

Electric Field-Associated Deformation of Polyelectrolyte Gel Near a Phase Transition Point

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SYNOPSIS

The influence of dc electric fields on sodium acrylate–acrylamide copolymer gel near a phase transition point in acetone–water mixtures containing NaOH was studied. In the mixtures free of NaOH, the shrunken-state gel near a phase transition point was not influenced by dc electric fields, while the swollen-state gel near it shrank from its part facing to the positive electrode in dc electric fields. In the presence of NaOH, unprecedented swelling of the shrunken-state gel has been observed. The swollen-state gel showed swelling or shrinking in the field. The type of deformation was determined by the concentration of NaOH. The drift of mobile ions played a role in the deformation. The shrinking occurred through the conformational change of polymer network caused by the drift. The swelling was observed by the change of the osmotic pressure based upon the ion concentration difference between the inside and the outside of a gel.

INTRODUCTION

Polyelectrolyte gel is a solid–liquid coexisting material consisting of crosslinked organic polymer chains with polyions and water as a solvent. It shrinks in an aqueous solution when the surrounding solution becomes poor solvent against the gel. In some cases the change of the solvent composition produces a drastic volume change. This phenomenon is called phase transition.¹ Polyelectrolyte gel also shows the phase transition when the temperature of the surrounding solution is changed. At a phase transition point, the gel has two states, swollen state and shrunken state. When the gel near a phase transition point receives a small change of the solvent composition or that of that temperature, it comes and goes between the swollen state and the shrunken state. It undergoes the volumetric change by the application of dc electric fields in the same way.

Concerning on the influence of electric field on polyelectrolyte gel, Tanaka has observed that par-

tially hydrolyzed polyacrylamide gel near a phase transition point in an acetone–water mixture was shrank by applying dc electric signals across the gel.² Hirotsu also³ reported that the electric field contracted an ionized poly(isopropyl acrylamide) gel near a phase transition point in water. Those shrinkings have been observed in the solutions free of electrolyte when the swollen-state gel is touching a pair of electrodes. The gels shrank at their anode side. In the previous article,⁴ Shiga and Kurauchi found that sodium acrylate–acrylamide copolymer gel (PAA gel) showed not only shrinking but swelling in electrolyte aqueous solutions under dc electric fields. The type of deformation depends on the concentration of electrolyte. When the concentration is high, the gel swells and it shrinks when low. The electric field-associated deformation has been observed when the gel is placed not touching the two electrodes. The obtained results suggest that the PAA gel near a solvent composition–phase transition point shows swelling in solutions with high contents of an electrolyte by the application of dc electric fields. In this study the deformation of the swollen-state PAA gels or the shrunken-state PAA gels near a phase transition point in acetone–water mixtures containing NaOH under the influence of dc electric fields was studied.

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DEFORMATION MECHANISM OF POLYELECTROLYTE GEL⁴

The deformation of polyelectrolyte gel by the application of dc electric fields is associated with the drift of ions. The drift of ions produces the changes of two factors. One is the change of the osmotic pressure of a gel due to the difference of ion concentrations between the inside and the outside of a gel. The other is the conformational change of crosslinked polymer chains due to pH change in the gel.

Consider the PAA gel with negatively charged polyions in NaOH aqueous solutions under dc electric fields. The deformation caused by the conformational change of crosslinked polymer chains due to the pH change has been observed in the solution free of NaOH or in the solution with low contents of NaOH. In the case of the PAA gel, the decrease of pH in the gel leads to a change of polyion, $-\text{COO}^- \text{Na}^+$ to $-\text{COOH}$. The change represents a change of strong polyelectrolyte to weak polyelectrolyte, and so it implies the decrease of the electrorepulsive interactions between polyions. The conformation of crosslinked polymer chains changes from an expanded state to a compact one, and then the gel shrinks.

The PAA gel also shows the deformation due to the osmotic pressure change of a gel in the solutions with high contents of NaOH. The deformation is explained by Flory's theory.⁵ Prior to the application of the field, the gel and the surrounding solution are under equilibrium as far as the swelling is concerned. When a dc electric field is applied across the gel, the counterions (Na^+) of polyions in the PAA gel move to the negative electrode, although the polyions are fixed immobile to the network. Mobile ions in the surrounding solution also move to the positive or negative electrodes at different speeds. Accompanying the drift of ions, water is dissociated into hydrogen ion and hydroxide ion, and then they are provided appropriately so as to maintain the electrical neutrality in the gel or in the solution. Therefore, the drift of mobile ions produces the change of the osmotic pressure due to the ion concentration difference between the inside and the outside of a gel. When the osmotic pressure increases, the gel swells, and it shrinks when the pressure decreases.

