

Synthesis and characterization of pH-sensitivity semi-IPN hydrogel based on hydrogen bond between poly(*N*-vinylpyrrolidone) and poly(acrylic acid)

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Received 8 September 2005; received in revised form 1 January 2006; accepted 9 January 2006

Abstract

A novel spherically shaped semi-interpenetrating network (semi-IPN) hydrogel, which is based on hydrogen bond between chemical crosslinked poly(*N*-vinylpyrrolidone) (PVP) and linear poly(acrylic acid) (PAA), was prepared. The semi-IPN hydrogel was synthesized by three steps: (1) linear PAA with different molecular weights were obtained by a reaction of free radical polymerization used 2,2'-azo-bis-isobutyronitrile (AIBN) as an initiator; (2) crosslinked PVP bead was obtained by a reaction of *N*-vinylpyrrolidone with AIBN used as an initiator and *N,N'*-methylene-bis-acrylamide (NNMBA) used as a crosslinker by the way of suspension polymerization; (3) complexation occurred between suitable amount of aqueous solution of PAA and the porous PVP bead and was stabilized by multiple frost–defrost, from this step the semi-IPN hydrogel was obtained. Fourier transform infrared spectroscopy (FTIR) and differential scanning calorimetry (DSC) proved the presence of the hydrogen bond in the hydrogel. The swelling behaviour of the hydrogel was studied in buffer solution with different pH and NaCl aqueous solution. The results showed that the semi-IPN hydrogel had excellent pH-sensitivity in the range of pH from 2.25 to 4.00 and the small molecule salt had little influence on the swelling behaviour of the semi-IPN hydrogel over the range of concentration of NaCl aqueous solution investigated. The results were confirmed further by scanning electron microscope (SEM). The mechanism of swelling and deswelling was discussed.

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Keywords: Semi-interpenetrating network; Poly(*N*-vinylpyrrolidone) hydrogel; Poly(acrylic acid)

1. Introduction

Hydrogels are one of the upcoming classes of polymer-based controlled-release drug delivery systems. Besides exhibiting swelling-controlled drug release, hydrogels also show stimuli responsive change in their structural network and the drug release. Because of large variations in physiological pH at various body sites in normal as well as pathological conditions, pH-responsive polymeric networks have been extensively studied [1–3]. 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 [4,5] or controls release system for drug delivery [6–9] because of their biocompatibility with the human body.

Hydrogels prepared by synthetic chemical reaction are insoluble due to the presence of chemical crosslinks (covalent bond) or physical crosslinks, such as entanglements or crystallites [10]. Unless the covalent bonds can be broken, these types of hydrogels do not dissolve in water or other organic solvents even upon heating. Physical hydrogels are hydrophilic networks comprised of an amorphous hydrophilic polymer phase held together by highly ordered aggregates of polymer chain segments arising from secondary molecular forces (for example, hydrogen bond) in conjunction with other types of molecular interaction. If the crosslinks are based on reversible physical interactions, such as hydrogen bond, ionic bond or van der waal' bond, which can be made or broken when the surroundings change, the responses of the hydrogels to external stimuli are often reversible [10]. In addition to conventional methods, hydrogels have also been constructed from interpolymer complexes and interpenetrating networks [11,12].

Recently, many of work did make the study of hydrogels based on complexation between PVP and PAA [11,13–15].

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Crosslinked complexes of PVP–PAA were prepared from a mixture of NVP, AA and ethyleneglycol dimethacrylates [14] and complexes of PVP–PAA from a mixture of NVP and AA were obtained [15]. In Ali's study [13] and Yaung's study [10], chelating poly(vinylpyrrolidone/acrylic acid) copolymer hydrogels were prepared from PVP with certain molecular weight and AA by radiation-induced copolymerization.

Semi-interpenetrating polymerization is a way of blending two polymers where only one is crosslinked in the presence of another to produce a mixture of fine morphology, additional noncovalent interaction between two polymers would influence the morphology and the thermal properties of the semi-IPN gel [16].

