Bending of Ionic Polymer Gel Caused by Swelling under Sinusoidally Varying Electric Fields

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SYNOPSIS

Deformation of poly(vinyl alcohol)–poly(sodium acrylate) composite hydrogel (PVA–PAA gel) under sinusoidally varying electric fields was studied in electrolyte solutions. The PVA–PAA gel was prepared by repeatedly freezing and thawing a mixed solution of PVA and polyacrylic acid. A cyclic bending–straightening motion of the PVA–PAA gel rods of about 1 mm in diameter have been observed in Na_2CO_3 aqueous solutions under the fields. The PVA–PAA gel had a response time of less than several hundreds milliseconds. The bending has also been observed in organic solvents containing an electrolyte when the organic solvent is electrolyzed. It was found that the motion of the gel under electric fields of less than 1 Hz occurred mainly through swelling due to the change of the osmotic pressure based upon the difference of the ion concentration. However, it has not been determined whether the motion at higher frequencies is caused by the osmotic effect. © 1993 John Wiley & Sons, Inc.

1. INTRODUCTION

Recent topics in polymer gel concern the deformation of ionic polymer hydrogels induced by the application of electric fields. Poly(vinyl alcohol)–poly(sodium acrylate) composite hydrogel (PVA–PAA gel) is a new type of ionic hydrogel prepared by the freezing–thawing process.[1,2] The structure of the PVA–PAA gel is analogous to that of the polyelectrolyte gel. Therefore, when the gel rod is placed parallel to a pair of electrodes, not touching them, it bends in electrolyte solutions under dc electric fields as does polyelectrolyte gel such as poly(sodium acrylate) gel.[3,4] The PVA–PAA gel shrinks where it faces the positive electrode in water and then bends toward the positive electrode like a bimetal. However, in solutions of basic electrolyte such as NaOH and Na_2CO_3, the gel swells at the positive electrode side and bends toward the negative electrode. The bending of the PVA–PAA gel in the presence of electrolyte is the deformation in a swelling and it has been qualitatively explained by a bending theory of polyelectrolyte gel based on the change of the osmotic pressure due to the difference of concentrations of ions between the inside and the outside of the gel.[5]

The attractive features in the bending caused by swelling are that the bending speed is in inverse proportion to the thickness of the gel rod and that no cracks observed in the polyelectrolyte gel have been produced in the bending because the PVA–PAA gel has good mechanical properties.[6,7] In addition, the deformed gel is straightened again at a same speed as bending when the polarity of the applied field is changed. These experimental results suggests that the slender PVA–PAA gel may respond to sinusoidally varying electric fields and show a bending–straightening motion cyclically. In this article, we prepared the PVA–PAA gel rods with diameters up to 3 mm and studied the deformation induced by sinusoidally varying electric fields.

2. BENDING THEORY[4]

Consider the bending of polyelectrolyte gel with negatively charged polyions such as poly(sodium acrylate) gel in electrolyte solutions. In the presence

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of electrolyte, the bending is the deformation caused by the swelling. It is related to the drift of the mobile ions in the gel. The osmotic pressure, π, due to the ion concentration difference between the inside and the outside of the gel, changes in dc electric fields. When π increases, the gel swells. When the gel is subjected to a dc electric field, counterions of polyions move toward the negative electrode while the polyions are immobile. The mobile ions in the surrounding solution also move toward their counterelectodes and come into the gel. Then, the osmotic pressure of the positive electrode side, π_1, increases and becomes larger than that of the negative electrode side, π_2. Therefore, the pressure difference, $\Delta\pi$ ($= \pi_1 - \pi_2$), occurs in the gel, and the gel is bent like a bimetal due to $\Delta\pi$. When $\Delta\pi > 0$ and $d\pi_1/dt > 0$, the gel swells and bends toward the negative electrode. It swells and bends toward the positive one when $\Delta\pi < 0$ and $d\pi_2/dt > 0$.

On bending of a gel in aqueous solutions with low contents of an electrolyte, $\Delta\pi$ is given approximately by a simple model based on the Donnan equilibrium [eq. (1)]:

$$\Delta\pi = 2RTC_p(V_2/V_1)ht(1 - ht), \quad *ht < 1 \qquad (1)$$

where R is the gas constant; T, the absolute temperature; C_p, the concentration of the polyion in a gel; V_2 and V_1, the volumes of a gel and of a surrounding solution; h, the transport rate of the counterion of the polyion from gel to solution or from solution to gel; and t, the time of applying an electric field.

