

## Research Article

# Long- and Intermediate-Range Correlations in Polymer-Containing Ionic Liquids

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Received 28 July 2011; Accepted 23 August 2011

Academic Editors: I. Anusiewicz, S. Sasaki, and D. Strout

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Structure on long- and intermediate-length scales in polymer-containing ionic liquids is investigated on the basis of the polymer integral equation method. The structural features of flexible homopolymer chains and the ions of the solvent are analyzed in reciprocal space using partial structure factors. There is a range of polymer concentrations at which the long-range correlations of polymer chains are observed. When these correlations are pronounced, the decrease of the characteristic scale of the long-range polymer ordering with increasing polymer concentration fits a power law. The effect of adding polymer chains upon the ordering of the ions of the solvent is also considered. Upon addition of a polymer, it is shown that long-range correlations of ions can arise, although the intermediate-range ordering typical of pure ionic liquids remains dominant and stable. The dependence of the characteristic scale of the long-range ordering of the ions of the solvent on the polymer concentration also fits a power law.

## 1. Introduction

Ionic liquids (ILs) have received considerable attention due to their unique physicochemical properties [1–6]. The polar nature of ILs makes them suitable for solvents and reaction media in a wide range of chemical processes. ILs dissolve a range of inorganic, organic, and polymeric materials at very high concentrations [7–11]. 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 [12–14], these organic salts have been the subject of many experimental and theoretical investigations over the past decade. The structure of ILs has been shown to exhibit unique spatial heterogeneity that results from their inherent polar/nonpolar phase separation [15–18].

For the last 10 years the area of application of ILs in polymer chemistry has been significantly enlarged [7, 14, 19, 20]. 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 [19]. ILs may be used as a medium in which polymerizations take place or into which a polymer may be dissolved or dispersed. The major reports on ILs and polymers have dealt with the use of ILs for polymerization solvents. IL functionality may also be incorporated into the polymer itself [7]. The combination of block copolymers and ILs results in a new class of functional materials with intricate structure on the nanometer scale [21]. There have been a few studies that refer to the phase behavior of copolymers in ILs [21–25]. A copolymer in an IL can serve as a model system for a proton exchange fuel cell membrane [21].

Despite the fact that ILs containing macromolecules as solutes are of considerable interest for polymer materials science, these systems are at an early stage of theoretical investigation. To the best of our knowledge, there had been no theoretical works that are focused specifically on the structural properties of ILs containing homopolymers until our early study was published [26]. 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 [27].

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 [7]. There has been little fundamental understanding of how the structure and chemical composition of ionic liquids govern polymer solubility [28]. 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 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 using the polymer integral equation or PRISM (polymer interaction site model) theory of Curro and Schweizer [29], which is an extension of the RISM theory of Chandler and Andersen [30]. This approach is believed to be well-suited for describing the equilibrium structure of polymer solutions including polyelectrolytes [31–33]. As to ILs, both one-dimensional RISM theory [34–36] and three dimensional generalization (3D-RISM) [37] were applied to imidazolium-based ILs. RISM theory was shown to adequately describe the liquid structure [34, 36] and solvation properties [35, 37] of ILs. Recently, we first used the PRISM theory to polymer-containing ILs [26].

Now there is an increasing number of papers using various simulation methods to investigate the structure of pure ILs or the solvation of small molecules in ILs [10, 11, 15–17, 38, 39]. However, the presence of polymer chains creates many obstacles to computer simulation. Analytically polymer-containing ILs are very complicated, too. At present, the PRISM theory seems to be the most powerful method for studying structural properties of 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.

## 2. Model and Method

To simulate ILs, multiscale coarse-graining (MS-CG) approaches based on the force-matching method have been developed [39]. In most MS-CG models, the cations are represented by linear chains and the anions are modeled by spherical sites. Many efforts have been made to develop more accurate MS-CG models. Indeed, the local structure of ILs (in particular, the local structure of the liquid around solutes) as well as accurate thermodynamic properties is sensitive to the type of force field and parameters used. Many simulation studies have used all-atom approaches and employed detailed molecular models for ILs. The question is how sensitive the structural characteristics describing the long- and intermediate-range ordering in polymer-containing ILs are to the level of detail. These properties are believed to be weakly sensitive. Moreover, there is a considerable risk that all-atom approaches generate results that are difficult to

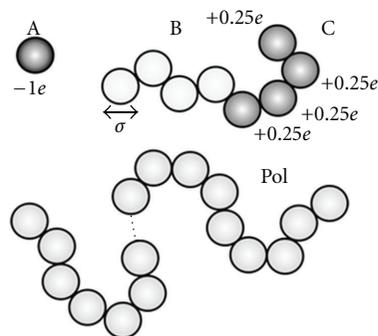


FIGURE 1: Model representation of a polymer-containing IL. The system consists of anions (a), cationic nonpolar tails (b), cationic polar groups (c), and polymer chains (Pol).

interpret, since the complexity of the models make it hard to separate the important physics from irrelevant details [40].