In this work, we want to develop a novel smart hydrogel, which has some reasonable biocompatibility and the responsiveness to external surroundings stimuli. So we used PVP as an essential material of gel-forming. We synthesized cross-linked PVP bead by the chemical reaction, then, we obtained the semi-IPN hydrogel based on complexation stabilized through the hydrogen bonds between the carboxylic acid groups on the PAA chain and carbonyl groups on the PVP networks at the low temperature. The semi-IPN hydrogel was studied by swelling measurements. The results were confirmed by FTIR, SEM and DSC measurements.

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'-Azo-bis-iso-butyronitrile (AIBN) and *N,N'*-methylene-bis-acrylamide (NNMBA) (C.P. grade) were recrystallized from 95% ethanol just before to use. The other reagents were A.P. grade and were used without further purification.

2.2. Preparation of PAA and PVP

The linear PAA with different molecular weights (the viscosity average molecular weight), $M_v(\text{PAA})$, and the linear homopolymer of *N*-vinyl-2-pyrrolidone, PVP-K30, were obtained in our laboratory during the previous experimental work (K30 means the viscosity average molecular weight of PVP is about 38,000) [17].

2.3. Preparation of crosslinked PVP beads

Crosslinked PVP beads were obtained from the process described as follow: to obtain a stable heterogeneous polymerization reaction system and avoid the hydrolysis of the monomer NVP [18], certain amount of K_2HPO_4 and Na_2SO_4 were dispersed into 5.5 mL distilled water, stirring till the mixture changed into homogeneous solution. And then certain amount of NVP, AIBN, PVP-K30 used as a surfactant and suitable amount of NNMBA were added into the above solution and stirred continually for 0.5 h under nitrogen blanket

to remove O_2 . The crosslinking reaction was maintained for 8 h in a 70 °C water bath equipped with a temperature controlled cell holder. Different mass ratios of NNMBA to NVP ($\text{MR} = W_{\text{NNMBA}}/W_{\text{NVP}} \times 100\%$) were used to modulate the crosslinking extent. The PVP beads were washed several times with distilled water to eliminate the unreacted reagents residues, and then they were dried under vacuum at room temperature for 72 h to constant weight. If a total drying is performed, the PVP bead's shape becomes analogous to a very thin disc.

2.4. Preparation of semi-IPN hydrogels

The dried PVP bead was immersed into an aqueous solution of PAA with certain molecular weight, $M_v(\text{PAA})$, according to suitable unit molar ratios of PAA to PVP ($R = n_{\text{PAA}}/n_{\text{PVP}} = 1:1$ or 2:1). Complexation between PAA and PVP occurred and was stabilized through multiple frosts and defrosts. After that, the swollen semi-IPN hydrogel was filtered to eliminate the solution excess, then, dried under reduced pressure at room temperature for 72 h to constant weight. The dried semi-IPN gel is no more spherical shape but analogous to a very thin disc.

2.5. Preparation of buffer solutions with different pH

Chlorine hydride/potassium acid pathalate, sodium hydrate/potassium acid pathalate and sodium hydrate/sodium dihydrogen phosphate were used to prepare buffer solutions with different pH ranged from 2 to 4, 4 to 6 and 6 to 8, respectively. Chlorine hydride and sodium hydrate were used to prepare solutions of pH 1.00 and 10.98, respectively. Sodium chloride was used to adjust ionic strength of solutions to 0.2 M; the pH of all solutions was determined by PHS-3B model pH meter.

2.6. Swelling studies

The swelling experiments were performed in distilled water and buffer solutions with different pH ranged from 1.00 to 10.98 at fixed ionic strength of $I = 0.2$ M or NaCl aqueous solution with different concentrations of NaCl (C_{NaCl}). The sample weighed previously was immersed in appropriate solution with the proportional of mass of xerogels to the mass of solution about 1:1000. Swelling continued to reach a constant weight of hydrogel. Before weighing the swollen sample, any surface water was removed with filter paper and then they were weighed on a sensitive balance.

