

# Deformation of Polyelectrolyte Gels under the Influence of Electric Field

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## Synopsis

Deformation of acrylic acid–acrylamide copolymer gels in an aqueous solution under the influence of a dc electric field was studied. In the electric field, the gel swells, shrinks, or bends. It depends on the concentration of polyion  $\text{coo}^-$  in the gel. When the concentration is low, the gel shrinks, and, when high, it swells. The gel which does not contain polyion is not influenced by the electric field. The long and thin gel is bent in an arc. The bent gel can be recovered to the original shape by removing the applied electric field or by changing the polarity of the applied electric field. The deformation is closely related to two substantial changes. One is the change of the osmotic pressure caused by the ion concentration difference between the inside and the outside of a gel. The other is the conformational change of the polymer network with decreasing of the polyion concentration.

## INTRODUCTION

Polyelectrolyte gels consist of a crosslinked polymer network with ionizable groups and a liquid phase. It is well known that they give a continuous or discontinuous volume change in the solution with temperature change<sup>1</sup> and solvent composition change.<sup>2</sup> It is also induced by applying a dc electric field to it.<sup>3</sup> The volume change of polymer gel shows the possibility of machinery systems which transduce a stimulus into mechanical energy. In the application, the best stimulus is an electric field because it can be controlled easily. In this paper, the deformation behavior induced by an electric field was studied experimentally as well as theoretically. Concerning the influence of an electric field on polymer gel, Tanaka reported the occurrence of shrinkage on partially hydrolyzed polyacrylamide gel in an acetone–water mixture. The present authors found a new type of deformation of polymer gel, bending, in an electric field.<sup>4</sup> According to them, sodium acrylate–acrylamide copolymer gel (PAA gel) was bent in an arc in aqueous solutions. Various polyelectrolyte gels were also deformed in the same way. The purpose of this paper is to present experimental results on the deformation of PAA gels in a dc electric field.

## EXPERIMENTAL

### Preparation of Gel

Five kinds of PAA gels were prepared by free radical polymerization. Acrylic acid (AA), acrylamide (AAm), sodium hydroxide, and *N,N*-methyl-enebisacrylamide (BAAM) were dissolved in distilled water. Table I shows

TABLE I  
Monomer Composition

No.	AA (mol)	AAM (mol)	BAAm (mol)	NaOH (mol)
1	0.1	0.1	0.001	0
2	0.1	0.1	0.001	0.02
3	0.1	0.1	0.001	0.04
4	0.1	0.1	0.001	0.06
5	0.1	0.1	0.001	0.10

monomer composition in the preparation of the gels. The total volume was 50 mL. After the addition of 50 mg of ammonium persulfate and 200  $\mu$ L of *N,N,N',N'*-tetramethylethylenediamine, the solution was poured into a plastic case and heated at 60°C for 3 h for gelation. In a flask, 1 g of the prepared gel was immersed into 200 mL of distilled water until it reached swelling equilibrium with water. After the equilibrium, the gel was used as a specimen and distilled water as an aqueous solution.

### Measurement of Deformation

The aqueous solution was poured into a plastic case equipped with two parallel platinum electrodes. The separation between them was 30 mm. The specimen was placed in the center of the case, and the voltage up to 60 V dc was applied across the solution between the electrodes.

## RESULTS AND DISCUSSION

### Deformation Behavior

Figures 1(a) and 1(b) show a PAA gel deformed by the applied electric field. The type of deformation depends on the concentration of polyion,  $-\text{COO}^- \text{Na}^+$ , in the gel. The gel which has a small amount of polyion (no. 2) shrinks from the anode side of it, while the gel with a large amount of polyion (nos. 4, 5) swells. The gel (no. 3) swells and shrinks continuously. The gel free of polyion is not influenced by the electric field. The long and thin gel is bent in an arc by applying the field to it (Fig. 2). In this deformation, both ends of the gel move toward the cathode. The gel gains weight while it is bending. This indicates that the bending is one of the swelling behaviors. The amount of the deflection increases gradually with time. The deflection is expressed in terms of the distance between the ends of a gel before and after bending, and the sign of the deflection is positive when a gel bends to the cathode. When the electric field is kept applied, both ends of the gel comes into contact with each other, and in some experiments the gel breaks after a while. But the specimens, nos. 2 and 3, turn back to the original shape and bend toward the anode with the length of time (Fig. 3). When the gel turn back, it loses weight. The deflections with time under various field intensities were examined.

