

Accounts

Polymers in Ionic Liquids: Dawn of Neoteric Solvents and Innovative Materials

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In this paper, we review recent advances in the use of polymers in ionic liquids (ILs) from the view point of the “*dawn of neoteric solvents and innovative materials*.” The first part of this paper presents a brief review of the solubility parameters of ILs, which are expected to serve as a qualitative guide for predicting polymer solubility in ILs; however, this concept cannot be used to rationalize a number of cases in which strong Coulombic interactions dominate the solubility parameters of the ILs. Thus, solubility of 24 different common synthetic polymers is experimentally demonstrated under dilute conditions (3 wt %) in four different common ILs. It is found that the Lewis basicities of the counter anions in the ILs play an important role in determining the solubility of the polymers. ILs can also be used as good solvents for low-solubility biopolymers and as good dispersion media of carbon nanotubes, which contributes to the fields of biorefinery processes and advanced materials. Certain combinations of polymers in ILs undergo phase separations as the temperature of the solutions is varied. The solubility of a nonionic polymer in water generally decreases with increasing temperature, and certain combinations exhibit lower critical solution temperature (LCST) phase separation, whereas the solubility of a polymer in an organic solvent generally increases with increasing temperature and in some cases upper critical solution temperature (UCST) phase separation is observed. Interestingly, both LCST and UCST phase separations are observed for certain polymers in ILs. After presenting possible explanations of the solubility of polymers in ILs, recent developments in the field of thermosensitive polymers in ILs are discussed from the perspective of materials science, where such phase separations are exploited to trigger abrupt changes in polymer properties. The final part of this review describes the thermosensitive self-assembly of block copolymers in ILs. Similar to conventional molecular solvents, block copolymers in ILs exhibit variable self-assemblies in solution and in the bulk.

1. Introduction

Ionic liquids (ILs) exhibit unique properties and, consequently, have been an area of intense focus. These properties include thermal and (electro)chemical stability, nonvolatility, nonflammability, and high ionic conductivity.^{1–3} ILs are generally regarded as environmentally benign green-solvents because of their unique characteristic of having a negligible vapor pressure, and as a promising class of functional liquids, applicable to the extraction and partitioning of various target molecules and for separation and storage of gases. The properties of ILs can be judiciously engineered from an infinite number of possible combinations of cations and anions. For this reason, ILs are referred to as “designer solvents” or “the third liquid,” following conventional water and organic solvents. From the standpoint of materials science, the combination of ILs and polymers is promising for the development of novel materials, given that certain polymers are soluble in ILs.^{4–7}

The discovery of ILs was first reported in 1914 by Walden, when he discovered a molten salt, ethylammonium nitrate,

having a melting point below room temperature. However, no significant attention was paid to the discovery of ILs for a long time afterwards.⁸ Renewed interest in studies on room-temperature ILs was awakened with the use of pyridinium or imidazolium salts with chloroaluminate anions, as reported by Wier et al. and Osteryoung et al., although these ILs were easily hydrolyzed by water.⁹ ILs have maintained their place of focus since Wilkes and co-workers reported air- and water-stable ILs containing the tetrafluoroborate anion (BF₄) in 1992.¹⁰ In 1993, the current authors published the first report on a polymer electrolyte having an exceptionally high ionic conductivity at that time, which was a molecular composite consisting of a chloroaluminate IL and a polymer.¹¹ To the best of our knowledge, this was the first report on the materialization of an IL/synthetic-polymer combination. Subsequently, we found that common vinyl monomers are widely soluble in common ILs and that they can be polymerized in ILs by free-radical polymerization.^{12,13} In certain cases, good compatibility of the resulting polymers with the ILs could be achieved, irrespective of the polymer concentration and temperature, and

polymer composites containing ILs (ion gels) could be obtained in such cases. This study was succeeded by many studies on new electrolyte materials based on molecularly designed task-specific ILs.^{14–20}

In addition to the above-mentioned polymer/IL compatible systems, certain polymers in ILs undergo phase separation with a variation in temperature. Numerous studies have demonstrated that such solubility changes of polymers in the relevant solvents induce volume phase transition of the corresponding polymer gels (solvent-swollen network polymers). In particular, polymer gels in aqueous solutions (hydrogels) have been proposed as smart or intelligent materials that may exhibit autonomous “sensing,” “processing,” and “action” responses to external stimuli. The phase separation and phase transition of polymers and polymer gels in nonvolatile ILs may afford novel materials and material systems that are functional over a wide range of temperature and pressure conditions, thereby generating considerable interest in these polymer/IL combinations. Stimuli-responsive polymers in ILs can be used as soft materials with no need for precautionary measures against solvent evaporation because of the nonvolatile nature of ILs.^{21,22} From the standpoint of fundamental science, it is exceptionally important to understand how the solubility of polymers in ILs is determined. Investigation of the phase behavior of polymers over a wide range of temperatures, using thermally stable ILs as solvents, is also important from the practical perspective.

Self-assembly based on intramolecular phase separation of block copolymers is another interesting topic in the field of polymer science.^{23–25} Recent development of living radical polymerization methods such as atom-transfer radical polymerization (ATRP),^{26,27} reversible addition fragmentation transfer (RAFT)²⁸ polymerization, and nitroxide-mediated polymerization (NMP),²⁹ has facilitated tremendous progress in the preparation of block copolymers with complex architectures. Bulk block copolymer melts and their concentrated solutions are macroscopically homogeneous but possess predictable structural heterogeneity on the scale of a few nanometers up to several micrometers. Such nanostructures have well-established ordered states termed cubic, lamellar, hexagonal, and bicontinuous phases. The composites formed when ILs are used as solvents for block copolymers consist of both IL-rich and polymer-rich domains. The former give the desirable functionality, whereas the latter furnish mechanical strength. A thermally induced change in the solubility of one segment of the block copolymers can open new avenues to the development of thermally processable ion gels.

In this paper, we comprehensively review recent developments in the studies of polymers in ILs. The compatibility of synthetic polymers with ILs is discussed in the first part of this review. An overview of the reported solubility parameters (SP) of ILs is also presented; however, the polymer solubility predicted based on these solubility parameters does not necessarily reflect the actual polymer solubility in the relevant ILs because of the presence of strong Coulombic interactions that dominate the SP. In contrast, Coulombic interactions frequently play only a minor role in determining the solubility of common nonionic polymers in ILs. In the second section, the phase separation of polymers in ILs is discussed. ILs provide

unusual microenvironments with high polarity and ionic strength as well as inhomogeneity on the nanoscale. The strongest interaction in ILs arises, as expected, from Coulombic forces. However, relatively weak but directional interactions such as hydrogen-bonds, van der Waals interactions, and cation– π interactions also play an important role in controlling the solubility of polymer solutes in ILs. The final part of this review presents a discourse on the self-assembly of block copolymers in ILs. When block copolymers consisting of thermosensitive segments are present in a self-assembly, the supramolecular structure may change with variations in temperature, which opens up the possibility of controlling the block copolymer assembly in ILs by use of external stimuli. Scheme 1 shows the chemical structures and the acronyms used to describe the cations and the anions of ILs throughout this paper. The chemical structures presented in Scheme 1 are by no means exhaustive, given that numerous ILs can be prepared by proper choice and variation of the cation and anion combinations.

2. Compatibility of Polymers in Ionic Liquids

2.1 Solubility Parameters of Ionic Liquids. In order for ILs to be used as solvents and additives for polymers, the compatibility of the polymers with the ILs is of paramount importance. Here, we present a brief overview of the relationship between the Hildebrand solubility parameter (SP) and polymer solubility. From the thermodynamic aspect, when the Gibbs free energy of mixing (ΔG_{mix}) of the polymer and solvent is negative, the resulting mixture is compatible:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

where ΔH_{mix} , T , and ΔS_{mix} are the enthalpy of mixing, absolute temperature, and entropy of mixing, respectively. ΔH_{mix} can be related to the SP as follows:

$$\Delta H_{\text{mix}} = (v_{\text{solvent}}x_{\text{solvent}} + v_{\text{polymer}}x_{\text{polymer}}) \times (\delta_{\text{solvent}} - \delta_{\text{polymer}})^2\phi_{\text{solvent}}\phi_{\text{polymer}} \quad (2)$$

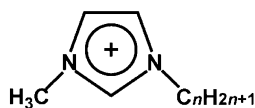
where v , x , δ , and ϕ are the molar volume (unit molar volume for polymer), mole fraction (unit mole fraction for polymer), SP, and volume fraction, respectively; subscripts denote each component in the mixture (polymer or solvent). Equation 2 shows that ΔH_{mix} is always positive, suggesting that the mixing process is endothermic. Therefore, if the δ values of the selected solvent and polymer are similar, ΔH_{mix} approaches zero, leading to $\Delta G_{\text{mix}} < 0$. Here, δ is defined as the square root of the cohesive energy density (CED), which is equal to the enthalpy of vaporization (ΔH_v) of a chemical compound:

$$\delta = (\text{CED})^{1/2} = [(\Delta H_v - RT)/v]^{1/2} \quad (3)$$

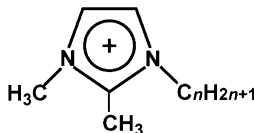
where R is the gas constant. Table 1 shows the SPs of some typical solvents.³⁰

The SP values for volatile solvents can be obtained directly from ΔH_v or vapor pressure–temperature data. However, because of the extremely low vapor pressure of ILs, the direct experimental measurement of ΔH_v is generally difficult. Thus, both indirect and direct estimations have been carried out. McLean, Gordon, and co-workers estimated the δ value of ILs indirectly using eq 4, which is generally applied to measuring the δ value for molecular solvents:³¹

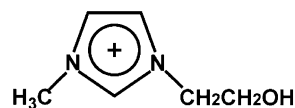
<Cation>



1-alkyl-3-methylimidazolium

[C_nmim]

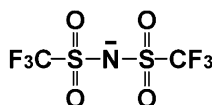
1-alkyl-2,3-dimethylimidazolium

[C_ndmim]

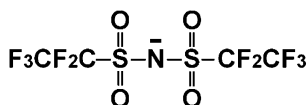
1-(2-hydroxyethyl)-3-methylimidazolium

[C₂OHmim]

<Anion>

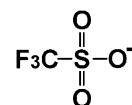
[NTf₂]

bis(trifluoromethanesulfonyl)amide



[BETf]

bis(pentafluoroethanesulfonyl)amide



[TfO]

trifluoromethanesulfonate

Scheme 1. Chemical structures and acronyms of the main ions discussed in this review.

