BRIEF REPORTS

Poisson's ratio in polymer gels near the phase-transition point

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Poisson's ratio, which was obtained by measuring swelling curves of free and radially constrained gels, has been investigated as a function of temperature and ionic strength for N-isopropylacrylamide (NIPA) gels and as a function of acetone concentration for polyacrylamide gels. It was found that the Poisson ratio exhibits a negative dip near the transition temperature for both neutral and ionic NIPA gels. The dip becomes deeper and shifts to a higher temperature as the ionic strength increases. The negative Poisson ratio of NIPA gels suggests that the bulk modulus is much smaller than the shear modulus as gels undergo the phase transition. The Poisson ratio of acrylamide gel, however, was found to be positive throughout the measured region.

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Under an external stimulus such as temperature and acetone concentration, polymer gels undergo a volume phase transition [1,2]. Since this transition involves a large deformation of the volume, the elastic quantities of gels must play a vital role at the critical point. The Poisson ratio (σ), one such quantity, characterizes the transverse deformation of materials under uniaxial pressure. The quantity σ is related to the shear (G) and bulk (K) modulus of the material by [3]

$$\sigma = \frac{1}{2}\frac{3K-2G}{3K+G} . \tag{1}$$

Therefore, σ depends on (K/G) only. Thermal dynamic stability conditions require that $-1 < \sigma < 0.5$ $(0 < K/G < \infty)$ for three-dimensional materials [3]. For most common materials, the Poisson ratio is positive, i.e., the sample undergoes a transverse contraction under axial stretching or a transverse expansion under axial compression. However, a few cases of negative Poisson ratio have been reported, including highly anisotropic crystals [4] and polymer foams with reentrance cells [5]. The Monte Carlo simulation also predicts possible negative Poisson ratio in the two-dimensional cyclic hexamers lattice [6].

Recently, Hirotsu measured the temperature dependence of the neutral N-isopropyacrylamide (NIPA) gel deformations (both axial and radial) under constant pressure [7]. By combining the bulk and shear elastic modulus, Hirotsu obtained negative Poisson ratio in neutral NIPA gels near the phase transition [7].

In this Brief Report, we report our direct measurement on the Poisson's ratio of ionic NIPA gels and neutral polyacrylamide (PAAM) gels. The method involves the measurements of gel equilibrium dimensions under uniform constraint that is achieved by covalently fixing the gel film onto a polyester sheet. The method has been previously tested for polyacrylamide-water gels [8]. The results are in excellent agreement with ones obtained by other methods. In Hirotsu's experiments, the sample was first dried so that it can be mounted to the instrument [7]. Although the drying process does not affect the apparent swelling properties of neutral NIPA gel, we have observed dramatic change in the degree of swelling from ionic gels that were first dried and then swelled. In our experiment, the gel sample does not have to be dried before the measurement.

The NIPA gel samples were made by free radical polymerization [2]. A mixture of 7.8 g of N-isopropylacrylamide (Kodak, Co.), 133 mg of methylene-bis-acrylamide as cross-linker, tetra-methyl-ethylene-diamine (240 μl) as accelerator, and sodium acrylate (SA), ionic group, were dissolved in 100 ml of deionized and distilled water. The concentration of SA (0–8 mM) was varied. Nitrogen gas was bubbled through the solution to remove dissolved oxygen. Then ammonium persulfate (40 mg) as an initiator was added to the solution.

A thin film of the solution was cast between a GelBond film (FMC, Co.) and a microslide with a fixed separation (0.996 mm). Since the GelBond film contains polymerization-active chemical groups, the bottom surface of the gel slab was thus covalently cross-linked to the GelBond film. For each gel slab fixed to GelBond, a companion free slab of the same chemical ingredient and same dimensions was made as well. The samples were left untouched for about 12 h before being transferred into a water bath to swell. After the samples had reached equilibrium, their thicknesses were measured by averaging over the thicknesses at three locations of the sample using a spherometer. The measurement accuracy was within 0.005 mm. The details of the method will be published elsewhere [8]. The temperature of samples was controlled by a circulation water bath (Brinkmann Lauda Super RM-6). A platinum resistor thermometer was used to monitor the temperature near the sample within 0.05 °C. The data were taken in a warm-up run with a rate of 0.1 °C/day near the phase-transition region.

The PAAM gel was made using the NIPA recipe with 7.8 g of N-isopropylacrylamide monomers replaced by 5 g of acrylamide monomers. The phase transition of PAAM gels was triggered by a change of acetone concentration in acetone-water mixture.