EXPERIMENTAL

PAA gel used was prepared by radical polymerization. In the vessel 0.02 mol of sodium acrylate, 0.08

mol of acrylamide, and 0.002 mol of *N,N'*-methylenebisacrylamide was dissolved in 50 mL of ion-exchanged distilled water. After the addition of 50 mg of ammonium persulfate and 200 μL of tetramethylethylenediamine, the solution was heated at 60°C for 3 h for gelation. The prepared gel was cut in weight of 1 g, and the one piece of the gel was immersed in 1000 mL of NaOH-acetone-water with the concentration of NaOH up to 0.0075 *M* to give the PAA gel.

The experiment of applying dc electric fields across the PAA gel was carried out at room temperature as follows. After the PAA gel reached a swelling equilibrium state with the surrounding solution, it was cut in any size. The gel was placed in a bath of the mixture in isolation from the positive and negative platinum electrodes, and then the voltage up to 120 V dc was applied between the electrodes (separation: 3 cm).

RESULTS

The PAA gel has exhibited a phase transition in NaOH-acetone-water mixtures. The acetone con-

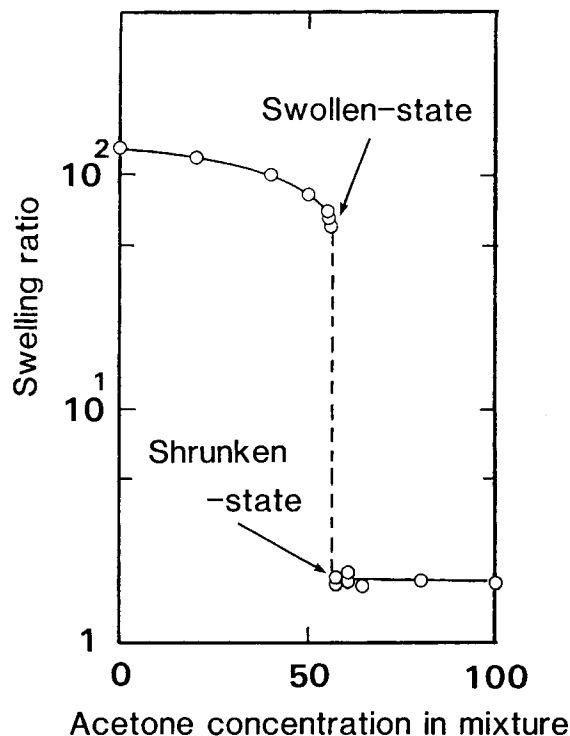


Figure 1 Swelling ratio (W_s/W_d) of sodium acrylate-acrylamide copolymer gel (PAA gel) in acetone-water mixtures containing NaOH. W_s and W_d represent the weights of the PAA gel swollen in solvent and of dried gel, respectively. The concentration of NaOH is 0.005 *M*.

centration at the phase transition is about 57% in all mixtures with NaOH concentration up to 0.0075 *M*. The swelling ratios (W_s/W_d) of the swollen-state gel at 56% of acetone concentration and of the shrunken-state gel at 58% in the mixture with 0.005 *M* of NaOH are 62 and 1.8, respectively (Fig. 1). Here, W_s and W_d represent the weights of PAA gel swollen in solvent and of dried gel.

Figure 2 shows the weight change of the swollen-state PAA gel at 56% of acetone concentration in the mixtures with the concentration of NaOH up to 0.005 *M* under the influence of a dc field with the intensity of 1.67 V/cm. The weight change was calculated by the following equation: $(W - W_0)/W_0 \times 100$, where W_0 and W represent the weights of the gel at imposing time of the electric field $t = 0$ and $t = t$, respectively. The swollen-state PAA gel shrinks or swells from its part facing to the positive electrode when it is subjected to the field. The type of deformation has been determined by the concentration of NaOH. The gel in the mixture free of NaOH shrinks as reported by Tanaka.² The gel also shrinks when the concentration of NaOH is less than 0.001 *M*. The shrinking speed and the amount of shrinking decrease with the increase in the NaOH concentration. On the other hand, the swollen-state PAA gel swells when the concentration is more than 0.0025 *M*. The shapes of the gel before or after applying an electric field are shown in Figures 3(a) and 3(b). The size of the PAA gel in Figure 3 is 5