Here, we use a very simple model which, nevertheless, accounts for the essential features of the ions of ILs, which are generally asymmetric and flexible, with delocalized electrostatic charges. Such a simple model of ILs has been shown to adequately describe the structural properties of pure ILs on intermediate lengthscales [36].

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 (Figure 1). Cations are considered as being constructed from four charged and four neutral spherical sites, arranged in a linear manner, with diameter  $\sigma$  and bond length  $\sigma$ . Anions are spherical interaction sites with diameter  $\sigma$ . The species diameter  $\sigma$  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  $N_{\text{Pol}} = 800$  spherical sites with diameter  $\sigma$  and bond length  $\sigma$ . Both cations and polymer chains are considered as freely jointed chains. The total number density is  $0.63\sigma^{-3}$ . Our choice of this value requires an explanation. The problem is what number density has to be chosen, as we do not consider any specific IL. However, using the data from publications on some model ionic liquids [34, 35] and the data from experiments, we have estimated the range of number densities for our model depending on the cationic tail length and temperature. The number density of  $0.63\sigma^{-3}$  falls within this range and provides 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 have shown. In our previous work [26], we adapted lower number density of  $0.54\sigma^{-3}$  to obtain liquid-like state of the model system in a broad range of parameters; however, the structural characteristics reported here coincide with those obtained for lower density. The temperature is equal to 350 K.

Polymer density (concentration) is measured in units of  $\sigma^{-3}$ .

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. These interactions may play an important role at interfaces, in determining the behavior of the IL double layer [40], in obtaining the right dynamics [10], and so forth. Our simple model relies on the assumption that the long-range ordering in polymer-containing ILs is insensitive to dispersion interactions. The interaction potential between any two species of IL  $\alpha$  and  $\beta$  separated by the distance  $r$  is given by

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

where  $q_\alpha$  and  $q_\beta$  are the charges on the interaction sites  $\alpha$  and  $\beta$ , respectively.

The solubility can be controlled by both the solute-cation and solute-anion interactions, which can be dominated, for instance, by hydrogen bonding. There have been surprisingly few studies relating to ionic liquid-polymer solute interactions. The nature of these interactions resulting in a strong association between the polymer chains and the ions of ILs can be manifold (multipolar interactions, hydrogen bonding, Lewis acid-base interaction, etc.). In order to provide good polymer solubility, we assume that specific interactions between polymer sites and the ions of the solvent are attractive and described by a Yukawa-type potential

$$u^{\text{attr}}(r) = \begin{cases} 0, & r > 5\sigma, \\ -\frac{\epsilon^{\text{attr}}\sigma}{r} \exp\left(\frac{-a(r-\sigma)}{\sigma}\right), & \sigma < r \leq 5\sigma. \end{cases} \quad (2)$$

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 [41]. It describes many physical phenomena and can be easily tuned to mimic different interactions. One can investigate the effect of both the strength and the range of the solute-solvent interaction on structural behavior of polymer-containing ILs. In addition to varying the strength of the solute-solvent interaction through  $\epsilon^{\text{attr}}$ , we can additionally vary the range of this interaction through  $a$ . 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.

We consider two cases: (I) polymer chains interact strongly with the charged cationic monomers (the PC system) and (II) polymer solutes interact with the anions (the PA system). For the PC system,  $u_{\text{PC}}^{\text{attr}}(r) \neq 0$ ,  $u_{\text{PA}}^{\text{attr}}(r) = 0$ , and vice versa for the PA system.

The polymer-polymer interaction is a hard-core repulsion.

In most cases a strong association between the charged cationic groups and a polymer is a result of the attractive interaction between the polymer monomers and the single site of the cationic head group. Despite the fact that such an assumption would be more natural, we introduce

specific interactions between the polymer monomers and all charged cationic sites. The reason is the restricted amount of components that can be explicitly considered in the frame of the PRISM method. The restriction is not fundamental but affects the convergence of the numerical procedure. This is why we cannot consider the polar cationic monomers as interaction sites of different types. In this connection, it is very instructive to compare the results obtained for the PC and PA systems. The number of associating sites of the solvent in the PA system is four-times smaller than in the PC system. This is exactly the case if there is only one associating site per cation. The difference in the internal structure of the anions and cations can have a significant effect on the local structure, but it is believed that this hardly affects the longer-range ordering. Thus, if the structural features are found to be the same in both cases, we will obtain a validation of the model used for PC systems.

