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Review

Macromolecules in Ionic Liquids: Progress, Challenges, and Opportunities

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ABSTRACT: Ionic liquids (ILs) are ambient temperature molten salts and have attracted considerable attention because of their unique properties such as nonflammability, negligible volatility, high ionic conductivity, and thermal stability. Here, we show that the combinations of macromolecules with ILs as solvents and additives could offer new progress, challenges, and opportunities in polymer materials science. Compatible binary systems, where ILs are solidified (gelled) by polymers, can be used as ion-conducting polymer electrolytes (ion gels). The ion transport in ion gels is found to be decoupled from the segmental motion of the polymers, leading to relatively high ionic conductivities even at their glass transition temperatures. The flexibility of the molecular design of ILs allows us to prepare many new ILs having electrochemical functionalities such as proton, electron, and lithium ion transport. The new ILs and their ion gels appear to be promising candidates as new materials for electrochemical applications. In contrast, certain combinations of macromolecules in ILs exhibit lower or upper critical solution temperature type phase separation by changing the temperature, where the phase separation temperatures are easily altered by the change in the polymer and IL structures. Moreover, cross-linked polymer gels in the ILs show reversible volume phase transition. The volume phase transition of polymer gels in ILs could usher in a new era of environmentally stable and smart gels since the swelling/shrinking behavior can be observed reversibly in an open atmosphere without the need to consider solvent evaporation, which is a serious drawback of conventional smart gel materials.

Introduction

Here, we introduce and summarize important issues on the topic of macromolecules in ionic liquids (ILs) including our recent studies. ILs consist entirely of ions and have attracted considerable attention because of their unique properties such as nonflammability, negligible volatility, high ion conductivity, thermal and chemical stability, and so on.[1–5] ILs are versatile liquids that have recently been utilized in many researches concerned with macromolecules.[6–9] The major reports on ILs and polymers have dealt with the use of ILs for polymerization solvents, such as free radical polymerization,[10] radical copolymerization and the determination of monomer reactivity ratios,[11] atom transfer radical polymerization[12] (ATRP[13]), reverse ATRP,[14] group transfer polymerization,[15] polycondensation,[16] and ring-opening polymerization.[17] Also, ILs are currently being used as solvent or additives for macromolecules. Since ILs offer great flexibility in designing cationic and anionic structures and their combinations, one can in principle manipulate their properties as required; therefore, they have been termed the "designers solvent." For instance, if a proper combination of the ions is selected, ILs can be used as solvents for poorly soluble macromolecules. Different research groups have reported that ILs having strong hydrogen-bond-accepting anions such as chloride and acetate anions can easily dissolve cellulose; ILs are thus expected to find applications in the processing of cellulose materials.[18] On the basis of this concept, many studies have been conducted on the solubilization of poorly soluble biopolymers such as silk,[19] wool,[20] keratin,[20] and oligosaccharides[21] in ILs. Carbon nanotubes (CNTs), which have large

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cohesive energy density owing to their very large surface area as well as strong $\pi-\pi$ interaction, tend to form bundles and have low dispersibility in solvents.[22] Nevertheless, CNTs can be dispersed in ILs, leading to the formation of bucky gels,[23] which have high electronic and ionic conductivity; CNTs can be used as the electrodes of an electric double-layer capacitor[24] and actuator.[25,26]

The study on the compatibility of common polymers in ILs has also attracted attention. The estimation of the solubility parameter (SP) is of great importance for considering the solubility of polymers in ILs.[27–29] A systematic screening of the compatibility of polymers in ILs was first carried out by Winterton et al.[30] They used imidazolium-based ILs as a porogen for cross-linked polymer catalytic membranes on the basis of results of the phenomenological study on the compatibility of polymer−IL composites. They also reported the temporal phase stability of many polymer−IL combinations. Due to low T_g of ILs, Brazel et al. proposed to use ILs as thermally stable plasticizer for PMMA.[6,31] From the viewpoint of the practical applications of ILs in materials such as polymer electrolyte membranes, separation membranes, and catalyst supports, ILs may be used in solid or quasi-solid states. There are important studies to prepare such materials from polymerizable ILs[32] and to apply them to the practical use[33–35] described above. The solubilization of macromolecules in ILs has also been emphasized with a view to the solidification (or gelation) of ILs while retaining their useful and unique characteristics.

In this study, we particularly focus on research topics concerning binary systems consisting of synthetic polymers and ILs. One topic deals with compatible binary systems, where ILs are solidified (gelled) by polymers. These binary systems can be used as ion-conducting polymer electrolytes having possible applications in electrochemical devices. The characteristic charge transport behavior of polymer electrolytes is presented. The other topic deals with polymer−IL binary systems, which exhibit phase separations depending on external stimuli such as temperature and light. Because of the nonvolatility of ILs, such systems appear to be promising as smart wet materials, particularly smart gels, which are free from the evaporation of the solvent.

Polymer Electrolytes: Compatible System between Polymers and Ionic Liquids

New Polymer Electrolytes Containing Ionic Liquids. The research on the compatibility of polymers in ILs is possibly the first step toward the fabrication of polymer electrolytes containing ILs, while retaining their useful characteristics. If electrochemically useful properties are molecularly designed in ILs, polymer electrolytes can play an important role in electrochemical energy conversion or energy storage devices. Conventionally, efforts have been made for the development of polymer electrolytes[36–38] obtained by doping high-melting-temperature (T_m) salts (not ILs) into flexible polymers that are capable of ion coordination. Studies have typically been conducted on polyethers[39,42] and, in some cases, on siloxane[43] or phosphazene[44] backbone polymers with polyether side chains. The ionic carrier mobility of such polymer electrolytes decreases with an increase in the salt concentration since the glass transition temperatures (T_g) of the polymer electrolytes increase simultaneously. A lithium cation in a polymer electrolyte, for example, strongly interacts with electron-donating oxygen atoms in a polyether matrix by the Lewis acid−base interaction. This interaction between the doped lithium cation and the polyether functions as a transient cross-linking point, resulting in an increase in T_g. Consequently, the ionic conductivity of high-T_m, salt-doped polymer electrolytes decreases after reaching a maximum, although the number of carrier ions increases with an increase in the salt concentration.

