SHORT COMMUNICATIONS

Volume Phase Transition of a Poly(*N*-isopropylacrylamide) Gel under Tension. Emergence of a New Critical Point

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The volume phase transition of polymer gels is one of the highlighted phenomena in the field of polymer physics, and extensive studies[1] have been made to clarify the origin and universality class of the transition. Poly(*N*-isopropylacrylamide) (PNIPA) gels with proper polymer concentrations and crosslink densities undergo the volume phase transition in water responding to an infinitesimal change of temperature, and the gels are widely used in the studies of the volume phase transition of polymer gels. A swollen phase is observed at low temperatures and at temperatures higher than the transition temperature (T_{tr}) a collapsed phase emerges for the PNIPA gels showing the volume phase transition, and T_{tr} lies around 35°C. The effects of applied tension on the volume phase transition have also been studied for the gels,[2—5] and the results show that the transition temperature and the degree of discontinuity increase with increasing tension as long as the applied tension is relatively low.[2—5] When the applied tension increases further both of the transition temperature and the degree of discontinuity level off,[3—5] but the information on the transition behavior under large extensions is still quite limited. It is very interesting and also important to examine how the PNIPA gels behave when high tension (or more exactly, high extensional stress) is applied to the gels. In this study we examine the effects of the higher tension on a PNIPA gel showing the volume phase transition in the stress-free state.

EXPERIMENTAL

A cylindrical PNIPA gel was prepared by copolymerizing *N*-isopropylacrylamide (NIPA) and *N*,*N'*-methylene-bis(acrylamide) (BIS) in distilled water. *N*,*N*,*N'*,*N'*-tetramethylethylenediamine was used as an accelerator. The molar ratio of NIPA to BIS was 60,

and the total monomer concentration in the pregel solution was 10 wt%. The pregel solution was poured into a glass tube and then the gelation was performed at 20°C. The cylindrical gel was washed in water to remove the reaction residues. The diameter of the specimen was *ca.* 200 μm at 30°C. The gel was fixed in a specially designed water bath, and tension was applied to the gel in water by using metal weights. Two types of weights, 37.5 mg and 77.5 mg, were used. The former weight is referred to as w_1 and the latter as w_2. The accuracy in controlling water temperature in the bath was ± 0.02°C. The local length (*l*), the distance between two marked points on the surface of the gel, and the diameter (*d*) were measured as a function of temperature in loaded as well as unloaded states. The local volume of the gel specimen (*V*) was calculated by

$$V = \frac{\pi d^2 l}{4} \qquad (1)$$

RESULTS AND DISCUSSION

Figure 1 shows the temperature (*T*) dependence of the local length for the PNIPA gel. Here, the normalized length (l/l_0) is used instead of *l* itself, l_0 being the value of *l* in the unloaded state at 31.0°C. The curve shifts to the higher length side as the applied weight increases. For each of the three curves, data points obtained on heating and on cooling appear to fall on a single curve over the *T* range examined, far from as well as near the transition point. The curve without loading shows a discontinuity at 33.65°C, and the discontinuous change of l/l_0 is observed at 33.81°C for the curve under loading of w_1. The transition temperature T_{tr} for the curve at w_1 is higher than that without loading. It is also clear that the degree of discontinuity at T_{tr} is
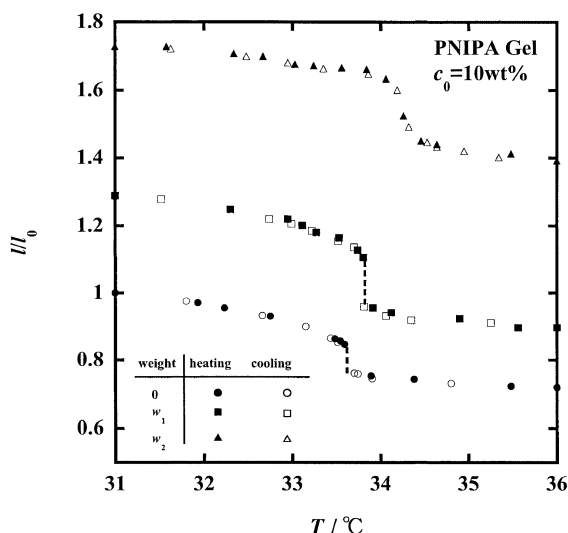
Figure 1. Temperature dependence curves of the normalized local length of the PNIPA gel.
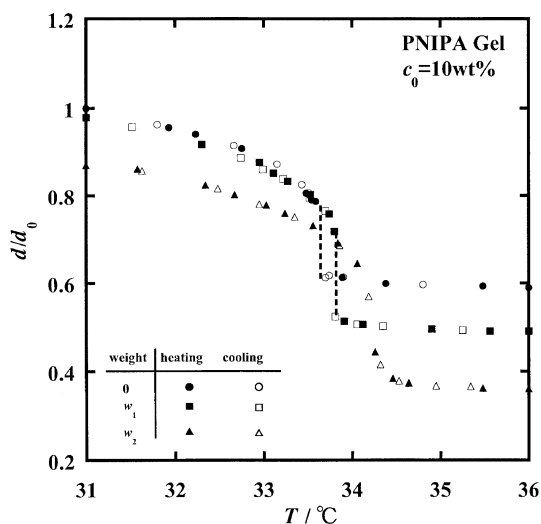

