Upper Critical Solution Temperature Behavior of Poly(*N*-isopropylacrylamide) in an Ionic Liquid and Preparation of Thermo-sensitive Nonvolatile Gels

Takeshi Ueki and Masayoshi Watanabe*
Department of Chemistry and Biotechnology, Yokohama National University,
79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501

(Received April 26, 2006; CL-060500; E-mail: mwatanab@ynu.ac.jp)

Poly(*N*-isopropylacrylamide) and its gels exhibited upper critical solution temperature behavior in a hydrophobic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide, which may be utilized to prepare stimuli-sensitive polymer systems without the problem of solvent evaporation.

Certain polymers greatly change their solubility in response to external stimuli such as temperature. Thermo-sensitive polymers and polymer gels have been recognized to have potential to be applied to switching or sensing materials by using this transition.[1] In particular, poly(*N*-isopropylacrylamide) (PNIPAm) and its gels, which exhibit lower critical solution temperature behavior in aqueous solutions around ambient temperature, have been extensively studied from the fundamental and practical points of view.[2] However, we have not been able to utilize such thermo-responsive materials in an open atmosphere or at high temperature for a long time, because of the problem of solvent evaporation.

Ionic liquids (ILs) are room-temperature molten salts and have drawn much attention because of their unique properties such as non-volatility, nonflammability, and chemical and thermal stability.[3] We have been interested in a combination of ILs with polymers, because the combination can afford new polymer gels[4] having electrochemically task-specific properties.[5] In this study, solubility and phase-behavior of different polymers in a common hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)imide (EMITFSI), are explored. From the results, a thermo-sensitive polymer gel in the IL is proposed.

Lewis acidity (acceptor number; AN) of typical imidazolium-based ILs, including EMITFSI, is higher than those of commonly used nonaqueous organic solvents, such as dimethyl sulfoxide, *N*,*N*-dimethylformamide, and acetone.[6] On the other hand, Lewis basicity (donor number; DN) of the ILs greatly changes, depending on the chemical structure of an anionic species.[7] EMITFSI has a high AN (=35), almost the same values as lower alcohols, whereas it has a relatively low DN (=11–12), similar to a DN of benzonitrile.[8] Solubility tests for different polymers in EMITFSI were performed.[9] Solubility of the polymers in the IL was judged with the naked eye.

Polymers that have functional groups enabling strong hydrogen bonding, such as poly(methacrylic acid), poly(acrylic acid), polyvinylalcohol, and poly(2-hydroxyethyl methacrylate), were not soluble in EMITFSI. On the contrary, polymethacrylates and polyacrylates were soluble in EMITFSI. For instance, poly(methyl methacrylate) (PMMA), poly(butyl methacrylate), and poly(2-ethylhexyl acrylate) were easily dissolved in the IL. Our NMR results indicate[4a] that the TFSI anion rather than the EMI cation preferentially interacts with the PMMA chain, possibly with the ester side chains, though EMITFSI has a relatively high AN, as mentioned. Interestingly, a PNIPAm/EMITFSI mixture showed upper critical solution temperature (UCST) behavior. PNIPAm ($M_n = 52{,}300$ g/mol, $M_w/M_n = 2.82$, where M_n and M_w are the number- and weight-average molecular weights, respectively.) is phase separated from EMITFSI at 34 °C (Figure 1), which is a completely opposite phenomenon of PNIPAm in aqueous solutions.[2] Until now, UCST phase separations of IL systems have only been observed for IL/alcohol or IL/water mixtures.[10] To our knowledge, this is the first observation of UCST phase separation of a polymer/IL system. The phase separation temperatures of the PNIPAm/IL system change with changing the molecular weight or concentration of PNIPAm. The higher the molecular weight or concentration is, the higher the phase-separation temperature becomes, which indicates a strong entropic contribution to the phase separation.

Although the solubility of PNIPAm in molecular solvents could not be correlated with the magnitude of the AN, it could be correlated with that of the DN. PNIPAm was easily soluble in an organic solvent having relatively high DNs. In low DN solvents such as chlorobenzene, nitrobenzene, nitromethane, and 1,2-dichloroethane, PNIPAm was not soluble at low temperatures; however, it became soluble with increasing temperature. PNIPAm also exhibited UCST phase separation in EMITFSI having a low DN, similarly in low DN organic solvents. These