The problem of decrease in the ionic conductivity can be overcome if the T_g values of polymer electrolytes do not increase upon salt doping. Low-T_m salts such as ILs or supercooled salts with low T_g have been employed for obtaining polymer electrolytes exhibiting high ionic conduc-

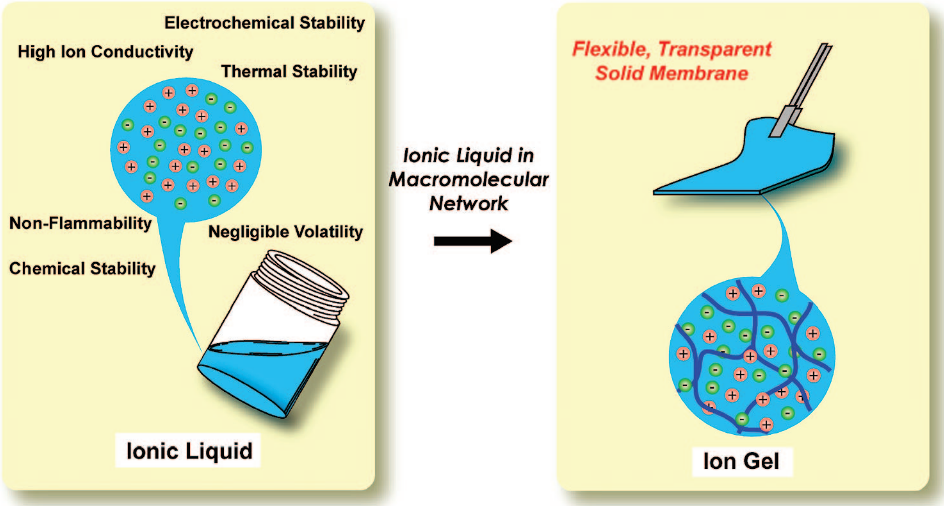

Figure 1. Preparation of ion gels (compatible binary systems between polymer networks and ionic liquids) by a variety of methods such as in situ radical polymerization of vinyl monomers in ionic liquids and sol–gel transition of macromolecules in ILs. The flexibility of molecular design of ionic liquids can facilitate various interesting applications of ion gels, particularly as ion-conducting polymer electrolytes.

tivity without increasing T_g by the salt doping.[45–47] Historically, studies on room temperature ILs started with using pyridinium or imidazolium salts with chloroaluminate anions, as reported by Wier et al. and Osteryoung et al., [47] although they were easily hydrolyzed by water. Polymer electrolytes containing room temperature ILs were first reported on such a system by our group.[10a] Successively, the study was expanded to polymer electrolytes containing chemically stable ILs.[10a,45,48] We found that common vinyl monomers were widely soluble in common ILs and that they could be polymerized by free-radical polymerization.[10a,48] In certain cases, surprisingly good compatibility of the resulting polymers with the ILs could be achieved irrespective of the polymer concentration and temperature (Figure 1). Typically, the polymerization of methyl methacrylate (MMA) in a common IL 1-ethyl-3-methyl imidazolium bis(trifluoromethane sulfone)imide ([C_2mim][NTf_2]) in the presence of a small amount of a cross-linker gives self-standing, flexible, and transparent polymer gels. The polymer and IL composite gels, which we term "ion gels", show a single T_g for a given range of [C_2mim][NTf_2] composition, and the T_g decreases with an increase in the mole fraction of [C_2mim][NTf_2] (Figure 2).[48] The dependence of T_g on the composition can be understood by the rationalization by the Gordon−Taylor equation[49] for copolymers and by the Fox equation[50] for plasticized polymers and copolymers. Both these equations are based on the assumption of the additivity of the free volume of the components. Therefore, the PMMA/[C_2mim][NTf_2] binary system appears to be a compatible one. Ion gels can be obtained in a wide [C_2mim][NTf_2]/[MMA] composition range from 1/9 to 7/3. The ionic conductivity of the ion gels with a high [C_2mim][NTf_2] composition becomes as high as 10^{-2} S cm^{-1} at ambient temperature, which is typical of solution conductivity. The Arrhenius plots of the conductivity can be effectively fitted to the Vogel–Tamman–Fulcher (VTF) equation.[51]

Decoupled Ionic Motion in Ion Gels. Polymer electrolytes consisting of network poly(ethylene oxide-*co*-propylene oxide) (P(EO/PO)) and Li[NTf_2] are selected as a reference for comparison purposes.[52] At ambient temperature, the conductivity of the PMMA/[C_2mim][NTf_2] electrolytes is higher than that of the P(EO/PO)/Li[NTf_2] electrolytes by a maximum of 3 orders of magnitude.[52] When the ideal glass transition temperature T_0 (one of the VTF fitting parameters) is compared with the experimentally obtained T_g, a difference in the ionic conduction is observed in these systems. In the P(EO/PO)/Li[NTf_2] electrolytes, T_0 and T_g increase in parallel with an increase in the salt concentration, and T_0 is lower than T_g by ca. 50 °C.[52] On the contrary, the difference between T_0 and T_g increases with decreasing [C_2mim][NTf_2] concentration in the PMMA/[C_2mim][NTf_2] electrolytes, with the observed difference in the studied concentration range reaching up to ca. 100 °C. Consequently, as shown in Figure 3,[52] the conductivities $\sigma(T_g)$ of the P(EO/PO)/Li[NTf_2] electrolytes at T_g are on the order of 10^{-14}−10^{-13} S cm^{-1} and gradually increase with increasing salt concentration, whereas those of the PMMA/[C_2mim][NTf_2] polymer electrolytes become 10^{-7} S cm^{-1} when the concentration of [C_2mim][NTf_2] is low. The $\sigma(T_g)$ values can be used for the approximation of the decoupling index (R_τ),

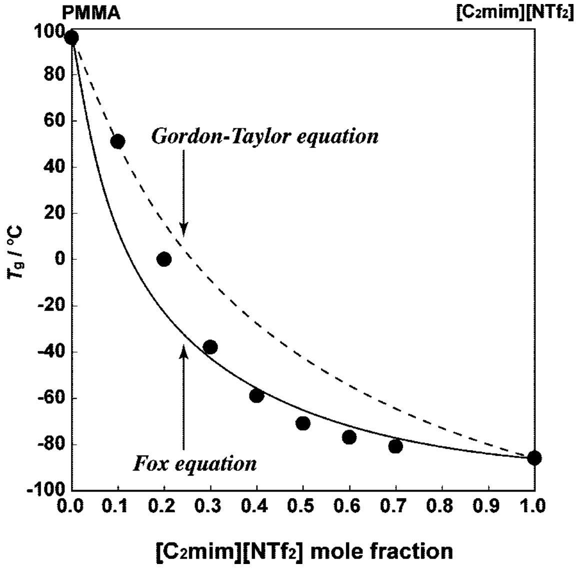

Figure 2. Glass transition temperatures (T_g) of PMMA network polymers with dissolved [C_2mim][NTf_2] as a function of [C_2mim][NTf_2] mole fraction. The points denote experimental T_g results, the broken lines denote the fitted profiles by the Gordon−Taylor equation, and the solid lines denote those by the Fox equation. Reproduced with permission from ref 48.

