Swelling Behavior of Polymer Gels with Built-In Anisotropy near the Volume-Phase Transition Point

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ABSTRACT: The swelling behavior of gels with built-in anisotropy is investigated near the volume-phase transition. The anisotropic gels consist of two interpenetrating polymer networks. One of them (*N*-isopropylacrylamide) is prestressed before the gelation of the other one (polyacrylamide) takes place, resulting in built-in anisotropy. It is found that these gels have a preferred direction for swelling: above the phase transition point, the gel swells more along the prestressed direction. The ratio of gel length (non-pre-stressed) to its diameter (prestressed) exhibits a stepwise change at T_c. The amplitude of such a change is proportional to the degree of initial stress. A theoretical model based on the free-energy consideration has been proposed and can be used to explain the experimental results.

I. Introduction

It has been shown that the gel volume-phase transition is Ising-like.[1] An analogy can be drawn between the gel volume-phase transition and the liquid−vapor transition. The gel-swollen phase (low polymer concentration) corresponds to the vapor phase and the gel-collapsed phase (high polymer concentration) corresponds to the liquid phase. Although the critical point of a liquid−vapor system can be approached either by an isochore path (constant volume) or an isobar path (constant pressure), the most practical path for a gel system is isobaric. Along the isobaric path, the volume of the sample is measured as a function of an external parameter (e.g., temperature,[1] solvent composition,[2] IR irradiation,[3] etc.). The kinetics of gel volume change involves absorbing/desorbing the solvent by the gel network, which is a collective diffusion process.[1,4,5] This process is slow, and is even slower near the critical point because of the softening of the network elasticity.[5]

Currently, most researches are focused on the volume-phase transition of conventional gels, which swell or shrink isotropically both near and away from the phase transition point. Under an external constraint such as stretching, compression, or surface bonding,[6−8] the isotropic symmetry may be broken. Anisotropic gels have been obtained by incorporating liquid crystals into gel networks.[9,10]

Here, we report the synthesis and study of new interpenetrating polymer network (IPN) gels with built-in anisotropy. The basic idea is to anisotropically constrain one of the network components before the gelation of the other network takes place. Once the gel of interpenetrating polymer networks is obtained, the external constraint is removed. The preconstrained network thus tends to regain its original shape, similar to the restoration of a compressed spring. This restoration will, however, be constrained by the other network, resulting in built-in anisotropy in both networks. In addition to improved mechanical properties which usually come from the reinforcement between two interpenetrating networks,[11] physical properties along the prestressed direction are expected to be different from those in other directions, in contrast to conventional gels which are isotropic materials.

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II. Theory

A. Swelling of Isotropic Gels. Usually, a polymer gel swells or shrinks isotropically. Li and Tanaka first introduced the isotropic condition.[5,12,13] Minimizing the total shear energy in response to any small change in shape under constant volume and using the collective diffusion equation,[4,14] Li and Tanaka derived the isotropic condition. For example, for an infinitely long cylindrical gel,

$$\frac{u_z(z,t)}{z} = \frac{u_r(a,t)}{a} \tag{1}$$

where $u_z(z,t)$ and $u_r(a,t)$ are the components of the displacement vector of the network **u** as the function of the position and time, a is the final radius of the gel cylinder, and r and z are radial and axial positions, respectively. This indicates that the relative change of the gel is isotropic, which has been confirmed by experiment. The collective diffusion equation, the isotropic condition, and the solvent motion have been further combined to form a theory of swelling kinetics of polymer gels.[15,16]

If only the surface and size of the sample are concerned and using diameter D instead, eq 1 can be written in another form:

$$\frac{L}{L_0} = \frac{D}{D_0} \tag{2}$$

where L_0 and D_0 are the length and diameter of the gel sample, respectively, at an initial time, while L and D are for a later time. Thus, the swelling ratios of a cylinder in the axial and radial directions are the same.

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For a cylindrical gel, define the ratio R as

$$R = \frac{L}{D} \tag{3}$$

Then eq 2 can be expressed as

$$\frac{R(T)}{R_0} = 1 \tag{4}$$

where T is an environmental parameter which could be temperature or ionic concentration. The change of the environment makes the gel shrink or swell, but R remains constant.

