

Electric-Field-Sensitive Polymers: Reversible Bending of Rod-Shaped Polymer Gels in Salt Solutions

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SYNOPSIS

Neutral gel (acrylamide [AAM] gel) and anionic gel (copolymer gel of 2-acrylamido-2-methyl-1-propane sulfonic acid [AMP₃SA] and butyl methacrylate [BMA]) were prepared to observe the bending phenomena in various salt solutions. The bending pattern of AAM gel was closely related to salts used in the aqueous media. The competition NMR technique was used to understand the interaction of salts with the polymer matrix. In the case of copolymer gel, the bending pattern did not show the salt dependence and the bending angle decreased after reaching a maximum. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

A gel is an intermediate form of matter between a solid and liquid. It can swell and shrink in the aqueous media and show discontinuous swelling under the external stimulus, which is called the phase transition.¹⁻³

The electric-field-induced deformation was first observed by Tanaka et al. who found the collapse of partially hydrolyzed acrylamide (AAM) gel in an acetone/water (50 vol %) binary mixture on the application of an electric field.³ Tanaka and co-workers suggested that the electric field pushed the negatively charged gel toward the anode and squeezed the anode side of the gel. Later, the work of Shiga et al. on bending of poly(vinyl alcohol)-poly(sodium acrylate) composite hydrogel in the electric field and the more fundamental work of Doi et al. on the deformation of ionic polymer gels by electric fields were performed.⁴⁻⁶ They pointed out that these phenomena were induced by the changes in the ionic distribution under the electric field. The work of Yuk and Lee on bending of AAM gel in NaCl aqueous solution also verified that the changes in the ionic distribution played a major role in the bending phenomena.⁷

The purpose of this article was to present the experimental results on the bending phenomena of the neutral and anionic polymer gels in various salt solutions with the application of electric field and to propose a mechanism of bending phenomenon. AAM gel was used as a neutral gel and a copolymer gel of 2-acrylamido-2-methyl-1-propane sulfonic acid (AMP₃SA) and butyl methacrylate (BMA) was used as an anionic gel.

EXPERIMENTAL

Reactants and Solvent

AAM monomer and salts used in the aqueous media were purchased from Junsei Chemical Co., Japan. *N,N'*-Methylenebisacrylamide (NMBAAm), AMP₃SA, BMA, ethylene glycol dimethacrylate (EGDMA), and ammonium peroxodisulfate (APS) were purchased from Aldrich. Azobisisobutyronitrile (AIBN) was purchased from Sigma. BMA was purified by distillation with reduced pressure under nitrogen and all other chemicals were used without further purification.

Gel Preparation

The AAM gel was prepared by free-radical polymerization. AAM (1.94 g), NMBAAm (0.06 g) as a

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cross-linker, and APS (0.01 g) as an initiator were dissolved in 40 mL water. The polymerization was carried out using UV irradiation. Irradiation was carried out with a high-pressure mercury lamp (USHIO, 1 kW).

The anionic gel, the copolymer of AMPSA and BMA, was synthesized using EGDMA as a cross-linker and AIBN as an initiator. The feed composition for AMPSA/BMA was a 3/1 (weight ratio). Monomers (10.0 g) were dissolved in DMF (20 mL) followed by the addition of EGDMA (0.12 g) and AIBN (0.01 g). The solution mixture was bubbled with dried nitrogen gas for 20 min to remove the oxygen. Polymerization was performed between two Mylar® sheets separated by a silicone rubber gasket and backed by glass plates at 60°C for 24 h. After polymerization, the gel was removed from the mold and soaked in a water/acetone (50/50 vol %) solvent mixture. The solvent mixture was replaced daily for 1 week to extract the unreacted compound. The prepared polymer gel was immersed in the salt solutions until use.