Figure 2. Temperature dependence curves of the normalized diameter of the PNIPA gel.

Figure 3. Temperature dependence curves of the normalized local volume of the PNIPA gel.

In Figure 3 the plots of V vs. T are shown for the gel specimen. The normalized volume V/V_0 is employed in this figure, V_0 being the volume without loading at $31.0°C$. The local volume increases with increasing tension at low temperatures (*i.e.*, in the swollen state) while the volume decreases with increasing tension in the collapsed state occurring at high temperatures. As can be seen from the comparison between the curves without and with loading of w_1, T_{tr}, and the degree of discontinuity in V increase by the addition of the weight w_1, although this is natural conclusion derived from the results shown in Figures 1 and 2. On the other hand, the curve at the highest load (w_2) gives a continuous $V-T$ curve.

As stated previously, the transition temperature T_{tr} and the degree of discontinuity for PNIPA gels showing the volume phase transition increase with increasing tension. A PNIPA gel undergoing the second order transition (continuous transition), although the gel was different in composition as well as in polymer concentration from that used in this study, changed to show the first order transition by increasing tension.[5] The gel must show a continuous volume change under compression, because the compressional force is negative tension. This suggests that a PNIPA gel undergoing the first order transition in the zero-stress state, corresponding to the gel used here, changes to show the second order transition at a certain compressional force (*i.e.*, critical force) and then to show the continuous volume change at larger compressional forces than the critical one. Until now, there has been little information on the shape of the unstable region far from the critical point, and the unstable region opposite to the critical point has been believed to be open from the analogy with the van der Waals fluids.[1,5] In this study, it was

enhanced by loading. The T dependence curve under loading of w_2 shows a steep change of length in the T range of $34.1–34.4°C$, but the change appears to be continuous. Figure 2 shows the T dependence curves of d for the gel specimen. Here, d is normalized by d_0, the diameter without loading at $31.0°C$, as is the case of l. From the comparison of the curves without and with loading of w_1, one can see that T_{tr} and also the degree of discontinuity increase by the addition of the small weight. The curve at w_1 is close in position to that without loading in the swollen state, namely in the low T region, but the curve is located in the low d region compared with the curve without loading. The curve at w_2 shows no discontinuity, and is located in the lower d side than the other two curves over almost the whole T range examined. The exception occurs only around $34°C$.
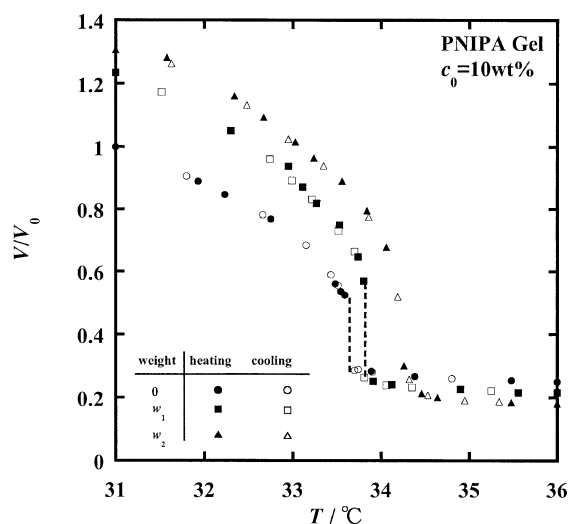
shown that the V–T curve (also l–T and d–T curves) at the larger weight (w_2) has no discontinuity, while the curves without a weight and with the smaller weight (w_1) have a discontinuity. The gel used in this study actually showed the discontinuity in the unloaded state, but the V–T curve for the gel in the low T side must become continuous if large compressional forces are applied to the gel, as stated above. In this case, the unstable region for the PNIPA gel system is closed and the gel system is concluded to have two critical points, although it is still unclear at present whether this can be applied to any kind of PNIPA gel.

REFERENCES

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