Table 1. Solubility Parameters (SP) of Typical Organic Solvents, Cited from Ref. 30

Solvent	SP /(cal cm ⁻³) ^{1/2}	Solvent	SP /(cal cm ⁻³) ^{1/2}
<i>n</i> -Hexane	7.3	Carbon disulfide	10.0
Diethyl ether	7.4	1,4-Dioxane	10.0
Cyclohexane	8.2	Acetic acid	10.2
Toluene	8.9	Acetaldehyde	10.3
Ethyl acetate	9.1	1-Butanol	11.4
Tetrahydrofuran	9.1	Ethyl alcohol	12.7
Benzene	9.2	Dimethyl sulfoxide	14.5
Chloroform	9.3	Methanol	14.5
Methylene chloride	9.7	Ethylene glycol	14.6
Acetone	9.9	Water	23.4

$$\log k_p = 2.15 + 1.18\pi^* + 0.07\delta \quad (4)$$

where k_p is a bimolecular rate constant for the reaction of singlet active oxygen ($^1\text{O}_2^*$) and 1,4-dimethylnaphthalene in a certain solvent. The Kamlet–Taft parameter, π^* , indicates the polarity of the solvent.³² The intrinsic viscosity method, which has been used for the determination of the SPs of polymers, has also been applied to the determination of the SPs of ILs using the following well-established relationship:³³

$$[\eta] = [\eta_{\max}] \exp[-A(\delta_{\text{solvent}} - \delta_{\text{IL}})] \quad (5)$$

where A is a constant, δ_{solvent} and δ_{IL} are the SPs of a volatile solvent and an IL, respectively, and $[\eta]$ is the intrinsic viscosity of an IL. The $[\eta]$ value is at a maximum when δ_{solvent} and δ_{IL} are coincident. Lee and co-workers used this relationship to determine the δ values of certain ILs.³⁴ Furthermore, Rebelo and co-workers directly determined the ΔH_v values of 1-alkylimidazolium-based ILs that have [NTf₂]⁻ as a counter anion;³⁵ this enables the determination of the δ values for the selected ILs using eq 3. It should be noted that the CED values

are frequently represented in units of kJ mol⁻¹, whereas SP values are in (cal cm⁻³)^{1/2}. The results of these pioneering studies are summarized in Table 2, and agreement can be found among the data even though different methodologies were used.

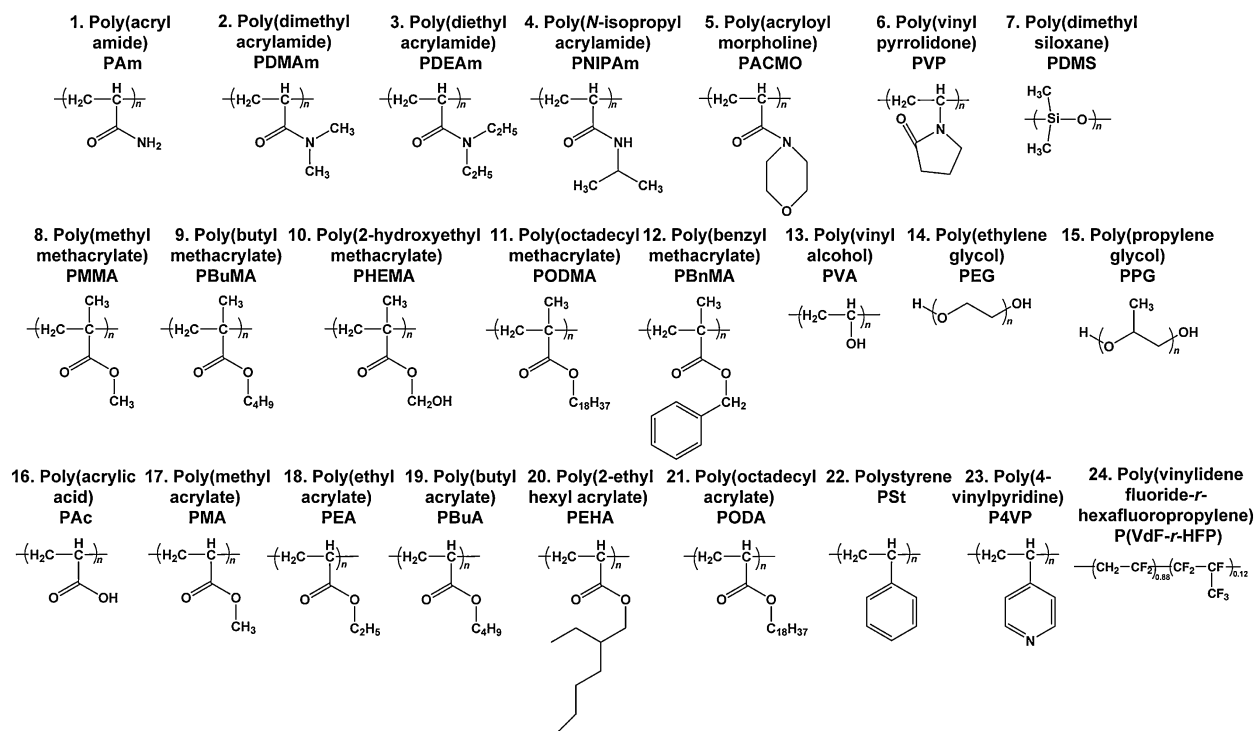
The SP values of ILs may sometimes be used for the design of ILs with specific solubilities as well as to indicate the compatibility of ILs with other solutes, including polymers. However, even the qualitative use of SPs eventually breaks down in the prediction of solute solubility in many cases. The assumptions of the theory are not consistent with the presence of any kind of strong or directional interactions, such as Coulombic and hydrogen-bonding interactions. The packing of dipoles can influence the entropy of mixing through the various orientational degrees of freedom. Thus far, precise information concerning the solubility and phase behavior of polymer/IL solutions has been obtained only by trial and error.

2.2 Phenomenological Aspects of Polymer Solubility in Ionic Liquids. Winterton and co-workers conducted an investigation of the compatibility of 51 different polymer/IL combinations for the purpose of catalytic membrane applications.³⁶ They screened the solubilities of 17 different polymers in three different ILs: 1-ethyl-3-methylimidazolium tetrafluoroborate, [C₂mim]BF₄, 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim]PF₆, and 1-methyl-3-octylimidazolium bis(trifluoromethanesulfonyl)amide, [C₈mim][NTf₂]. They also investigated the temporal stability of the polymer/IL composites over the course of 11–15 weeks and concluded that [C₈mim][NTf₂] appears to be the most effective solvent for a series of polymers.

In this account, we present a solubility study of 24 different polymers (3 wt %) in four selected ILs. Scheme 2 shows the chemical structures of the polymers and the corresponding entry numbers and acronyms. Table 3 summarizes the results of the solubility tests, along with the entry numbers of the

Table 2. Cohesive Energy Densities (CED) and Solubility Parameters (SP) of Selected ILs, Cited from Refs. 31, 34, and 35

	Cohesive energy density (CED)/kJ mol ⁻¹				Cohesive energy density (CED)/cal cm ⁻³				Solubility parameter (SP)/(cal cm ⁻³) ^{1/2}			
	Ref. 31	Ref. 34	Ref. 35		Ref. 31	Ref. 34	Ref. 35		Ref. 31	Ref. 34	Ref. 35	
			Exp.	Calc.			Exp.	Calc.			Exp.	Calc.
[C ₂ mim][NTf ₂]		196	136 ± 6	159 ± 10		184.7	128 ± 6	149 ± 10		13.6	11.4 ± 0.2	12.2 ± 0.4
[C ₃ mim][NTf ₂]			147 ± 6	172 ± 12								
[C ₄ mim][NTf ₂]	191	208	155 ± 6	174 ± 11	158.7	172.9	129 ± 6	145 ± 11	12.6	13.1	11.4 ± 0.2	12.0 ± 0.4
[C ₄ dmim][NTf ₂]	179											
[C ₅ mim][NTf ₂]			162 ± 6	179 ± 9								
[C ₆ mim][NTf ₂]		214	173 ± 6	184 ± 7		159.4	129 ± 6	137 ± 7		12.6	11.3 ± 0.1	11.7 ± 0.2
[C ₇ mim][NTf ₂]			180 ± 6	186 ± 10								
[C ₈ mim][NTf ₂]		226	192 ± 6	201 ± 6		151.9	129 ± 6	135 ± 6		12.3	11.3 ± 0.1	11.6 ± 0.2
[C ₄ mim]PF ₆	189	184			221	215.1			14.9	14.7		
[C ₆ mim]PF ₆		196				198.4				14.1		
[C ₈ mim]PF ₆		213				187.3				13.7		
[C ₄ mim][TfO]	139	149			146.1	156.6			12.1	12.5		
[C ₄ mim]BF ₄	201				261				16.2			
[C ₄ mim]SbF ₆	223											

**Scheme 2.** Chemical structures, acronyms, and entry numbers of polymers used for solubility tests in [C₂mim][NTf₂], [C₄mim][NTf₂], [C₄mim]PF₆, and [C₂mim]BF₄.

polymers and their SP values.^{30,37–45} The phenomenological experiment was carried out using commonly used ILs as solvents, i.e., [C₂mim][NTf₂], [C₄mim][NTf₂], [C₄mim]PF₆, and [C₂mim]BF₄ (Scheme 1). [C₂mim][NTf₂], [C₄mim][NTf₂], and [C₄mim]PF₆ are hydrophobic,⁴⁶ whereas [C₂mim]BF₄ is hydrophilic. It is generally difficult to judge the solubility of polymers in ILs at the equilibrium point because of the high viscosity of ILs, which makes the dynamics of polymer dissolution slow. In order to overcome the limitations imposed by this kinetic barrier, we applied the use of a cosolvent evaporation method, which is a common methodology used for

the preparation of polymer/IL binary systems. The general procedure for cosolvent evaporation based on the characteristic nonvolatile nature of ILs is as follows: (1) an organic solvent is used to prepare a homogeneous solution of a polymer; (2) an IL is added to the polymer organic solvent solution; and (3) after ensuring the transparency of the three-component mixture, the organic solvent is evaporated. In this study, methanol, acetone, chloroform, or tetrahydrofuran (THF) were used as volatile organic solvents. In the absence of an appropriate cosolvent capable of providing a homogeneous cosolvent/polymer/IL mixture solution, direct dissolution was carried out at 150 °C. It