Apparatus for Bending-angle Measurements

The apparatus for bending-angle measurements is shown schematically in Figure 1. The rod-shaped gel was placed between the positive and negative electrodes in a salt solution. The distance between the two electrodes was 10 mm. The gel was 30 mm in length and $5 \times 5 \text{ mm}^2$ in a cross-sectional area. The applied voltage was 20 V (DC).

Swelling Measurement

Swelling is defined as the weight of water uptake per unit weight of dried gel. The swelling of the anionic gel was measured as a function of pH by first wiping the excess surface water and weighing. The

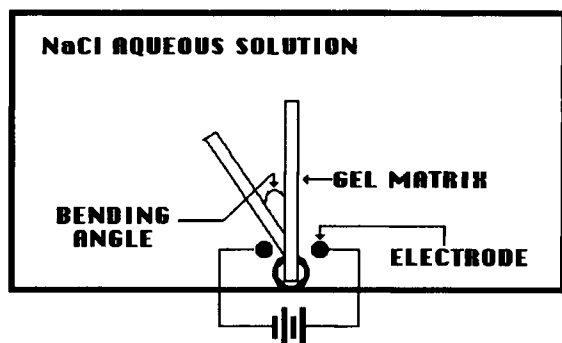


Figure 1 Schematic diagram of apparatus for bending-angle measurement.

pH of the aqueous solution was controlled by the addition of HCl. The total ionic strength of each aqueous media was adjusted to 0.1M with the calculated amount of NaCl.

pH Measurement

The pH change of aqueous media caused by the application of electric field was measured by taking 1 mL of aqueous medium after the application of the electric field for 20 min. Especially, the aqueous medium was taken directly from the aqueous medium-electrode interface using a syringe for the measurement of local pH around the electrode. The sampled aqueous media was diluted 10 times with a fresh salt solution to obtain a sufficient volume for pH measurement and assayed with a pH meter 245 (Corning).

Measurements of NMR Spectra

The NMR experiment was performed on a Bruker AM 300-MHz spectrometer operating at 60.0 MHz for ^{127}I . All the NMR spectra were obtained with spinning and field locking by placing D_2O , sealed in a 5 mm tube, in the middle of 10 mm sample tube in which the swollen gel was placed. The gel for the NMR measurement was prepared by drying the gel, grinding the dried gel into a powdery state, and immersing the gel powder in distilled water for equilibrium swelling. The temperature was controlled by flowing heated air around the sample tube located in the NMR probe head. The line widths at half-height were obtained by Lorentzian curve fitting.⁸ The errors in measuring the line width were estimated to be $\pm 2\%$ for ^{127}I -NMR.

RESULTS AND DISCUSSION

Bending of Neutral Gel

The bending of AAm gel used as a model neutral gel was observed in the aqueous solutions of KF, KCl, KBr, KI, KSCN, and KNO_3 . With the application of an electric field, the gel bent toward the negative electrode in KCl, KBr, and KI (denoted as KX) solutions and toward the positive electrode in KF, KSCN, and KNO_3 (denoted as KY) solutions as shown in Figure 2.

In the case of the KX solution, the following electrochemical reactions occur with the flow of electric

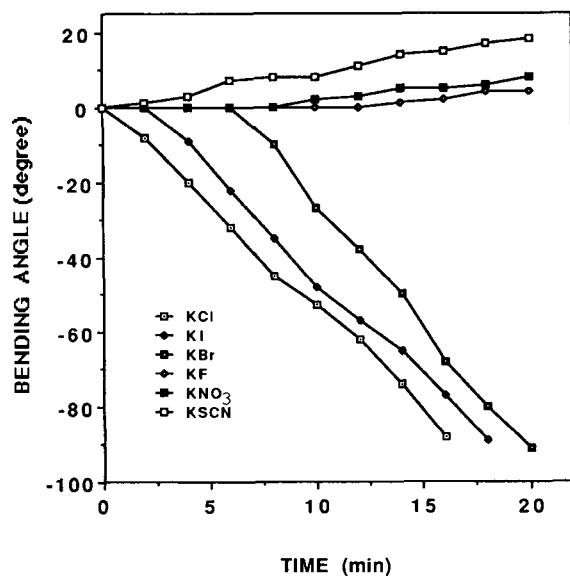
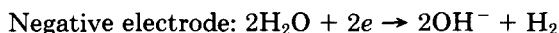
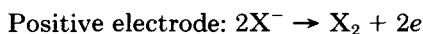


