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Polymer 43 (2002) 3101–3107

polymer

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Dependence of shrinking kinetics of poly(*N*-isopropylacrylamide) gels on preparation temperature

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Received 17 October 2001; received in revised form 18 December 2001; accepted 22 January 2002

Abstract

Preparation temperature dependence of equilibrium swelling degree and shrinking kinetics of poly(*N*-isopropylacrylamide) gel has been investigated by optical microscopic measurements. The degree of swelling, d/d_0, at 20 °C was found to be strongly dependent on the preparation temperature, T_{prep}, where d and d_0 are the diameter of gel during observation and preparation, respectively. The value of d/d_0 was about 1.2 for $T_{\text{prep}} = 20$ °C, but steeply increased by approaching the phase separation temperature ≈ 32.0 °C. Above 32.0 °C, d/d_0 decreases stepwise to 1.46. This upturn in d/d_0 was correlated with spatial inhomogeneities in gels. That is, the gel became opaque by increasing T_{prep}. Though the shrinking half-time, $t_{1/2}$, of gel was on the order of 500 min for $T_{\text{prep}} \leq 20$ °C, $t_{1/2}$ decreased to 2 min for $T_{\text{prep}} \geq 26$ °C. Hence, a rapid shrinking was attained by simply increasing T_{prep}. The physical implication of this rapid shrinking in gels was discussed in conjunction with the gel inhomogeneities and a thermodynamic theory of swelling equilibrium.

Keywords: Poly(*N*-isopropylacrylamide) gel; Inhomogeneities; Shrinking kinetics

1. Introduction

Water-soluble polymers carrying hydrophobic side groups often exhibit a strong temperature dependence. Those polymers undergo phase demixing in water by increasing temperature. In other words, these polymers have a lower critical solution temperature (LCST). One of the most typical examples is poly(*N*-isopropylacrylamide) (poly-NIPA) [1]. Hirokawa and Tanaka made a hydrogel from NIPA and found that the NIPA gels underwent a discrete volume transition at 33.8 °C from swollen to shrunken state [2]. This study triggered a numerous number of investigations on NIPA gels in order not only to understand the mechanism of volume phase transition, but also to develop functional materials, such as drug delivery systems, sensor, and actuators [3].

From the viewpoint of application, the rate of shrinking is a crucial issue. Since shrinking and swelling of a gel are diffusion-limited process, the rate is governed by diffusion of water (or solvent) through a network of polymer and is inversely proportional to the square of the characteristic size of the gel [4,5]. Hence, it has been believed that a down-sizing is the only way to increase the response rate of a gel. However, many investigators attained rapid shrinking by modifying methods of gel preparation. Kabra and Gehrke prepared a rapid-responsive NIPA gels by two-step polymerization [6]. The first 9 min of polymerization was conducted at 22 °C, much lower than its LCST, followed by second-stage polymerization at 37.9 °C for the next 24 h. The obtained gels were opaque and porous. The rate of shrinking was shortened by 3000 times compared with homogeneous NIPA gels prepared with the same composition at 22 °C. Yoshida et al. [7] prepared graft-copolymer gels and demonstrated that presence of free-end chains (i.e. graft chains) led to a rapid swelling. Kishi et al. reported that porous NIPA gels were formed by γ-ray irradiation and the gels exhibited a rapid shrinking by immersing in a hot water, e.g. 50 °C [8]. Zhang and Zhuo obtained a rapid shrinking NIPA gels by cold-treatment at −11 to −40 °C, followed by thawing at 24 °C [9]. Shibayama and Nagai studied cross-liker concentration, C_{BIS}, and NIPA concentration, C_{NIPA}, dependence of shrinking rate and reported that a rapid shrinking could be attained by lowering either C_{BIS} or C_{NIPA}, where BIS is the abbreviation of *N*,*N*′-methylenebisacrylamide (cross-linker) [10]. Okajima et al. reported that a rapid shrinking of NIPA gels could be achieved by controlling C_{BIS} lower than 3.45 mM or higher than

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PII: S0032-3861(02)00089-7

47.5 mM, while keeping C_{NIPA} being 700 mM [11]. These examples, particularly the last example, indicate that two types of inhomogeneities, such as topological inhomogeneities lacking of network structure and phase-separated structure consisting of polymer-rich domains and polymer-poor matrix, lead to a rapid shrinking of a gel.

