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Preparation and electrical sensitive behavior of poly (N-vinylpyrrolidone-co-acrylic acid) hydrogel with flexible chain nature

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ABSTRACT

On the basis of the existing knowledge of reactions and properties of poly (N-vinylpyrrolidone) (PVP) and poly (acrylic acid) (PAA), a novel pH- and electrical-sensitive poly (N-vinylpyrrolidone-co-acrylic acid) [poly (NVP-co-AA)] hydrogel was formulated and prepared from linear poly (NVP-co-AA). Gelation reaction was initiated by potassium persulfate (KPS) used as a radical initiator, and the mechanism of crosslinking reaction was investigated by FTIR and solid-state CP/MAS NMR techniques. The morphology of hydrogel with flexible chain nature and large free volume was verified by measurement of scanning electron microscope. The swelling behavior and bending phenomenon of the hydrogel were investigated. In the electric field, the gel bent toward cathode independently of the pH of buffer solution, applied voltage, crosslinking extent and polyion content in the backbone of gel. But the deflection and speed of the bending depended on them. Bending of poly (NVP-co-AA) gel was reinterpreted by bending theory of polyelectrolyte gel based upon the change of osmotic pressure, which is due to the difference of ion concentration between the sides facing anode and cathode.

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1. Introduction

Polymer hydrogels, which are three-dimensional polymeric networks formed from highly hydrophilic monomers rendered insoluble by hydrogen bond, electrostatic or covalent crosslinking [1], imbibe large amounts of water. Their high water content contributing to biocompatibility and soft elastomeric nature could ensure minimal mechanical and frictional irritation to surrounding tissues, as well as the low interfacial tension between the gel surface and

the aqueous surrounding fluids contributes to a reduction in protein adsorption and hence bio fouling and cell adhesion onto the gel [2–4].

Polymer hydrogel is a “soft material” capable of changing its volume and shape in response to environmental stimuli, such as an applied electric field, stress, light or changes in the temperature and pH value [5,6]. An electric field as a stimulus has advantages such as the availability of equipment, which allows precise control of the magnitude of current, duration of electric pulses, and intervals between pulses, etc. [3]. There have been a number of reports on electrically induced phenomena in charged polymer networks. Tanaka et al. [7] reported that a hydrolyzed acrylamide gel (approximately 20% of amide groups were converted to carboxyl groups) collapsed in an acetone/water (50 vol%) binary mixture on application of an electric field. Irie [8] reported bending behavior of

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acrylamide gel exposed to UV irradiation in an electric field. Wu et al. [9] reported the synthesis, structure and electric field sensitivity of polyacrylate/polyaniline (PAA/PANI) and poly (2-acrylamido-2-methyl propylsulfonic acid-acrylic acid)/polyaniline [P(AMPSAA)/PANI] conducting hydrogels with an interpenetrating polymer network (IPN) structure. Osada et al. [10] reported a model of an electrically driven “muscle”, made of water-swollen synthetic polymer gel, weakly crosslinked poly (2-acrylamido-2-methyl propane) sulphonic acid (PAMPS), which had motility when immersed in water.

With good biostability, biocompatibility, the sensitivity of hydrogels to electrical voltage or pH make gels promising materials for a broad range of applications for biological engineering, such as artificial muscles, drug delivery, and biosensors and bioactuators in biomicroelectro mechanical systems (BioMEMS) [11–15].

Hydrogels based on poly (N-vinylpyrrolidone) (PVP) have been applied successfully as local dressings on wound treatments, such as burns, skin's ulceration and postoperative dressings [16] or controls release system for drug delivery [17,18]. Recently, many of work did make the study of hydrogels based on complexation between PVP and PAA [19–22]. Crosslinked complexes of PVP-PAA were prepared from a mixture of NVP, AA and ethyleneglycol dimethacrylates [19] or a mixture of NVP and AA [20]. In Ali's study [21], chelating poly (N-vinylpyrrolidone/acrylic acid) copolymer hydrogels were prepared from PVP with certain molecular weight and AA by radiation-induced copolymerization. However, PVP dissolved in pure water does not exhibit a phase transition either at temperatures below the boiling point of water [19] or at pH [22]. Also, electric field sensitivity property of gel based on PVP has been rarely reported.

In this report, poly (N-vinylpyrrolidone-co-acrylic acid) [poly (NVP-co-AA)] hydrogel composed of flexible uncross-linked poly (acrylic acid) segments was prepared by a gelation process of linear statistical copolymer poly (NVP-co-AA). The reversible bending behavior of the gel induced by electric current in buffer solution was demonstrated, and a mechanism based on osmotic pressure theory for the bending phenomenon was proposed once again.

2. Experimental

2.1. Materials

N-vinylpyrrolidone (NVP) (98%, ACROS) and acrylic acid (AA) (A.P. grade) were distilled under reduced pressure to remove the stabilizer prior to use. 2,2'-Azobis-iso-butyronitrile (AIBN) and N,N'-methylene-bis-acrylamide (NNMBA) (C.P. grade) were recrystallized from 95% ethanol just before to use. Potassium persulfate (KPS) was recrystallized from distilled water. The other reagents were A.P. grade and used without further purification.