Figure 2 Bending angle of AAm gel in various salt solutions.

current:



As shown in Table I, the pH of the KX solution becomes basic, indicating the generation of an OH^- ion. In this case, the major mobile ions are K^+ and OH^- that move toward their counterelectrode. Because of the difference in diffusion coefficients of each mobile ion at $25^\circ C$, ionic concentration gradients are induced. Osmotic pressure on the positive electrode side (π_1) becomes larger than that on the negative electrode side (π_2), as shown schematically in Figure 3 (A). This osmotic pressure difference is the driving force for bending toward the negative electrode. It was also reported by us that the osmotic pressure difference caused by the ionic concentration gradients played a major role in the bending of AAm

Table I pH of Salt Solution with Application of Electric Current

	Before Reaction	After Reaction
KF	6.76	6.60
KCl	5.66	11.83
KBr	5.62	11.96
KI	5.43	12.41
KNO ₃	5.46	5.71
KSCN	5.48	1.82

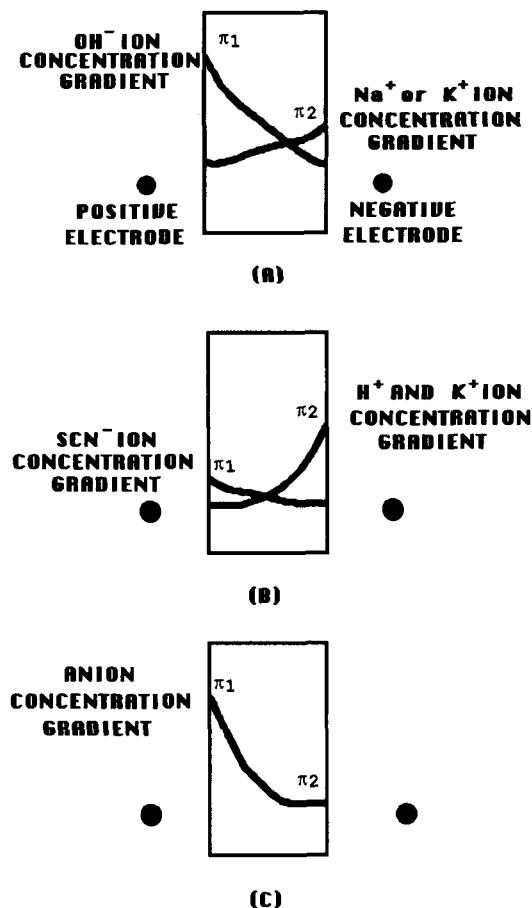


Figure 3 Schematic diagram illustrating the ionic concentration gradient in a gel matrix with the application of the electric field: (A) AAm gel in KX salt solutions; (B) AAm gel in KSCN solution; (C) copolymer gel in salts solution.

gel in NaCl aqueous solution induced by the electric field.⁷

The lag time was dependent on the anion of salt used in the experiment (see Fig. 2). To understand the relationship between the lag time in bending and the anion, the interaction of the anion with the polymer matrix was observed by the competition NMR technique. In the literature,⁹⁻¹⁰ the interaction between halide ions and polymer matrices has been shown to cause significant line broadening in halide NMR. Based on the competition NMR technique, the half-height line width in ^{127}I -NMR of aqueous halide-poly AAm gel was measured as presented in Table II. The NMR line width is much greater with poly(AAm) gel than without poly(AAm) in the halide solution and the difference between two under the same iodide concentration is the excess NMR line width. A 0.5 M KI solution used as a reference gave a half-height line width of 1660 Hz and the