When the polarity of the applied field is changed, mobile ions begin to return back to the starting point. In eq. (1), the transport rate is $-h$, and, therefore, the osmotic pressure difference, $\Delta\pi$, decreases gradually and then the deformed gel straightens again. Under a sinusoidally varying electric field, $E = E_0 \sin 2\pi ft$, the change of the polarity appears at regular intervals. Then, the gel bends and straightens cyclically. Under sinusoidally varying electric fields with high frequencies, the amount of ht is very small. So eq. (1) is reduced into eq. (2):

$$\Delta\pi = 2RTC_p(V_2/V_1)ht, \quad *ht < 1 \qquad (2)$$

The deflection of the bending, Y, is calculated by eq. (3). The deflection is expressed in terms of the distance between the ends of gel before and after bending. Equation (3) leads from the assumptions that the bending of a gel under an electric field is a bending in a three-point mechanical bending test and that $\Delta\pi$ is equal to a maximum tensile stress, σ, in the mechanical bending test:

$$\Delta\pi = \sigma = 6DEY/L^2 \qquad (3)$$

where E is the Young's modulus; D, the thickness; and L, the length of a gel rod before bending. The deflection of the bending motion is calculated by using eqs. (2) and (3):

$$Y = \frac{RT(V_2/V_1)C_phtL^2}{3DE} \qquad (4)$$

Here, C_pht represents the quantity of electricity, Q, in electrolyte solution under electric fields. Equation (4) says that Y is proportional to Q. It also says that the bending speed, dY/dt, is in inverse proportion to the thickness of the gel rod. The fibrous gel shows a higher response to an electric signal and largely deforms.

3. EXPERIMENTAL

3.1. Preparation of the PVA–PAA Gel

PVA with a viscosity-average degree of polymerization of 2500 with a degree of saponification of 99.5 mol % was supplied by Kuraray Co. Twenty-five percent of poly(acrylic acid) aqueous solution was from Waco Chemical Industories. Other inorganic and organic materials were commercially available.

The PVA–PAA gel was obtained as follows: In the vessel, 7.5 g of PVA was dissolved in 50 mL of a 30% dimethyl sulfoxide–70% water solvent. The PVA solution was added to 30 g of the 25% poly(acrylic acid) solution. The mixture was poured into micropipettes (Disposable Micropipette, Drummond Scientific Co.) and frozen at −50°C for 5 h. The frozen mixture was warmed up to room temperature at the rate of 5°C/h. When this freezing and thawing process was repeated twice, the mixtures changed into a gel. The prepared gels were finally immersed in a 0.02 M NaOH aqueous solution to yield the PVA–PAA gel.

3.2. Measurement of Bending

To begin electric field-applying measurements, the PVA–PAA gel rods were immersed in aqueous solutions of Na_2CO_3 up to 10 mM. After the gel rods obtained an equilibrium with the solution, the latter was poured into a plastic case equipped with two platinum electrodes (separation between electrodes:

60 mm). The immersed gel rod was set parallel to the electrodes, not touching them, in the center of the case. Then, sinusoidally varying electric fields with amplitudes up to 30 V/cm were applied across the gel between the electrodes. They were controlled by a Power Supply Control System (Arbitrary Function Generator HB-105 and Potentiostat HA-3001, Hokuto Denko Ltd.). The motion of the gel rod was recorded by a video camera (Compact Movie Camera NV-M50, Matsushita Electric Industrial Co.).

4. RESULTS AND DISCUSSION

4.1. Bending–Straightening Motion

We have observed that the PVA–PAA gel rod bends and straightens cyclically under sinusoidally varying electric fields. Figure 1 shows a photograph of the bent gel in motion. Figure 2 shows a response to an applied electric signal for a gel of 1.1 mm in diameter and 50 mm in length. When the electric signal is applied, the current of the system is measured. It is given by a sinusoidal-wave function with the amplitude of 375 mA. The gel rod has a good response to the signal. The deflection of the motion, Y, is written approximately by eq. (5):

$$Y = |17 \sin \pi t/2| \qquad (5)$$

The deflection reaches a maximum at a time $t = 1$ s and the gel rod bends semicircularly. The direction of the motion is defined by the polarity of the applied electric field as observed in dc electric fields.