The matrix PRISM equation is written as [29]

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

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 equation (3) is solved numerically with RLWC closure relation [42, 43]

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

where  $g(r) = h(r) + 1$  is the pair correlation function, matrix  $\mathbf{P}$  is defined as  $\mathbf{P} = \|u_{\alpha\beta}(r)/k_B T\|$ . In (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

$$\begin{aligned} h_{\alpha\beta}^{(\text{ref})}(r) &= -1, & r \leq \sigma_{\alpha\beta}, \\ c_{\alpha\beta}^{(\text{ref})}(r) &= 0, & r > \sigma_{\alpha\beta}. \end{aligned} \quad (5)$$

An implicit assumption in the standard PRISM calculations is that the probable polymer conformations in a dense, multimolecular system do not change greatly. The standard PRISM method is also valid for polymers consisting of large, bulky groups (e.g., polystyrene) as well as for charged polymers on condition that the conformational changes of polymer chains with changing parameters are not crucial. The lack of taking into account the conformational changes of polymer chains in our calculations was justified in the

previous work [26]. The conformational changes of the polymer chains in the IL under good solubility conditions cannot be crucial. To describe the chain conformation, a simplest freely jointed model with the fixed bond length  $b = \sigma$  is used. For this model, the spatial distribution of the pair of monomers  $i$  and  $j$  separated by  $n = |i - j|$  bonds in a given chain conformation is written in the reciprocal  $\mathbf{q}$  space as  $\hat{w}_{ij}(q) = [\sin(qb)/qb]^n$ .

### 3. Results and Discussions

The main parameters of the calculations are the polymer concentration  $\rho_{\text{Pol}}$  and the strength parameter  $\epsilon^{\text{attr}}$  of the Yukawa-type potential in (2) through which the strength of the solute-solvent interaction can be varied. Below,  $\epsilon^{\text{attr}}$  is measured in units of  $k_B T$ . The range parameter  $\alpha$  is taken to be 1 except the cases where the effect of the range of specific solute-solvent interactions on structural behavior is studied. All the results discussed in the present paper were obtained for sufficiently long polymer chains consisting of  $N_{\text{Pol}} = 800$  monomers. As has been shown in our previous work [26], the structural features of polymer-containing ILs on long- and intermediate-length scales can be obtained for polymer chains of sizes no less than approximately three correlation lengths of pure IL. The chosen chain length of 800 monomers satisfies this condition; therefore the results reported below one can extend over longer polymer chains.

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 2 presents the structure factors of polymer chains,  $S_{\text{Pol}}(q)$ , at varying the strength parameter  $\epsilon^{\text{attr}}$ . The appearance of the well-pronounced small-angle peak in the functions  $S_{\text{Pol}}(q)$  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) is equal to  $\approx 30\sigma$  for both the PC and PA systems and considerably exceeds the characteristic scale of the intermediate-range ordering in a pure IL [15–18, 36]. 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 [31]. 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 those that can be confined by the correlation spheres, the more prominent the liquid-like ordering of polymer chains.

The long-range correlations of the polymer chains are obviously caused by the presence of the attractive interaction between polymer monomers and the ions of the solvent. 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 strength parameter

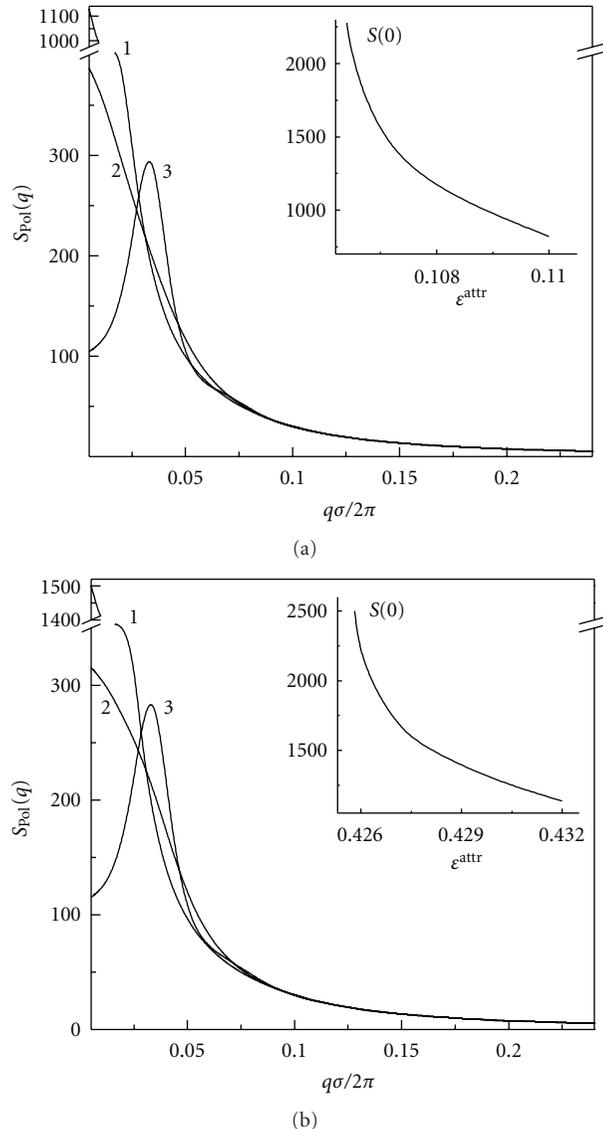


FIGURE 2: Partial structure factors of the polymer chains,  $S_{\text{Pol}}(q)$ , at various values of the strength parameter,  $\epsilon^{\text{attr}} = 0.108$  (1), 0.12 (2), and 0.25 (3) for the PC system (a) and  $\epsilon^{\text{attr}} = 0.43$  (1), 0.5 (2), and 0.8 (3) for the PA system (b) at  $\rho_{\text{Pol}} = 0.0135$ . Inset:  $S_{\text{Pol}}(q \rightarrow 0)$  as a function of  $\epsilon^{\text{attr}}$ .