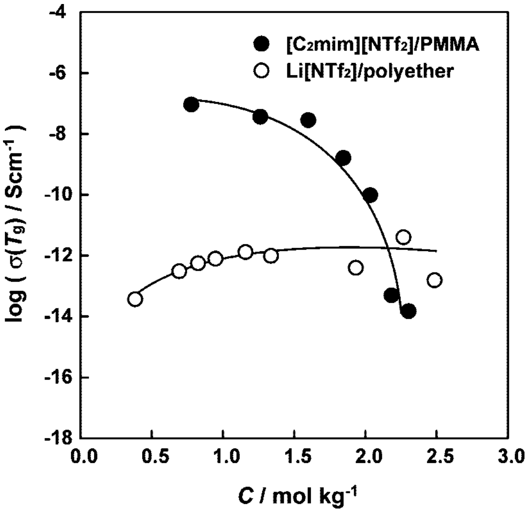

Figure 3. Ionic conductivities [$\sigma(T_g)$] of PMMA/[C_2mim][NTf_2] and P(EO/PO)/Li[NTf_2] polymer electrolytes at T_g as a function of salt concentration. Reproduced with permission from ref 52.

which is defined as the ratio of the conductivity relaxation time (σ_τ) to the structural relaxation time (τ_s), using the relationship[53]

$$\log R_\tau \approx 14.3 + \sigma(T_g) \qquad (1)$$

The log R_τ values of the P(EO/PO)/Li[NTf_2] and PMMA/[C_2mim][NTf_2] electrolytes are 0.3−1.3 and 0.3−7.3, respectively. Since T_g is an iso-free-volume state, a gradual increase in $\sigma(T_g)$ of the P(EO/PO)/Li[NTf_2] electrolytes on the order of 10^{-14}−10^{-13} S cm^{-1} reflects an increase in the number of carrier ions. In the P(EO/PO)/Li[NTf_2] electrolytes, the ions can be appreciably mobile by segmental motion due to the strong ion-dipole interaction, and the ionic motion is completely coupled with the segmental motion. In sharp contrast, $\sigma(T_g)$ of the PMMA/[C_2mim][NTf_2] electrolytes, which reaches 10^{-7} S cm^{-1}, indicates a decoupled ion transport from the segmental motion. This fact might be a new guideline to the design of high-performance polymer electrolytes. Since [C_2mim][NTf_2] exhibits self-dissociativity and may weakly interact with the PMMA chain, the constituting ions appear to be mobile even at T_g and do not couple with the segmental motion, unlike the behavior in the case of the P(EO/PO)/Li[NTf_2] electrolytes.

Lewis Acidity and Basicity to Understand Ion–Ion and Ion−Polymer Interactions. The physicochemical properties of ILs have been characterized by measuring their polarity,[54–56] dielectric constant,[57] and so on. We have proposed a new physicochemical parameter that represents the self-dissociativity of ILs,[58–60] that is, the molar conductivity ratio ($\Lambda_{imp}/\Lambda_{NMR}$), calculated from the molar conductivity measured by the electrochemical impedance method (Λ_{imp}) and estimated by pulse-field-gradient spin–echo (PGSE) NMR ionic self-diffusion coefficients and the Nernst–Einstein relation (Λ_{NMR}). Surprisingly, the conductivity ratios of typical ILs are rather high (0.5–0.8),[59] indicating that the ILs are dissociated into charged species even in the absence of the solvation by molecular solvents. The magnitude of the $\Lambda_{imp}/\Lambda_{NMR}$ is compared with solvatochromic polarity scales. The order of the ratio follows the inverse order of anionic Lewis basicity and cationic Lewis acidity for ILs having different anionic and cationic backbone structures with fixed counterparts, and it follows the order of magnitude of inductive and dispersive forces for various alkyl chains in the cations.[60]

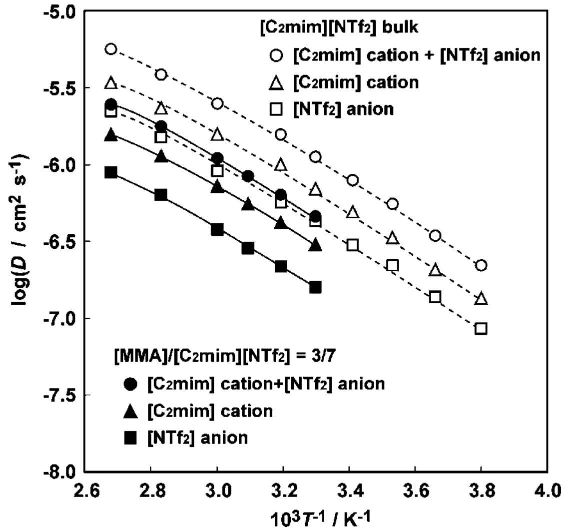

Figure 4. Temperature dependence of self-diffusion coefficients of [C_2mim] cation, [NTf_2] anion, and their summation for neat [C_2mim][NTf_2] and for PMMA/[C_2mim][NTf_2] electrolyte ([MMA]/[C_2mim][NTf_2]] = 3/7). Reproduced with permission from ref 48.

If we compare the properties of [C_2mim][NTf_2] and Li[NTf_2] using a scale of anionic Lewis basicity and cationic Lewis acidity, it is found that [C_2mim] and [NTf_2] are a very weak Lewis acid and base, respectively; however, the lithium cation is a strong Lewis acid and favors the interaction with a Lewis base. Regarding the host polymers PMMA and P(EO/PO), the latter polymer is characterized by high Lewis basicity in spite of its relatively low polarity. These characteristics also support the difference in decoupling indexes for the ionic conduction between the P(EO/PO)/Li[NTf_2] and PMMA/[C_2mim][NTf_2] electrolytes. We have successfully demonstrated that the doping of ILs into compatible polymers can be a new approach to obtain highly ion-conductive polymer electrolytes, where the ionic motion can be decoupled from the polymer segmental motion.[10a,48,52]

