

## Swelling of a Microgel with Immobilized Carbon Nanotubes in an Ionic Liquid

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We use a Flory–Huggins type approach to describe the swelling of a polymer microgel (a finite size network of polymer chains covalently bound with each other) with immobilized carbon nanotubes in an ionic liquid. The ionic liquid is modeled as a “two-component” solvent consisting of anions and cations. The anions and cations are assumed to have different affinities to the microgel. It is supposed that the carbon nanotubes form a conducting cluster interpenetrating the microgel. We show that if the difference of the Flory–Huggins parameters describing affinities of the anions and the cations to the microgel is high enough, the swelling ratio of the gel can depend on its size. The physical reason for the phenomenon is the violation of the cations and anions concentrations equality inside the gel that causes a shift of the free energy and can lead to a swelling-collapse transition. The segregation of cations and anions is different for microgels having different sizes because it is opposed by electrostatic field.

### Introduction

Ionic liquids (ILs) are substances solely composed of anions and cations that are nevertheless liquid at around (and often below) room temperature.<sup>1,2</sup> Probably the most important property of ILs discriminating them from nonionic solvents is their very low volatility.<sup>3,4</sup> Only several ILs could be distilled at high temperature and low pressure.<sup>5</sup> For this reason, ILs have become very popular as possible reaction media in environment-friendly (“green”) chemistry. Moreover, ILs can dissolve a wide range of both organic and inorganic substances<sup>1,6,7</sup> and, simultaneously, have excellent chemical and thermal stability which also makes them promising for chemical technologies. One of the most outstanding inventions connected with the high solvent power of ILs is the development of the new effective cellulose processing technique.<sup>8</sup> ILs mix of course with not all the substances. However, biphasic systems comprising an IL as one of the components are also promising in application to heterogeneous catalysis.<sup>7</sup> Another basic advantage of ILs lies in the possibility to produce ILs with predefined properties by means of combining different pairs of cations and anions.<sup>1,9</sup>

It is a marvel that besides the utilization as reaction media, ILs can find many other applications. For example, ILs can be used as proton-conducting media in fuel cells,<sup>10</sup> as lubricants, as plasticizers, and as heat transfer fluids.<sup>11</sup> Very interesting are phenomena connected with interaction of ILs and carbon nanotubes.<sup>12</sup> Single-wall carbon nanotubes (SWNTs) form a physical gel when being ground in an imidazolium ion-based IL (the so-called bucky gel).<sup>13</sup> Probably the cross-links between the SWNTs are formed by the ILs ions which are merely attracted to the SWNTs because the latter ones are conductors.<sup>12</sup> The same reason may explain the fact that an addition of a small amount of SWNTs to a gel formed by a polymerizable IL leads to a dramatic enhancement of the gel Young’s modulus.<sup>14</sup> The other interesting object created by using SWNTs and ILs is an actuator<sup>15</sup> which is a thin film consisting of three layers. The central layer is a polymer gel impregnated with an IL. The two

surface layers comprise the same components and a dispersion of SWNTs in addition. If a voltage is applied to the surface layers (the electrodes) the actuator bends in the direction of the cathode.

Despite the diversity of the chemical structures of the ILs, it is obvious that there are some common properties inherent to the ILs. One of the main goals of researchers is to explain or predict such properties. It seems evident that the first most important peculiarity of ILs is that they consist of two types of particles (the ions) which can possess significantly different properties but cannot segregate because of the electrostatic attraction. By employing this fact, we have proposed an explanation of ILs high solvent power.<sup>16</sup> In a subsequent publication,<sup>17</sup> we have shown that if affinities of an IL’s cations and anions to nonionic liquid molecules are different, then an electric double layer is to appear at the boundary of the two liquids. Such a double layer has been observed.<sup>18</sup> Moreover, we have demonstrated<sup>17,19</sup> that if the difference of the affinities is high enough, then a microheterogeneous structure is to be formed in the mixture of the IL and the nonionic liquid. Formation of such a microheterogeneous structure has been also predicted by means of computer simulation<sup>20</sup> and observed.<sup>21,22</sup>

In the present paper we extend the idea of our previous works<sup>17,19</sup> for the case when a finite-size network of covalently bound polymer chains acts as the second component in a binary system comprising an IL.

As a matter of fact, a number of investigations concerning the behavior of macroscopic polymer gels in ILs have been already carried out.<sup>23–25</sup> It has been experimentally demonstrated that solutions of polymers in ILs as well as in other solvents can show UCST- as well as LCST-type behavior.<sup>24,25</sup> Respectively, the polymer gels can undergo in ILs reversible discontinuous volume phase transitions.<sup>25</sup> They can either shrink or swell with the increase of temperature.

The UCST polymer–IL solution behavior and, respectively, the swelling of the polymer network in the IL with the increase of temperature is, so to say, the “classical behavior”. Such a behavior of polymers is normally observed in common organic solvents, and it can be explained by interplay of the entropic

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elasticity of the polymers and volume interactions of monomer units within the simplest lattice Flory–Huggins type approach.

The LCST polymer–IL solution behavior and, respectively, the shrinking of the polymer network in the IL with the increase of temperature is, so to say, an atypical behavior. It is observed in water solutions and is attributed to the formation of water molecules network induced by the hydrogen bonding.<sup>24</sup> It is very interesting and promising that ILs can also show this “water-like” behavior.

Anyway, neither the reversible swelling nor the reversible collapse of polymer networks in ILs with the increase of temperature are new in science, since these phenomena have been observed in other nonionic solvents and have been explained already long ago.<sup>26–31,35</sup>

The real novelty of polymer networks impregnated with ILs lies in the fact that ILs are stable, and, first of all, they are almost nonvolatile. This means that the gels are environmentally stable. Hence, a new generation of stable in open atmosphere smart gel materials can be created on basis of them (the serious drawback of conventional smart gel materials is the solvent evaporation<sup>25</sup>). The other innovation related with polymer/IL gels are the so-called “ion gels”.<sup>23,25</sup> That is, if the IL and the polymer covalently bound network are well compatible, the gel can be effectively used as an ion-conducting electrolyte. Moreover, its conductivity can turn out to be higher than that of a pure IL due to the fact that interactions of the IL and the polymer network prohibit formation in the IL of neutral ion clusters.<sup>23,25</sup>

In the present paper we consider the simple case when a covalently bound finite size network of *uncharged* polymer chains swells in IL with the increase of temperature. We use the standard methodology based on the Flory–Huggins-type lattice approach. The novelty of our study lies in the fact that we show that the state of the gel particle (collapsed or swollen) can depend not only on the temperature but *also on the size* of the particle (in other words, on the total number of monomer units it consists of). We demonstrate that this becomes possible if two conditions are fulfilled. First, the solvent is composed of ions, and the oppositely charged ions have different affinities to the polymer network of the gel. Second, the whole volume of the gel particle is equipotential. The latter condition is provided by the presence of SWNTs within the gel. Thus, we predict a new phenomenon related with the interplay of ILs and SWNTs. The only property of SWNTs used in our modeling is the fact that they are very thin and conducting.