$\epsilon^{\text{attr}}$  leads to a drastic increase of the value of the reduced compressibility, which is defined by the zero- $q$  limit of the structure factor (the insets in Figure 2). A drastic increase in this value with little decreasing  $\epsilon^{\text{attr}}$  indicates the tendency of the polymer chains toward macrophase separation.

Polymer solubility in our model IL is established for a PC system at much smaller values of  $\epsilon^{\text{attr}}$  compared to a PA system due to the higher concentration of charged cationic monomers compared to that of the anions. As a result, for a PA system the low- $q$  peak appears at much larger values of the strength parameter than for a PC system. Thus, decreasing the number of associating sites in the IL model leads to an increase in the strength of specific interactions at which polymer solubility is established.

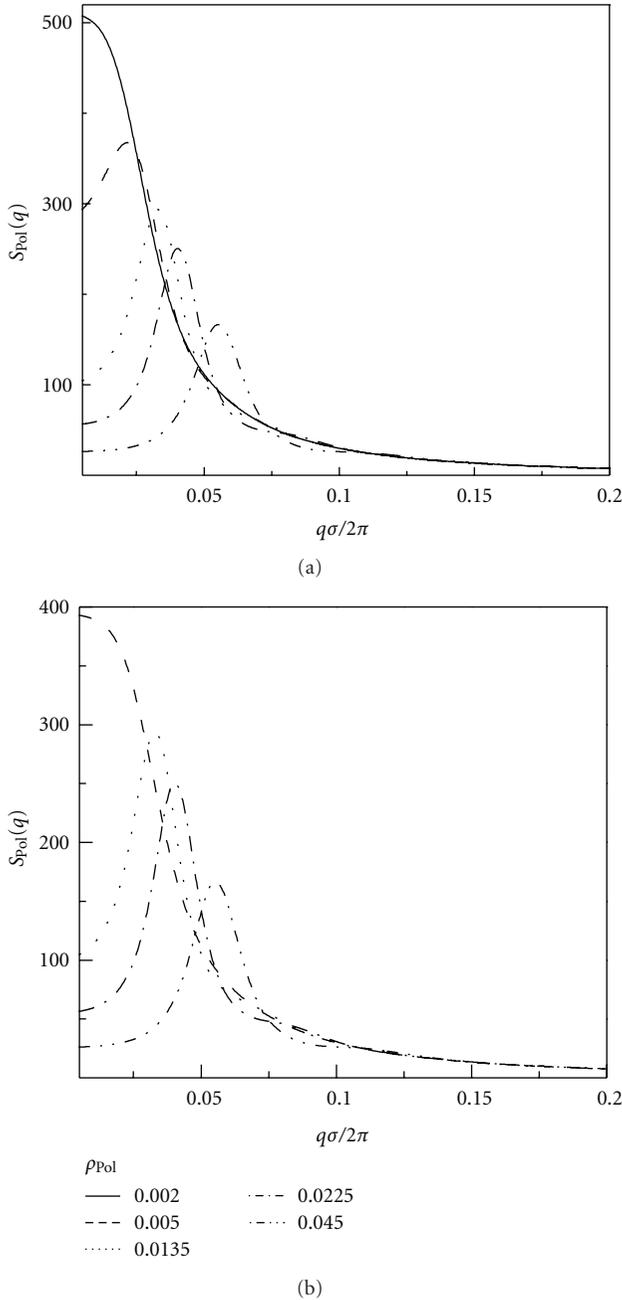


FIGURE 3: Partial structure factors of the polymer chains,  $S_{\text{Pol}}(q)$ , at varying the polymer density  $\rho_{\text{Pol}}$  for (a) the PC system at  $\epsilon^{\text{attr}} = 0.25$  and (b) the PA system at  $\epsilon^{\text{attr}} = 1.0$ .

Long-range correlations of the polymer chains appear at relatively high polymer concentrations corresponding to semidilute solutions. Figure 3 presents the polymer structure factors,  $S_{\text{Pol}}(q)$ , at various polymer densities  $\rho_{\text{Pol}}$  under good solubility conditions. In the PC system, the long-range ordering appears at lower polymer densities than in the PA system. The characteristic scale of the ordering,  $r^*$ , decreases with increasing polymer density, does not exceed the double size of the polymer chains, and does not take on a value less than half the size of the chains.

Figure 4 displays the dependence of the peak position,  $q^*$ , in the polymer structure factor on the polymer density,  $\rho_{\text{Pol}}$ , at different strength parameters  $\epsilon^{\text{attr}}$ . For both the PC and PA systems, there is a range of polymer density in which the  $q^*$  value increases with  $\rho_{\text{Pol}}$  as  $q^* \propto \rho_{\text{Pol}}^\nu$ , the exponents falling within the range [0.42; 0.45]. As can be seen from Figure 4(c), the peak positions at a fixed polymer density practically coincide for the PC and PA systems. Moreover, the close values of  $q^*$  were obtained when using the different range parameter of the Yukawa-type potential,  $\alpha = 2$ , and a 6-12-type Lennard-Jones potential. As the parameter  $\alpha$  is increased, the range of the solute-solvent interaction decreases. To gain good polymer solubility for the PC system, the corresponding increase in the interaction strength parameter  $\epsilon^{\text{attr}}$  should be of the order of 0.25 when going from  $\alpha = 1$  to  $\alpha = 2$ .

