tity ζ (the monomeric friction coefficient), we have chosen to determine the ratio (Γ_I/Γ_C) as a function of the term $2A_2MC$ for the two extreme compositions. At each concentration the ratio (Γ_I/Γ_C) was calculated using eq 41 and 42 of ref 1a, and these data are plotted in parts A and B of Figure 3. Included in each figure are the theoretical ratios (lines without points) shown as a function of $v\phi N = 2A_2M_wC$. Here v is the excluded-volume parameter, ϕ the total segment concentration in the system, and N is the number of monomers per chain. A_2 values were obtained from static light-scattering measurements on the binary system: matrix polymer/solvent. The A_2 values in the ternary systems used here with trace amounts of the probe should differ insignificantly for present purposes from those in the binary system. Benmouna et al. point out that $A_2M_wC^* = 1$, and thus all the points shown refer to the semidilute range for the fast mode (the matrix component) using this definition of overlap. In the figures, however, we have used the usual definition of overlap: $C^* = 3M/4\pi R_g^3N_A$ (where R_g is the radius of gyration and N_A Avogadro's number), which is approximately equal to the inverse intrinsic viscosity. Above C^*, semiquantitative agreement is found between theory and experiment for the absolute values of the self-diffusion coefficients, which is encouraging since existing theories of self-diffusion give only the scaling result. For comparison with the latter, the concentration exponent for self-diffusion may be derived, for example, from the data in Figure 3. The concentration dependence (and intercept) corresponding to the high-concentration matrix component is well-defined from both these experiments together with data from the binary system. Using the experimental values of Γ_C in conjunction with the predicted ratio (Γ_I/Γ_C) gave the data shown in Figure 4. At a given concentration, the experimental values of D_s are substantially smaller than those predicted. Both the theory points (A) and experimental points (B) are best represented by smooth curves.

Scaling theory[7] predicts a concentration dependence indicated by the inserted line of slope −1.75. As has been shown before,[8-10] this slope has been found to describe experimental findings only over a limited range of concentration. The reptation model,[11] however, provides a less good agreement with experiment.

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Communications to the Editor

Elastic Anomaly near the Critical Point of Volume Phase Transition in Polymer Gels

Poly(*N*-isopropylacrylamide)/water gel (abbreviated as NIPA/water gel) is an ideal system for detailed studies of the volume phase transition (or gel–gel transition) of polymer gels. This gel, with a neutral network and with a pure solvent (water), undergoes a nearly critical phase transition as a function of temperature around $T_0 = 33.6$ °C.[1-3] There has already been a considerable amount of work on this phase transition, though some of the most fundamental properties related to the phase transition have not been studied. For example, no measurement of the elastic moduli has yet been reported.

Because the volume phase transition of gels is essentially a phase-separation phenomenon, it would be reasonable to identify the order parameter of this phase transition as the concentration difference between the two phases on the coexistence line[3] and the variable conjugate to the order parameter as the chemical potential. On the basis of the linear relation between the osmotic pressure of gels and the chemical potential of solvent, we may take the osmotic pressure, Π, as the intensive variable conjugate to the order parameter. Hence, a divergence of the osmotic compressibility or in other words a complete softening of the osmotic bulk modulus is expected at the critical point of the volume transition. The importance of the elastic measurement can hence be understood.

The light-scattering (photon correlation) spectroscopy has widely been used to study viscoelastic properties of gels.[4,5] The quantity measured by this technique, however, is not the elastic modulus itself but is $[K + (4/3)\mu]/f$, where K is the bulk modulus, μ the shear modulus, and f the friction coefficient between polymer and solvent. Thus, the light-scattering experiment alone can determine neither the absolute values nor the temperature dependence of the elastic moduli of gel network.

Static stress–strain measurements have also been made on various gels.[6] Such measurements have so far been made on gels far from the transition point using a compressional stress. A gel plate with a surface area on the order of centimeters squared is sandwiched between parallel glass plates, and a change in thickness of the gel due to compression was measured. Unfortunately, however, this method cannot be applied to NIPA/water gel in the close vicinity of the phase transition for the following reason. When a gel plate is compressed perpen-

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dicular to the surface, the surface area of the plate inevitably changes (i.e., the Poisson's ratio is not zero). The problem is that this gel is very sticky near and above the transition temperature so that the surfaces of gel adhere to the glass plates and cannot freely change sizes when the gel is compressed. The surfaces of gel are thereby clamped, and the resultant inhomogeneous strain inside the gel alters the nature of the transition significantly. In fact, I observed[7] on a gel disk secured between a pair of parallel glass plates that the discontinuous transition disappeared even with a very small compressional stress, and only a broad changeover between the swollen and shrunken states took place. In this type of measurement, the effect of boundary clamping and the effect of compression are inevitably intermixed, and the former may become significant near the volume transition.

Previously[8] we observed that long and thin gel rods stretched uniaxially undergo a distinct first-order transition. On the basis of this observation, it is expected that if we hold a long gel rod at both its ends, apply tension on it, and measure the change of its size on the central portion, then the influence of the boundary clamping will be avoided and we will be able to obtain the elastic response of gel under homogeneous tension. This paper is a preliminary report of the successful application of this technique to NIPA/water gel.

