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Friction between a polymer network of poly(*N*-isopropylacrylamide) gels and solvent water was investigated. The gel was mechanically constrained in a glass capillary at gelation, and hydrostatic pressure was directly applied to the cross section of the cylinder. The temperature dependence of the flow velocity was extensively measured in the vicinity of the transition temperature for gels with different lengths, l_0 , at gelation. As the temperature increased, the friction slightly decreased at the transition point and increased rapidly in the collapsed phase. Although the flow velocity depended on l_0 , the friction in the vicinity of the transition point was well scaled by l_0 based on the Hagen-Poiseuille equation for the flux of water flow in a capillary. The results suggested that the assumption that the gel is a bundle of microcapillaries was applicable to the water flow through the hydrogel, which was largely deformed not only by the pressure applied to the solvent but also by the shrinking force caused by the temperature increment. Macroscopic deformation did not affect the friction between the three-dimensional polymer network and water. © 2006 American Institute of Physics. [DOI: 10.1063/1.2364893]

I. INTRODUCTION

Hydrogels are three-dimensional polymer networks containing a large amount of water. Because they exhibit many unique properties, they are attracting the interest of many researchers in various scientific and technological fields. Hydrogels are used as retainers of water and solutes for many practical applications, e.g., disposable diapers contain gel absorbents, and gels are used as drug carriers in anti-inflammatory analgesic cataplasms. Unlike a sponge and a dustcloth, hydrogels do not allow water and solutes to escape easily because the friction between the polymer network and water is extremely great.

Deswelling by an externally applied pressure on polyacrylamide (PAAm) gels was first investigated by Hecht and Geissler.¹⁻³ They reported the rate of deswelling of PAAm gels in contact with a semipermeable reverse osmosis membrane and they discussed the relationship of the experimental parameters, including the flow velocity, the applied pressure, the longitudinal elastic modulus of gel, and the friction coefficient between the polymer network and water. In 1991, Tokita and Tanaka investigated the relationship between the frictional property and static fluctuations of hydrogels^{4,5} and reported that the water flow is described by the classical model based on the Hagen-Poiseuille equation.⁶ They also confirmed that the friction between a polymer network of poly(*N*-isopropylacrylamide) (PNIPA) gel and water decreased many orders of magnitude as the critical temperature of the phase transition was approached.⁴ They proposed the fundamental physics of the phenomenon based on the critical phenomena of density fluctuations in gels;^{5,7,8} the polymer network density fluctuates dynamically near the critical

point, and water can pass through the dilute region of the polymer network. Recently, we developed a simple technique to obtain the friction coefficient between a polymer network and water in a hydrogel.⁹ Using this technique, in which the gel was mechanically constrained in a glass capillary at gelation, it was much easier to control the experimental conditions than it was in the above pioneering work.^{4,5} We used our technique to study the friction between a polymer network of PAAm gels and water. The effects of gel size (length and cross-section area) and the pressure applied to the solvent on the friction coefficients in PAAm gel were extensively examined and showed good agreement with the model from the flux of water flow in a capillary based on the Hagen-Poiseuille equation. Macroscopic deformation by pressure was found not to affect the model.

In this paper, we present the temperature dependence of the friction between a thermoresponsive polymer network and water in (PNIPA) gels measured by our simple clamp technique. We measured the absolute friction coefficient as well as its change in the vicinity of the transition temperature. In order to clarify macroscopic deformation induced not only by pressure applied to the solvent but also by the shrinking force caused by the temperature increment, we measured the friction of different lengths of gels prepared at gelation at a constant applied pressure.

II. EXPERIMENTAL AND MODEL GEL

A. Sample preparation and setup

The pregel solution of PNIPA gel was a mixture of PNIPA monomers (7.9 g, main constituent, Kohjin), *N,N'*-methylenebisacrylamide (133 mg, cross-linker, Wako), 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA-086, 30.6 mg, initiator, Wako), and *N,N,N',N'*-tetramethylethylenediamine (240 μ l, Wako) dissolved in

