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Preparation Pressure Dependence of Structure Inhomogeneities and Dynamic Fluctuations in Poly(*N*-isopropylacrylamide) Gels

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ABSTRACT: The structure inhomogeneities and dynamic fluctuations in poly(*N*-isopropylacrylamide) (PNIPA) gels have been investigated by dynamic light scattering as a function of gel-preparation pressure, P_{prep}. The ensemble average light scattered intensity ($\langle I\rangle_{\mathrm{E}}$), a measure of structure inhomogeneities, was found to be an increasing function of P_{prep} and diverged at $P_{\mathrm{prep}} = 168$ MPa. This indicates that PNIPA gels undergo phase separation by increasing P_{prep}. The corresponding PNIPA solution was transparent and had no P_{prep} dependence. It is concluded that the structure of gels depends not only on the pressure at observation P_{obs} but also on P_{prep}, and the inhomogeneities increase with P_{prep}. On the other hand, the dynamic fluctuations were independent of P_{prep}. This shows that cross-linking plays a major role in formation of built-in structure inhomogeneities.

Introduction

Poly(*N*-isopropylacrylamide) (PNIPA) gels are known to be environment-sensitive gels.[1,2] Upon a slight change of one of the environmental variables, such as temperature,[3,4] solvent composition,[5,6] and hydrostatic pressure,[7−9] PNIPA gels undergo either a swelling or shrinking transition. The environment sensitivity is mainly ascribed to the strong hydrophobicity of the *N*-isopropyl group located on the side chain. At lower temperatures (e.g., less than 32 °C), water molecules around an *N*-isopropyl group are ordered and form an iceberg structure[10] in order to minimize the number of contact with the hydrophobic group. However, this ordered structure is broken by thermal motion of water molecules when temperature is increased above the so-called volume phase transition temperature $T_{\mathrm{C}} \approx 33.6$ °C.[3] This leads to demixing between PNIPA and water. Although this process itself is thermoreversible, cross-links bestow a preparation history to a gel. For example, if a gel is prepared in a poor solvent, the chain conformation in the gel may be more compact than that prepared in a good solvent. Even if the gel is immersed in a good solvent, it still remembers how it was made. Hence, it can be stated that cross-links enable a gel to memorize its structure at preparation. Note that this is due not to a nonequilibrium effect (i.e., kinetic control) but to topological constraints (i.e., cross-linking). Hence, the gels can be in thermodynamic equilibrium with a memorizing capability as discussed by Panyukov and Rabin.[11]

Gels contain two types of concentration fluctuations. One is frozen inhomogeneity, and the other is thermal fluctuation.[12] Particularly, the frozen component in concentration fluctuations introduced by cross-linking has a strong preparation-temperature, T_{prep}, dependence, while the dynamic component in the concentration fluctuations does not have any significant T_{prep} dependence.[13] In the case of PNIPA gels, the higher the T_{prep}, the stronger the frozen inhomogeneities. On the other hand, poly(acrylamide) (PAM), which does not have hydrophobic groups on the side chains, has an opposite T_{prep} dependence compared to that of PNIPA.[14] The difference in the T_{prep} dependence is due to their LCST (lower critical solution temperature) and UCST (upper critical solution temperature) nature respectively for PNIPA and PAM.

Compared to the preparation temperature effects on gel inhomogeneities, pressure effects have been less elucidated. In contrast to the temperature dependence, the pressure dependence is more sophisticated as discussed by Otake et al.[15] for PNIPA solutions and by Kato and co-workers[16] for PNIPA gels. According to Kato, the Flory interaction parameter is a quadratic function of pressure, P ($=P_{\mathrm{obs}}$; the observation pressure), which results in a reentrant swelling−shrinking transition as P is increased. However, preparation pressure P_{prep} dependence of gel structure has never been discussed in the literature to our knowledge. In this paper, we demonstrate that P_{prep} is another key parameter affecting the microscopic structure of gels as well as macroscopic physical properties, such as transparency and swelling/shrinking kinetics.

Experimental Section

Samples. A series of poly(*N*-isopropylacrylamide) (PNIPA) gels were prepared by redox polymerization. Prescribed amounts of NIPA monomer (purchased from ACROS, U.S.A.) and *N*,*N*′-

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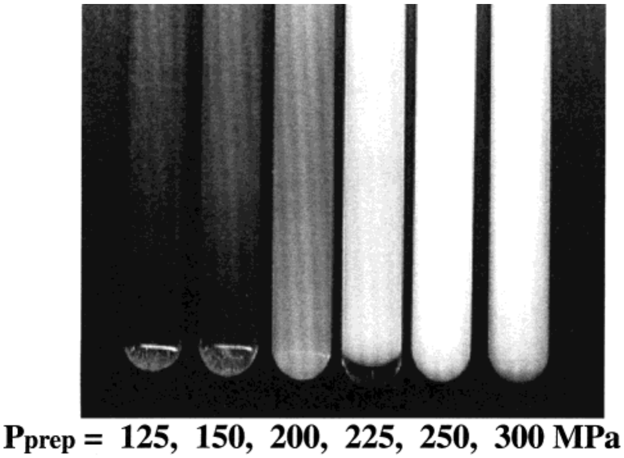

