

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Experiment Designs

In this work, many experimental parameters must be considered in order to find the best composition of the hydrogel and the best operational conditions. These parameters include the proportions of chitosan/PAA/barakol, the type and proportions of crosslinking agent, the NaCl concentrations, and electrical voltages.

In addition, other experiments have also been done including design and build the experiment equipments, finding the best shape and size of the hydrogel films and determine the best swelling time. The results of these finding were used in the following experiments.

The objective is to provide a hydrogel film with the most responsive to the electrical stimulus in terms of equilibrium bending angle, bending time, reverse bending time and number of repeated bending.

4.2 Electrochemical Studies of Barakol

Voltammogram of barakol is shown in Figure 4.1. The process was performed in the non-aqueous environment. The cyclic voltammogram exhibits redox wave corresponding to the reduction process at $E_1^{\circ} = -1.0$ V and the oxidation process at $E_2^{\circ} = -0.7$ V. They have been proposed that the charge transfer process at E_1° corresponds to the reduction of anhydrobarakol to anhydrobarakol radical and E_2° corresponds to the oxidation of anhydrobarakol radical to anhydrobarakol (Figure 4.2).

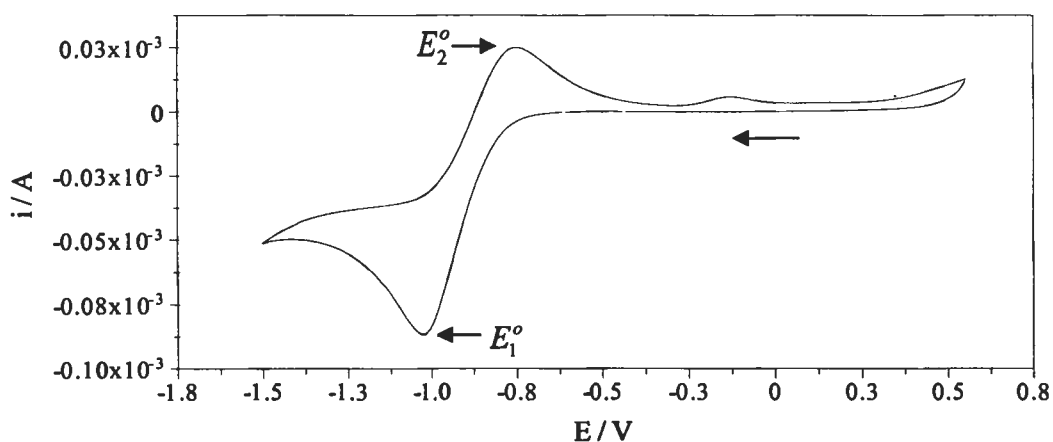


Figure 4.1 Cyclic voltammogram for 0.1 mM barakol at scan rate 0.2 V/s

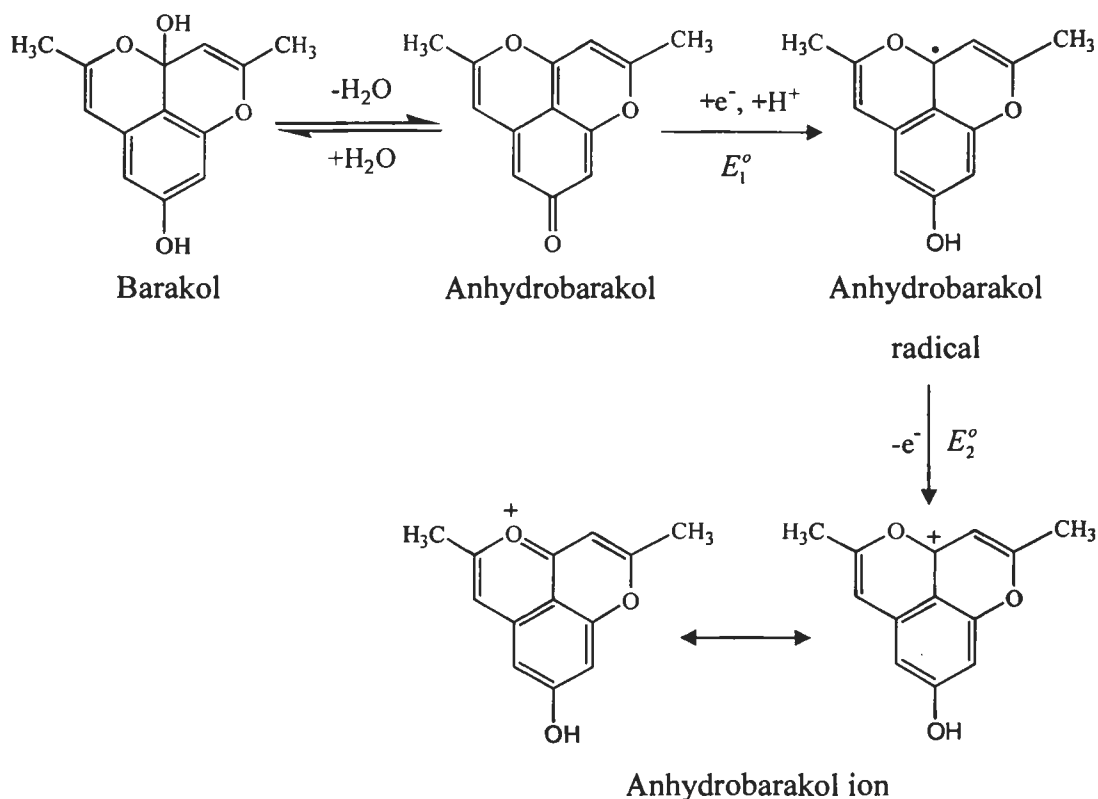


Figure 4.2 Proposed electrochemical steps of barakol

4.3 FT-IR Spectra

FT-IR spectra of hydrogel films prepared from chitosan and poly(acrylic acid) in various ratios can be seen in Figures 4.3 & 4.4. The IR spectrum of chitosan was showed in Figure 4.3 (a). The principle peaks were observed at wave numbers of 1575, 1657, 2875 and 3427 cm^{-1} . The peak showed the characteristic peak of N-H bending at 1575 cm^{-1} . The IR absorption peaks at 1657 and 2875 cm^{-1} were resulted from C=O of amide groups and $-\text{CH}_3$ stretching, respectively, that are occurred from the partial of chitin were not deacetylated. The characteristic peak is located at 3427 cm^{-1} is for a hydroxyl group.

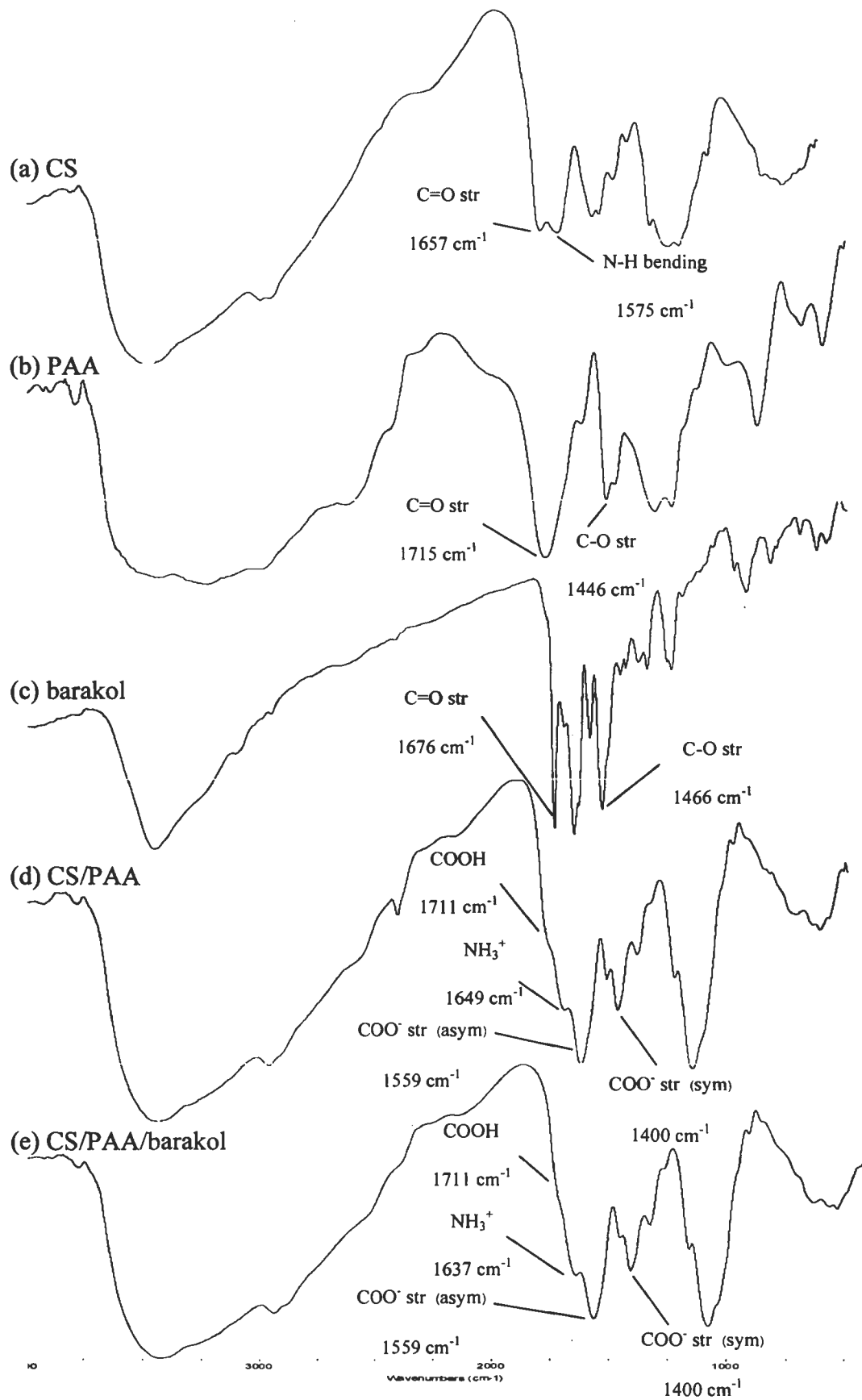


Figure 4.3 FT-IR spectra of (a) CS, (b) PAA, (c) barakol, (d) CS/PAA, (e) CS/PAA/barakol

The strongest peak, at 1715 cm^{-1} in the IR spectrum of poly(acrylic acid) (Figure 4.3 b), has been assigned to C=O stretching vibration of carboxylic acid groups. The IR peaks at 796 , 1446 cm^{-1} were resulted from C-H out of plane bending, coupled C-O stretching in COOH and the broad band at 3202 cm^{-1} resulted from -OH stretching that PAA can high absorbed humidity in air.

The IR spectrum of extracted barakol (yellow crystalline compound) is shown in Figure 4.3 (c). The spectrum showed broad absorption bands at 3443 cm^{-1} corresponding to an O-H stretching with the strong hydrogen bonding. The IR peaks at 1466 cm^{-1} was resulted from C-O stretching. The peak at 1676 cm^{-1} was assigned to the C=O stretching, indicating barakol is unstable and can be converted to anhydrobarakol.

FTIR spectra of chitosan/PAA can be seen in Figure 4.4 (d). In spectrum, two strong peaks at 1717 , 1559 cm^{-1} and 1400 cm^{-1} were observed due to the COOH group, asymmetrical and symmetrical stretching of COO^- group, respectively, while the peak at 1649 cm^{-1} was attributed to the formation of NH_3^+ groups. These facts confirmed that the carboxylic groups of PAA were dissociated to COO^- groups which complexed with protonated amino groups from chitosan through electrostatic interaction during the formation of the polyelectrolyte complex.^[42]

Figure 4.4 (e), (f), (g) and (h) depict the IR spectra of CS/PAA/barakol, CS/PAA/barakol/glutaraldehyde, CS/PAA/barakol/glutaric acid and CS/PAA/barakol/citric acid, respectively. The characteristic peaks were not shifted from their positions when compared to the IR spectra of the chitosan/poly(acrylic acid). However, in our experiment obvious differences between CS/PAA, CS/PAA/barakol, CS/PAA/barakol/glutaraldehyde, CS/PAA/barakol/glutaric acid, CS/PAA/barakol/citric acid could not be found from the IR spectra because the small amount of barakol; glutaraldehyde^[42], glutaric acid and citric acid content in the samples.

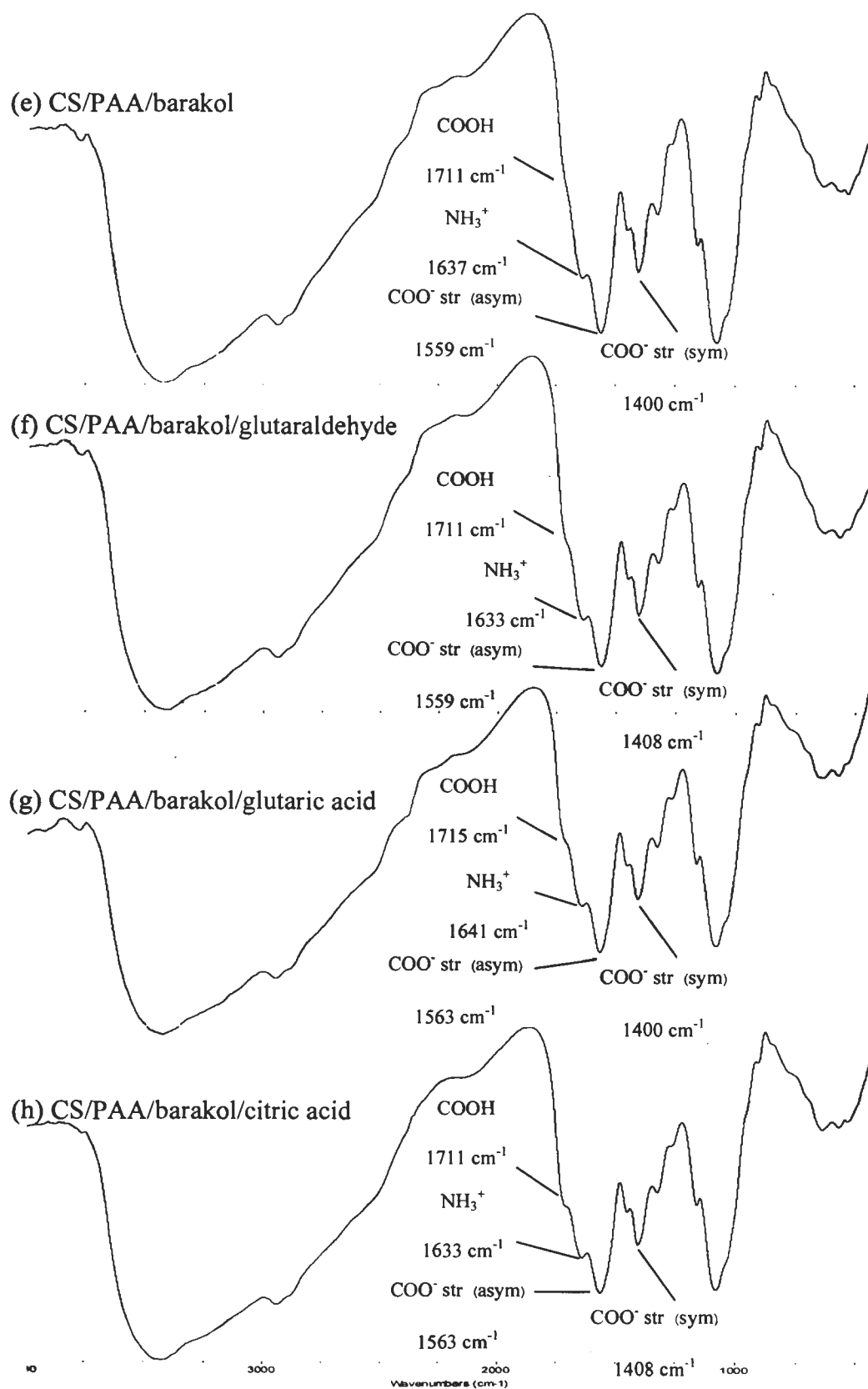


Figure 4.4 FT-IR spectra of (e) CS/PAA/barakol, (f) CS/PAA/barakol/glutaraldehyde, (g) CS/PAA/barakol/glutaric acid, (h) CS/PAA/barakol/citric acid

