Static and Dynamic Swelling Properties of Poly(*N*-isopropylacrylamide) Gels in the Swollen State

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(Received March 2, 2005; Accepted June 9, 2005; Published September 15, 2005)

ABSTRACT: Static and dynamic swelling properties of cylindrical poly(*N*-isopropylacrylamide) (PNIPA) gels in water as well as in liquid paraffin (non-solvent for PNIPA gels) have been investigated by using a laboratory-made magnetic force-driven rheometer. In static tests (under a constant stress), the length and diameter of the gel sample in water increase with time due to stress-induced swelling. Relaxation times of the stress-induced swelling in both directions are identical within experimental error. The Poisson ratio decreases from ~ 0.5 to ~ 0.2 with time just after the application of the magnetic force. The dynamic tests (under sinusoidal forces) reveal large differences in the swelling behavior of the gels in water and liquid paraffin. In liquid paraffin, amplitudes of strains parallel and perpendicular to elongation ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$, respectively) are independent of angular frequency (ω), giving the absolute value of dynamic Poisson ratio ($|\mu^*| = \varepsilon_{\perp}/\varepsilon_{\parallel}$) of ~ 0.47 . On the other hand, $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and $|\mu^*|$ in water significantly depend on ω due to the stress-induced swelling with a characteristic time. The dynamic Poisson ratio at $\omega \rightarrow \infty$ (short time limit) or $\omega \rightarrow 0$ (long time limit) agrees well with the corresponding Poisson's ratio obtained by the static tests. The phase lags of $\varepsilon_{\parallel}^*$ and $\varepsilon_{\perp}^*$ seeing from the stress wave ($\delta_{\parallel}$ and $\delta_{\perp}$, respectively) are independent of ω in liquid paraffin whereas $\varepsilon_{\parallel}^*$ and $\varepsilon_{\perp}^*$ move with keeping $|\delta_{\perp} - \delta_{\parallel}| = \pi$. In water, the $\delta_{\parallel}$ curve shows a minimum while the $\delta_{\perp}$ curve does a maximum at the same angular frequency. A characteristic time of swelling in the dynamic tests obtained as an inverse of the frequency accords well with the relaxation time in the static tests. [DOI 10.1295/polymj.37.694]

KEY WORDS Dynamic Swelling Behavior / Magnetic Force-Driven Rheometer / Poly(*N*-isopropylacrylamide) Gel / Poisson's Ratio /

Polymer gels vary the degree of swelling upon the change of circumstances. For example, hydrogels in aqueous media change the volume in response to the variation in temperature, pH, ionic strength, and so on.^{1–4} Among hydrogels, poly(*N*-isopropylacrylamide) (PNIPA) hydrogels have been paid much attention because the gels show the volume phase transition.^{1,3,4} The swollen phase emerges at low temperatures below *ca.* 35 °C, while the collapsed phase in the high temperature region. Many studies^{1–4} have been made to investigate the swelling properties of the PNIPA gels, but little is known on the properties of the gels in the collapsed state even at the present.^{5–7} Indeed the swelling properties in the swollen as well as collapsed phases have been studied by many research groups but the results were obtained through the static tests. Recently, we built up a new type of rheometer to examine the dynamic swelling properties of the PNIPA gels.⁸ In the previous paper⁸ we have reported the dynamic swelling properties of a PNIPA hydrogel using the laboratory-made rheometer as a preliminary study. The rheometer used in the study was a prototype and had several shortcomings to be improved. One major shortcoming was that the rheometer could not measure the time-dependence of the sample length in the stretching direction, causing

the uncertainty in determining the phase lag between strains parallel and perpendicular to elongation. In the present paper, we have improved this point by mounting a length-detection module on the prototype rheometer.