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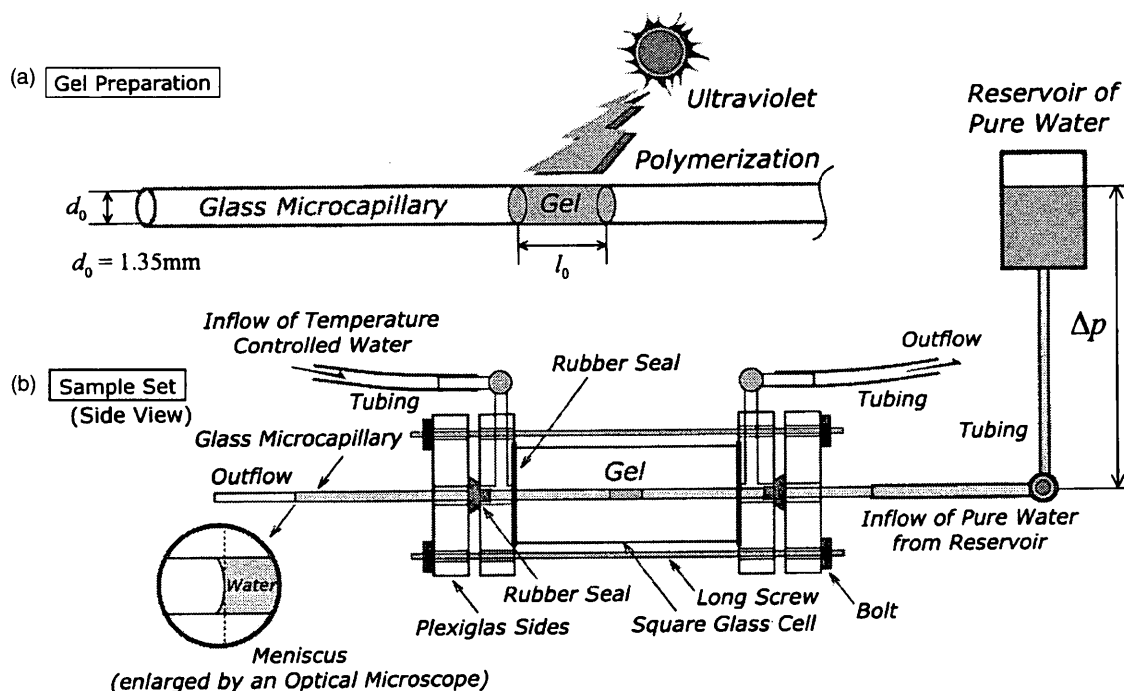


FIG. 1. Schematics of the sample preparation (a) and the sample setup (side view) (b), where the cell is made of glasses, bolted Plexiglas sides, tubing, and rubber seals.

100 g of pure water (de-ionized, distilled water).⁹ The pregel solution was injected into a glass capillary using a microsyringe. The length of each gel was changed by controlling the amount of pregel solution in the glass capillary at gelation. In order to chemically clamp the gel onto the inner surface of the glass capillary,^{10,11} bind silane (γ -methacryloxypropyltrimethoxysilane, Amersham Biosciences) was used to rinse the inner surface before the pregel solution was drawn into the capillary; the bind silane added reactive methacrylate groups onto the surfaces so that PNIPA became chemically bound to the groups during polymerization. Gelation was initiated by UV irradiation¹² (the wavelength was 365 nm and the intensity was 26–29 mW/cm²) on the capillary with the pregel solution. The irradiation time was 30 min at 25 °C (below the cloud point of PNIPA polymers).¹³

The experimental setup is shown in Fig. 1(b). The glass capillary with a gel adhered was encapsulated in a transparent square glass. One end of the capillary was connected to a reservoir of pure water. The temperature controlled water by the water bath with an accuracy of ± 0.05 °C was circulated within the square glass cell to control the temperature of the gel as well as the flow water. The pressure was adjusted by changing the water height from the water-outflow position to the top surface in the reservoir. The top surface area was much larger than the cross-section area of the capillary, and the decrease of the water height by the water flow through the gel could be neglected. The meniscus position was measured by an optical microscope connected to a calibrated charge-coupled device (CCD) camera and a video processor.

