Macromolecules **2002,** *35,* 857−860

Slow Relaxation of the Elastic *N*-Isopropylacrylamide Gel

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Received July 5, 2001; Revised Manuscript Received October 6, 2001

ABSTRACT: The tensile moduli of *N*-isopropylacrylamide (NIPA) gels having various cross-linking degrees, q, are measured at temperatures crossing over the volume phase transition temperature. The moduli increase with rising temperature to exhibit a transition at the volume phase transition temperature. The relaxation of the tensile modulus, $Y(t)$, of the shrunken gel can be fitted to $Y(t) = (Y_i - Y_e)(1 + t/\tau_1)^{-\beta} + Y_e$, which can be theoretically explained by a gel model consisting of dangling chain ends in cross-linking networks with topological constraints. The experiments show that the β value is proportional to $q^{0.4}$ and that the τ_1 and $(Y_i - Y_e)$ values are independent of q.

1. Introduction

The *N*-isopropylacrylamide (NIPA) gel is known to exhibit a volume phase transition with a change of temperature which has been intensively investigated.[1] The cooperative dehydration of the chain (divesting the hydrophobic isopropyl group of the clustered water molecules) coupled with the entropic force of chains, which shrinks the gel, induces the volume phase transition.[2] The dehydration is induced by the destabilization of the clustered water molecules surrounding the isopropyl group when their chemical potentials exceed that of the bulk water. The volume phase transition behavior of NIPA gel induced by the addition of salt[3,4] or saccharide[5] molecules to the solution surrounding the gel has been explained by the dehydration mechanism mentioned above.[6] The polymer chain is regarded as a copolymer composed of hydrated and dehydrated units, whose ratio changes with a change in the physicochemical condition such as temperature.

The gel in the swollen state can be considered to be similar to a semidilute polymer solutions in a good solvent. In the shrunken gel, most of water molecules are repelled from the gel. Therefore, the cross-linked and dangling chains in the shrunken gel are highly entangled with each other. Our knowledge is very poor about the mechanical properties due to the entanglement. As far as we know, little work has been done after Hirotsu's report[7] on the elastic anomaly for the volume phase transition of NIPA gels. The present study aims to clarify the elastic properties of the shrunken NIPA gel. We found that the tensile force responding to an elongation of the shrunken NIPA gel relaxed approximately according to a power function of t, $(t/\tau_1)^{-\beta}$, where t was the time following the elongation. It was also found that the β values depended on the cross-linking degree of network, q. The power function of t is interpreted as the relaxation of constraints of entangled dangling chains in the network.

2. Experiment

The NIPA gels were prepared by the radical copolymerization in aqueous solution of 1 M NIPA monomer and q M *N,N′*-methylenebis(acrylamide) (q = 0.00125, 0.0025, 0.005, 0.01, and 0.015) for 24 h at 5 °C. The polymerization was initiated by ammonium persulfate and accelerated by *N,N,N′,N′*-tetramethylethylenediamine. The rodlike gels synthesized in glass tubes (i.d. = 0.3 mm) were taken out of the tube, rinsed thoroughly, and dried. The NIPA monomer was purified by recrystallization from the mixture of *n*-hexane and toluene. All chemicals used were of reagent grade.

Figure 1 schematically shows an apparatus for the tensile force measurement of the rod gel. The electric resistance of a strain gage (AE-801 Capto Co., Norway), such as was used for measuring the tensile force of skeletal muscle fiber,[8] was transformed to the electric voltage which was monitored with a computer-aided instrument. A linear relation between the force and the voltage was checked before setting up the instrument. The force from 0.1 to 2000 dyn could be monitored with a time resolution of 0.1 ms using the present instrument. A rod gel was inserted into two platinum rings, each of which connected to the sensor and a translational stage through a platinum wire. For embedding the gel between the rings during measurements, the stoppers were made of silk strings carefully winding around the gel at its ends. The elongation length of the gel was adjusted with an accuracy of 10 μm by sliding the translational stage. The gel was elongated after equilibrating with the solution, and the tensile force was recorded with the computer-aided instrument after elongation. The temperature of the solution was controlled within 0.1 °C. The gel was elongated by a given distance (typically a few hundred micrometers) within 0.2 s. The force was found to decay to a constant tensile force, F_e, for about 500 s after the elongation. During the measurement, the holding gel was immersed in the solution. Figure 2 shows a plot of F_e against the distance between the rings. An inflection point gives a natural length of the gel, l_0. A linear relation between the l_0 and the radii of the tensile force free gel, r_0, at various temperatures was exhibited to pass through the origin. This indicates the spatial isotropy of the tensile force free gel. The Young's moduli Y_i at initial and Y_e at equilibrium are respectively obtained by using