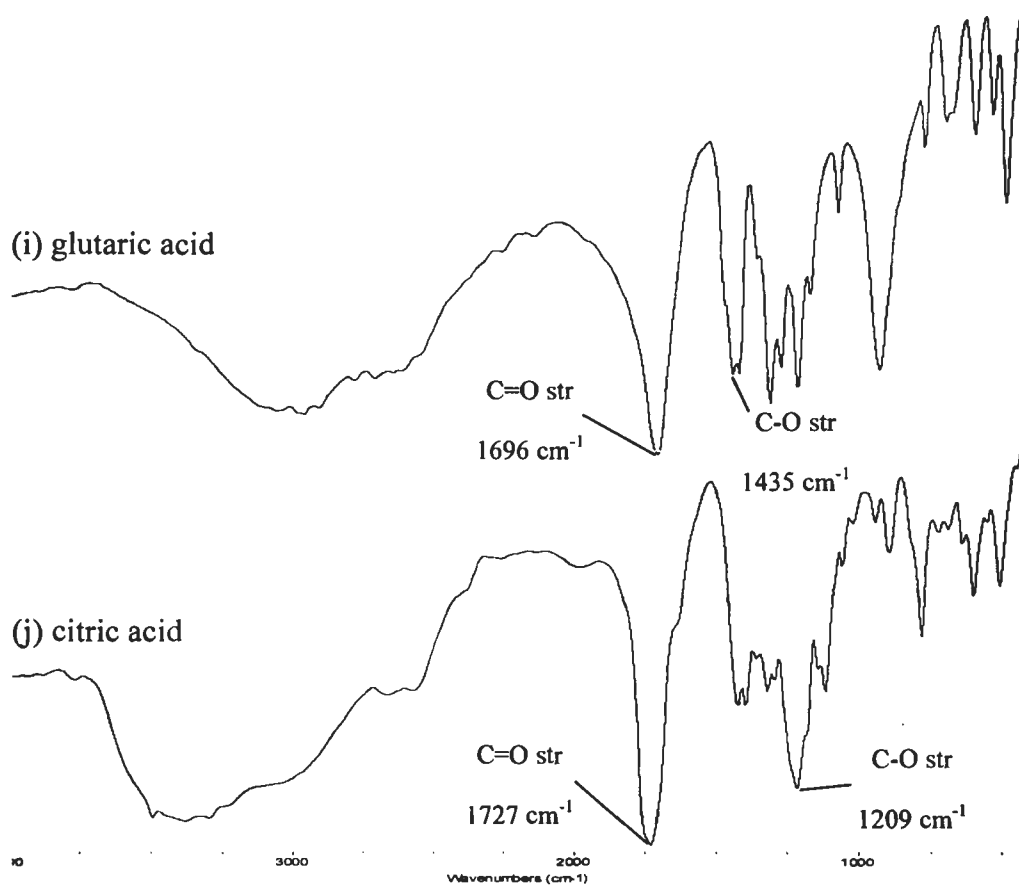


Figure 4.5 FT-IR spectra of (i) glutaric acid, (j) citric acid

The IR spectra of glutaric acid is illustrated in Figure 4.5 (i). The principle peaks were observed at wave number 921, 1696, 2898, 2960 and 3431 cm^{-1} . The peak at 921 and 1696 cm^{-1} were resulted from O-H out-of-plane bending and C=O of carboxylic acid, respectively. The IR absorption band at 2898 cm^{-1} (asym) and 2960 cm^{-1} (sym) were resulted from $-\text{CH}_2$ stretching. It showed the broad band at 3413 cm^{-1} was resulted from $-\text{OH}$ stretching.

Figure 4.5 (j) showed the IR spectra of citric acid. Because of the functional groups of citric acid to be similar to glutaric acid but citric acid have three C=O of carboxylic acid. So intensity of C-O, C=O stretching of carboxylic acid and hydroxyl group were increased at absorption band 1209, 1727 and 3381 cm^{-1} , respectively. The peak at 781 cm^{-1} was resulted from C-H out of plane bending.

4.4 Thermal Properties

The DSC thermograms of hydrogel films are shown in Figure 4.6 and 4.7.

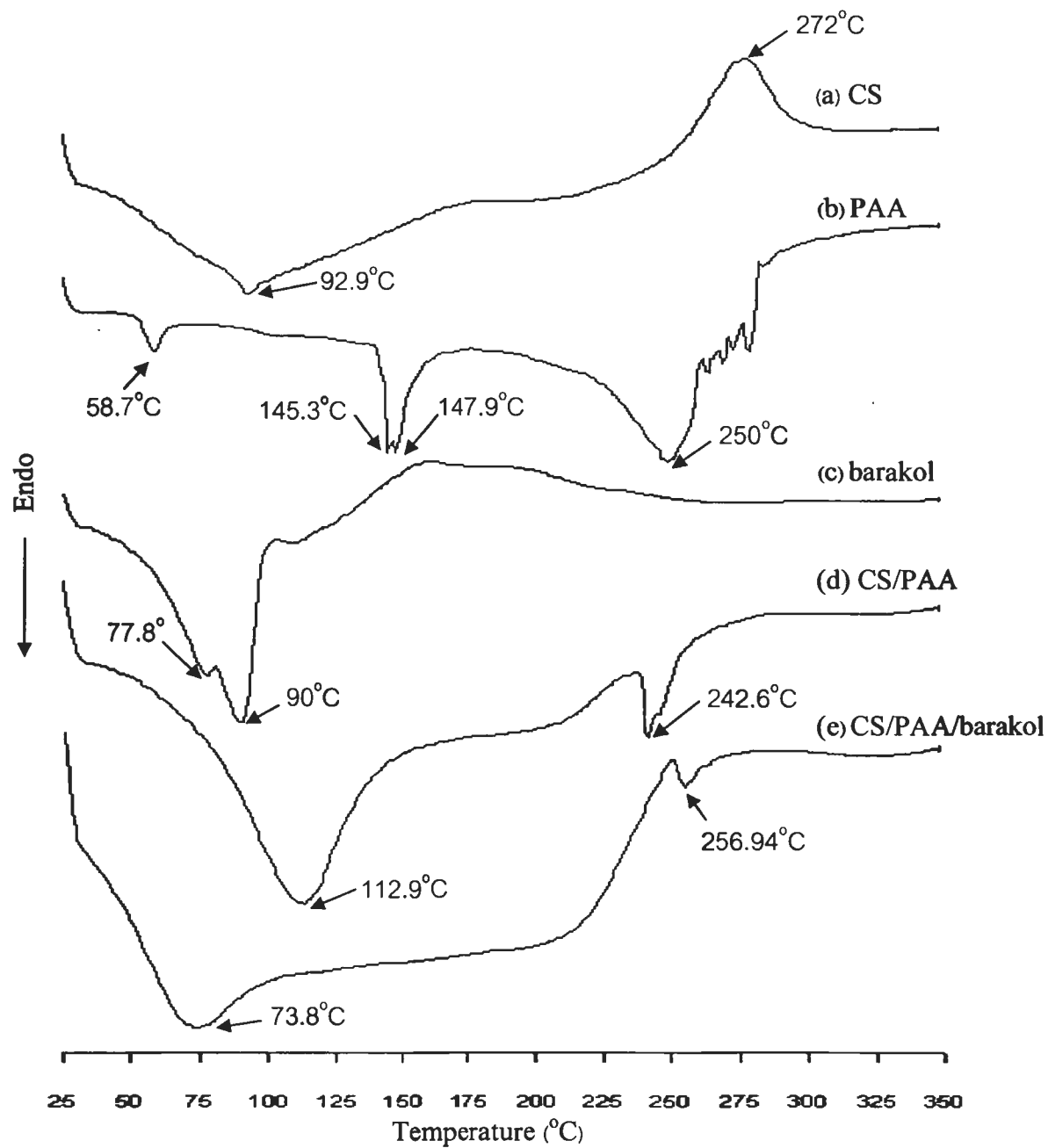


Figure 4.6 DSC thermograms of (a) CS, (b) PAA, (c) barakol, (d) CS/PAA, (e) CS/PAA/barakol

The DSC thermogram of pure barakol gave an endothermic peak at 77.8 °C and at 92.9 °C can be ascribed to the loss of water (Figure 4.6 (c)). Figure 4.6 (a), (b) exhibiting DSC thermogram of polyelectrolyte film. Chitosan film showed an endothermic peak at 92.9 °C can be ascribed to the loss of water. The second thermal event may be related to the decomposition of amine units with correspondent exothermic peak at 272 °C.^[43] However, the melting endotherm of chitosan was not observed by DSC although it has crystalline regions. This is due to the fact that chitosan has a rigid-rod backbone with a strong inter- and/or intra-molecular hydrogen bonding. Therefore, it degrades before melting. This characteristic is typical for many polysaccharides and their derivatives.^[44] In PAA, which is amorphous polymer, showed three endothermic peak at 58.7 °C, 145.3-147.9 °C, and 250 °C. At 58.7 °C showed removal of absorbed moisture or nonstructural water followed by a single endotherm, at 145.3-147.9 °C is glass temperature^[45] and at 250 °C are decomposition of PAA.^[44]

Figure 4.6 (d) exhibited that the endothermic peak of chitosan/PAA at 112.9 °C and that shifted from pure chitosan and PAA films. In general, it is known that interactions, for example, electrostatic interaction, hydrogen bonding between polymer chains contribute to the shifting of endothermic temperatures. In the case of polymer blend, two endothermic temperatures of polymers capable of interacting with another polymer shift to the inner side of endothermic temperatures of the two polymers. Chitosan and PAA in polyelectrolyte complexes have cationic and anionic groups, respectively, which can interact with each other, resulting in a shift of endothermic peaks of chitosan and PAA to the inner side of the two polymers as seen in Figure. 4.6 (d).

In Figure 4.6 (e) showed the DSC thermograms of chitosan/PAA/barakol film. Having barakol to chitosan/PAA film, the endothermic peak was shifted to the lower temperature when compared with pure chitosan/PAA film. Because barakol molecules can insert into structure between chitosan and PAA. Therefore electrostatic interaction in hydrogel film decreased, causing the temperature was

shifted. Figure 4.7 (e), (f), (g) and (h) depict the DSC thermograms of CS/PAA/barakol, CS/PAA/barakol/glutaraldehyde, CS/PAA/barakol/glutaric acid and CS/PAA/barakol/citric acid, respectively. The DSC thermograms of these hydrogel films were similar. The shapes and positions of the endothermic peaks were similar with a few differences. The DSC results showed that the interactions between polymer and crosslinking agents were very small and did not significantly affect thermal properties.

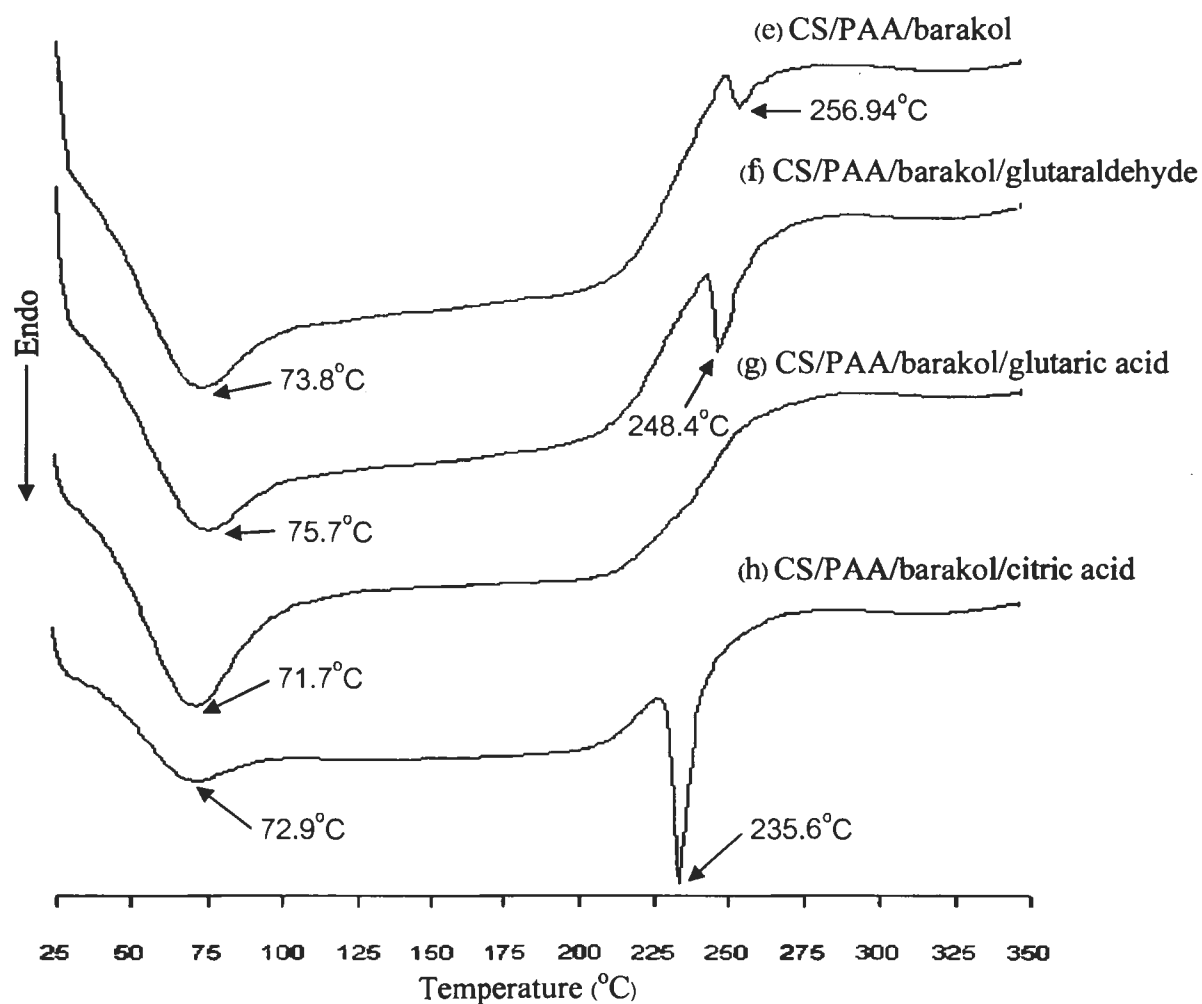


Figure 4.7 DSC thermograms of (e) CS/PAA/barakol, (f) CS/PAA/barakol/glutaraldehyde, (g) CS/PAA/barakol/glutaric acid, (h) CS/PAA/barakol/citric acid

4.5 Mechanical Properties

The tensile strength and elongation at break of the hydrogel films are shown in Figure 4.8.