B. Model gel

If the network is assumed to consist of N microcapillaries per unit area ($N = n/S$, where n is the number of capillar-

ies and S is the cross-sectional area) as a bundle of the microcapillaries with an inner diameter ξ , the applied pressure Δp can be expressed based on the Hagen-Poiseuille equation,⁶

$$p = \frac{32\eta}{\xi^2} u \alpha l_0 \equiv f u l_0, \quad (1)$$

$$f = \frac{32\alpha\eta}{\xi^2} \propto \frac{\eta}{\xi^2}, \quad (2)$$

where u is the average flow velocity, l_0 is the gel length at gelation, and η is the dynamic viscosity of the water. The length αl_0 indicates the average distance of total flow in the gel; α is a function of macroscopic deformation as well as temperature. One can see that u is proportional to Δp and inverse to f and l_0 , while f depends on η , α , and ξ but not on the gel size S and l_0 . From Eqs. (1) and (2), ξ can be estimated by measuring u at a constant Δp and determining l_0 .

In accordance with the previous report,⁹ the absolute f did not depend on the gel size S and Δp ; in the present study, S and Δp were fixed by using a capillary with d_0 (inner diameter of 1.35 mm) and a water height of 80 cm (7.8×10^4 dyn/cm²), respectively.

C. Pretreatment (long-time annealing)

In order to prevent the effect of residual chemicals, such as unreacted monomers, oligomers, cross-linkers, accelerators, and initiators in the as-prepared sample, the long-time water flow was conducted at room temperature (25 °C) for more than 1×10^5 s to reach the final steady state. This period was much larger than the relaxation time for the collective diffusion of polymer networks,^{14–19} i.e., it is an order of 10^4 s for a gel with a few millimeter size,^{17,18} and corre-

sponded for the meniscus position to move approximately the gel length (around l_0). In this long-time annealing, the residual chemicals were completely removed, and the pressure-induced network deformation along the flow direction was completed.

After the gel reached equilibrium at 25 °C in this initial treatment, the slope of the time evolution of the meniscus position yielded the absolute velocity u of the steady-state flow. Using Eqs. (1) and (2), f/η was calculated as a measure of ξ^2 , which is proportional to the inverse of the average pore areas (S/n or N^{-1}). While applying constant pressure, the temperature was very slowly increased in a step-by-step manner in the vicinity of the transition temperature. At each temperature, u was measured after the gel reached equilibrium. It took less than 5×10^2 s to reach the steady state, which was much smaller than the collective diffusion of polymer networks of a gel with a few millimeter size.^{14,17–19} This small relaxation time was caused by network diffusion at the inflow and outflow of the solvent water induced by the temperature change since small amounts of gel at the boundaries of the gel and water usually swell or collapse at the phase-transition point in minutes (or within an hour).¹⁷

III. RESULTS AND DISCUSSION

A. Macroscopic deformation by water pressure and shrinking of gels

In the present system, two types of deformations should be taken into account to understand the water flow because the gel was mechanically constrained onto the inner surface of the glass capillary. In the first type, the total density of the polymer network is slightly increased by the applied pressure along the flow direction since the gel is a dilute viscoelastic solid. After pretreatment (long-time annealing) at 25 °C, the deformation might reach equilibrium after a little water was squeezed out of the gel.²⁰ In the other type, the total density of the hydrophobic polymer network is slightly increased by the temperature increase since the networks of the free surfaces without mechanical constraints at the inflow and outflow of water could shrink. Moreover, the local networks in the bulk are deformed by the shrinkage because of the network inhomogeneity⁸ even though the total network density in the cross section remains constant except at the free surfaces. The effects of this shrinkage depend on the characteristic lengths of the gels at gelation. It is expected that these two deformations, caused by applied pressure and temperature-induced shrinkage, determine the average distance of total flow in the gel, αl_0 in Eq. (1), which is essential to understanding the friction of the thermoresponsive gels.