2.2. Preparation of poly (N-vinylpyrrolidone-co-acrylic acid) hydrogel

Firstly, linear poly (N-vinylpyrrolidone-co-acrylic acid) [poly (NVP-co-AA)] was prepared by free radical

copolymerization using AIBN as an initiator. Amounts of 15.5250 g NVP (0.13986 mol), 5.25 g AA (0.0729 mol), ω , the molar ratio of NVP unit to AA unit, is about 1.92), and 0.1560 g AIBN (1.0×10^{-3} mol) were dissolved in 20 mL anhydrous ethanol. A different mass value of NaOH (0.5833, 0.8750, 1.1666 and 1.7499 g) was used to modulate the degree of neutralization (20%, 30%, 40% and 60%) of AA, respectively. After thorough mixing, the copolymerization reaction was maintained for 2 h in a 70 °C water bath, and then the product poly (NVP-co-AA) was purified by multiple dissolutions ($\times 3$) in distilled water followed by precipitation into acetone. Then, poly (NVP-co-AA) was dried under vacuum at room temperature to constant weight.

Subsequently, 2.6500 g linear poly (NVP-co-AA), certain amounts of KPS and NNMBA (mass percentage of NNMBA to KPS is 10 wt%) were totally dissolved into 15.00 mL distilled water. The solution was poured into a glass model, and the model was sealed with sealant tape and placed in a 60 °C oven to initiate the crosslinking reaction of poly N-vinylpyrrolidone chain segments. Different mass percentages of KPS to NVP ($MR = W_{KPS}/W_{NVP} \times 100\% = 26.8, 33.5$ and 40.2 wt%) were used to modulate the crosslinking extent. The reaction was performed for 5 h, and then the product hydrogels were cut into strips with dimension of 11 mm \times 1 mm \times 1 mm.

2.3. Preparation of Britton–Robinson buffer solutions with different pH

Britton–Robinson (B–R) buffer solution was prepared from 0.4 M acetic acid, 0.4 M phosphoric acid, and 0.4 M boric acid that were adjusted to different pH values with 1 M NaOH or 1 M phosphoric acid. Sodium chloride was used to adjust ionic strength of solution to 0.0456 M; the pH of solution was determined by pHs-3B model pH meter.

2.4. Spectroscopic analysis

FTIR spectra of the final dried gels were recorded on a Thermo Nicolet Nexus 670 FTIR spectrometer at a resolution of 4 cm^{-1} . Solution NMR spectrum for linear PVP was recorded at room temperature (in D_2O) by using an AVANCE 600 NMR Spectrometer. Solid-state NMR experiment was carried out at ambient temperature on a Bruker Avance 400 MHz wide cavity solid-state NMR spectrometer operating at a ^{13}C resonance frequency of 400.13 MHz. Samples were analyzed under cross-polarization/magic-angle spinning (CP/MAS) conditions. The chemical shifts of all ^{13}C spectra were externally referenced to the carbon signal of TMS. The linear PVP was obtained by a free radical polymerization of NVP using AIBN as an initiator in distilled water. The product was purified by multiple dissolutions ($\times 3$) in distilled water followed by precipitation into acetone, then was dried under vacuum at room temperature to constant weight. The sample used for solid-state NMR measurement was obtained through a crosslinking reaction of linear PVP induced by KPS as mentioned above but without NNMBA. To remove the unreacted KPS, the hydrogel was extracted using Soxhlet extractor for 72 h in deionized water.

2.5. Determination of exact composition

The composition of linear poly (NVP-co-AA) was calculated by comparing the peak areas of the carbonyl group of PVP with the carboxylic acid and acrylate groups on the PAA chain shown in the FTIR spectrum as follows:

$$\omega = \frac{A_{NVP}}{A_{AA} + A_{Sodium\ AA}}$$

where ω is the molar ratio of NVP unit to AA unit; A_{NVP} , A_{AA} and $A_{Sodium\ AA}$ are the areas of the carbonyl group of PVP, the carboxylic acid and acrylate groups on the PAA chain, respectively. The area was calculated through Origin 8.0 after picking multiple peaks from a curve to fit Lorentz peak functions.

2.6. SEM measurement

Poly (NVP-co-AA) hydrogel with crosslinking extent $MR = 33.5\%$ was swollen completely in distilled water at room temperature, and then was freeze-dried under vacuum for 15 h with LABCONCO freeze dry system to avoid the collapse of porous structure after accelerated freezing by liquid nitrogen. The cross sectional morphology of the xerogel was determined using a scanning electron microscope, JSM-5600LV SEM.

2.7. Swelling studies

Poly (NVP-co-AA) gel with different crosslinking extents were allowed to swell in different pH buffer solutions under various electric fields. After the excess solution on the surface of the hydrogel strip had been removed with filter paper, the length of swollen samples was measured. The equilibrium swelling ratio was determined as follows:

$$\text{Swelling ratio} = (L_s - L_d)/L_d$$

where L_s is the length of the samples in swollen state, L_d is 11 mm, respectively.

2.8. Measurement of bending angle of poly (NVP-co-AA) hydrogel in an electric field

A schematic diagram of the equipment used for studying the electrical response of hydrogel is shown in Fig. 1 [23]. All hydrogel strips were 11 mm long, about 1 mm wide and 1 mm thick. Two parallel carbon electrodes, 50 mm apart, were immersed in the B–R buffer solutions with different pH and the hydrogel strip under investigation was mounted centrally between them. Upon application of a dc electric field, the deflection is expressed in terms of the degree of bending, θ , measured by reading the angle of deviation from the vertical position, and the sign of the value of deflection is positive when the hydrogel bent toward the right and negative when it bends toward the left. The bending behavior was recorded with a digital camera (Canon, Japan).