The inhomogeneities in gels are an attractive problem. Since a gel is a frozen system, at least topologically, the inhomogeneities strongly depend on the methods and ways of gel preparation. Temperature of gel preparation, T_{prep}, governs the physical properties of the resultant gel. The inhomogeneities, i.e. frozen-concentration fluctuations, are strong functions of T_{prep} [12,13]. Hirokawa et al. visualized inhomogeneities in NIPA gels prepared at different T_{prep}s by laser scanning confocal microscopy [14]. In this study, we focus on the shrinking kinetics of NIPA gels prepared at various T_{prep}s by taking account of the inhomogeneities in gels. A further investigation of inhomogeneities in NIPA gels with small-angle neutron scattering and dynamic light scattering will be reported elsewhere [15].

2. Experimental section

2.1. Samples

NIPA, kindly supplied from Kohjin Co. Ltd, Tokyo, was dissolved in toluene, followed by recrystallization in petroleum ether. The purified NIPA (690 mM) was dissolved in distilled water and chilled in refrigerator. Then, 8.62 mM of N,N'-methylenebisacrylamide (BIS), and 1.75 mM of ammonium persulfate (APS; initiator) were added to the solution. The temperature of the solution was adjusted to the desired temperatures, T_{prep} (5–35 °C). The polymerization was accelerated by adding and 8 mM N,N,N',N'-tetramethylethylenediamine (TEMED).

2.2. Swelling degree measurement

The sample was immersed in a thermostated chamber filled with distilled water. The degree of swelling was measured by monitoring the diameter of the cylindrical gel, d, via an inverted microscope (TMD300, Nikon, Japan) coupled with an image processor (Algas 2000, Hamamatsu Photonics, Japan). The temperature of the chamber was increased either stepwise with $\Delta T \leq 3$ °C by ensuring thermal equilibrium (quasi-static heating) or by temperature jump (T-jump) with $\Delta T \geq 20$ °C. The temperature step is defined by $\Delta T = T_{n+1} - T_n$, where T_{n+1} and T_n are the temperatures of the gel at the $(n+1)$th and nth steps, respectively. In the case of quasi-static heating, d was measured after an interval of 30 min, whenever the temperature was increased. Then, d was measured again after another interval of 30 min. If the difference in the values of d between two successive measurements was less than 5 μm, temperature was increased again and the same procedure was repeated. By this way, the quasi-static experiment on d was carried out. On the other hand, T-jump was carried out by switching the route of circulating water thermostated at two desired temperatures. The time required for a T-jump was about 1 min.

3. Results and discussion

3.1. Equilibrium swelling ratio

Fig. 1 shows d/d_0 at observation temperature, $T_{\mathrm{obs}} = 20$ °C, as a function of preparation temperature, T_{prep}. For $T_{\mathrm{prep}} \leq 23$ °C, d/d_0 remained rather constant at 1.2. This is due to the strong temperature dependence of the interaction parameter χ in the case of hydrophobically associated system, such as NIPA gels studied here. The χ is a weak function of temperature in the temperature region far below LCST, but it increases abruptly by approaching LCST. Hence, it is reasonable that gels prepared at these temperatures also have a similar tendency in their swelling behavior. However, d/d_0 steeply increased with d/d_0 for $T_{\mathrm{prep}} \geq 23$ °C, and reached a maximum value of 1.65 at 31.5 °C. Above 31.5 °C, d/d_0 decreased stepwise to 1.46. For the sake of discussion, we classified the swelling behavior of the PNIPA gel to four regimes depending on the values of d/d_0, i.e. I ($T_{\mathrm{prep}} \leq 23.0$ °C), II (23.0 °C < $T_{\mathrm{prep}} \leq 28.5$ °C), III ($T_{\mathrm{prep}} \approx 31.5$ °C), and IV ($T_{\mathrm{prep}} \geq 32.0$ °C). In Fig. 1, T_{prep} dependence of ensemble average scattered intensity $\langle I \rangle_{\mathrm{E}}$ at scattering angle of 90° is also plotted for the same systems reported elsewhere [12]. $\langle I \rangle_{\mathrm{E}}$ is a measure of spatial inhomogeneities. As shown in this figure, the two curves are strongly correlated, meaning that the higher the inhomogeneities, the larger is the d/d_0 for

