SPECIAL ISSUES -PROGRESS IN STRUCTURE ANALYSES OF POLYMERIC MATERIALS
BY SYNCHROTRON RADIATION AND NEUTRON BEAM-

Self-Assembling in Polymerization Processes of N-Isopropylacrylamide

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ABSTRACT: The self-assembling process during the polymerization of N-Isopropylacrylamide (NIPA) was investigated with time-resolved small angle X-ray scattering (SAXS). During the polymerization process at 35.0 °C which is above the cloud point curve of poly-N-Isopropylacrylamide (PNIPA)/water solution, the phase separation *via* spinodal decomposition occurs simultaneously. The SAXS profile can be well expressed by the sum of Porod law and Ornstein-Zernike form. The time changes in the parameters yielded by fitting can be divided into four regions: (i) Region I, $t < 130s$: In this region, The polymerization and the macrophase separation *via* spinodal decomposition progresses simultaneously. The molecular weight of PNIPA increases with time and the concentration difference between two phases increases with time. The domain formation from the concentration fluctuations is dominant. (ii) Region II, $130s < t < 350s$: Similar to Region I, The polymerization and the spinodal decomposition progresses simultaneously and the molecular weight of PNIPA increases with time and the concentration difference between two phases increases with time. However, the coarsening of the phase-separated structure becomes dominant rather than the domain formation. (iii) Region III, $350s < t < 1500s$: The polymerization has finished and the polymer rich and poor regions reach each equilibrium value. The coarsening still progresses in the time change in the structures in PNIPA/water systems. (iv) Region IV: $1500s < t$: The coarsening of the phase-separated structure is pinned down by the crosslink due to sequential hydrogen bond formation between polymer chains and water molecules.
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Poly(N-Isopropylacrylamide) (PNIPA)/water solution exhibits a lower critical solution temperature (LCST) type phase diagram with theta temperature being 30.5 °C.[1–5] Unlikely other polymer solution systems, the phase diagram of PNIPA/water solution is almost independent of molecular weight and the solution does not completely separate into two phases above its cloud point. Recently, Yoshizaki *et al.* investigated rather in detail the molecular weight dependence of aqueous solutions of PNIPA prepared by living anionic polymerization.[6] They found that the cloud point curve of PNIPA/water solution where the range of the molecular weight of PNIPA varies from 5.76×10^3 to 7.15×10^4 shifts upwards with increasing the molecular weight due to the effects of hydrophobic end group, which is contrary to the usual tendency of the molecular weight dependence of the polymer solution. It should be noted that they measured the transmittance of the solution with heating rate of 1.5 °C/h and defined the temperature where

the transmittance of the solution becomes as the cloud point of the solution. Theoretically, Okada and Tanaka investigated the phase diagram of PNIPA/water solution on the basis of cooperative hydration, or sequential hydrogen bond formation between polymer chains and water molecules.[7] They found that the strong cooperative hydration exists between PNIPA and water and leads to the LCST phase diagram with flat shape and only little molecular weight dependence.

The cooperative hydration may also affect the polymerization processes of PNIPA in water. If we polymerize NIPA above the cloud point curve, the macrophase separation is involved during the polymerization process of NIPA. Even though the polymerization is done below cloud point curve, the cooperative hydration may cause the self-assembling structure during the polymerization.

Thus, in this study, we investigated the polymerization process of NIPA in water after the onset of tem-

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perature-jump above the cloud point of PNIPA/water system by using time-resolved small-angle X-ray scattering (SAXS) and study the time changes in the self-assembled structure during the polymerization.

EXPERIMENTAL

Sample

First we prepared the monomer solution which contains N-Isopropylacrylamide (NIPA) (monomers, 1.47 M) and N,N',N',N'-tetramethyl ethylenediamine (accelerator, 17.8 mM). the monomer and the accelerator were dissolved into water purged with nitrogen. After addition of 17.5 mM ammonium peroxodisulfate (AP) solution to the monomer solution with the monomer solution/ the AP solution = 25/75 (v/v) at room temperature, the monomer solution was quickly transferred into a cell. Then the cell was put into the heater block heated at 35.0 °C for SAXS experiments.