As mentioned in the Introduction, the present technique can be easily applied to test samples with different l_0 ; three gels with different l_0 (with the same cross-sectional area) were prepared at the same time to study the dependence of l_0 on the water flow. As shown in Fig. 2, the effects of two types of deformation on the total network density decreased with increasing l_0 . In the case of deformation by applied pressure, the conformation change was larger at the water-inflow position of the gel but smaller at the water-outflow

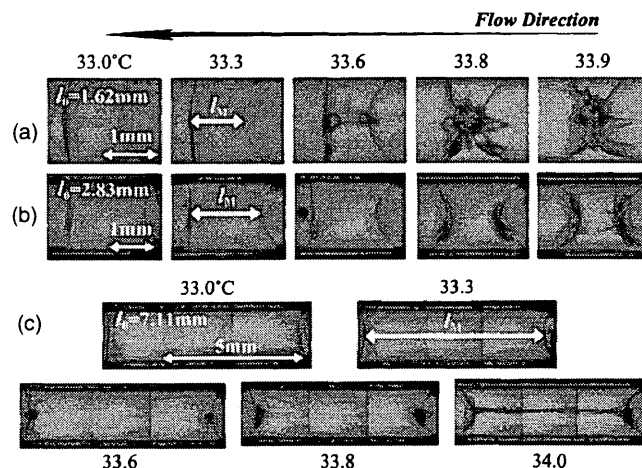


FIG. 2. Pictures of the PNIPa gel in glass capillaries with three different lengths ($l_0 = 1.62$, 2.83, and 7.11 mm) in which the gels were mechanically constrained at gelation. The temperature was increased with a minimum step of 0.1 °C in the vicinity of the transition temperature. For the longest gel, three pieces of photographs were connected.

position. The deformation at the outflow position was negligibly small, as seen in the pictures obtained at temperature below 33.6 °C (Fig. 2). In the case of deformation by temperature-induced shrinkage, the short gel ($l_0 = 1.62$ mm) totally shrank when the temperature approached the transition point T_0 , because l_0 was comparable to the inner diameter of the glass capillary, $d_0 (= 1.35$ mm). On the other hand, the longest gel ($l_0 = 7.11$ mm), which was much longer than d_0 , partly shrank, although the bulk network was not strongly affected.

B. Temperature dependence of u , l , and f/η

The average flow velocity u and the minimum length l_M (the distance between the centers of the water-inflow and -outflow surfaces, defined in Fig. 2) of these three samples were measured during heating processes. As shown in Fig. 3(a), u strongly depended on temperature and increased when the temperature approached T_0 . After reaching T_0 , it decreased rapidly below the initial value at 30 °C. Correspondingly, l_M decreased rapidly in the vicinity of T_0 [Fig. 3(b)]. It is noteworthy that the transition in this system was continuous in accordance with the previous reports for gels with mechanical constraints.^{10,11}

Regarding the temperature dependence of f , it has been well established that f depends on temperature because of the change in dynamic viscosity η and it is reasonable to plot f/η against temperature. Using the above results for u , f/η can be calculated based on Eq. (1) if we determine αl_0 , i.e., the average distance of the total flow in the gel (the water path length). In the previous reports, when f/η was calculated, it was assumed that αl_0 was roughly equal to l_0 (i.e., $\alpha = 1$). Since the size of the present PNIPa gel at around 30 °C is same as the size at gelation,¹¹ i.e., $l_0 = l_M$ at 30 °C, we compared the absolute f of three samples with the reported ones^{5,16} at 30 °C. The results showed that the three f/η were almost the same as 5×10^{13} cm⁻², which was

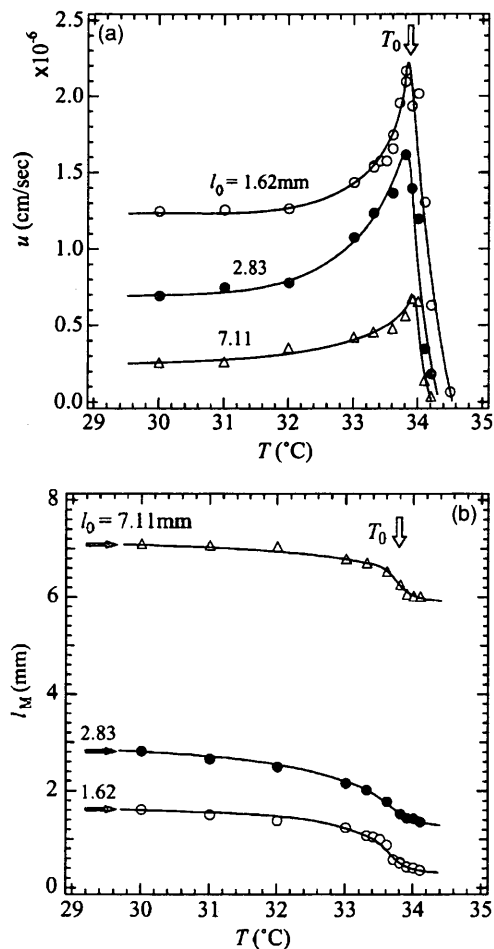


FIG. 3. Temperature dependence of the flow velocity, u , (a) and the minimum length, l_M (b) under the water height of 80 cm (7.8×10^4 dyn/cm 2).

approximately half the previously reported result (see discussion in Sec. III D).