Table 3. Results of Solubility Tests for 24 Different Polymers in Four Different Commonly Used Ionic Liquids^{a)}

Entry No.	1	2	3	4	5	6	7	8
Polymer	PAm	PDMAm	PDEAm	PNIPAm	PACMO	PVP	PDMS	PMMA
SP/(cal cm ⁻³) ^{1/2}	27.1 ³⁷	18.1 ³⁷	10.5 ³⁸	19.8 ³⁷	n.d.	14.7 ³⁹	7.4 ⁴⁰	8.9 ³⁰
[C ₂ mim][NTf ₂]	UCST	Yes	Yes	UCST	Yes	Yes	Yes	Yes
[C ₄ mim][NTf ₂]	UCST	Yes	Yes	UCST	Yes	Yes	Yes	Yes
[C ₄ mim]PF ₆	No	Yes	Yes	UCST	Yes	Yes	Yes	Yes
[C ₂ mim]BF ₄	No	Yes	No	UCST	No	Yes	No	No
Entry No.	9	10	11	12	13	14	15	16
Polymer	PBuMA	PHEMA	PODMA	PBnMA	PVA	PEG	PPG	PAC
SP/(cal cm ⁻³) ^{1/2}	9.0 ³⁰	16.8 ⁴¹	7.8 ³⁰	n.d.	10.6 ⁴²	9.8 ⁴³	8.0 ⁴⁴	n.d.
[C ₂ mim][NTf ₂]	Yes	No	UCST	LCST	No	Yes	No	No
[C ₄ mim][NTf ₂]	Yes	No	UCST	LCST	No	Yes	No	No
[C ₄ mim]PF ₆	Yes	No	UCST	LCST	No	Yes	No	No
[C ₂ mim]BF ₄	No	Yes	UCST	No	No	UCST	LCST	No
Entry No.	17	18	19	20	21	22	23	24
Polymer	PMA	PEA	PBuA	PEHA	PODA	PSt	P4VP	P(VdF- <i>r</i> -HFP)
SP/(cal cm ⁻³) ^{1/2}	8.9 ³⁰	8.9 ³⁰	10.0 ³⁰	9.0 ³⁰	n.d.	9.1 ³⁰	5.9 ⁴⁵	n.d.
[C ₂ mim][NTf ₂]	Yes	Yes	Yes	Yes	UCST	No	No	UCST (sol-gel)
[C ₄ mim][NTf ₂]	Yes	Yes	Yes	Yes	UCST	No	No	UCST (sol-gel)
[C ₄ mim]PF ₆	Yes	Yes	Yes	Yes	UCST	No	No	UCST (sol-gel)
[C ₂ mim]BF ₄	Yes	Yes	Yes	No	UCST	No	No	UCST (sol-gel)

a) Yes and No indicate compatible and incompatible, respectively. Numbers indicated by superscripts express reference numbers for the SP; PAm, PDMAm, PNIPAm from Ref. 37, PDEAm from Ref. 38, PVP from Ref. 39, PDMS from Ref. 40, PHEMA from Ref. 41, PVA from Ref. 42, PEG from Ref. 43, PPG from Ref. 44, P4VP from Ref. 45, and the other polymers from Ref. 30.

should be noted that the solubility of polymers depends strongly on not only the nature of the polymers themselves but also on the molecular weight of the polymer as well as the molecular weight distribution and concentration of the polymer. The solubility test for a combination of a polymer and a solvent therefore provides information that is strictly qualitative, and which is applicable only for a polymer of a certain molecular weight and molecular weight distribution at the specified concentration.

One may find from Table 3 that the solubility of the polymers in the [C₂mim][NTf₂] and [C₄mim][NTf₂] ILs is identical. Many studies have indicated that the solubility of polymers in ILs is predominantly governed by the structure of the anion rather than that of the cation. In contrast, the SP values do not prove useful in predicting the solubility of a polymer in an IL. For example, Table 3 shows that the solubilities of PMMA (Entry 8) and PSt (Entry 22), which have similar SP values of 8.9 and 9.1 (cal cm⁻³)^{1/2}, respectively, are quite different. Respectively, PMMA and PSt are compatible and incompatible with [C₂mim][NTf₂] (SP = 11–14 (cal cm⁻³)^{1/2}). It is reported that the SP values increase linearly with effective ionic concentration of the IL.⁴⁷ It should be noted that the ionic character of the ILs is strongly reflected in the SP values, so that the Hildebrand solubility parameters

for ILs may not have the same meaning as those for conventional molecular liquids, where Coulombic interactions are absent.

Polymer/IL solutions also exhibit a variety of phase behaviors. (Meth)acrylate polymers having short alkyl-side-chains, of which PMMA (Entry 8) is archetypal, are soluble in ILs having [NTf₂]⁻ and PF₆⁻ counter anions, whereas certain polymers exhibit abrupt solubility changes in ILs as the temperature is varied. For instance, (meth)acrylate polymers having long alkyl-chains (Entries 11 and 21) show upper-critical-solution-temperature (UCST) phase behavior in the ILs. The UCST phase behavior originates from the crystallization of long alkyl-side-chains at low temperatures. In this case, van der Waals interactions between the long polymer-alkyl-side-chains play an important role in polymer aggregation. At high temperatures, melting of the side chain causes the polymers to become soluble. The UCST solubility changes of PAm and PNIPAm (Entries 1 and 4) in ILs having the [NTf₂]⁻ anion appear to be brought about by competition between intra- and intermolecular hydrogen-bonding between the polymers and an increase in the entropy upon dissolution. When the amide hydrogen atom of the polymer is replaced by capping with a methyl or ethyl group, e.g., PDMAm (Entry 2) and PDEAm (Entry 3), the intra- and intermolecular hydrogen-bonding is

suppressed, resulting in compatibility with the ILs over a wide temperature range. PHEMA, PVA, and PAc (Entries 10, 13, and 16), which are strongly hydrogen-bonded polymers, are incompatible with the [NTf₂]-based ILs. It is interesting to note that [C₂mim][NTf₂], [C₄mim][NTf₂], and [C₄mim]PF₆ are good solvents for PACMO (Entry 5), which is known to be incompatible with many kinds of organic solvents. It was generally found that polymer solubility in [C₄mim]PF₆ is similar to that in [NTf₂]-based ILs.

For the series of (meth)acrylate polymers, the solubility in [C₂mim]BF₄ is poor in contrast to that in the hydrophobic ILs. However, PHEMA (Entry 10) was readily soluble in this IL. The BF₄ anion possesses hydrogen-bond acceptor ability, enabling it to interact with the hydroxy group of PHEMA. On the other hand, PVA and PAc (Entries 13 and 16) were not soluble in [C₂mim]BF₄, as was also the case when the corresponding hydrophobic ILs having the PF₆⁻ and [NTf₂]⁻ counter-ions were used. These results can be attributed to strong intra- and intermolecular hydrogen-bonding interactions. As is often the case for aqueous solutions of polymers, certain polymers such as PBnMA exhibit an LCST solubility change (Entry 12) in ILs; this is discussed in detail in Section 4.1. In addition, the sol–gel transition of P(VdF-*r*-HFP) that occurs in certain ILs with decreasing temperature enables the preparation of thermoreversible gels; this is described in Section 4.4.

3. Ionic Liquids as Solvents for Low-Solubility Biopolymers and Carbon Nanotubes

It is interesting to note that ILs can be used as good solvents for low-solubility biopolymers. The most renowned example is the use of ILs as solvents for cellulose. The use of ILs for cellulose processing was first demonstrated by Rogers and co-workers in 2002 (Table 4).⁴⁸ Cellulose, which is the most widely used biopolymer in industry, has six hydroxy groups in each unit (Figure 1), which results in extensive intra- and

intermolecular hydrogen-bonding. ILs having strong hydrogen-bond accepting anions such as chloride and acetate anions can solvate the hydroxy groups of cellulose, thereby enabling cellulose dissolution under relatively mild conditions. This concept is similar to that behind the well-known use of amide solvents such as dimethylacetamide and dimethylformamide with added LiCl for the dissolution of hydrogen-bonded polymers such as aromatic polyamides. The mechanism of cellulose dissolution in ILs has been studied in detail, using the temperature dependence of the relaxation time of the ¹³C and ^{35/37}Cl NMR signals.⁴⁹ In addition to the experimental approach, simulation studies on cellulose/IL combinations have also been carried out.⁵⁰ Cellulose processing using ILs is still ongoing and appears to be a promising area in biorefinery processes. Recently, ILs with alkyl phosphate, alkyl phosphonate, and alkyl phosphite anions that could dissolve cellulose more rapidly under milder conditions were developed by Ohno and co-workers.⁵¹ Based on a similar concept, many studies have been conducted on the solubilization of hydrogen-bonded hard-to-dissolve biopolymers such as silk,^{52,53} wool,^{54,55} keratin,⁵⁵ oligosaccharides,⁵⁶ and chitin⁵⁷ in ILs. Recently, certain proteins have been found to remain active for a long time in water/IL mixtures.^{58,59} Such studies are geared toward the eventual application of ILs in biochemical reactions and biopolymer preservation.

