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Communications to the Editor

Shape-Dependent Swelling and First-Order Phase Transition in Polymer Gels with an Ionized Network

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A number of experimental studies have already been made on swelling and volume phase transition of polymer gels. In most of these studies, cylindrical or spherical samples were used. This is because these shapes offer advantages of ease in handling samples as well as simplicity in theoretical analysis of the results. Of course, it has been taken for granted that the shape of the sample has no influence on the bulk equilibrium properties of the gels. Surprisingly, however, a simple experiment can show quite directly and unambiguously that the thermodynamic properties such as the degree of swelling and the phase transition temperature of ionized gels depend strongly on the sample shape. The purpose of this paper is to report on the observation of this very unusual phenomenon and to discuss its plausible mechanism.

Copolymer gels of *N*-isopropylacrylamide (NIPA) and acrylic acid (AA) were prepared in an aqueous solution as described before.[1-3] The pregel solution contained 680 mM NIPA, 20 mM AA, and 8.6 mM N,N'-methylenebisacrylamide (BIS; cross-linker). Cylindrical gels of various thickness were prepared using glass tubes as molds. The inner diameters of the glass tubes used were 0.2, 0.6, 1.0, 2.0, 3.5, and 4.5 mm. In addition, gel plates were also prepared using rectangular glass trays as molds. It was essential in the present experiment that all the samples be prepared from the same pregel solution at the same time, which assured that the compositions and structures of the gel network of all the samples were identical. Gelation occurred within 1 h at 15 °C, though gels were kept as they were for 2 days for cure. It was not difficult to remove gel cylinders from the molds, as they did not adhere tightly to the inner wall of the molds.

After taken out of the molds, gel cylinders were cut into pieces of 10–50 mm long, and gel plates were cut into rectangles with edges 5–30 mm. Then, they were put into a large amount of distilled water and kept at room temperature to assure equilibration. After more than 1 month, the linear sizes of these samples were measured with a microscope. The degree of swelling is represented by the swelling ratio α defined by $\alpha = L/L_0$, where L is the linear size of the gel after swelling and L_0 the value at the time of gelation. The result is shown in Figure 1. It is seen that α increases with the diameter of the cylinders. This result is surprising because it shows quite unambiguously that the swelling equilibrium of ionized gel cylinders depends strongly on their diameters, even though all the samples must have identical structure and composition. For plates, α was larger than that of the thickest cylinder measured and did not seem to depend on the length of the edges of the plates.

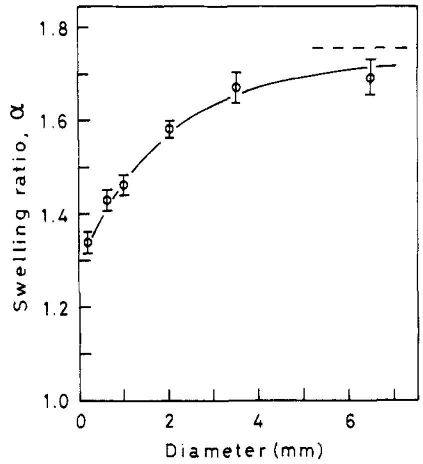

Figure 1. Linear swelling ratio of NIPA–AA copolymer gel cylinders at 20 °C as a function of diameter. A solid line is a guide for the eye. A dashed horizontal line denotes the value obtained on cubes and plates.

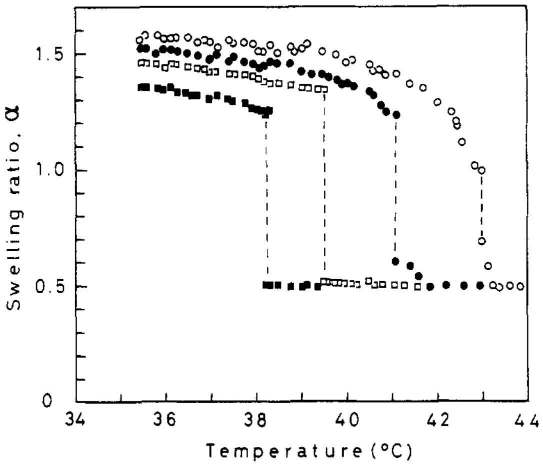

Figure 2. Linear swelling ratio of NIPA–AA copolymer gel cylinders as a function of temperature measured on heating. Diameters are 0.6 (■), 1.0 (□), 2.0 (●), and 3.5 mm (○).

