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Microscopic implication of rapid shrinking of comb-type grafted poly(*N*-isopropylacrylamide) hydrogels

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Abstract

The shrinking mechanism of comb-type grafted poly(*N*-isopropylacrylamide) gel was investigated by small-angle X-ray scattering (SAXS). The SAXS reveals that the microdomain structure with characteristic spacing of 460 Å is developed in the comb-type grafted poly(*N*-isopropylacrylamide) gel during the shrinking process. These observations suggest that the freely mobile characteristics of the grafted chains are expected to show the rapid dehydration to make tightly packed globules with temperature, followed by the subsequent hydrophobic intermolecular aggregation of the dehydrated graft chains. The dehydrated grafted chains created the hydrophobic cores, which enhance the hydrophobic aggregation of the networks. These aggregations of the NIPA chains contribute to an increase in void volume, which allow the gel having a pathway of water molecules by the phase separation.
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Keywords: Small-angle X-ray scattering; Comb-type grafted gel; Shrinking kinetics

1. Introduction

A gel system that swells and shrinks in response to the environmental stimuli could serve as the basis for applications of polymer gels, for example, as sensors, drug delivery devices and actuators [1–6]. However, since the process is diffusion-limited, the swelling and shrinking kinetics is strongly dependent on the size of gel. On the basis of the cooperative diffusion of polymer network in a medium, the characteristic time of gel swelling and shrinking is described as $\tau \approx R^2/D$, where R and D are the size of the gel and the cooperative diffusion coefficient of the polymer network, respectively [7]. For typical polymer gels, D is of the order of 10^{-7}–10^{-6} cm^2 s^{-1}, depending on polymer concentration, cross-linking density, etc. Since it is not easy to increase the value of D by a factor of 10^2 or more, a reduction of the gel size has been an only way to achieve quick response. Recently Okano et al. developed a novel architecture of *N*-isopropylacrylamide (NIPA) gel. They introduced comb-type NIPA polymer chains to NIPA gel network [6,8,9], and found the comb-type grafted NIPA gel (GG) exhibited drastic acceleration of the shrinking kinetics compared to conventional normal-type NIPA gel (NG). Our recent study on the dansyl-labeled comb-type grafted NIPA gel by the fluorescence spectroscopy suggests that the freely mobile grafted chains show the rapid dehydration, which enhances the dehydration of network chains of the gel [10]. The strong aggregation force is expected to induce the phase-separated structure during volume change, which contributes an increase in void volume within a gel, resulting in a rapid release of water. Small-angle X-ray scattering (SAXS) may provide powerful tools for studying these phenomena at the molecular level. In this study, we carried out SAXS to elucidate the temporal change in the microscopic structure of the comb-type grated NIPA gel due to temperature jump across its volume transition temperature.

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2. Experimental

2.1. Sample preparation

N-isopropylacrylamide (NIPA; Kohjin) was recrystallized from the mixture of toluene and *n*-hexane. *N*,*N*′-methylene-bis(acrylamide) (BIS; Kanto), *N*,*N*′-tetramethylethylenediamine (TEMED; Kanto) and ammonium persulfate (APS; Kanto) were used as received. NIPA macromonomer was synthesized by the esterification of acryloyl chloride with semi-telechelic NIPA polymer with a terminal hydroxyl end group, which was prepared by radical telomerization of NIPA monomer using 2-hydroxyethanethiol as a chain transfer agent [8,10]. The total amount of NIPA monomer unit (NIPA monomer + NIPA macromonomer) was kept constant, and the weight ratio of NIPA macromonomer to NIPA monomer was chosen to be 30% (w/w). The feed compositions are listed in Table 1. NG and GG (Fig. 1) were prepared by radical polymerization in distilled deionized water at 5 °C for 24 h initiated by APS/TEMED.

2.2. Measurement

The gel disks with 10 mm in diameter and 1 mm in thickness were used for the experiments. The gel sample was placed in a thermostated cell filled with distilled deionized water, the temperature of which was controlled to within 0.1 °C of the desired temperature. The temperature-jump (*T*-jump) experiments were carried out by exchanging the circulating water whose temperatures were set to the desired temperatures. The time required for the *T*-jump was about 30 s. The measurement was repeated at least three times and its average was used as the value of $d(t)$.