B. Swelling of Anisotropic Gels. Here, we extend the model proposed by Li and Tanaka to predict the swelling behavior of anisotropic gels. As the gel shrinks anisotropically, both its volume and shape are changed.

Let's define an anisotropic parameter A as

$$A = \frac{R}{R_0} - 1 \tag{5}$$

where the subscript "o" indicates the isotropic reference state at the gelation point of the individual polymer network. In general, the anisotropy of interpenetrating networks of two polymers α,β is related to R as

$$\frac{A_\alpha}{A_\beta} = \frac{R/R_{\alpha 0} - 1}{R/R_{\beta 0} - 1} \tag{6}$$

or

$$R = \frac{A_\alpha - B_\beta}{1/R_{\alpha 0} - 1/R_{\beta 0}} \tag{7}$$

Therefore, the value of $R = L/D$ is a function of the anisotropy parameter of the first network (A_α) and the second network (A_β).

Let us turn our attention to the free energy of the anisotropic gel. From the shear energy density

$$\epsilon = \mu\left(u_{ij} - \frac{1}{3}\delta_{ij}u_{kk}\right)^2 \tag{8}$$

the free energy per unit volume accumulated because of anisotropic swelling or shrinking can be derived as

$$f = \frac{2}{3}\mu_\alpha\left(\frac{D}{D_{\alpha 0}}\right)^2 {A_\alpha}^2 + \frac{2}{3}\mu_\beta\left(\frac{D}{D_{\beta 0}}\right)^2 {A_\beta}^2 \tag{9}$$

where f is the summation of the shear energy density of the network α and the network β. Detailed derivation of eqs 9−11 are given in the Appendix. By minimizing shear energy under constant volume, the relationship between the anisotropy parameter and the elastic shear modulus is expressed as

$$\mu_{\beta\alpha} = \frac{\mu_\beta}{\mu_\alpha} = -\frac{A_\alpha}{A_\beta}\left(\frac{D_{\beta 0}}{D_{\alpha 0}}\right)^2 \tag{10}$$

where μ_α and μ_β are the shear moduli for networks α and β, respectively. Furthermore, the ratio of the length over the diameter (L/D) is related to the shear modulus ratio $\mu_{\beta\alpha}$,

$$R = R_{\alpha 0}R_{\beta 0}\frac{{D_{\beta 0}}^2\mu_{\beta\alpha} + {D_{\alpha 0}}^2}{R_{\beta 0}{D_{\beta 0}}^2\mu_{\beta\alpha} + R_{\alpha 0}{D_{\alpha 0}}^2} \tag{11}$$

where $R_{\alpha 0}$, $R_{\beta 0}$, $D_{\alpha 0}$, and $D_{\beta 0}$ are all constants. Since $\mu_{\beta\alpha}$ is expected to change near the phase transition,[17] eq 11 explicitly shows that R will change if $\mu_{\beta\alpha}$ changes because of any external stimuli such as temperature or ionic concentration.

III. Experimental Section

The major steps proposed for the synthesis of anisotropic interpenetrating polymer network gels consisted of two steps. First, the *N*-isopropylacrylamide (NIPA) gel was made by free-radical polymerization. A mixture of 7.8 g of *N*-isopropylacrylamide, 133 mg of methylene-bis-acrylamide as the cross-linker, and tetra-methyl-ethylene-diamine (240 μL) as the accelerator was dissolved in 100 mL of deionized and distilled water. Nitrogen gas was bubbled through the solution to remove dissolved oxygen. The polymerization was initiated in glass tubes by adding 40 mg of ammonium persulfate. The NIPA gels were cylindrical with diameters ranging from 2 to 6 mm. The samples were kept in water for several days to wash out chemical residues. The NIPA gels were then dried slowly in a sealed glass container so that they shrank uniformly.