The dispersibility of carbon nanotubes (CNTs) in ILs,⁶⁰ found by Aida and co-workers, is also an interesting phenomenon, especially from the materials science perspective. CNTs have a large cohesive energy density as a result of their very large surface area and also exhibit strong π – π interactions, leading to the formation of bundles; hence, CNTs have low dispersibility in common solvents. CNTs can be finely dispersed in imidazolium ILs, possibly as a result of cation– π interactions; with increasing CNT concentrations, the mixtures form gels (“bucky gels”), which have high electrical conductivity as well as high ionic conductivity. Such composite materials consisting of CNTs and ILs have been employed in the electrodes of electric double-layer capacitors⁶¹ and actuators.^{62,63}

4. Phase Separation of Polymers in Ionic Liquids

4.1 LCST Phase Behavior of Methacrylate Polymers in Ionic Liquids. LCST phase behavior refers to the low-temperature mixing (soluble)/high-temperature demixing (insoluble) process. The LCST phase behavior is not phenomenologically and thermodynamically common. Based on the Flory–Huggins lattice model, the mixing entropy (ΔS_{mix}) in eq 1 is always positive. This indicates that ΔG_{mix} tends to become more negative when the temperature of the system is increased. In fact, such a simple model cannot describe the LCST phase behavior; nevertheless, there are a number of polymer/solvent mixtures which exhibit LCST phase behavior as the temperature is varied. LCST phase behavior is most often observed in aqueous polymer solutions. Poly(*N*-isopropylacrylamide) (PNIPAm) is the most well-known and the most extensively studied polymer exhibiting LCST phase behavior in aqueous media.⁶⁴ Because the phase-separation temperature of PNIPAm is close to room temperature,⁶⁵ the phase transitions of linear PNIPAm polymers, the related random

Table 4. Solubility of Pulp Cellulose in Ionic Liquids^{a)}

Ionic liquid	Method	Solubility/wt %
[C ₄ mim]Cl	heat (100 °C)	10
	heat (70 °C)	3
[C ₄ mim]Cl	heat (80 °C) + sonication	5
[C ₄ mim]Cl	microwave heating	25, clear
	3–5-s pulses	viscous solution
[C ₄ mim]Br	microwave	5–7
[C ₄ mim]SCN	microwave	5–7
[C ₄ mim][BF ₄]	microwave	insoluble
[C ₄ mim][PF ₆]	microwave	insoluble
[C ₆ mim]Cl	heat (100 °C)	5
[C ₈ mim]Cl	heat (100 °C)	slightly soluble

a) Reproduced with permission from Ref. 48.

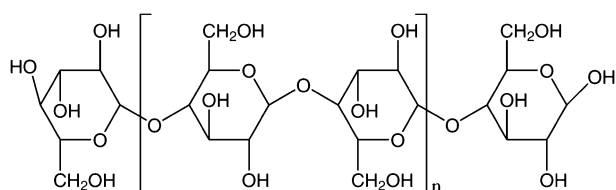


Figure 1. Chemical structure of cellulose.

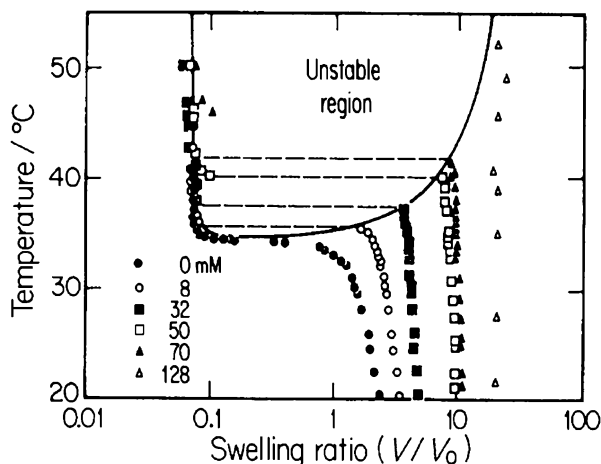


Figure 2. Volume phase transition of hydrogels of random copolymers consisting of NIPAm and sodium acrylate with different monomer compositions: 0, 8, 32, 50, 70, and 128 mM sodium acrylate. The total monomer concentration is 700 mM. Reproduced with permission from Ref. 65.

copolymers, and their gels have generated significant interest not only from the fundamental viewpoint but also from the application point of view. As mentioned before, thermosensitive PNIPAm gels have been proposed for use as “smart gels” with potential applicability in drug-delivery systems,^{66–70} optical devices,^{71,72} actuators,^{73–75} and sensing devices.^{76–78} Figure 2 shows the temperature-induced volume changes of a PNIPAm gel and its random copolymer gels with sodium acrylate in water. The figure illustrates that the volume of the gels changes dramatically at temperatures close to room temperature. With the exception of PNIPAm, other polymers reported so far which exhibit LCST phase behavior in aqueous solutions are polyether derivatives,^{79,80} cellulose derivatives,^{81,82} and betain polymers.⁸³ There have been many accounts of smart hydrogels that respond not only to temperature but also to light,^{84–86} electric fields,⁸⁷ magnetic fields,⁸⁸ pH,^{89–91} specific chemicals,^{92,93} and solvent compositions.⁹⁴

We found for the first time that poly(benzyl methacrylate) (PBnMA) exhibits LCST phase separation in an IL ($[C_n\text{mim}][\text{NTf}_2]$, $n = 1, 2, 4,$ and 6),²² as shown in Figure 3, where 100% transmittance indicates a transparent solution (soluble), whereas a transmittance lower than 100% indicates turbidity of the solution (phase separated). LCST phase behavior in media other than aqueous ones has seldom been encountered. Thermodynamic consideration of the LCST phase behavior shows that the essential requirements are a negative ΔS_{mix} in addition to a negative (exothermic) ΔH_{mix} in eq 1 for binary polymer/solvent systems. In other words, exothermic and structure-forming solvation must be present. When the entropic term ($-T\Delta S_{\text{mix}}$) exceeds the enthalpic term (ΔH_{mix}) in eq 1, with increasing temperature, desolvation of the polymer occurs, leading to LCST phase separation.⁹⁵ The negative ΔS_{mix} for well-known PNIPAm aqueous solutions is explained in terms of the hydrophobic hydration⁹⁶ of the isopropyl groups, resulting in formation of a cage-like ordered structure arising from hydrogen-bonding in the hydrated shells. On the other hand, a negative ΔH_{mix} is mainly attributed to the effects

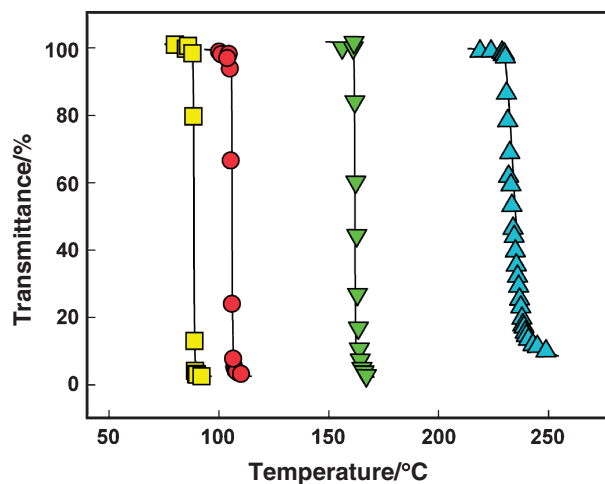


Figure 3. Temperature dependence of transmittance at 500 nm for PBnMA solutions in $[C_n\text{mim}][\text{NTf}_2]$. Yellow squares: $[C_1\text{mim}][\text{NTf}_2]$; red circles: $[C_2\text{mim}][\text{NTf}_2]$; green inverted triangles: $[C_4\text{mim}][\text{NTf}_2]$; blue triangles: $[C_6\text{mim}][\text{NTf}_2]$. Reproduced with permission from Ref. 22.

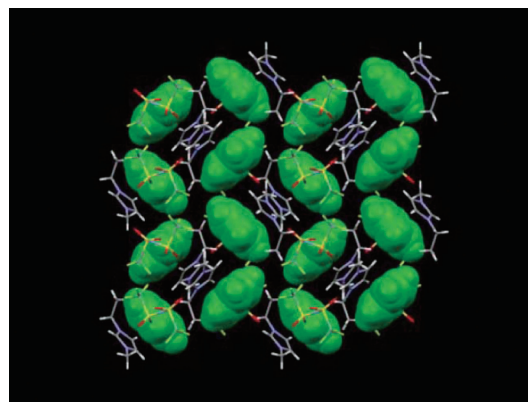


Figure 4. Snapshot of structure of $[C_2\text{mim}][\text{NTf}_2]$ /benzene monoclinic crystal, showing formation of tube-like structures of benzene (depicted in green) around IL ions. Reproduced with permission from Ref. 99.

of hydrogen-bonding interactions of the amide groups with water. The origin of the decrease in entropy upon mixing PBnMA with $[C_n\text{mim}][\text{NTf}_2]$ is still unclear; however, there have been a number of reports on the formation of structurally ordered aggregates in mixtures of aromatic compounds and ILs,^{97–100} i.e., the so-called “liquid clathrates” (Figure 4). We postulate that IL solvents form a structurally ordered solvation shell around the aromatic side chains of PBnMA, thereby decreasing the mixing entropy (negative ΔS_{mix}). At the same time, exothermic solvation (a negative ΔH_{mix}) may come from the interaction between the ester group and the IL (probably the anion). These thermodynamic aspects result in the observed LCST-type phase transition in the IL. This premise is strongly supported by the LCST-type phase separation of a random copolymer consisting of St and MMA (P(St-*r*-MMA)) with an approximately 50 mol % composition of St that has been observed in the $[C_2\text{mim}][\text{NTf}_2]$ IL.¹⁰¹ It is known that PSt is

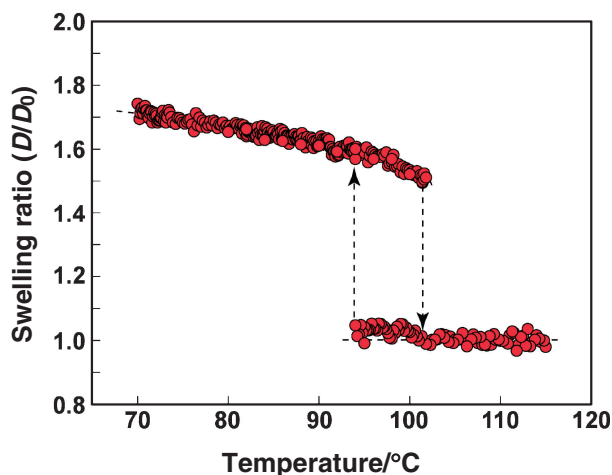


Figure 5. Equilibrium swelling ratio of PbnMA gel particles as a function of temperature in $[\text{C}_2\text{mim}][\text{NTf}_2]$. The swelling ratio represents the normalized gel diameter at each temperature divided by that at 100 °C. The temperature was increased in steps of 0.2 °C, and the measurements were performed after waiting for at least 1 h so that the gel particles could achieve equilibrium swelling. Reproduced with permission from Ref. 22.

insoluble and PMMA is freely soluble in this IL (Table 3). The coexistence of the aromatic unit, which causes a negative ΔS_{mix} , and the methacrylate unit, which causes a negative ΔH_{mix} , is essential for the appearance of LCST phase separation of this copolymer in an IL. Quite recently, LCST-type phase behavior has been reported for poly(*n*-butyl methacrylate) (PnBuMA),¹⁰² but the factors responsible for a negative ΔS_{mix} in this system are still unknown.