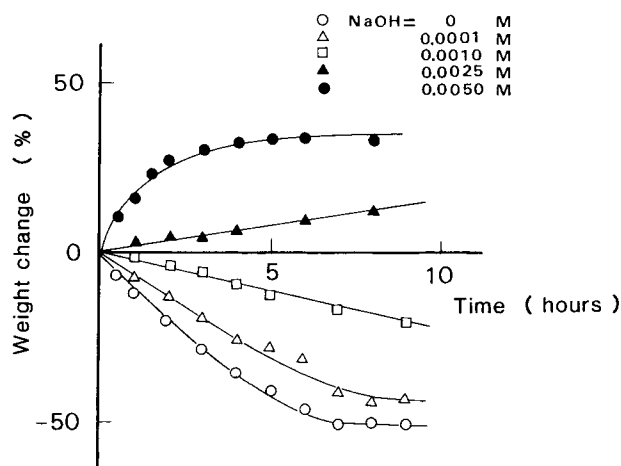
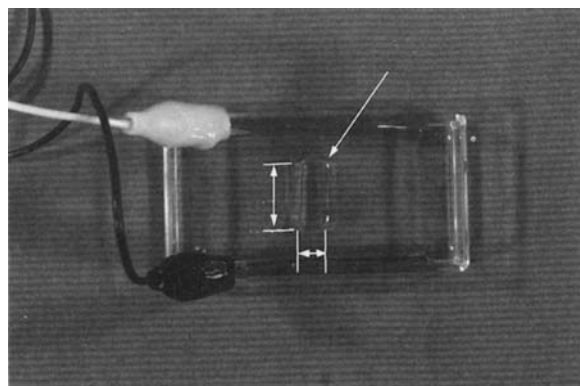
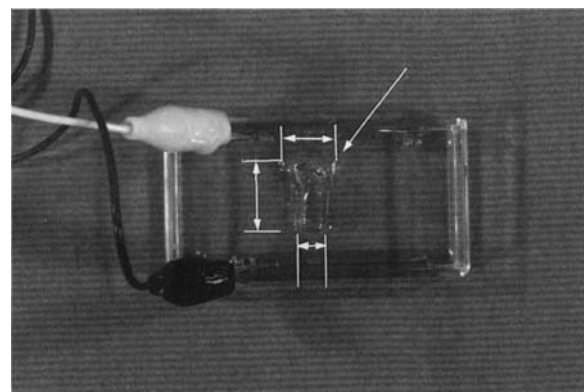


Figure 2 The weight changes of the PAA gels at 56% of acetone concentration in NaOH–acetone–water mixtures with NaOH concentration up to 0.005 *M* in a dc electric field of 0.67 V/cm. The weight change is calculated by an equation $(W - W_0)/W_0 \times 100$, where W_0 and W represent the weights of the PAA gel at the imposing time of the field, $t = 0$ and $t = t$.



a



b

Figure 3 The swelling of the swollen-state PAA gel in a dc electric field: (a) no field, (b) field applied. The field intensity is 1.67 V/cm. In Figures 3–6 the experiments have been made in the mixtures with 0.005 *M* of NaOH.

$\times 5 \times 15$ mm. It takes about 3 h to deform as shown in Figure 3(b). The swelling speed depends on not only the concentration of NaOH but the intensity of the applied field. Figure 4 shows the swelling ratios of the swollen-state gel in 0.005 *M* of NaOH at the imposing time of an electric field, $t = 10$ min, under electric fields up to 40 V/cm. The swelling ratio, which represents a swelling speed, increases with the intensity of the applied field. The obtained results in Figures 2 and 4 indicate that the diffusion of mobile ions plays an important role in the kinetics of the deformation.

The shrunken-state PAA gel near a phase transition point in the mixture free of NaOH is not influenced by dc electric fields. In the presence of