SAXS experiment

SAXS experiments were conducted at the BL45XU, SPring-8.[8] We used the CCD camera with Image-Intensifier.[9] The wavelength and the distance from sample to detector are respectively 1.1 Å and 2300 mm. The measurement time is 500 ms. It should be noted that it takes more than 30 min to measure the SAXS profiles of the NIPA solution by using conventional SAXS apparatus. Thus, the time-resolved SAXS experiment is impossible with conventional SAXS apparatus. We set two ion chambers at front and rear sides of the heater block to monitor the transmittance during polymerization processes. To avoid sample damage by the radiation of incident X-ray, we minimize the exposure time by synchronizing the beam shutter with CCD camera.

After the onset of the temperature jump, we measured the time changes in the scattered intensity with the scan rate being 10 s/scan. All scattered intensity profiles were corrected for background and then circularly averaged for further analyses.

RESULTS AND DISCUSSION

Figure 1 shows the time change in the scattering intensity $I(q,t)$ as a function of the magnitude of scattering vector q [$= (4\pi/\lambda)\sin(\theta/2)$, with θ being the scattering angle] after the onset of temperature jump to 35.0 °C, where the turbid solution was formed. At time $t > 84$s, $I(q)$ show q^{-4} dependence and obeys Porod law,[10] indicating that the macroscopic phase separation with sharp interface have already occur before the completion of the polymerization. As already described, the phase diagram of PNIPA/water system
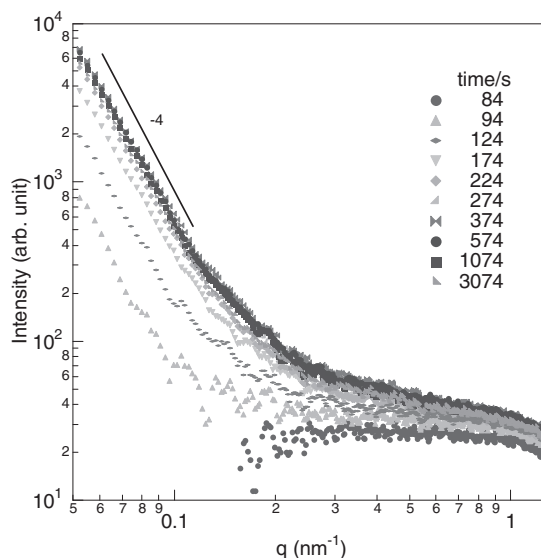

Figure 1. Time change in the scattered intensity plotted as a function of q during the polymerization processes at 35.0 °C.

is insensitive to molecular weight of PNIPA and the phase diagram with low molecular weight is lower than that of high molecular weight due to the effects of hydrophobic end group. Thus, the measured temperature 35.0 °C is above the spinodal temperature of the solution even though the molecular weight of PNIPA is still low. Therefore, once the polymerization occurs, the phase separation *via* spinodal decomposition progresses in PNIPA/water system almost simultaneously. Moreover the high mobility of low molecular weight PNIPA causes the fast dynamics of phase separation so that the phase-separated structure with sharp interface is well-formed at earlier time region. In order to analyze the change in the self-assembling structure of PNIPA/water system during polymerization, we assumed that the scattering function consists of the scattering intensity from the sharp interface of the phase-separated structure and the critical fluctuations in polymer rich region and can be described by the following sum of Porod law and Ornstein-Zernike form (OZ form):[11]

