Structural Study on the UCST-type Phase Separation of Poly(N-isopropylacrylamide) in Ionic Liquid

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Poly(N-isopropylacrylamide) (pNIPAm) is a well known polymer for its lower critical solution temperature (LCST) behavior in water. Until today, many researchers have studied the structure of pNIPAm aqueous solutions during phase separation process by differential scanning calorimetry, light scattering, small-angle neutron scattering (SANS), and so on. These pieces of information on temperature dependence of the structure of pNIPAm chain should be a significant insight for the applicational studies.

On the other hand, According to the report by Ueki and Watanabe, UCST-type phase separation of pNIPAm was observed in one of the ionic liquid (IL), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C2mIm+][TFSA-]).

In this study, we investigated the UCST-type phase separation of well-defined pNIPAm in [C2mIm+][TFSA-] in terms of structural viewpoints. SANS and DLS experiments were performed for pNIPAm/IL solutions with various molecular weights (Mw) and concentrations. From the experimental data, we discuss the characteristics of the phase separation of pNIPAm/[C2mIm+][TFSA-] system.

SANS experiments were carried out on High-flux Advanced Neutron Application Reactor (HANARO) located at Korea Atomic Energy Research Institute (KAERI), Korea. A monochromated cold neutron beam with an average neutron wavelength 6.00 angstrom was irradiated to the samples. The scattered neutrons were counted with a 2D detector. The sample concentrations were the same as the DLS experiment, i.e. 1, 3, 5 wt% for both 24, 100 kDa pNIPAm/the d8-[C2mIm+][TFSA-] solutions. The sample-to-detector distance (SDD) was chosen to be 7 m for all the 24 kDa samples, 1 wt% 100 kDa samples, and the other samples above 40 C, while 11 m for the other cases. After necessary corrections for open beam scattering, transmission, and detector inhomogeneities, the corrected scattering intensity functions were normalized to the absolute intensity scale.

Figure 1 shows (a) Rg, (b) xi, and (c) chi values obtained from the fitting analysis of SANS profiles as a function of temperature. It was found in Figure 1(a) that the Rg values became smaller as decreasing temperature, indicating that the pNIPAm chains gradually shrink with approaching the cloud points. The xi values of semi-dilute 100 kDa samples shown in Figure 1(b) become larger as decreasing temperature. This indicates an enhancement of concentration fluctuations by approaching the cloud point. The xi values, decrease at high temperatures as increasing concentration, which is a well-known behavior for semi-dilute polymer solutions in a good solvent. In Figure 1(c), it can be seen that the chi parameter becomes smaller with increasing temperature and approach 0.5 at around 45 C for 24 kDa, suggesting that the chi temperature in this system is ca. 45 C, which is in good agreement with the result shown in Figure 1(b). However, the chi temperature for 100 kDa is lower than that estimated from 24 kDa. One of the possible reasons is the effect of flexibility of pNIPAm chain, considering that a chi parame-

ter should be constant for a theoretical stiff polymer.

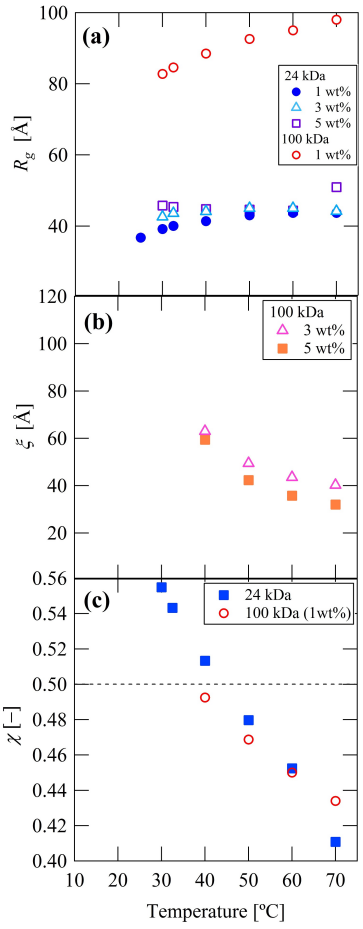

Fig. 1. Temperature dependence of (a) Rg, (b) xi, and (c) chi obtained from SANS data. The solid line indicates chi=0.5