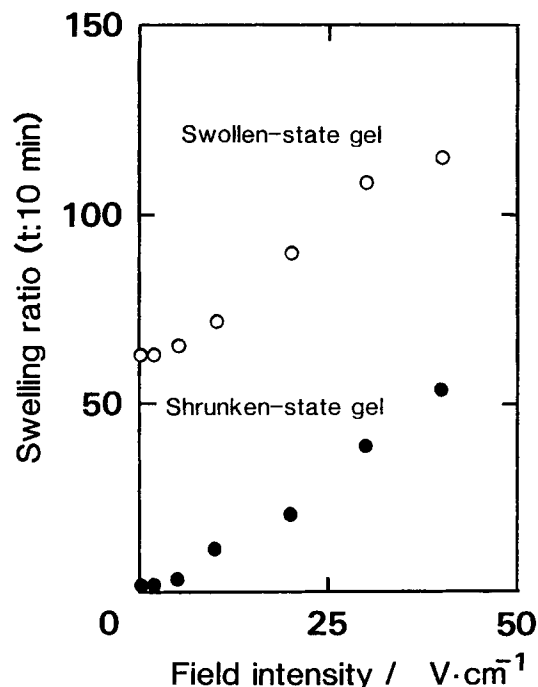


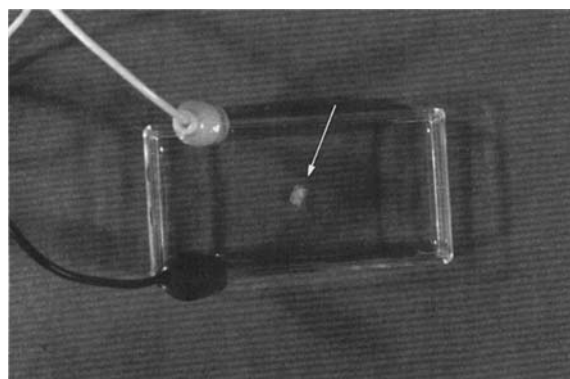
Figure 4 Effect of the field intensity on the swelling speed. The swelling ratio ($t = 10$ min) is the swelling ratio in 10 mins under an electric field, which represents swelling speed.

NaOH, the gel has not also responded to the electric signals of less than 0.67 V/cm. However, the shrunken-state PAA gel shows swelling under a dc electric fields [Figs. 5(a) and 5(b)]. The observed swelling is a large and unprecedented deformation. The swelling ratio of the shrunken-state gel changes from 1.8 to 76. The latter swelling ratio is more than that of the swollen-state gel at 56% of acetone as shown in Fig. 1. The swelling speed has been controlled by the intensity of the applied field (Fig. 4). It is also influenced by the NaOH concentration. The speed is practically proportional to the NaOH concentration.

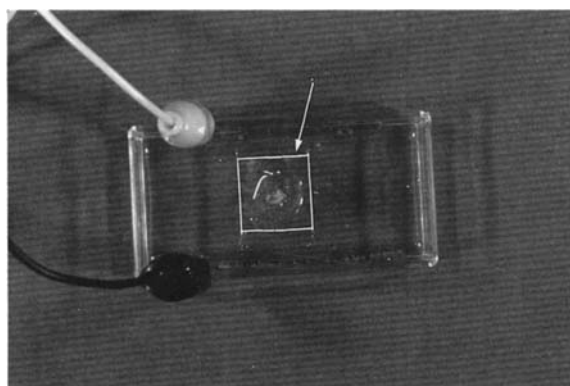
The shrunken-state gel at 58% of acetone concentration near a phase transition point swells in a dc electric field, but the gels have not been influenced by the electric field in the mixture of the acetone concentration of more than 60% regardless of the presence of NaOH. The result says that the electric field enhances the volume of the gel and shifts the acetone concentration at a phase transition from 57 to 60%.

Figure 6 indicates the reversing behavior of the deformed gels by removing the applied field or by changing the polarity of the applied field. The deformed gels near a phase transition point by the ap-

plication of an electric field return to the starting shapes slowly when the applied field is removed. If the acetone is evaporated from the mixture by the electric field and the swelling of the gel is based upon the evaporation of acetone, the deformed gel cannot go back to the starting state before applying an electric field. So the result says that the swelling is not induced by the evaporation of acetone. The reversing behavior of the gels has also been observed when the current direction is varied. The gels shrink, but they swell again in 15 min. This swelling is the same deformation as the swelling observed before varying the current direction. Figure 6 suggests that the swelling is induced by the drift of ions in dc electric fields.



a



b

Figure 5 The swelling of the shrunken-state PAA gel in a dc electric field with the intensity of 10 V/cm: (a) no field, (b) field applied.