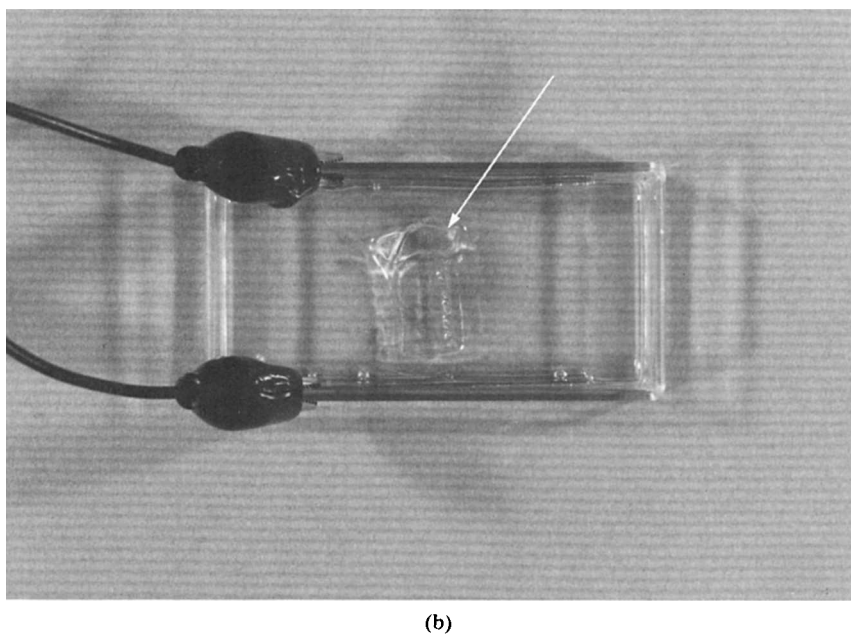
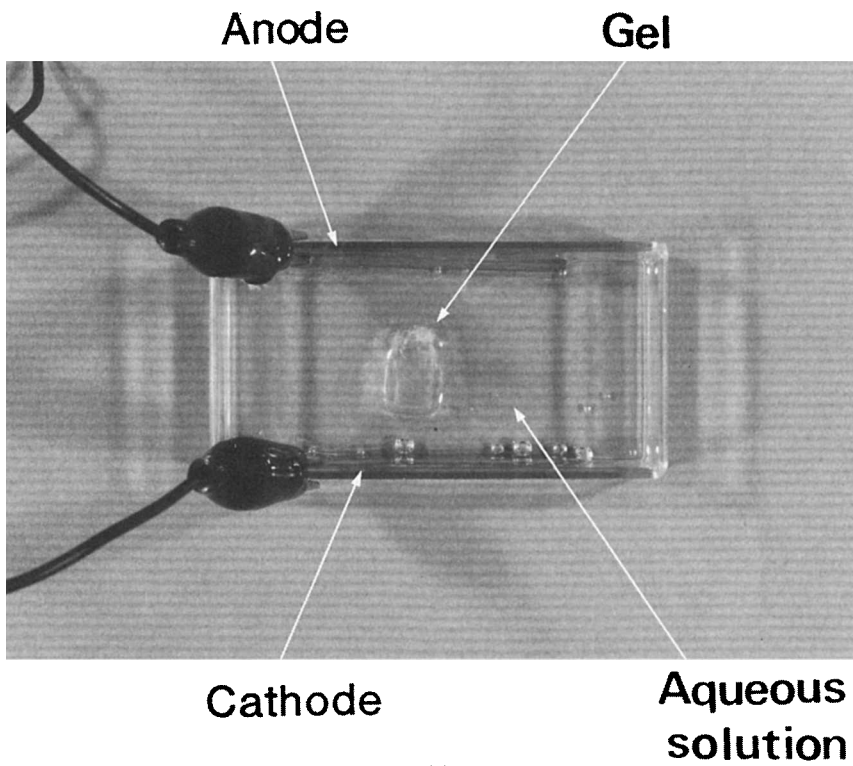


Fig. 1. Photographs of deformed gel: (a) shrinking (no. 2); (b) swelling (no. 5).

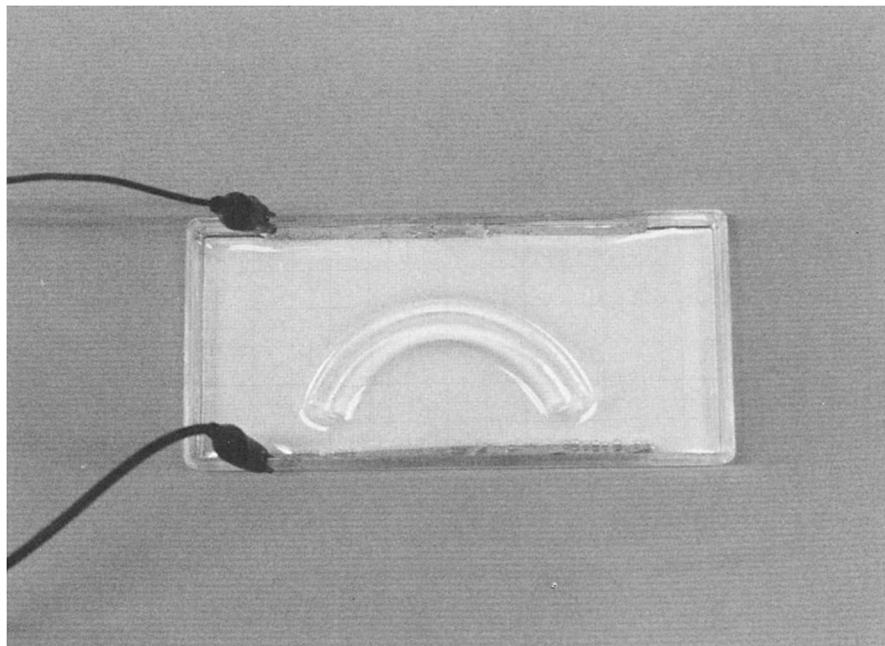
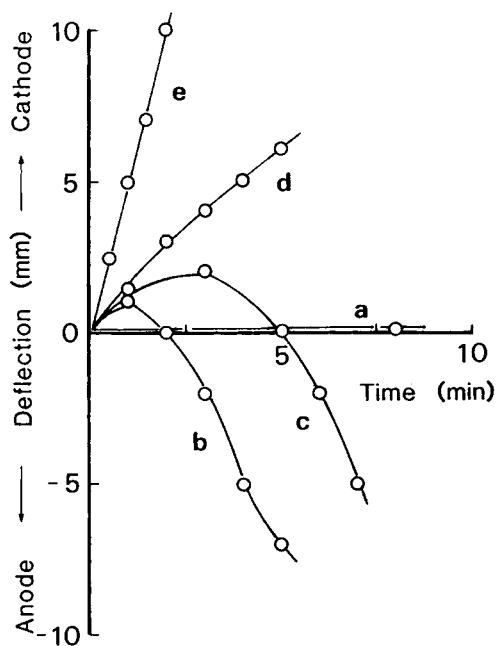


Fig. 2. Bending motion of the gel (no. 5) in the electric field.