2.7. FTIR measurements

Fourier transform infrared spectroscopy (FTIR) was carried out with Nicolet NEXUS 670 FT-IR Spectrometer. The samples dried completely and ground to fine power, then push down to piece blending with KBr.

Table 1
Compositions of crosslinked PVP beads (AIBN/NVP=0.03 wt%, PVP/NVP=0.17 wt%, $K_2HPO_4/Na_2SO_4/H_2O=0.0632/0.0421/1$ g/g/mL)

| | | | | | | | |
|-----------------|-------|-------|-------|-------|-------|-------|-------|
| NNMBA/NVP (wt%) | 0.331 | 0.519 | 0.602 | 0.648 | 0.698 | 0.904 | 1.746 |
| PVP | PVP1 | PVP2 | PVP3 | PVP4 | PVP5 | PVP6 | PVP7 |

2.8. SEM measurements

Two hydrogels were swollen completely in the buffer solutions of pH 2.07 and 10.98 ($I=0.2$ M) at 37 °C, respectively, and were freeze-dried for 15 h with LABCONCO freeze dry system to avoid the collapse of porous structure. Then the surface morphology of the zero-gels was determined using a scanning electron microscope, JSM-5600LV SEM (Japan).

2.9. Determination of glass transition temperature (T_g) and water states in the hydrogel

The measurements of determination of glass transition temperature (T_g) and water states in the hydrogel were carried out using a Sapphire DSC (Perkin–Elmer, America). Typical procedure for T_g was described as follows: first, the dried samples were heated to 260 °C at 50 °C/min and then were cooled to 30 °C at 20 °C/min. This procedure ensured that the samples had the same thermal history; second, the samples were reheated to 260 °C at 20 °C/min. The onset of the abrupt decrease in the heat flow was taken as T_g . For the measurement of water states, the process is that initially the swollen sample (or distilled water) was frozen to –100 °C and held for 10 min using liquid nitrogen, and then heated to 25 °C at 1 °C/min. The whole process was conducted under nitrogen blanket to avoid sample degradation.

3. Results and discussion

3.1. The composition of sample

Tables 1 and 2 show the different compositions of the crosslinked PVP beads and the semi-IPN hydrogels, respectively. For example, the semi-IPN1 hydrogel is made of

Table 2
Compositions of the semi-IPN hydrogels based on hydrogen bond between the crosslinked PVP beads and linear PAA ($R=n_{PAA}/n_{PVP}=1:1$)

| PVP | M_v (PAA) (g/mol) | | | |
|------|---------------------|---------------------|-------------------|--------------------|
| | 20.99×10^4 | 10.04×10^4 | 7.8×10^4 | 4.89×10^4 |
| PVP1 | – | Semi-IPN1 | – | – |
| PVP2 | – | Semi-IPN2 | – | – |
| PVP3 | – | Semi-IPN3 | – | – |
| PVP4 | Semi-IPN(1) | Semi-IPN4 | Semi-IPN(2) | Semi-IPN(3) |
| PVP5 | – | Semi-IPN5 | – | – |
| PVP6 | – | Semi-IPN6 | – | – |
| PVP7 | – | Semi-IPN7 | – | – |

–, the samples were not synthesized.

crosslinked PVP1 bead and linear PAA with molecular weight 10.04×10^4 g/mol, and the unit molar ratio of PAA to PVP is 1:1.

3.2. FTIR analysis

In order to obtain the information about the structure of the semi-IPN hydrogel, we carried out the FTIR spectra of PVP6 hydrogel and the semi-IPN6 hydrogel made of PVP6 bead and PAA with molecular weight of 10.04×10^4 g/mol ($R=n_{PAA}/n_{PVP}=1:1$). The result for the semi-IPN6 hydrogel is shown in Fig. 1. We know that the carbonyl group of PVP exhibits a stretching vibration peak between 1650 and 1680 cm^{-1} and the carbonyl group of carboxylic acid group on the PAA chain exhibits a peak at approximate 1750 cm^{-1} from the literatures [8,10,14,15]. When the carbonyl group forms intermolecular bond (such as hydrogen bond), there is a negative shift exhibited in the FTIR Spectrum. In our work, the carbonyl group exhibits a peak at 1658.60 cm^{-1} for PVP6 hydrogel but a peak at 1643.80 cm^{-1} for the semi-IPN6 hydrogel, this negative shift from 1658.60 to 1643.80 cm^{-1} signify that intermolecular hydrogen bond occurred in the formation of the semi-IPN hydrogel as shown in Eq (1) [17] and Scheme 1.