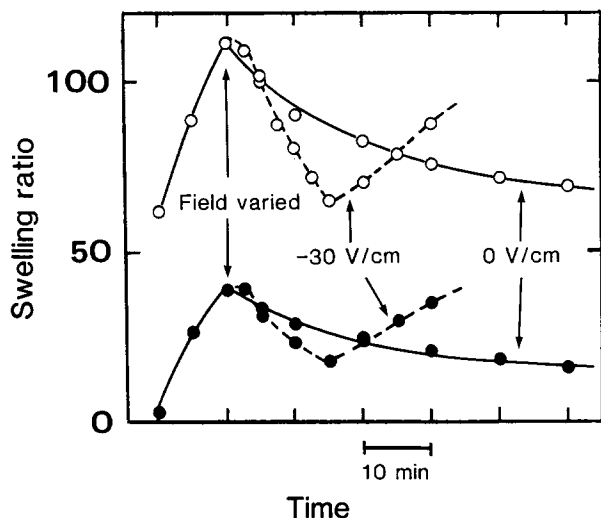


Figure 6 The deformation behavior of the deformed gels by removing the applied electric field, 30 V/cm or by changing the polarity of the applied field, 30 V/cm; (○) the swollen-state gel and (●) the shrunken-state gel. The solid and the dotted lines represent the changes of the swelling ratio under 0 V/cm and under -30 V/cm, respectively.

DISCUSSION

Deformation Mechanism of Swollen-State Gel

To understand the mechanism of the deformation UV spectra of the gels before and after applying an electric field were measured using an UV-VI spectrophotometer (Otsuka Electronics Ltd., SM-401). As shown in Figure 7, two peaks of the optical density near 210 and 300 nm have been observed in every specimen. The former and the latter peaks reflect the $n \rightarrow \pi^*$ absorption bands of carbonyl groups in polyions and in acetone, respectively. The negative sign of the peak near 300 nm says that the acetone concentration in gel is lower than that in the surrounding solution.

In the spectrum of the gel after shrinking induced by electric fields in the mixture free of NaOH, the peak near 210 nm becomes broad in comparison with the peak in no field. It is well-known that the PAA gel changes the kind of polyions from $-\text{COO}^- \text{Na}^+$ to $-\text{COOH}$ in HCl solutions and then shrinks. Furthermore it shows a shift of the peak due to the $n \rightarrow \pi^*$ absorption band of polyion (Fig. 8). Based on the data in Figure 8, the broad peak near 210 nm of the spectrum, C, in Figure 7 suggests that two kinds of polyion, $-\text{COO}^- \text{Na}^+$ and $-\text{COOH}$, exist together. So it seems that the shrinking of the swollen-state PAA gel by an electric field in the mixture

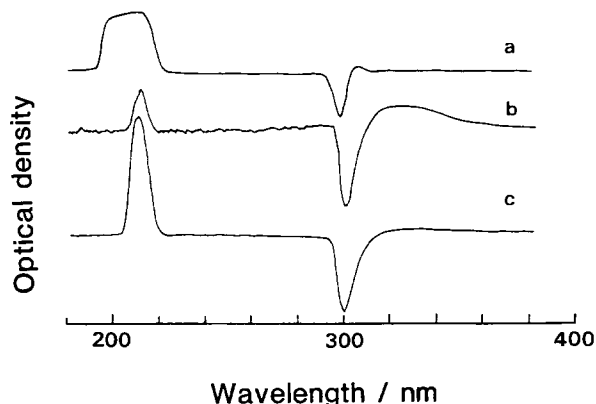


Figure 7 UV spectra of the swollen-state gels: (a) after shrinking by the application of an electric field in the mixture free of NaOH, (b) after swelling in the NaOH-acetone-water mixture, and (c) before applying an electric field. The negative sign of the peak near 300 nm says that the acetone concentration in the gel is lower than that in the surrounding solution.

free of NaOH occurs through the conformational change of the polymer chains due to a change of polyion from $-\text{COO}^- \text{Na}^+$ to $-\text{COOH}$. This change is observed at the positive electrode side because sodium ions move to the negative electrode.

