New Method for Measuring Poisson's Ratio in Polymer Gels

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SYNOPSIS

A new method for measuring the Poisson's ratio of polymer gels has been proposed and has been experimentally demonstrated. The method is based on different swelling behaviors of free and constrained gels. The Poisson's ratio of polyacrylamide gel, as a function of crosslinker concentration, has been measured using this method and has been found to be sensitive to the amount of polymerization initiator. The results are compared with results determined by other methods. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The Poisson's ratio ν, which is a combination of the (static) shear and bulk moduli, is one of the most important quantities of a gel network system.[1,2] It characterizes the response of a material under anisotropic external pressure. The fact that ν is a function of the ratio of material moduli makes it ideal for studying the scaling behavior of mechanical properties of gels.[3-5] Poisson's ratio plays a vital role in many phenomena, for example, the bending of polyelectrolyte gels in electric field,[6] gel surface pattern formation,[7] network swelling kinetics,[8,9] and gel volume phase transition.[10,11] Some of these phenomena have potential applications in the areas of artificial muscle, actuators, switches, controlled release, and membrane separations. In the semidilute regime, the quality of a gel solvent [good, theta (Θ), or poor] can be reflected by the Poisson's ratio of the gel.[2,12,13]

For a homogeneously elongated rod, with uniform elongational force applied to its ends, Poisson's ratio ν happens to be (one can consider this as the definition of ν),[14]

$$\nu = -\frac{u_{xx}}{u_{zz}} \qquad (1)$$

where u_{xx} and u_{zz} are strains perpendicular and par-

allel to the elongation, respectively. The ν is related to the shear (G) and bulk (K) modulus of the material by

$$\nu = \frac{1}{2} \frac{3K - 2G}{3K + G} \qquad (2)$$

Therefore, ν is a function of (K/G) only. The range of ν is $-1 \leq \nu \leq \frac{1}{2}$. Note that the Poisson's ratio can be expressed in terms of any two of the following moduli: Lame's constant, Young's modulus, bulk modulus, and shear modulus. In this article, we choose to express the Poisson's ratio in terms of the bulk and shear moduli.

The measurement of the shear modulus, G, of gels is often straightforward. Most of the methods involve measuring the instantaneous elongation/compression of a gel sample under known pressure.[1] With these methods, it is critical to complete the measurement quickly, before the sample changes volume. Another problem often encountered is friction between the sample and instrument, causing the sample to have nonuniform strain (e.g., a cylindrical sample could become drum-shaped under pressure). The bulk modulus of gels can be directly measured by the osmotic pressure method, which involves the measurement of change in gel volume under known osmotic pressure from the surrounding polymer solution.[4,5] Light scattering techniques have also been used to measure indirectly the longitudinal modulus.[1,5] However, due to the inevitable inhomogeneity of the system, an average over many

scattering volumes is often required in order to achieve a meaningful result. Other methods, used in measuring gel mechanical properties, include shear wave and ultrasound propagations and small angle neutron and X-ray scatterings.

The Poisson's ratio in gels can be obtained by measuring G and K separately,[1,2,4,5] or by measuring the swelling kinetics of gels.[8,9] It can also be obtained directly by measuring the equilibrium deformation of the gel under uniform elongation[10] or compression.[10,11] In the elongation experiment, the sample is usually dried first, so that it can be fixed onto the stretching instrument. However, it is conceivable that the drying process may change the sample mechanical properties and therefore influence the measured results (we have observed a significant swelling ratio reduction with ionic gel samples after going through a room-temperature drying process). In the equilibrium compression experiment, nonuniform deformation often occurs, making data analysis difficult.

In this article, we report a simple, yet nonambiguous, method for measuring Poisson's ratio of gels. This method involves the measurement of gel equilibrium dimensions under uniform constraint. The uniform constraint is achieved by covalently fixing the gel film onto a polyester sheet. The gel sample does not have to be dried before the measurement. Using this method, we measured the Poisson's ratio of polyacrylamide (PAAM) gel as a function of crosslinker concentration. Our results will be compared with the results measured by other methods.