In our previous report [17], we believe a cooperative interaction existing through the formation of hydrogen bond between PVP and PAA. In this work, the linear PAA entangle with PVP network chains like a reptile chain [19], and the cooperative interaction makes the amorphous hydrophilic PAA chain hold together with PVP by rather orderly aggregates of polymer segments arising from hydrogen bond.

Meanwhile, it is also evidence that a small shoulder appeared at about 1730.25 cm^{-1} corresponding to stretching

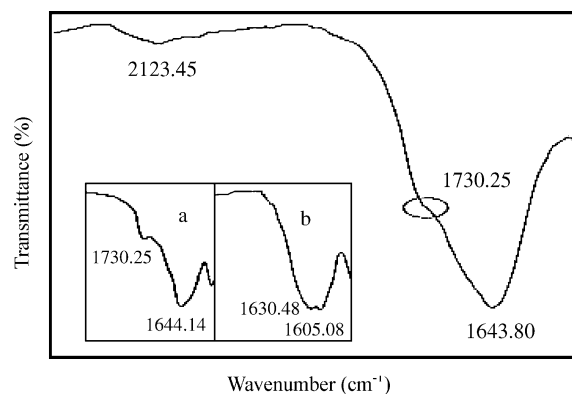
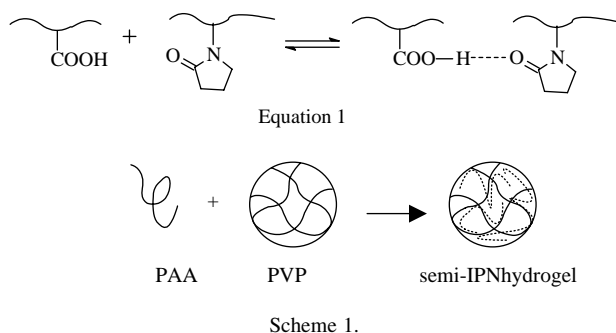


Fig. 1. FTIR spectra of the semi-IPN6 hydrogel. Inset: (a) the semi-IPN6 hydrogel swollen in buffer solution of pH 2.25 at 37 °C; (b) the semi-IPN6 hydrogel swollen in buffer solution of pH 10.98 at 37 °C.



vibration of carbonyl group of carboxylic acid group on the PAA chain, which further illustrated that some intermolecular hydrogen bond did occur and the complexation formed between PVP bead and PAA [10,14,15,20].

3.3. Glass transition temperature

Although the semi-IPN gel is a crosslinked polymer, the higher swelling degree of the hydrogel is defined in this work (the result is discussed in detail below) suggesting the flexibility and the favorable elasticity of the polymer segment. So the dried semi-IPN gel should show obviously glass transition temperature (T_g), meanwhile, the value of T_g would be influenced by the formation of the hydrogen bond, which would retard the movement of polymer segment and result in an increasing of T_g [16,22]. In our current work, the T_g of the dried gels are increasing from 182.2 to 183.9 °C, and then to 186.3 °C corresponding to the PVP4 gel, the semi-IPN4 gel ($R=1:1$) and the semi-IPN4 gel ($R=2:1$), respectively. This further testifies the hydrogen bond existing in the semi-IPN gel and the higher crosslinking density of the semi-IPN gel. The results are shown in Fig. 2.