The dried NIPA network was placed in glass tubes and immersed into a solution, containing 5 g of acrylamide, 133 mg of methylene-bis-acrylamide, 240 μL tetra-methyl-ethylene-diamine, and 100 mL of deionized and distilled water. The swelling of the NIPA network was constrained mechanically by the glass tube in the radial direction. The constraint was varied by using glass tubes with different diameters. The NIPA network was allowed to swell in the acrylamide solution for about 3 days. The polymerization of acrylamide was then initiated by immersing the sample in a 70 °C thermal bath. The gelation was completed in about 1 h, forming interpenetrating networks of acrylamide gel (PAAM) and NIPA gel. For a NIPA gel of a large size, while undergoing an immediate increase from a temperature below T_c to a temperature above T_c, the gel volume stays nearly unchanged for an extremely long time (about several days). This is referred to as the frozen effect.[17] The IPN sample was slightly milky and was harder than either the NIPA or PAAM gel. The major steps were shown schematically in Figure 1.

Once the IPN gels were obtained, the external mechanical constraint (glass tube) was removed. The preconstrained network NIPA thus tended to regain its original shape, similar to the behavior of a compressed spring. This restoration was, however, opposed by the network PAAM. The interaction of NIPA and PAAM resulted in different stresses in different directions. The most pronounced differences are in the directions parallel and perpendicular to the prestressed direction. To measure the temperature-dependent swelling curve, the sample temperature was controlled by a circulation water bath (Brinkmam Lauda Super RM-6) and was stable to 0.1 °C over 24 h.

IV. Results and Discussion

Figure 2 shows the anisotropy parameters A as a function of the diameter of samples (the tube diameter). The values of A inside the tube were measured before the tube was broken, while those of A outside the tube were measured after the tube was broken to release the external constraint. All anisotropy parameter approaches zero as the tube's diameter increases, because the constraint disappears when the tube's diameter is larger than the sample's diameter. Because of both the shear modulus and the unknown friction between the glass wall and the gel surface, the constraint can not

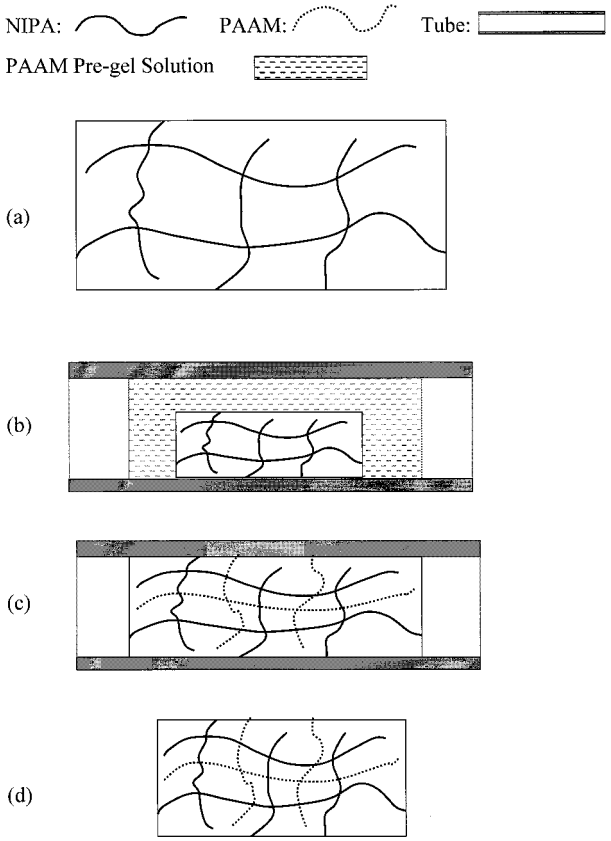

Figure 1. Sketch of the synthesis of anisotropic interpenetrating networks (a) fully swollen gel network α. (b) Dried gel network α is placed in a glass tube whose diameter is smaller than that of the fully swollen gel α. (c) After the α network is fully swollen in the pregel solution of the second network β, the gelation of the β network is initiated. In this study, the α network is NIPA and the β network is PAAM. (d) Removing the glass tube.