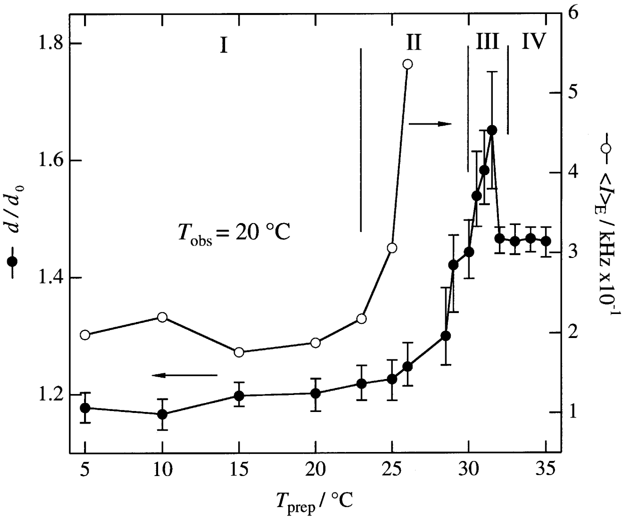

Fig. 1. T_{prep} dependence of the linear swelling ratio, d/d_0, of NIPA gels at observation temperature, $T_{\mathrm{obs}} = 20$ °C. The T_{prep} dependence was classified to four regimes I–IV depending on the values of d/d_0, regimes I ($T_{\mathrm{prep}} \geq 23.0$ °C), II (23.0 °C < $T_{\mathrm{prep}} \leq 28.5$ °C), III ($T_{\mathrm{prep}} \approx 31.5$ °C), and IV (31.5 °C < T_{prep}). The variation of the ensemble average scattered intensity, $\langle I \rangle_{\mathrm{E}}$, is also plotted as a function of T_{prep}.

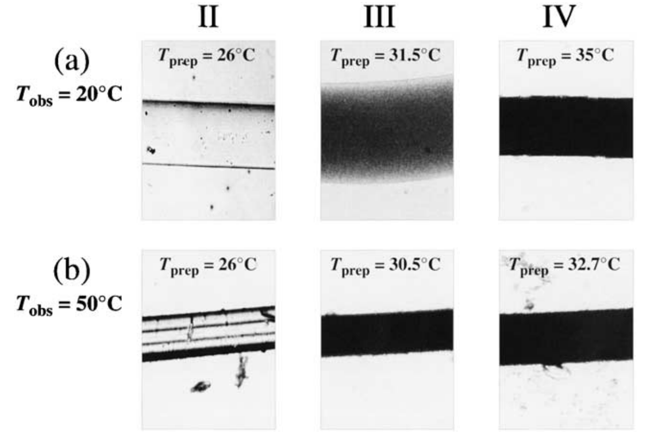

Fig. 2. Photographs of NIPA gels prepared at different T_{prep}s in swollen state (upper) at $T_{obs} = 20$ °C and those in shrunken state $T_{obs} = 50$ °C (lower). The gel with $T_{prep} = 20$ °C is transparent at both swollen and shrunken states, indicating that the gel is rather homogeneous at least in the spatial order of the wavelength of visible light. On the other hand, the gels prepared at 31.5 and 35 °C were opaque. This means that these gels are inherently inhomogeneous, i.e. phase separated.

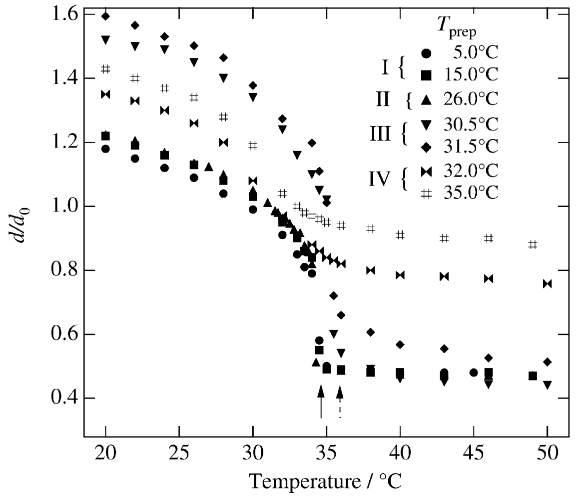

Fig. 3. Equilibrium swelling degrees, d/d_0, of NIPA gels prepared at various T_{prep}s as a function of temperature ($= T_{obs}$). The arrows indicate the temperature of volume phase transition, T_{tr}. Note that the gels prepared at $T_{prep} = 32.0$ and 35.0 °C (regime IV) underwent a continuous transition.