3.4. Swelling behaviour of the samples in distilled water

The PVP hydrogel was characterized by measuring the equilibrium swelling degree in distilled water and the results

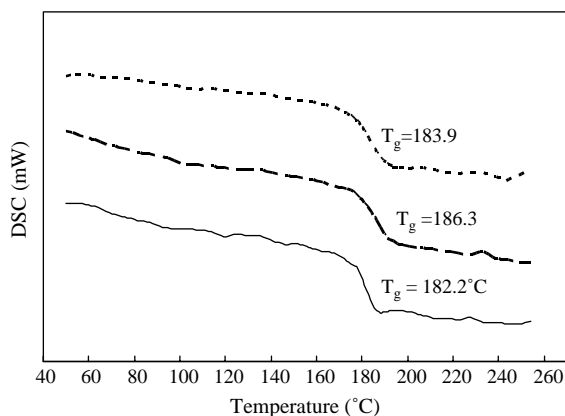


Fig. 2. DSC curves of the dried gels: (---) the semi-IPN gel with $R=n_{\text{PAA}}/n_{\text{PVP}}=1:1$, $T_g=183.9$ °C; (- - -) the semi-IPN gel with $R=n_{\text{PAA}}/n_{\text{PVP}}=2:1$, $T_g=186.3$ °C; (—) PVP4 gel, $T_g=182.2$ °C.

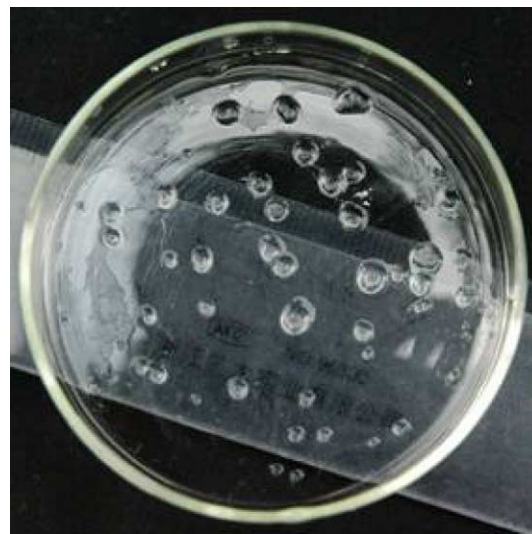


Fig. 3. Typical swelling characteristic of PVP hydrogel. The sample was swollen in distilled water.

are reported in Figs. 3 and 4. Fig. 3 shows the typical swelling properties of PVP bead swollen in distilled water. The diameter of swollen hydrogel bead is about 2–4 mm. Fig. 4 shows the variation of equilibrium swelling degree (SW_{eq}) in distilled water at 37 °C as a function of the mass ratio of NNMB to NVP (MR) for samples PVP1-7 hydrogel with different amounts of crosslinker. The curve in this figure indicates an optimum quantity of crosslinker. When MR is less than this optimum value, the number of effective net-chain in the hydrogel will increase with the increasing of MR. However, the further increase of the MR does increase the crosslinked density and results in a lower equilibrium swelling degree [23].

In order to determine the effect of the mass ratio of NNMB to NVP (MR) and the unit molar ratio of PAA to PVP (R) on the characterization of the network structure of the semi-IPN1-7 hydrogel made of PVP1-7 and PAA with molecular weight of 10.04×10^4 g/mol, the experiments of equilibrium swelling degree (SW_{eq}) versus MR and R were measured in distilled

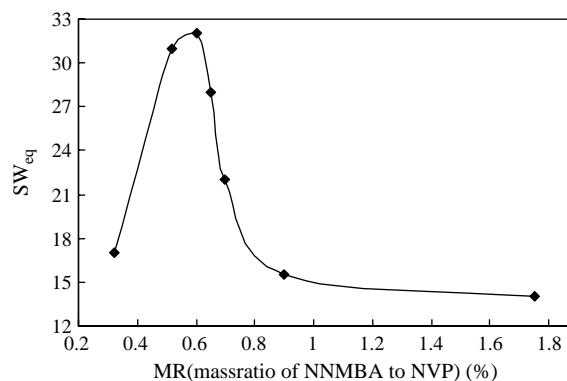


Fig. 4. Equilibrium swelling degree (SW_{eq}) versus the mass ratio of NNMB to NVP (MR) for samples of PVP1-7 hydrogels measured in distilled water at 37 °C.