## Model

The IL is treated as a “two-component” mixture including anions and cations which move independently. Thus, our approach is different from the one used in refs 32 and 33 where cation and anion of an IL are treated as a single molecular entity. For the sake of simplicity, it is assumed that the cations and the anions are spheres of the same diameter  $a$ . It is also supposed for simplicity that the cations and the anions do not form ion pairs, clusters, networks produced by hydrogen bonding, etc.

The behavior of a single microscopic gel particle immersed in an IL (let us term it for short in the following text just as “gel”) with embedded SWNTs is investigated. To be more precise, the gel is composed of an IL, an uncharged polymer chain, and carbon nanotubes. The IL plays the role of the solvent and occupies the major part of the gel volume (if the latter one is in the swollen state). The major part of the rest of the gel’s volume is occupied by the uncharged polymer chains that form a covalently bound network. This polymer chains network

provides the structural integrity and the elasticity of the gel. SWNTs are the minor (but very important) component of the gel. They are just admixed to the gel and are not obligatory, somehow (chemically or via ions<sup>13</sup>) attached to each other or to the polymer chains. Even if they are not attached to the polymer network, they cannot diffuse from it in the outer solution because they are very long. It is supposed that the SWNTs are distributed uniformly over the gel volume and that they are arbitrarily oriented. On the one hand, the concentration of SWNTs in the gel is supposed to be high enough, so that they form a percolation cluster, and the whole volume of the gel can be considered as an equipotential one. On the other hand, the concentration of SWNTs has to be small enough to provide their arbitrary orientation. To fulfill these conditions, the volume fraction of the SWNTs in the microgel,  $\Phi_{\text{SWNT}}$ , has to satisfy inequalities  $d^2/L^2 < \Phi_{\text{SWNT}} < d/L$ , where each tube is approximated by a rod of the diameter  $d$  and the length  $L$ . These inequalities mean that  $\Phi_{\text{SWNT}}$  has to be larger than the overlap volume fraction of the rods but smaller than the value for the nematic ordering of the rods.<sup>34</sup> Immobilization of the SWNTs in the microgel is possible if their length exceeds the mesh size of the network  $R, L \gg R$ : the longer the SWNTs, the lower their mobility within the microgel. Maximum value of the mesh size  $R \sim aN^{3/5}$  is attained in the swollen state. Here  $N$  is the number of segments in the subchain of the network, each segment of the size  $a$ . Thus, the polymer volume fraction in the swollen state  $\Phi_{\text{gel}} \sim a^3 N/R^3 \sim 1/N^{4/5}$  is always much larger than  $\Phi_{\text{SWNT}}$ ,  $\Phi_{\text{gel}} \sim (a/R)^{4/3} \gg (d/L)^{4/3} \geq \Phi_{\text{SWNT}} > (d/L)^2$ . So, the interpenetrating polymer network and the percolation cluster of SWNTs can be treated as just the whole network of the gel (let us term it for short in the following text just as “gel network”), in which the polymer is responsible for the elasticity and for van der Waals interactions with the IL’s ions and the SWNTs provide the conductivity.

The elastic free energy of the microgel  $F^{\text{el}}$  can be quantified by the simplest expression<sup>35</sup>

$$\frac{F^{\text{el}}}{kT} = \frac{3}{2}M\left((\alpha)^2 + \left(\frac{1}{\alpha}\right)^2\right) \quad (1)$$

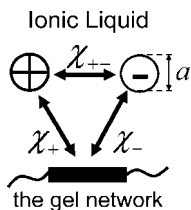
where  $M$  is the total number of the gel subchains and  $\alpha$  is the gel swelling ratio which relates the polymer volume fraction in the swollen gel,  $\Phi_{\text{gel}}$ , with the fraction in the gel in the reference state,  $\Phi_{\text{gel}}^0$ , in the following way:

$$\Phi_{\text{gel}} = \Phi_{\text{gel}}^0/\alpha^3 \quad (2)$$

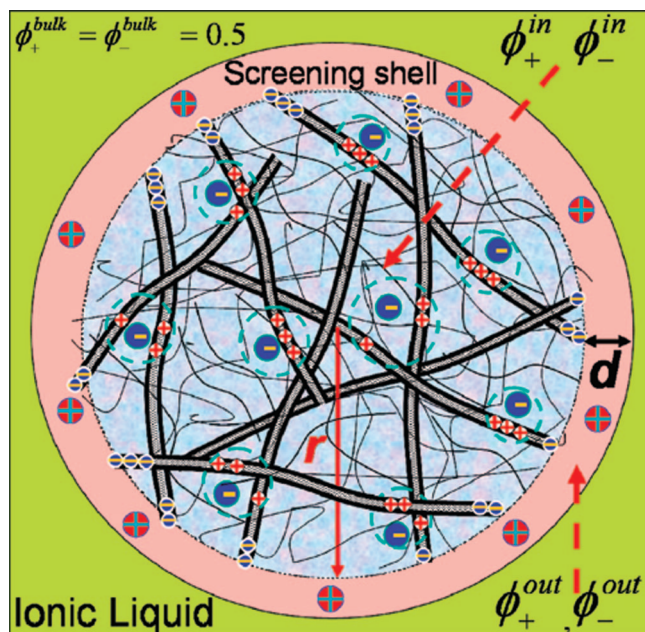
The reference state of the gel is determined as the state in which the gel’s subchains have the Gaussian size.

Let us introduce the Flory–Huggins parameters  $\chi_{+-}$ ,  $\chi_{+}$ , and  $\chi_{-}$  which characterize the van der Waals interactions of the cations with the anions, of the cations with the gel network, and of the anions with the gel network, respectively. The meaning of these parameters is represented schematically in the Figure 1. Let us also introduce the parameters  $\tilde{\chi} = \chi - \chi_{+-}/4$  and  $\chi = (\chi_{+} + \chi_{-})/2$ .