Figure 1. Series of photographs of PNIPA gels prepared at different pressures, i.e., $P_{\mathrm{prep}} = 125$, 150, 200, 225, 250, and 300 MPa.

methylenebis(acrylamide) (BIS; cross-linker, Wako Chemicals) were dissolved in distilled water (total volume 50 mL), whose concentrations were 700 and 8.63 mM, respectively. By adding 1.7 mM of ammonium persulfate (initiator; Wako Chemicals) and 3.0 mM of *N*,*N*,*N*′,*N*′-tetramethylenediamine (accelerator; Wako Chemicals) to the solution, polymerization was initiated. The polymerization was carried out in a 10 mm test tube at room temperature (20 ± 1 °C) under several pressures which were applied by a wet-bag type cold isostatic pressing equipment (Dr. CIP; Kobe Steel Ltd.) for 24 h. The preparation pressure, P_{prep}, was varied from 0.1 to 300 MPa. Samples for kinetics measurements were made in a glass tube with 2.06 mm i.d. The prepared gels were washed with a large amount of distilled water and cut into 10 mm long cylindrical pieces at swelling equilibrium.

Dynamic Light Scattering (DLS). Dynamic light scattering measurements were carried out on an ALV-DLS/SLS5000 (ALV) with a 22 mW He−Ne laser (Uniphase, U.S.A.). All DLS measurements were made on reactor batch samples at 20 °C, and the scattering angle was fixed to be 90°. All of the scattered intensities were normalized with a monitor intensity.

Swelling kinetics Measurement. The sample was immersed in a thermostated chamber filled with distilled water. Temperature-jump experiments were carried out by exchanging the circulating waters whose temperatures were set to two desired temperatures. The time required for temperature jumps was about 1 min. Images of gels were recorded on videotapes by an inverted microscope (TMD300, Nikon) coupled with an image processor (Algas 2000, Hamamatsu Photonics). The swelling ratio, d/d_0, was obtained by measuring the diameter of cylindrical gel, d, where d_0 is the diameter of the gel at preparation ($d_0 = 2.06$ mm).

Results and Discussion

Phase Separation and Memory Effect. Figure 1 shows a series of photographs of PNIPA gels prepared at different pressures, i.e., $P_{\mathrm{prep}} = 125$, 150, 200, 225, 250, and 300 MPa. As shown in the figure, the gels become turbid with increasing P_{prep}. Note that all of these pictures were taken at atmospheric pressure (the observation pressure, $P_{\mathrm{obs}} = 0.1$ MPa). Therefore, this figure indicates that these gels have a memory of the pressures at which they were made. This type of memory effect may be ascribed to the introduction of cross-links during polymerization process.

To examine this conjecture, we compared turbidities of a PNIPA gel and a corresponding PNIPA solution. Figure 2 shows photographs of PNIPA gel ($C_{\mathrm{NIPA}} = 700$ mM, $C_{\mathrm{BIS}} = 8.63$ mM) and PNIPA solution ($C_{\mathrm{NIPA}} = 700$ mM, $C_{\mathrm{BIS}} = 0$ mM). Both were prepared at $P_{\mathrm{prep}} = 250$ MPa. As shown here, the PNIPA solution is transparent. That is, the PNIPA solution does not have memory how it was made. On the other hand, the PNIPA gel is opaque, indicating that the gel remains in a phase-separated state even after releasing the applied pressure. Therefore, it is clear that gels have a capability of memorizing its environment at preparation. It is needless to mention that the memorizing capability is a result of frozen topology, i.e., cross-linking.

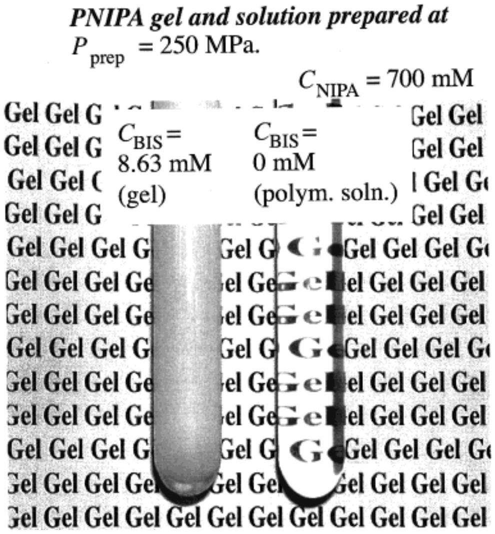

Figure 2. Comparison of photographs of PNIPA gel ($C_{\mathrm{NIPA}} = 700$ mM, $C_{\mathrm{BIS}} = 8.63$ mM) and PNIPA solution ($C_{\mathrm{NIPA}} = 700$ mM, $C_{\mathrm{BIS}} = 0$ mM).

