Structure Relaxation of Hydrophobically Aggregated Poly(*N*-isopropylacrylamide) in Water

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Introduction. Poly(*N*-isopropylacrylamide) (PNIPAM) in water undergoes a coil-to-globule transition at about 32 °C with elevating temperature.[1−3] This is mainly due to the dissociation of ordered water molecules surrounding hydrophobic *N*-isopropyl groups. In the case of PNIPAM gels, which are usually prepared by polymerizing NIPAM monomers in the presence of a cross-linker, a volume transition takes place from a swollen state to a collapsed state at a temperature, T_c, which is slightly above the coil−globule transition temperature. The dissociation enthalpy is large enough to be detected with a conventional differential scanning calorimeter (DSC).[4−6] We have conducted a series of studies on polymer concentration dependence[6] and comonomer dependence of PNIPAM gels by DSC.[7] During these experiments, we have found that successive DSC runs for PNIPAM solutions exhibit poor reproducibility in both the endotherm and the transition temperature. This is observed exclusively in PNIPAM solutions but not in PNIPAM gels. However, reproducibility is recovered by aging the solution sample at a temperature lower than the transition temperature. This phenomenon indicates that it takes a certain time for PNIPAM solutions to recover the hydrated structure after a DSC run. In this communication, we focus on the difference in the structure relaxation after thermal treatment (DSC run) and discuss the relaxation phenomenon in conjunction with the cooperativity of gel networks.

Experimental Section. NIPAM monomers (Kohjin Chemical Co. Ltd.), purified by recrystallization, were dissolved in deionized water, and a 690 mM NIPAM solution was prepared. Ammonium persulfate (APS) was then added to the solution. The polymerization was initiated with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) at 20 °C for 20 h after the pregel solution was degassed, and a PNIPAM solution was prepared. For the preparation of gel samples, *N*,*N*′-methylenebis-(acrylamide) (BIS) (cross-linker) was also added to the NIPAM monomer solution, followed by the same procedure as in the case of the PNIPAM solution. The concentrations of these reagents were 31.4 (BIS), 1.75 (APS), and 8 mM (TEMED). Gels were immersed in deionized water for a week to remove unreacted residue. DSC measurements were carried out with a DSC3100 (Mac Science Co. Ltd.). The polymer concentration was adjusted by moisturizing a dried gel or dried polymers in a sealed DSC sample pan. The sample was allowed to equilibrate for a few days to obtain a homogeneous gel or solution. A piece of thus prepared samples of about 10 mg was crimped in a sealed pan, and DSC thermograms were taken at a heating rate of 3 °C/min.

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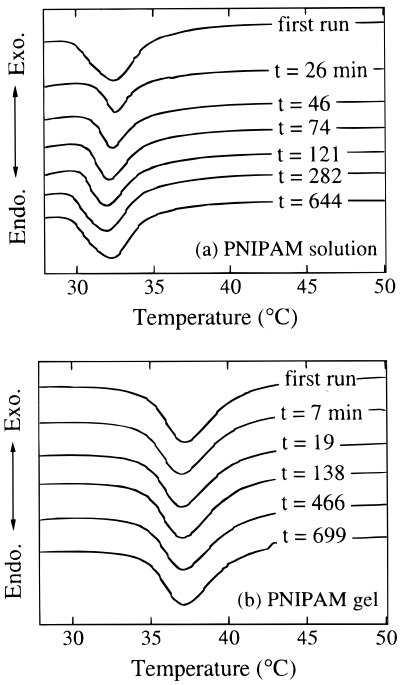

Figure 1. DSC thermograms of (a) PNIPAM solutions and (b) PNIPAM gels. The term "first run" indicates a virgin sample. After a DSC scanning of a first-run sample, the DSC pan was rapidly cooled to ambient temperature and aged for a given time, *t*. Successive DSC scanning was then conducted.

The temperature range was 20−60 °C. No noticeable change in the weight of the sample pan was detected before and after a DSC run, indicating no water evaporation took place during the DSC run. The concentration was determined by weighing the contents in the pan before and after drying.

