

## FOCUS REVIEW

# Stimuli-responsive polymers in ionic liquids

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The solidification of ionic liquids (ILs) in combination with synthetic polymers has been closely investigated for membrane applications, such as in plastic electronics for energy conversion/storage purposes, gas separations and actuators, owing to the versatile structure designability and unique properties of ILs. The possible combinations of ILs with polymers are not simply limited to the use of compatible components; stimuli-responsive synthetic polymers that undergo changes in solubility in response to external stimuli in ILs are now being recognized as a novel platform for creating intelligent soft materials. As a consequence of the nonvolatility and wide liquid temperature range of ILs, smart wet materials consisting of polymer–IL combinations can be employed under an open atmosphere over prolonged time periods and can also permit wide operating temperature and pressure conditions without solvent evaporation, a serious drawback of traditional smart wet (soft) materials. This review focuses on the thermodynamic aspects of and recent developments in stimuli-responsive polymers in ILs as a new class of intelligent soft materials.

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**Keywords:** block copolymers; gels; ionic liquids; LCST; self-organization; UCST; volume phase transition

## INTRODUCTION

Ionic liquids (ILs) are ambient-temperature molten salts possessing unique properties, such as high ion conductivity, electrochemical stability, nonvolatility, nonflammability and high solvation for specific solutes.<sup>1,2</sup> Since their recognition as both environmentally benign ‘green’ liquids and as a third solvent group—separate from water and organic solvents—ILs have been widely applied as a high ion-conductive medium for energy storage materials,<sup>3–5</sup> as reaction or extraction solvents for organic synthesis<sup>6–8</sup> and for use under vacuum conditions,<sup>9,10</sup> where other common solvents cannot be used because of evaporation concerns. In polymer science, ILs have received a great deal of attention as solvents for polymerization;<sup>11,12</sup> for the solubilization of sparingly soluble polymers such as cellulose,<sup>13–15</sup> silk<sup>16</sup> and wool;<sup>17</sup> as a dispersing medium for carbon nanotubes;<sup>18</sup> and as a preservation medium for biopolymers, such as proteins<sup>19–21</sup> and DNA.<sup>22,23</sup> Furthermore, the combination of (quasi) solid-state materials with ILs permits the fabrication of useful soft materials because the ILs can be tailored to exhibit specific properties. The scope and utility of composite ILs with synthetic polymers is ever-expanding; novel classes of solid-state electrolytes,<sup>24–26</sup> organic thin-film transistors,<sup>27</sup> gas separation membranes<sup>28</sup> and catalytic membranes<sup>29,30</sup> are currently under extensive development. The combination of ILs with light and inexpensive synthetic polymers is considered one of the more effective methodologies for achieving (quasi) solid materials from ILs.<sup>3,4,24,25,31</sup> Extensive reviews addressing the functionalization and compatibility of ILs with synthetic polymers are now available.<sup>24,25,31,32</sup> This article focuses especially on the recent progress and perspectives in stimuli-responsive polymers in ILs.

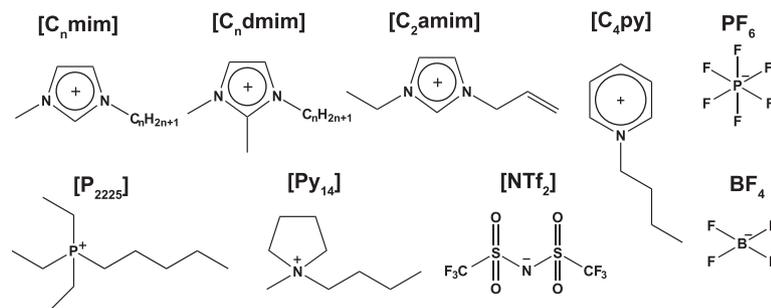
Although numerous efforts have been devoted to realizing smart soft materials by utilizing the phase changes of polymers (gels) in either water or common organic solvents,<sup>33–38</sup> studies of wet stimuli-responsive materials containing ILs remain in a preliminary stage. Because typical ILs are thermally stable and have extremely wide liquid temperature ranges, smart soft materials composed of ILs can be used under an open atmosphere over extended time periods without concerns about solvent evaporation and are not limited by operating temperatures or pressure conditions under which common solvents might not be ensured fluidity. Moreover, from the perspective of fundamental polymer science, it is important to understand how polymers dissolve and change in solubility in response to external stimuli in ILs, a medium consisting entirely of ions. Scheme 1 summarizes the structures and abbreviations of the polymers, cations and anions discussed in this article.