The phase-separation temperature of PbnMA is found to be greatly affected by small changes in the chemical structure of the IL as well as by small structural modifications of the aromatic side chains of the polymer.¹⁰³ This is supplementary evidence to substantiate the strong effect of a nanoenvironment around the aromatic side chain on the polymer phase behavior. A large change in the phase-separation temperature caused by a small change in the IL structure or the polymer structure of the PbnMA/IL composite is qualitatively explained by the approximately 10 times smaller entropy and enthalpy changes for the demixing of that system compared with those observed for PNIPAm in an aqueous solution,¹⁰⁴ which was obtained from a thermodynamic study¹⁰⁵ using superhigh-sensitivity DSC measurements.^{106,107} A small change in ΔS_{mix} and ΔH_{mix} for PbnMA in an IL can induce a large change in the phase-separation temperatures resulting from minor structural changes in the polymers as well as the IL. By using the significant structural dependence of the phase-separation temperature, we succeeded in demonstrating photoswitching of the phase-separation temperature of photochromic polymers in ILs. An azobenzene-containing PbnMA copolymer (P(AzoMA-*r*-BnMA)) exhibits a large phase-separation temperature difference in $[\text{C}_2\text{mim}][\text{NTf}_2]$, depending on the photoisomerization state of azobenzene.¹⁰⁸ It was also found that a PbnMA gel in $[\text{C}_2\text{mim}][\text{NTf}_2]$ exhibits volume phase transition (Figure 5), similar to PNIPAm gels in water (Figure 2). To the best of our

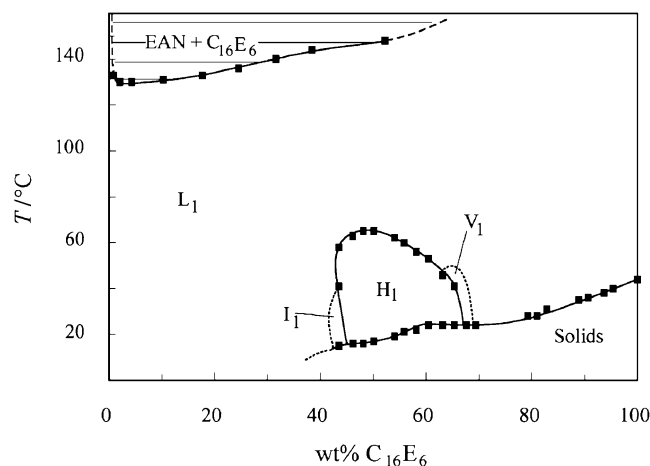


Figure 6. Phase diagram of binary poly(oxyethylene) alkyl ether nonionic surfactant (C16E6)/ethylammonium nitrate system, where 16 and 6 denote alkyl chain length and degrees of ethoxylation, respectively. L_1 , I_1 , H_1 , and V_1 indicate isotropic liquid, discrete cubic, hexagonal, and bicontinuous cubic phases, respectively. Reproduced with permission from Ref. 109.

knowledge, this represents the first report of the first-order volume phase transition of a neutral polymer network in a charged solvent, i.e., IL.

Stimuli-responsive polymers and polymer gels in nonvolatile, nonflammable, and thermally stable ILs would offer new soft and wet materials that may find many practical applications because of the wide range of temperatures that can be employed without solvent evaporation. One of our primary objectives is to control the LCST phase-separation temperatures and to accelerate the kinetics of solvation/desolvation and swelling/deswelling of polymers and polymer gels in neoteric IL solvents.

4.2 LCST Phase Behavior of Polyethers in Ionic Liquids.

Polyethers also exhibit interesting phase behavior in ILs. Warr and co-workers mapped out the phase behavior of PEO-based nonionic surfactants in ethylammonium nitrate ($[\text{EtNH}_3][\text{NO}_3]$, EAN), as shown in Figure 6.¹⁰⁹ They discussed the stability of a variety of lyotropic liquid crystals formed by a number of surfactants and found the pattern of self-assembly behavior and mesophase formation to be strikingly similar to that observed in water.¹¹⁰ In their first report published in 2005, they indicated LCST phase behavior in a nonionic surfactant/ $[\text{EtNH}_3][\text{NO}_3]$ combination, as shown in the low-surfactant concentration and high-temperature region of Figure 6. Lauth-Viguerie and co-workers reported lyotropic liquid crystal formation of nonionic surfactants in ILs.¹¹¹ They also demonstrated the LCST behavior of a polyether-based polymer in an IL.

We previously reported that polyethers prepared by anionic ring-opening polymerization of monosubstituted epoxy compounds, such as poly(ethyl glycidyl ether) (PEGE), poly(glycidyl methyl ether) (PGME), and poly(ethoxyethyl glycidyl ether) (PEEGE), undergo LCST phase separation in water.⁷⁹ It was also found recently that such polyethers exhibit LCST phase behavior in certain ILs and the full phase-diagrams of PEGE in $[\text{C}_2\text{mim}][\text{NTf}_2]$ have been elucidated.^{112,113} By using PEGEs having different molecular

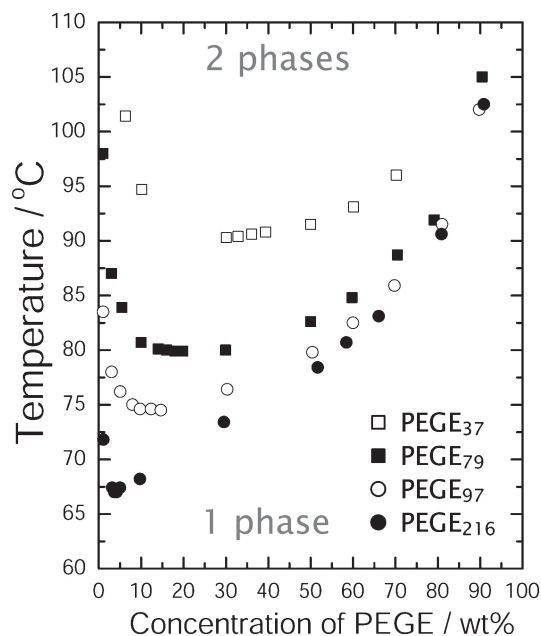


Figure 7. Phase diagrams for different molecular weight poly(ethyl glycidyl ether)s (PEGEs) and $[C_2mim][NTf_2]$. Reproduced with permission from Ref. 112.

weights with narrow molecular weight distributions, the effect of the molecular weight on the LCST phase behavior was investigated (Figure 7). The LCST phase-separation temperatures are also greatly altered, depending on the hydrogen-bonding ability of the cations. For example, when an imidazolium-based IL is used as the solvent, the 1H NMR chemical shift of the imidazolium ring proton at the 2-position exhibits a pronounced downfield shift with an increase in the concentration of PEGE in the IL. In addition, the LCST phase-separation temperatures of $[C_n dmim]$ -based ILs are markedly decreased compared to those observed for $[C_n mim]$ -based ILs, and ILs based on aliphatic ammonium cations are not compatible with these polyethers, indicating that the hydrogen-bond donor ability of the IL cations plays a crucial role in determining the LCST phase-separation temperatures. It is interesting to note that the LCST phase-separation temperatures of methacrylate-based polymers in imidazolium ILs are relatively unaffected by whether or not the cations of the ILs possess hydrogen-bond donor ability. An increase in the polarity of the polyethers (oxygen weight fraction) results in increased miscibility with the ILs and a higher LCST phase-separation temperature. The miscibility of the mixtures is also affected to a considerable extent by the Lewis basicity of the anions in the ILs; basic anions decrease the miscibility by interrupting the hydrogen-bonding interaction between the polyethers and ILs. The hydrogen-bonding interaction between the oxygen atoms in the polyethers and the aromatic hydrogen atoms on the cations in the ILs plays an important role in the LCST phase behavior of the mixtures. These results also imply that highly directional hydrogen-bonds between the ether oxygen atoms and the acidic cationic protons contribute to negative changes in both ΔS_{mix} and ΔH_{mix} for the mixing between polyethers and ILs, where the operational mechanisms of LCST phase separation completely differs from those of

methacrylate-based polymers. An MD simulation study performed by Ribeiro and co-workers revealed the formation of short- or middle-range structural order in the mixtures containing the PEO oligomer and $[C_n mim]$ cation of the IL.¹¹⁴ This simulation study also supports the role of hydrogen-bonds between PEO derivatives and ILs in decreasing the mixing entropy. Most recently, several groups reported the LCST phase behavior of PEO in other ILs, for example, $[C_n mim]Cl$ and $[C_n mim]BF_4$, where $n = 2$ and 4.¹¹⁵ Such liquid–liquid phase separation of polyether/IL mixtures can potentially be used for biopolymer processing, as suggested by Rogers and co-workers.¹¹⁶ Liquid–liquid phase separation of polyethers and ILs also represents a promising platform for achieving novel extraction and reaction media.

The importance of hydrogen-bonds for LCST phase separation was first reported in a low-molecular-weight system for quasi-binary solutions consisting of a $[C_4mim][NTf_2]/[C_5mim][NTf_2]$ IL mixture and a $CHCl_3/CCl_4$ organic solvent mixture by Rebelo, Seddon, and co-workers in 2005. This system shows LCST phase behavior, and the importance of oriented solvation via hydrogen-bonding between Cl atoms in the organic solvent and the acidic hydrogen atoms of the imidazolium ring of the IL was illustrated (Figure 8).¹¹⁷

4.3 UCST Phase Behavior of Polymers in Ionic Liquids.

Comprehensive studies of UCST phase behavior were conducted by Brennecke and co-workers using low-molecular-weight alcohols in ILs.¹¹⁸ From this study, it was found that: 1) the UCST increases (mutual miscibility decreases) as the alkyl chain length of the alcohols increases, 2) the UCST decreases (mutual miscibility increases) as the alkyl chain length of the IL cations increases, 3) the UCST decreases (mutual miscibility increases) as the hydrogen-bond accepting ability (Lewis basicity) of the counter anion increases. When the chemical structures of the cation of the IL and the alcohol were fixed, UCST was found to decrease in the order $PF_6 > BF_4 > [NTf_2] > [TfO] > N(CN)_2$.