Results and Discussion. Figure 1 shows a series of DSC thermograms for (a) PNIPAM solutions and (b) PNIPAM gels. The polymer concentrations of both gels and solutions were roughly the same, about 40 wt %. The "first run" means a DSC thermogram taken on a virgin sample. The curves with time (*t*) denote thermograms taken on a sample aged at 20 °C for time *t* after completion of the previous run (up to 60 °C). In the case of the PNIPAM solution, the endothermic peak is noticeably suppressed for $t = 26$ min. This suppression is gradually recovered by increasing *t*. At $t = 644$ min, the thermogram becomes quite similar to that for the first run. Note that the transition temperature, which we define as the intersection of the extrapolated baseline and the tangent line of the peak, also depends on *t*. On the other hand, thermograms for the gels seem to be invariant with respect to *t*.

Figure 2 shows the aging time dependence of the enthalpy of dissociation per mole of gel or solution, $\Delta H(t)$. It is clear that $\Delta H(t)$ for the gel is independent of *t*, whereas $\Delta H(t)$ for the solution is a strong function of *t*. The data point at $t = 0$ ($\equiv -0$) is for the first run. Note that $\Delta H(t)$ for the solution gradually approaches that for $\Delta H(-0)$, i.e., $\Delta H(t) \rightarrow \Delta H_\infty \cong \Delta H(-0)$. Figure 3 shows the variation of the transition temperature, T_c, as a function of *t*. Similarly to the t dependence of $\Delta H(t)$, a clear *t* dependence of T_c is observed exclusively in the PNIPAM solution.

The variation of ΔH and T_c with *t* for the PNIPAM solution is ascribed to structure relaxation. If this process can be assumed to be a single relaxation process,

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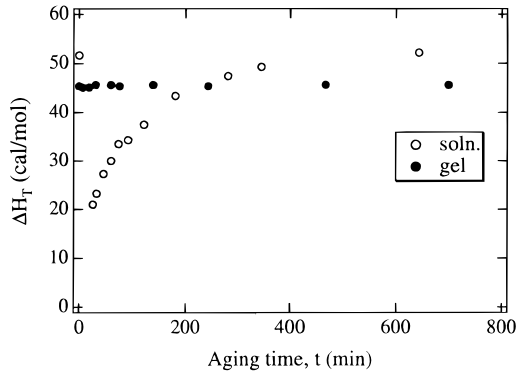

Figure 2. Aging time, t, dependence of the enthalpy of dehydration, $\Delta H(t)$, for PNIPAM gels (●) and for PNIPAM solutions (○).

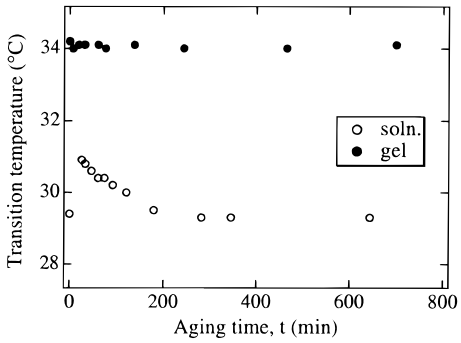

Figure 3. Aging time, t, dependence of the transition temperature, T_c, for PNIPAM gels (●) and for PNIPAM solutions (○).

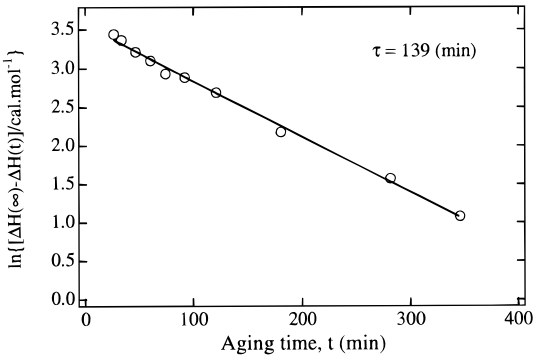

Figure 4. Semilogarithmic plot of the difference of the enthalpy of dehydration vs aging time, t, for PNIPAM solution. The relaxation time, τ, is estimated to be 139 min.

the following relation is given:

$$\ln[\Delta H_\infty - \Delta H(t)] = -\frac{t}{\tau} + \ln[\Delta H_\infty - \Delta H(t \to +0)] \quad (1)$$

where $\Delta H(t)$ is the enthalpy of dehydration aged for time t, and ΔH_∞ is equal to ΔH at large t. $\Delta H(t \to +0)$ is the value of ΔH at infinitesimally small t. τ is the relaxation time, which characterizes the structure relaxation by thermal fluctuations and rehydration.