## THERMOSENSITIVE POLYMERS IN ILS

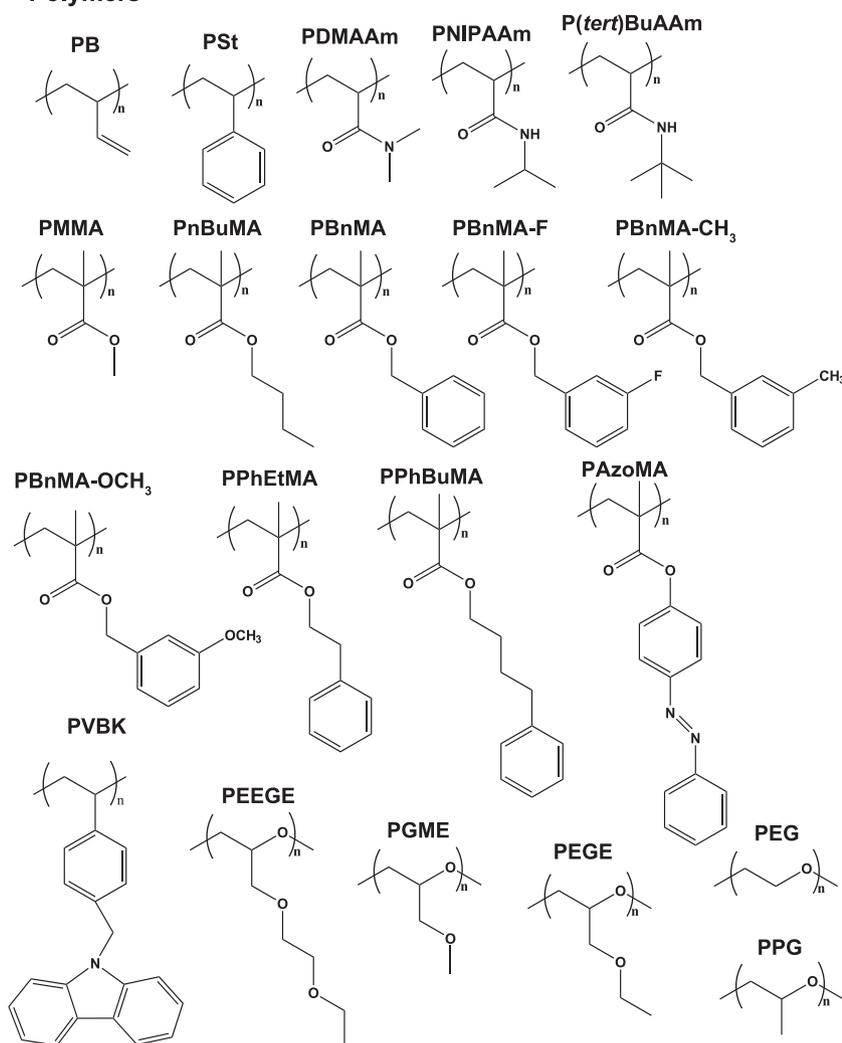
### Phase behavior of polyacrylamides and polymethacrylates in ILS

In 2006, we reported for the first time that poly(*N*-isopropylacrylamide) (PNIPAAm) exhibits an upper critical solution temperature (UCST)-type phase separation in a typical hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ([C<sub>2</sub>mim][NTf<sub>2</sub>]) (Figure 1a).<sup>39</sup> PNIPAAm is presently the most famous and widely studied thermosensitive polymer, as it shows a lower critical solution temperature (LCST)-type phase separation in aqueous solutions at approximately body temperature.<sup>33</sup> Although the UCST phase transition is not a rare phase behavior for nonaqueous polymer solutions, as discussed below, it is interesting to note that PNIPAAm

## &lt;Cations &amp; Anions&gt;



## &lt;Polymers&gt;



**Scheme 1** Chemical structures and abbreviations of the cations, anions and polymers discussed in this article.

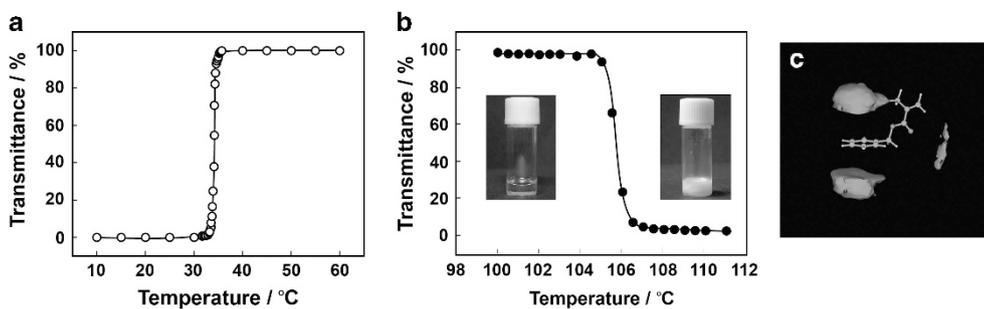
in an IL exhibits completely opposite phase transitions as those observed in aqueous solutions.<sup>40</sup>

To determine the temperature dependence of the mutual solubility of a polymer and a solvent, the Gibbs free energy of mixing ( $\Delta G_{\text{mix}}$ ) is considered that is expressed by the following relation:

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

where  $\Delta H_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  are the enthalpy and entropy of mixing, respectively, and  $T$  is the absolute temperature. When the  $\Delta G_{\text{mix}}$  value

of the system is negative, the polymer and solvent spontaneously mix together to produce a homogeneous transparent solution, whereas at positive  $\Delta G_{\text{mix}}$  values, the polymer solution becomes turbid because of the phase separation of the polymer and the solvent. According to the traditional lattice model established by Flory and Huggins,  $\Delta S_{\text{mix}}$  values are always estimated as positive. Therefore, the product of  $T$  and  $\Delta S_{\text{mix}}$  should always be positive, and the absolute value of the second term on the right-hand side of Equation (1) becomes larger with increasing temperature, leading to a negative  $\Delta G_{\text{mix}}$ . This



**Figure 1** (a) Upper critical solution temperature (UCST)-type phase behavior of poly(*N*-isopropylacrylamide) (PNIPAAm; 1 wt%) and (b) lower critical solution temperature (LCST)-type phase behavior of poly(benzyl methacrylate) (PBnMA; 3 wt%) [C<sub>2</sub>mim][NTf<sub>2</sub>] solutions, together with photographs depicting the appearance of PBnMA solutions below and above the transition temperature. (c) Space-distribution functions for the center of mass of the [C<sub>2</sub>mim] cation around monomeric BnMA. The clouds represent the iso-probability surfaces of a 1.8-fold larger probability density relative to the bulk. Reproduced with permission from Ueki *et al.*<sup>39,50</sup> and Matsugami *et al.*<sup>53</sup> A full color version of this figure is available at the *Polymer Journal* online.