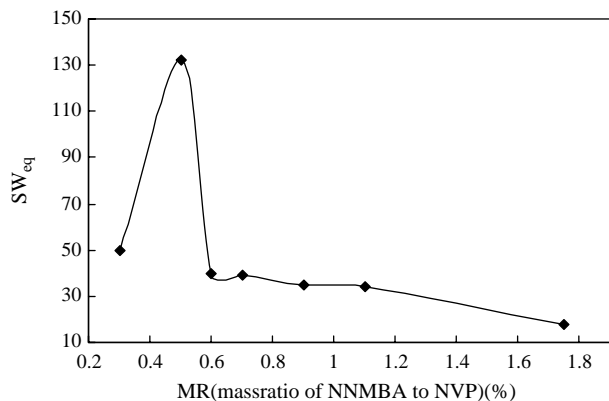


Fig. 5. Equilibrium swelling degree (SW_{eq}) versus the mass ratio of NNMBA to NVP (MR) for samples of the semi-IPN1-7 hydrogels measured in distilled water at 37 °C.

water and the results are shown in Figs. 5 and 6, respectively. Fig. 5 shows exactly the same pattern as Fig. 4, however, the SW_{eq} are much higher due to the more hydrophilic PAA was used as the component of the semi-IPN hydrogel. Fig. 6 shows the SW_{eq} dependence on R . First, when R is higher than 1:1, the SW_{eq} of the semi-IPN4 hydrogel is lower than that of the semi-IPN4 hydrogel which $R = 1:1$. This is because of an increasing of crosslinked density attributing to the formation of higher concentration complexation between PVP bead and PAA, as well as the formation of higher concentration physics entanglements of polymer chains. But for the results of a lower equilibrium swelling degree concerning $R < 1:1$, this because that the effective net-chain in the hydrogel is deficiency. All these lead to a lower equilibrium swelling degree.

3.5. Swelling behaviour of the samples in buffer solutions with different pH

Fig. 7 shows the equilibrium swelling degree (SW_{eq}) of PVP6 hydrogel and the semi-IPN6 hydrogel versus pH of swelling medium, the experiments were measured in buffer solutions with different pH at 37 °C. From this we can see that (1) the swelling behaviour of the PVP6 hydrogel is

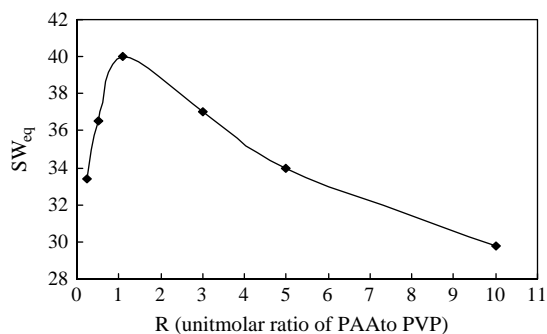


Fig. 6. Equilibrium swelling degree (SW_{eq}) versus the unit molar ratio of PAA to PVP (R) for sample of the semi-IPN4 hydrogel measured in distilled water at 37 °C.

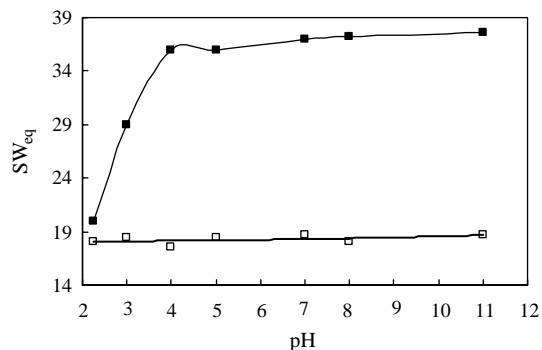
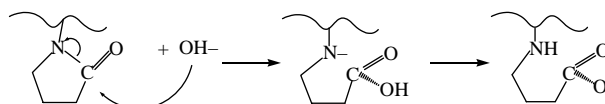