3. Results and discussion

3.1. Formulation and characterization

It is found that the responsive behavior of hydrogels immersed in a bath solution under an externally applied electric field are affected by many parameters, including the fixed charge density, exterior solution concentration, ionic valence, externally applied voltage, and so forth [6,24]. The ionic conduction, which is a transport process occurring under an applied electric field, can be rationalized in a dependence of hydrogels responsive behaviors upon the ionic mobility. Andreas Killis et al. have demonstrated that there exists a direct relationship between the ion conduction and viscoelastic properties of the networks, and the diffusion of ions is dependent on free volume [25]. In this report, formulation of a new poly (NVP-co-AA) hydrogel with flexible chain nature and large free volume was done from existing knowledge of reactions and properties of poly (N-vinylpyrrolidone) (PVP). At 60 °C, KPS would decompose into the sulfate anion radical. It is well known that the anion radical can not only react with π bond of vinyl monomer through an addition process, but also capture the active tert-hydrogen atom to generate free radical. Compared with PAA, PVP does easily form free radical, which is stabilized by an electron-donating resonance effect from nitrogen atom but PAA cannot, it was experimentally proved in this work. Therefore, the crosslink reaction among PVP chain segments has performed efficiently through bimolecular termination of free radical or initiating NNMBA to form covalent crosslinks. The gelation reaction and the structure of poly (NVP-co-AA) hydrogel, which is composed of crosslinked PVP network and uncrosslinked PAA chain segments, can be represented by Scheme 1.

The changes in the PVP chains before and after gelation are studied by solution and CP/MAS solid-state NMR spectroscopy. The results are shown in Fig. 2a for linear PVP dissolved in D₂O and Fig. 2b for pure PVP xerogel crosslinked by KPS inducing, respectively. Assignments of the peaks are facilitated by references 26 and 27. Thus, for linear PVP before gelation, as shown in Fig. 2a, the side-chain pyrrolidone ring's methylene carbons are assigned to $\delta 17.60$ (⁴CH₂), $\delta 31.34$ (⁵CH₂), and $\delta 42.61$ (³CH₂) ppm (see numbering in Fig. 2a), respectively. The main chain methylene carbon (¹CH₂) signal is assigned to the weak peak around $\delta 17.60$ ppm overlaid with the peak of ⁴CH₂, while the main chain methine carbon (²CH) is located at 44 ppm. The peak at 177.48 ppm is attributed to the carbonyl carbon in the pyrrolidone ring of PVP. As for the peaks appearing at 30.21 and 215.40 ppm may be attributed to the residual acetone, which was used as precipitator during the purification process of linear PVP.

As can be seen in Fig. 2b for PVP xerogel, a new peak is clearly observed near 81.79 ppm in the gel spectrum, which is a signal from the quaternary carbon atom (C⁺) groups in the newly-formed cross bond. The change is excellently consistent with the fact that the ²CH group partly converted into quaternary carbon atom C⁺ groups in the main chain. The carbonyl carbon peak at 215.40 ppm disappeared after crosslinking. This may be attributed to the purification process of PVP hydrogel

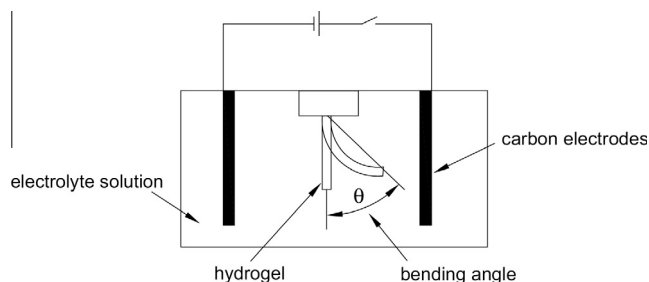
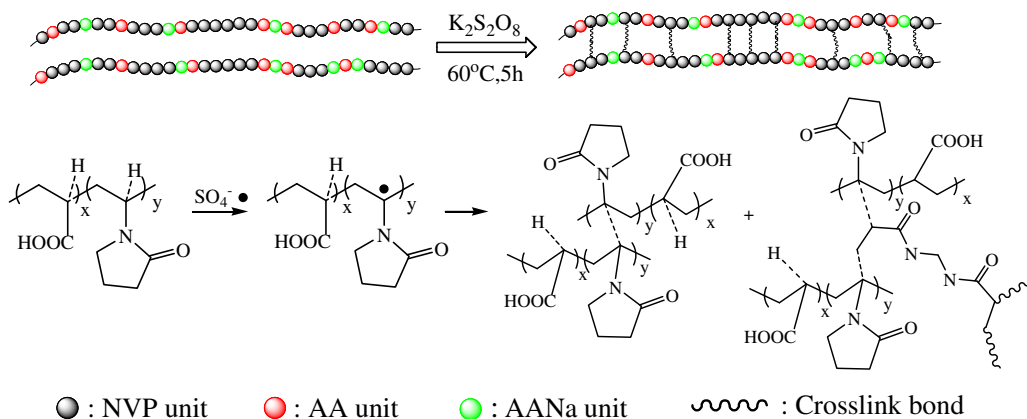


Fig. 1. Schematic diagram for testing the bending behavior of hydrogels.



Scheme 1. The crosslinking reaction for poly (NVP-co-AA) gel initiated by KPS.

by Soxhlet extractor with distilled water as extraction solvent.