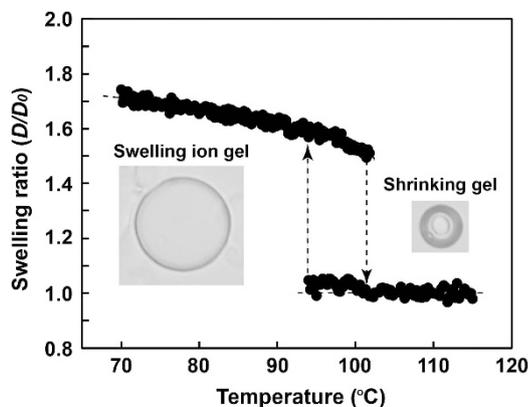
consideration supports the thermodynamic conditions in observations of UCST phase separations that are achieved by a  $\Delta H_{\text{mix}}$  that is positive and moderately smaller than the product of  $T$  and  $\Delta S_{\text{mix}}$ . In certain ILs, NIPAAm or related (meth)acrylamide derivatives that display both hydrogen-bond-donating and accepting components are found to show UCST behavior.<sup>24</sup> These polymers exhibit inter/intramolecular hydrogen bonding among the chains at lower temperatures, satisfying the conditions of a positive  $\Delta H_{\text{mix}}$  that is larger than  $T\Delta S_{\text{mix}}$  that results in phase separation at lower temperatures. However, once the temperature increases, the absolute value of the entropic term  $T\Delta S_{\text{mix}}$  overcomes that of  $\Delta H_{\text{mix}}$ , and the solution becomes homogeneously mixed. Certain methacrylates having longer alkyl chains, such as poly(octadecyl (meth)acrylates) that are capable of aggregating via van der Waals interactions, are also known to exhibit UCST phase transitions in certain ILs.<sup>24</sup> The polymer phase behavior in an IL is also strongly dependent on the polymer structure as well as on the structure of the IL, especially the anionic structure that governs its Lewis basicity. In the case of low-molecular-weight substances, Heintz *et al.*,<sup>41–45</sup> Domanska *et al.*<sup>46,47</sup> Brenecke *et al.*<sup>48,49</sup> actively investigated the UCST phase behaviors of alcohol IL solutions and concluded that hydrogen bonding as well as van der Waals interactions between the polymer and the IL play an important role in their mutual solubility.

In contrast, from a thermodynamic perspective of the LCST phase transition, both  $\Delta H_{\text{mix}}$  and  $\Delta S_{\text{mix}}$  must be negative so that  $\Delta G_{\text{mix}}$  satisfies the condition of transitioning from positive to negative with increasing temperature. The suggestion of entropic contributions by Flory and Huggins cannot completely describe the phase separations occurring at higher temperatures; nevertheless, we sometimes observe LCST-type phase transitions in real aqueous polymer solutions or certain polymer blend systems that seems to be a rare occurrence from a thermodynamic point of view. We have reported LCST phase separations in a polymer IL solution; poly(benzyl methacrylate) (PBnMA) exhibits LCST phase behavior in certain ILs,<sup>50–52</sup> similar to the phase behaviors of the widely studied aqueous PNIPAAm solution (Figure 1b). We are interested in the factors governing the mixing entropy of solutions for the PBnMA/[C<sub>*n*</sub>mim][NTf<sub>2</sub>] system. With regard to the LCST phase behavior of PNIPAAm aqueous solutions, it is generally accepted that structure-forming solvation events such as specific hydration around the hydrophobic isopropyl side chain, that is, hydrophobic hydration, decrease the entropy of the solution.<sup>33</sup> In the case of a PBnMA/[C<sub>*n*</sub>mim][NTf<sub>2</sub>] solution showing LCST phase behavior, it is possible that PBnMA and/or ILs form

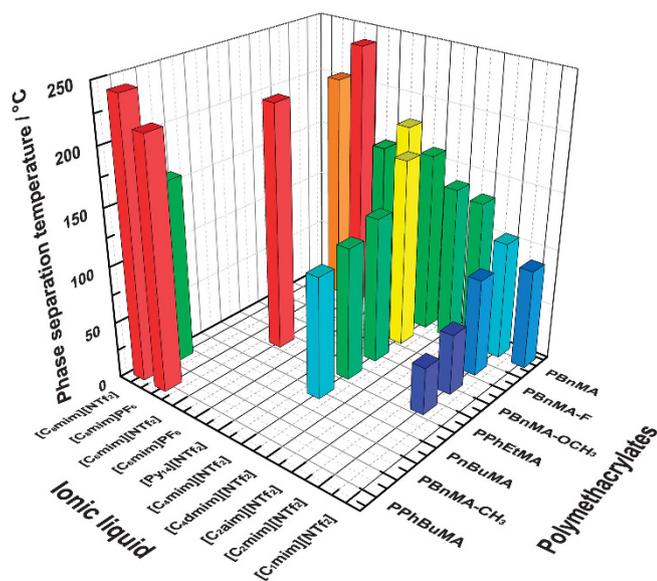
certain types of ordered structures in solution to decrease the mixing entropy. Recently, Fujii and coworkers<sup>53</sup> investigated the specific solvation of [C<sub>2</sub>mim][NTf<sub>2</sub>] for the monomeric BnMA structure using high-energy X-ray diffraction with the aid of a molecular-dynamics simulation. They found that the [C<sub>2</sub>mim] cation is distributed in an orderly manner above and below the benzyl group within BnMA, whereas the [NTf<sub>2</sub>] anion is distributed around the equatorial position of the benzyl group where no cation distribution is found, indicating a weak interaction between [NTf<sub>2</sub>] and BnMA (Figure 1c). ILs are also known to form liquid clathrate structures through contact with aromatic compounds such as benzene, toluene and xylene,<sup>54–57</sup> driven primarily by cation- $\pi$  interactions.<sup>58</sup> It has been revealed that the ordered structural formation of a microscopic solvation structure of an imidazolium cation and aromatic side chain in PBnMA/[C<sub>2</sub>mim][NTf<sub>2</sub>] solution decreases the mixing entropy to produce LCST phase behavior, an effect similar to the formation of hydrophobic hydration shells within a PNIPAAm aqueous solution. We further evaluated the phase behavior of a crosslinked PBnMA network swollen with ILs. The PBnMA ion gels in [C<sub>2</sub>mim][NTf<sub>2</sub>] clearly exhibit low-temperature swollen and high-temperature shrunken phases with a phase-transition temperature of  $\sim 100$  °C (Figure 2); the phase transition is discontinuous and reversible with increases and decreases in temperature, respectively.<sup>50</sup> The phase-transition behavior also exhibits a large hysteresis loop, implying the occurrence of a first-order transition.<sup>59</sup> Although there had been many experimental examples in which PNIPAAm-based hydrogels exhibited volume phase transitions in aqueous solution, this was the first report on the volume phase transition of a neutral polymer network in an IL that consists entirely of ions. Because ion gels consist of thermally stable, nonvolatile and moisture-insensitive components, their use could enable the development of environmentally stable smart gel materials for a variety of purposes.