$T_{prep} \leq 25$ °C. Note that light scattering measurement to obtain $\langle I \rangle_E$ was not possible for $T_{prep} > 26$ °C, because $\langle I \rangle_E$ exceeded the detection limit of the scattered light intensity. This results from increasing inhomogeneities by approaching LCST. The inhomogeneities increase by approaching LCST and a phase separation occurs at LCST.

In Fig. 2(a), photographs of the PNIPA gels in these regimes are shown. In regime II, the gel was transparent. The gel in regime III was hazy. The gels in regime IV, on the other hand, were opaque. Note that the gel was elastic in regime I, but became viscoelastic in regime II and III, and even sticky in regime IV. Fig. 2(b) shows the optical photographs of the gels classified to regimes II–IV in the shrunken state. The gel in regime I was transparent, indicating that the gel was more or less homogeneous. However, those in II–IV were opaque. The change in optical and mechanical properties suggests that the gels prepared at high temperatures were inhomogeneous.

Fig. 3 shows the variations of equilibrium swelling ratio, d/d_0, for NIPA gels prepared at different T_{prep}s. The gels, classified to I ($T_{prep} = 5$, 15 °C) and II ($T_{prep} = 26.0$ °C), showed a discontinuous volume transition at the transition temperature, $T_{tr} \approx 34.5$ °C from swollen to shrunken state as indicated with an arrow. The gels in regime III ($T_{prep} = 30.5$, 31.5 °C) exhibited a similar behavior to the gels in I and II, but the transition temperature was higher by ca. 1 °C as indicated with dashed arrow. The swelling ratio of the gels in regime IV ($T_{prep} = 32.0$, 35.0 °C) was lower at $T < T_{tr}$ than those of regime III and underwent a continuous transition. In addition, the value of d/d_0 at $T > T_{tr}$ was much larger than those in I–III. It should be noted here that a very small temperature change, i.e. 0.5 °C, was necessary to change the swelling properties of the gel from regime III to IV. It is noteworthy to mention that the gels in regime I and II were thermoreversible with respect to the swelling ratio, whereas that in regime III and IV did not go back to the original value of d/d_0, but reached a lower value by lowering temperature to 20 °C as shown in Fig. 4.

3.2. Kinetics of shrinking

Shrinking kinetics experiments were carried out for NIPA gels prepared at various T_{prep}s by temperature jump from 20 to 45 °C. Fig. 5 shows optical photographs for gels in regime I–IV undergoing shrinking transition. As shown in the figure, the shapes of gels during shrinking process greatly depend on T_{prep}. The gel prepared at 20 °C (regime I) was transparent after 2 min of T-jump and the size did not change so much in 2 min. Characteristic bubble formation took place for the gel with $T_{prep} = 26.0$ °C (regime II), which is a similar phenomenon observed in NIPA gels with lower C_{BIS} ($\leq$4 mM) or C_{NIPA} ($\leq$400 mM), or in the case with higher destination temperature of T-jump [10]. By further increasing T_{prep} (regime III), a quick shrinking leads to a collapse of gel with an irregular shape. The gel with $T_{prep} = 31.5$ °C underwent an opaque transition accompanied by transformation to an irregular shape. The category

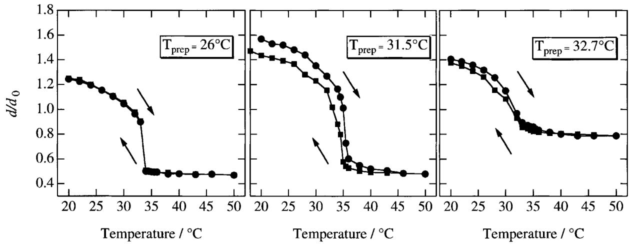

Fig. 4. Variation of d/d_0, of NIPA gels prepared at various T_{prep}s during heating and cooling processes. A hysteresis loop appeared for the gels in regime III ($T_{prep} = 31.5$ °C) and regime IV (32.7 °C).