Interestingly, as shown in Table 2, LCST and UCST phase behaviors have both been observed for polymers/IL mixtures. The first report of the UCST phase behavior of PNIPAm in $[C_2mim][NTf_2]$ was presented by the current authors;²¹ this behavior was of particular interest because it is the complete opposite of the well-known LCST phase-separation phenomenon of this polymer in water. The discovery of the UCST phase behavior of PNIPAm was used in the thermal control of block copolymer self-assemblies in ILs and to develop a thermoreversible ion gel (vide infra).^{119,120}

The investigation of PNIPAm solubility in a variety of organic solvents having different donor numbers (DNs) revealed that the UCST phase-separation temperature of PNIPAm increases with an increase in the DN, which corresponds to the Lewis basicity of the solvents.²¹ It is assumed that the interaction of the PNIPAm polymer chain with solvents having higher DN is enthalpically favored, resulting in the formation of homogeneous solutions. PNIPAm can dissolve in a solvent with a low DN at higher temperatures, because a positive entropic term ($T\Delta S_{mix}$) compensates for a positive enthalpic term (ΔH_{mix}). The phase-separation temperature of PNIPAm depends strongly on both the concentration and molecular weight (and M_n distribution) of the polymer.

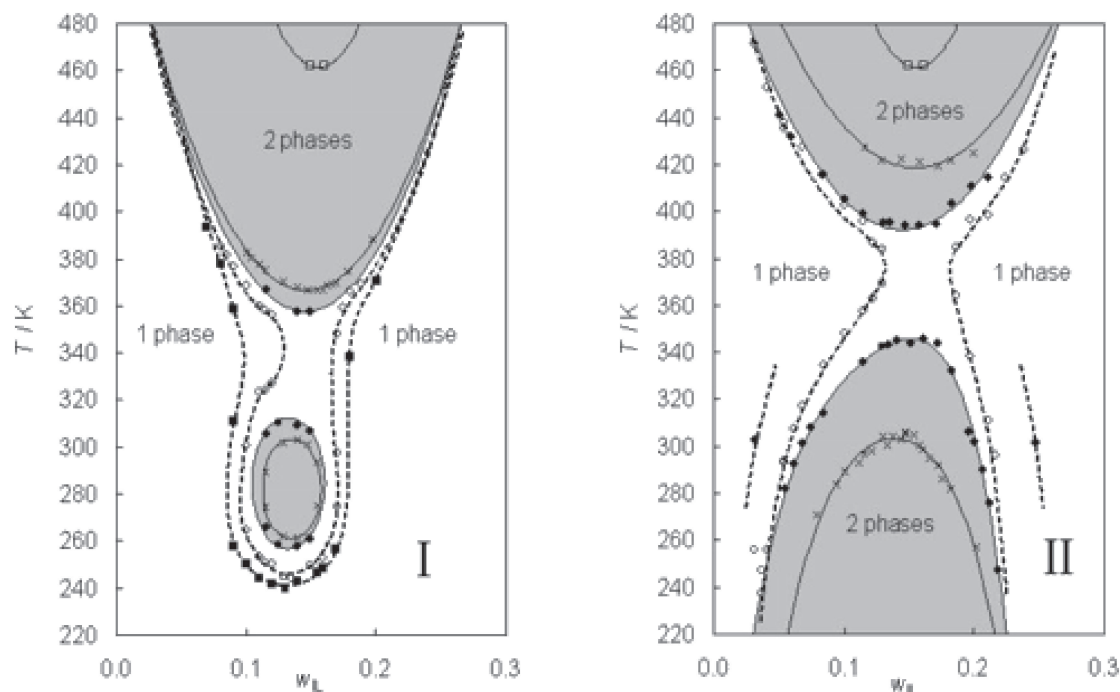


Figure 8. Phase diagrams of $[C_n\text{mim}][\text{NTf}_2]/\text{CH}_x\text{Cl}_{4-x}$ quasi-binary mixture systems. w_{IL} : weight fraction of IL. In system I (left), $x = 1$; open squares: $n = 5.000$; crosses: $n = 4.337$; closed circles: $n = 4.330$; open circles: $n = 4.320$; closed squares: $n = 4.300$. In system II (right), $n = 5$; c is the weight percentage ratio of CCl_4 in CHCl_3 , open squares: $c = 0\%$; crosses: $c = 6.5\%$; closed circles: $c = 7.6\%$; open circles: $c = 8.0\%$; closed diamonds: $c = 10.5\%$. Reproduced with permission from Ref. 117.

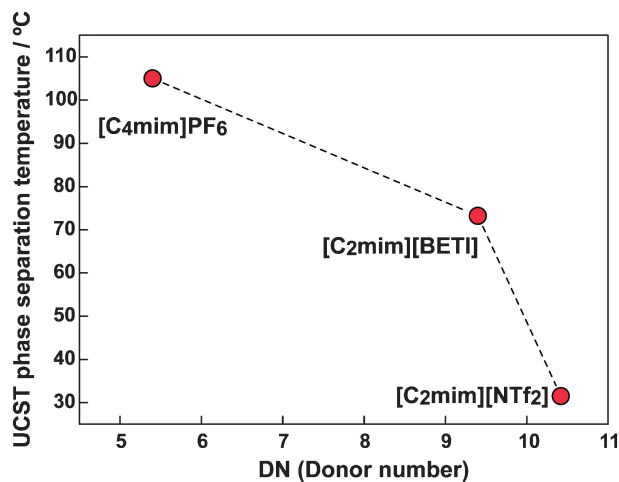


Figure 9. Relationship between UCST phase-separation temperature of 3 wt% PNIPAm ($M_n = 40$ kDa, PDI = 1.19) solutions in $[\text{C}_2\text{mim}][\text{NTf}_2]$, $[\text{C}_4\text{mim}][\text{PF}_6]$, and $[\text{C}_2\text{mim}][\text{BETI}]$, respectively, and the solvent donor number.

Figure 9 shows the relationship between the UCST phase-separation temperature and the donor number of ILs, using a PNIPAm sample which was made by RAFT polymerization and which has a relatively narrow polydispersity index (40 kDa, PDI = 1.19). The DN of the ILs could be quantitatively determined from the absorption maximum of a classic copper complex dye dissolved in the various ILs by exploiting the well-known correlation between the absorption maxima of the copper complex and the DN of common organic

solvents.¹²¹ Figure 9 illustrates that the UCST phase-separation temperature of PNIPAm in the ILs also decreases with an increase in the DN. However, it should be noted here that the phase-separation temperature changes between ILs even with identical anions if the cationic structure is altered.

Table 3 illustrates that there are several polymers other than PNIPAm that show UCST phase behavior in ILs. In polymer/common organic solvent mixtures, UCST phase changes are the type most frequently observed. However, as pointed out previously, both UCST and LCST phase behaviors have been observed for polymers in ILs. ILs consist entirely of ions, and, thus, the main force operating between the ions is the Coulombic interaction, which is a nondirectional and long-range force. However, the ions in ILs are frequently organic ions, and, therefore, strongly directional interactions between the ions and solutes in the ILs, such as hydrogen-bonds, cation- π interactions, π - π interactions, and van der Waals interactions may also exist. These directional interactions in addition to the strong Coulombic interaction can induce structure-forming solvation for certain solutes, which induces a negative ΔS_{mix} and results in LCST phase behavior. Furthermore, because the ILs consist of organic ions, they may also function like organic solvents with certain solutes, in which case UCST phase behavior can be observed. These bilateral characteristics of ILs classify them as unique liquid media for polymer solvation and thus account for both the UCST and LCST phase behaviors.

4.4 Sol-Gel Transition of Polymers in Ionic Liquids.

Random copolymers composed of vinylidene fluoride and hexafluoropropylene (Entry 24 in Table 3, P(VdF-*r*-HFP)) undergo sol-gel transitions (of their solutions) with decreasing

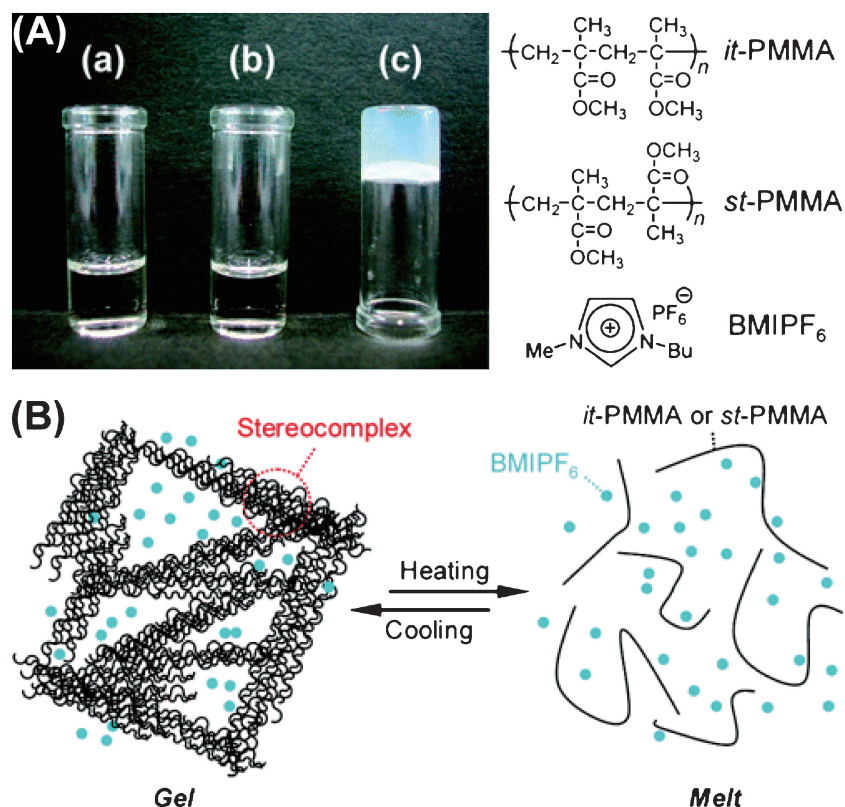


Figure 10. (A) Photograph of *it*-PMMA (a), *st*-PMMA (b), and their stereocomplex (*it/st* = 1/2 in unit molar base) (c) in [C₄mim]PF₆. (B) Conceptual illustration of thermoreversible ion gel by stereocomplex formation. Reproduced with permission from Ref. 128.