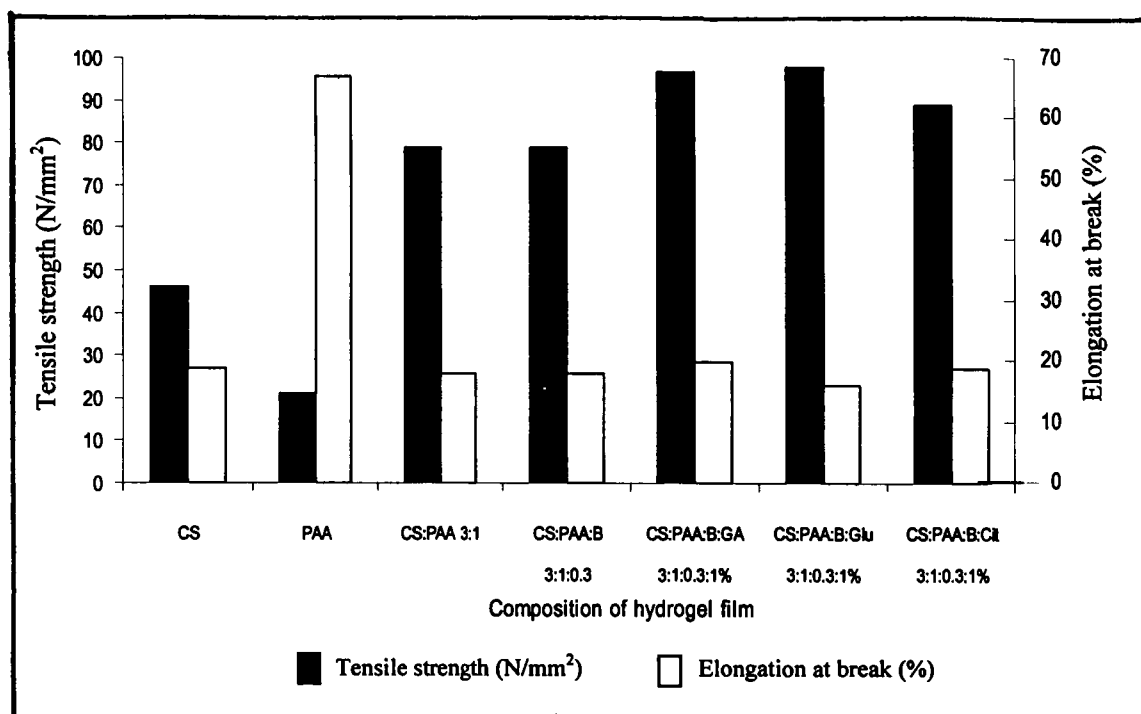


Figure 4.8 Mechanical properties of hydrogel films

The mechanical property of the hydrogel films is another important factor when used for electrical response. The chitosan film has greater tensile strength and less elongation at break than PAA. Chitosan-PAA complex film, which is a polyelectrolyte complex, exhibited an increased tensile strength and decreased elongation at break compared to pure chitosan and pure PAA, respectively. The tensile strength and the elongation at break of CS/PAA containing barakol are not significantly different from CS/PAA without barakol, indicating that the mechanical properties of hydrogel film were not affected by barakol.

The hydrogel films with different types of crosslinking agents (fixed at 1% by weight) reveal that the films have greater tensile strengths than those of other

non crosslinked hydrogel films. Whereas their elongation at break are the same. The increase of tensile strength could be explained by a chitosan network is formed between its polyelectrolyte chains; the pulling force on the crosslinked hydrogel films would be distributed on the chitosan network.^[47] The crosslinked hydrogel films would then withstand a stronger pulling force than the non crosslinked hydrogel films

4.6 Swelling Properties

The hydrogel films exhibited sensitivity to electrolyte concentration causing swelling behavior. The effect of the concentration of NaCl solution on the equilibrium swelling was observed at room temperature. The weight of completely dried samples was measured directly, and the samples were dipped into a petri dish filled with NaCl solution with different concentrations at room temperature.

4.6.1 Swelling properties of hydrogel films with various proportions of chitosan/poly(acrylic acid)

The equilibrium swelling ratio of the pure chitosan and pure poly(acrylic acid) hydrogel film could not be measured because the chitosan was shattered and PAA was dissolved when they were immersed in water and NaCl solution.

The equilibrium swelling ratio of the CS/PAA hydrogel in deionized water and NaCl aqueous solutions of 0.3, 0.6, 0.9, 1.2, 1.5 wt% concentrations are given in Figure 4.9.

The CS/PAA hydrogel exhibited the electrolyte concentration sensitive swelling behavior. The CS/PAA hydrogel swelled rapidly and reached equilibrium within 25 minutes. These swelling ratios of CS/PAA hydrogel varied from about 33% to 163%. For the swelling characteristic of 1:1 and 2:1 CS:PAA in response to NaCl concentration, their swelling ratio was lower than the others because the $-\text{NH}_3^+$ group

in the chitosan and the -COO^- group in the PAA of hydrogel formed polyelectrolyte complex with comparable proportions of the different charges. The electrostatic interaction between the different charges of polymers caused the shortening of intermolecule distances. The swelling ratio of 2:1 and 1:1 hydrogel increases when the concentration of NaCl solution is increased, probably due to the dissociation of ionic bonds between -COO^- and -NH_3^+ in the hydrogel. The -COO^- group of PAA became $\text{-COO}^-\text{Na}^+$ group, -NH_3^+ group of CS became $\text{-NH}_3^+\text{Cl}^-$ group. Therefore, electrostatic interactions in the hydrogel decrease, causing the hydrogel to swell.

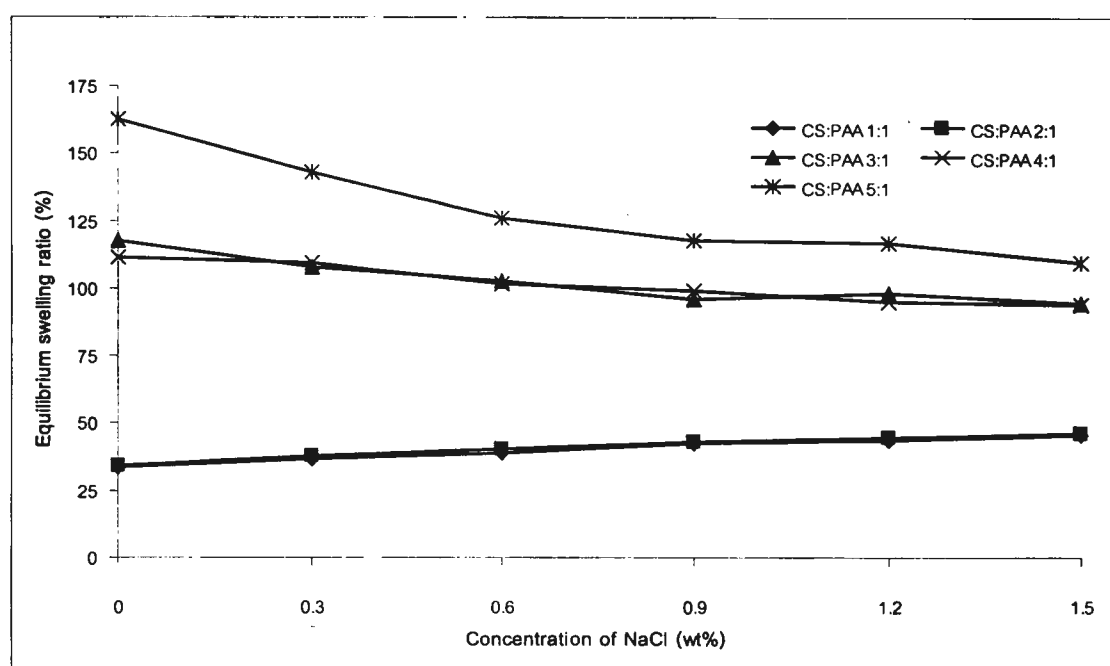


Figure 4.9 Equilibrium swelling ratio of hydrogel films with various proportions of CS/PAA as a function of NaCl concentrations at room temperature. a) CS:PAA 1:1 b) CS:PAA 2:1 c) CS:PAA 3:1 d) CS:PAA 4:1 e) CS:PAA 5:1

The swelling ratio of the 5:1 CS/PAA was higher than that of the 4:1, 3:1, 2:1 and 1:1. It was observed that an increase in the proportion of chitosan in the hydrogel films led to an increase in the equilibrium swelling ratio. This was probably because chitosan had a large proportion of hydrophilic part, that make it able to absorb water into the hydrogel. Therefore, 5:1 CS/PAA retained a large amount of water in the tested samples.

In contrast to 1:1 and 2:1 CS/PAA, the CS/PAA 3:1, 4:1 and 5:1 had a higher swelling ratio in water than that of in 0.3, 0.6, 0.9, 1.2 and 1.5%wt NaCl, because of the Donan osmotic pressure, an increase of excess concentration of NaCl in solution leads to a decrease of osmotic pressure within the hydrogel, causing the gel to shrink.^[2-3]

4.6.2 Swelling properties of hydrogel films with various amounts of barakol in solution

From the previous study (Formulation A-G), it was found that the proportion of 3/1 (w/w) chitosan/PAA (Formulation D) showed the most suitable electrical response behavior. Therefore, various amounts of barakol were added to 3:1 chitosan/PAA solutions to study the influences of the swelling ratio (Figure 4.10). The swollen barakol-CS/PAA hydrogel films in solution were softer than swollen CS/PAA hydrogel films without barakol. The swelling ratio of chitosan/PAA hydrogel films containing 0.05% and 0.1% of barakol are lower than that of chitosan/PAA hydrogel films. Because the molecular structure of barakol is planar; that makes them possible to get into the structure between the chitosan and PAA chains and participate strong H-bonds with CS/PAA network, forming strong polyelectrolyte complex. Therefore, sodium ions and chloride ions are hardly enter to the hydrogel.

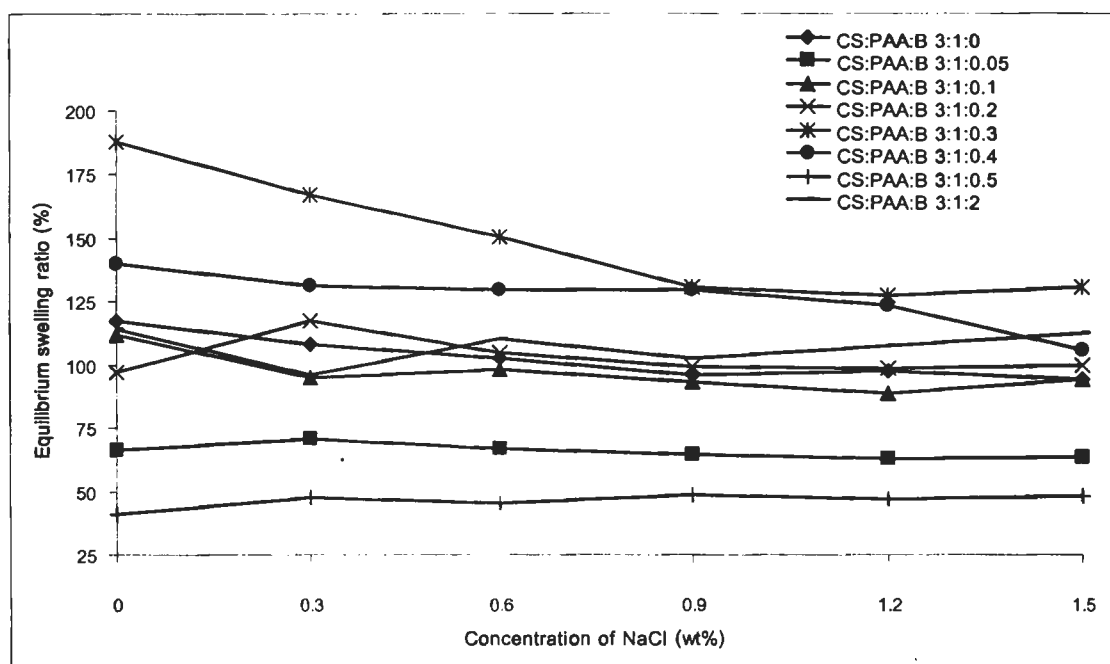


Figure 4.10 Equilibrium swelling ratio of hydrogel films with various amounts of barakol as a function of NaCl concentrations at room temperature. a) CS:PAA:barakol 3:1:0 b) CS:PAA:barakol 3:1:0.05 c) CS:PAA:barakol 3:1:0.1 d) CS:PAA:barakol 3:1:0.2 e) CS:PAA:barakol 3:1:0.3 f) CS:PAA:barakol 3:1:0.4 g) CS:PAA:barakol 3:1:0.5 h) CS:PAA:barakol 3:1:2

In cases of CS/PAA containing 0.3 and 0.2% (w/w) barakol, the swelling ratios were higher than that of the 0.1 and 0.05% (w/w) barakol, respectively. It was observed that an increase of barakol in hydrogel lead to an increase in the equilibrium swelling ratio. Because the molecular structure of barakol is planar and got into the network of the hydrogel, the network of polymer were forced to separate apart from each other. The sodium and chloride ions can easily move into the hydrogel. Therefore, electrostatic interaction in the hydrogel decreases, causing the hydrogel to swell. The swelling ratio of hydrogel decreases when the amount of barakol in hydrogel film was increased to 0.4, 0.5 and 2% (w/w). In addition, another possibility is that barakol can dissolve in NaCl aqueous solution, and form an anhydrobarakol hydrochloride (Figure 4.11), decreasing the amount of Cl^- in the medium bath. Therefore there were less chloride ions that could be moved into the CS/PAA hydrogel films.