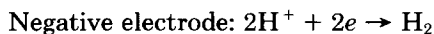
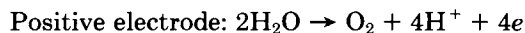
Table II Line Width of ^{127}I -NMR in Halide-AAM Gel System (Unit: Hz)

	Half-height Line Width	Excess Line Width
0.5 M KI solution (reference)	1660	—
KCl-KI-AAM gel	7810	6150
KI-AAM gel	7380	5720
KBr-KI-AAM gel	6830	5170

0.5 M KI-poly AAM gel gave a half-height line width of 7380 Hz, resulting in an excess NMR line width of 5720 Hz, whereas the excess NMR line width decreased to 5170 Hz when 0.5 M KBr was added into the solution.

This decrease in the excess NMR line width is due to the competition between Br^- and I^- for the same binding site of poly (AAM). Such a successive comparison of the ^{127}I -NMR line width gave us the order of binding affinity: $\text{Br}^- > \text{I}^- > \text{Cl}^-$. The electrochemical reaction at the positive electrode and the induction of ionic concentration gradient were hindered by the binding of anion to the polymer matrix. This effect was most significant in the presence of Br^- ion, resulting in the longest lag time in the bending phenomena.

pH changes of KF and KNO_3 solutions were not observed, but that of the KSCN solution was significant, as shown in Table I. The minimal electrochemical reaction occurred in KF and KNO_3 solutions, resulting in a minimal bending angle, as shown in Figure 2. In the case of the KSCN solution, the following electrochemical reaction occurs with the flow of electric current:



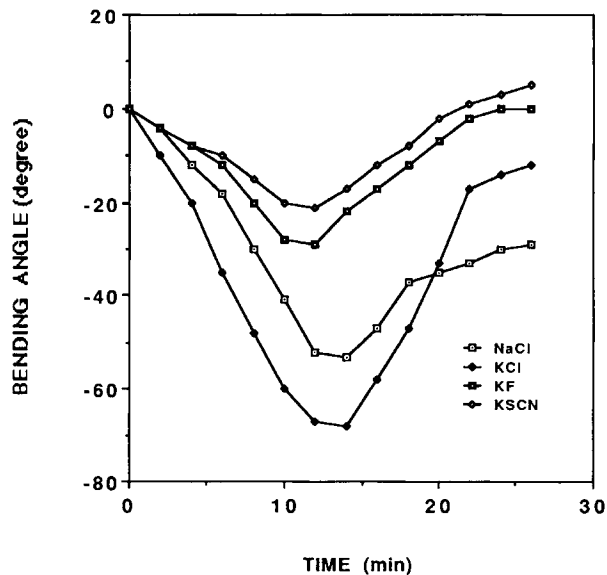
In this case, the mobile ions are K^+ , Y^- , and H^+ and they move toward their counterelectrode. Because the H^+ ion has the largest value of the diffusion coefficient in the aqueous solution at 25°C, the ionic concentration gradients are induced and the osmotic pressure on the positive electrode side (π_1) becomes smaller than that on the negative electrode side (π_2), as shown schematically in Figure 3(B). This osmotic pressure difference results in the bending toward the positive electrode.

Bending of the Anionic Gel

The copolymer gel of AMPSA and BMA was used as a model anionic gel. The role of BMA is to provide the mechanical strength to the gel matrix. As shown in Figure 4, the anionic gel bent toward the negative electrode with the application of the electric field and the bending angle decreased after reaching a maximum. The pattern of the bending phenomena did not exhibit any salt dependence, contrary to the results in Figure 2.