The analysis of the PGSE-NMR measurements of the PMMA/[C_2mim][NTf_2] electrolytes enables us to understand the ionic diffusion dynamics in ion gels (Figure 4).[48] The diffusion coefficient of the [C_2mim] cation is greater than that of the [NTf_2] anion in the ion gel. The same tendency is also observed in neat [C_2mim][NTf_2]. The number of carrier ions (n) in the neat IL and in the ion gel can be calculated using the Nernst–Einstein equation

$$n = (\sigma\, kT)/[q^2(D_{\text{cation}} + D_{\text{anion}})] \qquad (2)$$

where σ is the ionic conductivity, T is the absolute temperature, q is the electric charge on an ionic carrier, and D_{cation} and D_{anion} are the diffusion coefficients of the [C_2mim] cation and [NTf_2] anion, respectively. Figure 5 shows the relationship between the number of carrier ions, estimated by equation (2), and the mole fraction of [C_2mim][NTf_2] in the ion gel.[48] [C_2mim][NTf_2] dissociates into individual carrier ions, although the self-dissociation is not perfect. It is interesting to note that the incorporation of the PMMA matrix into the IL results in the promotion of ion dissociation, which causes an increase in the number of carrier ions. The values of D_{cation}, D_{anion}, and their sum ($D_{\text{cation}} + D_{\text{anion}}$) decrease with a decrease in the [C_2mim][NTf_2] fraction in the ion gel. However, the decrease in the D value of the [NTf_2] anion is more than the decrease in the D value of the [C_2mim] cation.[48] This implies that the interaction between the [NTf_2] anion and the polymer matrix is stronger than that between the [C_2mim] cation and the PMMA

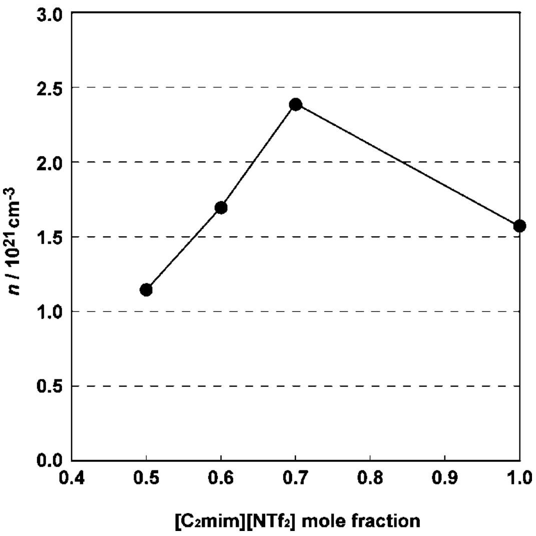

Figure 5. Number of carrier ions in PMMA/[C_2mim][NTf_2] electrolytes as a function of [C_2mim][NTf_2] mole fraction at 30 °C. Reproduced with permission from ref 48.

matrix, although both the interactions are unlikely to be as strong as those observed in the P(EO/PO)/ Li[NTf_2] electrolytes.

Charge Transport in Ionic Liquids. The nonvolatility and high thermal stability of the liquids incorporated in network polymers are fascinating characteristics of ion gels, which discriminate them from conventional polymer gels. Moreover, ion gels consisting of nonflammable ILs and polymer matrices can afford electrolytes that are safer than conventional electrolyte materials such as flammable organic electrolyte solutions. Our group has focused on the emerging field of ILs and ion gels for their application in energy devices.[61–63] Since task-specific properties such as proton conduction, lithium ion conduction, and electron transport can be designed into ILs on a molecular level, the scope and utility of the ion gels as new polymer electrolytes will immediately expand to fuel cells,[61] lithium batteries,[62] and solar cells. [63] In particular, proton-conducting and electron-transporting ILs are potentially applicable to nonhumidified medium-temperature fuel cells and dye-sensitized solar cells (DSSCs). Here, we show that interesting charge transport mechanisms occur in these ILs, where the charge transport is carried out by not only common physical diffusion (vehicle mechanism) but also structure diffusion (Grotthuss mechanism).

Proton Transport in Protic Ionic Liquids. In acidic aqueous solutions, it is well-known that proton transport can occur by proton hopping between hydrogen-bonded water molecules and hydronium ions (Grotthuss mechanism[64]) as well as by the simple diffusion and migration of hydronium ions (vehicle mechanism[65]) (Figure 6). The proton conduction based on the Grotthuss mechanism would be highly effective when the proton transport by the vehicle mechanism is decelerated by the high viscosity of the media, typically in polymer electrolytes. The concept of proton carriers other than water molecules, such as phosphoric acid and imidazole, has been proposed by Kreuer et al.[65–69] We have reported the electrochemical and thermal properties of protic ILs consisting of imidazole ([Im]) and other amines and a super strong acid bis(trifluoromethane sulfone-)imide (H[NTf_2]), which can conduct protons under anhydrous conditions and can function as a proton conductor for medium-temperature fuel cells, working at temperatures higher than 100 °C. [61] Although there had been several reports on protic ILs obtained from the mixtures of imidazole derivatives and monoprotic acids such as HBF_4, HPF_6, and H[NTf_2],[70] the detailed proton transfer mechanism in these protic ILs was not understood. The ionic conductivity of binary mixtures of [Im]/H[NTf_2] is high; moreover, the conductivity increases with an increase in the composition of [Im] in the mixtures and reaches a maximum in base-rich compositions (Figure 7).[61a] The ionic conductivity of the [Im]/H[NTf_2] mixtures containing 90 mol % of [Im] approaches 0.1 S cm^{-1} at 120 °C, which is comparable to that of a typical acidic aqueous solution.[61a] If the ionic conductivity of the [Im]/H[NTf_2] binary mixtures depends only on the migration of [NTf_2] anions and H[Im] cations, the number of carrier ions in the mixtures becomes maximum at the equimolar point of [Im] and H[NTf_2]. In sharp contrast, the increase in ionic conductivity with an increase in the [Im] mole fraction indicates enhanced ionic mobility.

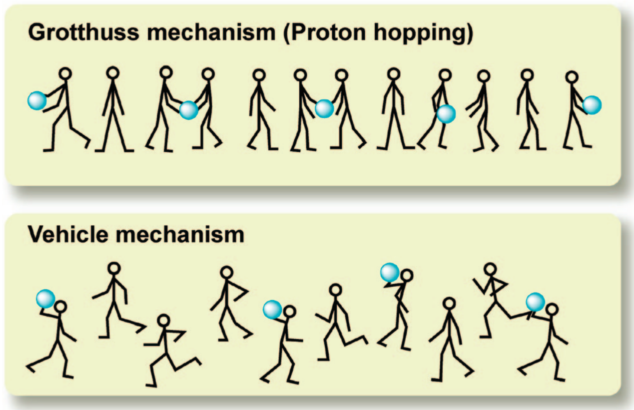

Figure 6. Illustration of proton transport in acidic aqueous solutions and in protic ionic liquids. [60] Top: Grotthuss mechanism; the protons are passed along hydrogen bonds. Bottom: Vehicle mechanism; the proton movement occurs with the aid of a moving "vehicle," e.g., H_2O and [Im].

