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Lower Critical Solution Temperature Behavior of Linear Polymers in Ionic Liquids and the Corresponding Volume Phase Transition of Polymer Gels

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Poly(benzyl methacrylate) (PBzMA) and its copolymers exhibit lower critical solution temperature (LCST)-type phase separation in common hydrophobic ionic liquids (ILs) such as 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ([C₂mim][NTf₂]). The turbidity measurements for PBzMA/IL mixed systems reveal that the LCST-type phase separation temperatures change significantly with the changes in the chemical structures of polymers and ILs. Moreover, cross-linked PBzMA gels show reversible and discontinuous volume phase transition in [C₂mim][NTf₂] with the changes in temperature.

In this study, we report the experimental observations of the unique phase behavior of linear polymers and cross-linked polymer gels in ionic liquids (ILs) as solvents. Poly(benzyl methacrylate) (PBzMA) and its copolymers exhibit lower critical solution temperature (LCST)-type phase separation in common hydrophobic ILs. Moreover, cross-linked PBzMA gels show reversible and discontinuous volume phase transition in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide ([C₂mim][NTf₂]) with the change in temperature. Because ILs are, in general, thermally and chemically stable and have negligible vapor pressure, these phase transitions could be utilized to develop stimuli-responsive smart materials,¹ such as actuators, optical devices, and switching devices. In particular, the phase transition of polymer gels in ILs could usher in a new era of environmentally stable polymer gels, since this phenomenon can be reversibly observed in an open atmosphere without the need to consider solvent evaporation, which is a serious drawback of conventional smart gel materials.

The LCST-type phase separations have been mainly observed in aqueous polymer (both synthetic polymer and biopolymer) solutions.² It would be a rare phenomenon for the mixing Gibbs free energy (ΔG_{mix}) to change from negative to positive with an increase in the temperature. From a thermodynamic viewpoint, the LCST-type phase separation phenomenon can occur under conditions where both enthalpy (ΔH_{mix}) and entropy (ΔS_{mix}) upon mixing become negative, and the entropic contribution ($\Delta S_{\text{mix}}T$) to ΔG_{mix} overwhelms ΔH_{mix} . In the case of aqueous polymer solutions, the LCST-type phase separation is induced by the specific characteristics of water molecules. Liquid water, referred to as “eccentric entropy liquid,” is composed of free water molecules and iceberg-like structured clusters,³ which are formed by cooperative hydrogen bonding. When a hydrophobic molecule is added to water, water molecules bind together to

enhance the structural order, resulting in a negative ΔS_{mix} (hydrophobic hydration).³ Several synthetic polymers are known to reversibly exhibit the LCST-type phase separation in aqueous media.^{2,4} In particular, poly(*N*-isopropylacrylamide) (PNIPAm) and its gels have been studied extensively² to gain a fundamental understanding of the phase behavior and also to investigate their potential application as smart materials. The LCST-type phase separation of a PNIPAm aqueous solution is induced by negative ΔS_{mix} , where water molecules form well-ordered structural hydration shells around the hydrophobic isopropyl groups. These structural shells have been suggested to have a clathrate-like structure.²

ILs are room-temperature molten salts and have attracted much attention because of their unique properties.^{5–8} Extensive studies have been performed to elucidate the relationship between the physicochemical properties and the structure of ILs.^{5–9} Among these are the phase behavior studies for IL/organic solvent mixtures.¹⁰ An interesting result is that certain IL/aromatic systems form liquid clathrate phases via associative interactions between aromatic molecules and salt ions, which separate the cation–anion packing interaction to a sufficient degree such that localized cage structures are formed.¹¹ For example, in a clathrate consisting of 1,2-dimethylimidazolium hexafluorophosphate and benzene,

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the aromatic solute is trapped in the solid state forming a crystalline 2:1 inclusion compound.^{11a,12} It is also noteworthy that LCST-type phase diagrams are observed for the binary and quasi-binary liquid solutions consisting of imidazolium-based ILs and chloroform/tetrachloromethane. It is pointed out that the hydrogen bonding between the π -system of the imidazolium ring and the H atom in chloroform together with that between the acidic H atom in the same imidazolium cation and the Cl atom leads to the liquid–liquid structuring effect in these systems.^{10a} These observations reveal that ILs and certain organic solvents form ordered phases upon mixing.