Gels were prepared from monomers of NIPA (Kodak Co.) and a cross-linker *N,N'*-methylenebisacrylamide (BIS; Wako Chemicals Co.) by radical polymerization in an aqueous solution. The pregel solution contained 0.7 mol/L of NIPA and 8.4×10^{-3} mol/L of BIS. Details of the preparation are described in ref 2. Gels used in the present experiments were of cylindrical shape with a diameter $D_0 = 2.0$ mm and a length $L_0 \simeq 15$ mm, where the subscript 0 means the sizes at the time of gelation. The method of holding gel rods and of imposing tension on them are described in ref 8.

The measurements were made of the diameter D and the length L with a specicially designed microscope, which had a horizontal optical axis and was equipped with an attachment (Model OSM, Olympus Co.) to measure small displacements. This microscope allowed us to measure the size of a gel rod while it was placed in an aquarium. With a magnification of 40, the accuracy of the measurement was better than ±3 μm. Hereafter, we use the subscript t to denote the size of the gel under tension and the subscript f to denote the size without tension. If we know D_f, L_f, D_t, L_t, and the value of the applied tension, we can calculate all the elastic moduli of the gel.

The actual procedure of the measurement was as follows. A couple of gel rods were swollen to equilibrium without tension in distilled water at 32.5 °C (T_r, the reference temperature), and their D_f and L_f were measured. The values of D_f measured on two rods usually coincided within ±0.5%. It should be mentioned that the length L measured was not the whole length of the rod but a distance between a pair of very slight scars or flaws (less than 10 μm in size) on the surface of the middle part of the rod. These scars or flaws, which may probably be formed during gelation due to imperfections on the inner surface of glass capillaries, were, of course, not frequently found. If an appropriate pair of marks was not found, the gel rod had to be replaced by a new one until a satisfactory one was met.

After the measurement at T_r, a weight (~0.7 g) was attached to one of the rods (rod A) on its lower end, while the other rod (B) was left free. Then the temperature of the aquarium was increased slightly (0.1 °C or less), and after about 24 h D_t and L_t of rod A and D_f and L_f of rod B were measured. The values of D_f and L_f of rod A at this temperature T, i.e., the diameter and the length rod A would have if it had been free, were calculated from the measured values of D_f and L_f of both rods at T_r, and those of rod B at T, through the proportionality relation. This procedure is justified because both rods were prepared at the same time from the same pregel solution in the same capillary, and hence both should have the same swelling properties. The measurements at each temperature were made after a long equilibration time (1 day or more); hence, I believe that the elastic constants determined are equilibrium ones. The temperature of the aquarium was controlled to within ±0.03 °C.

Figure 1 shows the diameter of the gel rod measured without tension. A slightly discontinuous transition takes place at $T_0 = 33.8$ °C. Figure 2 shows K and μ measured with an applied tension of $F_0 \simeq 0.2$ Pa. With this value

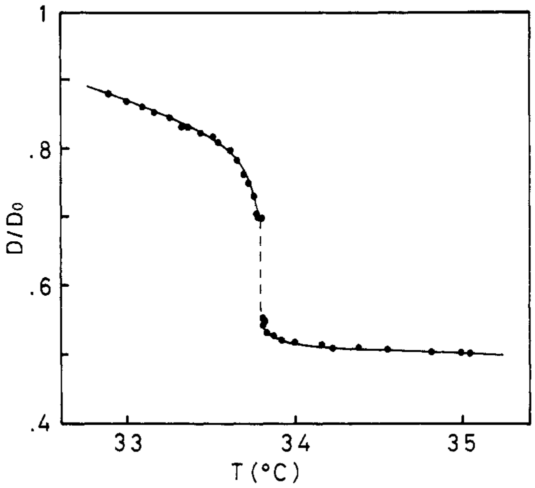

Figure 1. Diameter of free gel rod as a function of temperature showing a discontinuous phase transition at ~33.8 °C. D_0 is the diameter at the time of gelation.

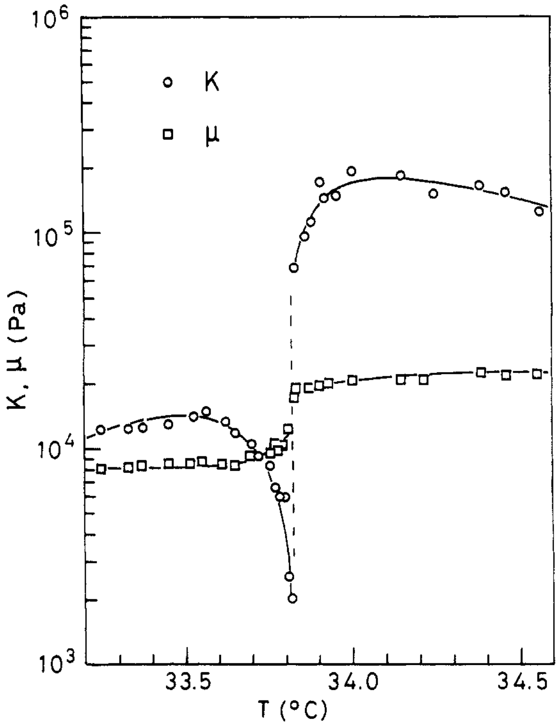

Figure 2. Bulk modulus, K, and shear modulus, μ, as a function of temperature. Lines are guides for the eye.

