

Osmotic Poisson's Ratio and Equilibrium Stress of Poly(acrylamide) Gels

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(Received May 31, 1996)

KEY WORDS Polymer Gel / Swelling under Elongation / Osmotic Poisson's Ratio / Equilibrium Stress /

Polymer gels have been recognized as a unique and interesting soft material, and the physical and mechanical properties of polymer gels have been investigated by many researchers.^{1–3} Experimental and theoretical studies, especially, on the volume phase transition¹ and swelling kinetics,^{1,2} have been carried out intensively. The physical properties of polymer gels have become clear. We have already shown⁴ that the swelling kinetics of polymer gels can be written by two types of diffusion equations, *i.e.*, the equations of longitudinal and transverse modes. The former determines the time evolution of the volume of gels from the initial to final state, and the latter the time dependence of the change of shape. We also found that the uniaxially stretched gel in solvent swells gradually until equilibrium under the deformation is attained.⁴ When a gel sample is deformed quickly in solvent, the state just after the application of the strain, which we call hereafter the initial state, must be determined by the material nature of the gel used. For example, in the case that a gel specimen is stretched uniaxially, the initial dimension of the specimen perpendicular to the elongation is determined by Poisson's ratio as a material constant (μ_0). This holds so long as the time for swelling is long enough compared with the time required for the mechanical measurement to estimate Poisson's ratio, and this situation is easily attained by employing a larger size of polymer gel.

On the other hand, the final state, *i.e.*, the state realized at long time limit after the application of the deformation, will be determined not only by the mechanical properties of the gel (for example, μ_∞ of the gels), but also by thermodynamic properties of the system under deformation. The polymer gel and surrounding solvent molecules compose a semi-open system and the solvent molecules can move through the interface between gel and solvent during long time when the solvent motion is favored. Osmotic Poisson ratio (μ_∞) defined for uniaxially deformed gels in solvent at long time limit reflects the thermodynamic properties of the semi-open system.

The equilibrium elongational stress (σ_∞) has also been affected by the thermodynamic properties of the system. Using the initial elongational stress (σ_0) and σ_∞ , we can define the relative stress reduction $(\sigma_0 - \sigma_\infty)/\sigma_0$. This quantity is also affected by the thermodynamic properties of the gel system. Although μ_∞ , and σ_∞ or $(\sigma_0 - \sigma_\infty)/\sigma_0$ are fundamental quantities for describing

the physical and mechanical properties of polymer gels at equilibrium, there are few studies on those values.^{4–7} The aim of the present study is to investigate the values of μ_∞ and $(\sigma_0 - \sigma_\infty)/\sigma_0$ for poly(acrylamide) (PAAm) gels, and to compare those with the theoretical predictions shown in a previous paper.⁴

EXPERIMENTAL

PAAm gels used in this study were prepared by employing a radical polymerization technique. Acrylamide (AAM), methylenebisacrylamide (MBA; crosslinker), and ammoniumpersulfate (initiator) were dissolved in distilled water at room temperature. The molar ratio of MBA to AAM and that of initiator to AAM were 0.002 and 0.006, respectively. The solution was poured in a metal mold in order to obtain a rectangular specimen. The gelation was performed at 33°C. After being removed from the mold, the gel specimen was immersed in distilled water until the equilibrium swelling was achieved. The sample name in Table I contains three digits. The left two digits represent the initial concentration of AAM in 10 kg m^{-3} , and the rest the serial number. The cross-sectional area of the rectangular sample, after equilibrium swelling, was square in shape and was about $3 \text{ mm} \times 3 \text{ mm}$ for PAAm277 and PAAm278, *ca.* $6 \text{ mm} \times 6 \text{ mm}$ for PAAm275 and PAAm276, and *ca.* $9 \text{ mm} \times 9 \text{ mm}$ for the other samples. The gel specimens were elongated in water at 25°C by using an Orientec RTM-250 tensile tester with a specially designed water bath, and time dependence of the tension was monitored. Two types of strain were defined for the stretched direction; one is the global strain and was calculated by using the cross-head distance, and the other is the local strain and was calculated from the distance between two marked points at the center of the gel sample by using a magnified video picture on the monitor screen. On the other hand, only the local strain, which was determined by the dimensional change of the gel in the central region, was employed for the direction perpendicular to the elongation. The global strain initially applied to the gel samples was fixed to be 10%. The local strains were used for calculation of μ_∞ , while the global strains were used for calculation of the initial Young's modulus (E_0).

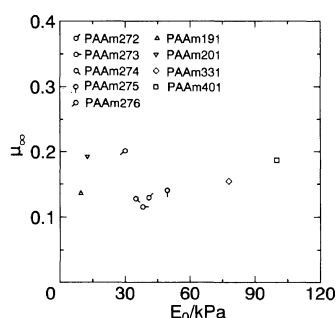
RESULTS

The experimental results on the values of μ_∞ and $(\sigma_0 - \sigma_\infty)/\sigma_0$ for the PAAm gels are summarized in Table

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Table I. Sample name, initial Young's modulus (E_0), osmotic Poisson's ratio (μ_∞), and relative stress reduction $((\sigma_0 - \sigma_\infty)/\sigma_0)$ for poly(acrylamide) (PAAm) gels

Sample	E_0/kPa^a	μ_∞	$(\sigma_0 - \sigma_\infty)/\sigma_0$
PAAm271	22.9	—	0.271
PAAm272	41.0	0.130	0.164
PAAm273	38.2	0.116	0.173
PAAm274	35.0	0.128	0.282
PAAm275	49.5	0.141	0.215
PAAm276	30.0	0.202	0.199
PAAm277	43.0	—	0.194
PAAm278	31.0	—	0.138
PAAm191	9.6	—	0.242
PAAm201	12.5	0.136	0.149
PAAm331	78.0	0.155	0.216
PAAm401	100	0.187	0.146

^a Calculated by using global strain.**Figure 1.** Osmotic Poisson's ratio (μ_∞) of poly(acrylamide) (PAAm) gels plotted against initial Young's modulus (E_0).