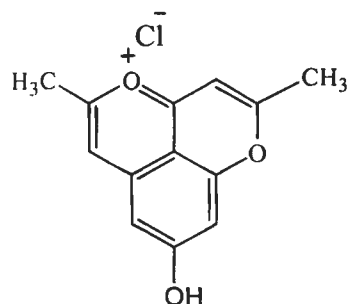


Figure 4.11 Chemical structure of anhydrobarakol hydrochloride

4.6.3 Swelling properties of hydrogel films with various amounts of cross-linking agent in solution

Various amounts of glutaraldehyde were added to CS:PAA:B 3:1:0.3 (Formulation K) to study its influences to the swelling ratio. Figure 4.12 shows the swelling behaviour of various amounts of barakol-chitosan/PAA hydrogel films with glutaraldehyde crosslinking agent (0% to 1%) (Formulation O-T) in different concentration of NaCl solution.

The swelling ratio is very much dependent on the concentration of external solution. Swelling ratio of the cross-linked barakol-CS/PAA film was lower than that of the non cross-linked barakol-CS/PAA film. When glutaraldehyde was crosslinked with chitosan, the swelling ratio is lower because the $-\text{NH}_3^+$ group in chitosan of hydrogel formed covalent bond, leading to the formation of an imine group, causing shortening of intermolecule distances of chitosan in hydrogel and thus a decreasing equilibrium swelling ratio. The swelling ratio of hydrogel decreases when the amounts of glutaraldehyde in hydrogel film was less than 1% by weight, while the swelling ratio increased when an amount of the glutaraldehyde was equal to or more than 1% by weight. The increase of the amount of the glutaraldehyde results in an decrease of the electrostatic interaction between chitosan and PAA in hydrogel. However, the repulsion interaction between negative charges of PAA increased, causing the hydrogel to swell. The barakol-chitosan/PAA hydrogel films with 2 and 5% (w/w) glutaraldehyde (Formulation G and H) could not be prepared as a film

because the large amounts of cross-linking agent caused the hydrogel to be fast crosslinked.

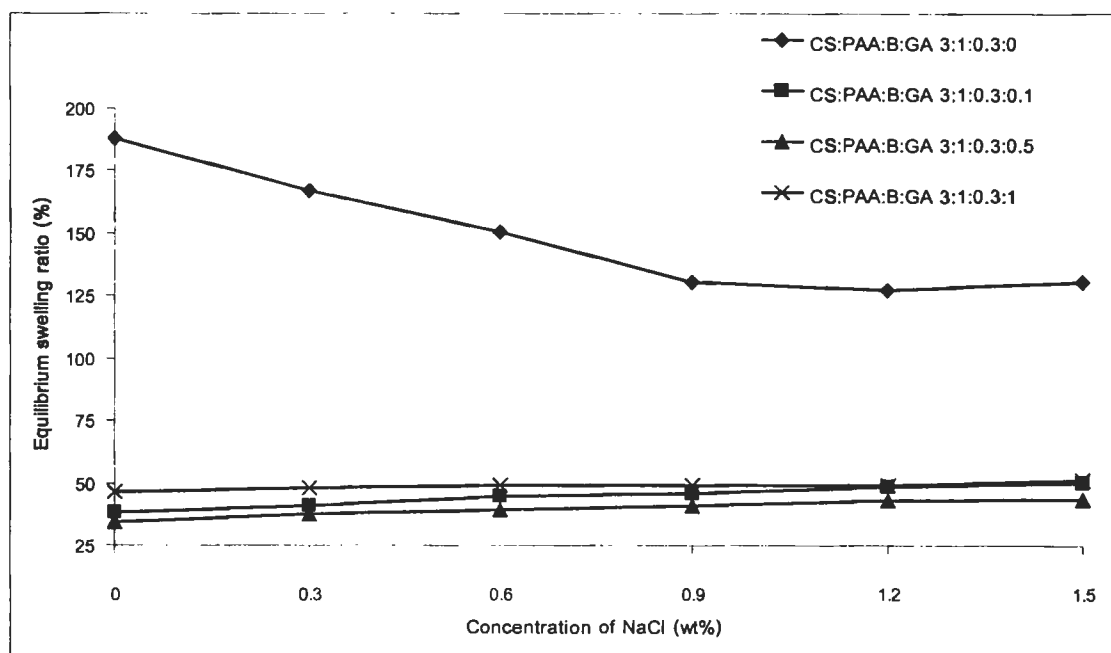


Figure 4.12 Equilibrium swelling ratio of hydrogel films with various amount of glutaraldehyde as a function of NaCl concentrations at room temperature. a) CS:PAA:B:GA 3:1:0.3:0 b) CS:PAA:B:GA 3:1:0.3:0.01 c) CS:PAA:B:GA 3:1:0.3:0.5 d) CS:PAA:B:GA 13:1:0.3:1

4.6.4 Swelling properties of hydrogel films with various types of cross-linking agent in solution

Charge density in hydrogel is an important factor in the electrostatic interactions that had effects on the swelling ratio. Figure 4.13 (Formulation K, R, U and V) shows the swelling properties of hydrogel films with various types of cross-linking agent in solution. Glutaraldehyde, glutaric acid and citric acid were used as a crosslink agent in this study. Glutaraldehyde is a covalent crosslinking agent but glutaric acid and citric acid are an ionic crosslinking agent. The structure of citric acid contains a larges number of carboxylic acid groups than that of glutaric acid. Therefore, when it was crosslinked with chitosan, electrostatic interactions in

hydrogel was increased, causing the hydrogel to shrink more than using glutaric acid as a crosslinking agent.

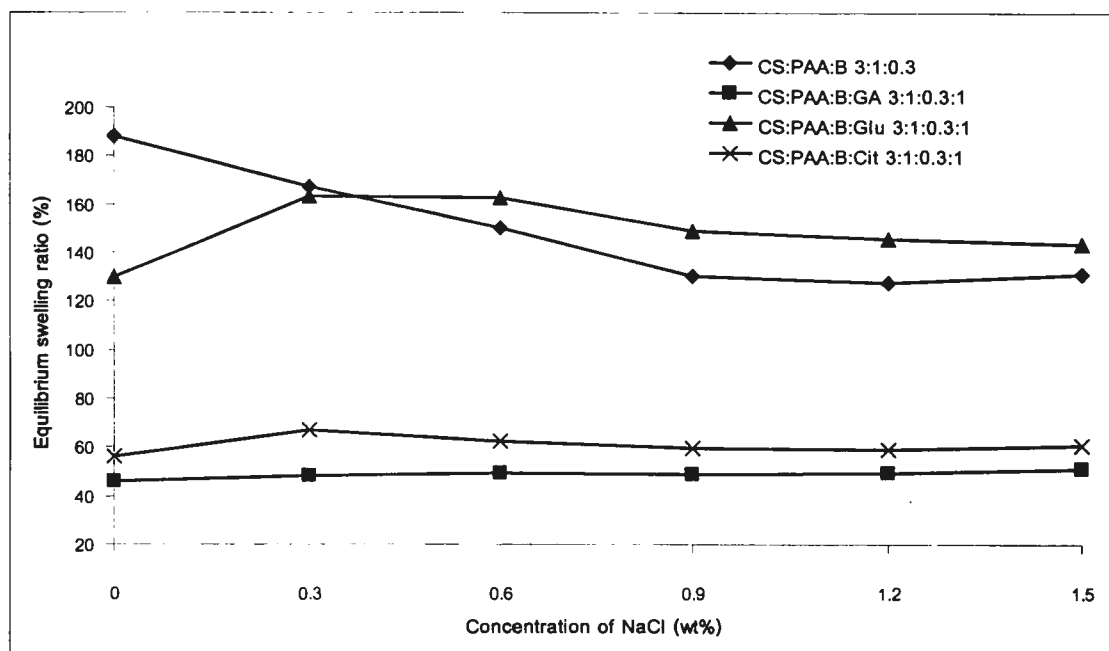
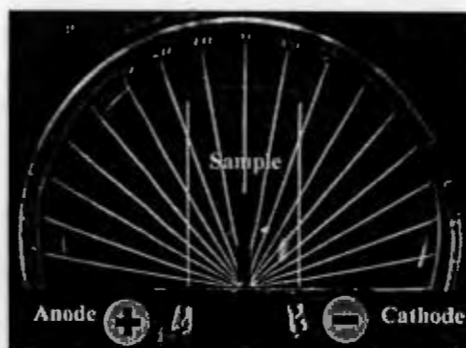


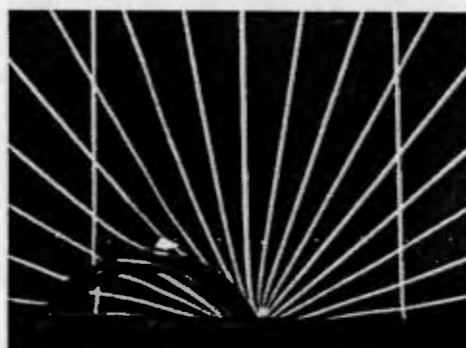
Figure 4.13 Equilibrium swelling ratio of hydrogel films with various types of cross-linking agent as a function of NaCl concentrations at room temperature. a) CS:PAA:B 3:1:0.3 b) CS:PAA:B:Glutaraldehyde 3:1:0.3:1 c) CS:PAA:B:Glutaric acid 3:1:0.3:1 d) CS:PAA:B:Citric acid 3:1:0.3:1

4.7 Bending Properties

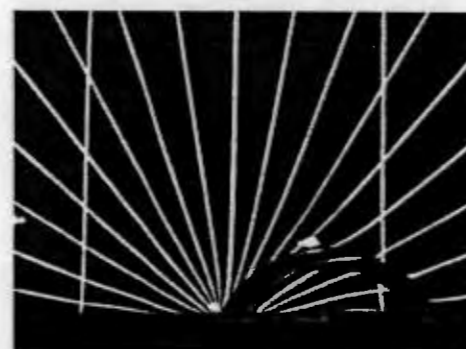
The electroactive behaviour of the CS/PAA hydrogel was studied. The hydrogel showed significant and quick bending towards the negative electrode when an external electric field was applied. When the electric stimulus was removed, the CS/PAA hydrogel returned to its original position. Also, if the polarity of the electric field was switched, the CS/PAA hydrogel film bent in the opposite direction (Figure 4.14).



(a)



(b)



(c)

Figure 4.14 Electric-current-sensitive bending phenomena (a) original position, (b) bending towards the left side and (c) bending towards the right side

There are three competing forces acting on the gel polymer network:^[5] (i) the rubber elasticity, (ii) the polymer-polymer affinity, and (iii) the ion pressure. These forces, collectively called the osmotic pressure, determined the equilibrium state of the gel, namely, the osmotic pressure (π) is given as the sum of π_1 , π_2 , and π_3 , which corresponded to the osmotic pressure due to the rubber elasticity,

the solubility of the solvent in the polymer chain, and the ion concentration difference between the inside and outside of the gel, respectively. The swelling of a polyelectrolyte gel can be explained by Flory's theory of osmotic pressure between the hydrogel and the surrounding solution, π .

$$\pi = [\ln(1-\nu) + \nu + \chi\nu^2]RT/V_1 + (\nu^{1/3} - \nu/2)RT\nu_e/V_0 + (\sum C_i - \sum C_j)RT$$

Where ν is the volume fraction of the polymer network; χ , the solubility parameter; V_0 , the volume of the polymer network under the dry condition; ν_e , the number of chains; V_1 , the molar volume of the gel; R , the gas constant; and T , the temperature. Since the composition between these forces determines the osmotic pressure, changing balance of these forces induces the volume change of the gel polymer network. The osmotic pressure (π) of the gel is equal to that of the surrounding aqueous solution, π_0 , at equilibrium. Therefore, π_1 , π_2 , and π_3 have definite values. When an electric field is applied on the charged gel in the aqueous solution, the counterion of the polyion, which is an ionic group in the polymer network, moves toward their electrode, while the polyion remains immobile. Also the free ions in the surrounding solution moved toward their counter electrodes and entered the gel. Thus, the osmotic pressure of the gel polymer network near the positive electrode increases and becomes larger than that of the negative electrode side. Consequently, the osmotic pressure difference occurs within the gel, and it is the driving force of bending toward the negative electrode.

Another factor that influenced the bending phenomenon of a gel may be the local pH gradient attributed to water electrolysis. Several researchers reported that ions produced by electrochemical reactions and the movement of ions toward the counterelectrodes induced the pH gradient inside the gel matrix under the flow of electric current. When an electric field was applied to the gel immersed in a NaCl electrolyte solution, electrochemical reactions occurred.



On the effect of bending with mobile ion, when electric current was applied. The mobile ions (Na^+ and OH^-) move toward their counterelectrodes (Figure 4.15).