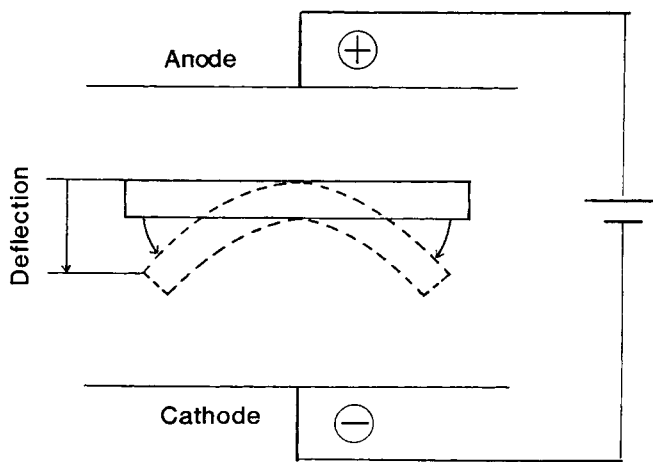
The bending was not induced when the applied voltage was less than 2 V. The bending rate before the maximum deflection was found to be proportional to the field intensity. Figure 4 shows the deformation of the specimens, nos. 2 and 5, after the removal of the electric field. Each specimen recovers the original shape slowly. Figure 5 shows the response of bending for the specimen, no. 4, under a cyclically varying electric field from 20 to  $-20$  V/cm every 2 min. The deformed gel can be recovered to its original shape by changing the polarity of the applied voltage. Hysteresis has not been observed. Figure 5 tells that the deflection is kept constant against the repeating. It also shows that the deformation of polymer gel may be induced by an ac electric field.

### Bending Mechanism

The swelling behavior of the polymer gel can be explained by Flory's theory of the osmotic pressure.<sup>5</sup> In present experiments, the deformation is related to the application of an electric field, which causes the ion's shift in the polymer gel. So the osmotic pressure  $\pi$  associated with ion concentration should be considered. When a dc electric field is applied between electrodes, mobile ions move toward their counterelectrode. As the result,  $\pi$  changes. When  $\pi$  increases with time, a gel swells. But it shrinks when  $\pi$  decreases with time. Then the osmotic pressure of the anode side  $\pi_1$  seems not to be equal to that of the cathode side  $\pi_2$ . A polymer gel is bent like a bimetal by swelling or shrinking due to the osmotic pressure difference,  $\Delta\pi = \pi_1 - \pi_2$ .



(a)



(b)

Fig. 3. (a) Deflection vs. the exposed time to the electric field, 10 V/cm. Specimen: a, no. 1; b, no. 2; c, no. 3; d, no. 4; e, no. 5. (b) Deflection of bending. Deflection is expressed in terms of the distance between the ends of a gel before and after bending. When a gel bends to the cathode side, the sign of the deflection is defined positive.

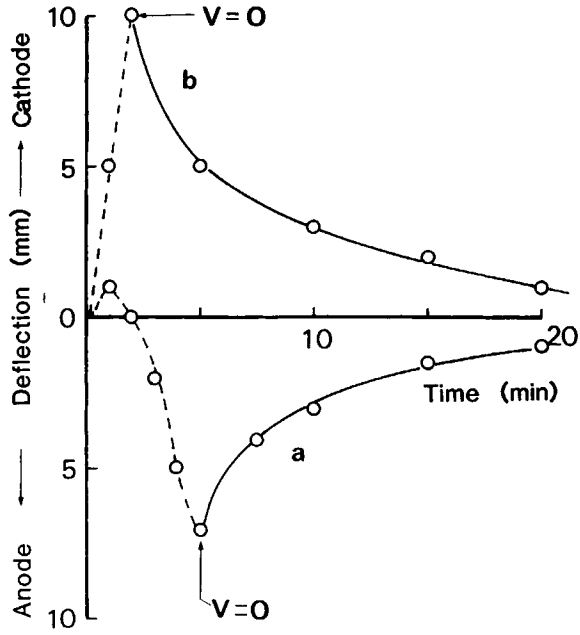


Fig. 4. Deformation behavior after the removal of the electric field. Specimen: (a) no. 2; (b) no. 5.

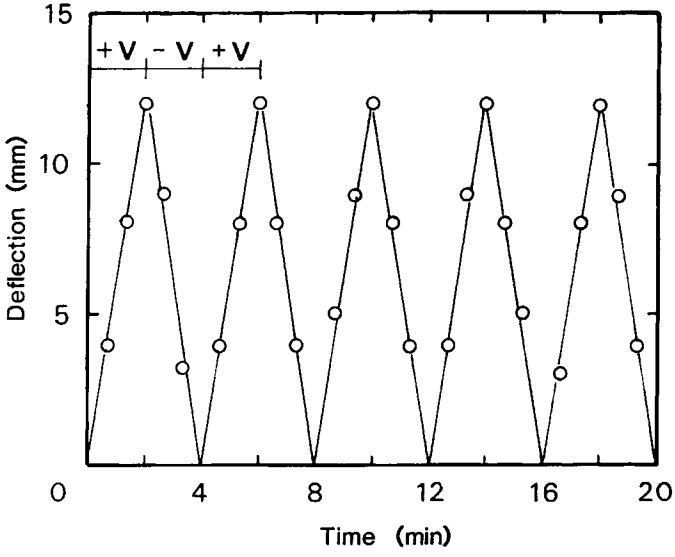


Fig. 5. Response of bending for the specimen (no. 4) under a cyclically varying electric field from 20 to  $-20$  V/cm every 2 min.

*Osmotic Pressure Difference*

The osmotic pressure should be given approximately by a simple model based on Donnan equilibrium as follows.