Thus, in the presence of specific interactions between the polymer chains and the ions of IL, there is a range of polymer concentrations at which the long-range correlations of polymer chains are observed. The characteristic scale of the long-range ordering slightly depends on the strength and range of specific interactions as well as the type of the ions associating with the polymer chains. When the long-range correlations are pronounced, the decrease of the characteristic scale of the ordering with increasing polymer concentration fits the power law dependence. The latter is the main finding of the present work while the fact of the independence of the long-range structural features from the type of solute-solvent interactions under good solubility conditions seems to be quite obvious. However, this result is also presented here because the question of what potential is suitable for describing the solute-solvent interactions when studying the long-range correlations has often arisen.

To explain the power law dependences of  $q^*$  on  $\rho_{\text{Pol}}$ , 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  $q^* \propto \rho^\nu$  depends on the concentration, solvent quality, and so forth [39]. The exponents obtained in our calculations belongs to the range of possible values for semidilute polyelectrolyte solutions. The point is that, as the interaction between the polymer and the ions of the solvent is attractive, the polymer molecule in an IL can be considered as a weakly charged chain, the anions or polar cationic groups playing the role of “induced” charges. The longer the polymer chain, the more uniform the distribution of the ions 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 [26]. This analogy between our system and a polyelectrolyte solution, however, is limited to the polymer concentrations at which the Debye screening lengths for these systems are of the same order. Indeed, the long-range ordering of polyelectrolyte chains in a dilute solution is well-pronounced while we have found no long-range correlations in polymer-containing ILs in this concentration range.

Let us now consider the effect of the adding of polymer chains on the ordering of the ions of the solvent. To this end, the structure factors of polar cationic groups,  $S_C(q)$ , are