Figure 3 indicates the maximum deflection in each cycle. It has been given at a time $t = 2n - 1$ (n: positive number). It is kept constant until the fourth cycle of the motion. However, it decreases gradually with the cycle of the motion over the fifth cycle, and then it becomes a constant value of 8 mm, which is one-half of the maximum deflection in the first cycle. The deflection at a time $t = 2n$, which reflects the amount of hysteresis in the straightening motion, is plotted in Figure 3. When $Y = 0$, the gel rod straightens again. The negative sign of the deflection means that the gel rod bends toward the other side of initial bending. At the fifth cycle, hysteresis has been observed for the first time. The amount of hysteresis increases with the repeat cycles. However, the distance of the movement at the end of each cycle is kept constant. This means that the gel has maintained a good response to electric fields against the repeat of motion.

According to eq. (4), the speed of the bending–straightening motion depends on the thickness of the gel rod under sinusoidally varying electric fields. The relationship between the diameter of the gel rod and the maximum deflection observed in the first cycle of the motion under a field of 30 V/cm

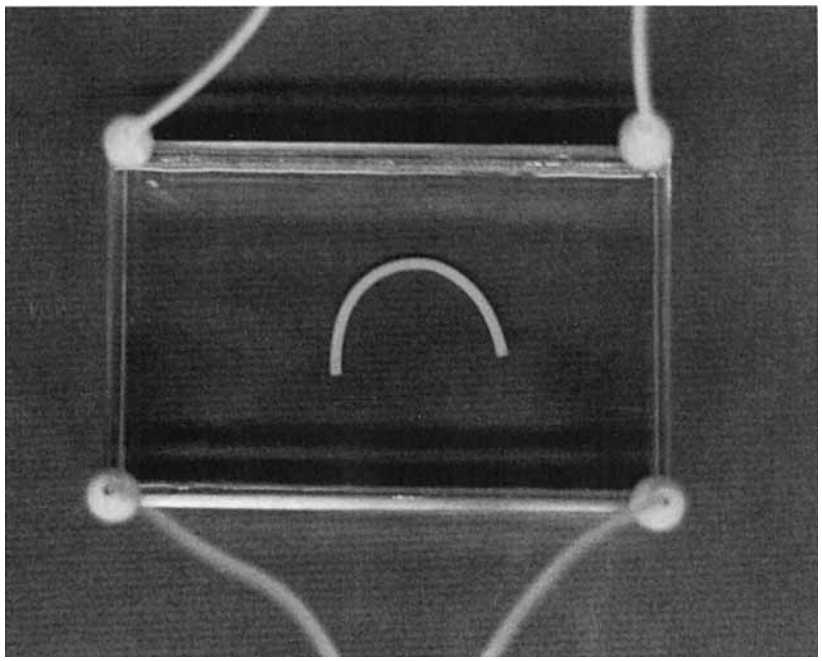

Figure 1 Photograph of the bending of the PVA–PAA gel under a sinusoidally varying electric field. In all bending tests, the length of the specimens is 50 mm.

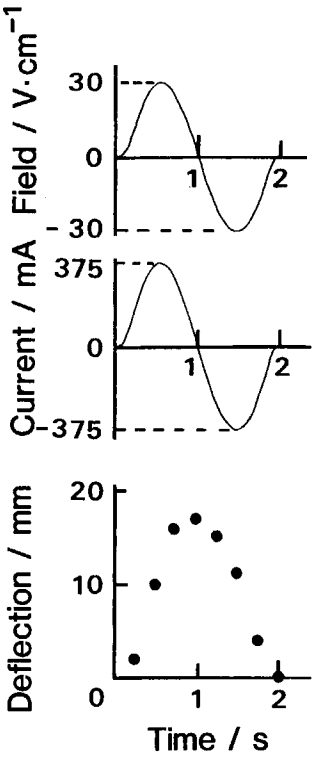

Figure 2 Deflection–time curve of the PVA–PAA gel rod of 1.1 mm diameter. In Figures 2–4, the experiments have been made under 30 sin π t (V/cm). In Figures 2–7, the concentration of Na_2CO_3 is 10 mM.

