Thermo-Responsive Phase Behavior of Polymer in Ionic Liquid

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Recently, it was reported that poly(benzyl methacrylate) (PBnMA) and its derivatives show a lower critical solution temperature (LCST)-type phase separation in a hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C2mIm+][TFSA-]) (Ueki, T and Watanabe, M., Langmuir, 23, 988(2007), Kodama, K et al., Langmuir, 25, 3820(2009)). Such thermo-responsive polymer-IL systems are expected as novel polymer materials having unique properties of ILs, such as nonvolatility, nonflammability and high ion conductivity. However, structural information about the mechanism of phase separation is not adequate at the present stage. We carried out small-angle neutron scattering (SANS) experiment for one of the derivatives of PBnMA, poly(2-phenylethyl methacrylate) (PPhEtMA) in deuterated ionic liquid, d8-[C2mIm+][TFSA-] at High-Flux Isotope Reactor in Oak Ridge National Laboratory, USA (06/03/2015 – 08/03/2015). d8-[C2mIm+][TFSA-] was prepared by the procedure established in our research group. Fig. 1(a) shows the SANS profiles of 3 wt% PPhEtMA solution of d8-[C2mIm+][TFSA-] at various temperatures, 288 K – 310 K. As can be seen from the figure, steep upturn was observed when temperature is larger than Tc (307 K in d8-[C2mIm+][TFSA-]), indicating the appearance of large aggregates in this region. We carried out further analysis for SANS profiles by using a Zimm plot. Fig. 1(b), (c) show the Zimm plots for T=288 K and T=303 K, respectively. The slope of A2, the concentration dependence, i.e., changes its sign from positive to negative at T=303 K as shown in the figure. The estimated absolute value of A2 is significantly smaller than the corresponding one of previously reported poly(N-isopropylacrylamide) (PNIPAm) in d8-[C2mIm+][TFSA-] system (Asai, H. et al., Macromolecules, 46, 1101(2013)). In addition, it is previously reported that enthalpy of demixing in PBnMA/[C2mIm+][TFSA-] solution is smaller than the corresponding one of PNIPAm/[C2mIm+][TFSA-] solution (Ueki, T. et al., Pure Appl. Chem., 81, 1829(2009)).The difference between A2s of PPhEtMA/[C2mIm+][TFSA-] and PNIPAm/d8-[C2mIm+][TFSA-] solutions can be explained by the difference in interaction energy between polymer and IL.

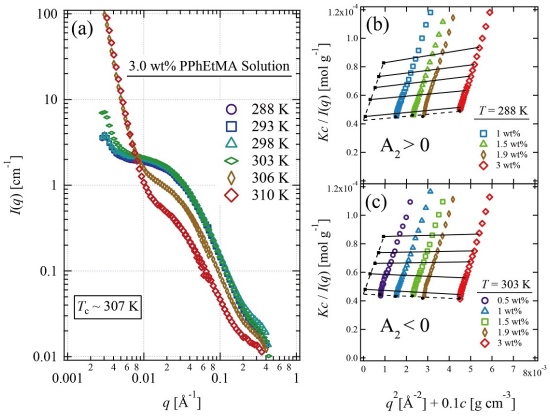

Fig. 1. (a) SANS profiles of 3 wt% PPhEtMA/d8-[C2mIm+][TFSA-] solution at T = 288 K – 310 K. Zimm plot for 0.5 wt% – 3 wt% PPhEtMA/d8-[C2mIm+][TFSA-] solutions at (b) 288 K and (c) 303 K are also shown.