It is supposed for definiteness that the affinity of the anions to the gel network is higher than the affinity of the cations, i.e.,  $\chi_{+} > \chi_{-}$ . As a consequence, because the anions are attracted stronger to the gel network than the cations, the concentration of the anions inside the gel turns out to be a bit higher than the concentration of the cations; i.e., a number of uncompensated anions appear inside the gel. It has to be noticed that in our



**Figure 1.** Schematic diagram representing parameters used for description of the van der Waals interactions in the system.



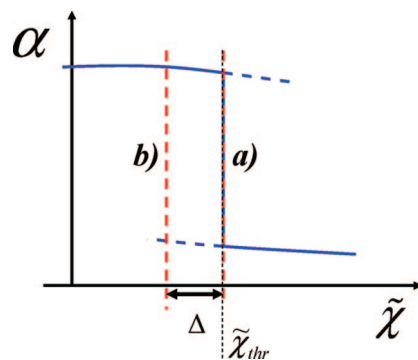
**Figure 2.** Schematic illustration of the considered model of the microgel with immobilized SWNTs immersed in an IL. The thin black curves represent the polymer network of the gel. The thick lines represent the SWNTs. Uncompensated ions of the IL are represented by larger circles with the corresponding sign. The smaller circles with the corresponding sign represent the charge induced on the SWNTs.

model cations and anions are interchangeable and the condition  $\chi_{+} < \chi_{-}$  would mean an existence of excess cations within the gel.

An electrostatic field cannot appear in the volume of a conducting network. Therefore, each of the uncompensated anions is screened by the charge induced on the network. Hence, the uncompensated anions do not repel each other and for this reason they are spread uniformly over the gel. The charge opposite to this screening charge is distributed over the nanotubes tips at the surface of the gel. The charge of the gel is equal to the total charge of the uncompensated anions inside it.

The charge produced by the uncompensated anions of the gel is screened by a shell containing uncompensated cations. It is supposed that the uncompensated cations are spread uniformly over the screening envelope (shell) of the gel. Total charge of the gel and the shell is equal to zero. The boundaries between the gel and the shell and between the shell and the outer solution (pure IL) are sharp. In the outer solution cations and anions are compensated and their volume fractions are equal.

The model of the system is presented schematically in Figure 2. The uncompensated cations and anions are represented by spheres (large ones) marked with the corresponding signs. The compensated ions are not illustrated. The charges induced on the network of carbon nanotubes are represented by the small spheres marked with the corresponding signs.



**Figure 3.** Dependence of the swelling ratio  $\alpha$  of a microgel with immobilized carbon nanotubes immersed in an IL on its affinity to the IL as a whole characterized by the parameter  $\tilde{\chi}$  (a) in the hypothetical case when the cations and the anions of the IL cannot segregate and (b) in the case when the cations and the anions are segregated.

Let us briefly set out the main idea of the predicted phenomenon. Hypothetically, if concentrations of the cations and the anions in all the points of the system were always same, then the uncharged gel would behave in the IL as in a normal one-component solvent<sup>35</sup> interaction of which with the gel network is characterized by the parameter  $\tilde{\chi}$ . If the subchains of the gel are stiff enough, then the dependence of the gel swelling ratio  $\alpha$  on the parameter  $\tilde{\chi}$  would be like the one presented in the Figure 3 (curve *a*). When  $\tilde{\chi}$  exceeds some certain threshold value  $\tilde{\chi}_{thr}$ , the gel collapses. This dependence would be valid for any sample of the gel independently of the number of subchains it consists of.

But in reality, if the anions of an IL have a higher affinity to the gel network than the cations, the concentrations of the cations and of the anions are different in the gel. As a result, the free energy is less than in the case of equal concentrations. The higher the density of the gel network inside the gel is, the stronger is the violation of the concentrations equality and the larger is the decrease of the free energy as compared to the case of equal concentrations. Thus, the collapsed state happens to be more energetically favorable. This means that the value of the parameter  $\tilde{\chi}$ , at which in reality the collapsed and the swollen states of the gel are in equilibrium, is less by a value  $\Delta$  than  $\tilde{\chi}_{thr}$  (see Figure 3, curve *b*).

Segregation of the cations and the anions is opposed by electrostatic field appearing in the screening shell of the gel. The decrease of the total system free energy with the increase of the anions concentration inside the gel is due to the decrease of the part of the free energy corresponding to the contact van der Waals interactions. The latter decrease is roughly proportional to the concentration of the uncompensated anions inside the gel and to the volume of the gel. On the other hand, if the concentration of the uncompensated anions inside the gel is fixed, the energy of the electrostatic field of the screening shell per unit volume of the gel grows with the growth of the volume. Hence, the larger the gel particle is, the stronger is the influence of the electrostatic field, and the less is the equilibrium concentration of uncompensated anions inside the particle.

This means that the larger the number of subchains in a gel is, the smaller is the shift  $\Delta$  of the  $\tilde{\chi}$  threshold value from the value  $\tilde{\chi}_{thr}$  corresponding to the case of a normal one-component solvent. If the gel is very large then the electrostatic field completely prevents any segregation of oppositely charged ions inside the gel, and the gel behaves in the IL as in a normal one-component solvent, i.e.,  $\Delta = 0$ . One more interesting fact follows from the foregoing speculations. If  $\tilde{\chi}$  is a bit less than



$\tilde{\chi}_{\text{thr}}$  then the state of the gel can depend on the number of subchains it consists of. That is, a gel composed of a smaller number of subchains can be in the collapsed state in the IL while a gel composed of a larger number of subchains is in the swollen state.

Now let us present the idea in a more rigorous way. In the considered model the system consists of, so to say, three zones: the gel, the screening shell, and the outer solution (see Figure 2). The zones are spatially homogeneous. The free energy  $F^{\text{tot}}$  of the system consists of the electrostatic field energy  $F^{\text{el-st}}$ , the entropic contribution  $F^{\text{ent}}$ , the contribution  $F^{\text{int}}$  caused by Van der Waals interactions, the surface energy  $F^{\text{surf}}$ , and the elastic free energy  $F^{\text{el}}$  (see eq 1).