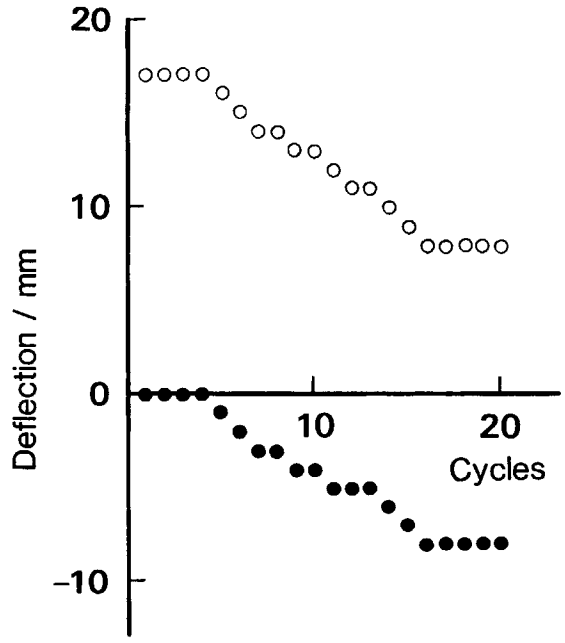

Figure 3 Deflections in the bending–straightening motion at times (○) $t = 2n - 1$ and (●) $t = 2n$ (n: positive number). The former deflection shows a maximum deflection and the latter reflects hysteresis in the motion.

and 0.5 Hz is shown in Figure 4. The maximum deflection, Y_{max}, has been observed at $t = 1$ s in every specimen, and so it represents a bending speed. In Figure 4, the solid line represents calculated values by $Y_{max} = 16/D$. Here, D is the diameter of the rod. The experimental results on the speed of the motion is qualitatively in inverse proportion to the diameter as predicted from eq. (4). Under 30 sin πt, the gel rods with diameters up to 2.4 mm respond to the field. The slenderer the gel, the better the response. For the rod of 2.4 mm in diameter, a small vibration has been observed at both ends of the rod. The rods with the diameter of about 1 mm show 20–22 mm of deflection. This means that the rod bends circularly or that it can be folded in two within 1 s.

Equation (4) shows that the speed of the bending–straightening motion depends not only on the diameter of the gel rod but on the quantity of electricity. We have already reported that the speed is proportional to the quantity of electricity, Q, in dc electric fields. Under sinusoidally varying electric fields, Q, is given by eq. (6):

$$Q = \int Idt = (E_0 d/R) \int_0^{1/2f} (\sin 2\pi ft)\, dt$$

$$= E_0 d/\pi R f \quad (6)$$

Here, I is the current; t, the imposing time to electric field; d, the distance between electrodes; and R, the resistance of the solution. Equation (6) suggests that the motion speeds down as the frequency increases or as the amplitude decreases. Figure 5 shows the

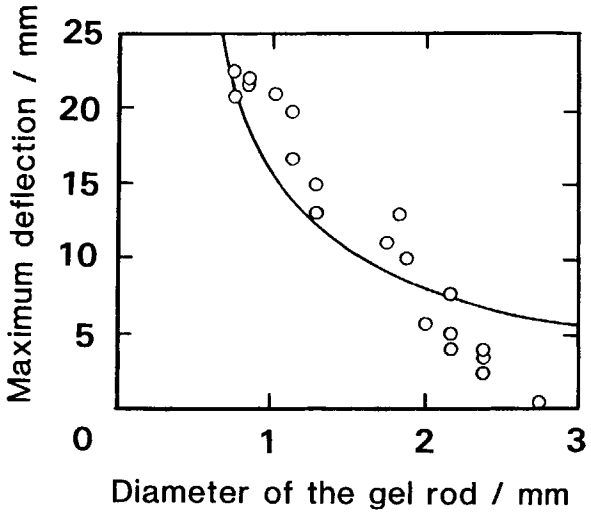

Figure 4 Effect of the diameter of the gel rod on the bending speed. The solid line is given by $Y_{max} = 16/D$, where Y_{max} is the maximum deflection and D the diameter.