Kinetics of swelling of gels has been studied by many researchers. The first theory for the swelling kinetics of gels was proposed for spherical gels by Tanaka and Fillmore.⁹ The swelling of spherical gels proceeds isotropically because the spherical shape which has originally no anisotropy is automatically maintained during the swelling process. The T–F theory was developed to the swelling kinetics of long cylindrical gels with infinite length.^{10,11} The theory suggests that the anisotropic swelling process takes place because the diffusion constants in the radial and axial directions are different. This anisotropic swelling process originates from the anisotropic shape of the gels. The diffusion in the radial direction is expected to be of the longitudinal mode, the diffusion in the axial direction being the transversal mode.^{10,11} The diffusion in the longitudinal mode is faster than that in the transversal mode although the expected difference is not large.^{10,11} The improved apparatus may detect the difference in the rates between the two diffusion modes. Several studies have investigated the swelling

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behavior of gels under constant strains or stresses.⁵⁻⁷ In the present study, we have made the first experiment measuring the dimensional changes in both radial and axial directions during the stress-induced swelling. In this paper we have investigated static and dynamic swelling properties of PNIPA hydrogels in the swollen state and compared the results obtained by the dynamic tests with those by the static tests.

DEFINITION OF DYNAMIC POISSON'S RATIO

Within the framework of the infinitesimal deformation theory,¹² the Poisson ratio (μ) is defined in terms of (static) strains. Hereafter, we consider the uniaxial deformation as a simplest case. Letting $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ be respectively the strains parallel and perpendicular to elongation, μ is defined by

$$\mu = -\frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} \quad (1a)$$

In our previous paper, we adopted the above definition even for the dynamic Poisson ratio; *i.e.*, $\mu^* = -\varepsilon_{\perp}^*/\varepsilon_{\parallel}^*$. In the case of the dynamic mechanical measurements, however, it appears to be more convenient to define the (dynamic) Poisson ratio (μ^*) as

$$\mu^* = \frac{\varepsilon_{\perp}^*}{\varepsilon_{\parallel}^*} \quad (1b)$$

because the negative sign appearing in eq 1a can be absorbed in the complex number μ^* . Phase lags of $\varepsilon_{\parallel}^*$ and $\varepsilon_{\perp}^*$ from the stress wave, $\delta_{\parallel}$ and $\delta_{\perp}$ respectively, are defined with the following equations.

$$\varepsilon_{\parallel}^* = \varepsilon_{\parallel} \exp[i(\omega t + \delta_{\parallel})] \quad (2a)$$

$$\varepsilon_{\perp}^* = \varepsilon_{\perp} \exp[i(\omega t + \delta_{\perp})] \quad (2b)$$

$$\begin{aligned} \mu^* &= \frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} \exp[i(\delta_{\perp} - \delta_{\parallel})] \\ &= -\frac{\varepsilon_{\perp}}{\varepsilon_{\parallel}} \exp[i(\delta_{\perp} - \delta_{\parallel} + \pi)] \end{aligned} \quad (2c)$$

Now, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are the amplitudes of the strains parallel and perpendicular to elongation, respectively. The quantities ω and t stand for the angular frequency and time, respectively. It is clear that $-\pi/2 \leq \delta_{\parallel} \leq 0$ for viscoelastic bodies, but the range of $\delta_{\perp}$ is not explicitly clear so that we assume $-\pi < \delta_{\perp} \leq \pi$. Equation 2c leads to the relation that $|\mu^*| = \varepsilon_{\perp}/\varepsilon_{\parallel}$. Figure 1 shows a schematic representation of $\delta_{\parallel}$ and $\delta_{\perp}$ in the complex plane.

EXPERIMENTAL

Gel Samples

Poly(*N*-isopropylacrylamide) (PNIPA) gels were prepared by radical copolymerization of *N*-isopropyl-

Figure 1. A relation between $\delta_{\parallel}$ and $\delta_{\perp}$ (phase lags for $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ seeing from the stress wave, respectively) in the complex plane with $-\pi/2 \leq \delta_{\parallel} \leq 0$ and $-\pi < \delta_{\perp} \leq \pi$.

acrylamide (NIPA) and *N,N'*-methylenebis(acrylamide) (BIS). The reagents, NIPA and BIS, were dissolved in distilled water under nitrogen atmosphere. The total monomer concentration of NIPA and BIS was fixed to be 13 wt %, and the molar ratio [NIPA]/[BIS], which is a measure of the crosslink density, was also fixed to be 53. After ammonium peroxodisulfate (initiator) and *N,N,N',N'*-tetramethylethylenediamine (accelerator) were added into the solution, the pregel solution was transferred into glass capillaries with the inner diameter of $\sim 500 \mu\text{m}$ and then the gelation was performed. The time for gelation was settled to be 24 h. The cylindrical gel samples were removed from the capillaries and were poured into hot distilled water ($\sim 50^\circ\text{C}$) to eliminate the unreacted reagents. Two gel samples were used for the mechanical tests: One is used for the measurements in water and the other for the measurements in liquid paraffin. Both have the same total monomer content and [NIPA]/[BIS] ratio. The length and diameter of the gel samples at 25°C were *ca.* 20 mm and *ca.* 400 μm , respectively.