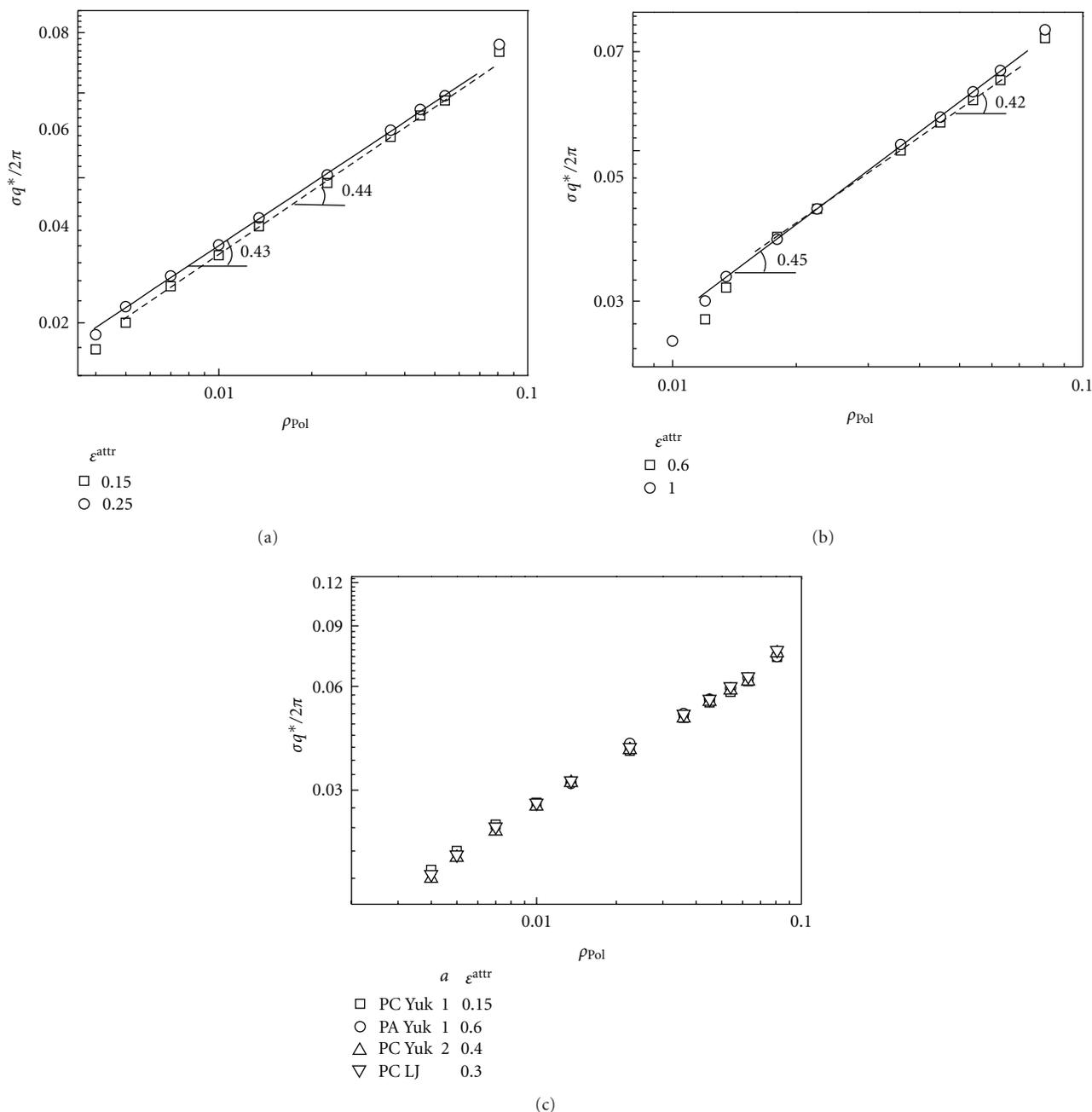


FIGURE 4: Variation of the peak position,  $q^*$ , in the structure factors  $S_{Pol}(q)$  with polymer density  $\rho_{Pol}$  for (a) the PC system, (b) PA system, (c) PC system at various parameters of Yukawa-type potential (Yuk) and for a 6-12 type Lennard-Jones potential (LJ) and for the PA system at  $\alpha = 1$ . The graphs are plotted in the double-logarithmic scale.

shown in Figure 5. 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. Moreover, the peaks reflecting the long- and intermediate-range ordering are only shown in Figure 5.

The peak in the structure factor of a pure IL (Figure 5(a)) reflects an intermediate-range ordering. The characteristic scale of the ordering defined by the position of this peak is equal to  $6.9\sigma$ . As one can see from the 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. As can be seen from Figure 5(a), a prepeak in  $S_C(q)$  appears at lower  $q$  both for the PC and PA systems. The position of this prepeak nearly coincides with the position

