

## Evolution of heterogeneity and gelation of poly(*N*-isopropylacrylamide) aqueous solution at a temperature below cloud point

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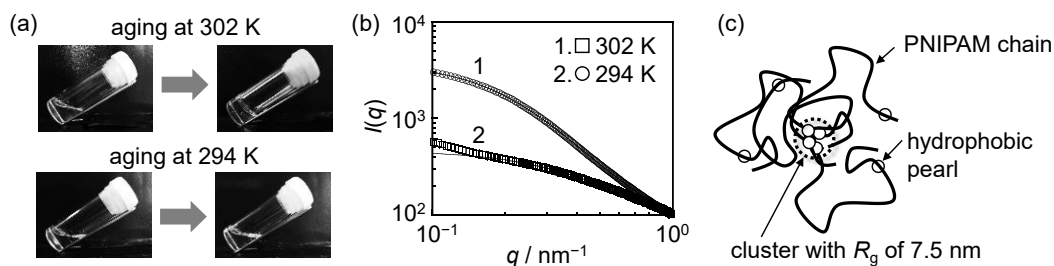
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Poly(*N*-isopropylacrylamide) (PNIPAM) is a representative thermoresponsive polymer, and its aqueous solution becomes phase separated at a temperature higher than the cloud point ( $T_{cp}$ ). To further promote the use of PNIPAM as a functional material, its phase behavior should be understood as a first benchmark. Previously, it was pointed out that the viscosity of a PNIPAM aqueous solution with a relatively higher concentration dramatically increased with temperature near to the  $T_{cp}$ . Although the origin of the peculiar viscosity increase just below the  $T_{cp}$  is a key to understanding the phase behavior, it remains unclear at the moment. Thus, it is necessary to examine the structure and physical properties of the PNIPAM solution a temperature just below the  $T_{cp}$  on various length scales. In this study, we report on the structure and physical properties examined by small-angle X-ray scattering (SAXS) measurement in conjunction with a particle tracking, in which the thermal motion of probe particles in the solution was tracked.

An aqueous solution with a concentration of 10 wt% was prepared from atactic PNIPAM with a number-average molecular weight of 193k and a polydispersity index of 2.2. The  $T_{cp}$  of the PNIPAM solution was determined by monitoring the light transmittance at a wavelength of 633 nm passing through the solution, as a function of temperature. A temperature ( $T_{cp}'$ ), at which the transmittance started to decrease upon heating, was collected at different heating rates ( $\nu$ ). By extrapolating the  $T_{cp}'$  value to  $\nu = 0$ , the  $T_{cp}$  value was determined to be 304 K. SAXS experiments were performed at the BL03XU in SPring-8, Japan.

Fig. 1(a) shows photographic images of the time-variation in the physical state of the PNIPAM-water mixtures. When the PNIPAM-water mixture was aged for 3 h at 302 K, which was just below the  $T_{cp}$ , it turned into a transparent gel without any loss of transparency. Such a gelation was not observed at 294 K. Fig. 1(b) shows SAXS profiles for the mixtures that were aged for 3 h at 302 and 294 K. The contribution of water to the scattering for the sample was subtracted. In general, a scattering from the polymer chains in semi-dilute solution, where the polymer concentration is above the overlap concentration, can be described by the Ornstein-Zernike (OZ) function. In fact, the experimental data obtained for the mixture aged at 294 K could be reproduced by the OZ function, as drawn by solid lines in the panel (b). The value of  $\zeta$ , which corresponded to the average size of blobs consisting of polymer segments, was 2.6 nm. On the other hand, the data for 302 K could not be fitted by the OZ function. The scattering intensity in the range smaller than  $0.6 \text{ nm}^{-1}$  was intensified. To express the data in the small  $q$  region, the scattering function based on the Guinier model, which was used for an aqueous solution of isotactic PNIPAM, was included as an additional term [1]. The  $\zeta$  and  $R_g$  values obtained by the curve fitting were 5.9 and 7.5 nm, respectively. According to the previous result, the  $R_g$  value should correspond to the size of the clusters formed by intermolecular association of segments, as shown in Fig. 1(c). In the presentation, the results of the particle tracking will be also given to discuss a



**Figure 1.** (a) Photographic images and (b) SAXS profiles for the PNIPAM–water mixtures aged for 3 h at 294 and 302 K. (c) Schematic illustration of the aggregation structure in the PNIPAM–water mixture aged at 302 K.

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