$$Y_i = \frac{\lambda F_i}{\pi r_0^{\,2}(\lambda - 1)} \tag{1}$$

and

$$Y_e = \frac{\lambda F_e}{\pi r_0^{\,2}(\lambda - 1)} \tag{2}$$

Here λ is an elongational ratio defined as $\lambda = l/l_0$. The typical λ value was about 1.1 in the present experiment. The difference between the observed radii of the gels before and after the elongation was compatible with an experimental error. Variations of the observed Y_i and Y_e values were within 10% when λ values changed from 1.05 to 1.2. It should be mentioned that

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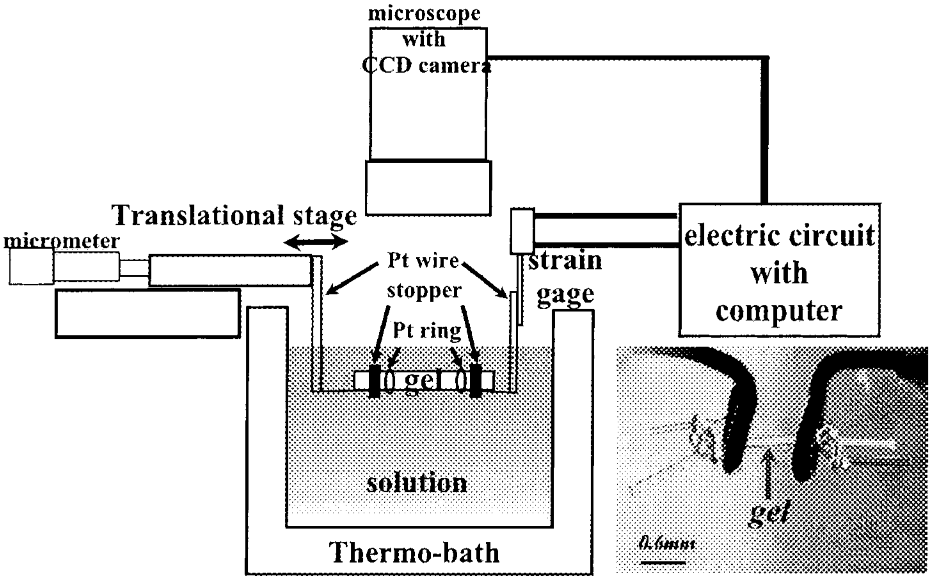

Figure 1. Schematic figure of the tension meter. The tensile force is measured by a strain gauge, which is monitored by a computer. Two platinum rings, which connect to the strain gauge and a translational stage, support a rod gel, at the ends of which knots are made of silk strings as stoppers in elongating it. The gel length is controlled by sliding the translational stage. The size of the gel is measured by using a computer-aided camera combined with a microscope. The temperature of the solution is controlled within 0.1 °C.

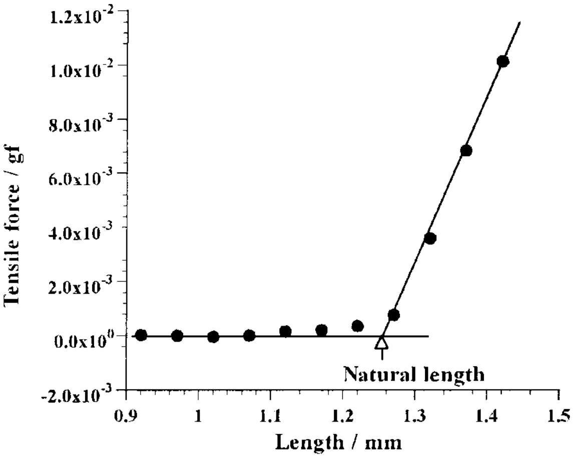

Figure 2. Equilibrating tensile force and the distance between the rings. An arrow indicates a natural length of the gel, l_0.