### Control of LCST-type phase transition of polymethacrylates in ILs

To control the nature of smart soft materials via the phase behaviors of the component polymers (gels) in ILs, controlling the phase-transition temperature is of great importance. The phase behaviors of polymers in ILs are reported to be controllable by modifying the polymer chemical structures<sup>50,51,60,61</sup> as well as the structures of the ILs<sup>50,62</sup> in a wide temperature range. Figure 3 and Table 1 summarize previously reported temperatures for LCST phase transitions and the chemical structures of the corresponding polymers and ILs. The phase-transition temperature of a polymer in an IL is strongly



**Figure 2** Swelling curve of a poly(benzyl methacrylate) (PBnMA) ion gel particle in  $[C_2mim][NTf_2]$  as a function of temperature. Photograph insets (left to right) show the PBnMA ion gel below (swelling) and above (shrinking) the phase-transition temperature, respectively. The swelling ratio represents the normalized gel diameter at each temperature divided by  $100^\circ C$ . The PBnMA ion gel was obtained by *in situ* suspension polymerization using continuous and dispersion phases of water and water-immiscible  $[C_2mim][NTf_2]$ , respectively. The  $[C_2mim][NTf_2]$  phase contains BnMA monomers (700 mM), ethylene glycol dimethacrylate (28 mM) as a crosslinker and 2,2-diethoxyacetophenone (7 mM) as a photo initiator in the feed. Reproduced with permission from Ueki *et al.*<sup>50</sup> A full color version of this figure is available at the *Polymer Journal* online.



**Figure 3** Summary of lower critical solution temperature (LCST)-type phase-separation temperatures for previously reported polymethacrylates in a series of ionic liquids (ILs). The bar color indicates the phase-separation temperature in each combination of polymer and IL, as follows: cobalt,  $\sim 50^\circ C$ ; dark blue,  $\sim 70^\circ C$ ; light blue,  $\sim 95^\circ C$ ; light green,  $\sim 120^\circ C$ ; dark green,  $\sim 150^\circ C$ ; yellow,  $\sim 170^\circ C$ ; orange,  $\sim 200$  and  $\sim 250^\circ C$ .

dependent not only on the nature of the polymer itself but also on the polymer molecular weight (distribution) and concentration. The data presented in Figure 3 and Table 1 therefore provide information that is strictly qualitative and is applicable only to a polymer of a certain molecular weight (distribution) at the specified concentration. We can identify tendencies in the phase-separation temperature changes of a

**Table 1** Previously reported LCST-type phase separation temperatures of polymers in ILs

Polymer	Solvent	MW/kDa	PDI	Conc./wt%	$T_c / ^\circ C$	Reference
PnBuMA	$[C_4mim]PF_6$	13	1.28	2	136.5	65
PnBuMA	$[C_4mim]PF_6$	48	1.38	2	108	65
PBnMA	$[C_1mim][NTf_2]$	28	2.76	3	89	50
PBnMA	$[C_2mim][NTf_2]$	28	2.76	3	105	50
PBnMA	$[C_2amim][NTf_2]$	28	2.76	3	133	62
PBnMA	$[C_3dmim][NTf_2]$	28	2.76	3	138	62
PBnMA	$[C_4mim][NTf_2]$	28	2.76	3	161	50
PBnMA	$[Py_{14}][NTf_2]$	28	2.76	3	180	62
PBnMA	$[C_6mim][NTf_2]$	28	2.76	3	239	50
PBnMA	$[C_6mim]PF_6$	28	2.76	3	155	62
PBnMA	$[C_8mim]PF_6$	28	2.76	3	205	62
PBnMA-OCH <sub>3</sub>	$[C_2mim][NTf_2]$	73	2.28	3	54	60
PBnMA-OCH <sub>3</sub>	$[C_4mim][NTf_2]$	73	2.28	3	130	60
PBnMA-F	$[C_2mim][NTf_2]$	74	1.94	3	87	60
PBnMA-F	$[C_4mim][NTf_2]$	74	1.94	3	168	60
PPhEtMA	$[C_2mim][NTf_2]$	76	1.91	3	42	60
PPhEtMA	$[C_4mim][NTf_2]$	76	1.91	3	118	60
PPhEtMA	$[C_6mim][NTf_2]$	76	1.91	3	218	60
PPhBuMA	$[C_6mim][NTf_2]$	51	1.93	3	144	60
PPhBuMA	$[C_8mim][NTf_2]$	51	1.93	3	242	60
PBnMA-CH <sub>3</sub>	$[C_8mim][NTf_2]$	75	1.74	3	162	60
P(St <sub>1.6-r</sub> -BnMA)	$[C_2mim][NTf_2]$	19	2.34	3	101.4	50
P(St <sub>3.7-r</sub> -BnMA)	$[C_2mim][NTf_2]$	13	1.88	3	69.9	50
P(MMA <sub>5.1-r</sub> -BnMA)	$[C_2mim][NTf_2]$	21	2.22	3	122.3	50
P(MMA <sub>10.0-r</sub> -BnMA)	$[C_2mim][NTf_2]$	21	2.15	3	135.2	50
P(trans-AzoMA <sub>1.9-r</sub> -BnMA)	$[C_2mim][NTf_2]$	45	2.9	3	102.9	67
P(trans-AzoMA <sub>3.0-r</sub> -BnMA)	$[C_2mim][NTf_2]$	44	2.8	3	103.1	67
P(trans-AzoMA <sub>4.1-r</sub> -BnMA)	$[C_2mim][NTf_2]$	47	3.0	3	102.0	67
P(cis-AzoMA <sub>1.9-r</sub> -BnMA)	$[C_2mim][NTf_2]$	45	2.9	3	91.1	67
P(cis-AzoMA <sub>3.0-r</sub> -BnMA)	$[C_2mim][NTf_2]$	44	2.8	3	84.4	67
P(cis-AzoMA <sub>4.1-r</sub> -BnMA)	$[C_2mim][NTf_2]$	47	3.0	3	80.3	67
P(VBK <sub>4-r</sub> -BnMA)	$[C_2mim][NTf_2]$	9.9	1.41	3	86	61
P(VBK <sub>9-r</sub> -BnMA)	$[C_2mim][NTf_2]$	6.7	1.39	3	68	61
PEG	$[C_2mim]BF_4$	5	1.07	9	164	63
PEG	$[C_2mim]BF_4$	20	1.14	2	163	63
PEG	$[C_4mim]BF_4$	20	1.14	2	209	63
PPG	$[C_4mim][NTf_2]$	3.9	1.15	10	48	72
PGME	$[C_4mim]PF_6$	3	1.19	10	53.5	72
PEGE	$[C_2mim][NTf_2]$	3.8	1.15	6	101.9	71
PEGE	$[C_2mim][NTf_2]$	8.1	1.19	3	87.8	71
PEGE	$[C_2mim][NTf_2]$	10	1.26	3	78.1	71
PEGE	$[C_2mim][NTf_2]$	22	1.75	3	67.5	71
PEGE	$[C_1mim][NTf_2]$	8.1	1.19	3	85.2	72
PEGE	$[C_3mim][NTf_2]$	8.1	1.19	3	132.9	72
PEGE	$[C_4mim][NTf_2]$	8.1	1.19	5	174.8	72
PEGE	$[C_4dmim][NTf_2]$	8.1	1.19	3	31.0	72
PEGE	$[C_5dmim][NTf_2]$	8.1	1.19	3	93.3	72
PEGE	$[C_6dmim][NTf_2]$	8.1	1.19	5	155.0	72
PEEGE	$[C_4mim]PF_6$	3.2	1.17	10	56	72