Uncompensated electrostatic charge is formed at the surface of the gel and in the screening shell (see Figure 2). With relation to the electrostatics, the system can be approximated as a charged sphere of the radius  $r$  (the radius of the gel) with uniformly distributed surface charge which is surrounded by an oppositely uniformly charged spherical shell (the screening shell of the gel) having the thickness  $d$ . The energy of the electrostatic field of such a system has a standard form:

$$\frac{F^{\text{el-st}}}{kT} = q^2 u \frac{a}{2r} \frac{\omega^6}{(\omega^3 - 1)^2} \left[ 1 - \frac{1}{\omega} + \frac{1}{5} \frac{\omega^5 - 1}{\omega^6} - \frac{\omega^2 - 1}{\omega^3} \right] \quad (3)$$

where  $\omega$  is the ratio of the outer shell radius to the gel radius,  $\omega = (r + d)/r$ ,  $q$  is dimensionless total charge of the gel measured in units of the elementary charge  $e$ , and the dimensionless parameter  $u = e^2/kT\epsilon a$  is the ratio of the absolute value of the electrostatic interaction energy of two neighboring ions to the thermal energy ( $\epsilon$  is the dielectric constant of the IL). The charge  $q$  of the gel can be expressed via the volume fraction of uncompensated anions inside the gel  $\Phi$ :

$$q = \frac{4}{3} \pi \Phi \frac{r^3}{a^3} \quad (4)$$

The entropic contribution to the free energy is caused by translational motion of the cations and the anions. In the framework of the lattice model, it takes the form:

$$\frac{F^{\text{ent}} a^3}{kT} = \frac{4}{3} \pi r^3 (\phi_+^{\text{in}} \ln \phi_+^{\text{in}} + \phi_-^{\text{in}} \ln \phi_-^{\text{in}}) + \frac{4}{3} \pi r^3 (\omega^3 - 1) \times (\phi_+^{\text{out}} \ln \phi_+^{\text{out}} + \phi_-^{\text{out}} \ln \phi_-^{\text{out}}) - \left( V - \frac{4}{3} \pi r^3 \omega^3 \right) \ln 2 \quad (5)$$

where the three terms correspond to the translational motion of the ions within the gel, the screening shell, and the outer solution, respectively. Here  $V$  is the volume of the system which is considered to be fixed. The multiplier  $\ln 2$  in the last term of eq 5 means that the volume fractions of the cations and the anions in the outer solution are equal to 0.5.  $\phi_+^{\text{in}}$ ,  $\phi_-^{\text{in}}$  and  $\phi_+^{\text{out}}$ ,  $\phi_-^{\text{out}}$  are the volume fractions of the cations and of the anions in the gel and in the shell, respectively, which have different values due to the local violation of the electric neutrality. They are connected with the variables  $\Phi$  and  $\omega$  via the following equations:

$$\begin{aligned} \phi_+^{\text{in}} &= (1 - \Phi_{\text{gel}} - \Phi)/2; & \phi_-^{\text{in}} &= (1 - \Phi_{\text{gel}} + \Phi)/2 \\ \phi_+^{\text{out}} &= \frac{1}{2} + \frac{\Phi}{2(\omega^3 - 1)}; & \phi_-^{\text{out}} &= \frac{1}{2} - \frac{\Phi}{2(\omega^3 - 1)} \end{aligned} \quad (6)$$

In a similar way, the contribution of the van der Waals interactions is expressed as

$$\begin{aligned} \frac{F^{\text{int}} a^3}{kT} &= \frac{4}{3} \pi r^3 (\chi_{+-} \phi_+^{\text{in}} \phi_-^{\text{in}} + \chi_{+-} \phi_+^{\text{in}} \Phi_{\text{gel}} + \chi_{+-} \phi_-^{\text{in}} \Phi_{\text{gel}}) + \\ &\frac{4}{3} \pi r^3 (\omega^3 - 1) \chi_{+-} \phi_+^{\text{out}} \phi_-^{\text{out}} + \left( V - \frac{4}{3} \pi r^3 \omega^3 \right) \chi_{+-} / 4 \end{aligned} \quad (7)$$

It has to be noticed that the excluded volume of each segment of the gel is assumed to be equal to  $a^3$ .

The last contribution to the total free energy is the surface free energy  $F^{\text{surf}}$ . In our model, we deal with two interfaces: (i) between the gel and the screening shell and (ii) between the shell and the outer solution. The interfaces are supposed to be very narrow, and the corresponding surface energy is described by the following expression derivation of which is presented in Appendix 1.

$$\begin{aligned} \frac{F^{\text{surf}}}{kT} &= \frac{2\pi r^2}{3a^2} [\chi_{+-} \Phi_{\text{gel}} (\phi_+^{\text{out}} - \phi_+^{\text{in}}) + \chi_{+-} \Phi_{\text{gel}} (\phi_-^{\text{out}} - \phi_-^{\text{in}}) + \\ &\chi_{+-} (\phi_+^{\text{in}} \phi_-^{\text{out}} + \phi_-^{\text{in}} \phi_+^{\text{out}} - \phi_+^{\text{out}} \phi_-^{\text{out}} - \phi_-^{\text{in}} \phi_+^{\text{in}}) + \\ &\omega^2 \chi_{+-} (0.25 - \phi_+^{\text{out}} \phi_-^{\text{out}})] \end{aligned} \quad (8)$$

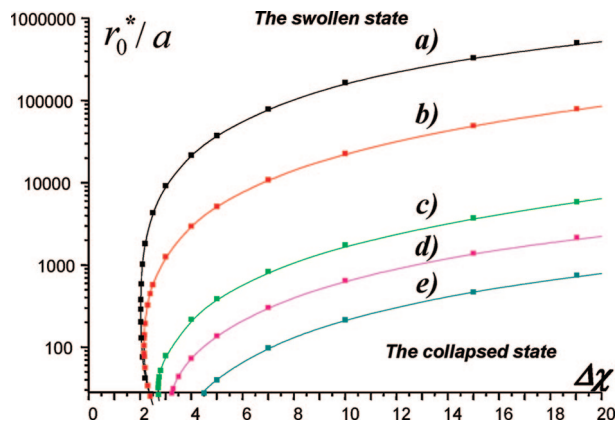
The parameters characterizing the system are  $\Phi_{\text{gel}}^0$  (see eq 2),  $u$  (see eq 3),  $\tilde{\chi}$ ,  $\chi_{+-}$ ,  $\Delta\chi$ ,  $r_0/a$ , and  $N$ . The parameter  $\Delta\chi = (\chi_+ - \chi_-)/2$  represents the difference in affinities of the IL's anions and the IL's cations to the network of the gel.  $N$  is the number of effective monomer units in the gel's subchain.  $r_0/a$  is the dimensionless radius of the microgel when it is in the reference state. Let us denote shortly the value  $r_0$  as *reference-state radius*. This parameter determines in our model the size of the gel. It is connected with the number  $M$  of subchains the gel consists of via the following expression:

$$r_0/a = (3MN/4\pi\Phi_{\text{gel}}^0)^{1/3} \quad (9)$$

At the given set of the parameters values, the equilibrium values of the variables  $\alpha$ ,  $\Phi$ , and  $\omega$  determining the state of the system are calculated via numerical minimization of the free energy  $F^{\text{tot}}$ . In the course of the calculations, it has been taken into account that the minimal possible thickness  $d$  of the screening shell is equal to the size of an ion  $a$ . Otherwise, it would obviously have no physical meaning. For the sake of simplicity, the parameter  $\chi_{+-}$  is supposed to be equal to zero.