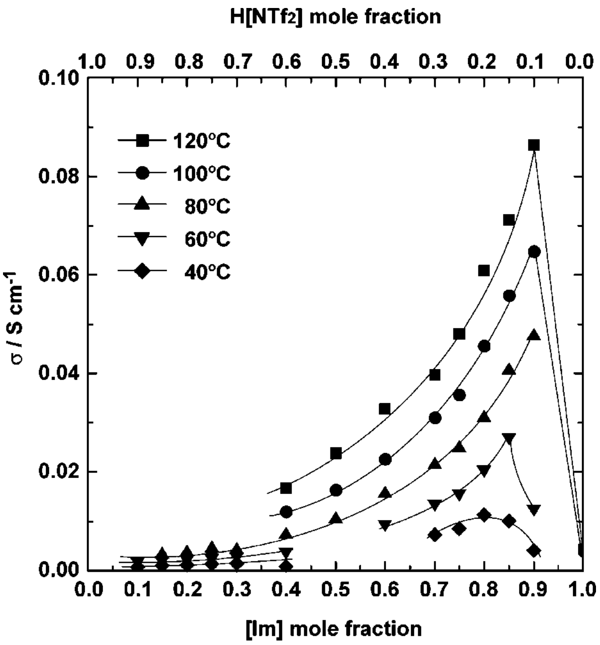

Figure 7. Ionic conductivity (σ) as a function of [Im] mole fraction for [Im]/H[NTf_2] binary mixtures at different temperatures. Reproduced with permission from ref 61a.

Kreuer et al. have already pointed out that the proton transport between protonated [Im] (H[Im] cation) and neat [Im] plays an important role for the intermolecular proton transfer and

Table 1. PGSE-NMR diffusion coefficients for [Im]/H[NTf$_2$] ionic liquid mixtures at 30 °C.

	D/10^{-7} cm^2 s^{-1}				
[Im]/H[NTf$_2$]	[Im](^{1}H)[a]	H[Im](^{1}H)[b]	[NTf$_2$](^{19}F)[c]	D_{H^+}/10^{-7} cm^2 s^{-1}	$D_{\mathrm{H}^+}/D_{[\mathrm{Im}]}$(^{1}H)
8/2	5.7	6.3	3.7	8.1	1.4
7/3	3.8	4.1	2.5	4.5	1.2

[a] From ^{1}H attached to carbon atoms of imidazole. [b] From ^{1}H attached to nitrogen atom of imidazole. [c] From ^{19}F of [NTf$_2$].

enhances the proton conduction at an optimum composition.[68] Thus, the conductivity is due to not only the migration of the ionic species (H[Im] cation and [NTf$_2$] anion) but also the intermolecular proton transfer. The H[Im] cations in neat [Im] accelerate the proton transfer dominantly via the Grotthuss mechanism in [Im] excess compositions. The proton conduction, therefore, appears to follow a combination of the Grotthuss and vehicle mechanisms, and which mechanism dominates the conduction is dependent on the composition. The increase in the [Im] mole fraction from the equimolar salt renders dominant conducting properties to change from the vehicle to the Grotthuss mechanism.

The PGSE-NMR measurements of the [Im]/H[NTf$_2$] binary mixtures reveal detailed information about the proton transport. The measured self-diffusion coefficients in base-rich compositions are summarized in Table 1.[61a] The self-diffusion coefficient $D_{\mathrm{H[Im]}}$ of ^{1}H attached to the nitrogen atom of [Im] is greater than that attached to the carbon atoms of [Im] ($D_{[\mathrm{Im}]}$). This difference indicates the existence of a rapid intermolecular proton transfer. Since the experimental $D_{\mathrm{H[Im]}}$ values include the contributions from both H[Im] and neat [Im], the H$^+$ diffusion coefficient (D_{H^+}) is calculated from the experimental diffusion coefficients ($D_{[\mathrm{Im}]}$ and $D_{\mathrm{H[Im]}}$).[61a] The ratios of the proton diffusion (D_{H^+}) to the matrix diffusion ($D_{[\mathrm{Im}]}$) coefficients are 1.4 and 1.2 (Table 1), and the higher value of the ratio for a higher [Im] content corresponds to an increase in the conductivity (Figure 7). If $D_{[\mathrm{Im}]}$ is assumed to be the same as the self-diffusion coefficient of the imidazolium cation (vehicle mechanism), the proton transfer by the intermolecular proton exchange process (Grotthuss mechanism) enhances D_{H^+} by a factor of 1.4 and 1.2 for [Im]/H[NTf$_2$] compositions of 8/2 and 7/3, respectively. The proton transference numbers are 0.7 and 0.6 for the [Im]-rich compositions of 8/2 and 7/3, respectively, which indicate that the dominant conductive species is protons.

Furthermore, the protic ILs are electroactive at platinum electrodes for both hydrogen oxidation and oxygen reduction reactions, which opens up the possibility of their use as fuel cell electrolytes at medium temperatures.[61] In the [Im]/H[NTf$_2$] fuel cell system, the [Im] molecule functions as not only a proton carrier such as water in acidic electrolytes but also a H$^+$ donor and acceptor for O$_2$ reduction and H$_2$ oxidation reactions, respectively. Proton conduction by the Grotthuss mechanism involves intermolecular proton transfer and structural reorganization by the processes of breaking and formation of hydrogen bonds. The concept of proton-conducting ILs may be used in compatible polymers for the construction of proton conducting membranes, and further, an acidic and/or basic site can be affixed to a polymer backbone.[61,68] These findings may open up a new field of fuel cells under nonhumidifying conditions, which can be operated at temperatures higher than 100 °C.

