LCST Phase Behavior of Poly(benzyl methacrylate) in Room-temperature Ionic Liquid studied by SANS

Shibayama M.(A), Fujii K.(A), Matsunaga T.(A), Ueki T.(B), Watanabe M.(B)
(A) Institute for Solid State Physics, The University of Tokyo. (B) Yokohama National University

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. We have recently reported that poly(benzyl methacrylate), PBnMA shows an LCST 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 PBnMA in [C2mIm][TFSA] solution and the LCST 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 SANS profiles, I(q)s observed for fully deuterated IL ([C2mim]-d11[TFSA]) containing 3 wt% PBnMA polymers in the temperature range of 298 - 373 K. As seen, the I(Q)s were kept practically unchanged in the temperature range between 298 and 363 K, while they suddenly changed at 363 K. This indicates that the LCST behavior of PBnMA-IL solution is a first order phase transition, which is consistent with dynamic light scattering (DLS) results. The SANS profiles below 363 K were well represented by theoretical Debye scattering function (solid line), and then the radius of gyration, Rg was estimated to be almost constant, i.e., 40 - 45 . With regard to T > 363 K, 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), PNIPAm solutions as a typical LCST system. It was found that the specific solvation of PBnMA by solvent IL plays an essential role on the phase behavior.

[1] Ueki T., Karino T., Kobayashi Y., Shibayama M., Watanabe M., J. Phys. Chem. B 2007, 111, 4750.
[2] Ueki T., Watanabe M., Macromolecules 2008, 41, 3739.
[3] Shibayama M., Matsunaga T., and Nagao M. J. App. Cryst. 2009, 42, 621.

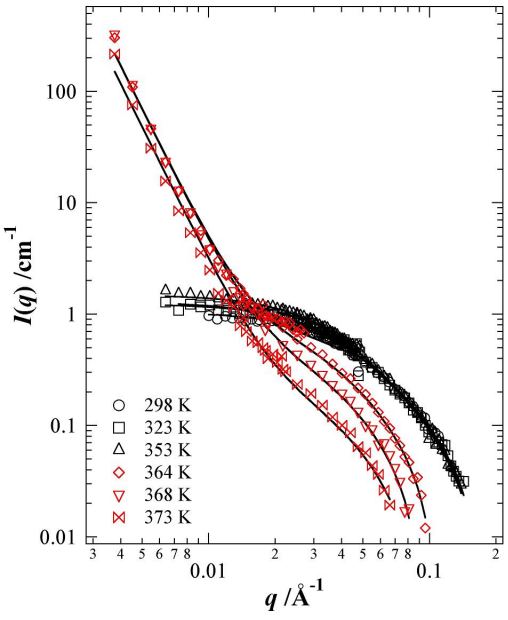

Fig. 1. SANS profiles observed in the PBnMA-[C2mim][TFSA] solution at various temperatures.