For simplicity, polymer gel and aqueous solution are assumed to be composed of three parts, A, B, and C, in turn from the anode side. Consider a system with one kind of mobile cation. When the electric field is applied between the electrodes, cation moves toward the cathode and therefore the cation concentration gradient occurs. For rough approximation, the concentration is assumed to change abruptly across the boundary between the parts and is also assumed to be uniform in any of A, B, and C. Furthermore, the transport rates of the cation from A to B and B to C are assumed to be all the same ( $= h$ ). On these assumptions, the cation concentration in each part is given by

$$C_A(t) = C_A(1 - ht) \quad (1)$$

$$C_B(t) = C_B(1 - ht) + C_A \frac{V_A}{V_B} ht(1 - ht) \quad (2)$$

$$C_C(t) = C_C + C_B \frac{V_B}{V_C} ht + C_A \frac{V_A}{V_C} h^2 t^2 \quad (3)$$

where  $C_i$  and  $C_i(t)$ , with  $i = A, B, C$ , are the cation concentrations in  $i$  part at time  $t = 0$  and  $t = t$ ,  $V_i$  is the volume of the  $i$  part, and  $t$  is the exposed time to an electric field. In eqs. (1)–(3), ion–ion interaction are all neglected. As the osmotic pressure  $\pi$  obeys van 't Hoff's law,  $\Delta\pi$  is given.

$$\begin{aligned} \Delta\pi &= \pi_1 - \pi_2 \\ &= RT[C_B(t) - C_A(t)] - RT[C_B(t) - C_C(t)] \\ &= RT \left[ C_C + C_B \frac{V_B}{V_C} ht + C_A \frac{V_A}{V_C} h^2 t^2 - C_A(1 - ht) \right] \end{aligned} \quad (4)$$

where  $\pi_1$ ,  $\pi_2$  are the osmotic pressure of the anode side and that of the cathode side between a gel and a solution, respectively.  $R$  is the gas constant, and  $T$  is the absolute temperature.

A system with one kind of cation  $M^+$  and one kind of anion  $N^-$  will be dealt with as follows: In this system  $M^+$  moves toward the cathode and  $N^-$  toward the anode, and therefore the ion concentration gradients of  $M^+$  and  $N^-$  are induced by the electric field. Electrical neutrality must exist in any part. So water resolves into  $H^+$  and  $OH^-$ , distributed to satisfy this requirement.

Therefore,  $\Delta\pi$  is given.

$$\Delta\pi = RT \sum_k [C_{k,C}(t) - C_{k,A}(t)] \quad (5)$$

where  $C_{k,C}(t)$  and  $C_{k,A}(t)$ , where  $k = M^+$ ,  $N^-$ ,  $H^+$ , and  $OH^-$ , are the concentrations of  $k$  species in C and A parts at time  $t = t$ .

Since

$$\begin{aligned} C_{M,C}(t) &= C_{OH,C}(t), & C_{M,A}(t) &= C_{OH,A}(t) \\ C_{N,C}(t) &= C_{H,C}(t), & C_{N,A}(t) &= C_{H,A}(t) \end{aligned}$$

eq. (5) is changed into

$$\begin{aligned} \Delta\pi &= 2RT \left[ C_{M,C} + C_{M,B} \frac{V_B}{V_C} h_M t + C_{M,A} \frac{V_A}{V_C} h_M^2 t^2 - C_{M,A}(1 - h_M t) \right] \\ &\quad - 2RT \left[ C_{N,A} + C_{N,B} \frac{V_B}{V_A} h_N t + C_{N,C} \frac{V_C}{V_A} h_N^2 t^2 - C_{N,C}(1 - h_N t) \right] \quad (6) \end{aligned}$$

In a system with  $i$  kinds of cations and  $j$  kinds of anions,  $\Delta\pi$  is given in a similar way as mentioned above.  $\Delta\pi$  is expressed as follows:

$$\begin{aligned} \Delta\pi &= 2RT \sum_i \left[ C_{i,C} + C_{i,B} \frac{V_B}{V_C} h_i t + C_{i,A} \frac{V_A}{V_C} h_i^2 t^2 - C_{i,A}(1 - h_i t) \right] \\ &\quad - 2RT \sum_j \left[ C_{j,A} + C_{j,B} \frac{V_B}{V_A} h_j t + C_{j,C} \frac{V_C}{V_A} h_j^2 t^2 - C_{j,C}(1 - h_j t) \right] \quad (7) \end{aligned}$$

Here  $C_{i,x}$  is the ion concentration of species  $i$  in the  $x$  part,  $x = A, B, C$ , at time  $t = 0$ ,  $h_i$  is the transport rate of species  $i$  between parts. In bending, the pressure difference is balanced by the stress caused by the strain on the polymer gel. We assume that the bending of a gel under an electric field is equal to the bending in a three-point mechanical bending test, and that  $\Delta\pi$  is equal to the maximum tensile stress,  $\sigma$ , in a three-point bending test. So the following is derived:

$$\Delta\pi = \sigma = 6DEY/L^2 \quad (8)$$

where  $E$  is Young's modulus,  $Y$  is the amount of the deflection,  $D$  is the thickness, and  $L$  is the length of a polymer gel before bending. By the use of eqs. (7) and (8), the deflection and the bending direction can be given. When  $\Delta\pi > 0$ , a polymer gel is bent toward the cathode by the electric field, and when  $\Delta\pi < 0$ , it is bent toward the anode. When  $\Delta\pi > 0$  and  $d\pi_1/dt > 0$  or when  $\Delta\pi < 0$  and  $d\pi_2/dt > 0$ , a polymer gel swells and bends.