The thickness of free (h_0, plus signs) and constrained NIPA gels (h, open circles) are shown in Fig. 1 as a function of temperature at various ionic concentrations. The thicknesses of the samples decrease as temperature increases. Following convention, we take the point at which the size of the sample shows the largest change as the transition temperature T_c. The fixed gels have higher transition temperature than their companions, the free gels. The increase of T_c is apparently caused by the radial stretching pressure generated by the constraint. This effect is similar to the change of phase-transition temperature of gels under uniaxial pressure [9]. The difference of transition temperatures between free and cons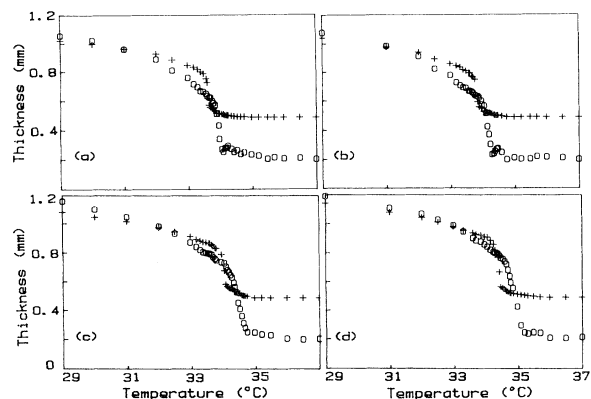trained samples becomes larger as the ionic concentration increases. There are three intersections between h_0 and h for all NIPA samples studied. At the first crossover point, both fixed and free samples reach the same thickness, which is the same as the thickness of samples when being made. This shows that the constraint from GelBond is zero at this point. For temperatures lower than the first crossover point, the constraint corresponds to a compressional pressure; above this point, the constraint corresponds to a stretching pressure. The other two crossover points are located on either side of the phase-transition temperature. These two points indicate the beginning and the end of the negative Poisson ratio region, respectively.

Since the gel is mechanically fixed at a lower surface, it is forced to swell in the direction perpendicular to the surface. The constraint can be viewed as a radial external pressure applied to the samples [8]. Using boundary conditions and the general stress(σ_{ik})-strain(u_{ik}) relation [3] with Einstein summation convention,

$$u_{ik} = \frac{1}{9K}\delta_{ik}\sigma_{11} + \frac{1}{2G}(\sigma_{ik} - \tfrac{1}{3}\delta_{ik}\sigma_{11}) , \qquad (2)$$

the Poisson ratio (σ) can be derived as [8]

$$\sigma = \frac{u_{zz}}{u_{zz} - 2u_{xx}} . \qquad (3)$$

The physical meaning of Poisson's ratio is illustrated in Fig. 2. In this figure, u_{zz}/u_{xx} (dashed line) and σ (solid line) are plotted as a function of K/G using Eqs. (1) and (3). For most materials, radial compression ($u_{xx} < 0$) results in an axial expansion ($u_{zz} > 0$), i.e., $u_{zz}/u_{xx} < 0$. This corresponds to $\sigma > 0$, or $K/G > \frac{2}{3}$. Rarely, a radial compression yields axial compression, i.e., $u_{zz}/u_{xx} > 0$. This corresponds to $\sigma < 0$, or $K/G < \frac{2}{3}$.

For small deformation, we have

$$u_{zz} = \frac{h - h_0}{h_0} , \qquad (4)$$

$$u_{xx} = \frac{L_1 - L_0}{L_0} = \frac{h_1 - h_0}{h_0} , \qquad (5)$$

FIG. 1. The thickness of free (h_0, plus signs) and constrained (h, open circles) NIPA gel films as a function of temperature. All samples had a thickness (h_1) of 0.996 mm when being made. The concentration of sodium acrylate varies: (a) 0 mM, (b) 2 mM, (c) 4 mM, (d) 8 mM. There are three intersections between h and h_0 for all samples.
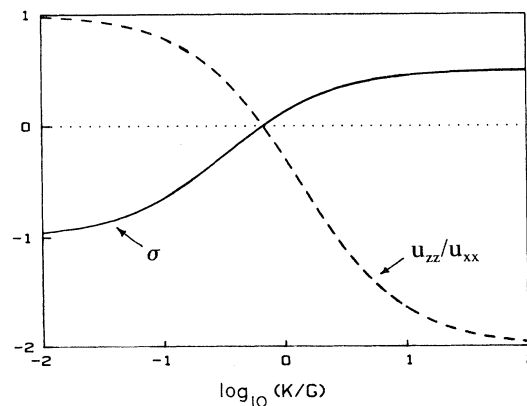