## Results and Discussion

Results of our calculations are presented in Figure 4. Let us explain its meaning. As has been already mentioned, a gel composed of a smaller number  $M$  of subchains (and hence having smaller reference-state radius  $r_0$ ) can be in the collapsed state in an IL while a gel of the same composition having a larger  $M$  is in the swollen state in the same IL. Thus, there exists the threshold value  $r_0^*$  of the reference-state radius demarcating the smaller gels that are to collapse and the larger gels that are to be swollen in the IL. Figure 4 represents the dependence of



**Figure 4.** Dependence of the threshold value  $r_0^*$  of the reference-state radius of the gel on the parameter  $\Delta\chi$  which describes difference in affinities of the IL's anions and the IL's cations to the gel network.  $\Phi_{\text{gel}}^0 = 0.003$ ,  $Nv/a^3 = 100$ ,  $u = 1$ ,  $\chi_{+-} = 0$ ,  $\tilde{\chi}_{\text{thr}} = 1.45964$ . (a)  $\Delta = 6.4 \times 10^{-4}$ ; (b)  $\Delta = 4.6 \times 10^{-3}$ ; (c)  $\Delta = 6.0 \times 10^{-2}$ ; (d)  $\Delta = 0.16$ ; (e)  $\Delta = 0.46$ . In the case considered, the number of the gel's subchains,  $M$ , is equal to 1 at  $r_0 = 20a$ . If at the given value of  $\Delta$  a point is under the corresponding curve the corresponding to the point microgel is in the collapsed state. If the point is over the curve the microgel is in the swollen state.

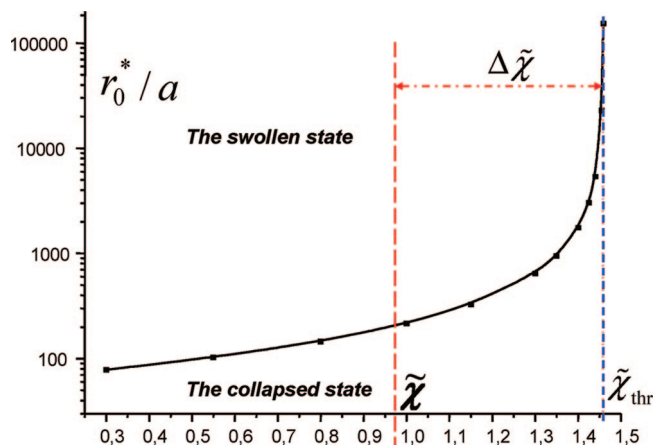
the threshold value  $r_0^*$  on the parameter  $\Delta\chi$ . Different curves correspond to the different values of  $\Delta$ . In other words, Figure 4 is a phase diagram in the coordinates  $(\Delta\chi, r_0)$  which has the following physical meaning. Let us take for example the value of  $\Delta$  equal to 0.06. If a point on the phase diagram is located below the curve c, then the gel having the corresponding reference-state radius  $r_0$  will be in the collapsed state in the IL, if the difference in affinities of its cations and anions to the gel network is characterized by the corresponding value  $\Delta\chi$ . If the point is above the curve, then the gel will be in the swollen state in this IL. It follows from the Figure 4 that if a synthesized sample of the gel is ground down and the obtained dispersion is immersed in an IL, it is possible that the smaller gel particles will collapse and the larger ones will be in the swollen state.

One can see in the figure that the higher  $\Delta\chi$  is, the larger is the value  $r_0^*$ , i.e., the larger is the maximal size of a collapsed gel. The maximal size of a collapsed gel also increases when  $\tilde{\chi}$  approaches the value  $\tilde{\chi}_{\text{thr}}$  corresponding to the collapse transition of the gel in a normal one-component solvent.

From Figure 4, it becomes evident why the word “microgel” and not just a “gel” appears in the title of the paper. The radius of the gel is measured in units of diameter  $a$  of an ion. Since the average size of IL's ions is large enough, it can be supposed that  $a$  is of order of 1 nm. One can see then in Figure 4 that a normal value of  $r_0^*$  is of the order of 1  $\mu\text{m}$ . Therefore, the predicted phenomenon most probably can be observed for small microgel particles.

However, if  $\tilde{\chi}$  is very close to  $\tilde{\chi}_{\text{thr}}$  the threshold value  $r_0^*$  of the gel reference-state radius can be rather large. For example, in the case represented by the curve a it reaches 1 mm. In theory, if  $\tilde{\chi}$  tends to  $\tilde{\chi}_{\text{thr}}$ , the maximal size of a collapsed gel tends to infinity. Let us also note that the minimal reference-state radius of the gel that has physical meaning is the one at which the gel consists of only single subchain. For the case presented in Figure 4, this radius is equal to  $20a$ .

Figure 5 represents the dependence of threshold value  $r_0^*$  of the gel reference-state radius on  $\tilde{\chi}$  at a fixed value of  $\Delta\chi$ . Actually, the figure repeats the data presented in Figure 4. In Figure 5 one can see again that when  $\tilde{\chi}$  approaches the value  $\tilde{\chi}_{\text{thr}}$ ,  $r_0^*$  grows. It can be seen that it grows asymptotically.



**Figure 5.** Dependence of the threshold value  $r_0^*$  of the reference-state radius of the gel on the parameter  $\tilde{\chi}$ .  $\Delta\chi = 10$ ,  $\Phi_{\text{gel}}^0 = 0.003$ ,  $Nv/a^3 = 100$ ,  $u = 1$ ,  $\chi_{+-} = 0$ ,  $\tilde{\chi}_{\text{thr}} = 1.45964$ . In the case considered, the number  $M$  of the gel's subchains is equal to 1 at  $r_0 = 20a$ . If a point is under the curve the corresponding to the point microgel is in the collapsed state. If the point is over the curve the microgel is in the swollen state.