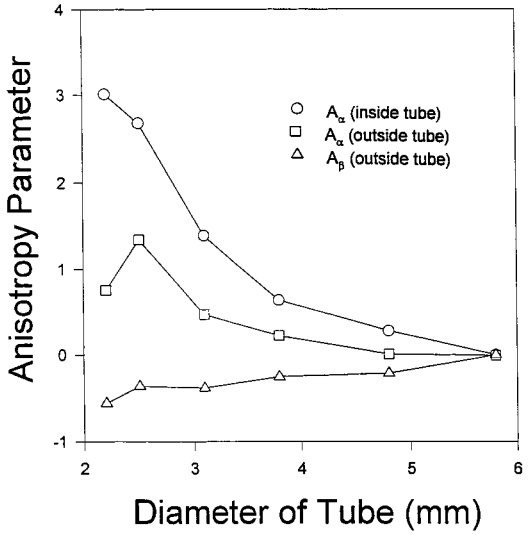

Figure 2. The anisotropy parameter versus the diameter of the tubes: (○) A_α anisotropy parameter of NIPA inside the tube, (□) A_α anisotropy parameter of NIPA outside the tube, and (△) A_β anisotropy parameter of PAAM outside the tube.

be calculated for the gel swelling along the axial direction. Therefore, the initial anisotropic parameters have to be experimentally determined.

Figure 3 shows the ratio of swelling $(L/L_0)/(D/D_0)$ as a function of temperature. Here, the ratio of swelling is

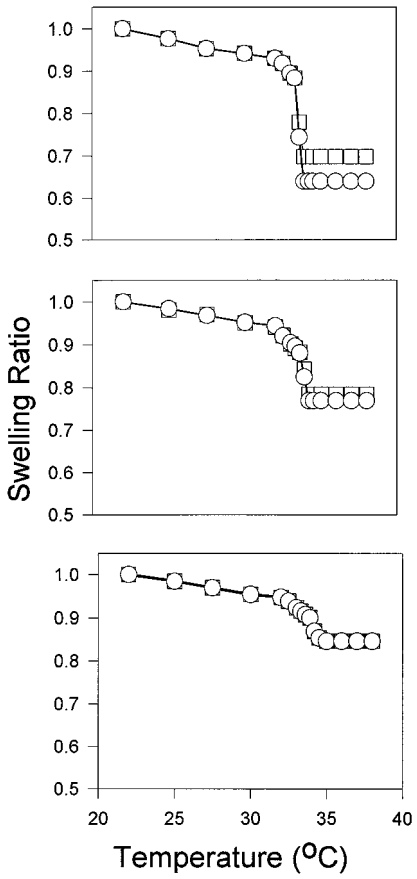

Figure 3. Swelling ratio of the samples is plotted as a function of temperature. Top figure: the sample with the 2.2 mm diameter tube. Middle figure: the sample with the 3.8 mm diameter tube. Bottom figure: the sample with the 5.8 mm diameter tube. In these figures, the symbol "□"corresponds to length and "○" to the diameter.

defined as the ratio of the relative length L/L_0 to the relative diameter D/D_0, with the value of length L_0 and D_0 at room temperature as the reference values. Below the phase transition temperature T_c, L/L_0 equals D/D_0. After the temperature is increased above the phase transition point, the gel sample shrinks because of the volume phase transition of the NIPA network. Both swelling ratios along the axial and radial directions decrease stepwise. As the tube's diameter becomes larger, the difference between the swelling ratios along two directions becomes smaller as shown in Figure 3.

In Figure 4, the equilibrium ratio R of the anisotropic gel is plotted as a function of temperature for various diameters of the prestressing tubes. For samples with a constraint (i.e., a small tube diameter (<6 mm)), the R (L/D) value exhibits a stepwise decrease near 34 °C. When the tube diameter is the same as or larger than the size (6 mm) of the fully swollen gel, the ratios of L/D remain unchanged around the phase transition point. Here, the ratio R is normalized by the ratio at room temperature, designated by R_{rt}.

It is known that the NIPA gel is sensitive to temperature, while the PAAM gel is not. The shear modulus of the NIPA gel shows a stepwise increase near the transition point,[19,20] while that of the PAAM gel remains a constant in the same temperature range. This fact is sketched in Figure 5 a, where the shear modulus data for NIPA and PAAM gels are taken from refs 20 and 21, respectively. Notice that $A_\alpha > 0$ for the NIPA gel and $A_\beta < 0$ for the PAAM gel above the transition point.