FIG. 2. Poisson's ratio (solid line) and u_{zz}/u_{xx} (dashed line) are plotted as a function of K/G. Zero is indicated by a dotted line.
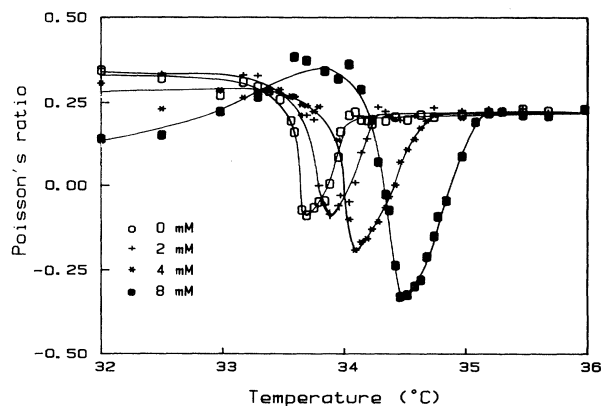
FIG. 3. The Poisson ratio of NIPA gels as a function of temperature for various sodium acrylate concentration: ($\bigcirc$) 0 mM, ($+$) 2 mM, ($*$) 4 mM, and ($\bullet$) 8 mM.

where h_1 is the thickness of the samples at preparation and h_0 and h are the thicknesses of the free and fixed samples, respectively. Using h_0 and h measured and Eqs. (3)–(5), the Poisson ratio of NIPA gels was obtained as is shown in Fig. 3 as a function of temperature for four different ionic concentrations. The Poisson ratio shows negative values for all NIPA samples studied near the critical point.

After the first intersection, the sample is under stretching ($u_{xx} > 0$). As temperature is far from the transition, $u_{zz} < 0$, the sample stretches in x-y plane while its equilibrium dimension along z direction shrinks, corresponding to a positive Poisson ratio. As the temperature nears the phase transition, $u_{zz} > 0$, the sample expands in both x-y plane and z direction. This yields the negative Poisson values. It has been pointed out that near the volume phase-transition point of a gel, the bulk modulus of it approaches zero while the shear modulus remains finite [10,7,9]. Therefore, near the critical point, $K/G \to 0$, and $\sigma \to -1$. In fact, near the critical point, $\sigma = -1$ is directly responsible for the slowing down of volume change kinetics [11].

As shown in Fig. 3, Poisson's ratio shows a dip near T_c. This dip approaches a larger negative number and shifts to a higher temperature as the ionic strength increases. The behavior of σ suggests that adding a small amount of ionic groups into NIPA gels moves the weakly discontinuous transition toward a continuous one. Furthermore, the ionization may also modify the polymer network, producing modulated structures [12]. This modification may also make the gel system closer to the critical point.

The thicknesses of free and constrained neutral PAAM gels were also measured as a function of acetone concentration in acetone-water mixture as shown in Fig. 4(a). The corresponding Poisson ratio is plotted in Fig. 4(b).
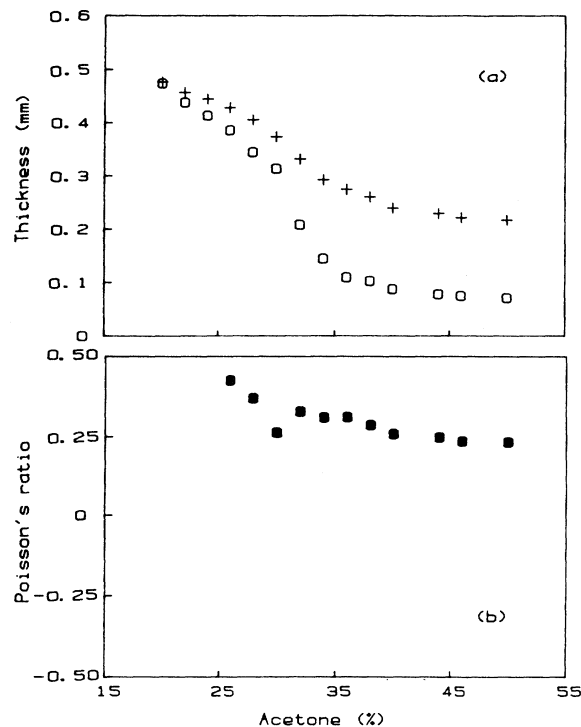

FIG. 4. (a) The thickness of free (h_0, plus signs) and constrained (h, open circles) PAAM gel films as a function of acetone concentration (wt. %) in water-acetone mixture. The phase-transition acetone concentration is around 30%. The samples had a thickness (h_1) of 0.457 mm when being made. There is only one intersection between h and h_0 in the entire region measured. (b) The Poisson ratio of the PAAM gel is plotted as a function of acetone concentration. No negative Poisson ratio was observed near the transition concentration.

In contrast to NIPA gels, PAAM gels have only one intersection between h and h_0. Poisson's ratio is positive over the entire range measured as shown in Fig. 4(b). Poisson's ratio has no anomaly near the transition point, which is around 30% acetone concentration. This appears to indicate that the phase transition in PAAM and NIPA may be quite different.

In conclusion, Poisson's ratio was obtained from the measurement of the swelling curves of free and constrained polymer gels. The Poisson ratio of NIPA gels exhibits a negative dip near the phase transition and the position of the dip shifts to a higher temperature as ionic concentration increases. In contrast to NIPA gels, the Poisson ratio of neutral PAAM shows no negative values throughout the measured transition region.

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