

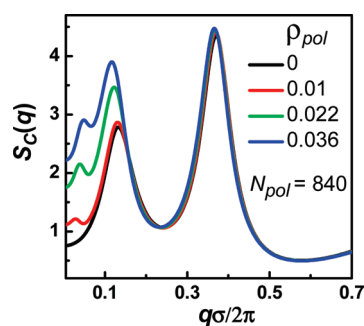


Figure 3. Partial structure factors of polar cationic groups, $S_c(q)$, at various polymer densities ρ_{pol} .

Note that the characteristic scale of long-range polymer correlations is much larger than that of intermediate-range ordering in a pure IL.^{30,34–38} Figure 3 demonstrates the partial structure factors of polar cationic groups, $S_c(q)$, at various polymer densities and particularly for a pure IL ($\rho_{\text{pol}} = 0$). The structure factors of anions have peaks at the same wave numbers in the entire range of parameters considered in this work, with the difference in intensity. Therefore, we do not give an example of the structure factors for anions as well as for nonpolar cationic groups. The behavior of the structure factors of the latter is somewhat different with changing parameters; however, the analysis of these distinctions is not the main goal of the present paper.

The first peak in the structure factor of a pure IL reflects an intermediate-range ordering. The characteristic scale of the ordering defined by the position of this peak is equal to 7.5σ . As one can see from the two preceding figures, the structure factors of polymer chains do not reveal this correlation size but a much larger one. At the same time, the adding of polymer chains can influence the ordering of ionic components. At $\rho_{\text{pol}} \geq 0.01$ (Figure 3), a prepeak in $S_c(q)$ appears at lower q . The position of this prepeak nearly coincides with the position of the small-angle peak in the polymer structure factor. Obviously, the main contribution to the new peak in $S_c(q)$ comes from long-range correlations of polymer chains. With increasing polymer density, the prepeak position has shifted to higher q , whereas the position of the first dominating peak has shifted to lower q . The question of the evolution of these peaks with further increasing polymer density remains open because of the problems concerned with the numerical solution of the integral equations.

As has been already shown above (Figure 1), the position of the low- q peak in the polymer structure factor shifts to larger wave numbers with increasing polymer density. Figure 4 displays the dependence of the characteristic scale of the ordering of polymer chains, r_{pol}^* , on the polymer density, ρ_{pol} , at various lengths of the chains, N_{pol} . For the three longest chains, there is a range of polymer density in which the r_{pol}^* value decreases with increasing ρ_{pol} as $r_{\text{pol}}^* \propto \rho_{\text{pol}}^{-\nu}$, the exponents being close to 0.4. The sizes of these polymer chains are much larger (more than 3 times) than the correlation size of pure solvent. The polymer density at which the long-range correlations of polymer chains become remarkable decreases with increasing chain length. To explain the

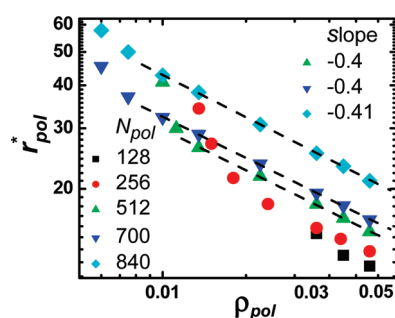


Figure 4. Variation of the characteristic scale, r^* , of the polymer ordering with density ρ_{pol} for various lengths of polymer chains, N_{pol} . The graphs are plotted in the double-logarithmic scale.

power dependences of r^*_{pol} on ρ_{pol} , it is appropriate to draw an analogy between the system studied in the present paper and a polyelectrolyte solution. The exponent in the well-known scaling form for polyelectrolytes $r^* \propto \rho^{-\nu}$ depends on the concentration, solvent quality, etc.³⁹ The exponent 0.4 obtained in our calculations belongs to the range of possible values for polyelectrolyte solutions. The point is that, as the interaction between the polymer and cationic polar groups is attractive, the polymer molecule in an IL can be considered as a weakly charged chain, the cationic heads playing the role of “induced” charges. The longer the polymer chain, the more uniform the distribution of the polar cationic groups along the chain. That is why the power dependence of the characteristic scale of polymer ordering on the polymer density is observed at relatively long chains.

In conclusion, we have shown that, in a polymer-containing IL under good polymer solubility conditions, there is a range of polymer concentrations at which the long-range correlations of flexible polymer chains are observed. The main finding is the power dependence of the characteristic scale of the long-range polymer ordering on the polymer density at relatively long lengths of polymer chains. While the long-range correlations of the chains are caused by the ionic correlations owing to attractive interaction between the polar cationic groups and polymer molecules, the characteristic scale of the ordering of polymer chains is much larger than that of intermediate-range ordering of ions. The structure factors of polar cationic groups also reflect the appearance of the longer range correlations, although the intermediate-range ordering typical of pure ILs remains dominant. One of the main conclusions of the present work is that the structural features of polymer-containing ILs depend on the length of polymer chains. One should not extend the results obtained for chains of sizes less than approximately three correlation lengths of pure IL over longer polymer chains.

One of the interesting issues remaining open includes the effect of the length of the nonpolar cationic tail on the structural properties of polymer-containing ILs. The challenge is the investigation of the structural behavior of polymer-containing ILs at lower temperatures, when the segregation of the ions can occur. Finally, forthcoming works will include an atomistic simulation for developing more realistic models of the system.

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