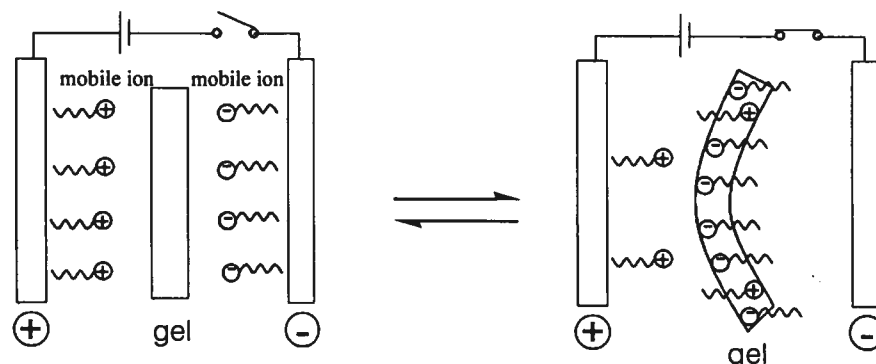


Figure 4.15 Schematic illustration of bending mechanism under electric field

The diffusion coefficient of OH^- in aqueous solution at infinite dilution at 25°C is 5 times larger than that of Na^+ .^[25] As a consequence, ion concentration gradients are induced and the osmotic pressure on the positive electrode side (π_1) becomes larger than that on the negative side (π_2), as shown schematically in Figure 4.16. This osmotic pressure difference is the driving force of bending toward the negative electrode

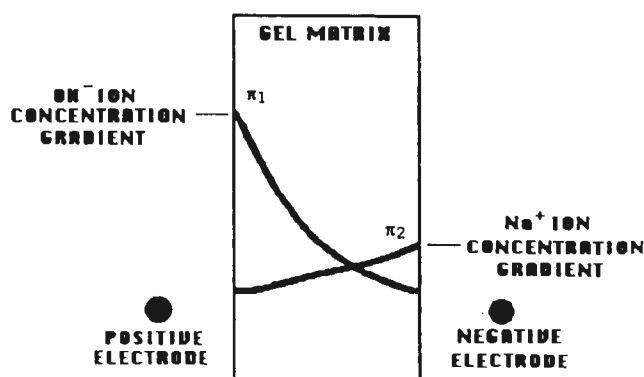


Figure 4.16 Schematic diagram illustrating the ion concentration gradient in a gel matrix on passage of electric current^[25]

4.7.1 Bending behavior of hydrogel films with various proportions of chitosan/poly(acrylic acid) under fixed electric field

The hydrogel films were allowed to reach their swelling equilibrium in the corresponding bath medium before electric stimulation. As soon as an electric field was applied, this equilibrium could not be maintained. The influence of medium ionic concentration on the bending behaviors of the hydrogel films in response to an electric stimulation was studied by varying the concentration of NaCl solution from 0 to 1.5% by weight while keeping the other conditions constant.

When the chitosan/PAA hydrogel films in the NaCl electrolyte solution are subjected to an electric field, the hydrogel films bent toward the negative electrode (cathode). All of them separated into two parts of chitosan and PAA (Figure 4.17) because the chitosan/PAA hydrogel were not well blended as a polyelectrolyte complex. The chitosan/PAA hydrogel films was not strong enough to hold the two parts together.

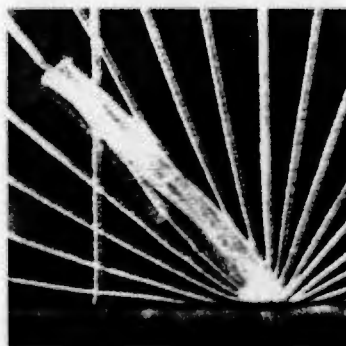


Figure 4.17 The film was separated into two parts

The 1:1 and 2:1 chitosan/PAA (Formulation B-C) films twisted and deformed when applying an electric field (Figure 4.18). If the amount of chitosan is increased, the strength of the hydrogel films increased because of stronger electrostatic interactions between chitosan and PAA. We have found that the 3:1 CS/PAA hydrogel films (Formulation D), showed significantly faster bending

towards the negative electrode than the 4:1 and 5:1 (Formulation E-F) CS/PAA hydrogel films. (Figure 4.19).

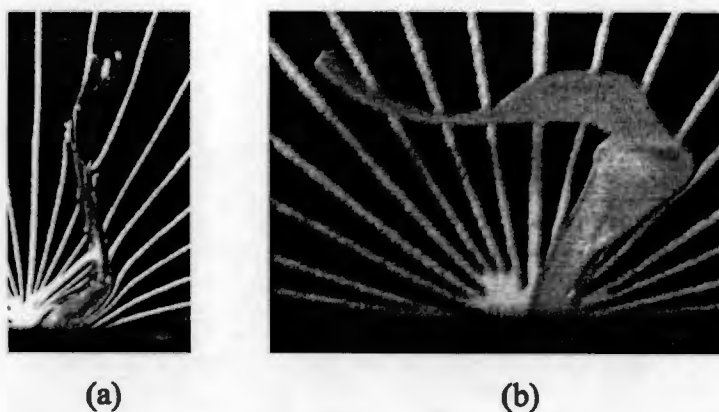


Figure 4.18 Twisted film (a) and deformation (b) of the hydrogel film

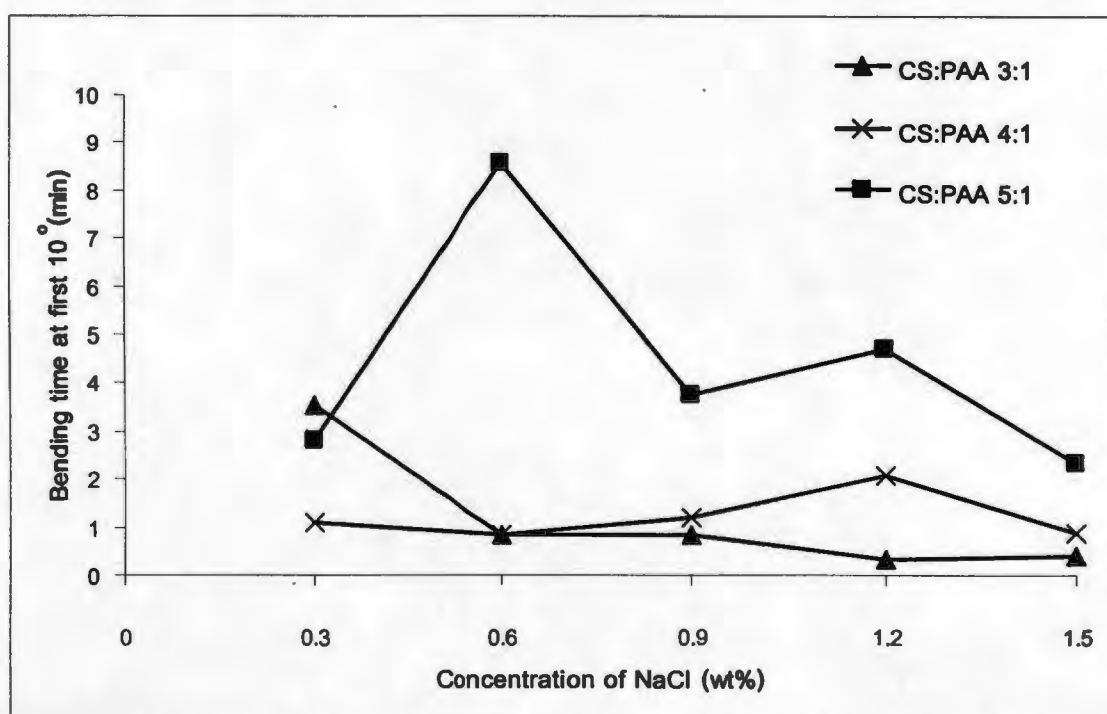


Figure 4.19 Effect of CS/PAA on the bending time (min) of the first 10 degree in aqueous NaCl solutions at 25 V

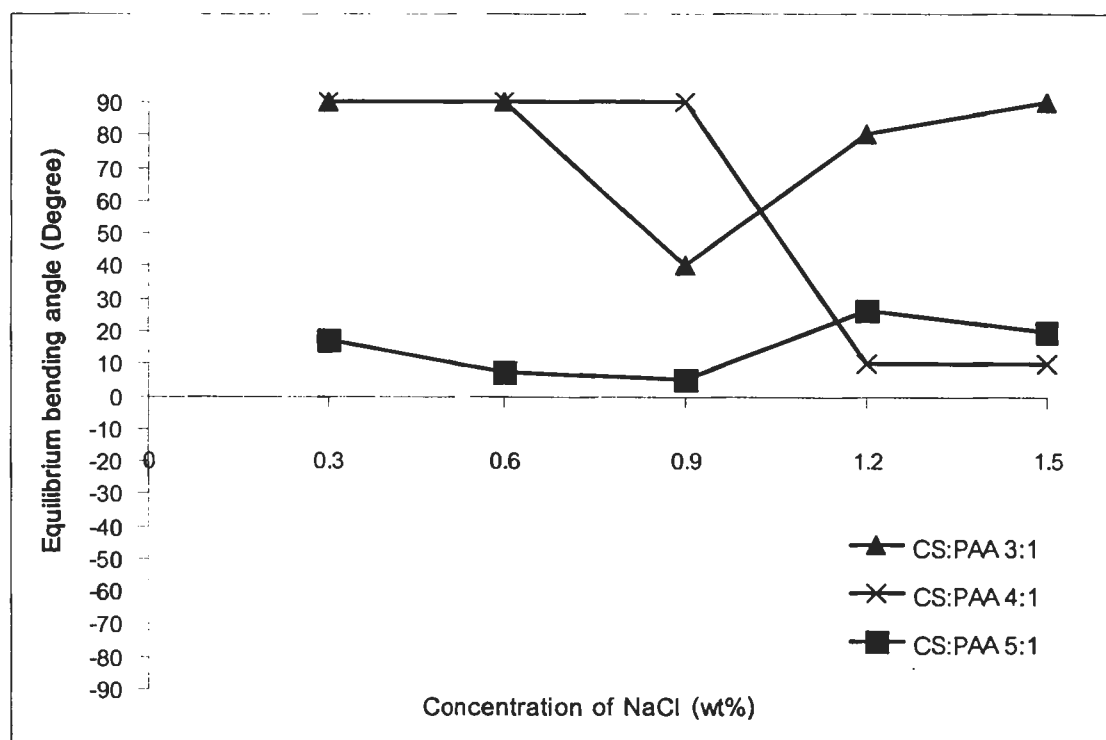


Figure 4.20 Effect of CS/PAA on the equilibrium bending angle in aqueous NaCl solutions at 25 V

Figure 4.20 shows the equilibrium bending angles of chitosan/PAA hydrogel films in the different concentrations of NaCl at 25 V. The 3:1 ratio of CS/PAA hydrogel film showed the highest equilibrium bending angle in the concentration of 0.3, 0.6 and 1.5% (w/w) NaCl solutions. When the electric stimulus was removed, the 3:1 CS/PAA hydrogel film returned to its original position but with other ratios of CS/PAA the hydrogel films returned very little.

The bending speed and the bending angle were very much dependent on the concentration of external solution. This could be explained as follows; the increase of the electrolyte concentration in the solution induced an increase of free ions moving from the surrounding solution towards their counter electrodes or into the hydrogel film. As a result, this enhanced the swelling property of the hydrogel film and increased the bending angle. However, as the concentration went on increasing, after a critical concentration, the shielding effect of the polyanion by the

ions in the electrolyte solution came into play and this led to a reduction in electrostatic repulsion of the polyions and a decrease in the degree of bending. In such a situation, the network could shrink into a more compact structure making ion diffusion through the gel more difficult. Thus, it took longer time to generate the ionic gradient and accompanying swelling (osmotic pressure), causing the gel to bend more slowly.

The 3:1 ratio of CS/PAA hydrogel film was chosen for the next studies because it showed the optimum angle and speed of bending. As shown in Figure 4.9, the swelling ratio of the 3:1 CS/PAA hydrogel film in the solution with a higher and lower concentration of electrolyte was greater than that of a solution with a 0.9% (w/w) electrolyte concentration. Therefore, if the swelling ratio is compared to the bending angle results depending on the concentration of the solution (Figure 4.20), it could be considered that swelling of the hydrogel film according to the concentration of the NaCl solution significantly affected the bending behavior of the hydrogel film.

4.7.2 Bending behavior of various proportions of barakol in chitosan/poly(acrylic acid) hydrogel films under fixed electric field

The 3:1 ratio of chitosan/PAA hydrogel films was used for the formulation H to N (see Table 3.3, (chapter 3)). These formulations were added with various 0.05-2 % (w/w) barakol.

When, the electric field was applied. Most hydrogel films bend toward the negative electrode (cathode). All the CS/PAA hydrogel films containing barakol were not separated into two parts of chitosan and PAA, in contrast to CS/PAA hydrogel films without barakol. Because barakol can intercalate into the structural network between chitosan and PAA and thus participated in strong H-bonding

with CS/PAA hydrogel films. This probably increased the strength of the hydrogel films as can be seen that hydrogel films containing barakol bent more slowly than the CS/PAA hydrogel films without barakol (Figure 4.21).

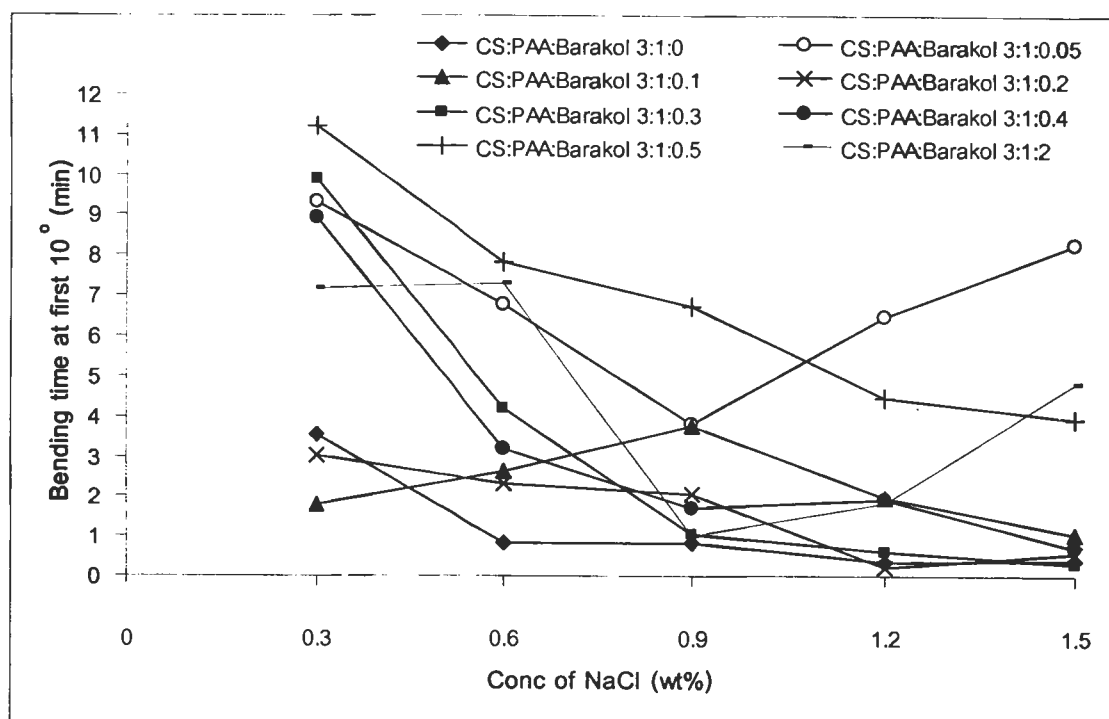


Figure 4.21 Effect of barakol on the bending time (min) of the first 10 degree in aqueous NaCl solutions at 25 V