$$I(q) = Aq^{-4} + \frac{I(0)}{1 + q^2\xi^2}, \qquad (1)$$

where A is proportional to interfacial area per unit volume and the square of the amplitude of the electron density difference between polymer rich region and poor region, $I(0)$ represents the osmotic compressibility of the polymer rich region, and ξ is the correlation length of the polymer rich region corresponding to the distance between entanglements. The first term of the right hand in Eq. (1) represents the scattering function of the sharp interface while the second term corresponds to the concentration fluctuations in polymer rich region or OZ form. Figure 2 shows the fitting re-
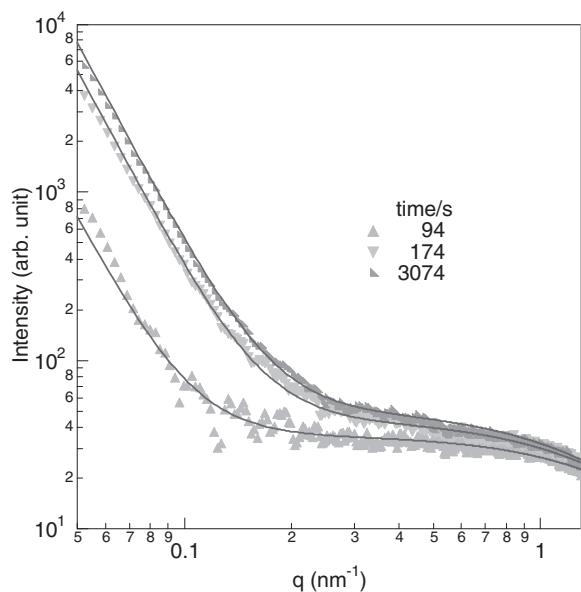
Figure 2. Fitting results of the scattering function with Eq. (1). Solid line correspond to the fitting results.
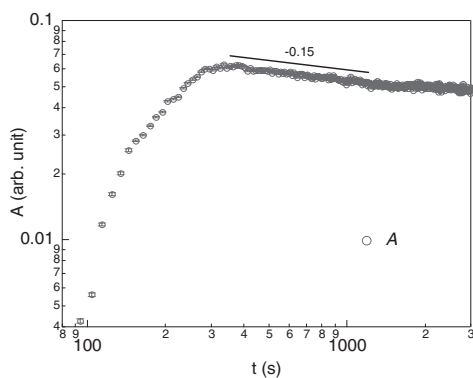

Figure 3. Time change in A in double logarithmic scale.

sults of the scattering function with Eq. (1). We found Eq. (1) can well describe the experimental results at $t > 84s$ and yielded the changes in the parameters A, $I(0)$, and ξ, with time.

Figure 3 shows the time change in A. The time change in A can be divided into four region: 1) Region I ($t < 130s$). In Region I the value of A rapidly increases with time. 2) Region II ($130 < t < 350s$). the value of A still increases with time but the rate of increase becomes slower than that in Region I. 3) Region III ($350 < t < 1500s$). In this region, the value of A decreases gradually with time. 4) Region IV ($1500s < t$). the value of A becomes almost constant. As already described above, A is proportional to i) the square of the amplitude of the electron density difference between polymer rich region and polymer poor region, and ii) the interface area per unit volume. The formation of phase-separated structure from concentration fluctuations increases the interface area per unit volume, while the coarsening of the phase-sepa-

rated structure causes the decreases of the interface area per unit volume. As for the square of the amplitude of the electron density difference, the square of the amplitude increases with time at earlier time region since the amplitude of the concentration fluctuations increases with time in the early and intermediate stage of spinodal decomposition.[12,13] On the other hand, the square of the amplitude becomes constant with time at later time region where the polymer rich and poor regions reach each equilibrium value.

At $t < 350s$ or Region I and II, the increase in the amplitude of the electron density difference becomes dominant in the change in A, reflecting that the difference between coexisting points at polymer rich and poor region widens with increasing molecular weight of PNIPA and that the phase separation processes is in the intermediate stage. In Region I, the domain formation is dominant while the coarsening process is then dominant in Region II. Thus, the increase rate changes between Region I and II. In region III, the polymerization has finished so that coexisting points at polymer rich and poor region does not grow further. Thus the coarsening of the phase-separated structure becomes dominant in the change in A, resulting A decreases with time. The change in A with time obeys the following power law of t:

$$A \sim t^{-0.15} \tag{2}$$

According to the previous result on spinodal decomposition of polymer blends, A is proportional to t^{-1} if the hydrodynamic interaction is important in the coarsening processes of spinodal decomposition.[13] The power law observed in PNIPA/water at $t > 350s$ is much smaller that t^{-1}. Moreover, it is well-known that the PNIPA/water solution can not separate into two phases macroscopically although usual polymer solutions can completely separate into two phases. These facts indicate that the crosslink within polymers occurs even though the solution does not contain crosslinker used for the formation of PNIPA gel. The crosslink may occur by sequential hydrogen bond formation between polymer chains and water molecules proposed by Okada and Tanaka.[7] In Region IV, the crosslink has been well-developed and pinned down the growth phase-separated structure. Thus, the value of A becomes constant with time.