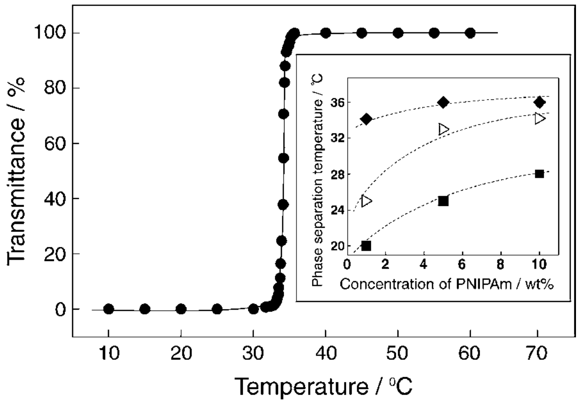

Figure 1. Temperature dependence of transmittance at 500 nm for 1 wt % poly(*N*-isopropylacrylamide) (PNIPAm) solution in EMITFSI. The transmittance of the EMITFSI/PNIPAm solutions was monitored at 500 nm with a cooling/heating rate of 0.5 °C/min. Inset shows a phase diagram for EMITFSI/PNIPAm solutions. UCST-type phase-separation temperatures clearly change with changing the molecular weight or concentration of PNIPAm. (■; $M_n = 15400$ g/mol, $M_w/M_n = 1.64$, ▷; $M_n = 38{,}900$ g/mol, $M_w/M_n = 2.17$, ◆; $M_n = 52{,}300$ g/mol, $M_w/M_n = 2.62$).

results imply that the solvent Lewis basicity strongly affects PNIPAm solubility. If there is only weak Lewis base/acid interaction between EMITFSI and PNIPAm, the solubility increase with increasing temperature can be mainly ascribed to an entropy effect. It has been also reported that solute solubility in ILs is strongly affected by the anionic structures.[11] The aforementioned PMMA solubility in EMITFSI also supports preferential interaction of the anion to the polymer chain.[4a]

The unique phase behavior of PNIPAm in EMITFSI prompted us to prepare PNIPAm gels and to measure the swelling change in the IL. Since the IL has several ten times higher viscosity than that of common molecular solvents, the time to reach equilibrium swelling state for the gels in the IL is prolonged, as expected by the Tanaka–Fillmore theory.[12] In order to easily attain the equilibrium swelling state, the size of gels for the measurements was made small by using the double template method.[13] Small PNIPAm gel particles were prepared in macroporous polystyrene (MP-PSt). The MP-PSt was prepared by using a silica colloid (diameter = 10 µm) crystal as template, followed by etching of the silica particles. An ethanolic solution, containing NIPAm monomer (1 M), *N*,*N′*-methylenebisacrylamide (67 mM), and 2,2-diethoxyacetophenone (10 mM), was infiltrated into the MP-PSt and was polymerized by photoinitiated radical polymerization. Dissolution of the MP-PSt by toluene gave PNIPAm gel particles of 10 µm. The ethanol solvent in the PNIPAm gel particles was replaced by EMITFSI, to obtain a PNIPAm gel particle suspension in EMITFSI. A droplet of the microspherical gel dispersion in EMITFSI was placed onto a concave slide glass. The slide glass was set onto a hot stage, which was allowed to control temperature up to 400 °C. Equilibrium diameters of the microgels were measured by using a digital microscope. We experimentally confirmed that the gels of such size could reach the equilibrium state rapidly, even in the viscous IL.

Figure 2 shows the relationship between the equilibrium diameter of a PNIPAm gel particle in EMITFSI and temperature. The temperature was changed by 10 °C step, and the measurements were carried out after waiting for at least 10 min in order to reach the equilibrium swelling state. The PNIPAm gel is shrunken at low temperatures, starts to swell at 50 °C, and is completely swollen at ca. 200 °C. The swelling and deswelling processes were reversible with rising and descending temperatures. The starting swelling-temperature (50 °C) is considerably higher than the phase-separation temperature observed in Figure 1 (34 °C), and the transition from the shrunken to swollen phases is much broader than that seen in the solution (Figure 1). These phenomena seem to be caused by the reduced conformational entropic effect for the gel, due to its extremely high molecular weight. The swelling ratio (relative size of the gels) could be easily tuned by changing monomer and/or cross-linker concentrations at the preparation, as has been recognized for the preparation of conventional hydrogels.[14] It is also interesting to note that the gel/IL system is stable up to 230 °C. The gel/IL systems are curious in terms of nonvolatility and thermal stability of the components, which may become a great advantage when these systems find applications as smart gel devices in an open atmosphere or at high temperature.

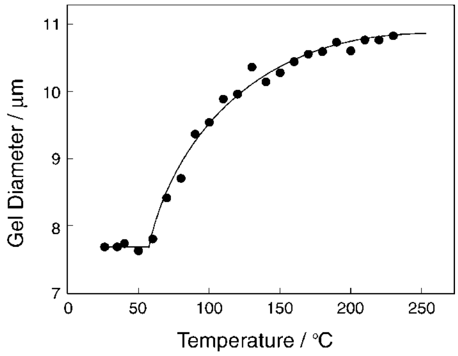

Figure 2. The equilibrium diameter of a PNIPAm gel particle in EMTIFSI as a function of temperature.