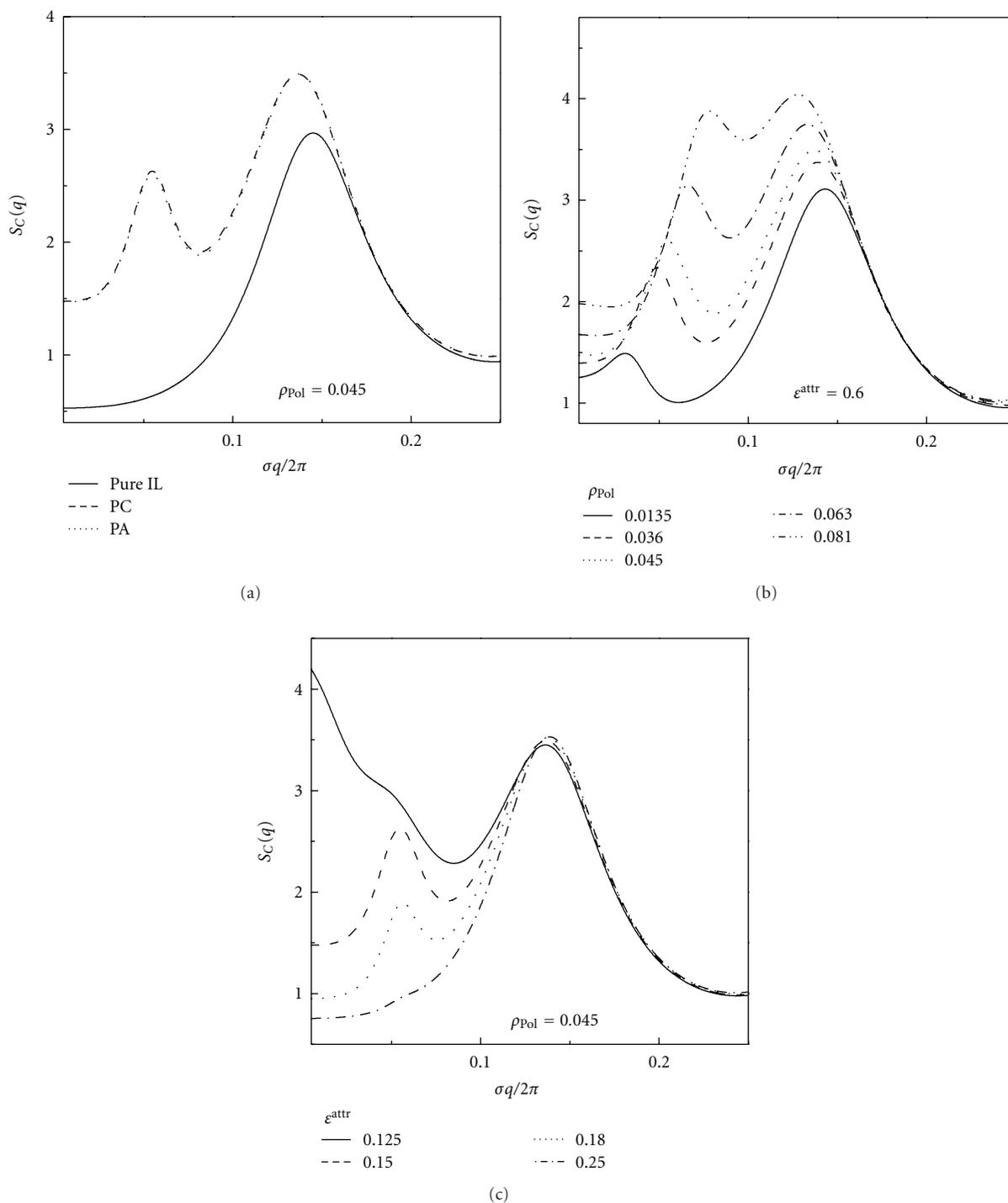


FIGURE 5: Partial structure factors of polar cationic groups,  $S_C(q)$ , (a) for a pure IL in comparison with the PC and PA systems at  $\rho_{\text{Pol}} = 0.045$ ; (b) for the PA system at varying the polymer density  $\rho_{\text{Pol}}$  at  $\epsilon^{\text{attr}} = 0.6$ ; (c) for the PC system at varying the strength parameter  $\epsilon^{\text{attr}}$  at  $\rho_{\text{Pol}} = 0.045$ .

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. Thus, the adding of polymer chains can lead to the appearance of the long-range ordering of the ions of an IL, but for all that the intermediate-range ordering remains dominant.

With increasing polymer density (Figure 5(b)), the pre-peak position has shifted to higher  $q$  whereas the position of the 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. The

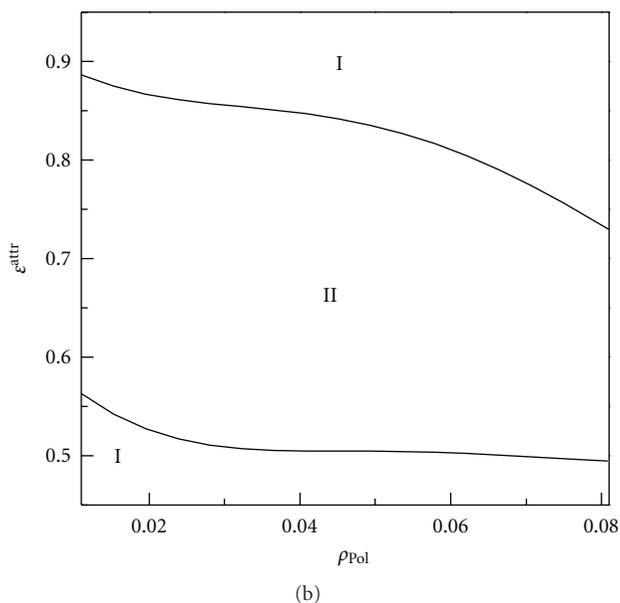
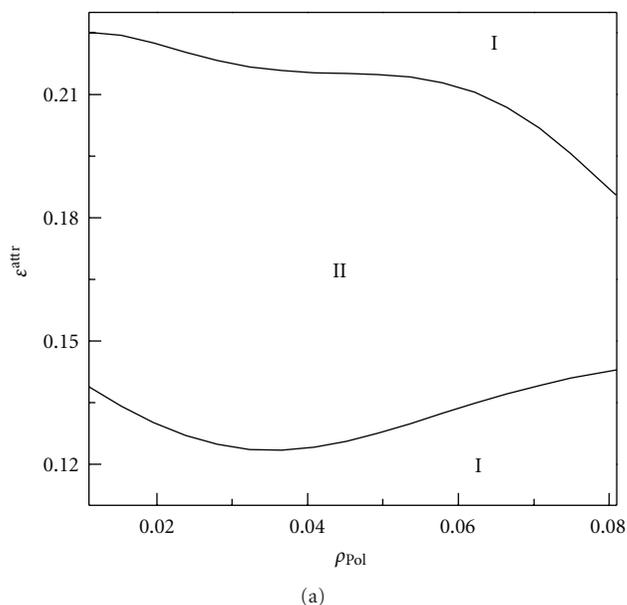


FIGURE 6: Structure diagrams for the (a) PC and (b) PA systems. In regions I, there is no low- $k$  prepeak in the structure factor  $S_C(q)$ . In region II, the function  $S_C(q)$  exhibits the prepeak.

changes in the structure factors with increasing the polymer density and strength parameter for the PC and PA systems are identical; therefore, with changing a chosen parameter, the structure factors either for the PC or PA system are shown.

Figure 5(c) presents the structure factors  $S_C(q)$  at varying the strength parameter  $\epsilon^{\text{attr}}$ . The low- $q$  prepeak appears at some value of  $\epsilon^{\text{attr}}$  and becomes more prominent with increasing the strength parameter. However, further increasing  $\epsilon^{\text{attr}}$  leads to a decrease in the intensity of the prepeak, and finally the prepeak gradually disappears.