In the calculation of the temperature dependence of f/η (other than 30 $^{\circ}\text{C}$), on the other hand, two characteristic gel lengths could be used; the minimum length l_M [Fig. 3(b)] and the gel length at gelation l_0 (independent of temperature). First of all, the temperature dependence of f/η was calculated by substituting l_M for αl_0 in Eq. (1), which is shown in Fig. 4(a). With increasing temperature, the f/η of the longest gel slightly decreased and showed a dip at T_0 , while the f/η of the shortest gel slightly increased and showed a steep increase in the vicinity of T_0 . These results indicated that the average ξ in response to the temperature change was strongly affected by l_M ; the water path length in the present system was not related to l_M in the capillary model based on the Hagen-Poiseuille equation. The results of the calculation by substituting l_0 for αl_0 in Eq. (1) are shown in Fig. 4(b). In this figure, all data were traced roughly on a single line, consistent with the prediction of resulting from Eq. (1); the average f and ξ did not depend on l_0 . The water path length was found to be determined by l_0 in the capillary model.

It is noteworthy that the water path was expected to be not straight but winding in the network, and the above value of f/η was an underestimate because of $\alpha l_0 > l_0 \geq l_M$; the real f/η should be larger and ξ should be smaller than the above estimation on the assumption of $\alpha l_0 = l_0$. Although the

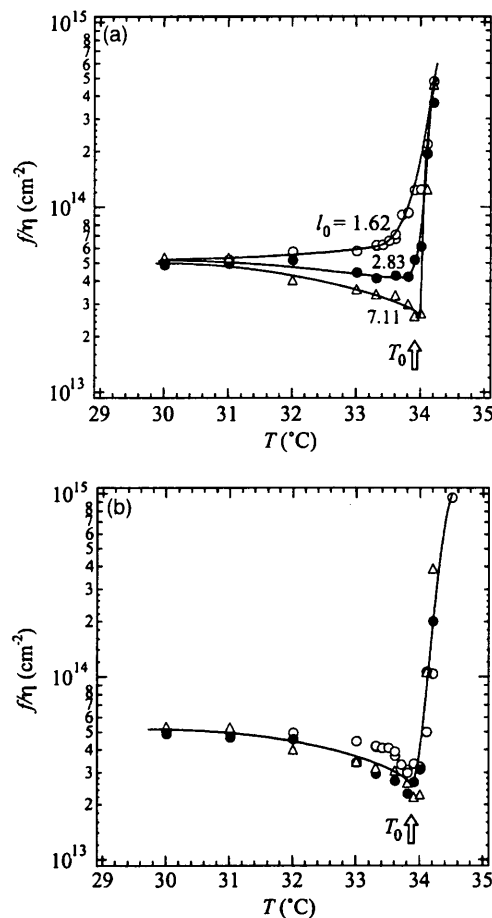


FIG. 4. Temperature dependence of f/η calculated using the data in Fig. 3 by substituting l_M (a) and l_0 (b) for αl_0 in Eq. (1) under the water height of 80 cm (7.8×10^4 dyn/cm 2).

degree of macroscopic deformation should affect the water path length, the above results indicated that the water flow can be predicted by Eq. (2); α/ξ^2 should be kept constant to give a constant f for the different degrees of deformation.