Financial support by Grant-in-Aid for Scientific Research from the MEXT (#A-16205024 and #452-17073009) is greatly acknowledged. T. U. acknowledges JSPS for financial support.

References and Notes

1 a) Y. Osada, Y. Matsuda, *Nature* **1995**, *376*, 219. b) R. Yoshida, T. Takahashi, T. Yamaguchi, H. Ichijo, *J. Am. Chem. Soc.* **1996**, *118*, 5134. c) J. M. Weissman, H. B. Sunkara, A. S. Tse, S. A. Asher, *Science* **1996**, *274*, 959. d) Y. Takeoka, M. Watanabe, *Adv. Mater.* **2003**, *15*, 199. e) D. Nakayama, Y. Takeoka, M. Watanabe, K. Kataoka, *Angew. Chem., Int. Ed.* **2003**, *42*, 4197. f) R. Akashi, H. Tsutsui, A. Komura, *Adv. Mater.* **2002**, *14*, 1808.

2 H. G. Schild, *Prog. Polym. Sci.* **1992**, *17*, 163, and references therein.

3 a) *Ionic Liquids in Synthesis*, ed. by P. Wasserscheid, T. Welton, Wiley-VCH, Weinheim, Germany, **2003**. b) T. Welton, *Chem. Rev.* **1999**, *99*, 2071.

4 a) M. A. B. H. Susan, T. Kaneko, A. Noda, M. Watanabe, *J. Am. Chem. Soc.* **2005**, *127*, 4976. b) A. Noda, M. Watanabe, *Electrochim. Acta* **2000**, *45*, 1187.

5 a) A. Noda, M. A. B. H. Susan, K. Kudo, S. Mitsushima, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* **2003**, *107*, 4024. b) M. A. B. H. Susan, A. Noda, S. Mitsushima, M. Watanabe, *Chem. Commun.* **2003**, 938. c) R. Kawano, M. Watanabe, *Chem. Commun.* **2005**, 2107. d) H. Shobukawa, H. Tokuda, M. A. B. H. Susan, M. Watanabe, *Electrochim. Acta* **2005**, *50*, 3872.

6 a) S. N. V. K. Aki, J. F. Brennecke, A. Samanta, *Chem. Commun.* **2001**, 413. b) J. L. Kaar, A. M. Jesionowski, J. A. Berberich, R. Moulton, A. J. Russell, *J. Am. Chem. Soc.* **2003**, *125*, 4125.

7 a) W. Linert, R. F. Jameson, A. Taha, *J. Chem. Soc., Dalton Trans.* **1993**, 3181. b) M. J. Muldoon, C. M. Gordon, I. R. Dunkin, *J. Chem. Soc., Perkin Trans. 2* **2001**, 433. c) L. Crowhurst, P. R. Mawdsley, J. M. P. Arlandis, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790.

8 The detailed polarity study of ILs will be published elsewhere.

9 P. Snedden, A. I. Cooper, K. Scott, N. Winterton, *Macromolecules* **2003**, *36*, 4549.

10 a) V. N-Visak, J. M. S. S. Esperança, L. P. N. Rebelo, M. N. da Ponte, H. J. R. Guedes, K. R. Seddon, J. Szydilouski, *Phys. Chem. Chem. Phys.* **2002**, *4*, 1701. b) J. M. Crosthwaite, S. N. V. K. Aki, E. J. Maginn, J. F. Brennecke, *J. Phys. Chem. B* **2003**, *108*, 5113.

11 a) J. L. Anderson, J. Ding, T. Welton, D. W. Armstrong, *J. Am. Chem. Soc.* **2002**, *124*, 14247. b) R. P. Swatloski, S. K. Spear, J. D. Holbrey, R. D. Rogers, *J. Am. Chem. Soc.* **2002**, *124*, 4974.

12 T. Tanaka, D. J. Fillmore, *J. Chem. Phys.* **1979**, *70*, 1214.

13 M. Kumoda, Y. Takeoka, M. Watanabe, *Langmuir* **2003**, *19*, 525.

14 a) L. Bromberg, A. Y. Grosberg, E. S. Matsuo, Y. Suzuki, T. Tanaka, *J. Chem. Phys.* **1997**, *106*, 2906. b) J. P. Baker, L. H. Hong, H. W. Blanch, J. M. Prausnitz, *Macromolecules* **1994**, *27*, 1446.

Published on the web (Advance View) July 22, 2006; doi:10.1246/cl.2006.964