*Comparison with Experiment*

**Bending in Aqueous Solutions.** Let us calculate the amount of the deflection of the specimen, no. 4, in the aqueous solution under the electric field, 10 V/cm. The specimen is in equilibrium with the aqueous solution before submitting to the electric field and so the initial conditions are as follows:

- (\*) Ions are  $H^+$ ,  $Na^+$ ,  $OH^-$ , and polyion  $P^-$ .
- (\*)  $C_{OH,B} = C_{H,B} = 10^{-7}$  mol/cm<sup>3</sup>,  $C_{P,B} = C_{Na,B}$ ,  $C_{Na,B} \gg C_{H,B}$ .
- (\*) The concentration of  $Na^+$  inside the specimen is larger than that outside it.  $C_{Na,B} > C_{Na,A}$  or  $C_{Na,C}$ .
- (\*) For convenience,  $C_{i,A} = C_{i,C}$ , where  $i = H^+$ ,  $Na^+$ ,  $OH^-$ , and  $V_A = V_C$ .

Since  $P^-$  is an immobile ion,  $h_P$  is zero. Using  $h_P = 0$  and initial conditions, eq. (7) is approximately reduced to

$$\Delta\pi = 2RTC_{P,B} \frac{V_B}{V_C} h_{Na} t (1 - h_{Na} t) \quad (9)$$

By combining eqs. (8) and (9), the deflection is obtained:

$$Y = \frac{RTC_{P,B} V_B h_{Na} t (1 - h_{Na} t)}{3DEV_C} \quad (10)$$

In calculating  $Y$ ,  $R = 8.31 \times 10^7$  dyn/cm<sup>2</sup>,  $T = 298$  K,  $V_B/V_C = 0.4$ ,  $D = 5$  mm,  $L = 50$  mm,  $C_{P,B} = 3.53 \times 10^{-5}$  mol/cm<sup>3</sup>,  $E = 1.8 \times 10^5$  dyn/cm<sup>2</sup>, and  $h_{Na} = 8.9 \times 10^{-5}$  1/s were used.  $h_{Na}$  was obtained from measuring the concentration of  $Na^+$  at time = 60 s in the C part by a microprocessor ionalyzer (Orion Research), and from using

$$C_C(t) = C_C + C_{P,B} \frac{V_B}{V_C} h_{Na} t \quad (11)$$

In Figure 6, calculated and experimental values of  $Y$  are given as a function of the exposure time to the electric field. Calculated values are qualitatively in good agreement with the experimental.

Consider changes in swelling. Equation (9) states that the sign of  $\Delta\pi$  is positive. Therefore, the gel swells when  $d\pi_1/dt > 0$ .  $\pi_1$  at time =  $t$  is given by

$$\begin{aligned} \pi_1 &= RT [C_B(t) - C_A(t)] \\ &= RT \left[ C_{Na,B} (1 - h_{Na} t) + C_{Na,A} \frac{V_A}{V_B} h_{Na} t (1 - h_{Na} t) \right. \\ &\quad \left. + C_{Na,A} \frac{V_A}{V_B} h_{OH} t (1 - h_{OH} t) \right. \\ &\quad \left. - C_{Na,A} (1 - h_{Na} t) - C_{Na,A} h_{OH}^2 t^2 \right] \quad (12) \end{aligned}$$

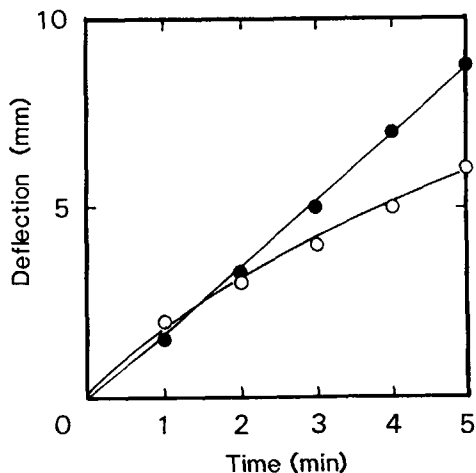


Fig. 6. Deflection time curves of the specimen (no. 4) under 10 V/cm; (○) experimentally obtained; (●) calculated by eq. (7).

Here  $h_{\text{OH}}$  is the transport rate of  $\text{OH}^-$ . So,  $d\pi_1/dt$  is as follows:

$$\frac{d\pi_1}{dt} = RT \left[ -C_{\text{Na},\text{B}}h_{\text{Na}} + C_{\text{Na},\text{A}} \frac{V_{\text{A}}}{V_{\text{B}}} (h_{\text{Na}} - 2h_{\text{Na}}^2 t) \right. \\ \left. + C_{\text{Na},\text{A}} \frac{V_{\text{A}}}{V_{\text{B}}} (h_{\text{OH}} - 2h_{\text{OH}}^2 t) + C_{\text{Na},\text{A}}h_{\text{Na}} - 2C_{\text{Na},\text{A}}h_{\text{OH}}^2 t \right]$$

Since  $h_{\text{Na}} \gg h_{\text{Na}}^2$ ,  $h_{\text{OH}} \gg h_{\text{OH}}^2$ ,  $h_{\text{OH}} > h_{\text{Na}}$

$$\frac{d\pi_1}{dt} = RT \left[ C_{\text{Na},\text{A}} \left( h_{\text{Na}} + \frac{V_{\text{A}}}{V_{\text{B}}} h_{\text{Na}} + \frac{V_{\text{A}}}{V_{\text{B}}} h_{\text{OH}} \right) - C_{\text{Na},\text{B}}h_{\text{Na}} \right] \\ > RTh_{\text{Na}} \left[ C_{\text{Na},\text{A}} \left( 1 + \frac{2V_{\text{A}}}{V_{\text{B}}} \right) - C_{\text{Na},\text{B}} \right] \quad (13)$$

In calculating  $d\pi_1/dt$ , we measured the value of pH in the A part. The value was 8.9, and, therefore,  $C_{\text{Na},\text{A}}$  is  $7.94 \times 10^{-6}$  mol/cm<sup>3</sup>.