Electron Transport in Redox Ionic Liquids. An I$^-$/I$_3^-$ redox couple plays an important role in the charge transport in the electrolytes of DSSCs. In their pioneering work, Grätzel et al. have reported that a Grotthuss-like mechanism possibly contributes to the charge transport of an I$^-$/I$_3^-$ redox couple in the IL 1-hexyl-3-methylimidazolium iodide.[71] Our electrochemical study has revealed that the exchange reactions between an I$^-$/I$_3^-$ redox couple contribute to the charge transport only in an IL solvent.[63f] An ultramicroelectrode technique is employed for the electrochemical measurements in order to discriminate the contribution of the exchange reaction from that of the physical diffusion. The apparent diffusion coefficient (D_{app}), which is the summation of the exchange reaction (D_{ex}) and physical diffusion (D_{phys}), of the I$^-$/I$_3^-$ redox couple ([C$_2$mim]I/I$_2$ mixture) is evaluated for [C$_2$mim][NTf$_2$] and for polyethylene glycol dimethylether (PEGDE, nominal molecular weight of 500). The viscosities of [C$_2$mim][NTf$_2$] and PEGDE at 30 °C are 27 and 19 mPa s, respectively. A proper comparison of the electrochemical results of these two liquids can be made because of their good redox couple solubilities and similarities in their viscosities. When D_{ex} significantly contributes to the charge transport, D_{app} can be expressed by the Dahms-Ruff equation:

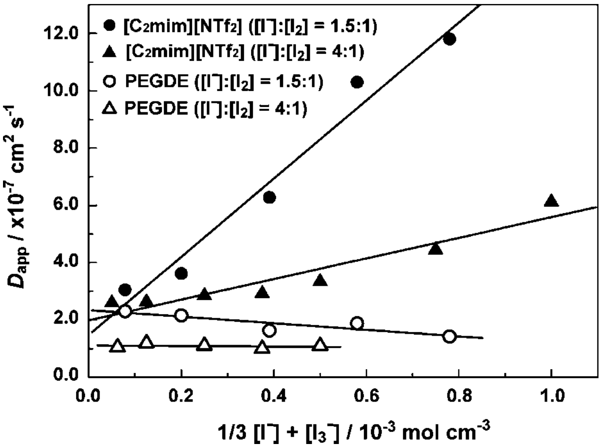

Figure 8. Relationship between D_{app} calculated from the limiting currents of the steady-state voltammetry and the concentration of the I/I$_3^-$ redox couple with different molar ratios dissolved in [C$_2$mim][NTf$_2$] and PEGDE. Reproduced with permission from ref 63f.

$$D_{\mathrm{app}} = D_{\mathrm{ex}} + D_{\mathrm{phys}} = (1/6)k_{\mathrm{ex}}\delta^2 c + D_{\mathrm{phys}} \tag{3}$$

where k_{ex} is the exchange reaction rate constant, δ is the center-to-center intersite distance during the exchange reaction, and c is the concentration of the redox couple. When the exchange reaction does not contribute to the overall transport process, D_{app} is independent of the concentration as long as the viscosity does not change. The concentration dependence of D_{app} of the redox couple in [C$_2$mim][NTf$_2$] and PEGDE is shown in Figure 8. D_{app} proportionally increases with the concentration when [C$_2$mim][NTf$_2$] is used as an electrolyte, indicating that the exchange reaction between the redox couple (I$^-$/I$_3^-$) can occur as estimated by equation (3). In contrast, D_{app} is constant or decreases slightly with increasing concentration of the redox couple in PEGDE because the viscosity increases slightly with the concentration. It appears to be difficult for I$^-$ and I$_3^-$ to collide with each other in the molecular solvent since both the reactants are negatively charged. However, the self-dissociativity of the IL is high, and its ionic strength is very high. The redox couple in the IL exists in a strong ionic field, and the electrostatic charge can be screened. Consequently, the two negatively charged ions (I$^-$ and I$_3^-$) appear to collide with each other more easily in the IL than in the molecular liquid by "the kinetic salt effect."[63f,72]

The additional charge transport based on the Grotthuss mechanism accelerates the redox charge transport in ILs, which enhances the performance of the DSSCs containing ILs. In spite of the high viscosities of the IL electrolytes, the DSSCs exhibit relatively high performances. In particular, the photocurrent of the DSSCs is greater than 80% of that of the cell containing a standard organic electrolyte solution, although the viscosity of the IL electrolytes is more than 10 times higher than that of the standard electrolyte.[63b] Furthermore, this kind of charge transport effectively occurs in IL crystal electrolytes[63e,g] in ILs gelled by the addition of nanoparticles[63i] and also in polymer electrolytes.

Phase Changes of Macromolecules in Ionic Liquids

Sol–Gel Transition of Polymers in Ionic Liquids. Most studies on the combined use of ILs with polymers have dealt with polymer−IL compatible systems; however, there have been several studies on the utilization of the phase changes or phase separation of a polymer in an IL. The sol–gel transition of polymers in ILs has attracted attention with a view to simply fabricating polymer electrolyte membranes. Poly[(vinylidene fluoride)-*co*-hexafluoropropylene] [P(VdF-*co*-HFP)] has been found to undergo a thermoreversible sol–gel transition in a variety of organic solvents.[73,74] Carlin et al. first reported the high ionic conductivity of a polymer electrolyte membrane consisting of P(VdF-*co*-HFP) and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([C_2mim][TfO]).[75a] In addition, polymer gels comprising P(VdF-*co*-HFP) and imidazolium-type ILs were widely studied as highly ion-conductive polymer electrolyte membranes.[75–78] The mechanism of gelation of P(VdF-*co*-HFP) in certain solvents is considered to be caused by the phase separation of the polymer from the solvents by cooling followed by the growth of spherulites. Therefore, the resulting membranes frequently have a porous structure owing to the aggregation of the spherulites. A similar sol–gel transition of P(VdF-*co*-HFP) appears to occur in IL solvents.

A unique membrane assembly that utilizes the phase change and/or phase separation of a polymer in an IL has recently been reported. Yashima et al. have successfully obtained a new ion gel that is a stereocomplex between isotactic- and syndiotactic-PMMA in ILs, such as 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim]PF_6).[79] Lodge et al. have reported the self-assembly of poly(1,2-butadiene)-*block*-PEO diblock copolymers (PB-*b*-PEO) in [C_4mim]PF_6 solvent.[80] A well-designed AB diblock copolymer having both a solvatophobic PB segment as the A block and solvatophilic PEO segment as the B block forms universal micellar structures (spherical and wormlike micelles and bilayered vesicles) by varying the length of the B block while maintaining the length of the A block constant. A recent research conducted by Lodge et al. has also suggested a new method for developing an ion gel triggered by the microphase separation of triblock copolymers.[81] The self-assembly of polystyrene-*b*-PEO-*b*-polystyrene triblock copolymers in [C_4mim]PF_6 yields highly ion-conductive polymer electrolyte membranes. Physical gelation by the self-assembly of the triblock copolymers in [C_4mim]PF_6 can be achieved by the addition of a small amount of the block copolymer, as low as 5 wt %, and this gelation is attributable to the microphase separation of solvatophobic styrene segments at both ends of each copolymer.[81] Other researches have reported the micelle formation of surfactants and block copolymers in ILs.[82–85] All these efforts imply that the macrophase or microphase separation of polymers in ILs provides opportunities for obtaining interesting materials as well as basic knowledge about the phase behavior of polymers in ILs.