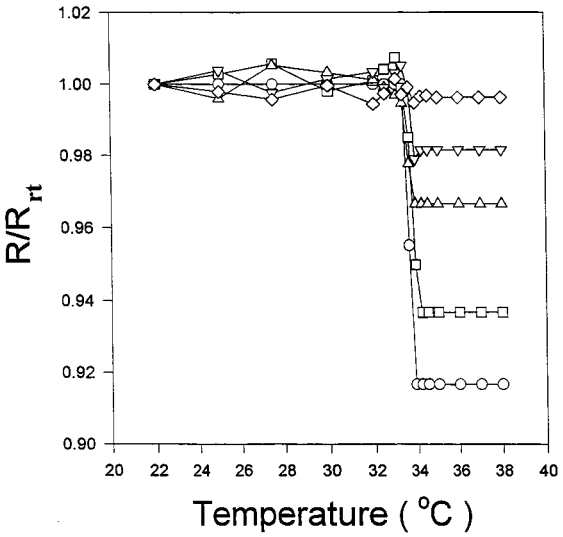

Figure 4. The temperature dependence of the swelling ratio $R = L/D$ of the anisotropy NIPA/PAAM gel in water. The ratio of length to diameter, which is normalized by the ratio R_{rt} at room temperature, is plotted as a function of temperature for various tube diameters: (○) 2.2 mm, (□) 2.5 mm, (△) 3.1 mm, (▽) 3.8 mm, and (◇) 5.8 mm.

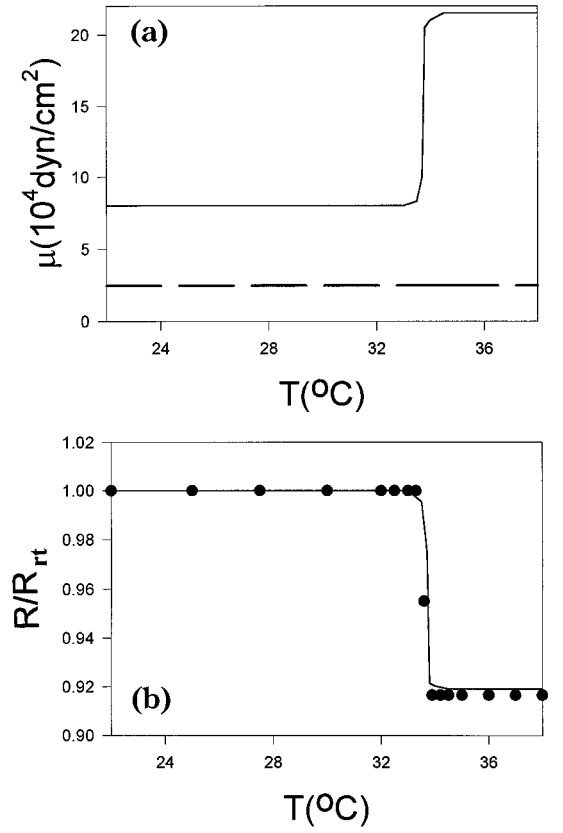

Figure 5. (a) The shear moduli of NIPA (solid line) and PAAM (broken line). The data are taken from refs 18 and 19, respectively. (b) The values of R/R_{rt} are calculated from eq 11. Shear moduli data in Figure 5a and the constant parameters from the sample whose constraining tube diameter is 2.2 mm. The result is plotted versus temperature. The corresponding experimental result for this sample (which is one curve of Figure 4) is plotted here by the solid dot for easy comparison.

Using eq 11, shear moduli data in Figure 5a, and the constant parameters from the sample whose constraining tube diameter is 2.2 mm, the values of R/R_{rt} are calculated and plotted as a function of temperature in Figure 5b. The corresponding experimental data for the same sample is also plotted in the figure by solid dots for comparison. They are in an excellent agreement.