The FTIR spectra of linear poly (NVP-co-AA) before gelation and poly (NVP-co-AA) gel with molar ratio of NVP to AA 2:1 (feed ratio) after crosslinking were carried out. The results are shown in Fig. 3a and b, respectively. We know that the carbonyl group of PVP exhibits a stretching vibration peak between 1650 and 1680 cm^{-1} and the group of carboxylic acid on the PAA chain exhibits a peak at approximate 1750 cm^{-1} from the literatures [19]. When the carbonyl group forms intermolecular hydrogen bond, there is a negative shift exhibited in the FTIR spectrum. In this work, the carbonyl group exhibits a peak at 1654.02 for poly (NVP-co-AA) before gelation but a peak at 1634.07 cm^{-1} for the polymeric gel, this negative shift from 1654.02 to 1634.07 cm^{-1} signify that a stronger intermolecular interaction after gelation than that before. Strong shoulder appearing at about 1713.85 cm^{-1} , which may be corresponded to stretching vibration of the carbonyl group of carboxylic acid on the PAA segments, further illustrated that intermolecular hydrogen bond did occur. In sum, FTIR spectroscopic analysis surprisingly showed no significant changes in the polymer before and after crosslinking by KPS inducing except for the changes in the intensity. Implying that no new groups formed during the process of gelation in which the predominant change is the formation of carbon–carbon cross bonds.

The composition of linear poly (NVP-co-AA), ω , is about 1.05. This was determined by comparing the area of the stretching vibration peak of the carbonyl group of PVP at 1654.02 with that of carboxylic acid group at about 1713.85 cm^{-1} and the asymmetrically stretching vibration of carboxylate ion appearing at about 1571.75 cm^{-1} on the PAA chain. The area was calculated automatically through Origin 8.0 after picking multiple peaks from a curve to fit Lorentz peak function as shown in Fig. 4. The difference of ω between 1.92 determined from feed ratio of NVP to AA units and 1.05 calculated from FTIR may be ascribed to the different active of NVP and sodium AA. For example, it is deduced that the reactivity ratio of NVP and sodium AA is 0.808 and 3.296 respectively, by the mathematical method of Fineman Ross, Kelen-Tüdös and YBR, via the aid of test results of element analysis [26].

Cross sectional morphology of poly (NVP-co-AA) hydrogel with crosslinking extents MR = 33.5% is shown in Fig. 5 after swelling completely in distilled water. From this we can see that the hydrogel exhibits certain uniform and porous three-dimensional network structure. This may be owing to the effective crosslinking bond triggered by KPS. From these we would easy to understand that the elastic nature and large free volume displayed by poly (NVP-co-AA) hydrogel, which would be favorable for the movement of polymer chain segments and migration of charged particles in the inner of the hydrogel [27].

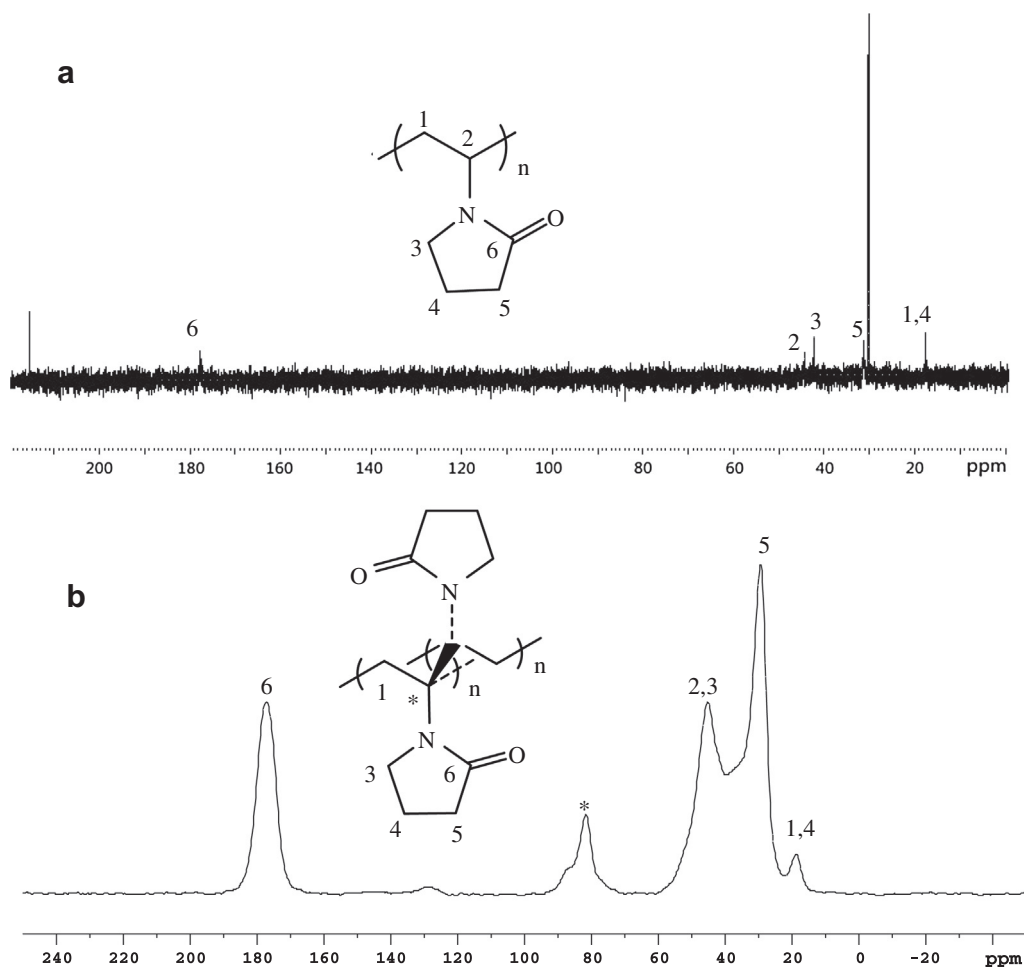


Fig. 2. ^{13}C NMR spectrum of linear PVP dissolved in D_2O at room temperature (a), and solid-state ^{13}C NMR spectrum of crosslinked PVP initiated by KPS, and (b) at room temperature.