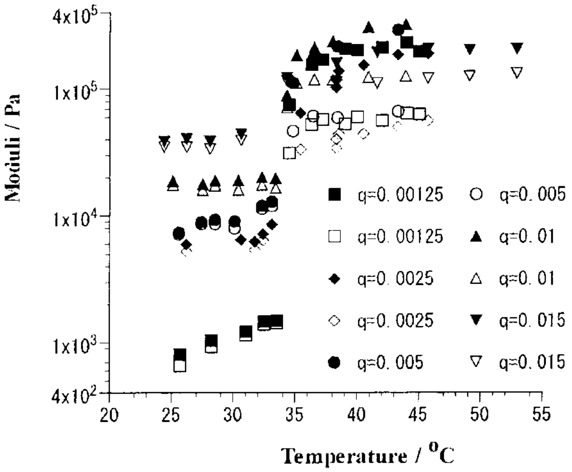

Figure 3. Young's moduli as functions of the temperature. The closed and open symbols represent the Young's moduli Y_i at the initial and Y_e at the equilibrium, respectively.

the Y_e value obtained from the tensile force coincided with the Y_e value obtained from the slope in Figure 2.

3. Results

The values of Y_i and Y_e plotted against the temperature are shown in Figure 3. The moduli of the swollen gels increase monotonically with temperature. An increase in the degree of dehydration of chain due to decreasing the chemical potential of water molecules induces an increase in the elasticity with temperature. The moduli jump up at the volume phase transition points of gels as shown in Figure 3. The transition in moduli is a reflection of the transition in the degree of dehydration of the chains. It should be mentioned that the measured values of Y_i and Y_e for the apparently opaque gel during the transition from the swollen to the shrunken states were less than half of those of the shrunken gel shown in Figure 3. The Y_i value of the shrunken gel increases dramatically for about 40 °C above the transition temperature and then levels off above that, while the changes in the Y_e value with temperature are very small, as shown in Figure 3.

The decaying functions from Y_i to Y_e for the shrunken gels are different from those for the swollen gels. Figure 4 shows the log−log plots of the normalized relaxation moduli, $\Delta Y(t)/\Delta Y(0)$, of the shrunken gels at about 42 °C against time t after the elongation, where $\Delta Y(t) = Y(t) - Y_e$. The relaxation force decays according to a power function of t, $(t/\tau_1)^{-\beta}$, at t larger than 0.2 s. Figure 5 shows the semilog plot of normalized relaxation moduli, $\Delta Y(t)/\Delta Y(0)$, of the swollen gel ($q = 0.01$; diameter $= 250$ μm) at 33.4 °C against the time t. A decay function of the relaxation force has the appearance of an exponential of t, $e^{-\Gamma t}$, although the data shown in Figure 5 fluctuate because of the small $\Delta Y(t)$ values.

4. Discussion

The elastic force decay of the power function of t is similar to the stress relaxation of an elastomer,[9] which

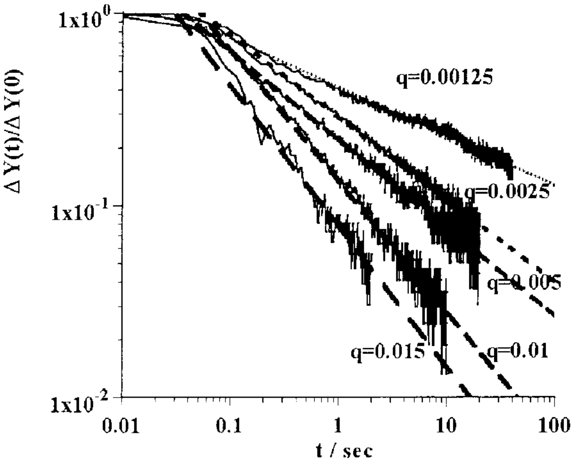

Figure 4. Relaxation behavior of Young's moduli of the shrunken gels at about 42 °C. The ordinate is the normalized relaxation moduli, $\Delta Y(t)/\Delta Y(0)$, where $\Delta Y(t) = Y(t) - Y_e$. Broken lines represent the functions of $(t/\tau_1)^{-\beta}$.