UCST-Type Phase Behavior in Ionic Liquids. Poly(*N*-isopropylacrylamide) (PNIPAm) is a well-known polymer that undergoes solid–liquid phase separation in water in response to temperature. A PNIPAm aqueous solution exhibits low-temperature transparency and high-temperature turbidity, in other words, lower critical solution temperature (LCST)-type phase separation at ambient temperature.[86] Such a phase change of a polymer solution and polymer gel is of great interest from the thermodynamic viewpoint[87,88] as well as with regard to the construction of smart materials that are capable of exhibiting certain functions in response to external stimuli. Numerous investigations have been attempted to develop smart materials such as actuators,[89] drug delivery systems,[90] optical devices,[91] and sensing materials[92,93] by using the phase changes of polymers and polymer gels in aqueous solutions.

In our recent work, we have discovered that PNIPAm in [C_2mim][NTf_2] exhibits an upper critical solution temperature (UCST)-type phase separation.[94] This is an interesting phenomenon because it is completely opposite to the phase behavior of a PNIPAm aqueous solution. A qualitative comparison of the results of the solvatochromic and turbidity measurements indicates that the anionic structure of ILs mainly governs the phase behavior of the polymer in an IL. This result is consistent with that of other researches on the solubilization of polymers in ILs.[18–21,27–30] The phase change of a polymer in an IL would also be used in task-specific ion gel materials. The thermosensitivity of PNIPAm in [C_2mim][NTf_2] has recently been utilized in a thermoreversible ion gel with high ion conductivity.[95] This is achieved by the use of a [C_2mim][NTf_2] solution of an ABA triblock copolymer that has a thermosensitive PNIPAm segment as the A block and an IL-compatible PEO segment as the B block (PNIPAm-*b*-PEO-*b*-PNIPAm triblock copolymer).

LCST-type Phase Behavior in Ionic Liquids. We have observed the experimental LCST-type phase separation of certain polymers in ILs, which is similar to the phase behavior of a PNIPAm aqueous solution. Poly(benzyl methacrylate) (PBnMA)[96] and analogous copolymers[97] exhibit the LCST-type phase separation in common hydrophobic ILs, typically in [C_2mim][NTf_2] (Figure 9). From a thermodynamic viewpoint, the LCST-type phase separation phenomenon can occur under conditions where both the enthalpy change (ΔH_{mix}) and the entropy change (ΔS_{mix}) become negative upon mixing and the entropic contribution ($\Delta S_{\mathrm{mix}}T$) to the Gibbs energy change (ΔG_{mix}) becomes greater than ΔH_{mix}. The LCST-type phase separation of a PNIPAm aqueous solution, for example, has been attributed to the formation of a clathrate-like structure of water around the isopropyl group due to hydrophobic hydration, leading to a decrease in the mixing entropy.[86] Thus far, there is no data indicating that ΔS_{mix} of the PBnMA/[C_2mim][NTf_2] solution is negative, although recent studies suggest that aromatic compounds can form a liquid clathrate structure[98–100] with ILs by the cation−π interaction[101] between an IL cation and an aromatic compound. The recently reported LCST-type phase behavior of aromatic substances (benzene, toluene, α-methyl styrene) has revealed decreasing entropy of the solution due to the formation of the liquid clathrate of an aromatic compound and an IL cation.[102,103] It could be possible that a well-ordered solvation shell by the cations of ILs is formed around the aromatic side chain, similar to the case of the hydrophobic hydration of a PNIPAm aqueous solution.

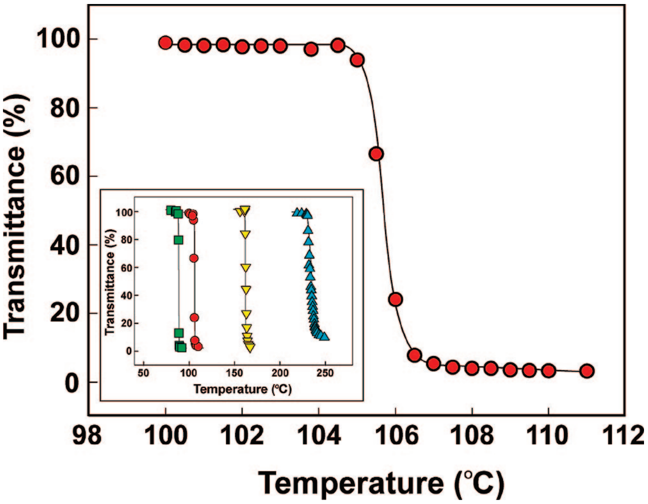

Figure 9. Temperature dependence of transmittance at 500 nm for a PBnMA solution in [C_2mim][NTf_2]. A transmittance of 100% indicates a single-phase (transparent) solution, while that of 0% indicates a phase-separated (turbid) one. The inset shows the comparison of the turbidity measurements for PBnMA solutions in [$C_n$mim][NTf_2]. Green square, [C_1mim][NTf_2]; red circle, [C_2mim][NTf_2]; yellow inverted triangle, [C_4mim][NTf_2]; and blue triangle, [C_6mim][NTf_2]. [$C_n$mim] represents the 1-alkyl-3-methylimidazolium cation.

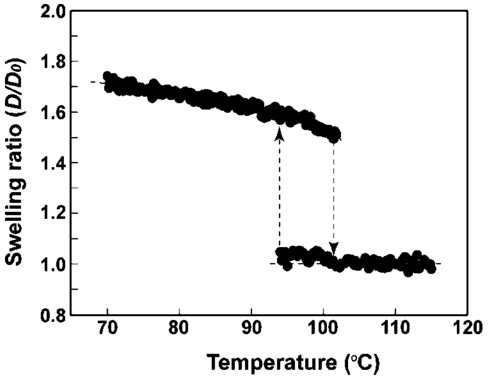

Figure 10. Equilibrium swelling ratio of a PBnMA gel particle in [C_2mim][NTf_2] as a function of temperature. The swelling ratio indicates the ratio of the normalized gel diameter at a particular temperature to that at 100 °C. The temperature is changed in increments of 0.2 °C, and the measurements are performed after waiting for at least 1 h so that the gel particles can achieve equilibrium swelling. Reproduced with permission from ref 96.