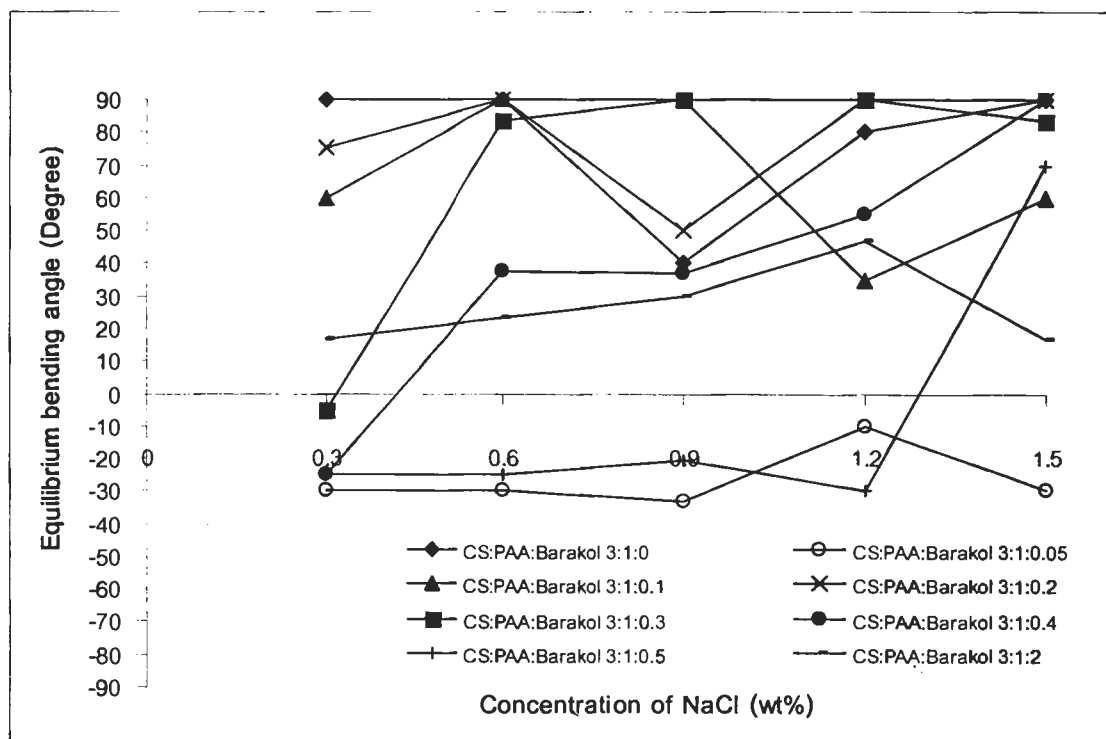


Figure 4.22 Effect of barakol on the equilibrium bending angle in aqueous NaCl solutions at 25 V

Figure 4.22 shows the equilibrium bending angle of the chitosan/PAA hydrogel films containing various amounts of barakol in different concentration of NaCl at 25 V. When the electric stimulus was removed, the 3:1 ratio of CS/PAA hydrogel films containing barakol could return to its original position. The CS/PAA hydrogel films with 0.2-0.3% (w/w) barakol present faster bending speed and the higher bending angle. This can be explained that the swelling ratios of the CS/PAA hydrogel films containing 0.3 and 0.2% (w/w) barakol were higher than other compositions. Therefore, sodium ions and chloride ions easily enter the hydrogels.

In addition, the barakol molecule can be oxidized (Figure 4.23). The structure of oxidized barakol is commonly used as a reflection on its importance in natural electron transfer systems. It helps the electricity, sodium ions and chloride ions easily move into the hydrogel, causing the hydrogel to have higher ion

concentration difference between the inside and outside of the hydrogel. As a consequence, the bending speed was faster and the bending angle was wider.

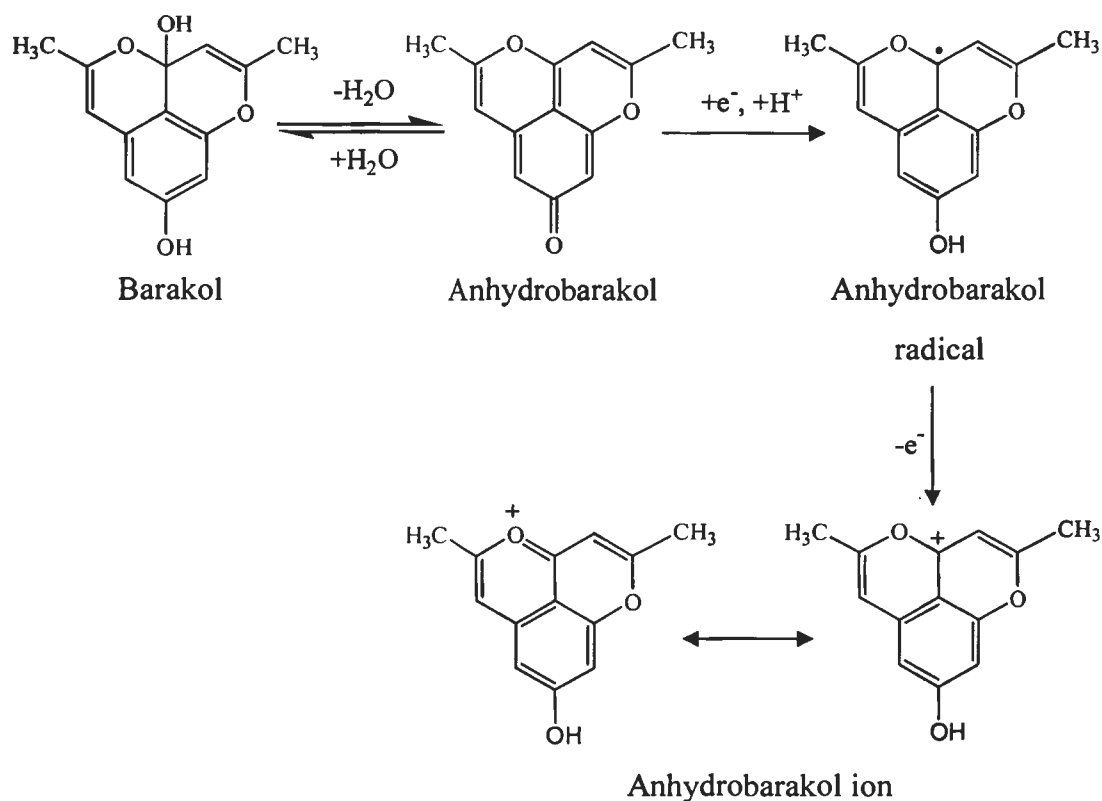


Figure 4.23 Suggested reduction and oxidation of anhydrobarakol

The 3:1 CS/PAA hydrogel film with 0.3% (w/w) barakol showed the highest equilibrium bending angle in the most concentration of NaCl solutions. So, the 3:1 ratio of CS/PAA with 0.3% (w/w) barakol was chosen for further studies because it showed the optimum angle and speed of bending. As shown in Figure 4.10, the swelling ratio of the 3:1 CS/PAA hydrogel film with 0.3% (w/w) barakol in the solution with lower concentration of electrolyte was greater than that of a solution with a higher electrolyte concentration. Therefore, if the swelling ratio is compared to the bending angle results depending on the concentration of the solution (Figure 4.22), it could be considered that swelling of the hydrogel film according to the concentration of the NaCl solution does significantly affect the bending behavior of the hydrogel film.

4.7.3 Bending behavior of various proportions of glutaraldehyde in chitosan/poly(acrylic acid) hydrogel films under fixed electric field

The 3:1 ratio of chitosan/PAA hydrogel films containing 0.3% (w/w) barakol was used for the formulation O to T (see Table 3.4, (chapter 3)). These formulations were crosslinked with various 0.1-5% (w/w based on the weight of chitosan) glutaraldehyde.

When the electric field was applied to each concentration of NaCl solution, Most hydrogel films bent toward the negative electrode (cathode). All of them did not separate into two parts of chitosan and PAA because the glutaraldehyde formed covalent crosslink with chitosan. Its advantage is the increasing of the strength of the films and makes them possible to repeat bending many times. But, the disadvantages of this hydrogel film is, the bending time was longer and the maximum bending angle of hydrogel films were decreases (Figure 4.24 and 4.25). Comparison of 1% glutaraldehyde crosslinked hydrogel film without barakol and with barakol in 0.9% (w/w) NaCl solution showed the maximum bending angles were the same but the bending times of crosslinked hydrogel film containing barakol were shorter. All of them confirmed that barakol contributed to the rapid bending, and glutaraldehyde helped increasing repeated bendings.

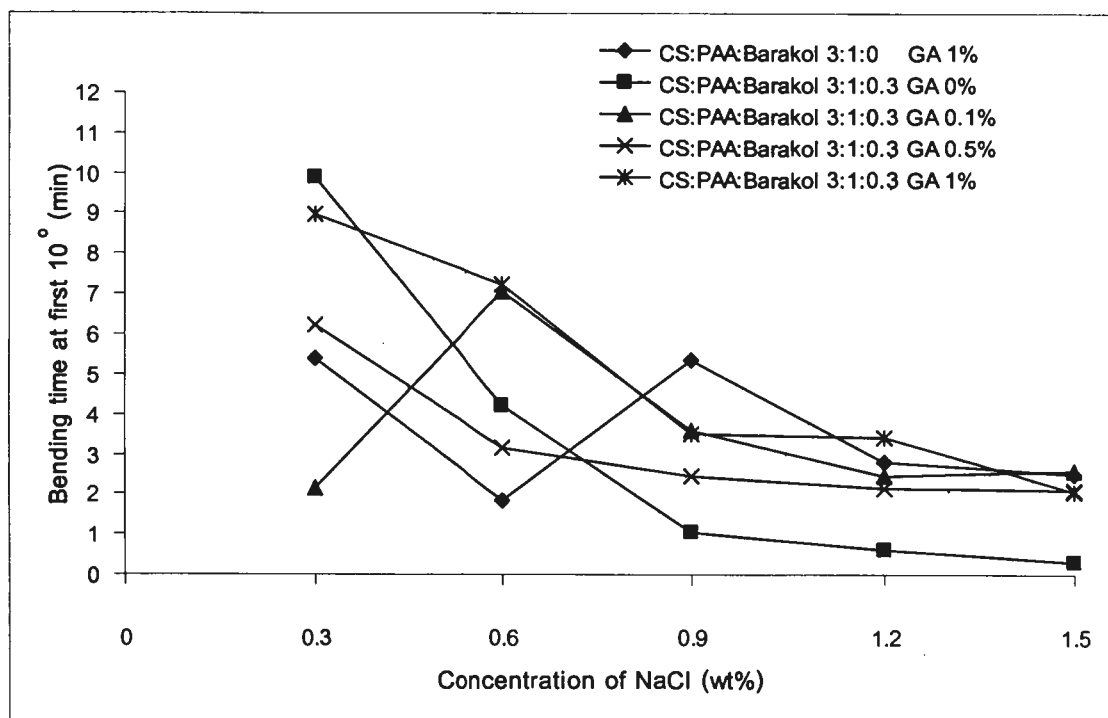


Figure 4.24 Effect of glutaraldehyde on the bending time (min) of the first 10 degree in aqueous NaCl solutions at 25 V

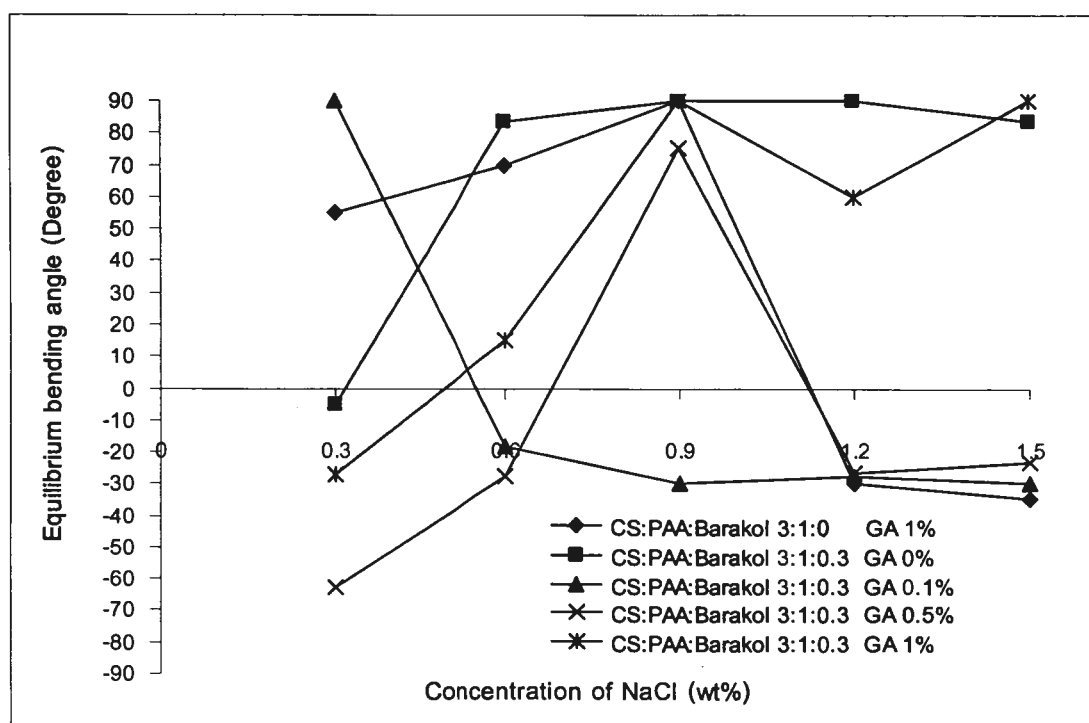


Figure 4.25 Effect of glutaraldehyde on the equilibrium bending angle in aqueous NaCl solutions at 25 V

The 0.3% (w/w) barakol-CS/PAA hydrogel films crosslinked with 1% glutaraldehyde showed the highest equilibrium bending angle at 90°. The shortest bending time to 90° and reverse bending time to 0° are 8 seconds and 27 seconds, respectively. The number of repeated bending was up to 46 times in 0.9% (w/w) NaCl solution (Figure 4.26). Therefore, this composition was chosen for further studies because it showed the most optimum angle and the highest speed of bending. As shown in Figure 4.12, the swelling ratio of the 0.3% (w/w) barakol-CS/PAA hydrogel films crosslinked with 1% glutaraldehyde in the solution with higher concentration of electrolyte was greater than that of a solution with a lower electrolyte concentration. Therefore, if the swelling ratio was compared to the bending angle results depending on the concentration of the solution (Figure 4.25), it could be considered that swelling of the hydrogel film according to the concentration of the NaCl solution does significantly affect the bending behavior of the hydrogel film.

