

Thermodynamical Study on Phase Behavior of Thermo-responsive Polymer in Hydrophobic Ionic Liquids.

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Ionic liquids (ILs) are molten salts having their melting points near room temperature. Recently, it was reported that poly(benzyl methacrylate) (PBnMA) and its derivatives show a lower critical solution temperature (LCST)-type phase separation in ILs. Interestingly, the phase separation temperature (T_c) of the thermo-responsive polymers in IL systems strongly depends on both chemical structures of the polymer and the ILs; one of the PBnMA-derivatives, PPhEtMA (see Fig. 1(a)) exhibits LCST-type phase behavior at 315 K, 391 K, and 393 K in [C₂mIm][TFSA], [C₄mIm][TFSA], and [Py₁₄][TFSA], respectively. Such a tendency indicates that the macroscopic phase behavior of the systems is controlled by microscopic molecular interactions. In the present study, we carried out small-angle neutron scattering (SANS) experiments for PPhEtMA in deuterated ILs, (1) *d*₈-[C₂mIm][TFSA], (2) *d*₁₂-[C₄mIm][TFSA], and (3) *d*₉-[Py₁₄][TFSA] to investigate the correlation between microscopic polymer-IL interactions and the LCST-type phase behavior. Here, in comparison with system (1), we examined the effect of (2) the side chain length and (3) the existence or absence of π -conjugated electron system in the IL cation. Fig. 2(b) shows a representative SANS profiles at elevated temperatures which are close to the cloud point. As shown, the scattering intensity at the low- q region gradually increased with temperature indicating that the excluded volume effect of polymer chains decrease with temperature. The effective Flory-Huggins interaction parameter, $\chi_{\text{eff}}(T)$, was estimated by a curve fitting procedure. Furthermore, the enthalpic (χ_{eff}^H) and the entropic (χ_{eff}^S) contribution to $\chi_{\text{eff}}(T)$

were obtained as an intercept and a slope of a $\chi_{\text{eff}}(T)$ vs $1/T$ plot, respectively. As a result, both of χ_{eff}^H and χ_{eff}^S systematically varied with the chemical structure of the ILs. To obtain a precise interpretation to the variation of χ_{eff}^H and χ_{eff}^S , we carried out high-energy X-ray total scattering (HEXTS) experiment to investigate the microscopic solvation structure. The analysis of the obtained HEXTS data is now in progress. After completing the analysis, we will be able to understand the macroscopic phase behavior of the thermo-responsive polymer in IL systems from a viewpoint of the microscopic molecular interactions.

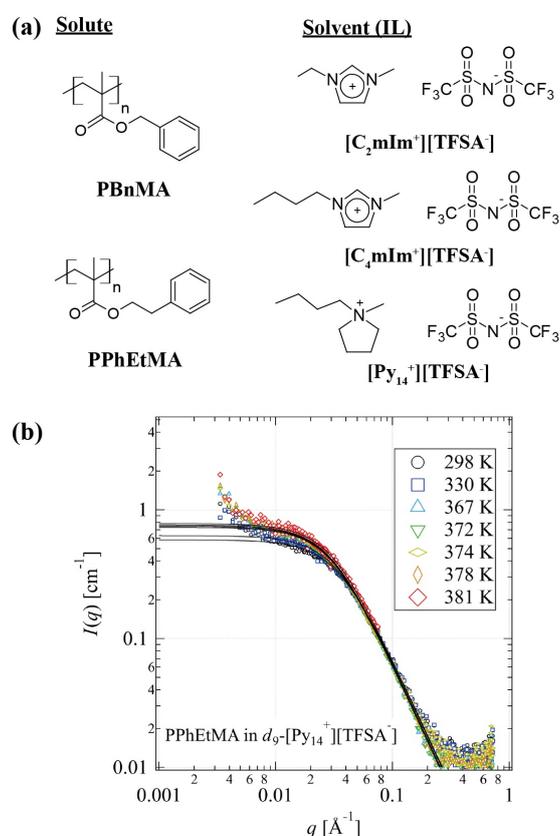


Fig. 1. (a) Chemical structures of polymers and ILs. (b) A representative SANS profiles obtained for PPhEtMA in *d*₉-[Py₁₄][TFSA] solution.