The unique phase change of the PBnMA linear polymer in the ILs has further encouraged us to evaluate the phase behavior of the cross-linked polymer gels in [C_2mim][NTf_2], as inferred from the size (volume) of the gels. The PBnMA gel in [C_2mim][NTf_2] exhibits low-temperature swollen and high-temperature shrunken phases with a phase transition temperature of ca. 100 °C (Figure 10). Smart hydrogel materials[89–93] have not been used successfully in an open atmosphere for a long duration and in a wide range of temperatures because of the properties (volatility and phase change, e.g., freezing) of the solvent within the polymer networks. The volume phase transition of polymer gels in ILs could usher in a new era of environmentally stable polymer gels since the swelling/shrinking behavior can be observed reversibly in an open atmosphere without the need to consider solvent evaporation, which is a serious drawback of conventional smart gel materials. Furthermore, the phase separation temperature of a polymer in an IL could be easily controlled by copolymerization with a solvatophilic or solvatophobic comonomer.[96] The copolymerization of styrene with BnMA leads to a decrease in the phase separation temperature of the resulting copolymers in [C_2mim][NTf_2]; in contrast, the phase separation temperature of P(BnMA-*co*-MMA) increases. The shift in the phase separation temperatures of the BnMA copolymers in each case becomes larger with an increase in the comonomer composition in the copolymer. These results imply that the phase change temperature of a stimuli responsive ion gel can be manipulated by the copolymerization method, as observed in the aqueous polymer solution.[104]

Interestingly, the phase separation temperature of PBnMA also changes significantly with the chemical structure of the IL solvent. The inset of Figure 9 shows the results of the turbidity measurements for a PBnMA (3 wt %) solution in ILs, which consists of imidazolium cations having different alkyl chain lengths and the same [NTf_2] anion. The phase separation in the PBnMA solutions of imidazolium ILs having longer alkyl chains occurs at a high temperature. The difference between the phase separation temperatures of PBnMA/[C_6mim][NTf_2] and PBnMA/[C_1mim][NTf_2] is greater than 100 °C. An increase in the LCST-type phase separation temperature implies an increase in the affinity of the solute and solvent. Rebelo et al. have observed that the LCST-type phase separation temperatures of ILs/organic solvent mixtures increase with the length of the alkyl chain on the imidazolium cation.[103] The UCST-type phase separation is also observed in certain alcohol/IL mixtures.[105–109] The UCST of a solution comprising a mixture of butanol and IL clearly decreases with an increase in the length of the alkyl chain attached to the imidazolium cation. Brennecke et al. have claimed that the attractive van der Waals dispersion interaction between the alkyl chains on the imidazolium cation and the butyl group strengthens with an increase in the number of alkyl carbon atoms in the imidazolium cation.[105] Although the factors affecting the phase separation temperature of the alkyl chain attached to the imidazolium cation have not yet been understood, the tendency for the LCST-type phase separation temperature of PBnMA/[$C_n$mim][NTf_2] to increase with increasing alkyl chain length appears to be caused by the enhancement of mixing enthalpy. The nano-ordered dynamic domain structure of the ILs[110] decreases their entropy, and the dissolution of PBnMA in these ILs might enhance their structural order, although the exact entropic contribution of the PBnMA/IL solutions cannot be described here. To understand the unique LCST-type phase behavior, we are now investigating ultrasensitive differential scanning calorimetry (DSC) of the polymer–IL solutions.

Concluding Remarks

In this study, we have dealt with macromolecules in ILs particularly as new materials from the perspective of the progress, challenges, and opportunities. The compatible binary systems between an IL and a polymer can afford ion-conductive polymer electrolytes (ion gels). The ion transport in the ion gels is found to be decoupled from the segmental motion of the polymers, leading to relatively high ionic conductivities even at their T_gs. Decoupled ion transport has not been observed in conventional polymer electrolytes consisting of ion-coordinating polymers and high-T_m salts, typically polyethers and lithium salts, where the ion transport is strongly coupled with the segmental motion. The difference in the ion-conducting behavior appears to be understood in terms of the interaction between the ions and the polymers, which can be rationalized by Lewis acid–base interactions. Common ILs comprise weak Lewis acidic cations and weak Lewis basic anions and are self-dissociative, which causes the interaction between the ions and the polymers to be very weak consequently resulting in decoupled ion transport. The flexibility of the molecular design of ILs in polymers provides many new ILs having electrochemical functionalities such as proton, electron, and lithium ion transport. The new ILs and their ion gels appear to be promising candidates as new materials for the electrochemical applications.

We have also found that certain combinations of macromolecules in ILs exhibit the UCST- and LCST-type phase separations by changing the temperature. The phase separation temperatures are easily altered by the change in the polymer and IL structures, although the phase separation and thermodynamics have not yet been understood quantitatively. Moreover, cross-linked polymer gels in the ILs show a reversible volume phase transition. As ILs are, in general, thermally and chemically stable and have negligible vapor pressure, these phase transitions could be utilized for developing stimuli-responsive smart materials such as actuators, optical devices, and switching devices. In particular, the polymer gel system could enable the development of environmentally stable smart gel materials for a variety of purposes.

Finally, we would like to point out some similarities between ILs and water. Water is the most common solvent; however, it has extraordinary properties compared to other typical molecular solvents. Due to its strong hydrogen bonding ability, water, the so-called "eccentric entropy liquid," exhibits specific physical chemical properties such as a high boiling point, high viscosity, and surface tension. Water exists as a mixture of free water molecules and hydrogen-bonded water clusters; however, they are exchanging with each other on a time scale of 10^{-12} s. The most important interaction in ILs is the Coulombic interaction between the constituent ions.[59c] ILs appear to be a mixture of free ions and ionic aggregates or clusters, in a manner similar to water.[59,60] The notable characteristics of ILs, such as nonflammability, nonvolatility, relatively high ionic conductivity, and chemical stability, are basically attributable to their ionic nature. [60] The Coulombic interaction itself has no directionality; however, there exist additional molecular interactions in ILs, such as hydrogen bonding interaction, cation−π interaction, van der Waals inductive and dispersion interactions, and so on. The combination of the strong Coulombic interaction and weak directional interaction may induce the formation of structures in ILs and IL/solute mixtures. A further understanding of such interactions appears to be essential for the development of new materials based on macromolecules and ILs. From a practical point of view, toxicity and biodegradability and expensiveness of ILs should also be addressed and resolved to enable further development.

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