The SAXS experiment was carried out with the BL-10C installed at Photon Factory (Tsukuba, Japan). An incident X-ray beam from the synchrotron orbital radiation was monochromatized to 1.49 Å. The scattered X-ray was detected by a one-dimensional position-sensitive proportional counter positioned at 1 m from the sample: the magnitude of the observed scattering vector ranged from 0.008 to 0.15 $Å^{-1}$. The gel samples were sealed in a cell, the temperature of which was controlled to within 0.1 °C of the desired temperature. The intensities were accumulated for 600 s in order to assure sufficient statistical accuracy without degrading the gel samples by X-ray irradiation. The scattered intensities were corrected for the cell scattering and absorption, and then normalized with the thickness of the sample and irradiated time.

Table 1
Feed composition for preparation of NIPA normal-type gel (NG) and comb-type grafted NIPA gel (GG)

Sample code	NG	GG
NIPA monomer (g)	15.60	10.92
NIPA macromonomer (g)[a]	–	4.68
BIS (g)	0.266	0.266
TEMED (μl)	48	48
APS (g)	0.008	0.008
Water (ml)	100	100

[a] $M_w = 7340$, $M_n = 5170$, $M_w/M_n = 1.42$. The molecular weight distribution of NIPA macromonomer was determined by gel permeation chromatography apparatus (TOSOH SC-8020 system) in DMF with 10 mM LiCl. Calibration was carried out with monodisperse poly(ethylene glycol) standards purchased from TOSOH Corp.

3. Results and Discussions

The kinetics of swelling of gel was treated by Tanaka and Fillmore [7]. The time variation of the gel size, e.g. the gel diameter, could be described by a single-exponential function

$$\frac{d(t)-d(\infty)}{d(0)-d(\infty)} = \frac{d(t)/d(0)-d(\infty)/d(0)}{d(0)/d(0)-d(\infty)/d(0)} \approx \frac{6}{\pi^2}\exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where $d(t)$ is the gel diameter at time t and τ is the characteristic time for swelling. Fig. 2 shows the variation of the degrees of swelling, $d(t)/d(0)$, of the NG and GG after *T*-jump from 10 to 35 °C. In the case of NG, the swelling ratio is satisfactorily reproduced by Eq. (1). The evaluated value of the collective diffusion coefficient of the gel network, D for NG is 6.9×10^{-7} cm^2 s^{-1}. In the case of GG, however, the analysis with a single-exponential function (Eq. (1)) found to be no more applicable. This is due to the fact that the theory is limited to the linear regime and the collective diffusion constant is assumed to be invariant upon shrinking/swelling [7]. It has been confirmed Eq. (1) was also valid for the shrinking kinetics as far as the shrinking did not accompany phase separation. Therefore we define the time required for half- shrinking, $t_{1/2}$, as follows [11]:

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

The values of the time required for half-shrinking, $t_{1/2}$, for NG and GG after *T*-jump from 10 to 35 °C are 4000 and 100 s, respectively. The shrinking kinetics for GG compares approximately 40 times accelerated with that for NG. The rapid shrinking of the comb-type grafted NIPA gel is expected to originate in a microphase-separated structure during volume change. We carried out, therefore, the SAXS experiment to confirm the microscopic structure of the gels. Fig. 3 shows the SAXS intensity profiles for NG and GG equilibrated at 10 and 35 °C. When cross-links are introduced to polymer solution, the concentration fluctuations are perturbed. Geissler et al. proposed that the scattering intensity from an uncharged gel could be described by a sum of dynamic and static components

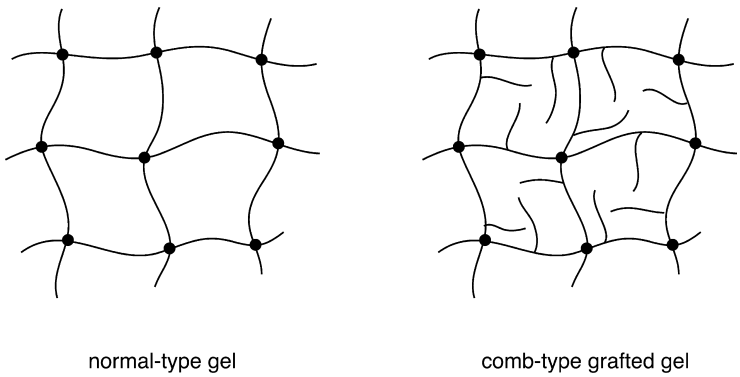

Fig. 1. Schematic illustrations of structures for NG and GG.