A gradual disappearance of the low- $q$  prepeak in the structure factors of the ions of the solvent with strengthening the polymer-solvent interactions seems to be a nontrivial

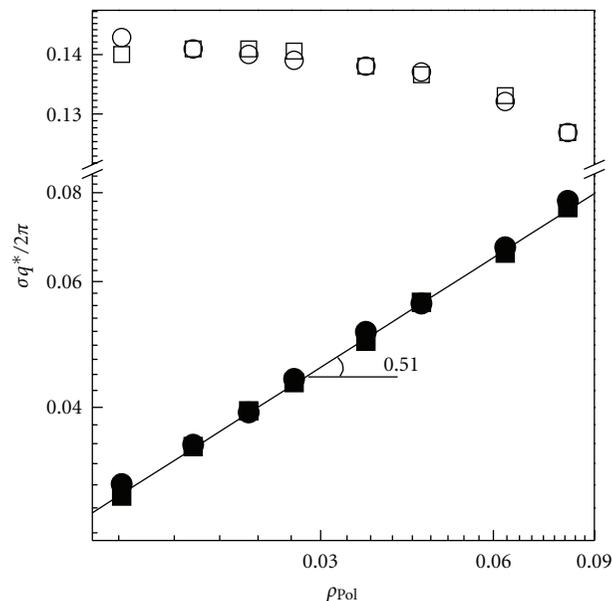


FIGURE 7: Variation of the position,  $q^*$ , of the prepeak (solid symbols) and the peak associated with the intermediate-range ordering (open symbols) in the structure factors  $S_C(q)$  with polymer density  $\rho_{\text{Pol}}$  for the PC system at  $\epsilon^{\text{attr}} = 0.15$  (circles) and PA system at  $\epsilon^{\text{attr}} = 0.6$  (squares). The graphs are plotted in the double-logarithmic scale.

fact. The polymer densities  $\rho_{\text{Pol}}$  and strength parameters  $\epsilon^{\text{attr}}$ , at which the structure factors  $S_C(q)$  have the prepeak, belong to the region II in Figure 6. At any of polymer densities, the long-range correlations of cations and anions disappear at relatively strong polymer-ion interactions. To explain this fact let us consider the behavior of the intermediate-range ordering with increasing the strength parameters  $\epsilon^{\text{attr}}$ . As can be seen from Figure 5(c), strengthening the interaction between the polymer chains and the ions of the solvent, neither the position nor intensity of the peak that reflects the ordering of charged cationic monomers on intermediate length scales changes. Thus, the intermediate-range ordering is stable when the polymer-solvent interaction is strengthened. The polymer monomers do not penetrate into the polar domains forming by cations and anions but localize in a close vicinity. In this case, the more contacts between the polymer chains and the ions of the solvent, the weaker the influence of the polymer chains on the ordering of the ions. Increasing the strength parameter obviously leads to an increase in contacts, and consequently, to a gradual disappearance of the long-range correlations of the ions of the solvent. The long-range ordering of polymer chains stays well-pronounced.

The analysis of the structure factors  $S_C(q)$  (Figure 5(b)) has shown that the positions of the low- $q$  prepeak and the peak associated with the intermediate-range ordering depend on the polymer density. Figure 7 illustrates the variation of the positions of these peaks with  $\rho_{\text{Pol}}$ . The position of the low- $q$  prepeak follows the power law  $q^* \propto \rho_{\text{Pol}}^\nu$ , the exponent being close to 0.51 both for the PC and PA systems. This value of  $\nu$  is a little larger than the exponents

obtained for the polymer chains. The structural features of the ions of the solvent upon addition of a polymer are identical for the PC and PA systems as in the case of the structural behavior of the polymer chains.

Thus, in a polymer-containing IL, under good polymer solubility conditions, the features of long- and intermediate-range correlations of both the polymer chains and the ions of the solvent hardly depend on what species of solvent form the association with a polymer.

#### 4. Conclusions

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 law dependence of the characteristic scale of the long-range polymer ordering on the polymer density. While the long-range correlations of the chains are caused by the ionic correlations owing to attractive polymer-solvent interaction, the characteristic scale of the ordering of polymer chains is much larger than that of intermediate-range ordering of ions.

The adding of polymer chains can influence the ordering of ionic components. The structure factors of the ions of the solvent also reflect the appearance of long-range correlations, although the intermediate-range ordering typical of pure ILs remains dominant. However, strengthening the polymer-solvent interaction leads to a gradual disappearance of the long-range ordering of ions. When the long-range ordering is observed, the decrease of the characteristic scale of this ordering with increasing polymer concentration also fits a power law.

Further work is needed to study the effects of the length of the nonpolar cationic tail on the structural properties of polymer-containing ILs. It should be stressed, however, that one cannot easily disregard the presence of dispersion forces when considering ILs containing long cationic tails.

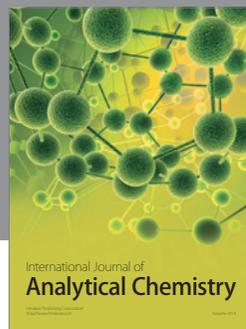
#### Acknowledgment

This work was supported by the Russian Foundation for Basic Research (Project no. 09-03-00030).

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