**TABLE 1**

| $\Delta\chi$ | $r_0^*\Delta/a$ |            |
|--------------|-----------------|------------|
|              | numerical       | analytical |
| 5            | 20              | 21.8       |
| 10           | 100             | 111        |
| 20           | 350             | 398        |

It has been noticed that for a fixed value of  $\Delta\chi$  the product  $r_0^*\Delta$  is approximately constant. We have also explained why it happens so by means of analytical calculations; see Appendix 2. The average values of the product  $r_0^*\Delta$  obtained numerically for three different values of  $\Delta\chi$  and the corresponding values obtained analytically (see eq A2.13) are presented in the Table 1.

## Conclusions

We developed a theory of swelling of a microgel with immobilized SWNTs in an IL. The cations and anions of the IL were supposed to have different affinities to the gel network. The difference in affinities leads to the segregation of the cations and the anions inside the gel and appearance of uncompensated ions therein. The conducting network formed by SWNTs screens the charge of each uncompensated ion inside the gel and thus does not allow the uncompensated ions to repel each other and concentrate near the surface of the gel. Total charge of the gel is screened by a shell saturated with uncompensated ions charged oppositely. Violation of the cations and anions concentrations equality leads to the shift of the system's free energy and as a result it turns out that the swelling ratio of the gel can depend on its size.

If the affinity of the IL as a whole to the network of the gel is a bit higher than the affinity of a one-component solvent to the network of the gel at which the gel would collapse, then a smaller gel is in the collapsed state in this IL and a larger gel is in the swollen state in this IL. Maximal size of a collapsed gel increases with increase of the difference in the affinities of the IL's anions and cations to the network of the gel. Maximal radius of a collapsed gel grows asymptotically as the affinity of the IL as a whole to the network of the gel approaches the value at which the gel would collapse in a normal one-component solvent.

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## Appendix 1

Let us suppose that there are two neighboring volumes of mixtures (two phases), each consisting of the same  $N$  different enumerated components volume fractions of which in the two phases are equal to  $\phi_1^i$  and  $\phi_2^i$ , correspondingly. Let us suppose that the boundary between the phases is infinitely thin. Let us imagine that the whole volume of the system is divided into elementary cells and each of them contains one molecule of a component. Thus, it is supposed that molecules of all the components have the same size. Let us denote as  $J^{ij}$  the interaction energy of two adjacent cells in the case if the molecules of the components  $i$  and  $j$  are located inside these cells. Let us suppose that the interface is flat and  $S$  is its area.

The energy of interaction of adjacent cells belonging to the two different phases, i.e., the energy of contacts within the interface, is equal to

$$E_{pq} = \frac{S}{a^2} \sum_{i=1}^N \sum_{j=1}^N J^{ij} \phi_p^i \phi_q^j \quad (\text{A1.1})$$

where  $p \equiv 1$  and  $q \equiv 2$ . The contact of the two different mixtures can be produced, for example, in the following way. Two volumes of the two different mixtures are divided by a plane in two parts each. After that the two parts of the first type are brought in contact with the two parts of the second type. This means that with emerging of the contact between the two different mixtures two other contacts between similar mixtures disappear. The area of each of the disappeared contacts is 2 times less than the area of the appeared contact. Hence, the energy of the phase boundary is

$$E_{\text{surf}} = E_{pq}|_{p=1, q=2} - \frac{1}{2}E_{pq}|_{p=1, q=1} - \frac{1}{2}E_{pq}|_{p=2, q=2} \quad (\text{A1.2})$$

Let us introduce the following substitutions for all the pairs of molecules of the types E and F (E, F = A, B, or C):

$$\chi_{\text{EF}} = 6 \left( J^{\text{EF}} - \frac{J^{\text{EE}} + J^{\text{FF}}}{2} \right) / kT \quad (\text{A1.3})$$

where  $\chi_{\text{EF}}$  is the Flory–Huggins parameter characterizing the van der Waals interaction of the two molecules of the types E and F. With the help of eq A1.3 the expression A1.2 can be transformed into the following one:

$$\frac{F_{\text{surf}}}{kT} = \frac{S}{6a^2} \sum_{i=1}^N \sum_{j=1}^N \chi_{ij} \left( \phi_1^i \phi_2^j - \frac{1}{2} \phi_1^i \phi_1^j - \frac{1}{2} \phi_2^i \phi_2^j \right) \quad (\text{A1.4})$$

By using eq A1.4 one can obtain eq 8.

## Appendix 2

The gel is considered to be close to the collapse–swelling transition. In fact the swelling ratio of the gel in the swollen state is close to the one the gel would have in the swollen state if the parameter  $\Delta\chi$  were equal to zero. Same concerns the swelling ratio of the gel in its collapsed state. In other words, segregation of the cations and the anions inside the gel shifts the value of  $\tilde{\chi}$  at which the transition of the gel between the collapsed and the swollen states takes place, but it does not change significantly the swelling ratios of the gel in the two states.

Therefore, it can be roughly supposed that the two values  $\alpha_{\text{col}}$  and  $\alpha_{\text{sw}}$  of the gel swelling ratio in the collapsed and the swollen states, correspondingly, are just equal to the ones the gel would have if  $\Delta\chi = 0$ . In the swollen state the concentration of uncompensated anions inside the gel as well as the caused by it change of the system's free energy is much less than in the collapsed state, since the concentration of the gel chains inside the gel is much less in the swollen state than in the collapsed state. That is why let us take into account only the break in the cations and the anions concentrations equality in the collapsed state.

If  $\Delta\chi = 0$  and  $\tilde{\chi} = \tilde{\chi}_{\text{thr}}$ , then the free energies corresponding to the collapsed and the swollen states of the gel are equal. If the parameter  $\tilde{\chi}$  is decreased by  $\Delta$ , then due to the change of the energies of van der Waals interactions the free energy of the swollen state becomes less than the free energy of the collapsed state by

$$\frac{\Delta F^{\text{normal}}}{kT} = \frac{4\pi r_0^3 \Delta}{3a^3} \Phi_{\text{gel}} \left( \frac{\Phi_{\text{gel}}^0}{\alpha_{\text{col}}^3} - \frac{\Phi_{\text{gel}}^0}{\alpha_{\text{sw}}^3} \right) = \frac{4\pi r_0^3 \Delta}{3a^3} (\Phi_{\text{gel}}^0)^2 \left( \frac{1}{\alpha_{\text{col}}^3} - \frac{1}{\alpha_{\text{sw}}^3} \right) \quad (\text{A2.1})$$

In fact, change of  $\tilde{\chi}$  leads to changes of the swelling ratios of the gel in the collapsed and in the swollen states. This, in its turn causes an extra additive to the difference of the free energies in the two states. But it can be shown that the latter one is negligible as compared to the contribution (A2.1).