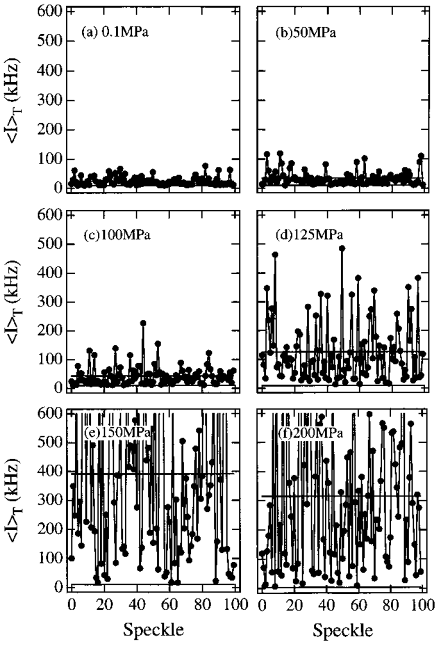

Figure 3. Variations of time-average scattered intensity, $\langle I \rangle_T$, obtained at various sample positions for PNIPA gels prepared at $P_{\mathrm{prep}} = 0.1$, 50, 100, 125, 150, and 200 MPa.

Figure 3 shows variations of time-average scattered intensity, $\langle I \rangle_T$, obtained at various sample positions for PNIPA gels prepared at $P_{\mathrm{prep}} = 0.1$, 50, 100, 125, 150, and 200 MPa. The scattering angle was 90°, and 100 data points were chosen randomly in each sample. The upper horizontal line denotes ensemble average scat-

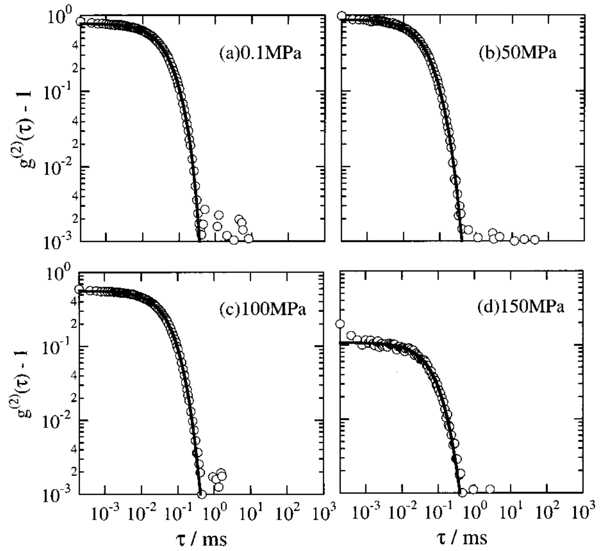

Figure 4. Intensity−time correlation functions (ICFs), $g^{(2)}(\tau)$, for PNIPA gels prepared at $P_{\mathrm{prep}} = 0.1$, 50, 100, and 150 MPa.

tered intensity, $\langle I\rangle_E$, obtained by simply averaging $\langle I\rangle_T$ over 100 data points. The lower horizontal line indicates the contribution of dynamic fluctuations, $\langle I_F\rangle_T$, as will be discussed later. As shown in the figure, $\langle I\rangle_T$ fluctuates with sample positions as are called speckles.[17] The speckles increase with P_{prep}. For $P_{\mathrm{prep}} > 200$ MPa, the gels are no more transparent as shown in Figure 1. Hence, quantitative analyses were limited for gels with $P_{\mathrm{prep}} < 150$ MPa.

Dynamic Light Scattering and Intensity Decomposition. Figure 4 shows the intensity−time correlation functions (ICFs), $g^{(2)}(\tau)$

$$g^{(2)}(\tau) = \beta\sigma_I^{2} \exp(-2D_A q^2 \tau) + 1 \qquad (1)$$

for PNIPA gels prepared at $P_{\mathrm{prep}} = 0.1$, 50, 100, and 150 MPa, where β is the instrumental coherence factor close to unity ($\beta \approx 0.95$), q is the scattering vector, τ is the relaxation time, σ_I^2 is the initial amplitude of ICF, and D_A is the apparent diffusion coefficient. Note that in the case of gels σ_I^2 and D_A vary depending on the sample position, i.e., $0 < \sigma_I^2 < 1$ and $D < D_A < 2D$, where D is the collective diffusion coefficient of the gel.[18] As shown by the solid line in the figure, $g^{(2)}(\tau)$'s were fitted with a single-exponential function given by eq 1. Thus, D_A, and σ_I^2 were evaluated at different 100 sample positions for each sample, from which the intensity component of the dynamic fluctuations was obtained via

$$\sigma_I^{2} = X(2 - X), \quad X \equiv \langle I_F\rangle_T/\langle I\rangle_T \qquad (2)$$

where $\langle I_F\rangle_T$ is the intensity component of dynamic fluctuations. According to the partial heterodyne analysis proposed by Joosten et al.,[19] the following equation is obtained:[18,20]

$$\frac{\langle I\rangle_T}{D_A} = \frac{2}{D}\langle I\rangle_T - \frac{\langle I_F\rangle_T}{D} \qquad (3)$$