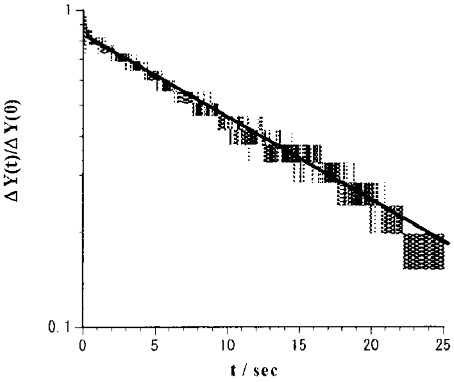

Figure 5. Relaxation behavior of Young's moduli of the swollen gel ($q = 0.01$; diameter = 250 μm) at 33.4 °C. The ordinate is the normalized relaxation moduli, $\Delta Y(t)/\Delta Y(0)$, where $\Delta Y(t) = Y(t) - Y_e$. A solid line represents the function of $e^{-\Gamma t}$.

is described as $E(t) = E_\infty[1 + (t/\tau_1)^{-\beta}]$. Pincus et al.[10] have assigned the relaxation to the liberation of dangling chains from the topological constraints in the network. There should exist dangling chains in the present gel. We are tentatively regarding the relaxation of the tensile force of the shrunken gel as due to the liberation of stress of dangling chains. When the gel is elongated, the dangling chain is deformed as shown by a faint bold line in Figure 6b. The deformation of the dangling chains induces the strong tensile force of the network. The dangling chains can reptate in the network and liberate the stress as depicted by a bold line shown in Figure 6c, because its one end is un-cross-linked. In the shrunken gel network, a time, t, for l units of the deformed dangling chain having n units to reach equilibrium is given by $t = \tau_1 \exp(\alpha l)$ according to the reptation model proposed by de Gennes,[11] where τ_1 and α, respectively, are a primary time of the reptation and a characteristic density of the mesh which constrains the dangling chains. Since the equilibrating part of the dangling chains provides little stress to the network, the stress induced by the dangling chains deformed initially can be given by some function of $n - l(t)$, $g(n - l(t))$. Here $l(t) = \alpha^{-1} \ln(t/\tau_1)$. The existing probability of the dangling end having n units $P(n)$ is approximately given as $P(n) = q(1 - q)^{n-1}$. Therefore, the relaxation modulus, $E_d(t)$, of the gel with a dangling chain density of ν_d can be given by

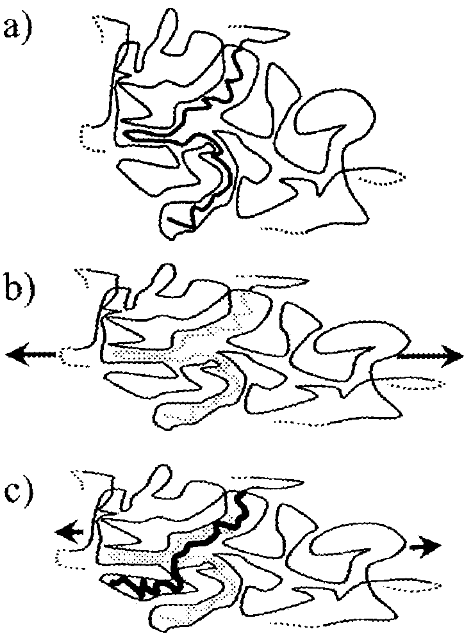

Figure 6. Schematic picture of the model consisting of dangling chain ends in the network with topological constraints. (a) A dangling chain (a bold line) is entangled with the other chains before applying the tensile force. (b) The dangling chain (a bold faint line) is deformed together with the surrounding chains just after applying the tensile force. (c) The deformation of dangling chain (a bold faint line) is relaxing (a bold thick line) to reach a new stress-free state.

$$E_d(t) = (\nu_d)^{2/3} \sum_{n=l(t)}^{\infty} P(n)\, g(n - l(t))/(\lambda - 1) \approx (\nu_d)^{2/3} \langle g \rangle/(\lambda - 1)(t/\tau_1)^{-q/\alpha} \quad (3)$$

where

$$\langle g \rangle = q(1 - q)^{-1} \sum_{m=1}^{\infty} g(m)(1 - q)^m \quad (4)$$

and $\langle g \rangle$ is proportional to $\lambda - 1$. Equation 3 is valid at t larger than τ_1 and $E_d(0) = (\nu_d)^{2/3}\langle g \rangle/(\lambda - 1)$ since $l(0) = 0$. The tensile force is a sum of the stresses due to the deformed cross-linked chains and the dangling chains described above. Accordingly the modulus is the sum of E_C and $E_d(t)$. Therefore, the following relations can be obtained:

$$Y_i = E_C + E_d(t{=}0) \quad (5a)$$

$$Y_e = E_C \quad (5b)$$

$$\beta = q/\alpha \quad (5c)$$

The values of $\Delta Y = Y_i - Y_e$ are plotted against temperature for the gels with various q values and are shown in Figure 7. It is obvious that the ΔY value of the shrunken gel is much larger than that of the swollen gel and independent of the q value. The ΔY value of the swollen gel depends on the q value as shown in Figure 7. This difference of the q value dependence indicates the difference in the mechanisms to induce the ΔY of the swollen and the shrunken gels. The different mechanisms can be also inferred from the difference in the relaxation functions shown in Figures 4 and 5.

