

SHORT COMMUNICATIONS

Dynamic Swelling Properties of a Poly(*N*-isopropylacrylamide) Gel Measured by a Magnetic Force-Driven Rheometer

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Polymer gels in solvent show an interesting response to external stimulus. For example, a gel changes the volume when mechanical stress is applied to the gel, and the rate of volume change strongly depends on the sample dimension. The volume change responding to the applied stress originates from the fact that the polymer network and solvent molecules form a thermodynamical semi-open system, and this phenomenon has been considered to be a typical example of the stress-diffusion coupling.¹ Studies on swelling kinetics of the polymer gels after the application of mechanical stimulus have been made by employing so-called static methods,^{2–5} such as continuous monitoring of the gel dimension after imposition of a step stress, and have shown that in the long time region the volume change can be written by a single exponential function; *i.e.*, a single characteristic (or, relaxation) time governs the volume change to a new equilibrium state under deformation in that time region.^{2–5} On the other hand, little is known on the swelling kinetics for the gels at short times, where a multi-exponential character is considered to become dominant for the volume change.^{3,6} Studies in terms of dynamic viscoelasticity will be very useful to give the full picture of the swelling kinetics of the polymer gels. Conventional rheometers, however, cannot be used for this purpose; the rheometers require relatively large gel specimens to detect the mechanical response but the large specimens move the relaxation time far away from the measurable frequency range of the rheometers. A new type of rheometer, applicable to very small gel specimens, is needed to investigate the dynamic swelling properties of polymer gels. In this study we have made a new apparatus to observe the dynamic swelling behavior of polymer gels, and examined the frequency dependence of the dynamic Poisson ratio for a poly(*N*-isopropylacrylamide) (PNIPA) gel. A phenomenological theory of linear viscoelas-

ticity to analyze the dynamic swelling behavior is also described briefly in this paper.

Consider a time (t) profile of strain in response to an applied elongational stress (σ) of the following form

$$\sigma = \sigma_S + \sigma_D^* \quad (1)$$

with $\sigma_D^* = \sigma_0 \exp(i\omega t)$. Here, σ_S is the magnitude of the static stress and σ_0 is the amplitude of the dynamic stress σ_D^* , ω being the angular frequency. The strain parallel to elongation ($\varepsilon_{//}$) can be divided into two components: the static and dynamic strains.

$$\varepsilon_{//} = \varepsilon_{//,S} + \varepsilon_{//,D}^* \quad (2)$$

In the steady state, σ_S and $\varepsilon_{//,S}$ are related by the following equation.

$$\varepsilon_{//,S} = \frac{1}{2(1 + \mu_\infty)G_\infty} \sigma_S \quad (3)$$

Here, μ_∞ and G_∞ are the Poisson ratio and shear modulus at equilibrium, respectively.³ Young's modulus is generally used for the uniaxial elongation. When the elongation induces the volume change due to re-swelling, however, it is convenient to separate formally the effect of volume change on deformation and the usual elasticity originating from the polymer network itself, so that the Poisson ratio and shear modulus are introduced in the above equation instead of Young's modulus. Similar to eq 3, σ_D^* and $\varepsilon_{//,D}^*$ can be connected with each other by

$$\varepsilon_{//,D}^* = \frac{1}{2(1 + \mu^*)G^*} \sigma_D^* \quad (4)$$

where μ^* and G^* are the complex Poisson ratio and shear modulus, respectively.

Hereafter, we focus on the dynamic stress-strain behavior of polymer gels in solvent. Using the strain perpendicular to elongation $\varepsilon_{\perp,D}^*$, eq 4 can be rewritten by

$$\varepsilon_{\perp,D}^* = \frac{-\mu^*}{2(1 + \mu^*)G^*} \sigma_D^* \quad (5)$$

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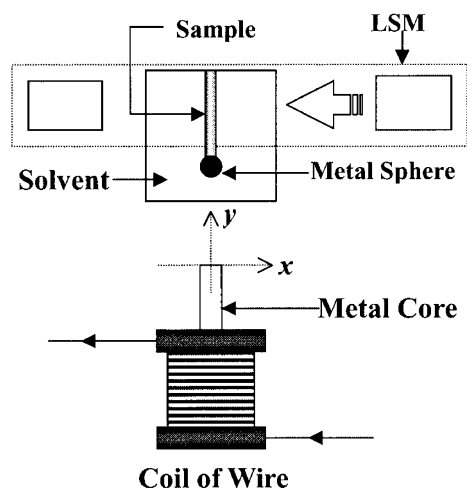