Figure 4 shows the changes in $I(0)$, and ξ with time. Similar to the case of A, the time change in $I(0)$ and ξ can be divided into the following four regions. 1) Region I ($t < 130s$). In Region I the values of $I(0)$ and ξ increase with time. 2) Region II ($130 < t < 350s$). The values of $I(0)$ and ξ still increase with time. The growth rate of ξ is the same rate in Region I while the growth rate of $I(0)$ becomes slower than that in Region I. 3) Region III ($350 < t < 1500s$). In this
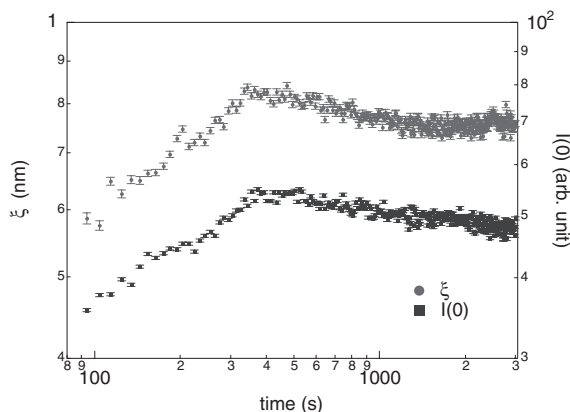
Figure 4. Time changes in $I(0)$ and ξ in double logarithmic scale.

region, the values of $I(0)$ and ξ decrease with time. 4) Region IV ($1500s < t$). The value of ξ becomes almost constant while the value of $I(0)$ still decreases with time. It is interesting that ξ is less than 1 nm at observed time region. This small correlation length suggests that the observed correlation length is not the network structures in PNIPA rich region. The fluctuations with small length scale may reflect the correlation of sequential hydrogen bond formation between polymer chains and water molecules. The sequential hydrogen bond has been reported by Hirashima and Suzuki.[14] The reason of the increases in $I(0)$ in Regions I and II is the decreases of the osmotic compressibility associating with the increases in molecular weight and concentration of PNIPA. The increase in ξ may reflect the increase the correlation length of sequential hydrogen bond formation between polymer chains and water molecules due to the increase in the molecular weight of PNIPA.

On the other hand, at $t > 350s$, the polymerization has finished and the polymer rich region become more dense with time. The crosslink occurs more tightly. The tight crosslink causes the increase in the osmotic compressibility thus the decrease in $I(0)$ with time. The decrease in ξ also may occur associating with the tight crosslink.

From the time changes in the parameters yielded by fitting, A, $I(0)$, and ξ, the polymerization process at $35.0\,^{\circ}C$ can be divided into the following four regions: (i) Region I, $t < 130s$: In this region, the polymerization and the macrophase separation *via* spinodal decomposition progress simultaneously. The molecular weight of PNIPA increases with time and the concentration difference between two phases increases with time. The domain formation from the concentration fluctuations is dominant. (ii) Region II, $130s < t < 350s$: Similar to Region I, The polymerization and the spinodal decomposition progress simultaneously and the molecular weight of PNIPA increases with

time and the concentration difference between two phases increases with time. However, the coarsening of the phase-separated structure becomes dominant rather than the domain formation. (iii) Region III, $350s < t < 1500s$: The polymerization has finished and the polymer rich and poor regions reach each equilibrium value. The coarsening still progresses in the time change in the structures in PNIPA/water systems. (iv) Region IV: $1500s < t$: The coarsening of the phase-separated structure is pinned down by the crosslink due to sequential hydrogen bond formation between polymer chains and water molecules.

CONCLUSION

We have investigated the polymerization processes of NIPA in water at $35.0\,^{\circ}C$ by using the time-resolved SAXS technique. We found that the phase-separated structure with sharp interface have been developed even in earlier time region of polymerization process. The scattering function at $t > 94\,s$ can be well described by the sum of Porod law and OZ form. We obtained the time changes in the characteristic parameters. From the time changes in the parameters, the polymerization process at $35.0\,^{\circ}C$ can be divided into the four regions described in the previous section.

In future work, we will compare the polymerization process of NIPA in water and the gelation processes of PNIPA/water system where we use the crosslinker.

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