Abbreviations: Conc., concentration; IL, ionic liquids; LCST, lower critical solution temperature; MW, molecular weight; PDI, polydispersity index. Numbers indicated after the monomers for a series of random copolymers denote the composition of the comonomer in mol%.

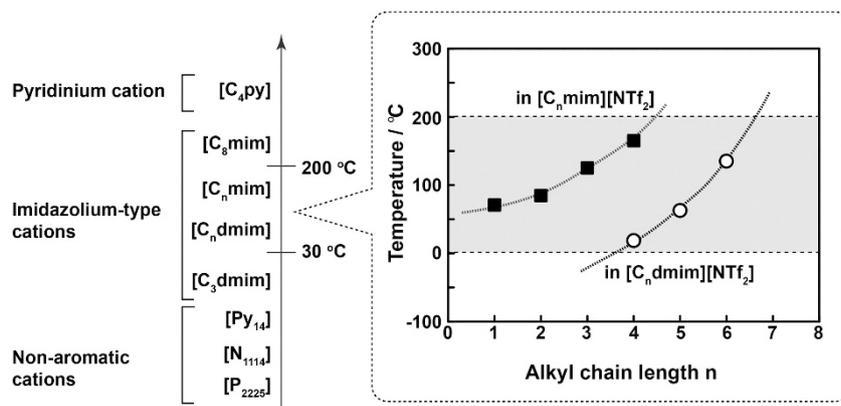
PBnMA homopolymer through systematically changing the chemical structure of the ILs as follows: 1. The phase-transition temperature increases with increasing alkyl chain length at the imidazolium ring 3-position; 2. the phase-transition temperature does not change

substantially if methyl substitution is present at the 2-position of the imidazolium ring, a position that is known to possess strong hydrogen-bond-donating ability; 3. the phase-transition temperature depends strongly not only on the cation structure but also on the anion structure in ILs. From the conditions stated in 1 and 2, it can be concluded that van der Waals interactions, rather than hydrogen bonding between polymers and ILs, seem to play an important role in determining the phase-transition temperature of methacrylate polymers in ILs. Although the anion structure does not seem to induce structure-ordering solvation to decrease the mixing entropy of the solution, the fact that the anion structure affects the phase-transition temperature implies that there are enthalpic contributions from anion solvation to the polymers. It is also likely that the structure-forming solvation of cations by the polymer can be altered by a change in the anionic structure that results in a changing phase-separation temperature. In terms of the continuous phase-transition temperature manipulation of polymers in ILs, the LCST phase transitions in PBNMA, PPhEtMA and PEG can be easily controlled using an IL blend.<sup>60,63–65</sup> Furthermore, the phase-transition temperature significantly decreases following chemical modification around the aromatic side chain, suggesting that the microscopic solvation of ILs around the aromatic units plays an important role in polymer phase behaviors in ILs. In particular, the LCST phase-transition temperature of PPhEtMA is as much as 63 °C lower than that of PBNMA,<sup>60</sup> however, the chemical structures of PPhEtMA and PBNMA differ by only one methylene spacer inserted between the aromatic group and the methacrylate main chain. These results also suggest that control over the LCST phase-transition temperature is not achieved by tailoring the electron density of the benzyl group through aromatic substitution but rather through steric hindrance. The phase changes of polymers in ILs are also controllable by the random copolymerization of different monomers in a similar manner used for traditional aqueous thermosensitive polymers,<sup>66</sup> however, the magnitude of the temperature change after the random copolymerization of polymers in ILs is much larger than that for thermosensitive random copolymers in aqueous solution. For example, due to the hydrophilicity of *N,N*-dimethylacrylamide (DMAAm), a random copolymer of NIPAAm and DMAAm (P(DMAAm<sub>10.0</sub>-*r*-NIPAAm)) is known to show a 5 °C higher LCST phase transition than the corresponding PNIPAAm homopolymer in aqueous solution.<sup>66</sup> Similarly, in a polymer [C<sub>2</sub>mim][NTf<sub>2</sub>] solution, a random copolymer consisting of BnMA and methyl methacrylate