Figure 5 shows the plots of $\langle I\rangle_T/D_A$ vs $\langle I\rangle_T$ for PNIPA gels prepared at $P_{\mathrm{prep}} = 0.1$ (atmospheric pressure) to 150 MPa, where K is the horizontal offset introduced to avoid overlap. As shown here, each set of the data points falls on a straight line, suggesting the validity of the partial heterodyne analysis. The width of data range in $\langle I\rangle_T$ indicates a degree of inhomogeneities; i.e., the wider the data range, the more inhomogeneous the gel is. In addition, it is noteworthy that the slope does not seem to depend on P_{prep}.

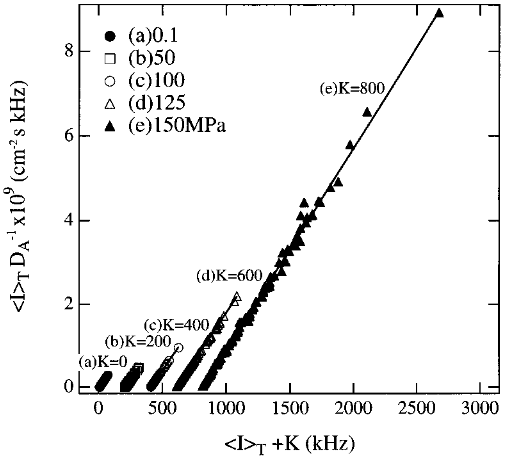

Figure 5. Plots of $\langle I\rangle_T/D_A$ vs $\langle I\rangle_T$ for PNIPA gels prepared at $P_{\mathrm{prep}} = 0.1$ (atmospheric pressure) to 150 MPa.

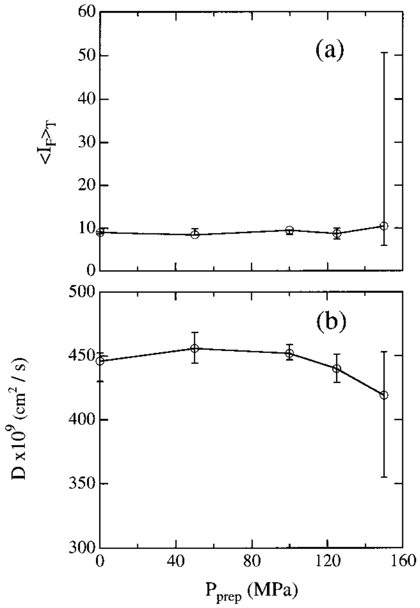

Figure 6. Variations of (a) $\langle I_F\rangle_T$ and (b) D with P_{prep}.

Figure 6 shows the variations of (a) $\langle I_F\rangle_T$ and (b) D, which are evaluated from the intercept and the slope in Figure 5, respectively. It should be stressed here that both $\langle I_F\rangle_T$ and D are independent of P_{prep}. These results are reasonable since both are dynamic properties and should not depend on P_{prep}. A similar phenomenon was observed in the preparation temperature dependence of PNIPA gels.[13,14] The evaluated value of D itself is 4.4×10^{-7} cm^2/s and is very close to a PNIPA gels with the same NIPA and BIS concentrations prepared at the atmospheric pressure, $P_{\mathrm{prep}} = 0.1$ MPa.[20] Hence, it is concluded that the dynamic properties are independent of P_{prep}. Now we discuss the P_{prep} dependence of the scattered intensity.

Divergence of Scattered Intensity and Reentrant Swelling Behavior. As discussed above, the scattered intensity from a gel can be decomposed to the dynamic, $\langle I_F\rangle_T$, and frozen components, $\langle I_C\rangle_E \equiv \langle I\rangle_E - \langle I_F\rangle_T$. The dynamic component of the scattered intensity

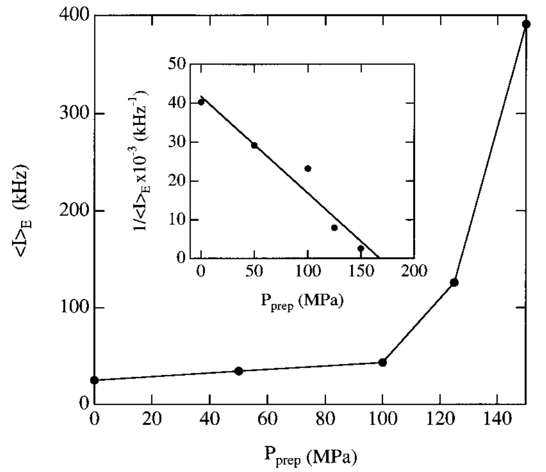

Figure 7. P_{prep} dependence of the ensemble average scattered intensity, $\langle I\rangle_{\mathrm{E}}$.