temperature in certain organic solvents and ILs. UCST phase separation of the polymer from the solution triggers the sol–gel transition of P(VdF-*r*-HFP), which is followed by the formation of spherulites in the solvents (including ILs), leading to gelation of the solutions.¹²² The sol–gel transition of P(VdF-*r*-HFP) has been proposed to be potentially applicable to processable ion gels, particularly for use in electrochemical devices. Trulove and co-workers reported the formation of P(VdF-*r*-HFP) gels in [C₃dmim][X] and [C₄dmim][Y] (where [X] = BF₄ or [NTf₂], Y = BF₄, [NTf₂], or PF₆).¹²³ In addition to that study, gel formation has also been reported for P(VdF-*r*-HFP) in [C₂mim][X] ([X] = [OTf] or BF₄),¹²⁴ [C₃dmim][X] ([X] = BF₄, [NTf₂], PF₆, or [OTf]),¹²⁵ and [1-hydroxyethyl-C₂mim][X] ([X] = BF₄ or PF₆).¹²⁶ The combination of P(VdF-*r*-HFP) and ILs appears to produce thermoreversible ion gels for a wide variety of ILs.

It is known that a mixture of isotactic-PMMA (*it*-PMMA) and syndiotactic-PMMA (*st*-PMMA) in a polar solvent forms a thermoreversible gel as a result of stereocomplex formation between the PMMAs.¹²⁷ Yashima and co-workers exploited this phenomenon in the development of a thermoreversible ion gel (Figure 10).¹²⁸ In contrast to the case of the thermoreversible P(VdF-*r*-HFP) gel, the gelation behavior of the stereocomplex of PMMA is strongly dependent on the anionic structures. When [C₄mim] is used as the cation and the counter anion is varied, the ILs with PF₆ or [NTf₂] anions produced thermoreversible ion gels, whereas use of an IL having the [OTf] anion did not result in the formation of an ion gel.

5. Self-Assembly of Block Copolymers in Ionic Liquids

A block copolymer is formed by the coupling of two or more chemically distinct polymer segments (blocks) in a linear and/or radial arrangement. When the repulsive interaction between connected blocks is sufficiently strong, microphase separation into periodic domains occurs, whether in the melt, solid, or solution state, although the segments remain tethered together. This subject matter has been comprehensively reviewed and is now a textbook topic.^{23–25} Spontaneous self-assembly of block copolymers has been regarded as a novel bottom-up strategy for nanopatterning techniques.^{129–134} Block copolymer self-assemblies have also been proposed for use in novel applications such as templates for nanoporous or mesoporous materials,¹³⁵ controlled arrangement for nanoparticle arrays,¹³⁶ and as hardeners for soft materials.¹³⁷ In addition, recent advances in the development of controlled polymerization protocols have enabled the straightforward synthesis of quite complicated block copolymer architectures, incorporating a wide selection of monomers, as mentioned in the introduction.

Block copolymers consisting of polyether segments have been extensively investigated because they have the advantages of being nontoxic and water soluble, as well as having a nonionic nature; these properties satisfy the requirements for drug-delivery or medical purposes. The most renowned of these is the P(EO-*b*-PO-*b*-EO) triblock copolymers, which are well known as *Pluronic* by their BASF trademark. The first reported

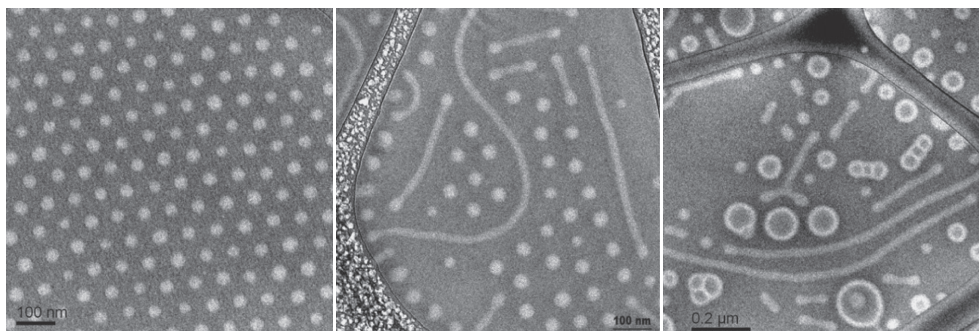


Figure 11. Cryo-TEM images for self-assembly of P(B-*b*-EO) in [C₄mim]PF₆. White dots (left), white strings (center), and white double circles (right) correspond to spherical micelles, cylindrical micelles, and bilayer vesicles, respectively. Reproduced with permission from Ref. 139.

block copolymer/IL mixture also consisted of polyether derivatives. In 2003, Armstrong and co-workers reported that adding a commercially available nonionic surfactant, Brij35 (alkyl-PEO), to [C₄mim]PF₆ or to [C₄mim]Cl resulted in surface-tension diminution.¹³⁸ They discussed the micellization behavior of the surfactant based on their results. A comprehensive study of the self-assembly of well-defined block copolymers in an IL was first conducted by Lodge and co-workers.¹³⁹ In that study, diblock copolymers with different total molecular weights, consisting of polybutadiene and PEO (P(B-*b*-EO)), which form micelles of a PB-core surrounded by a PEO-shell in [C₄mim]PF₆, were prepared. Changing the volume fraction of PEO in the diblock copolymers revealed the universal morphology of various micelles: spherical micelles, cylindrical micelles, and bilayer vesicles could be observed. The micellar structure was explored using both cryogenic transmission electron microscopy (cryo-TEM) and dynamic light-scattering (DLS) measurements, with excellent agreement between the results of the two techniques (Figure 11). Another related topic concerning the block copolymer/IL mixture is the discovery of “round-trip” micelles between water and hydrophobic ILs.^{140,141} The aggregation of triblock copolymers in ILs was further exploited with the aim of forming physical ion gels, where it was demonstrated that the P(St-*b*-EO-*b*-St) triblock copolymer and [C₄mim]PF₆ binary system yields a physical ion gel at block copolymer loadings as low as 5 wt%.¹⁴² As mentioned above, block copolymer melts, the solids or their concentrated solutions, are macroscopically homogeneous but possess predictable structural heterogeneity at length scales of a few nanometers up to several micrometers.^{143,144} Such nanostructures have well-known ordered states (cubic, lamellar, hexagonal, and bicontinuous phases). When ILs are used as solvents for block copolymer composites, the entire mixture possesses both IL-rich and polymer-rich domains. The former gives the desirable functionality, for example, ionic conductivity and selective gas permeability, while the latter gives mechanical strength,^{145,146} leading to applicability in areas such as plastic electronics.¹⁴⁷

The formation of thermoreversible ion gels by combining the block copolymer self-assembly and the UCST thermosensitivity of PNIPAm in ILs has also been proposed. A P(NIPAm-*b*-EO-*b*-NIPAm) triblock copolymer that exhibits a reversible sol-gel transition in which both ends of the triblock copolymer aggregate together to form physical crosslinking points below

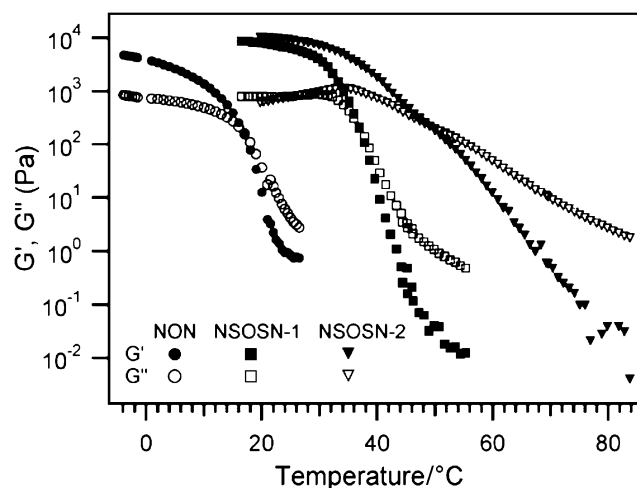


Figure 12. Temperature-dependent dynamic shear moduli (G' and G'') for three ion-gels (P(NIPAm_{4.3}-*b*-EO₂₀-*b*-NIPAm_{4.3}), P(NIPAm_{4.5}-*b*-St_{3.3}-*b*-EO₂₀-*b*-St_{3.3}-*b*-NIPAm_{4.5}), and P(NIPAm_{3.8}-*b*-St_{4.4}-*b*-EO₃₅-*b*-St_{3.8}-*b*-NIPAm_{4.4})), each with 10 wt% copolymer in [C₂mim][NTf₂]. The number shown after the name of the polymer indicates the molecular weight of the polymer (kDa). The measurements were taken at strain $\gamma = 2\%$, frequency $\omega = 0.1 \text{ rad s}^{-1}$, and heating rate = $1 \text{ }^\circ\text{C min}^{-1}$. Reproduced with permission from Ref. 120.

the UCST phase-separation temperature of PNIPAm is also known. As the temperature is increased above the UCST phase-transition temperature, melting of the gel can be observed. By incorporating the solvophobic PSt segment into the P(NIPAm-*b*-EO-*b*-NIPAm) triblock copolymers to produce well-defined P(NIPAm-*b*-St-*b*-EO-*b*-St-*b*-NIPAm) pentablock copolymers, the melting temperature of the resulting ion gels could be tuned over a wide temperature range (17–48 °C) (Figure 12). Thermoreversible ion gels offer the advantage of solvent-free processing during practical applications. Ion-gel formation by supramolecular self-assembly of block copolymers has also been conducted by the same group. Triblock copolymers consisting of poly(2-vinylpyridine) (P2VP) segments at both ends of the triblock and solvophilic poly(ethyl acrylate) as the middle block (P(2VP-*b*-EA-*b*-2VP)), were successfully prepared by RAFT polymerization. A solution containing 10 wt% P(2VP-*b*-EA-*b*-2VP) and 4 wt% poly(4-