(MMA), which is a solvophilic monomer toward [C<sub>2</sub>mim][NTf<sub>2</sub>] (P(MMA<sub>10.0</sub>-*r*-BnMA)), shows a higher phase-transition temperature. Compared with the P(DMAAm<sub>10.0</sub>-*r*-NIPAAm) system, the difference in magnitude of the phase-separation temperature is as large as 30 °C for P(MMA<sub>10.0</sub>-*r*-BnMA) in [C<sub>2</sub>mim][NTf<sub>2</sub>] solution.<sup>50</sup> Although the exact reason for the large phase-transition temperature difference in ILs in response to subtle chemical modification of the polymer is still unclear, a partial rationalization from a thermodynamic point of view has been proposed through a systematic comparison via high-sensitive differential scanning calorimetry analyses of thermosensitive polymers in both water and ILs.<sup>62</sup> Inspired by the unprecedented phenomenon whereby a tiny chemical modification can induce large changes in the phase-transition temperature of a polymer in an IL, optically triggered solubility changes of polymers in ILs were also proposed. Certain azobenzene-containing random copolymers of P(AzoMA-*r*-BnMA)<sup>67</sup> and P(AzoMA-*r*-NIPAAm)<sup>68</sup> in ILs have been reported to show a drastic change in LCST phase-transition temperature depending on the azobenzene composition as well as on the photochromic isomerization state of the chromophore in the random copolymer. The optically driven solubility changes of polymers in ILs can initiate photo-triggered volume phase transitions in ion gels<sup>69</sup> as well as the photo-induced self-assembly of block copolymers,<sup>70</sup> as briefly introduced in the section ‘Stimuli-responsive self-assembly of block copolymers and gels in ILs’.

#### Phase behavior of polyethers in ILs

Not limited to methacrylate and acrylamide backbone polymers, we have found that polyethers, such as poly(ethyl glycidyl ether) (PEGE), also show LCST phase transitions in ILs.<sup>71,72</sup> In the case of LCST phase behaviors in polyether IL solutions, directional solvation based on hydrogen bonding between the polyether and IL cations plays a crucial role in decreasing the mixing entropy of the solutions. Seddon, Rebelo and coworkers<sup>55</sup> have noted directional solvation based on hydrogen bonding as an important contribution to decreasing the mixing entropy for a quasi-binary solution of chlorine containing an organic solvent and imidazolium IL. We recently conducted a systematic investigation of the effect of chemical structure on LCST phase behaviors using five polyethers (PEG, PMGE, PEGE, PEEGE and PPG) in 14 different ILs (Figure 4).<sup>72</sup> For ILs containing the same anions, the polyethers were soluble in imidazolium- or pyridinium-based ILs and were insoluble in ammonium- or phosphonium-based ILs. An increase in the alkyl chain length in the imidazolium cation



**Figure 4** Solubility and lower critical solution temperature (LCST)-type phase-separation temperatures for 10 wt% poly(ethyl glycidyl ether) (PEGE) as a function of the cation structures of ionic liquids (ILs) containing [NTf<sub>2</sub>] anions at temperatures ranging from room temperature to 200 °C. Reproduced with permission from Kodama *et al.*<sup>72</sup>

and an increase in the polarity of the polyethers resulted in a higher LCST for phase separation, whereas, not surprisingly, the substitution of hydrogen atoms on the imidazolium ring with methyl groups resulted in a lower LCST for phase separation, suggesting the importance of hydrogen bonding for the LCST phase transition of polyethers in ILs. The hydrogen-bonding interactions between the oxygen atoms in the polyethers and the aromatic hydrogen atoms on the cations in the ILs can be qualitatively explained by the ranking of the LCST phase-transition temperatures of polyethers and ILs.

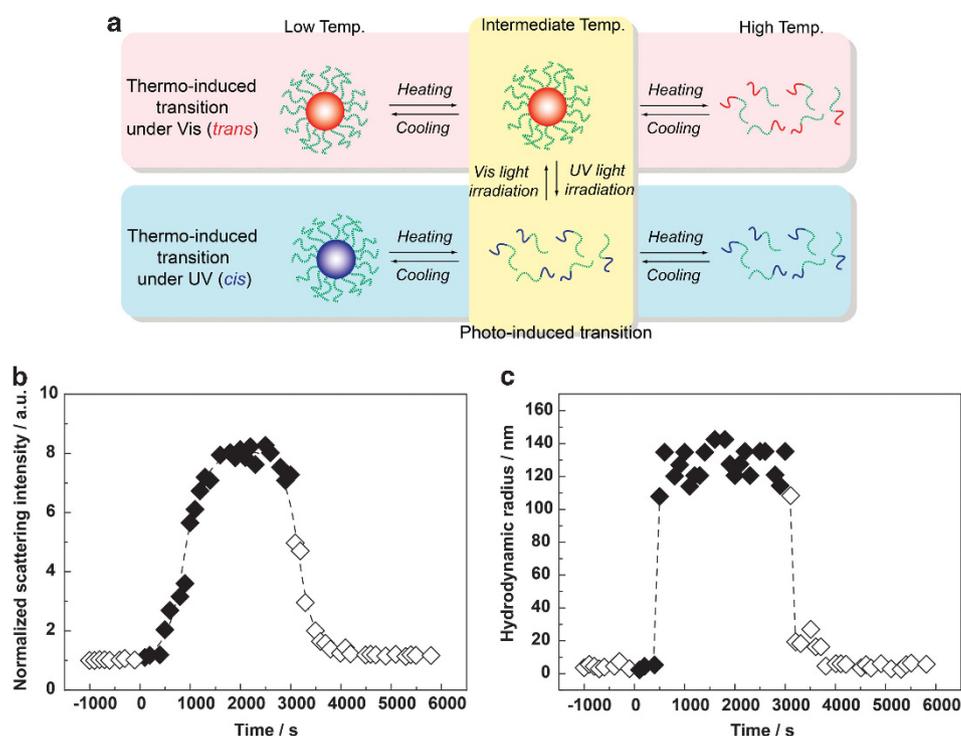
## FUNCTIONAL DESIGNS VIA STIMULI-RESPONSIVE POLYMERS IN ILS

### Stimuli-responsive self-assembly of block copolymers and gels in ILs

New materials utilizing the phase behaviors of polymers in ILs are now being designed on the basis of the unique properties of stimuli-sensitive polymers (gels) combined with ILs. The volume phase transition of a polymer gel can be applied to a variety of stimuli-responsive smart materials, such as actuators, optical devices and switching devices, all of which have been proposed for hydrogel systems—because the phenomenon can be reversibly observed in an open atmosphere without the occurrence of solvent evaporation, a serious drawback of conventional smart gel materials.