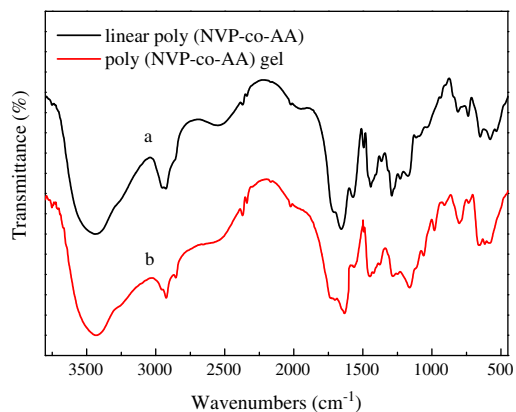


Fig. 3. FTIR spectra of linear poly (NVP-co-AA) solid before gelation (a), and poly (NVP-co-AA) gel after KPS initiate crosslinking (b).

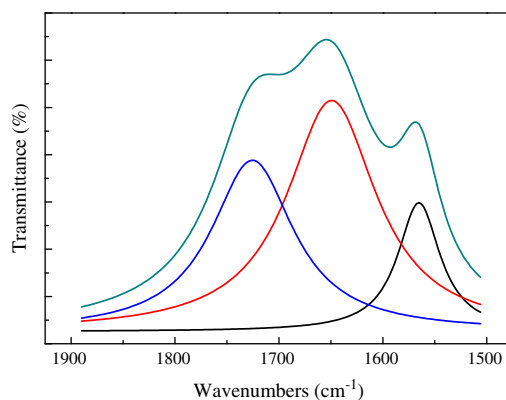


Fig. 4. Fitting peaks (Lorentz) obtained from Origin 8.0 Peak Analysis (R -Square is 0.99532).

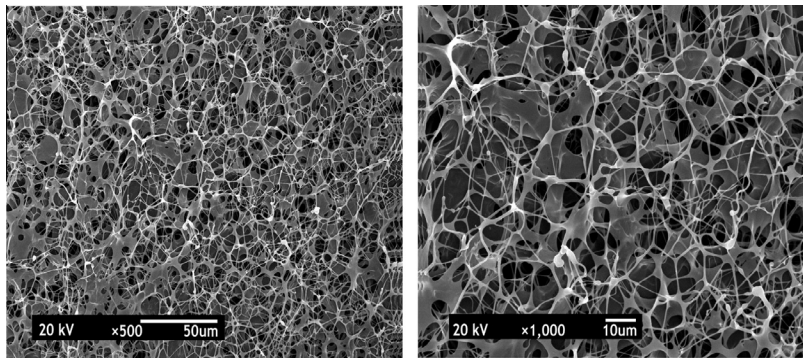


Fig. 5. The SEM micrograph of the poly (NVP-co-AA) hydrogels with MR = 33.5% after swelling in distilled water.

3.2. Swelling behavior of poly (NVP-co-AA) hydrogel in the electric field

Fig. 6 shows the variation of equilibrium swelling degree (SW_{eq}) of poly (NVP-co-AA) hydrogel with different crosslinking extents bathing in different pH B-R buffer solutions. The experiments were measured at room temperature when an electric field was applied. From this figure we can see that:

- (1) The swelling of poly (NVP-co-AA) hydrogel is largely dependent on the pH of bathing and the hydrogel shows a higher value of SW_{eq} at pH 7.96 and 10.88 than that of at pH 2.87 and 6.09, no matter what the crosslinking extent and voltage are. This behavior is typical property of pH-sensitive hydrogel [22]. The lower level of swelling degree may be considered to be due to the higher crosslinking density stemming from the formation of hydrogen bond among polymer chain segments. While the higher one at high pH is due to the dissociation of carboxylic acid groups, results in destruction of hydrogen bond and decrease of crosslinking density, the latter maximizes the free space that is favorable for swelling. Apart from this, the charge repulsion along PAA chain also results in the extension of polymer chains and an increase of SW_{eq} at high pH.
- (2) Exposure voltages applied during the measurement have also a great influence on the swelling. The increase in the applied voltage enhances the swelling. The swelling behavior of hydrogel in the electric field can be explained by Flory's theory of osmotic pressure [28,29]. When an electric field is applied, the counter ions of the polyions in the inner of hydrogel and the free ions in the solution move toward their counter-electrodes. At the same time, the electro neutrality property of the gel body must be hold. This would result in an ionic gradient within the hydrogel along the direction of the electric field. The ionic concentrations inside and outside the hydrogel are thereby different at the beginning of the swelling process, it turned out that the osmotic pressure originates in which and contributes to the