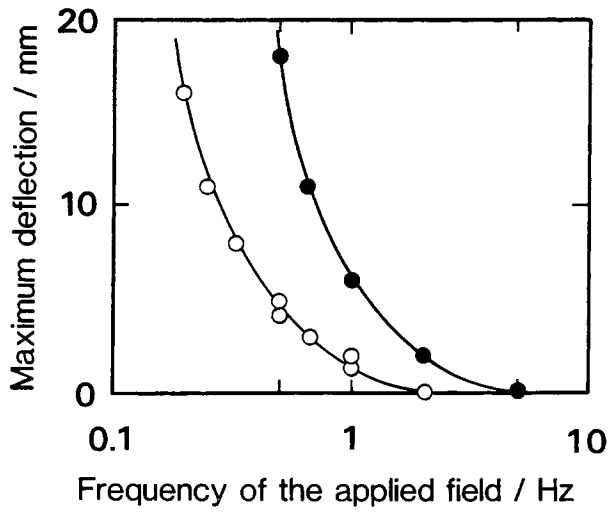

Figure 5 Relationship between the frequency of the applied field and the maximum deflection. The diameters of the gels are (●) 1.1 mm and (○) 2.2 mm.

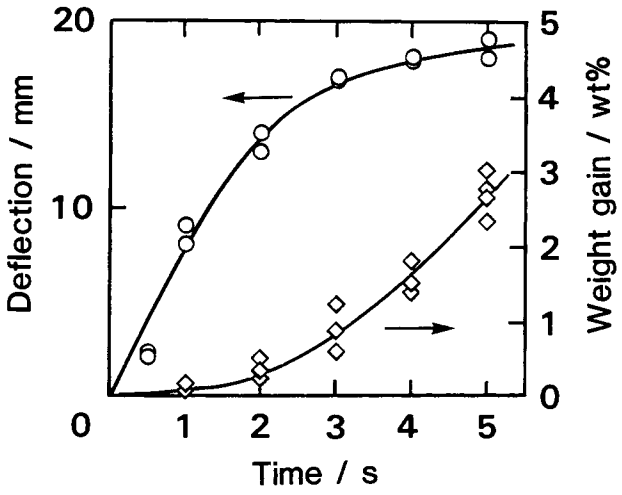

Figure 6 Deflection and weight gain of the PVA-PAA gel in a dc electric field of 30 V/cm. The weight gain (ΔW) was calculated by the following equation; $\Delta W = 100(W - W_0)/W_0$. Here, W_0 and W are the weights of the gel at times $t = 0$ and $t = t$.

effect of the frequency of the applied field on the maximum deflection, which represents a motion speed. As predicted from eq. (6), the speed decreases as the frequency of the applied field increases. The maximum deflection–frequency curve shifts to the higher frequency side as the diameter becomes smaller. The rod with the 1.1 mm diameter responds to a higher field of 4 Hz. Under a 4 Hz field, both ends of the rod has vibrated with a small deflection. The experimental results on the effect of the amplitude of the field on the maximum deflection is also in agreement with the predicted one from eq. (6). As the amplitude is increased, the maximum deflection–frequency curve shifts to the higher-frequency side. At 30 V/cm, the gel rod of 2.2 mm diameter responds to a 2 Hz signal. By calculating the response time of the PVA–PAA gel to electric fields, the gel has the response time of at least several hundreds milliseconds.

4.2. Mechanism of the Motion

To clarify whether the bending motion under sinusoidally varying electric fields occurs through swelling due to the osmotic effect, we have first done dc experiments and have compared them with the results in ac experiments. The dc experiments have been made under 30 V/cm in 10 mM Na_2CO_3 solution using the gel rod of length 50 mm and diameter 2.2 mm. Figure 6 shows a response to the dc electric field and the weight change of the gel on bending. The gel rod deflects by 18 mm in 3 s and the bending motion is caused by swelling. At 3 s, a weight gain of about 1 wt % has been observed. The ac experimental results are shown in Figure 5. When the gel showed a maxmum deflection at time $t = 5$ s under 0.2 Hz, a weight gain of 0.98 wt % was observed. The ac experimental result corresponds to the dc one. According to Figure 6, it is expected that the bending is caused by swelling under ac electric fields of more than 1 Hz. However, at higher frequencies, it is not determined whether the gel gains weight because the bending is too small. Figure 7 shows the effect of the concentration of Na_2CO_3 in