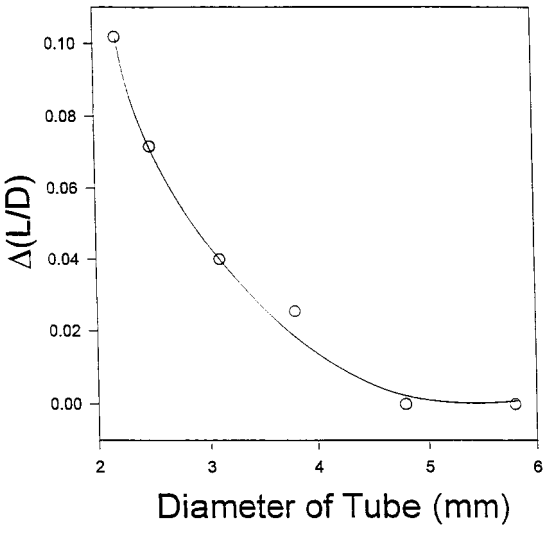

Figure 6. The change of the ratio of length to diameter at the transition temperature T_c is plotted versus the diameter of the tube. The solid line is a guide to the eye.

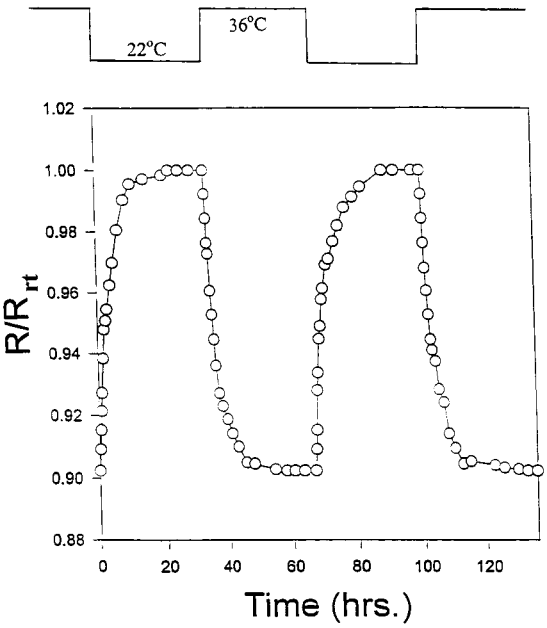

Figure 7. The normalized ratio of length to diameter of the sample with a 2.2 mm diameter of tube is plotted as a function of time as the temperature is switched between 22 and 36 °C. The temperature profile is represented by a solid line.

The change of the ratio of length to diameter at the transition temperature is plotted against the diameter of the tube as shown in Figure 6. The change of the ratio at the transition point decreases with the increase of the tube diameter. When the tube diameter is larger than 6 mm, the change of the ratio reaches zero, indicating isotropic shrinking.

The anisotropic swelling or shrinking of the gels is reversible. In Figure 7, the normalized ratio of length to diameter of the sample made with 2.2 mm tube diameter is plotted as a function of time. When the temperature of the sample was switched from 36 to 22 °C, the ratio L/D increases from 0.9 to 1.0. When the temperature of the sample was switched from 22 to 36 °C, the ratio L/D decreased from 1.0 to 0.9. When this

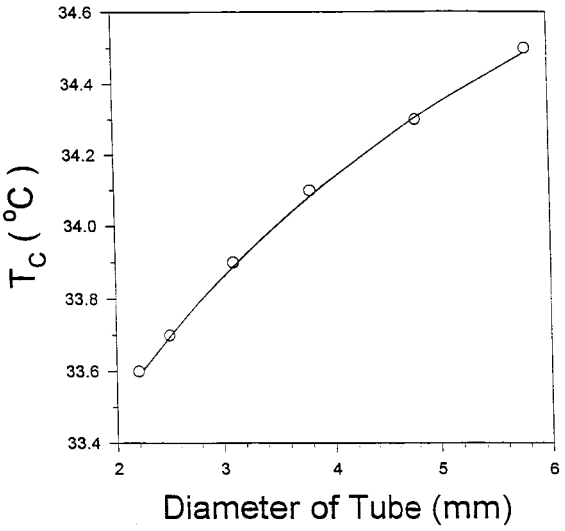

Figure 8. The phase transition temperature is plotted as a function of diameter of the tube. The solid line is a guide to the eye.

procedure was updated, the same result was obtained as indicated by the second cycle.