The compatibility of polymers in ILs has also been investigated.^{13–15} We have found that polymethacrylates and polyacrylates are easily soluble in common ILs,¹⁵ especially [C₂mim][NTf₂]. Poly(methyl methacrylate) (PMMA) and [C₂mim][NTf₂] make up a completely compatible binary system independent of compositions. Furthermore, the network polymers of PMMA containing the IL, named “ion-gels,” afford highly ion-conductive polymer electrolytes.¹⁴ On the other hand, polymers containing phenyl groups, especially polystyrene (PSt), are hardly soluble in common ILs. The previously mentioned PNIPAm has both a hydrophilic acrylamide structure and a hydrophobic isopropyl group in the same monomer unit. When benzyl groups, which induce structure formation in ILs, are incorporated into the polymethacrylate structure, LCST-type phase behavior in ILs, which is analogous to that of PNIPAm in water, appears to be realized. On the basis of this idea, the phase behavior in [C₂mim][NTf₂] and other imidazolium-based ILs for PBzMA and its polymer gels, which have both solvatophilic methacrylate and solvatophobic benzyl structures, has been investigated.

The ILs were prepared and characterized by a previously reported procedure.^{9,16} The PBzMA linear polymer prepared by conventional free radical polymerization was dissolved in the ILs by the cosolvent (tetrahydrofuran) evaporation method.^{15,17} A drop of the PBzMA/IL solution (3 wt %) was placed onto a concave slide glass and covered using a cover glass. The slide glass was set onto a hot stage (Imoto) that enabled temperature control up to 400 °C. The temperature was changed in increments of 0.2 °C, and the transmittance of the PBzMA/IL solutions was monitored at 500 nm after waiting for 4 min in order to detect the phase behavior of the solution. Almost no hysteresis was observed in the transmittance at this rate. In this study, the phase separation temperature (cloud point, T_c) was defined as the temperature at which the transmittance became 50%. The copolymers of BzMA with either St or MMA were also prepared and characterized by ¹H NMR, and their compositions were calculated based on the carbon content obtained from elemental analysis. The phase behavior in [C₂mim][NTf₂] was investigated in a similar manner.

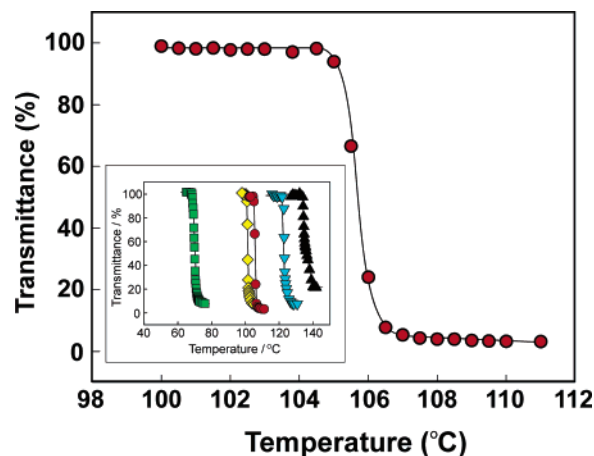


Figure 1. Temperature dependence of transmittance at 500 nm for a PBzMA solution in [C₂mim][NTf₂]. The transmittance of 100% indicates that the solution is a single-phase one (transparent), while that of 0% indicates that it is phase-separated (turbid). Inset shows the comparison of the turbidity measurements for BzMA copolymers with St or MMA. (red circle): PBzMA homopolymer, ($M_n = 28\,300$ g/mol, $M_w/M_n = 2.76$); (yellow diamond): P(BzMA-*co*-St) (1.6 mol %) ($M_n = 19\,100$ g/mol, $M_w/M_n = 2.34$); (green square): P(BzMA-*co*-St) (8.7 mol %), ($M_n = 13\,100$ g/mol, $M_w/M_n = 1.88$); (blue inverted triangle): P(BzMA-*co*-MMA) (5.1 mol %), ($M_n = 21\,600$ g/mol, $M_w/M_n = 2.22$); (black triangle): P(BzMA-*co*-MMA) (10 mol %), ($M_n = 21\,500$ g/mol, $M_w/M_n = 2.15$).