[12–15]

$$I(q) = I_{dyn}(q) + I_{st}(q) = \frac{I_L(0)}{1+\xi^2 q^2} + I_G(0)\exp[-\Xi^2 q^2] \quad (3)$$

where Ξ is the mean size of the solid-like (static) nonuniformity, and ξ is the correlation length. The Ornstein–Zernike expression (first term) in Eq. (3) corresponds to the thermal fluctuation in a semi-dilute polymer solution, where ξ is the mean distance between contact points [16]. The second term describes static concentration fluctuation, such as elastic constraints frozen-in by the cross-links or other structural features present in a particular gel.

As shown in Fig. 3, at swelling equilibrium at 10 and 35 °C, the scattered intensities for NG and GG monotonously decrease with the scattering magnitude q, and indicate the absence of microphase separated structure. The parameters deduced from the fits of the SAXS spectra to Eq. (3) are summarized in Table 2. In the swollen state at 10 °C, it is found that Ξ for NG and GG are almost identical, which indicates that the introducing of the graft chains does not induce the extra static inhomogeneity, namely the static inhomogeneity basically results in the distribution fluctuation of the cross-linkers in the pre-gel polymer solution. In contrast to Ξ, the difference in correlation length, ξ is probably due to the freely mobile characteristics of the NIPA graft chains. As the grafted chains are structurally separated from the backbone cross-linked network, they could behave the free polymer chains as in the polymer solution, which makes the dynamic fluctuation of the polymer density for the GG larger than that for NG. As shown in Fig. 3(c) and (d), in the collapsed state at 35 °C, remarkable decrease in the dynamic component of the scattering intensity was observed for NG and GG. With regard to the dynamic component due to the scattering of the solution like structure in the gel, it is reasonable that its contribution to the scattering intensity is neglected.

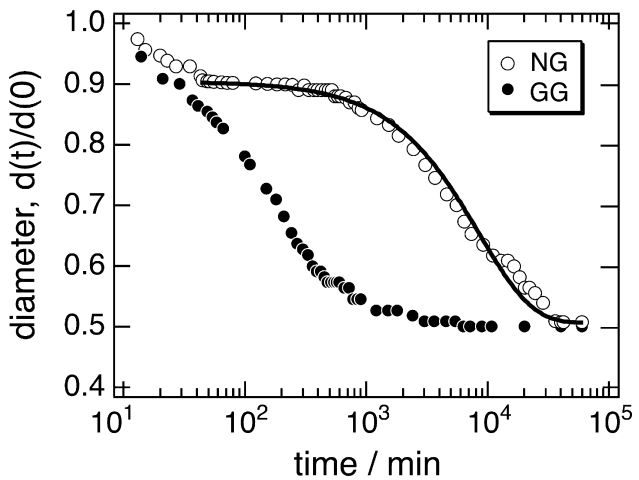

Fig. 2. The variation of the degrees of swelling, $d(t)/d(0)$, of the NG and GG after T-jump from 10 to 35 °C. The solid line is the fit with Eq. (1).

Fig. 4(a) shows the SAXS intensity profiles, illustrating the trends observed as the time after T-jump from 10 to 35 °C. The scattered intensities for NG monotonously decrease with the scattering magnitude q. It is remarkable for GG that a scattering peak appeared at $q = 0.014$ Å^{-1} at 10 min after T-jump. The intensity was increased with time, and was confirmed to reach a maximum at 420 min after T-jump, and the peak position unchanged until the GG reached the equilibrium state.

The Cahn–Hilliard theory is based on the linearization of a generalized diffusion equation and is considered to be applicable to the early stage of spinodal decomposition [17,18]. In this theory, the time dependence of the static structure factor after the system is quenched into the two-phase region should follow an exponential growth as

$$I(q,t) = I(q,0)\exp[2R(q)t] \quad (4)$$

with the $I(q,t)$ as the time dependent static structure factor.

Table 2
Scattering parameters from NIPA normal-type gel (NG) and comb-type grafted NIPA gel (GG) in equilibrium state at 10 and 35 °C

Sample	Temperature (°C)	ξ (Å)	Ξ (Å)
NG	10	41.0 ± 1.0	181 ± 1.4
	35	46.1 ± 2.7	159 ± 0.7
GG	10	59.3 ± 1.2	176 ± 1.6
	35	59.1 ± 5.4	160 ± 0.4