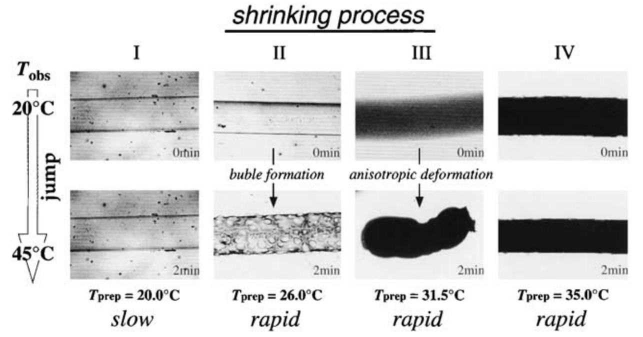

Fig. 5. Photographs of NIPA gels before and 2 min after T-jump from 20 to 45 °C. Characteristic bubble formation was exclusively observed for the gel in regime (II). In regime III, the shape of gel was highly deformed at the beginning of T-jump. On the other hand, the gel in regime IV kept its shape and only the diameter decreased in this time range. The shrinking behavior is qualitatively given by 'slow' or 'rapid'.

IV is characterized by isotropic shrinking by keeping the original shape. In regime IV, the gel was inherently opaque. In other words, the gel was phase separated even in the swollen state at 20 °C, which is also shown in Fig. 2(a) and (b). This phase-separate structure led to a rapid shrinking. Now, we discuss the kinetics of shrinking more quantitatively.

Fig. 6 shows the variation of d/d_0 after T-jump as a function of time. For gels in regime I ($T_{\mathrm{prep}} = 5.0$ and 20.0 °C) exhibited a slow shrinking, whereas the gels in II (25.0–28.5 °C), III (31.5 °C), and IV (35.0 °C) quickly shrank to the shrunken state. The rate of shrinking was characterized by the shrinking half-time, $t_{1/2}$, defined by [16]

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

Fig. 7 shows $t_{1/2}$ as a function of T_{prep}. As shown in this figure, the characteristic shrinking time, $t_{1/2}$, is very slow and is on the order of 10^2 min for $T_{\mathrm{prep}} < 23$ °C. This is due to that the shrinking kinetics is controlled by collective diffusion of polymer network as extensively discussed by Tanaka and Fillmore [4]. However, for $T_{\mathrm{prep}} \geq 25$ °C, $t_{1/2}$, drastically decreases for which is consistent with the anomalous change of $\langle I \rangle_{\mathrm{E}}$ with T_{prep} shown in Fig. 1. It is rather surprising that the rate of shrinking was accelerated by more than 300 times. A similar rapid shrinking behavior was observed for gels prepared with lower C_{NIPA}s and/or a lower C_{BIS}s as reported elsewhere [10]. In the case of this study, the origin of rapid shrinking is clearly ascribed to gel inhomogeneities by Fig. 5. This behavior is similar to the preparation pressure dependence of the shrinking kinetics as reported by Nakamoto et al. [17]. However, in the case of gels with lower BIS or NIPA concentrations, the origin of rapid shrinking seems to be different from those of gels prepared at higher temperatures, since the gels were transparent in the former case. It was conjectured that the topological inhomogeneities, or topological incompleteness, such as dangling chains, led to rapid shrinking. This speculation was supported by the reports by Yoshida et al. [7], who prepared PNIPA gels having a large number of graft chains. This type of gels contains a large portion of dangling chains and can be called a gel with topological incompleteness. The presence of this type of inhomogeneites is believed to be the origin of rapid shrinking.

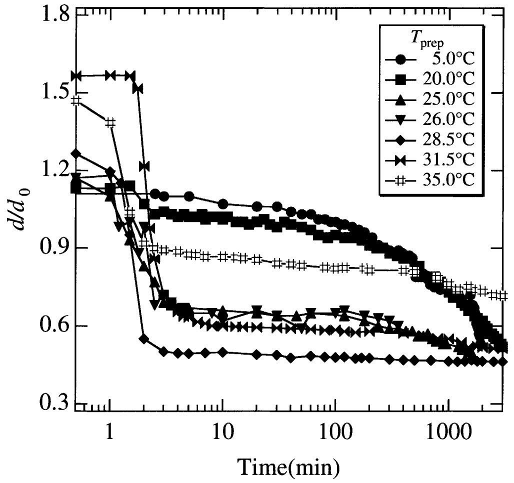

Fig. 6. Variation of d/d_0, of NIPA gels prepared at various T_{prep}s after T-jump from 20 to 45 °C.