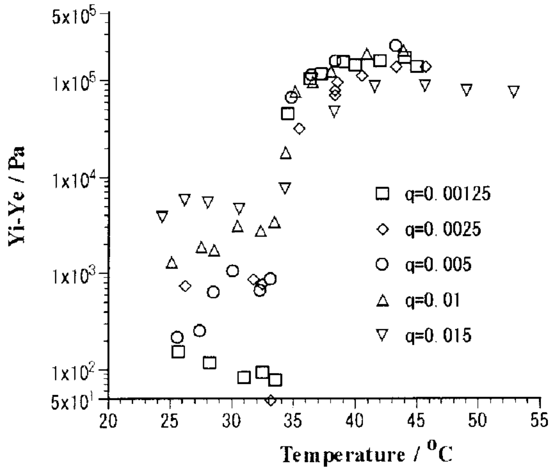

Figure 7. Temperature dependence of relaxing moduli $Y_i - Y_e$.

The q-independence of ΔY for the completely shrunken gel shown in Figure 7 indicates that $(\nu_d)^{2/3}\langle g\rangle$ in eq 3 is independent of q. The ν_d is considered to be proportional to q, since the observed gel volumes in the shrunken state are scarcely dependent on q. Then $\langle g\rangle$ should be proportional to $q^{-2/3}$. From eq 4 we can infer the proportionality of $g(m)$ to $q^{1/3}$ with assuming the proportionality of $g(m)$ to m, which makes the summation term in eq 4 proportional to $(1 - q)q^{-2}$. However, more experiments are needed for establishing the q independence of ΔY.

Figure 8 shows the plots of β and τ_1 against q. It is observed that β is approximately proportional to $q^{0.4}$ and that τ_1 is independent of q. On the basis of eq 5c, the former relation indicates $\alpha \propto q^{0.6}$. It is plausible that the characteristic mesh density α effectively increases with the cross-link density, which is proportional to q.

It is remarkable that the slowly decaying relaxation in the moduli of swollen gel can be described by the function $e^{-\Gamma t}$ as shown in Figure 5. The characteristic time of the decay Γ^{-1} is about 16 s. We might mention that Γa^2 is about 10^{-9} m^2 s^{-1}, where a is a radius of the rod gel. The value of 10^{-9} m^2 s^{-1} is close to the diffusion coefficient of a water molecule, $(2-3) \times 10^{-9}$ m^2 s^{-1}. This suggests that the elastic relaxation of the swollen gel is related to the diffusion of water molecules. However, further experiments are needed for assigning the relaxation mechanism.

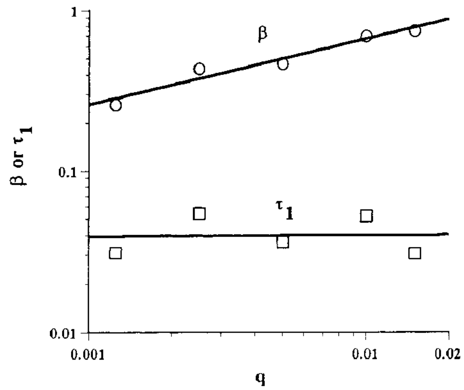

Figure 8. The q dependence of β and τ_1. The solid line on the symbols of circle represents a function of $q^{0.4}$.

Acknowledgment. The authors are very grateful to Professor K. Tawada of Kyushu University in Japan, Professor N. Thomas of University of Birmingham in UK, Professor M. Kawai of Iowa University in USA, and Dr. S. Kamimura of Tokyo University in Japan for their kind advice and help in constructing the apparatus for tensile force measurements. S. Koga is grateful to The Research Fellowship of Japan Society for the Promotion of Science for Young Scientists for partial financial support.

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