Macromolecules **1990,** *23,* 905–907

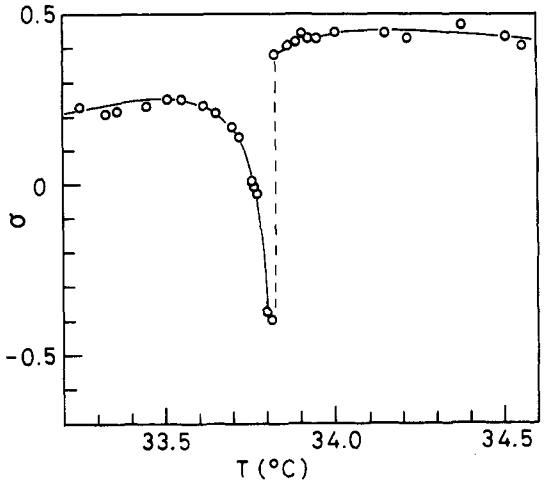

Figure 3. Poisson's ratio, σ as a function of temperature. Lines are guides for the eye.

of tension, the shift of transition temperature[8] was about 0.05 °C. A drastic softening of K toward T_0 both above and below T_0 is noted, though the softening is incomplete due to the first-order nature of the transition. On the contrary, μ shows only a small steplike anomaly at T_0.

The Poisson's ratio σ shows a very characteristic anomaly as shown in Figure 3. On approaching T_0 from below, σ decreases sharply and even becomes negative in the extreme vicinity of T_0. Negative Poisson's ratio demonstrates the fact that if we elongate the gel network in one direction, it elongates also in the perpendicular directions. Although the negative values of σ do not violate the stability condition, such values have not been found in any isotropic material so far.[10] (We should point out, however, that the equilibrium Poisson's ratio of gel network is somewhat different from the Poisson's ratio of conventional solids, because the amount of solvent contained in a gel is different before and after the deformation.)

In terms of K and μ, σ is expressed as

$$\sigma = (3K - 2\mu)/(6K + 2\mu) \qquad (1)$$

Thus we see that σ is negative when $\mu > 3K/2$. This condition is surely satisfied in the vicinity of the critical point of volume phase transition of gels, where K tends to zero while μ remains nearly constant.[11] The elastic stability condition limits σ to $-1 < \sigma < 0.5$.[10] We can see from eq 1 that $\sigma = -1$ corresponds to the volume instability ($K = 0$) and $\sigma = 0.5$ to the shear instability ($\mu = 0$). The drastic variation of σ around the volume transition will be more clearly seen if the gel undergoes a true critical transition. The measurement for this case is now in progress.

It has been demonstrated[8,12] that the anomalous swelling properties of NIPA/water gel can be explained fairly well within the Flory theory of gels provided that the empirically determined material parameters (the enthalpy and the entropy of solution) are used. We can indeed show that the free energy expression including the concentration-dependent polymer–solvent interaction parameter used in the previous studies[8,12] can reproduce quantitatively the present experimental results. The details will be reported elsewhere.

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Liquid-Crystalline Poly[oxybis(trimethylene) *p,p′*-bibenzoate]: Effect of the Central Ether Group

In recent years the interest in thermotropic mesogenic materials has grown extraordinarily. These compounds usually exhibit a mesophase at temperatures above the region of the crystalline solid and before the formation of an isotropic melt. Among them, aromatic polyesters constitute an important class of main-chain liquid-crystalline polymers but with the inconvenience of their very high melting points, sometimes not detected before the degradation of the sample.

One method of reducing the high melting points of all-aromatic, rodlike polyesters, so that the polymers will be sufficiently thermally stable to be injection molded or melt spun, is to introduce flexible aliphatic units into the polymer main chains. Poly(ether glycols) with an even number of carbons in the chain repeat segment, i.e., poly(oxyethylene glycol) or poly(oxytetramethylene glycol), have been widely used in the synthesis of polyesters. Less use has been done of the intermediate polyglycol, i.e., poly(oxytrimethylene glycol), which has an odd number of carbon atoms in the chain repeat unit.

On the other hand, polyoxetanes with the structural unit $-OCH_2CR_1R_2CH_2-$ are an interesting class of polyethers where the properties can be easily modified by changing the nature of the substituents R_1 and R_2. The parent compound of this series, poly(trimethylene oxide) (PTO) (or polyoxetane), exhibits one of the lowest characteristic ratios in polymers and a great flexibility.[1] This property can be modified by substituting the two hydro-

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