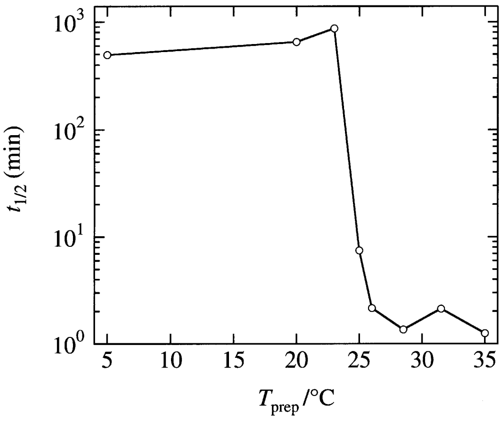

Fig. 7. T_{prep} dependence of the shrinking half-time, $t_{1/2}$.

On the basis of the experimental results disclosed earlier, we depicted the gel structures schematically in Fig. 8. When a NIPA gel is formed at a low temperature, e.g. at 20 °C or lower, the network structure is homogeneous. The gel can swell homogeneously by immersing in deionized water at the observation temperature $T_{\mathrm{obs}} = 20$ °C. However, gels prepared at higher temperatures, the network structure becomes inhomogeneous due to the LCST nature of poly-NIPA aqueous systems, resulting in a formation of polymer-rich domains or aggregates in the matrix of loosely tied network. Those domains are connected with 'tie-chains' as shown in the figure (regimes II and III) and form a loose network. It is expected that these domains are hard to swell, because of high polymer density and cross-linking, whereas the matrix part is capable of swelling as discussed

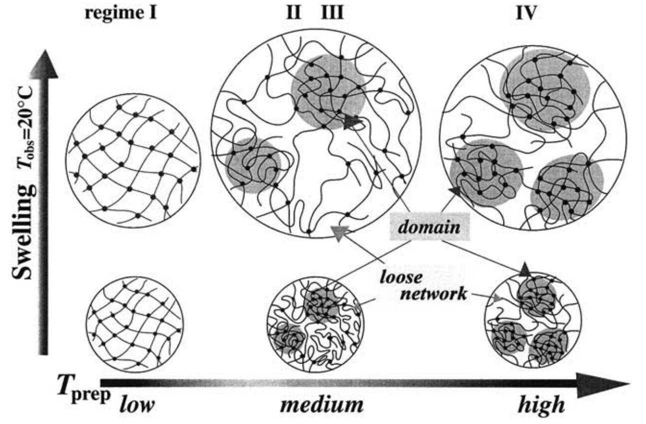

Fig. 8. Schematic models of NIPA gels prepared at various T_{prep}s. The gel network prepared at high temperatures (regimes II and III) is characterized by the presence of domains and loose network, which results in a larger swelling and rapid shrinking.

by Bastide and Leibler [18]. This is why a larger swelling ratio is observed for the gel prepared at higher T_{prep}. By further increasing T_{prep} (regime IV), however, gels loose tie-chains and a large portion of condensed domains looses inter-domain connection. These gels look opaque due to phase separation and even are porous. Therefore, these types of gels loose a swelling capability as a result. In addition, obviously, this situation leads to an irreversible swelling behavior by temperature up and down as shown in Fig. 4.

Fig. 9 shows destination temperature dependence of NIPA gels prepared at (a) $T_{prep} = 20.0$ °C, (b) 26.0 °C, and (c) 28.5 °C. In the case of (a), the change of kinetics from slow shrinking to rapid shrinking takes place at 50 °C-jump. However, by increasing T_{prep} to 26 and 28.5 °C, the destination temperature at which rapid shrinking took place shifted to lower temperatures, i.e. 45.0 °C, for the case of the gel with $T_{prep} = 26.0$ °C. Here, we define the term 'rapid shrinking' to be $t_{1/2} \leqslant 10^2$ min, e.g. $t_{1/2} \approx 10^0$ min. Interestingly, for the gel with $T_{prep} = 28.5$ °C exhibited a rapid shrinking at all the destination temperatures in the range of 35.0 °C. This observation disclosed that the higher the preparation temperature, the more inhomogeneous are the gels and the shrinking kinetics becomes independent of the destination temperature.