If the parameter  $\Delta\chi$  becomes larger than zero, then uncompensated anions appear in a collapsed gel (for a swollen gel we do not take this into account) which also leads to the change in its free energy. That is, the energy of van der Waals interactions inside the gel decreases by

$$\frac{\Delta F^{\text{int}}}{kT} = \Phi_{\text{gel}}^0 \frac{4}{3} \pi \frac{r_0^3}{a^3} \Phi \Delta\chi \quad (\text{A2.2})$$

The equivalence of the product  $r_0^* \Delta$  to a constant value is best fulfilled at large values of  $r_0^*$  and, therefore, this case is considered. At large values of  $r_0^*$  the thickness of the screening shell is larger than  $a$ . In this case, the value of  $\omega$  is almost equal to the minimal value  $(1 + \Phi)^{1/3}$  at which the shell is composed of cations only. Let us prove it by means of finding the equilibrium value of  $\omega$  corresponding to some fixed values of  $\alpha$  and  $\Phi$ . Let us suppose that

$$\omega = 1 + p \equiv 1 + \frac{1}{3}\Phi + p_1 \quad (\text{A2.3})$$

where  $p_1$  is a value that is much less than  $\Phi$ . Later on, we will prove that. As our numerical calculations have shown the volume fraction  $\Phi$  of the uncompensated anions inside the gel is small and hence  $p$  is small. Therefore, the energy of the electrostatic field can be expanded into a series of the value  $p$  powers and only the highest order term can be left:

$$\frac{F^{\text{el-st}}}{kT} = \frac{8}{27}\pi^2 \frac{r^5}{a^5} u \Phi^2 p \quad (\text{A2.4})$$

Taking into account that  $\Phi$  is small and  $p_1$  is much smaller than  $\Phi$ , one can obtain by means of an expansion that depending on  $p_1$  part of the free energy corresponding to the gel-shell interface is approximately equal to

$$\frac{\Delta F_{p_1}^{\text{surf}}}{kT} = -2\pi \frac{r^2}{a^2} \Delta \chi \Phi_{\text{gel}} \frac{1}{\Phi} p_1 \quad (\text{A2.5})$$

The last depending on the value of  $p_1$  part of the free energy is the one corresponding to the ions entropy in the shell. By means of the same procedure, one can obtain that it is approximately equal to

$$\frac{\Delta F^{\text{ent-shell}}}{kT} = 2\pi \frac{r^3}{a^3} p \frac{p_1}{\Phi} \left( \ln \left( \frac{3p_1}{2\Phi} \right) - 1 \right) \quad (\text{A2.6})$$

Finally, after taking the derivative over  $p_1$  of the sum of the expressions A2.4–A2.6 and equating it to zero one can obtain the equilibrium value of  $p_1$ :

$$\frac{p_1}{\Phi} = \frac{2}{3} \exp \left( \frac{\Delta \chi \Phi_{\text{gel}}}{\Phi r/a} - \frac{4}{27} \pi u \left( \frac{\Phi r}{a} \right)^2 \right) \quad (\text{A2.7})$$

The value expressed by the eq A2.7 is low for any considered set of parameters characterizing the system.

Since it can be supposed that  $\omega = (1 + \Phi)^{1/3}$ , the appearing due to ions segregation increase of the free energy entropic part corresponding to the zone occupied by the screening shell is equal to

$$\frac{\Delta F^{\text{ent-shell}}}{kT} = \frac{4}{3} \pi (\omega^3 - 1) \frac{r^3}{a^3} \ln 2 = \frac{4}{3} \pi \Phi \frac{r_0^3}{a^3} \alpha_{\text{col}}^3 \ln 2 \quad (\text{A2.8})$$

The volume fraction  $\Phi$  of the uncompensated anions inside the gel is small. Therefore, the eq A2.4 can be used for the description of the electrostatic field energy (by substituting  $p_1 = 0$ ).

By means of expanding into series of the value  $\Phi$  powers and leaving only the highest order term, one can obtain that the decrease of the entropic contribution to the free energy caused by translational motion of ions inside the gel is equal to

$$\frac{\Delta F^{\text{ent-gel}}}{kT} = \frac{2}{3} \pi \frac{r_0^3}{a^3} \alpha_{\text{col}}^3 \frac{\Phi^2}{1 - \Phi} \quad (\text{A2.9})$$

Since large values of  $r_0$  are considered, the contribution A2.9 is negligible as compared to the electrostatic contribution and

can be omitted. The last contribution to the change of the system free energy is the one corresponding to the interface between the gel and the shell:

$$\frac{\Delta F^{\text{surf}}}{kT} = \frac{2}{3} \pi \frac{r_0^2}{a^2} \Delta \chi \frac{\Phi_{\text{gel}}^0}{\alpha_{\text{col}}} \left( 1 + \Phi + \frac{\Phi_{\text{gel}}^0}{\alpha_{\text{col}}^3} \right) \quad (\text{A2.10})$$

If one now minimizes over  $\Phi$  composed of the contributions (A2.2), (A2.4), (A2.8), and (A2.10) to free energy corresponding to the collapsed state of the gel, one can obtain the following expression for the equilibrium value of  $\Phi$ :

$$\Phi^2 = \frac{9 \left( \Phi_{\text{gel}}^0 \Delta \chi \left[ 1 - \frac{1}{2r_0 \alpha_{\text{col}}} \right] - \alpha_{\text{col}}^3 \ln 2 \right)}{2\pi r_0^2 \alpha_{\text{col}}^5 u} \equiv \frac{C}{r_0^2} \quad (\text{A2.11})$$

In the expression A2.11 the value  $C$  has been introduced. In the considered case of large values of  $r_0$ , the term of the expression located in the square brackets and having  $r_0$  in the denominator can be omitted. Then,  $C$  does not depend on  $r_0$ .