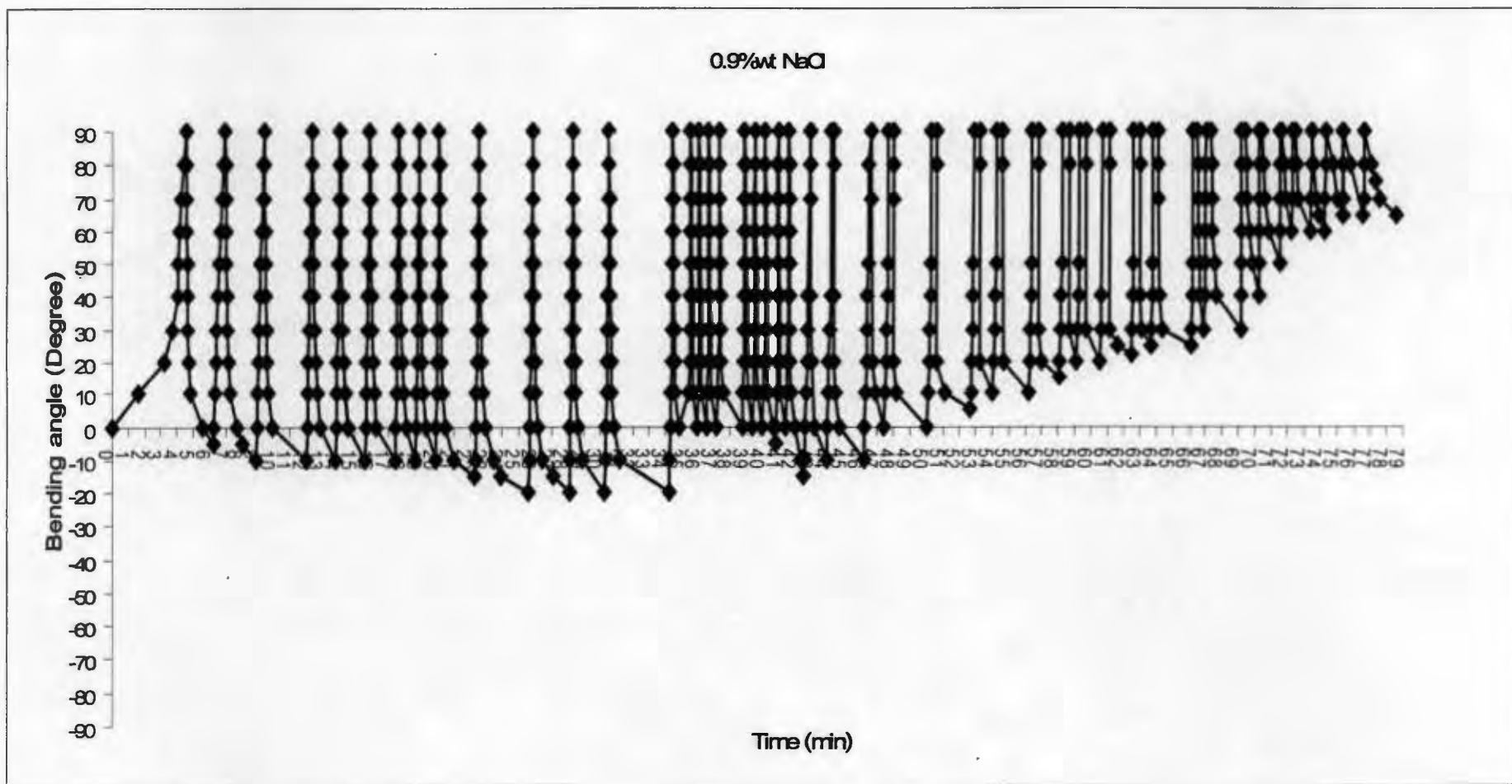


Figure 4.26 Reversible bending behavior of the 0.3% (w/w) barakol-CS/PAA hydrogel film with 1% glutaraldehyde in a 0.9 wt % NaCl solution with changes in the applied voltage (25 V)

4.7.4 Bending behavior of various crosslinking agent in chitosan/poly(acrylic acid) hydrogel films under fixed electric field

The compositions of chitosan/PAA hydrogel film used in this studied were showed in the formulations R, U and V (see Table 3.4, (chapter 3)). These formulations were prepared with various 1% crosslinking agents (glutaraldehyde, glutaric acid and citric acid).

When electric field was applied, Most of the hydrogel films bent toward the negative electrode (cathode). Most of them separated into two distinct parts of chitosan and PAA, except the hydrogel films crosslinked with glutaraldehyde. Glutaric acid and citric acid are ionic crosslinking agents, but glutaraldehyde is a covalent crosslinking agent. The properties of crosslinked hydrogel films are different depending on the types of crosslinking agent. The covalent crosslinked hydrogel films have interaction between polymers stronger than the ionic crosslinked hydrogel films. The bending times of the hydrogel films crosslinked with glutaraldehyde were more than that of the hydrogel crosslinked with citric acid and glutaric acid, respectively (Figure 4.27).

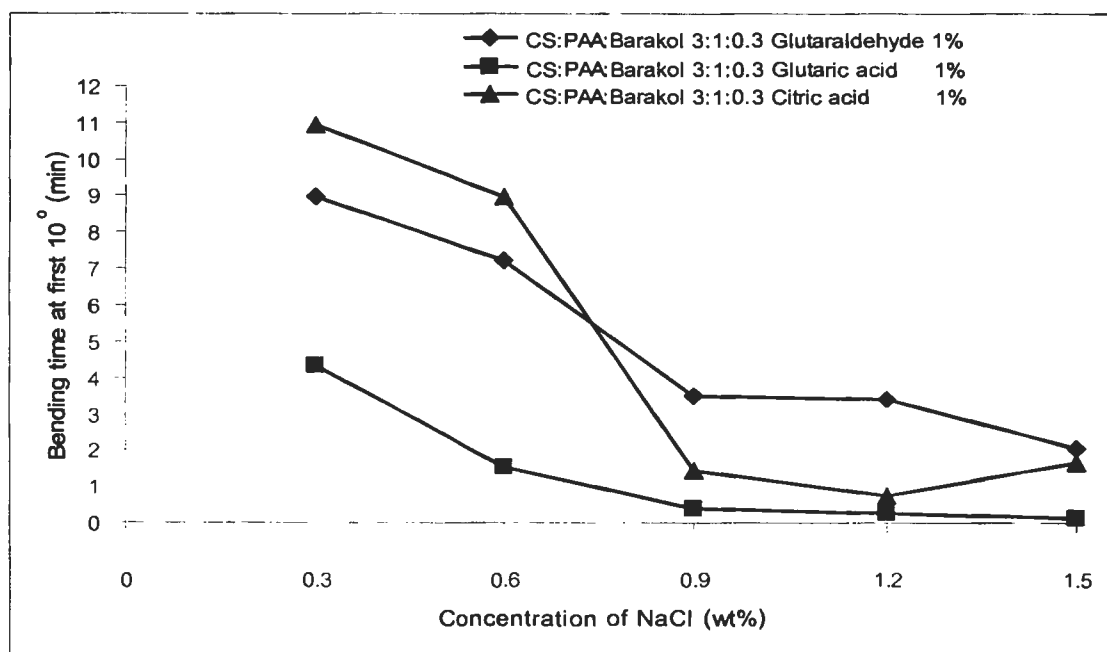


Figure 4.27 Effect of crosslinking agents on the bending time (min) of the first 10 degree in aqueous NaCl solutions at 25 V

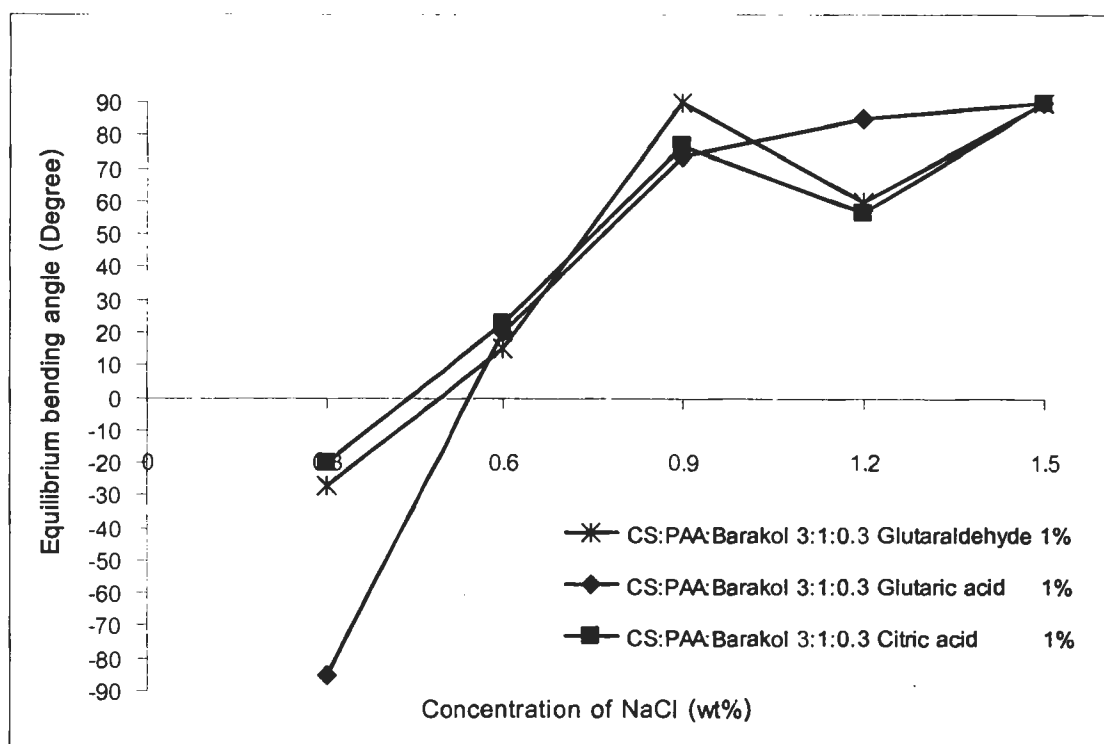


Figure 4.28 Effect of crosslinking agents on the equilibrium bending angle in aqueous NaCl solutions at 25 V

Although, the maximum bending angle of the ionic crosslinked hydrogel films and the covalent crosslinked hydrogel films were similar. The bending time to the first 10 degree of the ionic crosslinked chitosan/PAA hydrogel films was shorter than that of the covalent crosslinked films (Figure 4.28), but the covalent crosslinked chitosan/PAA hydrogel films gave the highest number of repeated bending.

The 0.3% (w/w) barakol-CS/PAA hydrogel films crosslinked with glutaraldehyde showed the best optimum angle and the highest speed of bending. Therefore, this composition was chosen for further studies.

4.7.5 Bending behavior of chitosan/poly(acrylic acid) hydrogel film under various voltages

Figure 4.29 shows the variation of the bending angle of the The 0.3% (w/w) barakol-CS/PAA hydrogel film crosslinked with 1% glutaraldehyde as a function of the applied voltage in aqueous 0.9 wt % NaCl.

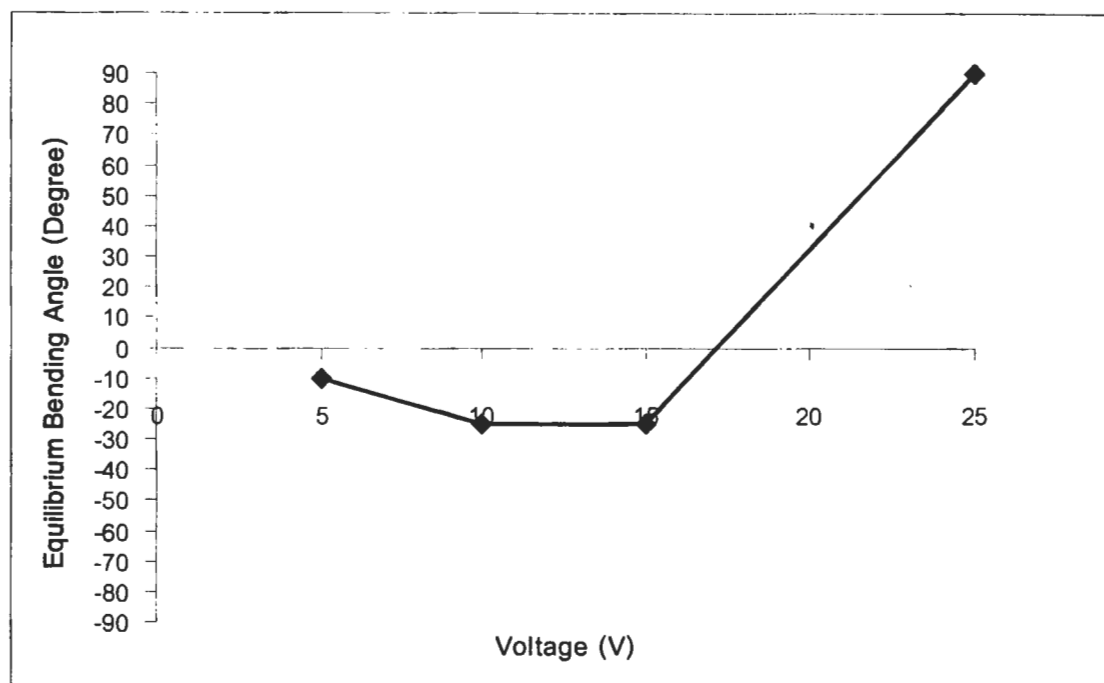
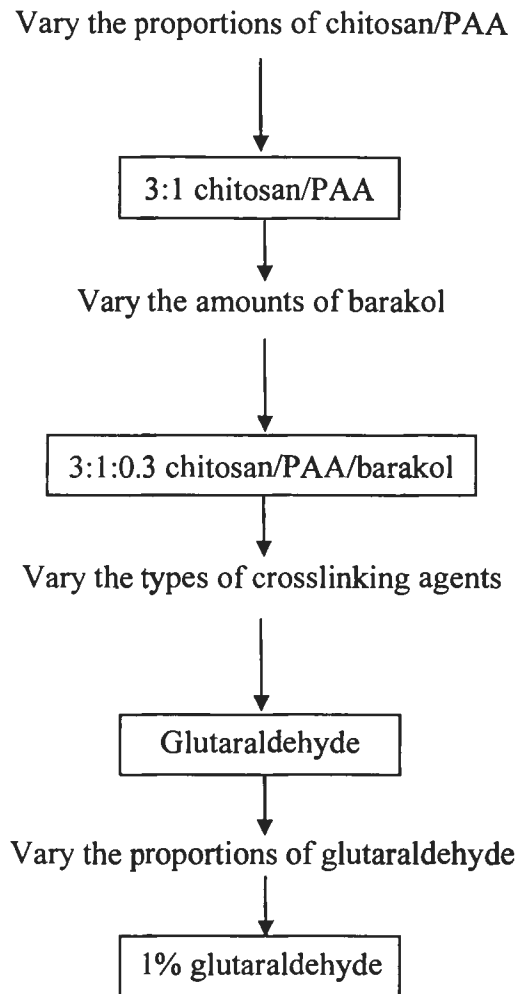


Figure 4.29 Bending of hydrogel film containing barakol in response to various amplitudes of the applied electric potential in 0.9 wt% NaCl solution.