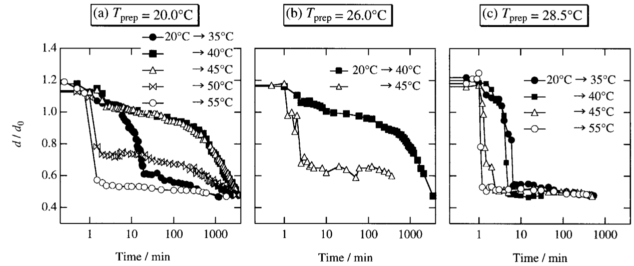

Fig. 9. Destination temperature dependence of shrinking processes after *T*-jump for NIPA gels prepared at various T_{prep}s.

The slow shrinking of PNIPA gels after *T*-jump across its phase separation temperature (≈32 °C) has often been interpreted as a skin formation on the surface, which prevents diffusion of water [19]. However, our observation on the destination-temperature dependence of shrinking kinetics in PNIPA gels suggests that such skin formation cannot apply the case studied in this work. For example, if a skin is formed by *T*-jump, the shrinking rate of PNIPA gel *T*-jumped to 55 °C should be noticeably slow. Note that a rapid shrinking is attained by either increasing T_{prep} or increasing the destination temperature. Fig. 9 strongly indicates that the shrinking kinetics is governed by the inhomogeneities of gels (which is T_{prep} dependent), as well as the destination temperature (thermodynamic driving force).

3.3. Swelling thermodynamics

In the case of gels having inhomogeneous structure schematically described in Fig. 8, theoretical prediction of equilibrium value of swelling degree is quite difficult. However, in this section, we try to reproduce the swelling curve in Fig. 3 by playing with the effective cross-linking density and interaction parameter. In one of previous papers, we proposed a modified Flory–Rehner theory of gel swelling, which is given by

$$\nu \frac{C_{\mathrm{NIPA}}}{C_{\mathrm{NIPA},0}} \left[\frac{1}{2}\left(\frac{\phi}{\phi_0}\right) - \left(\frac{\phi}{\phi_0}\right)^{1/3} \right] - \frac{1}{V_{\mathrm{s}}}[\phi + \ln(1-\phi) + \chi\phi^2] = 0 \tag{2}$$

where ν is the number of cross-links per unit volume, V_s is the molar volume of the solvent, and χ is the Flory's interaction parameter. ϕ and ϕ_0 are the network volume fractions at swelling equilibrium and the reference state, respectively, and are related to d/d_0 as follows:

$$\phi_0/\phi = (d/d_0)^3 \tag{3}$$

$C_{\mathrm{NIPA},0}$ is the reference NIPA concentration, which is a lower bound of NIPA concentration capable of gel formation. The cross-link density ν is the number of cross-links per unit volume and is stoichiometrically given by

$$\nu = \frac{2C_{\mathrm{BIS}}}{C_{\mathrm{NIPA}}} \frac{\phi_0}{V_{\mathrm{NIPA}}} = \frac{2C_{\mathrm{BIS}}}{1000} \tag{4}$$

In the modified Flory–Rehener theory [20], the factor, $C_{\mathrm{NIPA}}/C_{\mathrm{NIPA},0}$, was introduced to take into account of the effect of entrapped entanglements, which behaves as cross-links in the swollen state. We employed a concentration dependent χ parameter after the treatment of Erman and Flory [21] and Hirotsu [22] as follows:

$$\chi = \chi_1 + \phi\chi_2 \tag{5}$$

where χ_1 is temperature dependent and χ_2 is a constant. For poly-NIPA aqueous solutions, χ_1 is given by