Figure 1. Schematic representation of a magnetic force-driven rheometer.

because $\varepsilon_{\perp,D}^* = -\mu^* \varepsilon_{//,D}^*$. Setting $\varepsilon_{\perp,D}^* = -\varepsilon_0 \exp(-i\omega t + \delta)$ with an amplitude $\varepsilon_0 (> 0)$, then δ is given by

$$\delta = \arg \frac{\mu^*}{2(1 + \mu^*)G^*} \quad (6)$$

and the absolute value of $\mu^*/2(1 + \mu^*)G^*$ is given by

$$\left| \frac{\mu^*}{2(1 + \mu^*)G^*} \right| = \frac{\varepsilon_0}{\sigma_0} \quad (7)$$

The quantities δ and $|\mu^*/2(1 + \mu^*)G^*|$ are connected with each other through a Kramers–Kronig relation⁷ as follows:

$$\left| \frac{\mu^*}{2(1 + \mu^*)G^*} \right| = \exp\left(\frac{2}{\pi} \int_0^\infty \frac{s\delta(\omega)}{s^2 - \omega^2} ds\right) \quad (8)$$

A cylindrical PNIPA hydrogel was prepared by radical copolymerization of *N*-isopropylacrylamide [NIPA] and *N,N'*-methylene-bis(acrylamide) [BIS] in a capillary using ammonium peroxodisulfate as an initiator and distilled water as a solvent. In the reaction *N,N,N',N'*-tetramethylethylenediamine was used as an accelerator. The total monomer concentration (c_0) was 13 wt%, and the molar ratio [NIPA]/[BIS] was settled to be 53. The pregel solution was poured into a glass tube and the gelation was performed around 20 °C for 12 h. After gelation was completed the gel specimen was removed from the glass tube, and the gel was then immersed into distilled water and kept for 2 d to wash out residual agents. The diameter and length of the specimen at 23 °C were 540 μm and 21 mm, respectively.

Dynamic swelling experiments were carried out using a laboratory-made apparatus shown in Figure 1. A metal (tungsten carbide) sphere with diameter of 2.4 mm was fixed on one end of the cylindrical hydrogel specimen by using a commercially available adhesive, and the specimen was put into a solvent bath. A coil

of wire with a metal core was placed below the solvent bath. The solvents used were distilled water and liquid paraffin. Water is a good solvent for PNIPA, but liquid paraffin is a non-solvent for PNIPA and is also immiscible with water. The temperature of the solvent was controlled to be 23 °C. The current in the coil, synthesized by a function generator (Yokogawa, FG200) and then amplified by a power amplifier (NF, 4010 High Speed Power Amplifier/Bipolar Power Supply), generates an electromagnetic field. The force exerting on the metal sphere is a function of current I as well as position of the sphere \mathbf{r} . The applied current I had the form of

$$I(t) = A \sin \omega t + B \quad (9)$$

Here, A and B are constants with $B/A \approx 1$. The DC component was applied in order to stretch the gel specimen to small extent. For both solvents, the displacement of sphere due to the metal weight and DC was *ca.* 2 mm (*ca.* 10% in elongational strain). We neglected the position dependence of the alternative force because the displacement due to the alternative force was *ca.* ± 1 mm (which corresponds to the dynamic strain amplitude of *ca.* 5%). Since a swollen PNIPA gel with $c_0 = 10$ wt% showed the linear stress–strain behavior up to $\varepsilon_{//} = 0.35$,⁸ we assumed here that all mechanical measurements were made in the linear viscoelasticity regime although the total maximum strain reached to *ca.* 15%. In this case, the force F (or, the dynamic engineering stress acting on the gel) can be regarded to be proportional to I . The t -profile of diameter for specimen was monitored by a laser scan micrometer (LSM; Keyence, LS5500). The ω -scan was carried out from high to low ω , and at each ω a stationary part in the diameter curve was used for calculation. The measurements were made twice and the reproducibility was checked. The t -dependence curve of diameter was decomposed into Fourier series and the fundamental components were compared with the current wave to analyze the dynamic swelling properties of the gel by a combination of 2-channel analyzing recorder (Yokogawa, AR1100A) and PC.