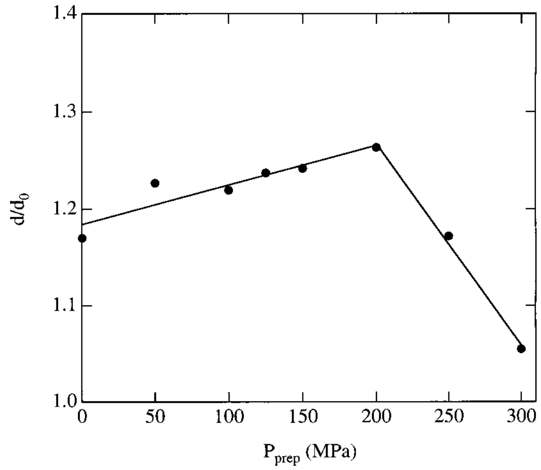

Figure 8. Degree of swelling, d/d_0, as a function of P_{prep} observed at 20 °C.

is related to the longitudinal osmotic modulus, M,

$$\langle I_{\mathrm{F}}\rangle_{\mathrm{T}} \sim \phi^2\left(\frac{\partial \Pi}{\partial \phi}\right)^{-1} = \frac{kT\phi^2}{M} \tag{4}$$

where ϕ is the volume fraction of the gel, Π is the osmotic pressure, k is the Boltzmann constant, and T is the absolute temperature. Since M diminishes at the phase separation point, $\langle I_{\mathrm{F}}\rangle_{\mathrm{T}}$ is expected to diverge as

$$\langle I_{\mathrm{F}}\rangle_{\mathrm{T}} \approx \epsilon^{-\gamma} \tag{5}$$

where γ is the critical exponent for the susceptibility (scattered intensity) and ϵ is the relative distance from the critical point, e.g., $\epsilon = |T - T_{\mathrm{C}}|/T_{\mathrm{C}}$ and $\epsilon = |P - P_{\mathrm{C}}|/P_{\mathrm{C}}$. Regarding the observation temperature dependence, a divergence of the scattered intensity was observed by Tanaka et al.[21] and Shibayama et al.[18] Note that the scattered intensity discussed in those papers included both dynamic and frozen components, i.e., $I \equiv \langle I\rangle_{\mathrm{E}}$. A small-angle neutron scattering study suggested that only the dynamic component diverged at the transition temperature.[22] However, it is now recognized that both dynamic fluctuations and frozen inhomogeneities diverge at the transition point.[23] This is due to the fact that both frozen inhomogeneities and dynamic fluctuations are strongly coupled with each other as predicted by Panyukov and Rabin[11] and as experimentally verified by Shibayama et al.[24]

In the case of the pressure dependence studied in this paper, data on the observation pressure dependence of the scattered intensity are not available at this stage. Hence, by knowing the fact that gels have a capability of memorizing the state of its preparation, the preparation pressure dependence of the scattered intensity was analyzed. Figure 7 shows P_{prep} dependence of the ensemble average scattered intensity, $\langle I\rangle_{\mathrm{E}}$. As shown in the figure, $\langle I\rangle_{\mathrm{E}}$ increases steeply for $P_{\mathrm{prep}} > 100$ MPa. The inset shows a plot of $1/\langle I\rangle_{\mathrm{E}}$ vs P_{prep}, which indicates a linear relationship between $1/\langle I\rangle_{\mathrm{E}}$ vs P_{prep} and $\langle I\rangle_{\mathrm{E}}$ diverges at $P_{\mathrm{prep}} = P_{\mathrm{prep,C}} = 168$ MPa. More rigorously speaking, it was found that the observed data are well fitted by

$$\langle I\rangle_{\mathrm{E}} \approx |P_{\mathrm{prep,C}} - P_{\mathrm{prep}}|^{-\gamma} \tag{6}$$

with $P_{\mathrm{prep,C}} = 168$ MPa and $\gamma \approx 1.3$. This fact may indicate that a phase separation in polymeric gels can be described by a three-dimensional Ising model.[25] The critical preparation pressure, $P_{\mathrm{prep,C}} \approx 168$ MPa, agrees with that reported by Otake, i.e., $P_{\mathrm{obs,C}} \approx 170$ MPa at 20 °C for PNIPA solutions (see Figure 2 of ref 15). Here, we assume that the critical observation pressure $P_{\mathrm{obs,C}}$ is the same as that at preparation $P_{\mathrm{prep,C}}$ for polymer solutions, and a gel has a memory at which the gel is made. It is needless to mention that the observation pressure dependence of the scattered intensity has to be investigated in order to confirm the class of this critical phenomenon. This will be an issue of the forthcoming paper.