C. On the scaling behavior of the friction

A schematic view of the macroscopic deformations of gels is shown in Figs. 5(a) and 5(b) based on the pictures in Fig. 2. Under such deformations, it was interesting to observe that the water flow showed good agreement with the prediction based on the Hagen-Poiseuille equation. This equation was originally derived to model a steady laminar flow of an incompressible fluid through a rigid-walled cylindrical tube. Assuming the network of gels as a bundle of microcapillaries with an inner diameter ξ , the present results indicated that the original water path length, αl_0 , at a fixed temperature was not affected by deformation (α was independent of the macroscopic size) or that α decreased in accordance with the decrease in ξ^2 [Fig. 5(c)]. In any case, it can be concluded that the microscopic change in the local density did not affect the macroscopic flow in the gel under the present experimental conditions and f/η was scaled against temperature in spite of the different l_0 .

Another important result of the heating process was the dip in f/η at T_0 [Fig. 4(b)], which indicated that ξ increased rapidly when the temperature approached T_0 . According to

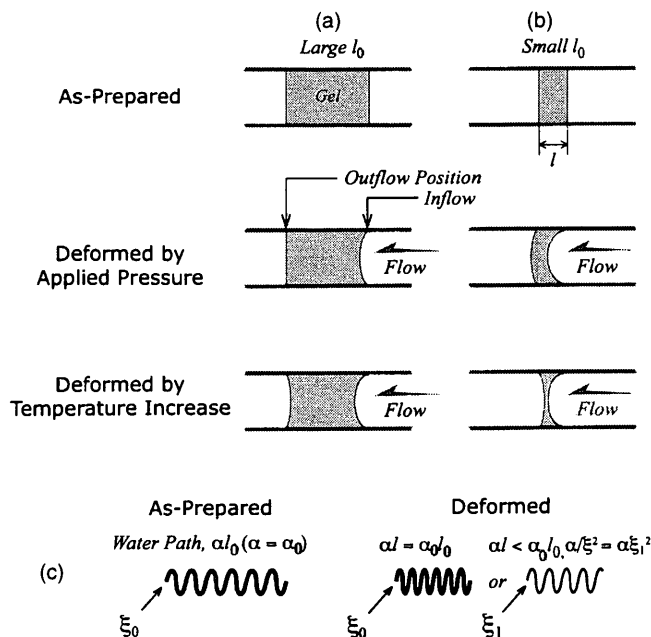


FIG. 5. Schematics of the macroscopic deformation of gels with different l_0 [(a) and (b)] and a schematic of a path of water flow (a microcapillary) (c).

the previous reports, the friction coefficient (or the pore size) obeyed the following temperature dependence.^{4,16}

$$\frac{f}{\eta} = \frac{32\alpha}{\xi^2} \propto \left(\frac{T_0 - T}{T_0} \right)^\nu, \quad (3)$$

where the reported exponent ($\nu=1/4$) was much smaller than the theoretical value ($\nu=5/8$) (Ref. 21) based on the three-dimensional Ising model.^{22,23} As pointed out in the previous reports,^{4,16} the discrepancy could be attributed to the fact that the gel was not prepared at the critical condition and that the phase separation took place in the metastable region before the gel reached the spinodal line. In order to test the transition behavior for the present system, an additional, detailed measurement was conducted in the vicinity of T_0 at smaller temperature increments on another sample prepared with the same recipe as the above three samples. The least-squares analysis of f/η to Eq. (3) was plotted in Fig. 6 together with the results of the above three samples. A result of $\nu=0.165$ (approximately 1/6), smaller than the theoretical result, was obtained.

D. On the principle of the water flow through PNIPa gels

The primary focus of this paper is to answer the following questions regarding the principle of water flow through phase-transition hydrogels: What determines the absolute value of f ? How can f be affected by the bulk phase change, including the collapsed phase, under mechanical constraint? It is important to examine the roles of the physical and chemical properties of polymer networks in determining the friction. Regarding the physical properties, the network density, which can be controlled by monomer concentrations at gelation, determined the average pore size far from T_0 with little effect on the mechanical constraint. In addition, the fact that the total network density of the gel was kept almost