The ω -dependence of the amplitude ε_0 for the gel specimen is demonstrated in Figure 2. Although the data points are a little scattered, ε_0 for liquid paraffin is almost independent of ω , remaining around 0.02. This means that nothing happens for the gel in liquid paraffin; *i.e.*, the gel cannot swell the solvent because liquid paraffin is a non-solvent for PNIPA. We have reported that the Poisson ratio of PNIPA gels (in a swollen state) as a material constant (μ_0) is ~ 0.45 .⁵ Combining the values of μ_0 and ε_0 , the dynamic strain amplitude parallel to oscillation $|\varepsilon_{//,D}^*|$ can be estimated to be 0.044, independently of ω . The value of ε_0 for water remains

constant, lying in the same level as for liquid paraffin, in the high ω region, indicating that the gel cannot swell in this time scale ($\sim 1/\omega$) even in water. The curve starts to decrease at about $\omega = 1 \times 10^{-3} \text{ s}^{-1}$ as ω decreases further. The decrease of ε_0 corresponds to the reduction of $|\mu^*|$, which means the increase of volume, with decreasing ω . In the low ω region the data points appear to give again a leveled-off value of 0.012, which leads the Poisson ratio of 0.27 if $|\varepsilon_{//,D}^*| = 0.044$ is used. The Poisson ratio estimated at the low ω limit is close to that reported as the equilibrium Poisson ratio for PNIPA gels (~ 0.25)⁵ and the low value of the Poisson ratio indicates that the hydrogel re-swells by the application of alternative tension.

Figure 3 shows the ω -dependence curves of $\tan \delta$ for the PNIPA gel. No ω -dependence is observed for liquid paraffin, supporting the result in Figure 2 that

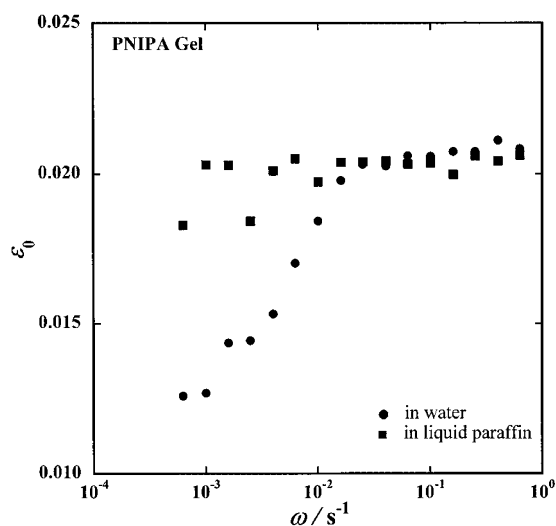


Figure 2. Angular frequency (ω) dispersion curves of ε_0 in liquid paraffin and in water.

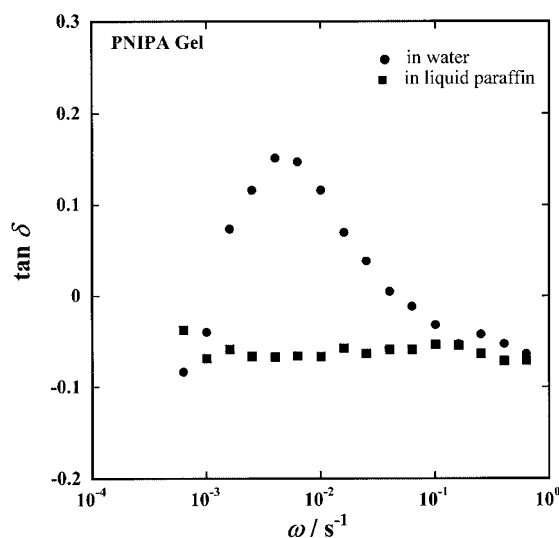


Figure 3. Angular frequency (ω) dispersion curves of $\tan \delta$ in liquid paraffin and in water.

the gel in the solvent does not re-swell even if the mechanical stress is applied to the gel. In liquid paraffin, the value of $\tan \delta$ must be determined by the ratio of G'' (loss modulus) to G' (storage modulus) of the network itself as in the case of usual viscoelastic bodies, although the current values become negative resulting from the introduction of δ to the strain part. The curve for water, on the other hand, shows a dispersion peak around $\omega = 5 \times 10^{-3} \text{ s}^{-1}$, which corresponds to the central domain of the ε_0 curve for water showing a large change. This indicates that the peak originates from the re-swelling of the gel specimen. The value of ω at the peak also gives a relaxation time (τ), defined as a reciprocal of ω at the peak position, of $2 \times 10^2 \text{ s}$, which agrees well with the longest relaxation time estimated from the static swelling experiment for the gel although we do not show the detailed data here. At the high ω limit, the value of $\tan \delta$ for water coincides with that for liquid paraffin because the gel cannot swell in this time scale. The $\tan \delta$ value for water also agrees with that for liquid paraffin at low ω . This may mean that the fully “re-swollen” gel can respond to the sinusoidal stress without phase lag.