The particle size of the polymer gels was reduced by in situ suspension polymerization. The continuous phase was deionized water with a dissolved non-ionic surfactant (KAO-Emalgen) as a polymeric stabilizer. The hydrophobic [C₂mim][NTf₂] phase containing BzMA (700 mM), ethylene glycol dimethacrylate (28 mM) as a cross-linker, and 2,2-diethoxyacetophenone (7 mM) as a photoinitiator was deaerated by a N₂ purge for 20 min and dispersed into the aqueous continuous phase by stirring. During the stirring, the reaction mixture was irradiated for 30 min at room-temperature using UV light. After the reaction, this mixture was filtered and washed with a large amount of deionized water. The PBzMA gel particles that remained on the membrane filter were redispersed in [C₂mim][NTf₂]. The volatile compounds in the dispersion were removed under reduced pressure at 70 °C for 24 h. Overhead-type mechanical agitation at 265 rpm gave us ion gel particles with a proper size for the microscopic observation. An average gel diameter calculated from 40 randomly selected gel particles was 9.8 μ m with a standard deviation of 3.5. The equilibrium diameter of the microspherical gel D under controlled temperatures was measured using a digital microscope (KEYENCE VH-8000). The temperature was changed in increments 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. The relative swelling ratio D/D_0 was determined, where D_0 is the gel particle diameter at 100 °C.

Figure 1 shows the transmittance at 500 nm for the PBzMA/[C₂mim][NTf₂] mixture as a function of temperature. The mixture exhibited LCST-type phase separation at 105 °C (T_c), where it is miscible below T_c but becomes phase-separated above T_c . In the miscible phase, it appears that certain ordered structures are formed, resulting in a negative ΔS_{mix} . It is plausible to consider the formation of a clathrate-like structure around the benzyl groups in the side chain, although there is no evidence that the PBzMA/[C₂mim][NTf₂] mixture has such structural order. It should also be pointed out here that certain polymers dissolved in organic solvents exhibit LCSTs without the aid of structure-forming solvations such as hydrophobic hydration.¹⁸ Figure 1 also shows the change in T_c with the change in the BzMA composition

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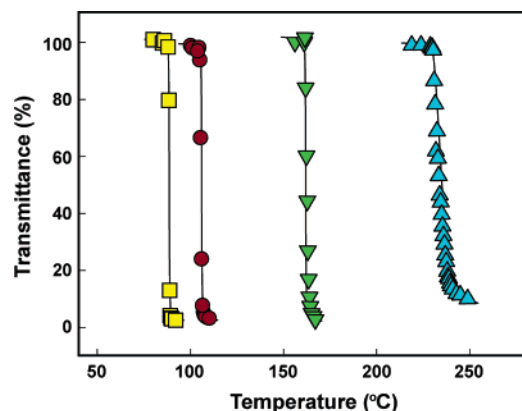


Figure 2. Temperature dependence of transmittance at 500 nm for a PBzMA solution in $[C_n\text{mim}][\text{NTf}_2]$. (yellow square): $[C_1\text{mim}][\text{NTf}_2]$; (red circle): $[C_2\text{mim}][\text{NTf}_2]$; (green inverted triangle): $[C_4\text{mim}][\text{NTf}_2]$; (blue triangle): $[C_6\text{mim}][\text{NTf}_2]$. $[C_n\text{mim}]$ represents the 1-alkyl-3-methylimidazolium cation.

where either solvophobic St or solvophilic MMA is copolymerized with BzMA. The T_c shifts to the lower temperature side with an increase in the St composition in $\text{P}(\text{BzMA-co-St})$, while it shifts to the higher temperature side with an increase in the MMA composition in $\text{P}(\text{BzMA-co-MMA})$, as expected. It is revealed that the LCST-type phase separation temperature of polymers in ILs can be easily controlled by copolymerization with solvophobic or solvophilic comonomers, as was observed in the case of PNIPAm copolymers in water.¹⁹