The thermosensitivity of diblock copolymers in ILs<sup>64,65,73,74</sup> and thermoreversible ion gels<sup>75–78</sup> based on their thermally induced association/dissociation of multiblock copolymers in ILs have also been investigated by several groups. With the main objective of material process engineering, the solidification of ILs triggered by thermal stimuli is promising. For the preparation of thermoreversible

ion gels, low-temperature-gel/high-temperature-sol systems have been realized by utilizing the UCST behaviors of PNIPAAm<sup>75,76</sup> or P(*tert*)BuAAm<sup>77</sup> as the thermosensitive blocks. We are interested in the formation of thermoreversible ion gels utilizing the LCST-based solubility changes of PBnMA<sup>79</sup> or PPhEtMA<sup>80</sup> that can impart low-temperature-sol/high-temperature-gel phase behaviors. Although numerous studies have been conducted on high-temperature-sol/low-temperature-gel systems in ILs using either organic gelators<sup>81–83</sup> or the crystallization of ethers<sup>84,85</sup> or F-containing polymers<sup>30,86,87</sup> in the absence of block copolymer self-assembly, the construction of high-temperature-gel systems remains challenging. In addition to utilizing the thermosensitivity of block copolymers in ILs, optically switchable ion gels, in which gel formation (or melting) is achieved under UV-visible light illumination, have the potential to open many opportunities for gel patterning in applications such as plastic electronics. The random copolymer consisting of methacrylates with an azobenzene side chain (AzoMA) and NIPAAm shows a distinct solubility difference in [C<sub>4</sub>mim]PF<sub>6</sub> depending on whether the photochromic azobenzene moiety is in the *trans* (ground) or *cis* (excited) state; the more polar *cis* form is generally more soluble.<sup>68</sup> The optically induced micellization/demicellization of an AB diblock copolymer consisting of polyethylene glycol (PEG) and P(AzoMA-*r*-NIPAAm) as the solvophilic and thermal/photosensitive segments, respectively, has been recently demonstrated (Figure 5).<sup>70</sup> The study of an ABA triblock copolymer containing P(AzoMA-*r*-NIPAAm) end blocks is presently ongoing; this system is expected to induce photo-triggered formation/breakage of physical crosslinking points in the concentrated polymer IL solution, leading to a photo-reversible ion gel. The novelty of such a photo-reversible gel is apparent because it has not yet been described in a polymer IL solution



**Figure 5** (a) Conceptual illustration of the micellization/demicellization of photo-responsive polymers and experimental results from the reversible photo-induced micellization/demicellization of PEG-*b*-P(AzoMA<sub>2,0</sub>-*r*-NIPAAm) micelles at aggregation temperatures between the *trans*- and *cis*-polymer bistable temperatures under ultraviolet (UV; open diamonds) or visible-light (closed diamonds) irradiation. (b) The normalized scattering intensity and (c) the hydrodynamic radius as a function of temperature are shown. Reproduced with permission from Ueki *et al.*<sup>70</sup>

nor in a traditional polymer solution using both aqueous and organic solvents.

### Thermosensitive colloid shuttle between water and IL interface

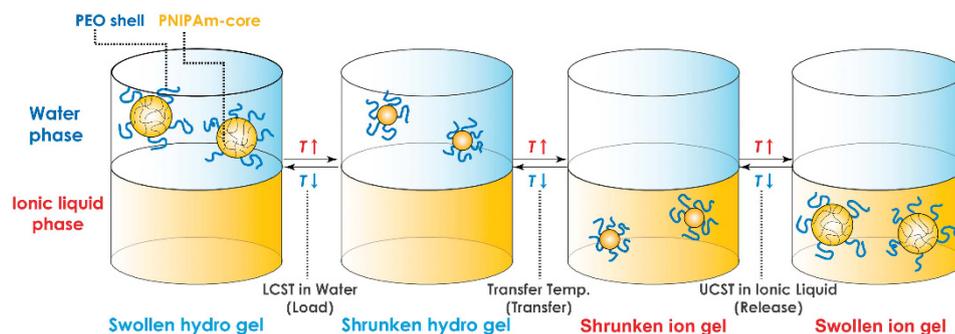
Thermosensitive so-called ‘round-trip’ colloids that partition between water and hydrophobic (water-immiscible) ILs have recently shown promise in the field of material science research directed at polymer–IL composites. He and Lodge<sup>88</sup> found for the first time that PB-*b*-PEG block copolymer micelles reversibly shuttle between the water and hydrophobic IL ([C<sub>2</sub>mim][NTf<sub>2</sub>]) interface in response to temperature changes, irrespective of micellar morphology. They revealed through successive nuclear magnetic resonance studies that reversible micelle transfer between the water and IL phases is based on the relative affinity changes of the corona PEG chains toward the water and IL solvents.<sup>89,90</sup> It is well known that PEG shows LCST phase behavior in aqueous solutions at relatively high temperatures, indicating that its solubility decreases with increasing temperature. On the other hand, the temperature-dependent change in the solubility of PEG toward [C<sub>2</sub>mim][NTf<sub>2</sub>] is not as significant. If the micelle surrounded by a well-solvated PEG shell is in the water phase, it can transfer across the interface between water and [C<sub>2</sub>mim][NTf<sub>2</sub>] at a higher temperature because PEG is more thermodynamically stable in the IL phase than in the upper water phase. Their findings strongly imply that all colloidal particles decorated with a PEG shell can exhibit ‘round-trip’ behaviors between water and IL phases through changes in temperature. Based on their pioneering findings, well-defined vesicles,<sup>91</sup> silica particles,<sup>92</sup> Pluronic micelles<sup>93</sup> and 2-oxazoline-modified micelles<sup>94</sup> have as been found to show similar reversible transfer behaviors between water and hydrophobic IL phases.