After substituting this equilibrium value of  $\Phi$  into eqs A2.2, A2.4, A2.8, and A2.10 and taking into account eq A2.1, one can get the following expression describing the difference of the free energies corresponding to the collapsed and to the swollen states:

$$\begin{aligned} \frac{\Delta F}{kT} = & \frac{4\pi r_0^3 \Delta}{3a^3} (\Phi_{\text{gel}}^0)^2 \left( \frac{1}{\alpha_{\text{col}}^3} - \frac{1}{\alpha_{\text{sw}}^3} \right) + \frac{4\pi r_0^3 \sqrt{C}}{3a^3 r_0} (\alpha_{\text{col}}^3 \ln 2 - \\ & \Phi_{\text{gel}}^0 \Delta \chi) + \frac{8}{81} \pi^2 r_0^5 \alpha_{\text{col}}^5 u \frac{C \sqrt{C}}{r_0^3} + \frac{2}{3} \pi r_0^2 \Delta \chi \frac{\Phi_{\text{gel}}^0}{\alpha_{\text{col}}} \left( 1 + \frac{\sqrt{C}}{r_0} \right) \end{aligned} \quad (\text{A2.12})$$

Finally, after equating to zero this difference, one can obtain the expression connecting the value of the parameter  $\Delta$  and the maximal reference-state radius  $r_0^*$  of a collapsed gel:

$$r_0^* \Delta = \frac{\frac{4}{27} C \sqrt{C} \pi \alpha_{\text{col}}^5 u - \frac{\Delta \chi \Phi_{\text{gel}}^0}{2 \alpha_{\text{col}}}}{(\Phi_{\text{gel}}^0)^2 \left( \frac{1}{\alpha_{\text{col}}^3} - \frac{1}{\alpha_{\text{sw}}^3} \right)} \quad (\text{A2.13})$$

Thus, it has been proven that at fixed values of the parameters  $\Phi_{\text{gel}}^0$ ,  $u$ ,  $\tilde{\chi}$ ,  $\chi_{+-} = 0$ ,  $\Delta \chi$ , and  $Nv/a^3$  the product  $r_0^* \Delta$  is a constant at large values of  $r_0^*$ .

## References and Notes

- (1) Scheldon, R. *Chem. Commun.* **2001**, 2399.
- (2) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley VCH: New York, 2002.
- (3) Welton, T. *Chem. Rev.* **1999**, 99, 2071.
- (4) Wasserscheid, P.; Keim, W. *Angew. Chem., Int Ed.* **2000**, 39, 3772.
- (5) Earle, M. J.; Esperanca, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. *Nature* **2006**, 439, 831.
- (6) Ding, J.; Welton, T.; Armstrong, D. *Anal. Chem.* **2004**, 76, 6819.
- (7) Dupont, J.; Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, 102, 3667.



- (8) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.
- (9) Canongia Lopes, J. N.; Cordeiro, T. C.; Esperanca, J. M. S. S.; Guedes, H. J. R.; Huq, S.; Rebelo, L. P. N.; Seddon, K. R. *J. Phys. Chem. B* **2005**, *109*, 3519.
- (10) Greaves, T. L.; Drummond, C. J. *Chem. Rev.* **2008**, *108*, 206.
- (11) Zhao, H. *Chem. Eng. Commun.* **2006**, *193*, 1660.
- (12) Dekker, C. *Phys. Today* **1999**, *52*, 22.
- (13) Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Tagikawa, T.; Ishii, N.; Aida, T. *Science* **2003**, *300*, 2072.
- (14) Fukushima, T.; Kosaka, A.; Yamamoto, Y.; Aimiya, T.; Notazawa, S.; Tagikawa, T.; Inabe, T.; Aida, T. *Small* **2006**, *2*, 554.
- (15) Fukushima, T.; Asaka, K.; Kosaka, A.; Aida, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 2410.
- (16) Aerov, A. A.; Khokhlov, A. R.; Potemkin, I. I. *J. Phys. Chem. B* **2006**, *110*, 16205.
- (17) Aerov, A. A.; Khokhlov, A. R.; Potemkin, I. I. *J. Phys. Chem. B* **2007**, *111*, 3462.
- (18) Ishimatsu, R.; Shigematsu, F.; Hakuto, T.; Nishi, N.; Kakiuchi, T. *Langmuir* **2007**, *23*, 925.
- (19) Aerov, A. A.; Khokhlov, A. R.; Potemkin, I. I. *J. Phys. Chem. B* **2007**, *111*, 10189–10193.
- (20) Canongia Lopes, J. N. A.; Gomes, M. F. C.; Padua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 16816.
- (21) Deetlefs, M.; Hardacre, C.; Nieuwenhuyzen, M.; Sheppard, O.; Soper, A. K. *J. Phys. Chem. B* **2005**, *109*, 1593.
- (22) Blesic, M.; Marques, M. H.; Plechkova, N. V.; Seddon, K. R.; Rebelo, L. P. N.; Lopes, A. *Green Chem.* **2007**, *9*, 481.
- (23) Susan, A. B.H.; Kaneko, T.; Noda, A.; Watanabe, M. *J. Am. Chem. Soc.* **2005**, *127*, 4976.
- (24) Ueki, T.; Watanabe, M. *Langmuir* **2007**, *23*, 988.
- (25) Ueki, T.; Watanabe, M. *Macromolecules* **2008**, *41*, 3739.
- (26) Tanaka, T.; Fillmore, D. J. *J. Chem. Phys.* **1979**, *70*, 1214.
- (27) Hirotsu, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
- (28) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
- (29) Aimiya, T.; Tanaka, T. *Macromolecules* **1978**, *20*, 1162.
- (30) Vasilevskaya, V. V.; Aerov, A. A.; Khokhlov, A. R. *J. Chem. Phys.* **2004**, *120*, 9321.
- (31) Bodrova, A. S.; Potemkin, I. I. *Polym. Sci. Ser. A* **2007**, *49*, 737.
- (32) Najdanovic-Visak, V.; Esperanca, J. M. S. S.; Rebelo, L. P. N.; da Ponte, M. N.; Guedes, H. J. R.; Seddon, K. R.; de Sousa, H. C.; Szydlowski, J. *J. Phys. Chem. B* **2003**, *107*, 12797.
- (33) Rebelo, L. P. N.; Najdanovic-Visak, V.; Visak, Z. P.; da Ponte, M. N.; Szydlowski, J.; Cerdeirina, C. A.; Troncoso, J.; Romani, L.; Esperanca, J. M. S. S.; Guedes, H. J. R.; de Sousa, H. C. *Green Chem.* **2004**, *6*, 369.
- (34) Onsager, L. *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
- (35) Grosberg, A. Yu.; Khokhlov, A. R. *Statistical Physycs of Macromolecules*; AIP Press: New York, 1994.

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