Investigation of how IL structures affect the phase behavior of PBzMA (Figure 2), where the alkyl chain length of the imidazolium substituent is altered with a fixed $[\text{NTf}_2]$ anion, could also yield interesting results. Figure 2 clearly indicates that PBzMA exhibits the LCST-type phase separation in a series of $[C_n\text{mim}][\text{NTf}_2]$ and that the T_c increases with the alkyl chain length. The exact reason for this phenomenon is still unclear. However, nanometer-scale structuring is predicted by a molecular simulation study.²⁰ In $[C_n\text{mim}]$ -based ILs, the aggregation of the alkyl-chain nonpolar groups becomes more pronounced with an increase in the alkyl chain length and induces the formation of phase-separated structures between the alkyl-chain group and the ionic channel formed by the imidazolium ring and counter anions.²⁰ Our conductivity and diffusivity study on $[C_n\text{mim}][\text{NTf}_2]$ also supports the aggregation of ions with the alkyl chain length.^{9a} The nanometer-ordered dynamic domain structure decreases the entropy of ILs, and the dissolution of PBzMA in these ILs might enhance their structural order, as in the case of the hydrophobic hydration of PNIPAm in an aqueous solution. On the other hand, the increase in the alkyl chain length appears to induce an increase in the van der Waals interaction between the cations and PBzMA.^{10b,e} A subtle balance between the entropy and enthalpy changes upon mixing causes the increase in T_c with the alkyl chain length.

The unique phase change of PBzMA and its copolymers in the ILs further encouraged us to evaluate the phase behavior of

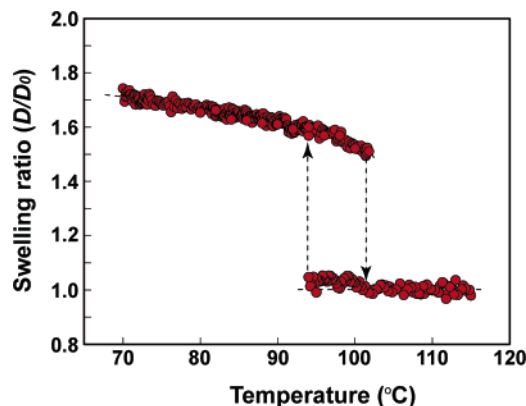


Figure 3. Equilibrium swelling ratio of a PBzMA gel particle as a function of temperature. The swelling ratio represents the normalized gel diameter at each temperature divided by that at 100 °C. The gel undergoes volume phase transition at ~ 100 °C. The temperature was changed in increments of 0.2 °C, and the measurements were performed after waiting for at least 1 h so that the gel particles could achieve equilibrium swelling.

cross-linked polymer gels in $[C_2\text{mim}][\text{NTf}_2]$, as inferred from the size (volume) of the gels. In order to easily attain the equilibrium swelling state,²¹ the particle size of the polymer gels was reduced by the suspension polymerization. The PBzMA gel in $[C_2\text{mim}][\text{NTf}_2]$ exhibits low-temperature swollen and high-temperature shrunken phases with a phase transition temperature of ~ 100 °C (Figure 3). The phase transition is discontinuous and reversible with increasing and decreasing temperatures, respectively, and with a hysteresis loop, implying that the transition could be a first-order one.²² Tanaka et al. predicted that all the polymer gels could exhibit continuous phase changes or discontinuous phase transitions resulting from a change in the balance of osmotic pressures,²³ and the result presented in this study is another example of the volume phase transition of polymer gels, that is, the phase transition of nonionic polymer gels in ILs. Since the polymer gel system presented in this paper consists of thermally stable, nonvolatile, and hydrophobic (water-immiscible) components, and the phase transition temperature can be controlled by the polymer and IL structures, it could enable the development of environmentally stable smart gel materials for a variety of purposes.

To the best of our knowledge, this is the first report on the experimental observations of LCST-phase behavior for polymers and polymer gels in ILs. This may underpin the understanding of polymer/IL systems and lead to the development of nonvolatile smart gel materials.

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