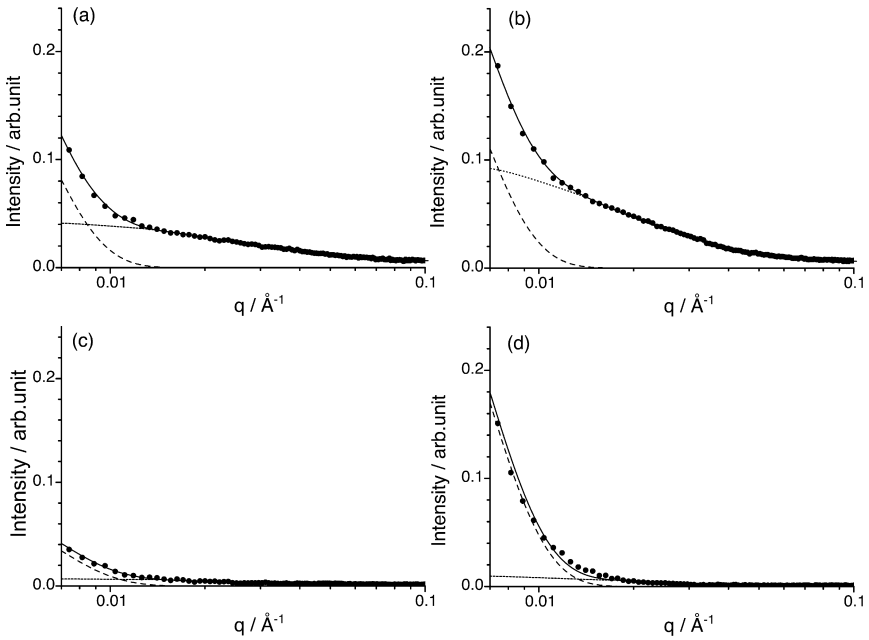

Fig. 3. SAXS intensity profiles and reconstructed spectra for NG and GG. The dotted curve represents the Lorentzian behavior with the correlation length ξ, the broken curve is the contribution of the solid-like (static) nonuniformity with the mean size Ξ, and the full curve is total intensity: (a) NG at 10 °C, (b) GG at 10 °C, (c) NG at 35 °C, (d) GG at 35 °C. The fitting parameters are summarized in Table 2.

Here $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering wave vector, with the incident beam wavelength λ and scattering angle θ. The growth rate $R(q)$ is given as

$$R(q) = -Dq^2(1 - \xi^2 q^2) \tag{5}$$

where $D(= -(\partial^2 f/\partial\phi^2)_0 \Lambda(q))$ is the effective diffusion constant. $(\partial^2 f/\partial\phi^2)_0$ is the second derivative of the free energy at the initial state and $\Lambda(q)$ is a Onsager coefficient. When the thermal fluctuation is included, Eq. (4) is modified and becomes:

$$I(q,t) = I_x(q) + [I(q,0) - I_x(q)]\exp[2R(q)t] \tag{6}$$

and

$$I_x(q) = -q^2\Lambda(q)/R(q) \tag{7}$$

Solid lines in Fig. 4(b) are the results of curve fitting for GG at the time after T-jump with Eq. (6). The amplitude of the static concentration fluctuation is very small, therefore the contribution of the solid-like (static) nonuniformity to