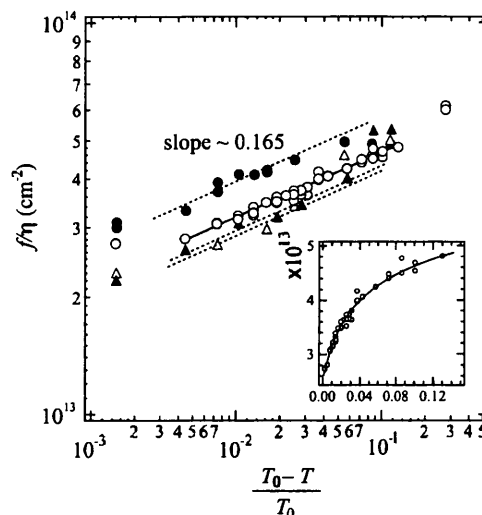


FIG. 6. The log-log plot of f/η as a function of the reduced temperature. The inset is the linear plot.

constant by mechanical constraint, except for slight changes at the free surfaces, was an important factor in determining the average pore size. Regarding the chemical properties, on the other hand, the hydrophobic-hydrophilic balance^{24,25} has some role in determining the friction; the number of water molecules that strongly interact with the polymer depends on the balance. With increasing hydrophobicity, the number of water molecules per PNIPa monomer unit of the network decreased, which enhanced the water flow, consequently, the friction decreased. Considering the results of a slight decrease of f/η and its steplike increase after the transition on the heating process, however, the change in f/η as a function of temperature was not attributed dominantly to the change in hydrophobicity since the balance would change monotonically against temperature but would not induce a dip or steplike increase of f/η . Therefore, the temperature dependence of f/η results mainly from the physical properties, and the network structure and the mechanical constraint have dominant roles in determining the friction.

Based on these findings, it is worth comparing the present results with those of the previous study.⁴ First of all, the present f/η of PNIPa gel at 30 °C was approximately twice as large as that of the one previously reported. We believe that the difference resulted from several technical factors, such as different cross-linking and clamping methods. The conventional cross-linking method was used in the previous study; the gelation initiated by adding ammonium persulfate induced slight ionization of the end points of the polymers at gelation. On the other hand, the gelation initiated by UV irradiation in the present experiment made the gel completely neutral. As for the clamping technique, l_0 was much smaller than d_0 in the previous experiment but much larger in the present one. It seems that the larger the ratio of l_0/d_0 is, the larger the average degree of the mechanical constraint becomes. Therefore, the effects of the mechanical constraint were efficiently reflected in the water flow in the present experiment. The present results, that is, the larger f/η and the smaller exponent ν than the reported ones, can be explained, respectively, by the neutral networks resulting

from the UV-initiated gelation and by the obstacle of the dynamic fluctuation by strong mechanical constraint in the present experiment.

Finally, the steep increase above T_0 will be briefly discussed. Since the gel was mechanically constrained, the total density did not largely change in the present experiment. Although inhomogeneity (dilute and dense regions) was enhanced in the cross section with increasing temperature, the steep increase indicated that the average pore size along the flow direction increased rapidly when the temperature exceeded T_0 . It is possible that water flowed through the dilute region at the expense of the long path length or the water flowed through the shortest path at the expense of a loss by the friction due to the flow through the dense region. As a result of the competition of the complicated flow mechanism, the average pore size could be determined, and it became very large in the collapsed phase.

In order to verify these considerations, simple techniques for experimental observations of stimulus-responsive gels with different degrees of inhomogeneity introduced at gelation are highly desired. The results of our study may assist in the creation of a new technology for the application of stimulus-responsive hydrogels to the design of a soft microvalve to control water flow through a hydrogel as a soft, simple microactuator. We are currently investigating how to control the water flow in the same system by introducing different inhomogeneities at gelation. The results will be published elsewhere.

IV. CONCLUSION

In this paper, the friction between a polymer network and water of poly(*N*-isopropylacrylamide) gel was measured under mechanical constraint. The experimental results agreed well with the prediction of the water flow in a capillary based on the Hagen-Poiseuille equation. Although the real network structure is much more complicated than the capillary model, it was found that α/ξ^2 was kept constant, justifying the consideration of the network of gels as a bundle of microcapillaries.

The macroscopic deformations caused not only by the pressure applied to the solvent but also by the shrinking

force due to the temperature increment did not affect the model and the water flow, which can be determined only by the length of the gel at gelation and the applied pressure. Since gels may be put to practical use under mechanical constraint, the present results are important for future applications. The technique presented here can be developed to design a device to control water flow through a hydrogel in spite of different conditions of mechanical deformation.

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