Figure 4 shows the fitted result of $\Delta H(t)$ with eq 1. The fitting seems to be satisfactory. The estimated τ is 139 min for the PNIPAM solution. This strongly suggests that it takes a certain amount of time, of the order of 2 h, for the PNIPAM solution to recover a hydrated structure. On the other hand, the gel does not require such a long time for structure relaxation.

Here we discuss the origin of the difference in the structure relaxation processes. Structure recovering of a PNIPAM aqueous system may take place by water diffusion into the polymer-rich phase. In the case of polymer gels, the time required for the structure relaxation can be estimated, provided the size of the gel is known. Suppose that a PNIPAM gel is in the the fully shrunken state just after a DSC run. On lowering the temperature, the gel starts to swell. However, the swelling kinetics is governed by collective diffusion of the network, as extensively discussed by Tanaka and co-workers.[8,9] The collective diffusion coefficient for PNIPAM gels is of the order of 10^{-7} cm^2/s. The size of a gel used for a DSC run is estimated to be of the order of 10^{-1} cm, because a 10 mg DSC sample has a volume of about 10×10^{-3} cm^3, which gives $10^{1/3} \times 10^{-1}$ cm. Thus, the time required for swelling equilibrium is estimated by

$$\tau = \frac{\langle x^2 \rangle}{6D} \approx \frac{(10^{1/3} \times 10^{-1})^2\ [\mathrm{cm}^2]}{6 \times 10^{-7}\ [\mathrm{cm}^2/\mathrm{s}]} \approx 7.74 \times 10^4\ \mathrm{s} \approx 21.5\ \mathrm{h} \quad (2)$$

This value does not agree to the experimental result at all. The experiment indicates that structural relaxation for the gel is complete in less than 7 min, since no relaxation kinetics was observed by DSC. This contradiction disproves the hypothesis, i.e., "the gel is in shrunken state after DSC run". It should be noted here that the heating rate is 3 °C/min. This means that it takes only 13.3 min to reach 60 °C after starting a DSC run from 20 °C. Though a gel sample for DSC is small, it is not small enough to follow the equilibrium size of gel during heating. Therefore, the gel undergoes a phase separation but not volume transition upon heating. If the gel does not shrink during a DSC run, it can recover its original size upon cooling within a time much smaller than that required for swelling. This is why no relaxation in ΔH was observed for gels. On the other hand, PNIPAM chains in a solution undergo collapse transition during a DSC run, and a polymer-rich phase is segregated from water. Thus, it takes a long time to recover its original state or, in other words, to dissolve again. It is obvious that the evaluated relaxation time, τ, may depend on the volume of the solution used for DSC experiment, thermal history, the molecular weight of the polymer, and so on. Therefore, τ is not a material constant. The important points in this work, however, are the following: (1) A thermosensitive gel is a quick responsive heat container which stores or releases heat according to temperature change of the environment. This results from a reversible phase separation/homogenization without significant change of gel volume. (2) The corresponding polymer solution does not have such a function because it takes a rather long time to recover a homogeneous solution from a hydrophobically aggregated structure.

We verified that ΔH for gels is substantially suppressed upon aging for a long enough time, e.g., 1 day, above the T_c. This verifies our hypothesis that a gel does not shrink enough during a DSC run. Systematic studies of the volume effect and thermal hysteresis effect on ΔH are now in progress.

Conclusion. A clear difference in the thermal properties is found between hydrogels and aqueous solutions of PNIPAM. The enthalpy of dissociation of water molecules surrounding hydrophobic groups of PNIPAM, ΔH, was dependent on the aging time t after the previous DSC run for the solution, but not for the gel. The relaxation time for the solution was 139 min. The

absence of the relaxation for the gel is explained by phase separation/homogenization without noticeable volume transition.

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