Since  $C_{\text{Na},\text{B}} = 3.53 \times 10^{-5}$  mol/cm<sup>3</sup>,  $V_{\text{A}}/V_{\text{B}} = 2.5$ ,

$$\frac{d\pi_1}{dt} > RTh_{\text{Na}} \left[ C_{\text{Na},\text{A}} \left( 1 + \frac{2V_{\text{A}}}{V_{\text{B}}} \right) - C_{\text{Na},\text{B}} \right] \\ = 1.23 \times 10^{-5} \cdot RTh_{\text{Na}} > 0$$

This result indicates that the gel (no. 4) swells under the influence of a dc electric field.

**Bending in NaOH Aqueous Solutions.** The amount of the deflection in NaOH aqueous solution was calculated by the use of eqs. (7) and (8). The

specimen, no. 4, is placed in aq NaOH, the concentration of which ranges from  $10^{-5}$  to  $10^{-1}M$  and soon the electric field is applied. The specimen is not in equilibrium with the solution and so the initial conditions are as follows:

- (\*) Ions are  $H^+$ ,  $Na^+$ ,  $OH^-$ , and  $P^-$ .
- (\*)  $C_{P,B} = C_{Na,B} \gg C_{H,B} = C_{OH,B}$ ,  $C_{H,A} \ll C_{Na,A}$ .
- (\*) For convenience,  $V_A = V_C$ ,  $C_{i,A} = C_{i,C}$ ,  $i = Na^+$ ,  $OH^-$ .

From initial conditions, eq. (7) is changed to

$$\Delta\pi = 2RT \left( C_{Na,A} h_{Na} t + C_{Na,A} h_{Na}^2 t^2 + C_{Na,B} \frac{V_B}{V_C} h_{Na} t \right) - 2RT \left( C_{OH,A} h_{OH} t + C_{OH,A} h_{OH}^2 t^2 + C_{OH,B} \frac{V_B}{V_C} h_{OH} t \right) \quad (14)$$

The values of  $h_{Na}$  and  $h_{OH}$  were evaluated as follows:  $h_{Na}$  was obtained by measuring the concentration of  $Na^+$  in the A part and using

$$C_{Na,A}(t) = C_{Na,A}(1 - h_{Na} t) \quad (15)$$

However,  $h_{OH}$  cannot be obtained in the same way because the concentration of  $OH^-$  changes so as to maintain  $[H^+][OH^-] = 10^{-14}$  constant. Therefore, the value of  $h_{OH}$  was evaluated as being proportional to the mobility [eq. (16)]:

$$h_{OH} = \frac{U_{OH}}{U_{Na}} h_{Na} \quad (16)$$

where  $U_{OH}$  and  $U_{Na}$  are the mobilities of  $OH^-$  and  $Na^+$ . In Table II, the values of  $h_{Na}$  and  $h_{OH}$  in aq NaOH in 10 V/cm are given. Using the values listed in Table II, the amount of  $Y$  after 5 min imposing of the electric field were calculated. Figure 7 shows the calculated and observed values of  $Y$  as a function of the NaOH concentration. Both are in good agreement. With the increase in the concentration, the amount of the deflection to the cathode increases rapidly. But above  $10^{-3}M$ , the gel is bent to the anode side.

TABLE II  
Transport Rate of Ions

NaOH Concn ( $M$ )	$h_{Na}$ ( $s^{-1}$ )	$h_{OH}$ ( $s^{-1}$ )
$10^{-5}$	$1.65 \times 10^{-5}$	$6.68 \times 10^{-5}$
$10^{-4}$	$8.93 \times 10^{-5}$	$3.53 \times 10^{-4}$
$10^{-3}$	$5.06 \times 10^{-4}$	$2.00 \times 10^{-3}$
$10^{-2}$	$2.67 \times 10^{-4}$	$1.08 \times 10^{-3}$
$10^{-1}$	$4.10 \times 10^{-3}$	$1.62 \times 10^{-2}$

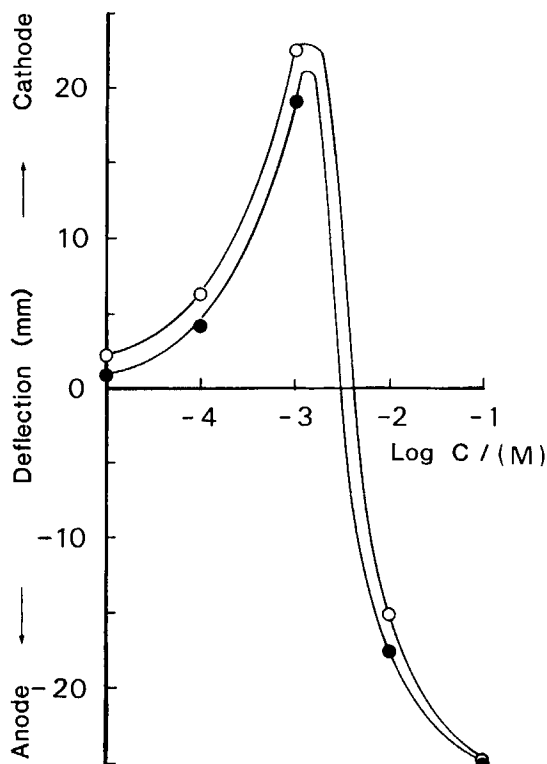


Fig. 7. Deflection after 5 min imposing of an electric field, 10 V/cm, in NaOH aqueous solution. Specimen, no. 4: (○) experiment; (●) calculation.