EXPERIMENTAL

The PAAM gel samples were made by free radical polymerization. A mixture of 5 grams of acrylamide (Bio-rad, Co.) and various amounts of methylenebisacrylamide (BIS; 45 to 500 mg) as crosslinker, and tetramethylethylenediamine (240 μL) as accelerator, was dissolved in 100 mL of deionized and distilled water. Nitrogen gas was bubbled through the solution to remove dissolved oxygen. The polymerization initiator, ammonium persulfate (AP), was added to the solution after the nitrogen bubbling. The solution was then transferred into a narrow gap (0.457 mm $\times$ 25 mm $\times$ 50 mm) between a GelBond sheet (FMC, Co.) and a microslide. The microslide was coated with a water-repelling chemical (Sigmacoat, Sigma Chemical, Co.) for easy separation from the gel film. The gel started to form in about 10 min. To observe the effect of initiator con-

centration, samples were prepared at two levels of AP (40 mg and 400 mg). Since the surface of the GelBond sheet contained polymerization-active chemical groups, it became covalently attached to the gel film.[15] The back of the GelBond was preglued onto a glass slide to keep it from bending. For each gel film fixed on GelBond, a companion free-gel film of the same chemical ingredient and the same dimension was made as well. The samples were left untouched for more than 12 h before being transferred to a water bath to swell to equilibrium at room temperature.

The samples were immersed in water for several days before being measured. The ones, constrained by attachment to the GelBond, can swell only in one direction. The free gels swelled isotropically in all directions.[16] Sketches of the swelling processes of constrained and free-gel films are shown in Figure 1. After the samples had reached equilibrium, their thicknesses were measured, using a spherometer. The accuracy of the measurement was within 0.005 mm. For each sample, thickness measurements were made at three different locations and the average was used in calculating the Poisson's ratio.

THEORETICAL CONSIDERATIONS

We will use Landau and Liftschitz's elasticity notation[14] in this article. The Einstein's summation convention will be applied to the dummy indices i, j, k, and l. The samples are assumed to be isotropic at preparation. We will label the direction, perpendicular to the gel film, as the z-direction. Since our samples are all thin gel films, the edge effect of constrained samples can be neglected and the deformation of the sample is, therefore, homogeneous, that is, the strain tensor u_{ik} is a constant throughout the sample. Furthermore, the only nonzero elements are $u_{xx} = u_{yy}$ and u_{zz}, as a result of the symmetry of the system. The stress tensor σ_{ik} is related to u_{ik} by

$$\sigma_{ik} = K u_{ll} \delta_{ik} + 2G(u_{ik} - \tfrac{1}{3} u_{ll} \delta_{ik}) \qquad (3)$$

where $\delta_{ik} = 1$, when $i = k$, and $\delta_{ik} = 0$ otherwise. Using this relation, we find that all off-diagonal stress tensor elements are zero. In fact, we will show that σ_{zz} is zero as well, leaving $\sigma_{xx} = \sigma_{yy}$ as the only nonzero elements.

Since σ_{zz} is a constant, it can be determined by the boundary condition $\sigma_{ik} n_k = P_i$, where n_k is the normal vector to the boundary and P_i the external

FREE GEL   **CONSTRAINED GEL**
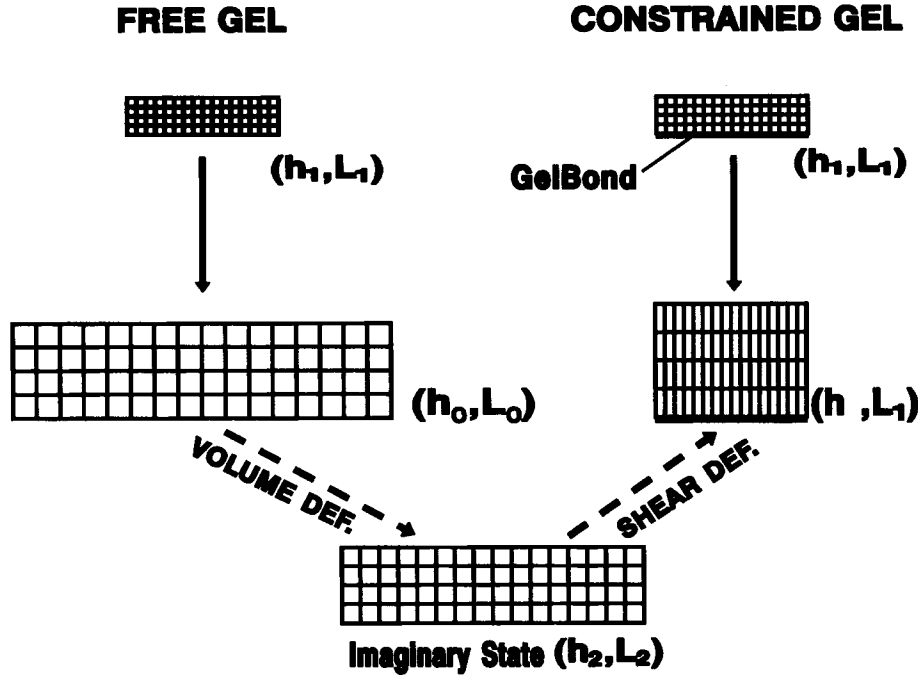
Figure 1   This is a schematic description of the cross section of samples at various stages. Free (a) and constrained (b) gel films of the same initial dimensions (h_1, L_1) were allowed to swell in water. The constrained gel film can only swell in one dimension $(h_1 \rightarrow h)$. An imaginary intermediate state (h_2, L_2) of the constrained gel is shown. The volume of the imaginary state is the same as that of the final state. The swollen state of the free gel film (h_0, L_0) was used as the reference state for the deformation of the constrained gel.