It is of interest to relate the inhomogeneities with the degree of swelling. Kato reported that a shrunken PNIPA gel underwent a swelling transition by increasing the observation pressure P_{obs}, followed by a gradual shrinking by further increase in P_{obs}.[8] This behavior was explained by a quadratic dependence of the Flory interaction parameter, χ, on P, i.e.,

$$\chi(T,P) = \chi_0(T) + \chi_1(T)P + \chi_2(T)P^2 \tag{7}$$

where $\chi_1(T) < 0$ and $\chi_2(T) > 0$. This unique solvation of PNIPA in water is ascribed to a structure formation of water molecules surrounding the hydrophobic group, i.e., N-isopropyl group. The reentrant swelling behavior indicates that there are two solvation mechanisms depending on P. If the solvation accompanies an iceberg formation of water molecules, a positive volume change in water, $\Delta V_{\mathrm{w}} > 0$, is expected. Therefore, the shrinking behavior at elevated pressure is accounted for by desolvation, i.e., destructuring of the iceberg structure, $(\partial \Delta V_{\mathrm{w}}/\partial P)_{\mathrm{T}} < 0$. The negative variation of χ in the intermediate P region, on the other hand, must be interpreted with a negative volume change of mixing, $\Delta V_{\mathrm{m}} < 0$ between NIPA segments and water molecules and $|\Delta V_{\mathrm{m}}| > |\Delta V_{\mathrm{w}}|$. As a matter of fact, Kato reported that $\Delta V_{\mathrm{m}} = -28$ mL/mol for PNIPA.[26] Here, ΔV_{m} is assumed to include the contribution of ΔV_{w}. The solvation of proteins also accompanies by a negative volume change of the order of $-(1-7) \times 10$ mL/mol.[27]

In Figure 8 is shown the degree of swelling, d/d_0, as a function of P_{prep} observed at 20 °C. Here, d/d_0 is the linear swelling ratio, which is an increasing function of P_{prep} for $P_{\mathrm{prep}} \leq 200$ MPa. However, d/d_0 decreases with P_{prep} for $P_{\mathrm{prep}} > 200$ MPa. The increase in d/d_0 with P_{prep} for $P_{\mathrm{prep}} < 200$ MPa, however, does not mean a decrease in χ with P_{prep}. Because the degree of inhomogeneities, i.e., $\langle I\rangle_E$, increases with P_{prep}, χ has to be an increasing function of P_{prep}. In this case, a swelling is expected by immersing in water at $P_{obs} = 0.1$ MPa because of a lowering in χ from $\chi(P_{prep})$ to $\chi(P_{obs})$. A similar swelling behavior is observed in the preparation temperature T_{prep} dependence.[28] In this case, χ is an increasing function of T, and $\Delta\chi \equiv \chi(T_{obs}) - \chi(T_{prep})$ is always negative. This results in an increase in swelling with increasing T_{prep} because a polymer chain has a tendency to expand by immersion in a solvent with a less value of χ. Therefore, in both cases, the T_{prep} (P_{prep}) dependence in the swelling behavior is opposite to the T_{obs} (P_{obs}) dependence.

The swelling behavior for $P_{prep} > 200$ MPa has a different story. For $P_{prep} > 200$ MPa, a phase separation takes place, and the gel consists of globules weakly connected with polymer chains. In the globule, polymer chains are tightly cross-linked. Such a gel does not have swelling capability. This is why the swelling degree decreases with P_{prep} for $P_{prep} > P_C$. An analogy is again found in PNIPA gels prepared at a temperature above the phase separation temperature.[29] Figure 9 shows the swelling curves for PNIPA gels prepared at $P_{prep} = 0.1$ and 250 MPa. The dashed and solid lines denote the results of curve fitting with the modified Flory−Rehner equation,[30]

$$\frac{\Pi}{RT} = -\frac{1}{V_s}[\phi + \ln(1-\phi) + \chi\phi^2] + \nu\frac{\phi_0}{\phi_{ref}}\left[\frac{1}{2}\left(\frac{\phi}{\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3}\right] \quad (8)$$

where R is the gas constant, V_s is the molar volume of the solvent, and ν is the number of effective polymer chains per unit volume. ϕ and ϕ_0 are the polymer volume fractions at swelling equilibrium and at the preparation, respectively. According to the modified Flory−Rehner equation,[30] the number density of cross-links is assume to be larger by the factor of ϕ_0/ϕ_{ref} than that calculated by stoichiometry due to entanglements, where ϕ_{ref} is the reference volume fraction. Here, ϕ_{ref} is regarded as the lowest polymer volume fraction for gelation, i.e., for infinite network formation. The thermodynamic properties, such as the osmotic pressure, can be assumed to be independent of P_{prep}. Hence, we set $\chi = \chi_P \equiv \chi(P_{prep} = 0.1\ \text{MPa})$. Here, the subscript P means that the (observation) pressure is fixed (cf. eq 7). It is known that the interaction parameter, χ_P, is concentration-dependent, having the following form[31]