The spectrum of the gel after swelling in NaOH solutions by the application of an electric field is similar to the spectrum of the gel before applying an electric field. It is found that the kind of the polyion has not been changed in the swelling. In the mixture containing NaOH, sodium ions in the surrounding solution come into the gel, however, the counterions of the polyions go out of the gel. When the drift rate of sodium ion from the solution to the gel is higher than that of the counterion of polyions from the gel to the solution, the concentration of

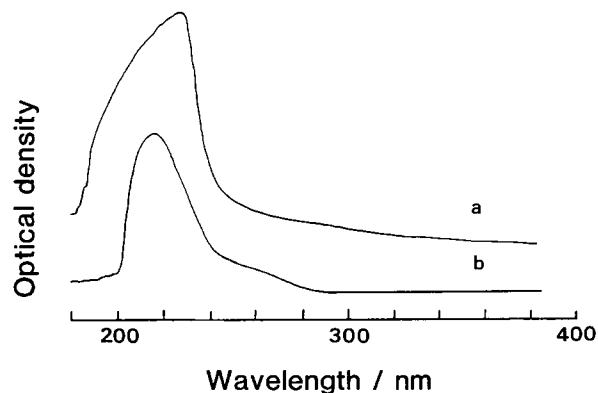


Figure 8 UV spectra of the PAA gels: (a) in 5mM HCl solution and (b) in 5mM NaOH solution.

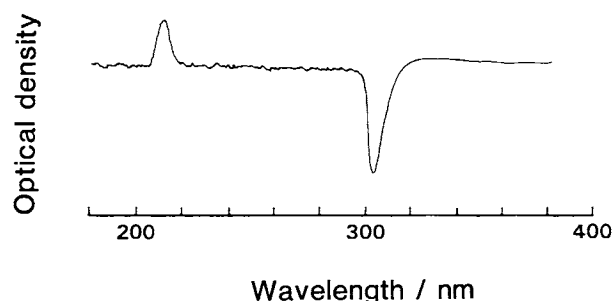


Figure 9 UV spectrum of the shrunken-state gel after large swelling by the application of an electric field.

$-\text{COO}^-\text{Na}^+$ remains constant immediately, and that of the mobile ions in the gel increases. Therefore, only the increase of the osmotic pressure due to the difference of ion concentrations between the inside and the outside of a gel is produced by electric fields. As the result, the gel swells. In the mixture with low contents of NaOH, the two factors, that is, the conformational change due to a change of polyion and the osmotic pressure change, are competing with each other. On the shrinking of the gel observed in mixtures with low contents of NaOH the effect of the conformational change is larger than that of the osmotic pressure change.

Deformation Mechanism of Shrunken-State Gel

When the acetone concentration in the mixture is more than 58%, the PAA gel shows the shrunken state. This phenomenon occurs mainly through decreasing the solubility of crosslinked polymer chain in solvent. In this state the polymer chain is in a compact form because the polyion is not dissociated, or Na^+ of the polyion exists close to $-\text{COO}^-$. The shrunken-state gel at the acetone concentration of more than 58% is considered to be not an ionic gel but a nonionic gel. When an electric field is applied across the gel, the gels at 58–60% of the acetone show a large swelling. To understand the deformation, a UV spectrum of the gel after a large swelling was measured (Fig. 9). It is found that the spectrum is similar to that of the swollen-state gel at 56% (Fig. 8), and that the gel after the large swelling keeps the polyions of $-\text{COONa}$ dissociated. So it is reasonable that the large swelling of the shrunken-state gel is caused by the dissociation of the polyion due to the drift of ions. When the acetone concentration is more than 60%, the gels have not been influenced by electric fields. This is because the ef-

fort of the drift of ions is smaller than that of the solubility of the polymer chains in solvent.

The shrunken-state PAA gel in the mixture free of NaOH does not shrink in dc electric fields like the swollen-state gel does. At 58–60% of acetone concentration, the polymer chain of the gel has already been in a compact form before applying an electric field. Therefore the volume change of the gel has not apparently been observed even if the conformational change of the polymer chain due to the change of the polyion from $-\text{COONa}$ to $-\text{COOH}$ is produced by the application of dc electric fields.

CONCLUSIONS

We have presented experimental results on electric field-associated deformation of the PAA gels near a phase transition point in NaOH–acetone–water mixtures. In the absence of NaOH, the shrinking of the swollen-state gel near a phase transition point has been observed as reported by Tanaka. The shrunken-state gel was not influenced by electric fields. In the presence of NaOH, the swollen-state PAA gel swells or shrinks in dc electric fields as predicted from the previous study.⁴ The type of deformation depends on the concentration of NaOH. We have made an observation on a new deformation of the shrunken-state gel. It shows large swelling from its part facing to the positive electrode under electric fields. The deformation is related to the drift of mobile ions, that is, the counterion of polyion in the PAA gel and free ions in the surrounding mixture. It is found that the deformation occurs through the conformational change of the polymer chain or the change of the osmotic pressure due to the concentration difference between the inside and outside of the gel.

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