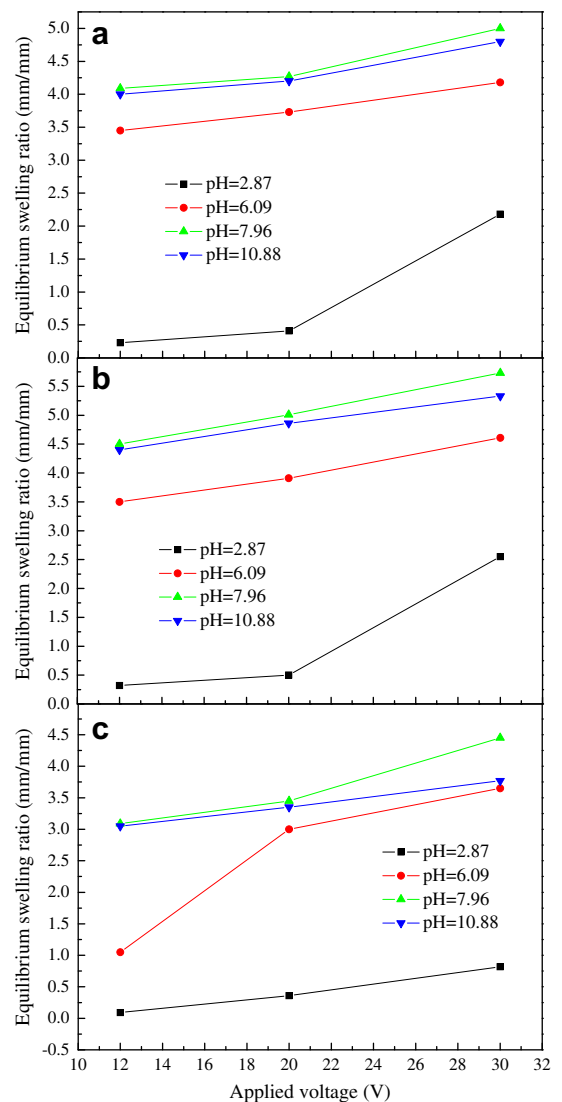


Fig. 6. Effects of pH of buffer solution, MR and applied voltage on the swelling ratio of poly (NVP-co-AA) gels at ND = 40%: (a): MR = 26.8%; (b): MR = 33.5%; (c): MR = 40.2% (ionic strength = 0.0456 M).

penetration of the solvent molecules, so hydrogel swells. It is understood easily that the higher applied voltage would lead to a higher number and migration rate of ion, and consequently the degree of swelling increase.

- (3) Another important factor influencing the swelling behavior of the poly (NVP-co-AA) hydrogel is crosslinking extent of the poly (NVP-co-AA) regulated by the mass percentages of KPS to NVP unit (MR). The curves shown in Fig. 6a–c indicate an optimum quantity of MR, which is 33.5%. When MR is less than 33.5%, the number of effective net-chain in the inner of hydrogel will be insufficient. On the contrary, a higher MR than 33.5% does increase the crosslinking density; the latter impedes the segmental motion, and contributes to a lower equilibrium swelling degree.

3.3. Bending behavior of poly (NVP-co-AA) hydrogel in the electric field

After applying a dc electric field to poly (NVP-co-AA) hydrogel strip in buffer solution, the response behavior of the hydrogel is dissimilar to CS/CMC hydrogel [23], which quick bent toward the anode or the cathode depending on the pH of the electrolytic solution bathing the gels. Also different from the AAC/VS hydrogel [24], PAA/PANI and P(AMPS-AA)/PANI IPN conducting hydrogels [9], they showed significant bending towards the anode when an electric field was applied to the hydrogel strip suspending in the electrolytic solution. In the present experiments, after an electric current passing, the strip shaped poly (NVP-co-AA) hydrogel matrix starts to bend toward the negative electrode. When the electric stimulus is removed, the hydrogel displaces to their original positions. Also, if the polarity of the electric field is altered, the hydrogel first becomes straight and then bends toward the opposite direction, as shown in Fig. 7.

The influence of applied voltages on the response to the electric stimulation is shown in Fig. 8. The data shows that the use of higher voltages either 20 or 30 V would speed up the response of the hydrogel, and it is found to be proportional to the field intensity [28]. Also, the increase in pH of buffer solution could improve the electroactive property of poly (NVP-co-AA) hydrogel and the results are shown in

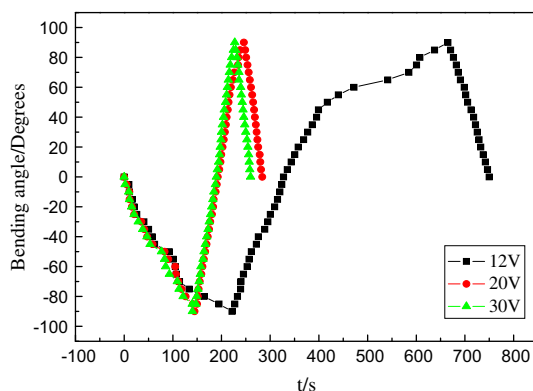


Fig. 8. Bending behavior of poly (NVP-co-AA) hydrogels with MR = 26.8% and ND = 40% bathing in pH 10.88 buffer solution under a cyclically varying electric field from positive to negative when various voltages were applied.

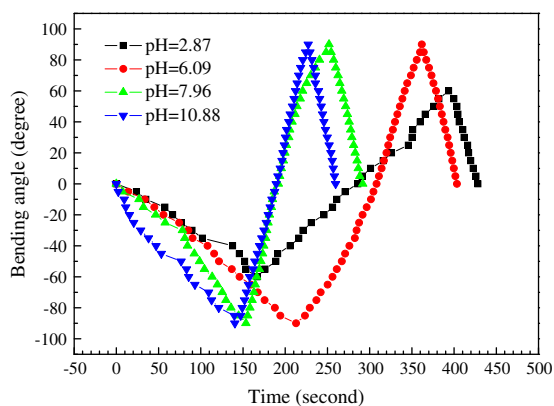


Fig. 9. Bending behavior of poly (NVP-co-AA) hydrogels with MR = 26.8% and ND = 40% bathing in buffer solutions with different pH under a cyclically varying electric field from 30 to -30 V.