$$\chi_P \equiv \chi(P{=}0.1\ \text{MPa}) = \chi_{P,1} + \phi\chi_{P,2} \quad (9)$$

where

$$\chi_{P,1} = (\Delta H - T\Delta S)/kT \quad (10)$$

and $\chi_{P,2}$ is a constant. ΔH and ΔS are the enthalpy and entropy per monomeric unit of the network related to the volume phase transition. The results of curve fitting are listed in Table 1. According to Table 1, it is clear that the absolute values of both ΔH and ΔS for the PNIPA gels prepared at $P_{prep} = 250$ MPa is smaller than those prepared at $P_{prep} = 0.1$ MPa. On the other hand, the measure of the degree of entanglements, ϕ_0/ϕ_{ref}, increases with P_{prep}. The relationship between inhomogeneities and the calorimetric parameters, i.e., ΔH and ΔS, was discussed for quenched and annealed PNIPA gels.[32] It was revealed that the absolute values of both ΔH and ΔS decrease by quenching. Therefore, these experimental results obtained in this work strongly indicate that the PNIPA gels prepared at $P_{prep} = 250$ MPa are more inhomogeneous than the gel prepared at $P_{prep} = 0.1$ MPa.

Table 1. Comparison of the Thermal Parameters for PNIPA Gels Prepared at Different Preparation Pressures

	$P_{prep} = 0.1$ MPa	$P_{prep} = 250$ MPa
ΔH (J)	-1.94×10^{-20}	-1.34×10^{-20}
ΔS (J)	-6.93×10^{-23}	-5.00×10^{-23}
ϕ_0/ϕ_{ref}	2.89	3.49
$\chi_{P,2}$	0.666	0.510

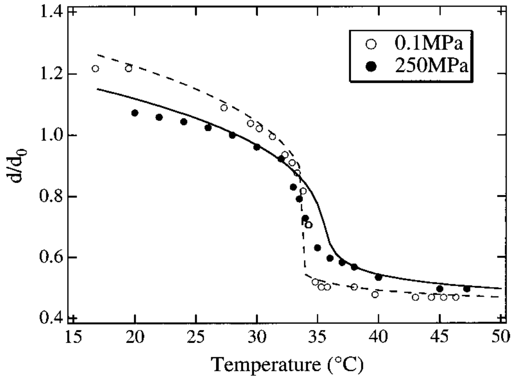

Figure 9. Temperature dependence of the degree of swelling, d/d_0, for PNIPA gels prepared at $P_{prep} = 0.1$ and 250 MPa. The dashed and solid lines denote the results of curve fitting for PNIPA gels prepared at $P_{prep} = 0.1$ and 250 MPa, respectively.

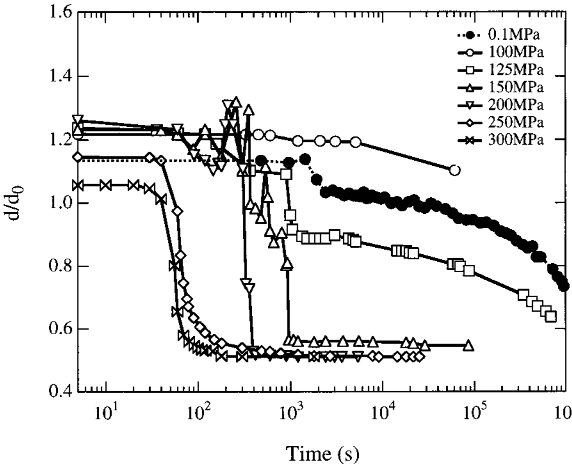

Figure 10. Variation of swelling degree, d/d_0, for PNIPA gels prepared at different P_{prep}'s as a function of time after temperature jump from 20 to 45 °C.

Shrinking Kinetics. To study the dynamics of structure change, pressure jump is more effective than temperature jump as demonstrated by Kojima et al.[33] However, in the case of gels with an ordinary size such as millimeters, the characterstic time of the swelling or shrinking kinetics is on the order of a few hundred seconds or more; a temperature jump is fast enough. In addition, since PNIPA undergoes volume phase transition upon temperature change, we employed a T-jump experiment in order to study the effect of preparation pressure on structure. Figure 10 shows the variation of swelling degree, d/d_0, for PNIPA gels prepared at different P_{prep}'s as a function of time after temperature jump from 20 to 45 °C. Interestingly, the shrinking behaviors can be classified to three categories. (1) The