stress (force per unit area) applied to the boundary. Since there is no external force on the top and bottom of the gel film along the z-direction $(P_z = 0)$, we have $\sigma_{zk}n_k = 0$. Using $n_x = n_y = 0$ and $n_z = 1$, we have $\sigma_{zz} = 0$. Therefore, we conclude that $\sigma_{xx} = \sigma_{yy} \equiv P$ are the only nonzero stress tensor elements. This indicates that the constraint of the samples from GelBond can be viewed as a radially applied external pressure P.

Substituting $\sigma_{xx} = P$ and $\sigma_{zz} = 0$ in eq. (3), we have

$$u_{xx} = \frac{P}{3}\frac{3K + 4G}{6KG},\tag{4}$$

$$u_{zz} = -\frac{P}{3}\frac{3K - 2G}{3KG}\tag{5}$$

Combining these results with eq. (2), one can easily verify that

$$\nu = \frac{u_{zz}}{u_{zz} - 2u_{xx}}\tag{6}$$

For a gel under small deformation,

$$u_{zz} = \frac{h - h_0}{h_0}\tag{7}$$

$$u_{xx} = \frac{L_1 - L_0}{L_0} = \frac{h_1}{h_0} - 1.\tag{8}$$

Where h and h_0 are the thickness of the fixed and free samples, respectively, and h_1 is the thickness of the samples at preparation $(h_1 = 0.457$ mm$)$. The measured h_0 and h of the samples with 40 mg/100 mL ammonium persulfate as a function of BIS concentration, are shown in Figure 2. The swelling ratios of these samples are all lower than their corresponding samples, initiated with 400 mg/100 mL ammonium persulfate. This indicates that these samples are better crosslinked. In both cases, h_0 and h decrease as BIS concentration increases.

RESULTS AND DISCUSSION

The change of the sample from the reference state (free gel state) to the final state (constrained gel
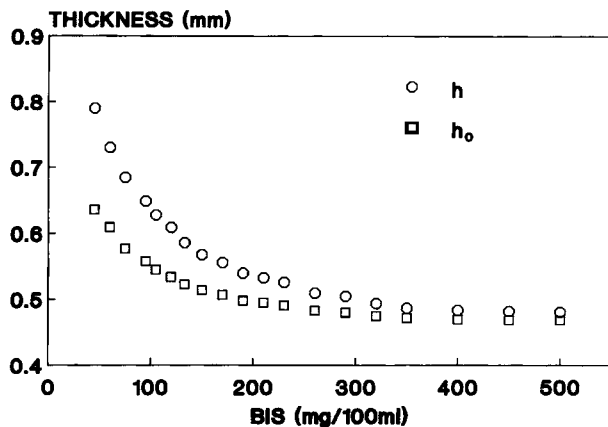
THICKNESS (mm)

Figure 2   The thickness of free swollen polyacrylamide gel films (h_0) and of constrained swollen polyacrylamide gel films (h) as a function of initial crosslinker (BIS) concentration. The samples were prepared with the ammonium persulfate (AP) initiator concentration equal to 40 mg/100 mL. The initial thicknesses (h_1) of all samples were equal 0.457 mm.

DEGREE OF DEFORMATION
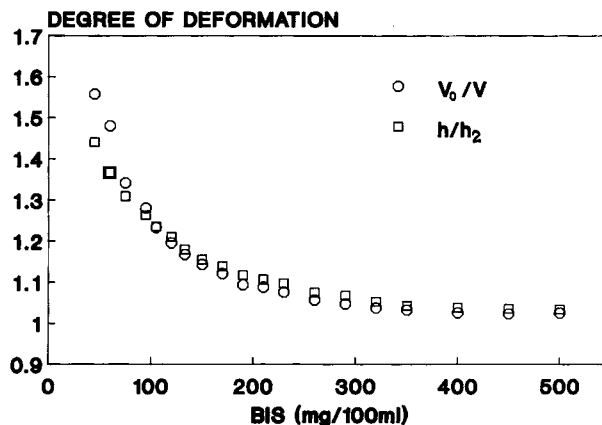
Figure 3   The degree of bulk (V_0/V) and shear (h/h_2) deformation of constrained polyacrylamide gel films of different crosslinker (BIS) concentration. The samples were the same as those used in Figure 2. Except for the first three samples with low BIS concentration, all relative deformations are smaller than 30%.