**Bending of Various Gels.** Equation (7) suggests that various polyelectrolyte gels may be bent in the aqueous solution by applying the electric field. In this article the bending of polymer gel composed of polyion ( $P^+$  or  $P^-$ ) and their counterions whose charge is monovalent ( $x^-$  or  $x^+$ ) is discussed. The initial conditions are the same as that mentioned about the bending of PAA gels in aqueous solutions. Hence eq. (7) is reduced to

$$\begin{aligned} \Delta\pi &= -2RTC_{P,B} \frac{V_B}{V_A} h_x t (1 - h_x t) && \text{(polycation gel, } P^+) \\ &= 2RTC_{P,B} \frac{V_B}{V_C} h_x t (1 - h_x t) && \text{(polyanion gel, } P^-) \end{aligned} \quad (17)$$

Since  $0 < h_x t < 1$ ,

$$\Delta\pi < 0 \quad \text{(polycation gel)}$$

$$\Delta\pi > 0 \quad \text{(polyanion gel)}$$

In eq. (15), polycation gel is considered to be bent to the anode side, and polyanion gel, to the cathode one. The bending of four kinds of polyelectrolyte

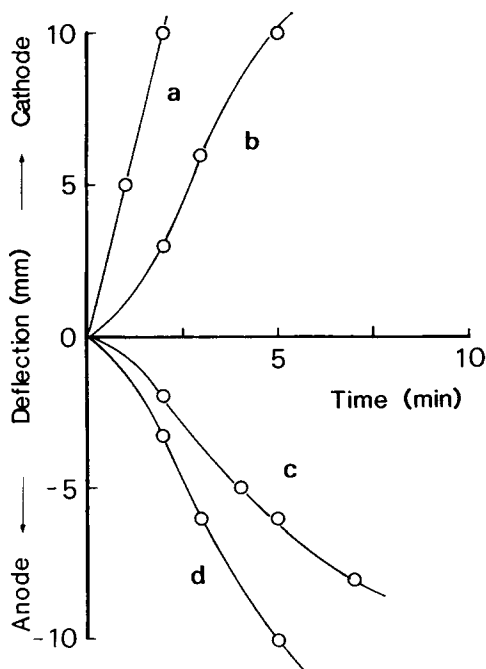


Fig. 8. Deflection time curves of various gels under 10 V/cm: (a) PSS gel; (b) TBAS gel; (c) PBVC gel; (d) METMA gel.

gels were examined: (a) poly(*p*-styrenesodiumsulfonate) gel (PSS gel), (b) *t*-butylacrylamidesodiumsulfonate-acrylamide copolymer gel (TBAS gel), (c) poly(*N*-benzyl-4-vinylpyrriidum) gel (PBVC gel), (d) methacryloyloxyethyltrimethylammonium-acrylamide copolymer gel (METMA gel). Figure 8 shows the experimental results. Polycation gels, (c) and (d), are bent to the anode, and polyanion gels, (a) and (b), to the cathode. These results are in accordance with the predictions from eq. (17).

From comparisons with the calculation and the experimental results, the proposed model seems to be rather good. So it is reasonable to assume that the driving force of bending is the osmotic pressure difference  $\Delta\pi$ . Figure 9 shows a schematic illustration of the bending mechanism. When dc electric field is applied, the osmotic pressure difference occurs in consequence of mobile ion transport. So the PAA gel swells at the anode side, and then it is bent toward the cathode.

As shown in Figure 3, the specimens, nos. 2 and 3, turn back the original shape and bend to the anode with the length of time. To account for this deformation behavior, the optical density at 225 nm for PAA gels due to the  $n \rightarrow \pi^*$  absorption band of polyion,  $\text{COO}^-$ , and the electric potential difference inside polymer gel in the presence of an externally applied electric field were measured. Figure 10 shows the variation of the optical density at 225 nm for the specimen (no. 2) in the electric field, 10 V/cm.

A marked decrease in the optical density occurs after 3 min imposing of an electric field. This result indicates that the concentration of  $\text{COO}^-$  decreases when the specimen begins to turn back.

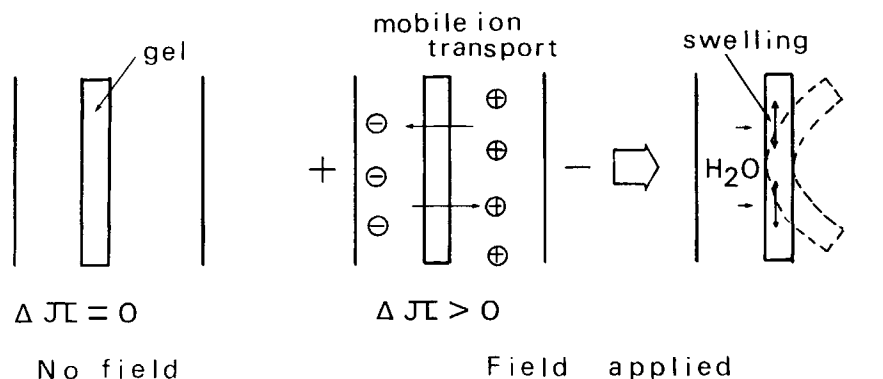


Fig. 9. Schematic illustration of bending mechanism.

The electric potential difference,  $V = V_A - V_B$ , between points A and B inside the specimen, no. 2, is shown in Figure 11. It abruptly increases after 3 min. This time agrees with that for the concentration of  $\text{coo}^-$  to decrease. The electric potential difference depends on the applied electric field and the concentration gradients of  $\text{coo}^-$  and  $\text{Na}^+$ . The electric field is kept constant in this study and therefore the cause of the increase of potential difference is that the concentration of  $\text{coo}^-$  at point A becomes lower than that at point B.