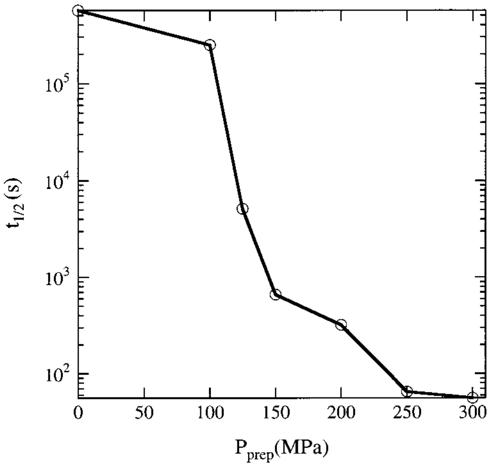

Figure 11. Variation of the half-shrinking time, $t_{1/2}$, as a function of P_{prep}.

shrinking process of gels prepared at $P_{prep} \leq 100$ MPa is very slow. Just after temperature jump, these gels become opaque, indicating occurrence of phase separation. The phase separation prevents the gel from shrinking. This type of shrinking process was observed for PNIPA gels prepared with relatively high C_{NIPA} and C_{BIS}, as reported elsewhere.[34] (2) On the other hand, the gel prepared at $P_{prep} = 125$ MPa shrank by exposing bubbles until $d/d_0 = 0.9$ at $t \approx 10^3$ s, followed by a very slow shrinking. Gels with $150 \leq P_{prep} \leq 200$ MPa shrank with bubbling, which led to an oscillation in d/d_0. This is again similar to the gels with low concentrations of C_{NIPA} and C_{BIS}.[34] (3) A very rapid shrinking without accompanying bubble formation was observed for gels with $P_{prep} \geq 250$ MPa. This observation also supports that the gels prepared at $P_{prep} \geq 200$ MPa are phase-separated and porous capable of rapid shrinking.

In the case of shrinking or swelling without accompanying phase separation, the change of the gel diameter can be described by the Tanaka–Fillmore equation,[35]

$$\frac{|d(t) - d(\infty)|}{|d(0) - d(\infty)|} \approx \frac{6}{\pi^2} \exp(-t/\alpha) \qquad (11)$$

where α is the characteristic time for shrinking. This means that the relative swelling ratio, i.e., the left-hand side of eq 11, decreases exponentially. However, such a behavior does not occur if a phase separation is involved as reported elsewhere.[34] Hence, we defined another characteristic time to describe gel shrinking, the half-shrinking time, $t_{1/2}$, as follows:

$$\frac{|d(t_{1/2}) - d(\infty)|}{|d(0) - d(\infty)|} = \frac{|d(t_{1/2})/d_0 - d(\infty)/d_0|}{|d(0)/d_0 - d(\infty)/d_0|} = \frac{1}{2} \qquad (12)$$

Figure 11 shows $t_{1/2}$ as a function of P_{prep}. As shown in this figure, the characteristic shrinking time, $t_{1/2}$, drastically decreases with P_{prep}. This means that the shrinking rate becomes very rapid by the factor of 10^4 as the preparation pressure is increased to 200 MPa or higher. It is needless to mention that this rapid shrinking is related to the phase separation of the gel appearing for $P_{prep} > 168$ MPa. It is known that a rapid shrinking in gels can be attained in (1) a gel having a large fraction of dangling chains[36,37] or a water pathway in the gel network or in (2) a gel prepared at certain conditions, such as at a low cross-linker concentration or a low monomer concentration.[34] It is disclosed here that the third category of gels undergoing a rapid shrinking is a phase-separated (opaque) gel corresponding to PNIPA gels prepared at $P_{prep} \geq 200$ MPa.

Conclusion

The preparation pressure dependence of PNIPA gels has been investigated by swelling and static-and-dynamic light scattering experiments. Static light scattering disclosed that the scattered intensity of PNIPA gels prepared at different P_{prep}'s diverged at $P_{prep,C} =$ 168 MPa with the critical exponent being 1.3, indicating that the system can be described by a three-dimensional Ising model. The swelling behavior at 20 °C is strongly coupled with the phase behavior. For $P_{prep} \leq 200$ MPa, which is close to $P_{prep,C}$, the swelling degree increased with P_{prep}, but decreased with P_{prep} for $P_{prep} > 200$ MPa. The ensemble average scattered intensity $\langle I \rangle_E$, a measure of frozen inhomogeneities, was an increasing function of P_{prep} for PNIPA gels. Such P_{prep} dependence was not observed in the corresponding PNIPA solutions. Therefore, it was concluded that cross-links play a significant role in memorizing the frozen inhomogeneities at preparation. Dynamic properties of PNIPA gels, on the other hand, did not depend on P_{prep} at least for $P_{prep} \leq 168$ MPa. It was also clarified that the frozen inhomogeneities affect the kinetics of gel shrinking. Phase-separated gels, i.e., opaque gels (prepared at 250 MPa), for example, have an extremely fast shrinking rate by a factor of 10^4 compared to transparent gel prepared at atmospheric pressure. These experimental evidences suggest that the structure and properties of gels prepared at high pressure is very different from those prepared at the atmospheric pressure, and cross-links maintain the gel structure at preparation even though pressure is released.

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