It is noted that the phase transition temperature T_c shifted up with increasing tube diameter, therefore, with decreasing constraint as shown in Figure 8. This may be because the relative density of the PAAM in the NIPA/PAAM interpenetrating networks increases with the tube diameter. Previous experiments have shown that the incorporation of PAAM in NIPA gels results in shifting T_c to a higher temperature.[22]

V. Conclusion

A new system with built-in anisotropy was synthesized and studied. This gel system consisted of interpenetrated polymer network (IPN) gels of polyacrylamide (PAAM) and *N*-isopropylacrylamide (NIPA). The NIPA network component was prestressed during the gelation of the other network (PAAM). The swelling property of the anisotropic IPN gels along the prestressed direction was different from that along other directions, in contrast to conventional gels that swell isotropically. It was found that the ratio (L/D) of length (L) and diameter (D) of IPN samples had stepwise changes as the samples were heated from below to above the volume phase transition temperature. A theoretical model has been proposed and is in agreement with the experimental results. The unique feature of the novel gel system is the preferential swelling in certain directions near the phase transition point. This feature could be useful for some chemomechanical devices.

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Appendix

For a cylindrical gel with the initial radius r_0 and the length $2h_0$, displacement vectors along the radial (u_r) and the axial (u_z) directions are defined as

$$u_r = cr \tag{A-1}$$

$$u_z = gz \tag{A-2}$$

From the definition, we know that $u_r(r_0) = r - r_0$ and $u_z(h_0) = h - h_0$. Therefore,

$$c = \frac{r}{r_0} - 1 = \frac{D}{D_0} - 1 \tag{A-3}$$

$$c = \frac{h}{h_0} - 1 = \frac{L}{L_0} - 1 \tag{A-4}$$

The elastic strains can be written as

$$u_{xx} = \frac{\partial u_x}{\partial x} = c \tag{A-5}$$

$$u_{yy} = \frac{\partial u_y}{\partial y} = c \tag{A-6}$$

$$u_{zz} = \frac{\partial u_z}{\partial z} = g \tag{A-7}$$

From eq 9, the shear energy density is

$$\epsilon = \mu\left[\left(u_{xx} - \frac{T}{3}\right)^2 + \left(u_{yy} - \frac{T}{3}\right)^2 + \left(u_{zz} - \frac{T}{3}\right)^2\right] \tag{A-8}$$

$$T = u_{xx} + u_{yy} + u_{zz} = 2c + g \tag{A-9}$$

Substitute eq A-3 ~ eq A-7 and eq A-9 into eq A-8, the shear energy density becomes

$$\epsilon = \frac{2}{3}\mu\left[\frac{D}{D_0} - \frac{L}{L_0}\right]^2 \tag{A-10}$$

From the definition of the anisotropic parameter A in eq 5, we have

$$\epsilon = \frac{2}{3}\mu\left(\frac{D}{D_0}\right)^2 A^2 \tag{A-11}$$

For the gel with the interpenetrating networks of α and β, the total shear energy density, f, is the sum of the individuals as shown in eq 10.

$$f = \frac{2}{3}\mu_\alpha\left(\frac{D}{D_{\alpha 0}}\right)^2 A_\alpha{}^2 + \frac{2}{3}\mu_\beta\left(\frac{D}{D_{\beta 0}}\right)^2 A_\beta{}^2 \tag{A-12}$$

After the glass tube is removed, the interpenetrating networks gel will change its shape under a constant volume. Minimizing the shear energy under a constant volume ($\mathrm{d}f/\mathrm{d}R = 0$), using relationships of $LD^2 = \text{const}$ and $\mathrm{d}D = -D\mathrm{d}R/(3R)$, and assuming that A is much smaller than 1, we obtained

$$\mu_{\beta\alpha} = -\frac{A_\alpha}{A_\beta}\left(\frac{D_{\beta 0}}{D_{\alpha 0}}\right)^2 \tag{A-13}$$

This equation is the same as eq 10 in the text. Com-

bining eq (A-13) and eq 8, we obtained

$$R = R_{\alpha 0} R_{\beta 0} \frac{D_{\beta 0}{}^2 \mu_{\beta\alpha} + D_{\alpha 0}{}^2}{R_{\beta 0} D_{\beta 0}{}^2 \mu_{\beta\alpha} + R_{\alpha 0} D_{\alpha 0}{}^2} \qquad \text{(A-14)}$$

which is eq 11 in the text.

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