On the basis of this concept, we recently proposed a thermoreversible nanogel shuttle between water and a hydrophobic IL phase, in which the nanogel consists of a crosslinked PNIPAAm core surrounded by a PEG shell.<sup>95</sup> By maintaining an ascending LCST-type phase-transition of PNIPAAm in water, one can construct novel nanogel systems that may potentially undergo unique load-transfer-release processes by simple temperature adjustments (Figure 6). Substrates in the water phase can be loaded into the nanogels at the LCST-type phase-transition (shrinking) temperature of PNIPAAm at lower temperatures, transported with the nanogels into the lower IL phase with an increase in temperature, and subsequently released at a higher (swelling) temperature as a result of the UCST nature of PNIPAAm in the IL phase. The thermal sensitivities of nanogels in

both water and IL phases as well as their transfer behaviors were confirmed to be reversible using the dynamic light scattering technique. The realization of intelligent nanogel cargo as a micro reactor<sup>95,96</sup> consisting of two types of ‘green’ liquids (that is, water and ILs) is a promising development in polymer/IL composite research.

### Surface modification of thermosensitive polymers in ILs

Interface modification with stimuli-responsive polymers in ILs is one of the more novel approaches in polymer–IL composite materials design. Guo, Jiang and coworkers<sup>97</sup> demonstrated that a PBnMA-modified nanoporous surface could act as a temperature-responsive ion gate for organic charge carriers that can be potentially operated over a wide temperature range. Such polymeric, brush-like surfaces are expected for use as intelligent molecular nanoactuators that can efficiently block ions in response to appropriate external stimuli, exhibiting functionalities similar to biological ion channels. Ueno, Watanabe and coworkers<sup>98</sup> reported interesting rheological and optical properties of thermosensitive polymers decorated with silica nanoparticles in an IL solvent. They successfully synthesized PBnMA-grafted silica nanoparticles via surface-initiated atom-transfer radical polymerization. When using silica particles at concentrations above 14.2 wt%, the composites show a nonbrilliant, angle-independent structural color caused by the scattering of coherent light from the short-range ordered glassy colloidal array.<sup>37,99</sup> Moreover, the concentrated PBnMA-modified silica nanoparticle solutions display interesting viscoelastic behavior in response to temperature. Both the storage ( $G'$ ) and loss ( $G''$ ) moduli first decrease up to the LCST phase-transition temperature (95 °C) and then increase at higher temperatures after passing through the minimum. Such a V-shaped rheological response can be interpreted in relation to the thermosensitivity of the PBnMA-grafted nanoparticles. At lower temperatures (below the LCST aggregation temperature of immobilized PBnMA), a repulsive interaction is at work among the PBnMA-grafted nanoparticles because of the effect of the excluded volume of grafted polymers. Hard-sphere repulsive particles are known to form colloidal glass at high particle concentrations, whereby the particles are trapped within cages formed by their nearest neighbors, showing solid-like properties. However, at higher temperatures (above the LCST phase-transition temperature), the collapse of the PBnMA-modified silica nanoparticles renders the steric hindrance of PBnMA ineffective, thus leading to gel formation because of the percolation of PBnMA-grafted nanoparticles into



**Figure 6** A conceptual illustration of a thermally driven load-transfer-release nanogel shuttle. The nanogel exhibits low-temperature-swollen/high-temperature-shrunken volume phase transitions in the upper aqueous phase and shows opposite phase behavior in the lower hydrophobic IL phase because of the dual thermosensitivity of poly(*N*-isopropylacrylamide) (PNIPAAm) in both phases. A nanogel surrounded by poly(ethylene glycol) (PEG) shells can transfer between the aqueous and ionic liquid (IL) phases. Reproduced with permission from Ueki *et al.*<sup>95</sup>

particulate networks. As a result of these unique optical and rheological properties as well as of the properties derived from the IL itself, thermosensitive soft glassy colloidal arrays are of significant interest as a new material for a wide range of applications, such as in functional fluids, color displays and electrochemical devices.

## CONCLUDING REMARKS

This article focused on the thermodynamic aspects of and recent developments in research directed at stimuli-responsive polymers in ILs. The most noteworthy properties of the IL itself are its thermal stability and wide liquid temperature range. By employing an IL as a solvent for smart soft materials, unprecedented applications can be afforded under a wide range of operating conditions, including wide temperature ranges or long-term operations under an open atmosphere, without concerns of solvent evaporation. Composite materials combining thermosensitive polymers with ILs show particular promise; however, there remains some ambiguity regarding precisely how such polymers behave in an IL solvent. For example, there is still no theoretical or experimental interpretation of the effect of osmotic pressure on volume phase transitions in ion gels; the osmotic pressure between the interior and exterior of the polymer network is believed to play a crucial role at the volume phase transition of well-established aqueous hydrogel systems consisting of a charged polymer network in a neutral solvent (water).<sup>100–102</sup> However, further investigation as well as basic interpretations of the mechanism of osmotic pressure in a neutral polymer (PBnMA) network in a charged solvent (IL) is still required to clarify its role in the volume phase transition of the PBnMA ion gel. On the other hand, from a material science point of view, polymers in ILs generally have a longer relaxation time and require prolonged periods to reach thermodynamic equilibrium as a result of the high viscosity of ILs. From the viewpoint of thermodynamic behavior in ILs, the polymer or its self-assembled structure is sometimes forced into not only the thermodynamic equilibrium phase but also its metastable state.<sup>69,103–105</sup> When designing stimuli-responsive polymers in ILs, it is necessary to suppress the viscosity of polymer–IL composites to achieve quick response times for the resulting soft materials. Although an increasing number of studies concern polymers and ILs, the research area of stimuli-responsive polymers in ILs remains in its infancy and has many years of progress, challenges and opportunities ahead from a fundamental as well as a material science point of view.

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