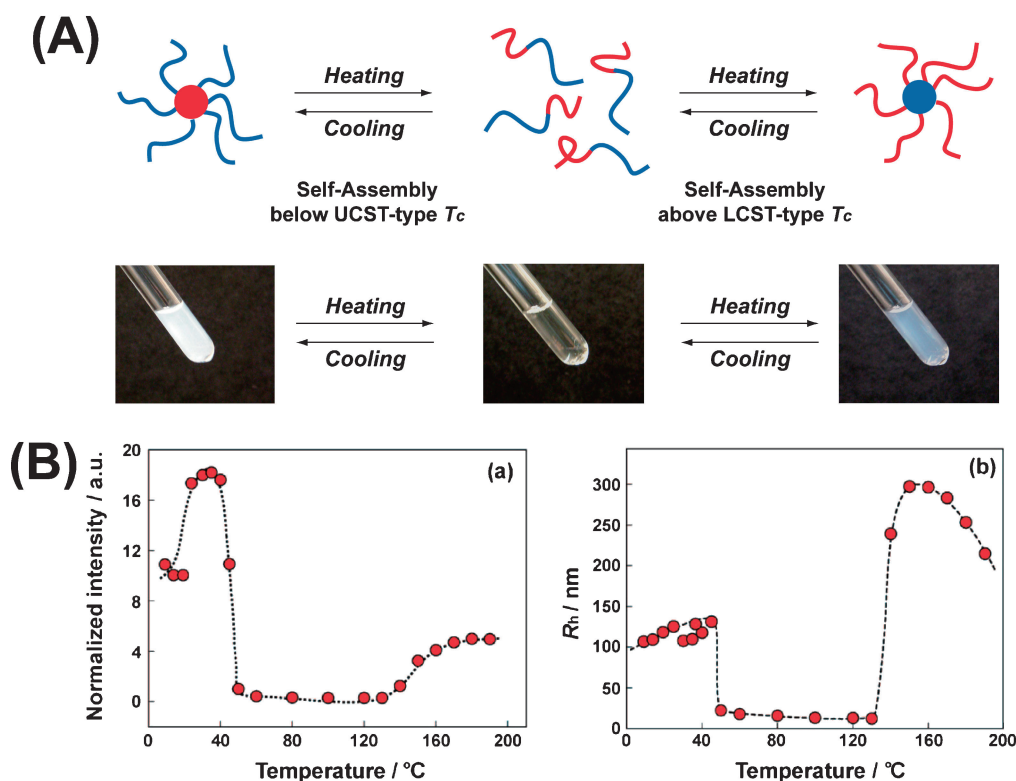


Figure 13. (A) Conceptual illustration of doubly thermosensitive self-assembly of block copolymer in IL (upper) and difference in appearance of block copolymer IL solution depending on sample temperature (lower). (B) Scattering intensity (a) and hydrodynamic radius (b) of PBnMA-*b*-P(NIPAm-*r*-AAm) 1 wt% solution in [C₂mim][NTf₂] as a function of temperature, determined by dynamic light-scattering measurements. Reproduced with permission from Ref. 150.

hydroxystyrene) (P4HSt) in [C₂mim][NTf₂] forms a thermoreversible supramolecular polymer network via hydrogen-bonds between proton-accepting P2VP segments and proton-donating P4HSt segments.¹⁴⁸

The transition phenomenon of low-temperature unimer/high-temperature aggregation behavior in ILs is also of great interest and has been demonstrated by the current authors by exploiting the LCST phase behavior of polymers in ILs. P(BnMA-*b*-MMA), where the MMA segment is solvophilic, exhibits this type of self-assembly in the hydrophobic IL [C₂mim][NTf₂].¹⁴⁹ In addition, doubly thermosensitive micellar aggregation in an IL (or IL mixtures) was also demonstrated using block copolymers consisting of segments that exhibit LCST and UCST. These polymers include P(BnMA-*b*-NIPAm) and P(BnMA-*b*-(NIPAm-*r*-AAm)). At temperatures below the UCST phase-separation temperatures of the PNIPAm or P(NIPAm-*r*-AAm) segments, PBnMA-shell micelles are formed. In contrast, at temperatures higher than the LCST phase-separation temperature of the PBnMA, PBnMA-core micelles are formed (Figure 13).¹⁵⁰ In other words, micelle/inverse-micelle transition occurs in an IL with temperature variations. It is known that diblock copolymers may form micelles and inverse-micelles, based on an appropriate choice of solvents. For example, P(St-*b*-B) diblock copolymers form micelles with either PSt-cores (in *n*-alkanes) or PB-cores (in dimethylformamide or methyl ethyl ketone).¹⁵¹ Diblock copolymers of PSt and polyisoprene (P(St-*b*-I)) also exhibit a similar reverse micellization in PSt-selective solvents (diethyl

phthalate and dimethyl phthalate) and in PI-selective solvents (tetradecane and squalane).¹⁵² The stimuli-sensitive micelle/inverse-micelle transition of a block copolymer in a single solvent is called “schizophrenic aggregation behavior,” which has only been reported for aqueous solutions, triggered by either pH or temperature.^{153–156} However, the micelle/unimer/inverse-micelle transition of doubly thermosensitive block copolymers has been observed for the first time in ILs.¹⁵⁰ Such unique self-assembly of block copolymers in ILs is of fundamental interest and at the same time offers a potential route to various smart materials.

6. Concluding Remarks

In this paper, the solubility, phase behavior, and self-assembly of polymers in ILs were comprehensively reviewed. The solubility of polymers in ILs was evaluated in the first section of the paper. Although Hildebrand SPs have frequently been used to account for the solubility of polymers in organic solvents, the SPs for ILs do not have the same significance as those for conventional molecular liquids and cannot be used to account for the solubility of solutes in ILs. This is because the ionic character of ILs is strongly reflected in the SP values, whereas the assumptions behind the Hildebrand SPs that are normally used to determine the polymer solubility in organic solvents, where Coulombic interactions are usually absent, do not account for the strong Coulombic interactions present in ILs. However, based on the empirical data obtained from a screening test of the compatibility of 24 different polymers in

four different ILs, it is found that the Lewis basicities of the counter anions in the ILs play an important role in determining the solubility of the polymers.

It is also important to note that ILs can be used as good solvents for low-solubility biopolymers and as good dispersion media for CNTs, which contributes to the fields of biorefinery processes and advanced materials. The most renowned example of the former is the use of ILs as solvents for cellulose. ILs having strong hydrogen-bond accepting anions such as chloride and acetate anions can solvate the hydroxy groups of cellulose, thereby enabling cellulose dissolution under relatively mild conditions. CNTs can be finely dispersed in imidazolium ILs, possibly as a result of cation- π interactions. The mixtures form gels with increasing CNT concentrations, which have high electrical conductivity as well as high ionic conductivity and are expected to be advanced functional materials.

Certain combinations of polymers in ILs exhibit temperature-dependent phase changes. Interestingly, both UCST phase behavior and LCST phase behavior were observed in polymer/IL binary mixtures. The UCST phase behavior is often observed for polymers in organic solvents and can be understood in terms of a positive enthalpic term (ΔH_{mix}) that is compensated for by a negative entropic term ($-T\Delta S_{\text{mix}}$) with increasing temperatures. In ILs, ΔH_{mix} appears to be greatly affected by the Lewis basicities of the anions. Conversely, the LCST phase behavior, which has largely been restricted to aqueous polymer solutions, is not compatible with the Flory-Huggins lattice model for describing the mixing entropy change because the essential requirements are a negative ΔS_{mix} in addition to a negative ΔH_{mix} . In other words, an exothermic and structure-forming solvation process should exist. When the entropic term ($-T\Delta S_{\text{mix}}$) overwhelms the enthalpic term (ΔH_{mix}) with increasing temperature, LCST phase separation occurs. The origin of structure-forming solvation in ILs is still not completely understood; however, the origin appears to vary depending on the polymer structures. In the case of PBnMA and its derivatives, IL solvents appear to induce structure-forming solvation around the aromatic side chains of PBnMA ("liquid clathrate") as a result of cation- π interactions. The coexistence of the aromatic unit, which causes a negative ΔS_{mix} , and the methacrylate unit, which causes a negative ΔH_{mix} , is essential for the appearance of the LCST phase separation of these polymers. In the case of polyethers, hydrogen-bonding interaction between acidic cationic protons and the ether oxygen atoms appears to be responsible for both the negative ΔS_{mix} and the negative ΔH_{mix} . ILs consist entirely of ions, and thus strong but nondirectional Coulombic interactions are present in their composites. In addition to this interaction, many weak but directional interactions such as hydrogen-bonding, cation- π , π - π , charge-transfer, and van der Waals interactions may operate between the ions as well as between the ions and the molecular solutes because ILs frequently consist of organic ions. The coexistence of strong and directional interactions may assist structure-forming solvation in ILs, as is the case in water.

In the latter part of this review, recent developments concerning phase transition and self-assembly of polymers in ILs were appraised. Studies on the stimuli-responsive (typically UCST and LCST) polymers and polymer gels in ILs are

expected to take a new direction in the development of "smart" materials which can be used over a wide range of temperatures and atmospheric conditions without solvent evaporation because of the nonvolatility of ILs. Liquid-liquid phase separation between polymer melts and ILs induced by temperature changes is promising for use in novel extraction or separation processes. Finally, self-assembly of block copolymers in ILs was discussed. The predictable structural heterogeneity caused by nanosegregation of block copolymers in ILs results in the formation of IL-rich and polymer-rich domains, both in dilute and concentrated solutions. In dilute solutions, block copolymers can self-assemble into a variety of micelles. If thermosensitive polymer segments are incorporated into the block copolymers, thermally induced self-assembly changes may be judiciously designed. Concentrated block polymers in ILs can give rise to thermoplastic or thermosetting ion gels with nanosegregated domains. The IL-rich domains may produce the desirable functionality, while the polymer-rich domains may furnish mechanical strength, thereby opening new avenues to the development of functional ion gels.

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