$$\chi_1 = (\Delta H - T\Delta S)/k_B T \tag{6}$$

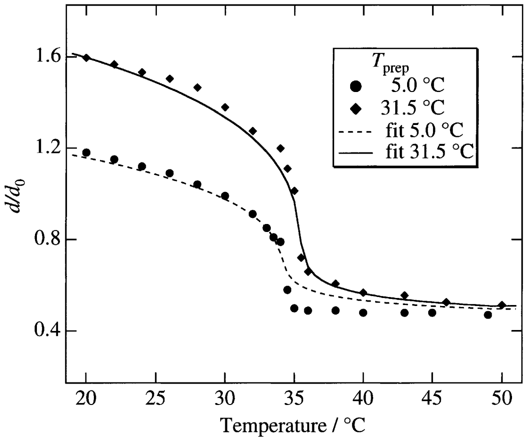

Fig. 10. Theoretical curves of equilibrium swelling degree, d/d_0, of NIPA gels prepared at $T_{prep} = 5.0$ and 31.5 °C with fitted parameters of (χ_2, C_{BIS}) = (0.51, 8.62 mM) and (0.42, 1.4 mM), respectively.

where ΔH and ΔS are the enthalpy and entropy per monomeric unit of network related to the volume phase transition, and k_B is the Boltzmann constant. By solving Eq. (2) numerically with given values of C_{NIPA} and $\Delta H = -12.46 \times 10^{-21}$ J and $\Delta S = -4.717 \times 10^{-23}$ J/K [22], we obtained the solid lines in Fig. 10. Here, the parameter set (χ_2,C_{BIS}) was floated. As shown in the figure, the variations of d/d_0 for gels with $T_{prep} = 5.0$ and 31.5 °C were reproduced by the theory with the set of (χ_2,C_{BIS}) = (0.51,8.62 mM) and (0.42, 1.4 mM), respectively. The lowering of χ_2 accounts for the upper shift of T_{tr}. The decrease of the fitted value of C_{BIS} means that the gel becomes more inhomogeneous with increasing T_{prep} and the effective number of cross-links is greatly reduced by formation of polymer-rich domains. The decrease of the value of C_{BIS} is a result of consumption of a large portion of BIS for making polymer-rich domains. This speculation is supported by the experimental evidence, i.e. an increase in the inhomogeneities (Fig. 1). Hence, the decrease does not mean formation of 'a loosely connected homogenous gel'. As depicted in Fig. 8, a gel can contain domains (or microdomains) in which the polymer concentration is slightly larger than the matrix due to introduction of cross-links. This type of domains is different from phase-separated domains, since the latter are formed as a result of phase separation. The former, on the other hand, is thermodynamically preferable to be as one phase, while their local concentrations are fixed by the cross-links. This result is consistent with the speculation shown in Fig. 8. Okajima et al. [11] reported that d/d_0 for NIPA gels increased by lowering C_{BIS}. This observation is also consistent with our results of experiment and simulation.

It is needless to mention that the theoretical consideration above is not a unique method to describe the swelling behavior of NIPA gels prepared at different T_{prep}s. Nonetheless, we believe that this trial gives a hint of understanding the effect of T_{prep}. A further theoretical investigation on the thermodynamics of gel swelling, which accounts for the inhomogeneities is strongly desired. A microscopic structure investigation in terms of small-angle neutron scattering, as well as dynamic light scattering will be reported in the near future [15].

4. Conclusions

Preparation temperature T_{prep} dependence of equilibrium gel swelling and kinetics of shrinking of NIPA gels was investigated. The swelling behavior was found to be strongly dependent on T_{prep}. The equilibrium swelling degree, d/d_0, in swollen state (e.g. at 20 °C) increases with T_{prep} up to $T_{prep} = 31.5$ °C, which is due to formation of a loosely connected network by clustering NIPA domains. For gels with $T_{prep} = 31.5$ °C, d/d_0 at 20 °C was significantly suppressed and a hysteresis appeared by temperature scan was repeated. This is explained as formation of incomplete network in which connectivity is locally lost. The preparation temperature T_{prep} dependence of the shrinking dynamics of NIPA gels exhibited a drastic change at $T_{prep} \approx 25$ °C. It took more than 500 min for gels prepared at $T_{prep} \leq 23$ °C to shrink, while those prepared at $T_{prep} \geq 25$ °C shrank to the shrunken state in a few minutes. This strong T_{prep} of shrinking kinetics was explained with a network model with spatial inhomogeneities, such as topological incompleteness and clustered structure. A thermodynamic consideration of swelling equilibrium also supported this model.

Acknowledgements

This work is partially supported by the Ministry of Education, Science, Sports and Culture, Japan (Grant-in-Aid, 12450388 and 13031019 to M.S.).

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