Apparatus

A laboratory-made magnetic force-driven (namely, a stress-controlled type) rheometer was used to investigate the static and dynamic swelling properties of the PNIPA gels. The rheometer was originally made in the previous study,⁷ where one emission-detector unit was employed to determine the time dependence of diameter. The rheometer was improved to determine the change of length as well as diameter in this study. The outline of the apparatus is shown in Figure 2. A metal (tungsten carbide) sphere was glued to one end of the gel using a cyanoacrylate-type adhesive. The gel with the metal sphere was put in a glass-made solvent bath comprising inner and outer compartments. The inner compartment, where the gels were immersed, was filled with a surrounding solvent: water (W) or liquid paraffin (LP). However, the solvent

Figure 2. Schematic representation of magnetic force-driven rheometer. FG; function generator; Amp; power amplifier; E; emitter part of laser scan micrometer; D; detector of laser scan micrometer; DR; Digital Recorder.

in the gels (“inside solvent”) was water throughout. The outside solvent LP is a non-solvent for the PNIPA gels.

Temperature-controlled water was circulated in the outer bath to keep temperature constant throughout the experiments. Magnetic force was applied to the metal sphere by controlling the current in the coil. The current wave was generated by a NF power amplifier (4010 High Speed Power Amplifier/Bipolar Power Supply) based on the voltage-wave designed by a Yokogawa function generator (FG200). The static stress acting to the gels is originated from DC in the coil, while the dynamic stress comes from AC. The dimension of the gels was measured as a function of time (t) by two sets of emission-detector units (Laser Scan Micrometer; Keyence, LS5500): One monitored the diameter and the other monitored the position of the metal sphere from the bottom of the bath (namely, the length of the gels). The wave-form data from the output of the detectors were recorded with a Yokogawa analyzing recorder (AR1100A) together with the wave-form data of the current in the coil. The swelling of the gels were equilibrated at 25 °C before the measurements, and thereafter the gels were transferred to the solvent bath of the rheometer. Details of the experimental conditions are the same as the previous paper.⁷

RESULTS AND DISCUSSION

Static Properties

Figure 3 shows the time dependence of dimensions of the gel sample in water after the imposition of the magnetic force. The gel remained in equilibrium ($l = 18.1$ mm and $d = 410$ μ m) in water by the weight of the metal sphere before the application of the mag-

Figure 3. Time (t) dependence of (a) length l and (b) diameter d of the PNIPA gel in water after the imposition of the magnetic force.

netic force. When DC is applied to the electromagnet at $t = 0$, the length l increases (Figure 3a) and the diameter d decreases (Figure 3b) instantaneously ($l = 19.5$ mm and $d = 393$ μ m). This must correspond to the usual elastic-deformation without swelling, because the value of Poisson's ratio in the instantaneous deformation was ~ 0.47 , as will be shown later. As can be seen from the figure, however, l and d change with t in the region of t up to ~ 200 s. These dimensional changes with t suggest that the stress-induced swelling¹⁰ occurs for the gel in water, because d increases with t in spite of the increase of l . Figure 4 shows the semi-logarithmic plots of l and d against t . Here, l_0 and l_∞ represent l at $t = +0$ (just after deformation) and $t \rightarrow \infty$, respectively. The quantities d_0 and d_∞ also have the same meanings as l_0 and l_∞ . In both plots, the data points appear to fall on a

Figure 4. Semi-logarithmic plots for (a) $(l_\infty - l)/(l_\infty - l_0)$ and (b) $(d_\infty - d)/(d_\infty - d_0)$ as a function of time (t). Here, l_0 and l_∞ represent l at $t = +0$ (just after deformation) and $t \rightarrow \infty$ in Figure 3, respectively. The quantities d_0 and d_∞ also have the same meanings as l_0 and l_∞ . The straight lines represent approximation of single-exponential.

straight line, indicating the t -dependence is approximated to be single-exponential for the length as well as the diameter. A relaxation time for the stress-induced swelling (τ) is evaluated from the slope of each line: $\tau \approx 85$ s for the length; $\tau \approx 70$ s for the diameter. The values of τ for the length and diameter should be considered identical in view of the experimental error in estimating τ , and thus the relaxation time in both directions is evaluated to be about 80 s.