As shown schematically in Figure 5, which presents the ionic environment, the concentration of the counterion (K^+) will not change significantly with the application of the electric field if electroneutrality is maintained. However, the concentration of the co-ion (F^- , Cl^- , Br^- , I^- , SCN^- , and NO_3^-) can vary significantly without violating electroneutrality. Based on this explanation, the co-ion concentration gradients are induced, as shown schematically in Figure 3(C). With application of the electric field, osmotic pressure on the positive electrode (π_1) becomes larger than that on the negative electrode (π_2). This osmotic pressure difference is the driving force of bending toward the negative electrode.

The changes in pH under the electric field will affect the swelling of the anionic gel. The swelling change of the gel as a function of pH is shown in Figure 6. The maximum swelling change was observed at pH 1–2, which reflected the ionization of sulfonic groups. Above pH 3, the swelling increased

**Figure 4** Bending angle of copolymer gel in various salt solutions.

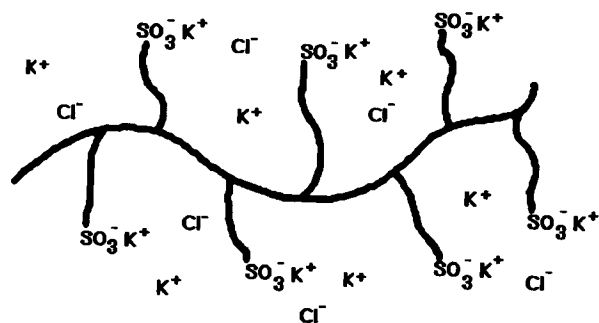


Figure 5 Schematic diagram illustrating the ionic environment of copolymer gel in the salt solution.

slightly. With application of the electric field, the pH of the aqueous media was approximately 1.5 around the positive electrode and 8.5 around the negative electrode. The H^+ ion generated around the positive electrode protonated the sulfonic groups of the gel matrix on the side of positive electrode, resulting in the deswelling. This deswelling of the gel matrix is the driving force of bending toward the positive electrode and results in the decrease of the bending angle after the maximum bending angle.

CONCLUSIONS

The bending phenomena of the AAm gel and the copolymer gel of AMPSA and BMA were studied in various salt solutions with the application of the electric field. The bending pattern of the AAm gel was closely related to the salts used in the aqueous media. With application of the electric field, the gel bent toward the negative electrode in KCl, KBr, and KI solutions and toward the positive electrode in KF, KSCN, and KNO_3 solutions. These phenomena could be explained in terms of the osmotic pressure difference caused by the ionic concentration gradients and the osmotic pressure difference was closely related to the major mobile ions generated in the electrochemical reactions.

The bending pattern of the copolymer gel did not show the salt dependence. With application of the electric field, the gel bent toward the negative electrode and the bending angle decreased after reaching a maximum. The osmotic pressure difference caused by the ionic concentration gradients without vio-

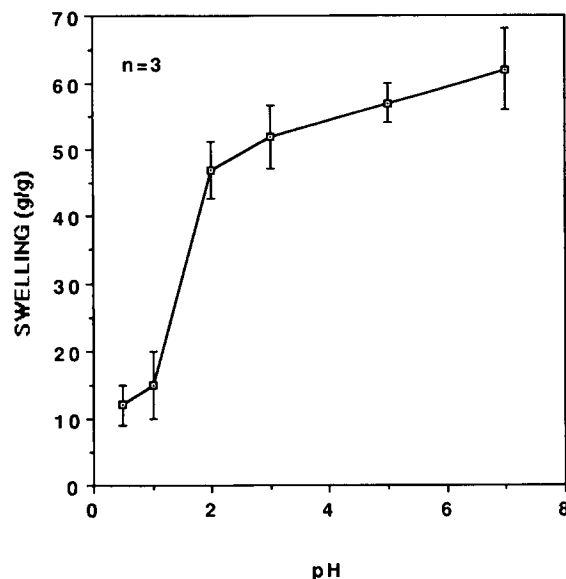


Figure 6 Swelling change of copolymer gel as a function of pH.

lating the electroneutrality and the swelling change of gel matrix in response to the pH change played the major roles in the bending phenomena.

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