Since the same current profile was applied in both experiments (in liquid paraffin and in water), a ratio of the dynamic strain in water to that in liquid paraffin (α^*) is given from eq 5 by

$$\alpha^* \equiv \alpha' + i\alpha'' = k_0 \left(\frac{\mu^*}{1 + \mu^*} \right) \quad (10)$$

if we assume that $G^*(\omega)$ is identical in both solvents. Here, $k_0 = (1 + \mu_0) / \mu_0 \approx 3.2$ (for $\mu_0 = 0.45$). The quantity G^* in water is basically changed with ω due to re-swelling, because the re-swelling lowers the polymer concentration (c) in the gel, which may consequently

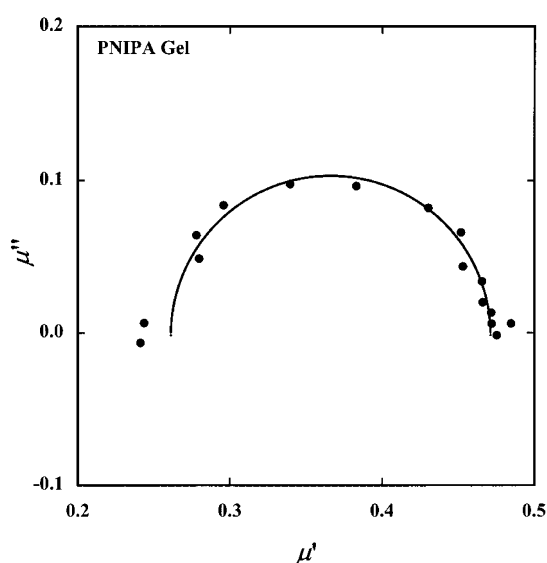


Figure 4. A Cole–Cole plot for μ^* for the PNIPA hydrogel.

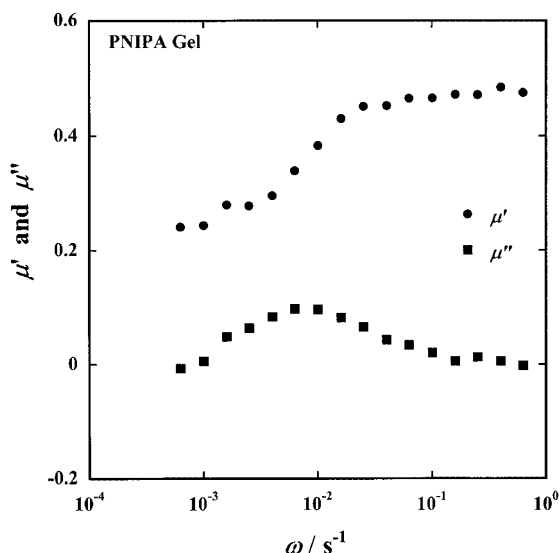


Figure 5. Angular frequency (ω) dispersion curves of μ' and μ'' for the PNIPA hydrogel.

reduce $|G^*|$ as $|G^*| \sim c^{1/3}$.⁹ However, when the degree of re-swelling is small, as is the case of this study (the degree of re-swelling by the static stress estimated by $(1-2\mu_\infty)\varepsilon_{//,S}$ lying around 0.02 in this study), the assumption that $G^*(\omega)$ is common for both solvents must be valid.

Eq 10 can be re-arranged by

$$\mu^* = \frac{\alpha^*}{k_0 - \alpha^*} \quad (11)$$

This means that the dispersion of α^* can be converted to that of μ^* , corresponding to a conformal mapping of α^* to μ^* . Figure 4 shows a Cole–Cole plot for μ^* . The curve in this figure corresponds to a half circle. The

data points fall on the curve, indicating that μ^* relaxes almost in a single mode of the Debye-type. This leads the following expression for μ^* .

$$\mu^* = \mu_0 + \frac{\mu_\infty - \mu_0}{1 + i\omega\tau} \quad (12)$$

It should be noted that in our notation $\mu_0 = \mu'(\omega \rightarrow \infty)$ and $\mu_\infty = \mu'(\omega = 0)$. The relaxation time τ in above equation may correspond to the longest relaxation time observed in the static swelling experiments. Finally, the ω -dispersion curves of μ' and μ'' are demonstrated in Figure 5. The shape of μ' curve resembles that of the ω -dispersion curve of ε_0 in Figure 2, the shape of μ'' being similar to that of the $\tan \delta$ curve in Figure 3.

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