Fig. 9. As increase of buffer solution pH from 2.87 to 6.09, 7.96 and then 10.88, both the bending angle and response speed increase dramatically. The deformation of hydrogel is associated with its swelling behavior that influenced by voltage and buffer solution pH as an electric field is applied. The tendency of bending is consistency with that of

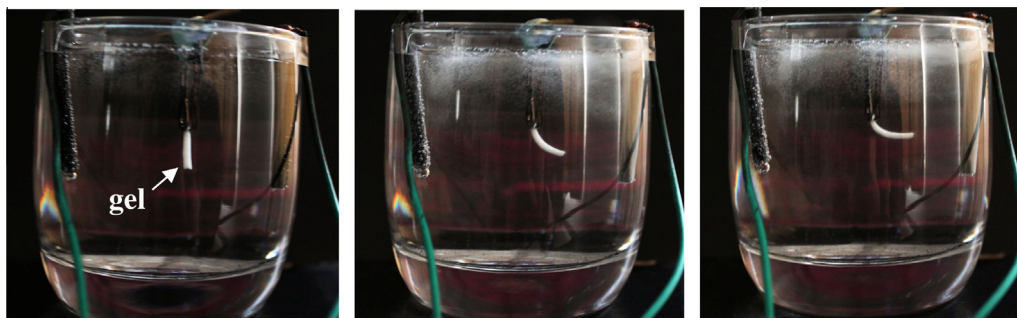


Fig. 7. Bending phenomena of poly (NVP-co-AA) hydrogel with MR = 26.8% and ND = 40% bathing in pH 7.96 buffer solution when a constant voltage of 30 V was applied.

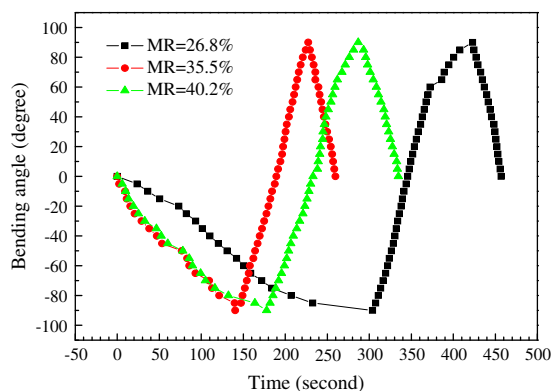


Fig. 10. Bending behavior of poly (NVP-co-AA) hydrogels with various MRs and ND = 40% bathing in pH 10.88 buffer solution under a cyclically varying electric field from 30 to -30 V.

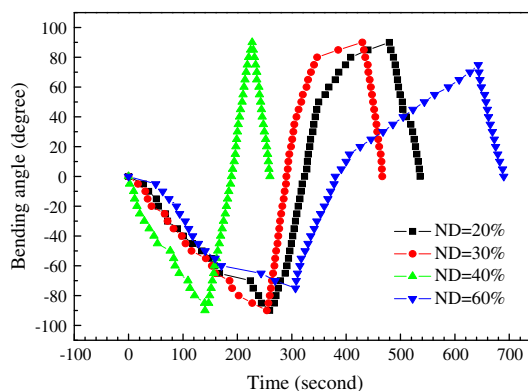


Fig. 11. Bending behavior of poly (NVP-co-AA) hydrogels with MR = 26.8% and various NDs bathing in pH 10.88 buffer solution under a cyclically varying electric field from 30 to -30 V.

swelling under same condition. So the hydrogel shows higher SW_{eq} , bending angle and response speed at pH 7.96 and 10.88 than that at pH 2.87 and 6.09 when the applied voltage is up to 20 V and 30 V. This indicates that the bending is one of the swelling behaviors.

The effect of the extent of crosslinking on the bending behavior of poly (NVP-co-AA) hydrogel is shown in Fig. 10. The bending angle and response speed first increase considerably as the crosslinking extent up to MR 33.5% from 26.8%, and then decrease slightly when one continue to up to MR 40.2%. Optimum mechanical properties given by an optimum crosslinking extent could explain the changes in the degree of deflection shown in this figure. Shiga and Kurauchi have used a three-point mechanical bending model to explain the bending behavior of gels [28,29]. That is, when hydrogels bend under electric stimulus, the osmotic pressure difference between the anode and the cathode sides, $\Delta\pi$, is balanced by the stress caused by the strain on the polymers. Therefore, in a three-point bending test, $\Delta\pi$ is equal to the maximum tensile stress σ .

$$\Delta\pi = \sigma = 6DEY/L^2$$

where E is Young's modulus, Y is the amount of the deflection (the distance between the ends of the polymer gel before and after bending), D is the thickness, and L is the length of the polymer gel before bending. When a constant value of electric field is applied to the hydrogel, $\Delta\pi$ is constant. And if the length and thickness of the hydrogel are also kept constant, the bending deflection would be in inverse proportion to its Young's modulus [23]. It is found that the crosslinking extent of MR 33.5% should give an optimum value of Young's modulus in the current test according to the discussions above. In addition, monomer unit molar ratio of NVP to AA should also influence the mechanical properties. These were not evaluated at present and would be discussed in detail in further work.

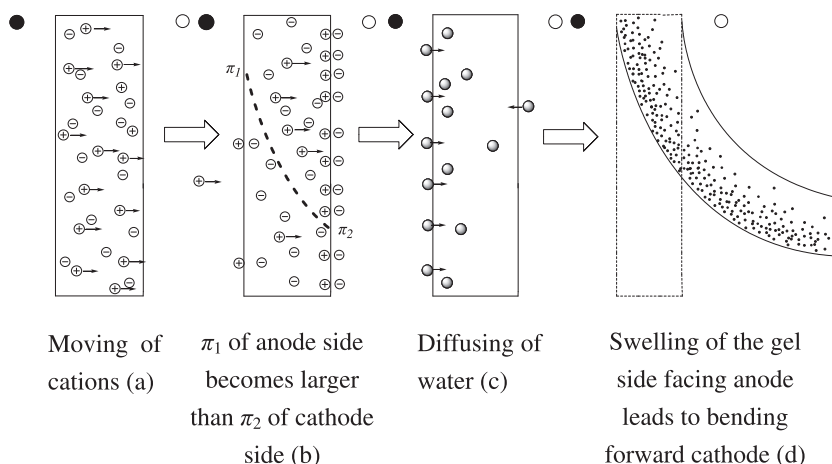
In Shiga and Kurauchi's study, the direction of deformation depended on the concentration of polyion, $-\text{COO}^-$, in the gel. The gel with a small amount of polyion (molar ratio of NaOH to AA was 20% in feed) shrank from the anode side of it, while the gel with a large amount of polyion (molar