As stated before, a theory^{10,11} predicts that the diffusion constants in the radial and axial directions differ for infinitely long cylindrical gels: The change in diameter by stress-induced swelling is governed by the longitudinal mode while the change in length

Figure 5. Time (t) dependence of Poisson's ratio (μ) obtained from the static test. Here, $\mu = -\Delta\varepsilon_\perp/\Delta\varepsilon_\parallel$ with $\Delta\varepsilon_\perp = \varepsilon_\perp(t) - \varepsilon_\perp(t = -0)$ and $\Delta\varepsilon_\parallel = \varepsilon_\parallel(t) - \varepsilon_\parallel(t = -0)$. The time at $t = -0$ stands for the time just before elongation by the magnetic force in Figure 3.

being by the transversal mode. On the basis of the theory, the ratio of the two diffusion constants (D_L/D_T), *i.e.*, the ratio of the relaxation times for the swelling in the two directions, is given by $D_L/D_T = 2(1 - \mu_\infty)/(1 - 2\mu_\infty)$, where μ_∞ is the equilibrium Poisson ratio.^{10,11} As will be shown later, the gel samples used in this study show $\mu_\infty = 1/5$ – $1/4$, giving the ratio D_L/D_T of $8/3$ – 3 . This indicates that the two modes of relaxations are distinguishable in principle. The relaxation times for l and d in the present experiments were identical within experimental error. The reason for the disagreement of the theoretical prediction and the experimental results is unclear at present. The aspect ratio in the present experiments ($l_0/d_0 \approx 30$) may still be insufficient to satisfy the condition of the infinite aspect ratio assumed in the theory. The theory does not give what value of aspect ratio is needed to observe the anisotropic swelling process. Further experiments using the gels with larger aspect ratios are needed to settle this issue.

In Figure 5 μ is plotted against t for the PNIPa gel in water. In this plot μ was defined by $\mu = -\Delta\varepsilon_\perp/\Delta\varepsilon_\parallel$ with $\Delta\varepsilon_\perp = \varepsilon_\perp(t) - \varepsilon_\perp(t = -0)$ and $\Delta\varepsilon_\parallel = \varepsilon_\parallel(t) - \varepsilon_\parallel(t = -0)$. The time at $t = -0$ stands for the time just before elongation by the magnetic force. This definition is a little different from the conventional one, but μ in the above definition is known to give the same value as from the conventional one as long as the deformation is small. Actually, the strains parallel to elongation in the present experiment never exceeded 20%, satisfying the condition of small deformation. At $t \approx 0$ μ lies around 0.47, and then μ decreases with increasing t . The value of μ at short

Figure 6. Angular frequency (ω) dependence of the dynamic strain amplitudes $\varepsilon_{||}$ and $\varepsilon_{\perp}$ for the PNIPA gel in water (●; $\varepsilon_{||}$; ■; $\varepsilon_{\perp}$) and in liquid paraffin (○; $\varepsilon_{||}$; □; $\varepsilon_{\perp}$).

times corresponds to the Poisson ratio as a material constant without swelling. The curve levels off at $t \approx 200$ s and the leveled-off value corresponding to the equilibrium Poisson ratio is estimated to be ~ 0.2 , clearly indicating that stress-induced swelling occurs in the gel in water and the time profile of μ is almost the same as those of l and d (Figure 3).