state) can be achieved by two imaginary steps, as shown in Figure 1. First, the reference state is isotropically shrunken by a factor of $(V/V_0)^{1/3}$, that is, h_0 shrank to $h_2 = h_0(V/V_0)^{1/3}$, and L_0 shrank to $L_2 = L_0(V/V_0)^{1/3}$. The volume of this shrunken state is obviously the same as the final constrained gel state. The second step is to elongate the scaled state (h_2, L_2) to the final state (h, L_1). In this step, the change of volume is zero, therefore it is a pure shear deformation. The degree of bulk (volume) and shear deformation of the system can, therefore, be represented by (V_0/V) and $h/h_2 = (V_0/V)^{1/3}(h/h_0)$. As shown in Figure 3, other than the samples with low BIS concentration, the bulk and shear deformations of our samples were both small (less than 30%), as compared with the deformation range used in other methods.[5] We expect that in the small deformation regime, the linear analysis we have outlined earlier should be valid. For the samples under large deformation, the nonlinear terms should be considered if more accurate analysis is desired.

Using the measured values for h_0 and h and eq. (6), Poisson's ratios of samples of both series were obtained and shown in Figure 4. The v values of the first series (AP = 40 mg/100 mL) are consistently higher than the second series (AP = 400 mg/100 mL). Upon increasing BIS concentration, the Poisson's ratio of both series initially increases. Since K/G is monotonically related to v, and the gel network concentration (inverse of volume swelling ratio) is monotonically related to BIS concentration,

this indicates that, as the network concentration increases, K increases more than G. This agrees with the fact that, in general, the bulk modulus K has a much stronger polymer concentration dependence than the shear modulus G. As the BIS concentration further increases, its crosslinking efficiency decreases, causing the v value to plateau. For semidilute gel in good solvent, v is expected to be around 0.278.[13]
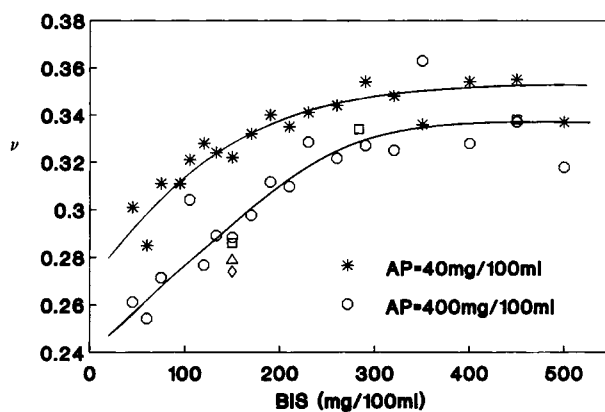
Figure 4   Poisson's ratio v of polyacrylamide gels of different crosslinker (BIS) concentration. The samples, made with lower ammonium persulfate concentration (40 mg/100 ml) have higher v values than the corresponding samples, made with higher ammonium persulfate concentration (400 mg/100 mL). The squares (□), the triangle (△), and the diamond (◇) were results obtained by Cohen et al.,[17] Peters and Candau,[8] and Geissler et al.,[5] respectively.

This corresponds to the BIS $\sim$ 110 mg/100 mL region for the AP = 400 mg/100 mL series, or the BIS $\sim$ 50 mg/100 mL region for the AP = 40 mg/mL series.

The results, obtained by Cohen et al., using the osmotic deswelling technique, are also plotted in Figure 4 for comparison. The result from the swelling kinetics technique by Peters and Candau,[8] and that from the combination of shear modulus and scattered light intensity by Geissler et al.[5] are also presented in Figure 4. The agreement between these results and our AP = 400 mg/100 mL series is excellent.

We would like to point out that this method, although simple, is limited by the fact that not all gels can be easily attached to a rigid substrate. Also, for any given system, the degree of deformation may not be easily controlled. When large deformation occurs, a nonlinear elasticity theory would be required when accurate quantitative information is desired.

CONCLUSION

In conclusion, we have demonstrated a new method to measure directly the Poisson's ratio of gels based on different swelling behaviors of constrained and free gel slabs. This method is precise and easy to use. The results from PAAM gels indicate that the mechanical properties of gels are sensitive to the polymerization parameters. Our results, at the higher level of ammonium persulfate (400 mg/100 mL), are in excellent agreement with previously reported values of ν.

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