I. The values of E_0 for PAAm271 to PAAm278 were a little scattered, although we tried to prepare the gels with almost the same E_0 by fixing the concentration of the reagents as well as the conditions for gelation. Comparing the E_0 values for the specimens differing in the AAm concentration, E_0 becomes higher with increasing AAm concentration. The plot of μ_∞ against E_0 is shown in Figure 1. The data points are a little scattered but they appear to be independent of the AAm concentration. The average value with the standard deviation is 0.149 ± 0.030 . Figure 2 shows the plot of $(\sigma_0 - \sigma_\infty)/\sigma_0$ against E_0 . The data points are also independent of E_0 in this region of E_0 . The average value of $(\sigma_0 - \sigma_\infty)/\sigma_0$ is 0.199 with the standard deviation 0.048.

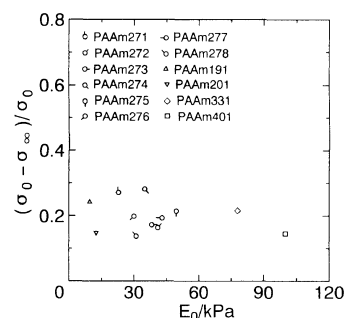
DISCUSSION

First, we compare the experimental values of μ_∞ and $(\sigma_0 - \sigma_\infty)/\sigma_0$ with theoretical ones shown in a previous paper,⁴ where an isotropic gel with low polymer concentration stretched uniaxially in solvent was considered. The gel was also assumed to be incompressible. Starting from the Flory-type Gibbs free energy per unit volume,^{4,8} the osmotic stresses parallel and perpendicular to the stretched direction (Π_{\parallel} and Π_{\perp} , respectively) are given by⁴

$$\Pi_{\parallel} = (5/2)G\varepsilon_{\parallel} + G\varepsilon_{\perp} - \sigma_{\infty} \quad (1)$$

$$\Pi_{\perp} = (1/2)G\varepsilon_{\parallel} + 3G\varepsilon_{\perp} \quad (2)$$

Here, G is the shear modulus. The quantities, ε_{\parallel} and ε_{\perp}

**Figure 2.** Relative stress reduction $((\sigma_0 - \sigma_\infty)/\sigma_0)$ of poly(acrylamide) (PAAm) gels plotted against initial Young's modulus (E_0).

are the strains parallel and perpendicular to the stretched direction at equilibrium. The above equations hold only for small ε_{\parallel} . At equilibrium, Π_{\parallel} and Π_{\perp} are zero. It is clear from eq 2 that $\mu_\infty = 1/6$,⁴ since μ_∞ is defined by $\mu_\infty = -\varepsilon_{\perp}/\varepsilon_{\parallel}$. The average value of μ_∞ for PAAm gels experimentally obtained in this study ($= 0.149$) coincides fairly well with the theoretical prediction ($\mu_\infty = 1/6 \cong 0.167$). Geissler *et al.*⁵⁻⁷ have reported $\mu_\infty = 0.275 \pm 0.011$ for PAAm gel in their latest work.⁵ Their value is high compared with that obtained in this study. Geissler *et al.* have estimated μ_∞ from the combination of two different moduli, while we measured the value directly from the dimensional change of the sample in solvent under uniaxial deformation. From eq 1 and 2, we have $\sigma_\infty = (7/3)G\varepsilon_{\parallel}$. The initial stress (σ_0) is given by $3G\varepsilon_{\parallel}$ when the gel is incompressible as assumed in the theory.⁴ In this case, $(\sigma_0 - \sigma_\infty)/\sigma_0$ results theoretically in the value of $2/9 \cong 0.222$. The average value of $(\sigma_0 - \sigma_\infty)/\sigma_0$ for the PAAm gels investigated here was 0.199, as shown previously. The difference in $(\sigma_0 - \sigma_\infty)/\sigma_0$ between experiment and theory is not so large. By using the value of $(\sigma_0 - \sigma_\infty)/\sigma_0$, we can also estimate μ_∞ for the PAAm gels by experiment when μ_0 is known, since $\sigma_0 = (1 + \mu_0)G\varepsilon_{\parallel}$ and $\sigma_\infty = (1 + \mu_\infty)\varepsilon_{\parallel}$. For the PAAm gels examined here, we have $(\mu_0 - \mu_\infty)/(1 + \mu_0) = 0.199$. The PAAm gels were not actually incompressible and μ_0 of the gels⁹ was about 0.46, which gives $\mu_0 \cong 0.17$. This is close to the value ($\mu_\infty = 0.149$) obtained directly by the ratio $(-\varepsilon_{\perp}/\varepsilon_{\parallel})$, indicating that the two values of μ_∞ obtained independently by experiment is consistent with each other.

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