

Kazu Hirose¹, Kenta Fujii², Takeshi Ueki³, Yuzo Kitazawa⁴, Masayoshi Watanabe⁴, Elliot Paul Gilbert⁵, and Mitsuhiro Shibayama¹

¹*Institute for Solid State Physics, The University of Tokyo, Japan*

²*Graduate School of Sciences and Technology, Yamaguchi University, Japan*

³*Polymer Materials Unit, National Institute for Materials Science, Japan*

⁴*Department of Chemistry and Biotechnology, Yokohama National University, Japan*

⁵*Bragg Institute, Australian Nuclear Science and Technology Organization, Australia*

Ionic liquids (ILs) are molten salts having their melting points near room temperature. ILs consist of only ion species, and thus they exhibit unique solvent properties such as high ion conductivity, negligible volatility and nonflammability. Recently, it was reported that poly(benzyl methacrylate) (PBnMA) and its derivatives show a lower critical solution temperature type phase separation in ILs. Interestingly, the phase separation temperature of the thermo-responsive polymers in IL systems strongly depends on both chemical structures of the polymer and the ILs. It indicates that macroscopic phase behavior of the systems is strongly affected by microscopic molecular interactions between polymers and ILs.

In this study, we performed small-angle neutron scattering (SANS) experiments on various PBnMA derivatives in deuterated IL solutions. The interaction parameter, χ between the polymers and the ILs was estimated from the obtained SANS profiles. Here, enthalpic (χ_H) and entropic (χ_S) contributions to χ were obtained from temperature dependence of χ . As a result, it was found that χ_H strongly depends on the chemical structure of the polymers and the ILs. Furthermore, microscopic solvation structure of the polymers in IL systems was investigated by high-energy X-ray total scattering measurement with the aid of molecular dynamics (MD) simulations. It was found that there is strong correlation between the value of χ_H and the microscopic solvation structure.