The equilibrium bending angle and bending speed increase with increasing voltage. However, bending is not observed in pure water, indicating that bending is induced by the electric current. The deformation of a polymer hydrogel under an electric field is due to the voltage-induced motion of ions and the concomitant expansion of one side of the polymer and contraction of the other. Also, the hydrogel film exhibited reversible bending behavior depending on the application of the electric field when the electric stimulus was removed; the hydrogel film was displaced to its original position.

4.8 Summary of the Experiments

: Summary of finding the best compositions.



: Summary of finding the best operational conditions.

- Vary size and shape: 25 x 2 mm, film
- Vary the distance between cathode and anode: 20 mm
- Vary NaCl concentration: 0.9% (w/w) NaCl
- Vary voltage: 25 V
- Vary swelling time: 22 hours

4.9 Performance Comparison to other State-of-the Art Methods

This study determined the relative performance trends of the prepared methods, equilibrium bending angle, bending time, reverse bending time and number of repeated bending. These performance indicators were compared with other hydrogels that have been reported.

The 0.3% (w/w) barakol-CS/PAA hydrogel films crosslinked with 1% glutaraldehyde showed the highest equilibrium bending angle at 90° . The shortest bending time to 90° and reverse bending time to 0° were 12 seconds and 32 seconds, respectively. The number of repeated bending was up to 46 times in 0.9% (w/w) NaCl solution (Figure 4.30).

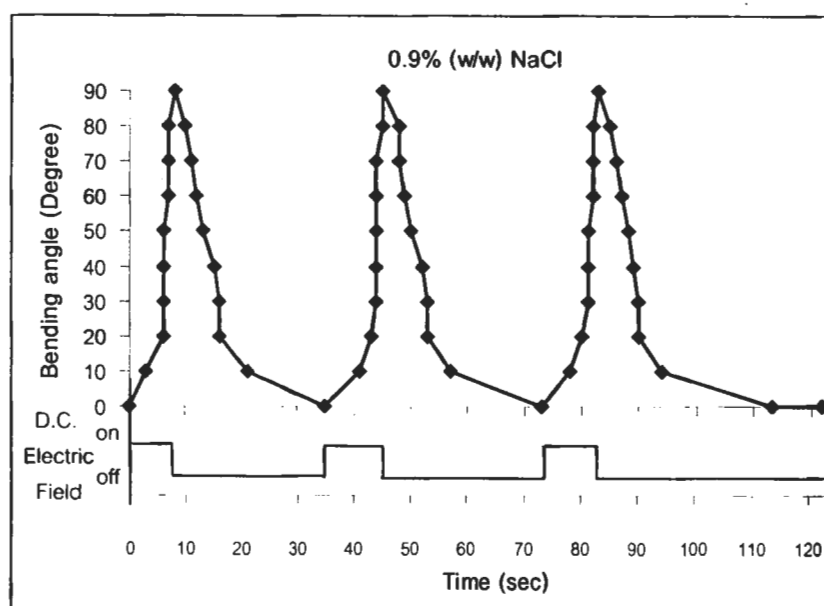


Figure 4.30 Reversible bending behavior of the 0.3% (w/w) barakol-CS/PAA hydrogel films crosslinked with 1% glutaraldehyde in a 0.9 wt % NaCl solution with changes in the applied voltage at 25 V

These results were compared to those of other works, as shown in Table 4.1.

Table 4.1 The comparative properties of various smart materials

No.	Compositions	Preparation method	Equilibrium bending angle (degree)	Bending time (sec)	Reverse bending time (sec)	Number of repeated bendings (Times)
1	barakol-CS/PAA	Blend	90°	8	27	46
2	PVA/CS	UV	120°	60	60	-a
3	SA/PDADMAC	UV	90°	20	30	-a
4	CS/PAN	Blend	30°	0.5	3.5	-a
5	PEGM/CS	UV	75°	720	-a	-a

^a not reported

In (2), Kim et al.^[2], a poly(vinyl alcohol)/chitosan (PVA/CS) IPN hydrogel was synthesized by an ultraviolet (UV) irradiation method. It exhibited the electro-sensitive behavior in an aqueous NaCl solution. The equilibrium bending angle was 120° . The bending time to 90° and reverse bending time from 90° to 0° were 14 seconds and 57 seconds, respectively (Figure 4.31).

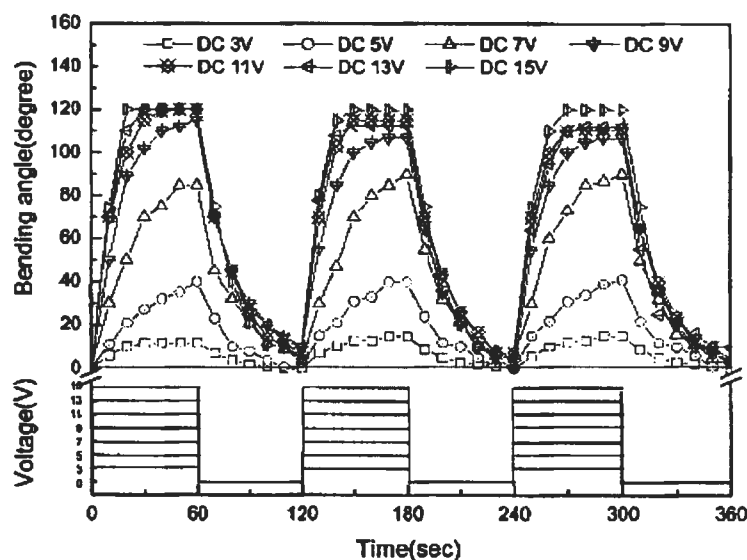


Figure 4.31 Variation of bending angle as a function of the applied voltage in aqueous NaCl at 0.9% by weight^[2]

The comparison showed that our hydrogel film could bend to 90° 1.75 times faster and bend back to 0° 2.2 times faster the PVA/CS hydrogel. Moreover, the barakol-CS/PAA hydrogel film was easily and more economically prepared by using a simple blending method. In contrast, the PVA/CS hydrogel film was synthesized from monomers by using UV irradiation method that used a special equipment.

In (3), Kim, S. J.^[48], an alginate/poly(diallyldimethylammonium chloride) (SA/PDADMAC) IPN hydrogel was prepared using a sequential IPN method. The diallyldimethylammonium chloride was crosslinked in the presence of sodium alginate, using ammonium peroxydisulfate, *N,N,N',N'*-tetramethyl ethylenediamine and *N,N'*-methylenebisacrylamide as initiator, accelerator and crosslinking agent. The equilibrium bending angle was 90°. The bending time to 90° and reverse bending time to 0° of the SA/PDADMAC hydrogel were 20 seconds and 50 seconds, respectively (Figure 4.32).

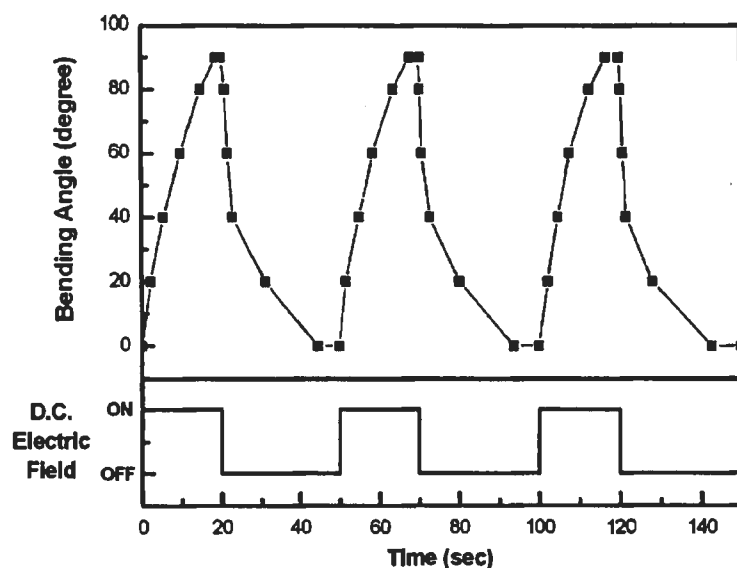


Figure 4.32 Reversible bending behavior of the SA/PDADMAC IPN in 0.6 wt.% HCl solution with changes in the applied voltage of 10V^[48]

The comparison showed that our hydrogel film could bend to 90° 2 times faster and bend back to 0° 1.5 times faster. In this case, SA/PDADMAC was prepared using a number of components in the formulations, that means increasing the costs. It was also prepared by the UV technique.

In (4), Kim, S. J.^[3] also reported the electrical response characterization of chitosan/polyacrylonitrile (CS/PAN) hydrogels in NaCl solutions. They found that the hydrogels have the equilibrium bending angle of only 30°. The bending time to 30° and reverse bending time to 0° of the CS/PAN hydrogel were 0.5 seconds and 4 seconds, respectively (Figure 4.33).

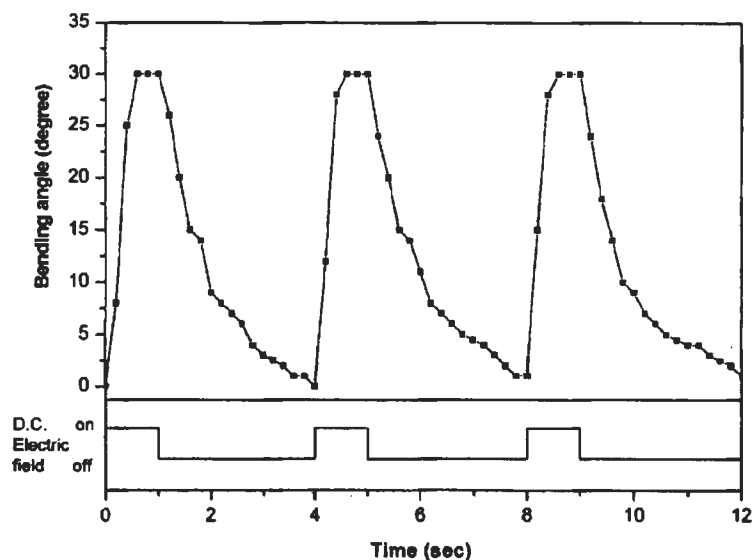


Figure 4.33 Reversible bending behavior of the semi-IPN in a 0.9 wt % NaCl solution with changes in the applied voltage (15 V)^[3]

Our hydrogel films could bend to 30° in 8 seconds and bend back from 30° to 0° in 19 seconds. In this case, the performance of the IPN film was significantly better than our hydrogel film. However, the maximum bending angle of CS/PAN film was only 30° which is less response to the electric applied. While the our reported films still showed the better performance than that of CS/PAN film, as our films could bending to 90°. Therefore, the CA/PAN film responded to electric field faster than any other films but its bending angle was less than any other film as well. In addition a disadvantage of CS/PAN is that polyacrylonitrile, used as a major component, was toxic and expensive. Therefore, its application areas are restricted.

In (5), S. Kaewpirom and S. Boonsang^[44] demonstrated that interpenetrating polymer network hydrogels composed of poly(ethylene glycol) macromer (PEGM) and chitosan (CS) and synthesized by UV irradiation of solutions in a mild aqueous media displayed mechano-electro-chemical (MEC) behaviors. They showed that the equilibrium bending angle of chitosan and PEGM/CS were 82° and 75°, respectively (Figure 4.34).

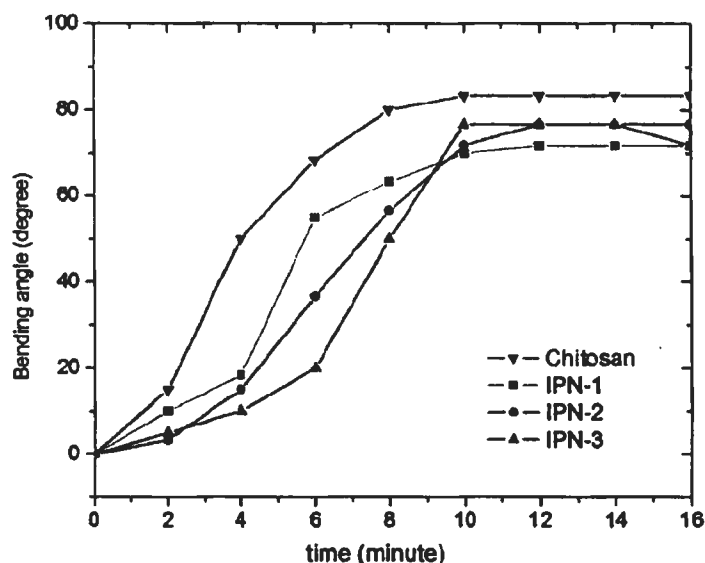


Figure 4.34 Effect of the hydrogel composition on bending behavior of swollen PEGM/chitosan hydrogels, in a 0.6% (w/v) NaCl solution, after applying electric current from a 25 V dc supply^[44]

The bending time to maximum bending angle of pure chitosan and PEGM/chitosan were 10 minutes and 12 minute, respectively. The comparison clearly showed that our hydrogel film was significantly superior in terms of bending time and the performance of bending angles than that of PEGM/CS.

Additionally, the previous works did not report the number of the repeated bendings. All of them presented only 3 times repeated bendings. And they did not mention about the operation-life time of the film. In our case, the 3% (w/w) barakol-CS/PAA hydrogel film (Figure 4.26) could maintain the sensitivity to the electric field through its lifetime. However, the reversibility (reversible bending angle) gradually degraded after 46 repeated bendings.