Because the above result was quite unexpected, it was suspected that glass walls of the molds have some special effect, which, for example, gives rise to a thick surface layer at the time of gelation. To test this speculation, I prepared gels using tubes made of materials other than glass. Materials tested were Teflon, polyvinyl, alumina-silicate ceramics, and stainless steel. Except for the case of stainless steel, gels could be removed from the molds quite easily. It turned out that α measured on these samples also showed clearly the shape dependence similar to that shown in Figure 1. Hence, it is unlikely that the observed shape dependence is due to the materials of the molds used in preparing gels.

Next I measured α as a function of temperature by the same method as described previously.[4,5] Samples used were cylindrical gels prepared using glass tubes. The results obtained on heating are shown in Figure 2, where dashed lines denote temperatures at which a nucleus of

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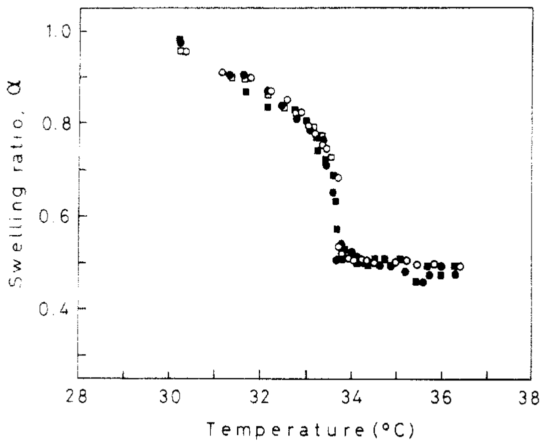

Figure 3. Linear swelling ratio of neutral NIPA gel cylinders as a function of temperature on heating. Diameters are 0.2 (■), 0.6 (□), 1.5 (●), and 3.5 mm (○).

the high-temperature phase first appears. Strictly, this temperature may not be equal to the transition temperature, because a relatively wide two-phase region exists around the first-order transition of gels. However, we will not go into such details here and regard this temperature as a first-order transition temperature. The most remarkable point of this result is that the transition temperature increases with the diameter of the cylinders.

For comparison, I made the same measurements as above on neutral NIPA gels. The neutral gel prepared contained 700 mM NIPA and 8.6 mM BIS. As in the case of ionized gels, cylindrical samples were prepared using glass tubes as molds. The results of measurement are shown in Figure 3. It is clear that both the swelling ratio and the transition temperature do not depend on diameter. Independent measurements showed that α measured on plates and cubes coincided with that measured on cylinders. We can say from these results that the shape-dependent properties observed in ionized gels are due to ions contained in them. Especially, ions in the surface region will play a decisive role.

Quantitative theory of the roles played by counterions and fixed ions in the swelling equilibrium of ionized gels has not been fully developed. Moreover, the surface state of ionized gels has not been studied at all. Hence, the unambiguous explanation for the present observation cannot be expected at the present stage. We will mention below some possible mechanisms which may explain the observed shape dependence. As noted above, it is plausible that ions in the surface region of ionized gels play a decisive role in the shape-dependent swelling and phase transition properties. There must be a surface layer in which the concentration of the ions (either or both of counterions and fixed ions) is different from that of bulk.

One conceivable origin of such a surface layer is the specific mold material which may have a significant influence on the polymerization–gelation reaction.[11] If different monomeric species constituting a copolymer gel have different affinities to mold materials, a portion of the network formed in the close vicinity of the wall will have different compositions from that formed in the bulk. If, in the present case, the concentration of the ionic species (acrylic acid) in the surface layer is smaller than that of the bulk, α in the surface layer will be smaller than the bulk value. Then, the free energy of the total sample will have a minimum at the value of α, which lies intermediate between the bulk and the surface values. As the sample size increases, the relative contribution from the surface layer to the total free energy of the sample decreases so that the equilibrium α of the whole sample approaches the bulk value. However, the present result shows that the observed shape dependence does not depend on the mold materials. Hence, it is unlikely that some specific interaction between mold materials and monomers is the origin of the observed shape dependence.