Dynamic Properties

Figure 6 shows the plots of dynamic strain amplitudes ($\varepsilon_{||}$ and $\varepsilon_{\perp}$) against ω for the PNIPA gel in W and LP. The gel in LP shows ω -dependence neither for $\varepsilon_{||}$ nor for $\varepsilon_{\perp}$, just behaving as a soft elastic body like a rubber. For the gel in W, however, a finite ω -dependence is observed in both $\varepsilon_{||}$ and $\varepsilon_{\perp}$; namely, $\varepsilon_{||}$ increases and $\varepsilon_{\perp}$ decreases with decreasing ω . Using $\varepsilon_{||}$ and $\varepsilon_{\perp}$, we can calculate the absolute value of the dynamic Poisson ratio ($|\mu^*|$). In Figure 7 $|\mu^*|$ is plotted against ω for the gel in W and LP. The curve indicates that no stress-induced swelling occurs for the gel in LP in the entire range of ω because the constant value estimated is ~ 0.47 , close to 0.5, which agrees well with the value obtained from the static experiments in the short time limit. On the other hand, μ of the gel in W is strongly ω -dependent. At high frequencies at $\omega > 0.1 \text{ s}^{-1}$, μ is close to 0.5 similarly to μ in LP because the time scale for the sinusoidal force ($\sim \omega^{-1}$) is sufficiently shorter than the characteristic time for stress-induced swelling (τ), *i.e.*, no occurrence of the stress-induced swelling. At frequencies at $\omega < 0.1 \text{ s}^{-1}$ where ω^{-1} is comparable to τ , the ω -dependence of μ becomes pronounced due to the emergence of the stress-induced swelling effect. The stress-induced swelling is equilibrated throughout

Figure 7. Angular frequency (ω) dependence of the absolute value of the dynamic Poisson ratio ($|\mu^*| = \varepsilon_{\perp}/\varepsilon_{||}$) for the gel in water (●) and in liquid paraffin (○).

Figure 8. Angular frequency (ω) dependence of the loss tangent of the phase lags $\tan \delta_{||}$ and $\tan \delta_{\perp}$ in water (●; $\tan \delta_{||}$; ■; $\tan \delta_{\perp}$) and in liquid paraffin (○; $\tan \delta_{||}$; □; $\tan \delta_{\perp}$). The values $\delta_{||}$ and $\delta_{\perp}$ are the phase lags of $\varepsilon_{||}^*$ and $\varepsilon_{\perp}^*$ seeing from the stress wave, respectively.

the oscillation at low ω ($< 0.01 \text{ s}^{-1}$) where ω^{-1} is much longer than τ , with the result that $|\mu^*|$ shows level-off. The leveled-off value of $|\mu^*|$ at low ω lies about 0.25, which is rather close to the value of μ obtained by the static measurements in the long time limit ($\mu \approx 0.2$).

Figure 8 shows the loss tangent of the phase lags ($\tan \delta_{||}$ and $\tan \delta_{\perp}$) as a function of ω . In LP, both of the loss tangents are almost the same and are constant independently of ω , lying around -0.1 . This non-zero value indicates that the gel is viscoelastic, and $\varepsilon_{||}^*$

and $\varepsilon_{\perp}^*$ move with t by keeping $|\delta_{\perp} - \delta_{\parallel}| = \pi$. The PNIPA gel in W, on the other hand, shows a maximum on the $\tan \delta_{\parallel}$ vs. ω plot and a minimum on the $\tan \delta_{\perp}$ vs. ω plots, reflecting the re-swelling by the applied force. The value of ω for the maximum is very close to that for the minimum. A characteristic time for swelling in the dynamic tests defined as the inverse of ω at the maximum (equivalently, at the minimum) is evaluated to be ~ 100 s both for the $\tan \delta_{\perp}$ and $\tan \delta_{\parallel}$ curves. The value is also close to the τ determined by the static tests (~ 80 s). The agreement ensures the accuracy as well as reliability of the dynamic measurements.

We would like to emphasize again that the relaxation observed stems from swelling, not from mechanical relaxation. This is also confirmed from the fact that τ is proportional to the square of the dimension of gels. A separate similar experiment shows $\tau \approx 180$ s for the gel with the larger initial diameter ($d^0 = 0.54$ mm). The ratio of τ ($180/100$) for the two gels is close to the square of the ratio of d^0 ($(0.54/0.42)^2 \approx 1.7$). It should be noticed that in the case of mechanical relaxation, the relaxation time is independent of the sample dimensions.

The influence of large applied stress reaching the nonlinear stress-strain regime on the stress-induced swelling is also an interesting issue to investigate, which will be studied in our future study.

Acknowledgment. This research was supported in part by the 21st century COE program "COE for a United Approach to New Materials Science" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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