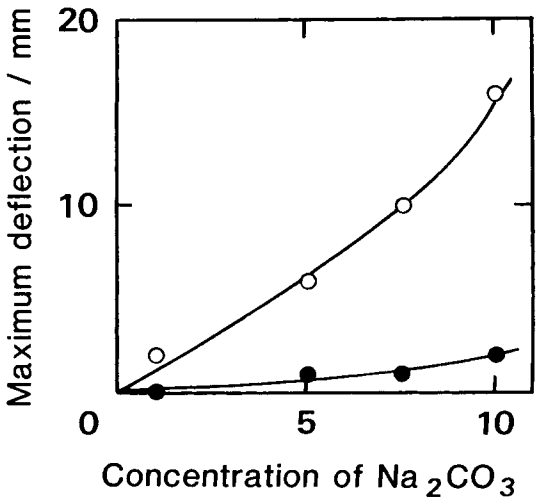

Figure 7 The effect of Na_2CO_3 concentration in the surrounding solution on the response to electric fields: (○) at 0.2 Hz; (●) at 1.0 Hz.

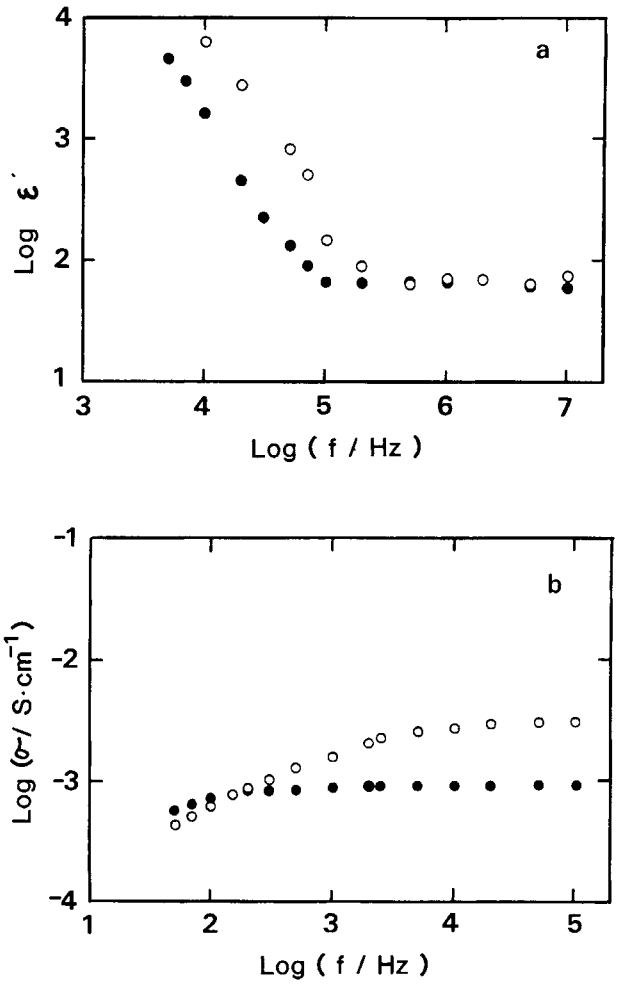

Figure 8 Electrical properties of (○) the PVA–PAA gel and of (●) 10 m*M* Na_2CO_3 aqueous solution: (a) the real part of complex dielectric constant (ϵ'); (b) ac conductivity (σ).

the surrounding solution on the response to electric fields of 0.2 and 1 Hz. The motion has been activated by the electrolyte, which means that the response is related to the drift of mobile ions and that the bending under electric fields of less than 1 Hz occurs through swelling due to the osmotic effect.

Next, we have attempted to examine the polarization effects of the gel and the surrounding solution on the bending–straightening motion. We have measured the real part of the complex dielectric constant (ϵ') and the ac conductivity (σ) of the PVA–PAA gel and 10 m*M* Na_2CO_3 aqueous solution using an impedance analyzer (Yokogawa Hewlett Packard Model 4192A). The gel plate (10 mm long, 10 mm wide, 2 mm thick) was sandwiched between two platinum electrodes and then a voltage of $V = V_0 \sin 2\pi ft$ (V_0 = 1 volt, f = 5 Hz–10 MHz) was applied between the electrodes. In the case of the 10 m*M* Na_2CO_3 solution, two platinum electrodes (10 mm long and 20 mm wide) were set separating only 40 mm in the Na_2CO_3 solution and the voltage was applied. ϵ' was calculated by regarding the gel or the solution as a parallel series composed of resistance and capacitance. At frequencies of less than 100 kHz, ϵ' increases with decreasing f (Fig. 8). Both the gel and solution have an ϵ' of more than 10^6 at 5 Hz. The dielectric increment in the gel is shown to be attributable to the distribution and the mobility of bound counterions of polyions.[8] It is caused by the mobilities of free ions in the solution. At higher frequencies, the oscillations of the counterions and the free ions cannot follow the field. This bring about dielectric dispersion.