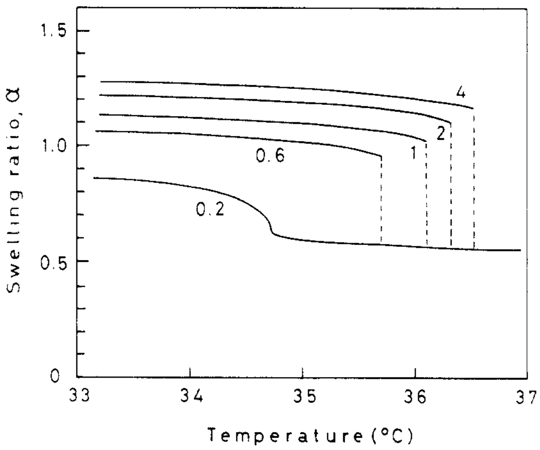

Figure 4. Swelling curves of ionized gel spheres calculated on the basis of the new equilibrium condition, eq 2. The numerals represent the diameter in millimeters. The dashed lines indicate transition temperatures determined by the Maxwell rule.

Another possible mechanism leading to the shape dependence is a surface-tension effect. We note that the surface tension of gels gives rise to the osmotic pressure which depends on the curvature of the surface. Consider, as the simplest example, a spherical gel immersed in solvent. It is easy to show that the surface tension yields an inward osmotic pressure given by

$$\pi_s = 2\gamma/\rho \qquad (1)$$

where γ is the surface tension and ρ is the radius of the sphere. Extending the conventional Flory-type theory of gels[4,6–8] to include this component, we can write the equilibrium condition as

$$\pi_m + \pi_e + \pi_i + \pi_s = 0 \qquad (2)$$

The first three terms represent mixing, elastic, and ionic contributions to the osmotic pressure, respectively, the expressions for which have already been given in many places.[4,6–8]

We can calculate the swelling curves of ionized gel spheres on the basis of eq 2. The typical results are shown in Figure 4. In this calculation, I put f (number of counterions per chain)[3,8] = 1.2, which corresponds to the ionic concentration of the present gel. The value of the surface tension was put rather arbitrarily as $\gamma = 1 \times 10^3$ dyn/cm. Other parameters were identical to those used in the previous calculations.[4] In a cylindrical gel, eqs 1 and 2 must be modified to allow for the uniaxial anisotropy of π_s. However, it can be shown that the total π, which is of course isotropic, does not differ much from that of spherical gels of the same radius. Hence, the result shown in Figure 4 can also be taken as roughly representing the behavior of cylindrical gels. We see that the qualitative features of the experimental results shown in Figure 2 are reproduced here.

Although it is not clear whether a large tension is really present at the ionized gel–solvent interface, we note here that there is at least one possible mechanism which can give rise to a surface tension in ionized gels but not in neutral gels. It is related to an electrical double layer at the gel–solvent interface. In a surface region of ionized gels, a part of the counterions will diffuse away to the outer solvent, leaving an excess charge on the surface.[9] This surface excess must be compensated for by free ions with an opposite charge in the outer solvent, and, thus, an electrical double layer should be formed at the interface. Thermodynamics of the polarizable interface[10] predicts that a surface tension γ_e given by $\gamma_e = \sigma_s \Delta V$ is induced, where σ_s is the surface charge and ΔV is the potential difference. However, it is not certain whether the surface tension as large as 10^3 dyn/cm can be induced by the above mechanism. A rough numerical estimate shows that γ on the order of 10^2 dyn/cm can be induced provided that a few tens of a percent of counterions contained in the surface layer with a depth of the Debye–Hückel length κ^{-1} (which amounts to less than 10^{-6} of counterions in the whole sample) flow out of the gels and form an electrical double layer.

I admit that the mechanism proposed above to interpret the present result should be regarded as tentative. Because of lack of experimental information on the surface state of ionized gels, we cannot give the correct, unambiguous explanation to the shape-dependent properties at the present stage. What I want to stress here is that the surface state of ionized gels needs special consideration and raises interesting problems in the physics of gels. Further studies on this subject are now in progress.

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Registry No. (NIPA)(AA) (copolymer), 79042-19-6.