To investigate the behavior of the specimen, no. 2, caused by decreasing the concentration of  $\text{coo}^-$ , the swelling ratio for PAA gel containing various amount of NaOH was measured. As shown in Figure 12, it drops rapidly below 20% concentration of NaOH. The concentration of NaOH is equal to that of  $\text{coo}^-$  and therefore this fact indicates that the gel shrinks when the concentration of  $\text{coo}^-$  goes below 20%. Then it can be concluded that the concentration of  $\text{coo}^-$  in the anode side of the gel decreases faster than that in the cathode side in an electric field. As a result, the gel begins to shrink at the anode side

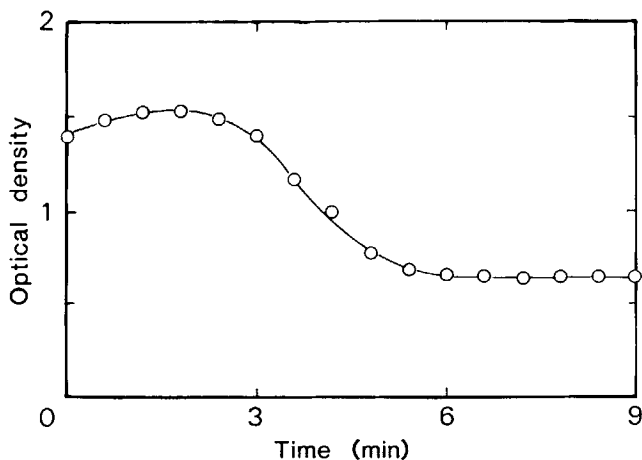


Fig. 10. Optical density at 225 nm vs. the exposed time to the electric field, 10 V/cm. Specimen, no. 2.

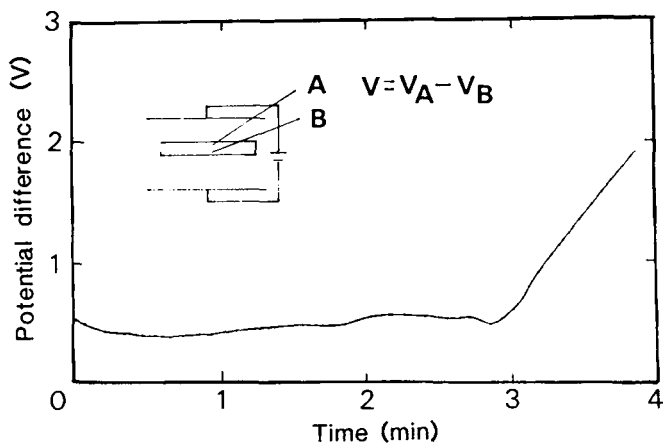


Fig. 11. A time course of potential difference between points A and B under 10 V/cm.

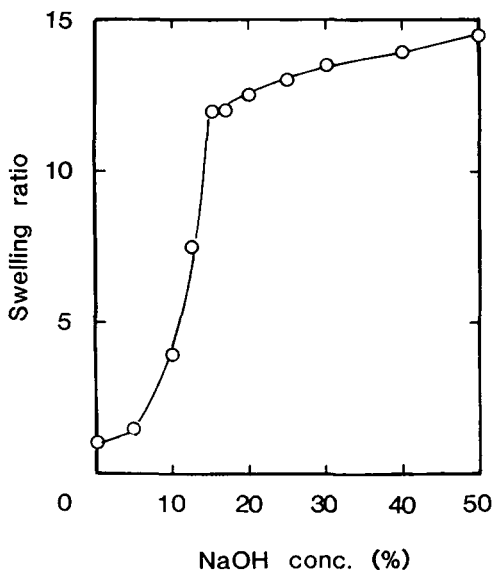


Fig. 12. Swelling ratio for gels containing various amounts of NaOH.

of it. So, the turn of the specimen, no. 2, occurs through the shrinking at the anode side of it (Fig. 13).

### CONCLUSIONS

The deformation of PAA gels in an aqueous solution under the influence of a dc electric field was studied. The following results were obtained:

1. The deformation induced by the electric field is swelling, shrinking, and bending.
2. The polyion plays an important role in the deformation. When the concentration of the polyion is low, the gel shrinks, and, when high, it swells. The gel free of polyion is not influenced by the electric field.

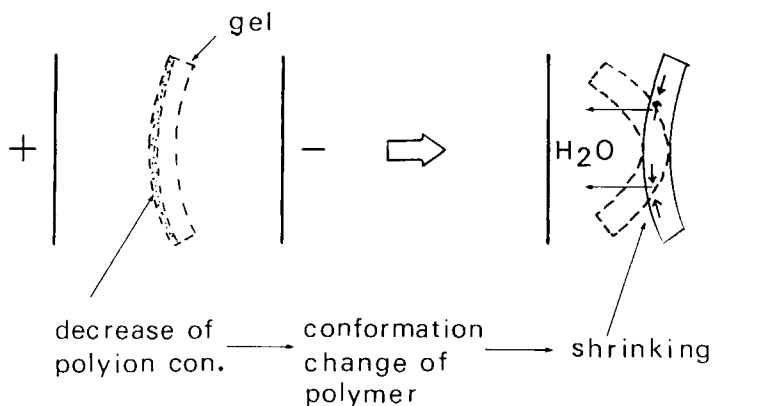


Fig. 13. Schematic illustration of mechanism of bending to the anode side.

3. The long and thin gel is bent by it.
4. The bending rate depends on the field intensity and the concentration of mobile ions in the solution.
5. The bent gel can be recovered to its original shape by removing the applied electric field or by changing the polarity of the applied electric field.
6. The deformation occurs through two substantial changes. One is the change of the osmotic pressure caused by the ion concentration difference between the inside and the outside a gel. The other is the conformational change of polymer network with decreasing of the polyion concentration.

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