ac Conductivities of the gel and the solution are shown in Figure 8(b). They have σ of 10^{-3}–10^{-4} s/cm. Figure 8(a) and (b) show that the gel and the solution have large polarizability and high conductivity. It is expected that the PVA–PAA gel responds to electric fields of more than 5 Hz if the bending–straightening motion of the PVA–PAA gel occurs through the solvent polarization effect or the polarization effect of the gel. However, the experimental results show (Figure 5) that the gel has not been influenced by electric fields of more than 5 Hz.

To investigate the solvent effect, electric field-associated motions of the gel in organic solvents were studied. A previous study showed that the electrolysis of water plays an important role in the bending under dc electric fields.[4] If it does, the motion will

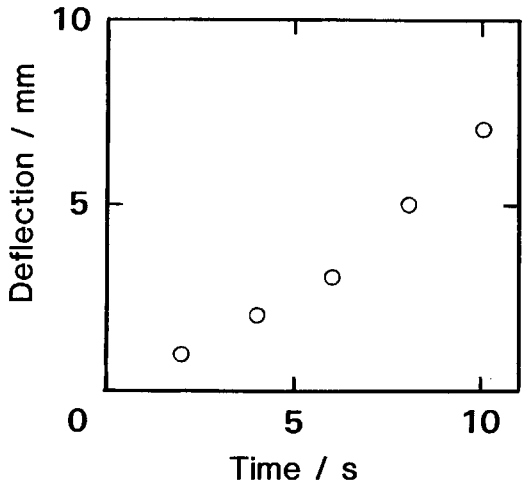

Figure 9 Deflection time curve under a dc field of 30 V/cm in 3 m*M* tetra-*n*-butylammonium perchlorate ethanol solution. The experiment was done as follows: The gel with 1.1 mm in diameter was set in the solution, and, immediately, the field was applied.

be observed in organic solvents when the solvent is electrolyzed. The experiments have been done as follows: The gel of 1.1 mm diameter was set in ethanol or benzene solutions containing tetra-*n*-butylammonium perchlorate of 0 and 3 m*M*, and, immediately, electric fields of 30 V/cm were applied because the gel began to shrink in the solvents. In the case of the solutions free of the electrolyte, the gel has not been influenced by electric fields. This result means that the polarization effect of the gel is negligible. In the benzene solution containing the electrolyte, the gel was not influenced by electric fields. The current has not been observed. On the other hand, in the ethanol solution, the motion has been observed in both dc and ac electric fields. Figure 9 shows the deflection–time curve in a dc electric field. There is 3.2 wt % of weight gain at 10 s. On bending in the ethanol solution, a current of 32 mA has also been carried out. The obtained results suggest that the bending process is related to the ions carrying the current and that it is driven by the electrolysis of the solvent. Therefore, it seems that the solvent polarization effect induced by electric fields on the motion is small.

5. CONCLUSION

The deformation of the PVA–PAA composite hydrogel in Na_2CO_3 aqueous solutions under sinusoidally varying electric fields has been studied. A cyclic bending–straightening motion has been observed in the gel rods of about 1 mm in diameter under the fields. The gel has responded to the fields up to 4 Hz and has a response time of less than several hundreds milliseconds to electric fields. The experimental results suggest that we need to prepare fibers or films of the gel to show a higher response to electric signals. In this study, the bending induced by electric fields has also been observed in ethanol containing an electrolyte. It was found that the bending process under sinusoidally varying electric fields is related to the ions carrying the current. It is reasonable that the bending–straightening motion under electric fields of less than 1 Hz occurs through swelling due to the osmotic effect. However, it has not been determined whether the motion at higher frequencies is caused by the osmotic effect.

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