

# UCST Phase Behavior of Poly(N-isopropylacrylamide) in Room-temperature Ionic Liquid studied by SANS

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It is well known that a lower critical solution temperature (LCST)-type phase behavior in a polymer solution can be often observed in aqueous medium, for example, Poly(N-isopropylacrylamide) (PNIPAm) in aqueous solution. We have reported that the PNIPAm shows an upper critical solution temperature (UCST)-type phase behavior in a hydrophobic room-temperature ionic liquid (IL) such as 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, [C2mIm][TFSA].[1,2] In this study, small-angle neutron scattering (SANS) were made on the PNIPAm in [C2mIm][TFSA] solution and the UCST phase behavior was characterized from the structural viewpoint.

SANS measurements were carried out using SANS-U spectrometer with the camera length 2 and 8 m. SANS profiles corrected for background using an empty cell were normalized with respect to the scattering of polyethylene as a secondary standard material. The SANS profiles thus obtained were further corrected for the incoherent scattering to obtain the scattering intensity,  $I(q)$ . [3]

Figure 1 shows typical SANS profile,  $I(Q)$  observed for fully deuterated IL ([C2mim]-d11[TFSA]) containing 1 wt% PNIPAm in the temperature range of 25 ? 78.9 C °. The  $I(Q)$  observed at 78.9 C ° showed a simple profile with relationship of  $I(Q) \propto Q^{-2}$ , which is typical for a dilute polymer solution system. The intensity in the  $I(Q)$  gradually increased with decreasing temperature down to 32.7 C °. The profile appreciably changed at 24.8 C °, indicating that phase separation occurs at this temperature. The SANS profiles below 32.7 C ° were successfully represented by

theoretical Debye scattering function (solid line). With regard to 24.8 C °, we tried to reproduce the observed  $I(q)$ s by using a sum of Debye and squared-Lorentz functions. The SANS result obtained here was compared with those in aqueous Poly(N-isopropylacrylamide) solutions in terms of polymer concentration and molecular weight dependence. It was found that the solvation of side-chain within PNIPAm by solvent IL or water plays an essential role on the phase behavior.

[1] T. Ueki and M. Watanabe, Chem. Lett. 2006, 35, 4750.

[2] T. Ueki and M. Watanabe, Macromolecules 2008, 41, 3739.

[3] Shibayama M., Matsunaga T., and Nagao M. J. App. Cryst. 2009, 42, 621.

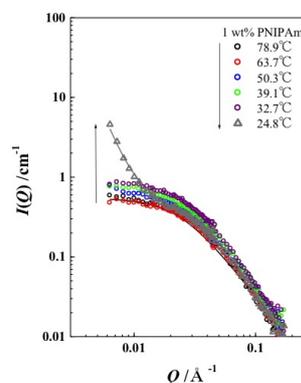


Fig. 1. SANS profiles observed for 1 wt% PNIPAm in deuterated ionic liquid.