ratios were 60% and 100% in feed) swelled. The gel, content of polyion was 40% modulated by molar ratio of NaOH to AA, swelled and shrank continuously [28]. But the gel free of polyion was not influenced by the electric field. Both ends of the gel should move toward the cathode if a long and thin gel was stimulated by applying the field to it. The gel gained weight while it was bending. As mentioned above, this indicates that the bending is one of the swelling behaviors. In the present work, the great influence of concentration of polyion defined by the neutralization degree of AA monomer on the response to the electric stimulation was evaluated. The bending angle and response speed of poly (NVP-co-AA) hydrogel bathing in pH 10.88 buffer solution under a cyclically varying electric field from 30 to -30 V are shown in Fig. 11. The data shows that the bending phenomena are not in agreement with that reported in literature [28]. What depended on the concentration of polyion is the bending angle and response time but not the direction of deformation. Larger amounts of polyion, molar ratio of NaOH to AA is 40% in feed, improves both the bending angle and the response speed as compared with that of less amounts of polyion, molar ratios are 20% and 30% in feed. However, it is worth noting that the further increase in polyion content reduces electroactive property for hydrogel with degree of neutralization of AA of 60%. This may be due to the decrease in reactivity ratio of sodium AA to NVP as an increase in neutralization degree of AA comonomer, which inevitably leads to a reduction of the polyion content in the hydrogel.

3.4. Proposing mechanism of bending

Under the influence of an electric field, electro responsive hydrogels generally swell, deswell or bend, depending on the shape of the gel and its position relative to the electrodes. Swelling and deswelling occur when the hydrogel lies perpendicular to the electrodes, whereas bending occurs when the main axis of the gel lies in parallel with (but does not touch) the electrodes [28,30], where a side of gel swells and the other shrinks.

The deformation and the swelling behavior of polyelectrolyte gel related to the application of electric fields can be



Scheme 2. Schematic illustration of bending mechanism (●: anode; ○: cathode; ⊕: freely mobile cation; ⊖: immobile polyion; ⊙: water molecule).

explained by Flory's theory of the osmotic pressure, π , which originated in the ion concentration difference between the inside and outside of the gel subjected to a dc electric field. When π increases, the gel swells, on the contrary the gel shrinks. As the poly (NVP-co-AA) gel strip with negatively charged polyion is placed parallelly between a pair of electrodes (Fig. 1) and a constant direct current is applied, the positively charged free ions migrate towards the cathode, whereas the polyion remains immobile. The counter ions in the inner of gel would not move out of it because of the electrostatic interaction between polyion and free cation, and for maintaining the electro-neutrality property of gel. Thus a concentration gradient of freely mobile cation is established and the concentration on the side facing negative electrode becomes larger than that on the opposite side as shown schematically in Scheme 2a and b. So the gel network on the cathode side is cationic. Simultaneously, the free ions in the solution also move toward their counter electrodes. Some of negatively charged ions can therefore bind to gel's surface facing the cathode, then, electric double layer will be induced at the interface between the gel and solution. As the results, the osmotic pressure of the positive electrode side, π_1 , becomes larger than that of the negative electrode side, π_2 , with time as shown in Scheme 2b. Consequently, the side of gel facing the anode swells easily as compared with the cathode side, and the gel would bend toward cathode.

Another explanation for the bending behavior of the poly (NVP-co-AA) gel in the electric field cannot be ignored. For polyanionic (NVP-co-AA) hydrogel, as we discussed above, a concentration gradient of freely mobile cation is established and the concentration on the negative electrode side larger than that on the positive side, so negatively charged groups on the polymer chain are balanced by the positively charged ions. This means that the charge repulsion along the PAA block can also be screened effectively, namely, coupling-coupling attraction increases on the side facing the cathode, accompanied by a decrease of electrostatic repulsion. But, they repel each other on the anode side. This makes the hydrogel shrinks on the

cathode side and swells on the anode side and it thereby bends toward the cathode side.

4. Conclusions

In this study we have developed a synthetic strategy to fabricate poly (NVP-co-AA) hydrogel by a gelation reaction of linear statistical copolymer of NVP and AA. The cross-linking process is triggered by using KPS as a radical initiator. The novel hydrogel presents porous and flexible chain structure consisting of crosslinked PVP network and uncrosslinked PAA segments, which is expected to be useful for the improvement of electric field sensitivity. When the poly (NVP-co-AA) hydrogel bathing in buffer solutions with different pH is subjected to an electric field, the hydrogel bends toward the cathode. The bending angle and bending speed of the hydrogel increase with increasing pH of buffer solution and applied voltage. The degree of neutralization of AA and crosslinking extent of PVP network also considerably affects the bending behavior. Therefore, the hydrogel can be useful for sensors, actuators, switches, or drug delivery systems. But, the influence of monomer unit molar ratio of AA to NVP on the response to the electric stimulation, the mechanical properties and the structure of the poly (NVP-co-AA) gel should be discussed in detail in the further.

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