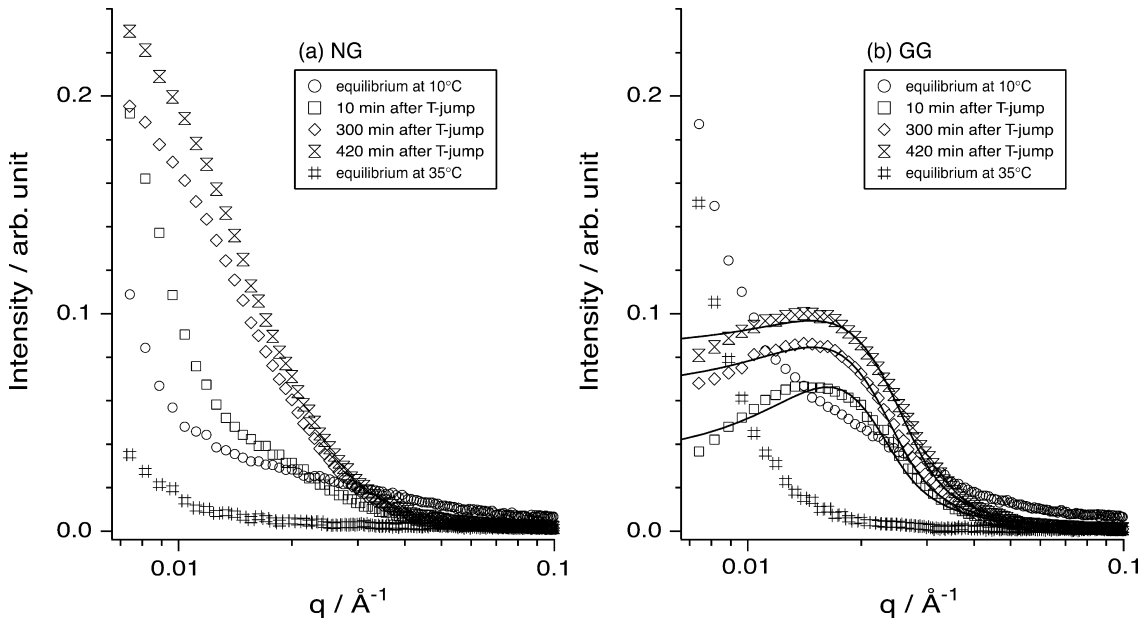

Fig. 4. (a) Time evolution of SAXS intensity profiles for (a) NG and (b) GG after T-jump from 10 to 35 °C. Solid lines in (b) are the results of curve fitting with Eq. (6).

$I(q,t)$ is negligible. The theoretical curves reasonably reproduce the observed scattering intensity functions. From the fitting results, the correlation length of the concentration fluctuation is evaluated to be $\xi = 49.5$ Å at each time after T-jump. This value is almost the same as the correlation length of the dynamic fluctuation for GG at equilibrium state summarized in Table 2. This indicates that the concentration fluctuation is mostly associated with individual network segment, and graft chains due to its freely mobile characteristics, and its amplitude increases by T-jump.

Contrary to GG, the scattered intensity for NG is still monotonous decreasing function of the scattering magnitude q, and the increase in the dynamic fluctuation is observed. The observed microphase separated structure that developed in GG during the shrinking process well explains the drastic acceleration of shrinking of GG compared to NG. These observations and our previous studies by fluorescence spectroscopy [10] suggest that the freely mobile characteristics of the grafted chains are expected to show the rapid dehydration to make tightly packed globules with temperature, followed by the subsequent hydrophobic intermolecular aggregation of the dehydrated graft chains. The dehydrated grafted chains created the hydrophobic cores, which enhance the hydrophobic aggregation of the networks. These aggregations of the NIPA chains contribute to an increase in void volume, which allow the gel having a pathway of water molecules by the phase separation.

Here we report the first SAXS observation of NG and GG to study its shrinking mechanism at microscopic level. A further investigation of the shrinking mechanism by means of the time-resolved SAXS and SANS is in progress and will be reported in a future publication.

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References

[1] Tanaka T. Phys Rev Lett 1978;40:820.
[2] Tanaka T, Fillmore DJ, Sun ST, Nishio I, Swislow G, Shah A. Phys Rev Lett 1980;45:1636.
[3] Hirokawa Y, Tanaka T. J Chem Phys 1984;81:6379.
[4] Kiler J, Scranton AB, Peppas NA. Macromolecules 1990;23:4944.
[5] Suzuki A, Tanaka T. Nature 1990;346:345.
[6] Yoshida R, Uchida K, Kaneko Y, Sakai K, Kikuchi A, Sakurai Y, Okano T. Nature 1995;374:240.
[7] Tanaka T, Fillmore D. J Chem Phys 1979;70:1214.
[8] Kaneko Y, Sakai K, Kikuchi A, Yoshida R, Sakurai Y, Okano T. Macromolecules 1995;28:7717.
[9] Kaneko Y, Nakamura S, Sakai K, Kikuchi A, Aoyagi T, Sakurai Y, Okano T. Polym Gels Networks 1998;6:333.
[10] Annaka M, Tanaka C, Nakahira T, Sugiyama M, Aoyagi T, Okano T. Macromolecules 2002;35:8173.
[11] Hirose H, Shibayama M. Macromolecules 1998;31:5336.
[12] Mallam S, Hecht AM, Renniie AR, Geissler E. Macromolecules 1991; 23:543.
[13] Horkey F, Hecht AM, Mallam S, Geissler E, Renniie AR. Macromolecules 1991;24:2896.
[14] Geissler E, Horkey F, Hecht AM. Phys Rev Lett 1993;645:71.
[15] Horkey F, Burchard W, Geissler E, Hecht AM. Macromolecules 1993; 26:1296.
[16] de Gennes PG. Scaling concepts in polymer physics. Ithaca, NY: Cornell University Press; 1979.
[17] Okada M, Han CC. J Chem Phys 1986;85:5317.
[18] Li Y, Wang G, Hu Z. Macromolecules 1995;28:4194.