Fig. 7. Equilibrium swelling degree (SW_{eq}) versus the pH of buffer solution for the samples at 37 °C. (■) the semi-IPN6 hydrogel; (□) the PVP6 hydrogel.

independence on pH, this clearly suggests that PVP hydrogel has no pH stimuli-responsive properties. (2) The semi-IPN6 hydrogel shows a lower SW_{eq} at pH 2–3 as compared with that of at pH 4–11 and an abrupt jump around pH 4. This behaviour is typical property of pH-sensitive hydrogel. The lower level of swelling degree is due to the higher crosslinked density stem from the formation of hydrogen bond and the physics entanglements between PVP segment and PAA chain, while the higher value of equilibrium swelling degree at high pH is due to the dissociation of carboxylic acid groups on the PAA chain at $pH \geq 4.00$, which results in the destruction of hydrogen bond and the decrease of crosslinked density. Meanwhile, the charge repulsion also results in an increasing of SW_{eq} that in our case is correlated to higher concentration COO^- groups, which not only stem from the dissociation of carboxylic acid group but also from the reaction of partially hydrolyze of γ -lactam group in the alkaline solutions described as in Scheme 2.

Additionally, the carboxylate ions attract the cation into the hydrogel replace the H^+ , this effectively raise the concentration of free ions inside the hydrogel and increase the swelling capacity [14].

For a weak polyelectrolyte, such as PAA, the number of ionic charge on the backbone of polymer depends on the pH of the solution. When the pH value is above the dissociated content of PAA, pK_a , a fraction of the carboxylic acid groups dissociate to form carboxylate ions. From potentiometric titration of the PAA, the pK_a value was found to be about 4.00 in a 0.2 M NaCl solution [10]. In $pH < 4.00$ buffer solutions, the carboxylic acid groups are undissociated, therefore, the hydrogen bond between PVP and PAA are expected to remain intact leading to a lower SW_{eq} . But in $pH \geq 4.00$ buffer solutions, the pK_a value is exceeded, and the carboxylic acid group would dissociate to form carboxylate ion which leads to a higher SW_{eq} .



Scheme 2.

Inset (a) and (b) of Fig. 1 show the stretching frequency of carbonyl group of the semi-IPN6 hydrogel after swollen in solutions of pH 2.25 and 10.98, respectively. From inset (a) we can see that the stretching frequency (1644.14 cm^{-1}) of carbonyl group in the semi-IPN6 hydrogel hardly changes (compared with 1643.80 cm^{-1}) and the shoulder at 1730.25 cm^{-1} corresponding to carboxylic acid group in the PAA chain still exists, this further illustrate the complexation and the physics entanglements at pH 2.25. However, in inset (b), the appearance of the peak at 1605.08 cm^{-1} corresponding to the asymmetrically stretching vibration of carboxylate ion and the disappearance of the shoulder at 1730.25 cm^{-1} clearly indicate the dissociation of carboxylic acid group and the partially hydrolyze of γ -lactam group at pH 10.98. The peak at 1630.48 cm^{-1} is difficult to explain at the moment, it may be the stretching frequency of carbonyl group of PVP markedly influenced by the surrounding.

Now, we can propose a model swelling and deswelling mechanism about the semi-IPN hydrogel, which is shown as the following Scheme 3.

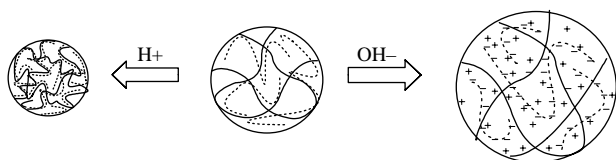
When $\text{pH} < 4.00$, the carboxylic acid group is undissociated, and the higher concentration hydrogen bond forms and leads to a rather compact conformation of the hydrogel and a low swelling degree. But in $\text{pH} \geq 4.00$ buffer solutions, the carboxylic acid group would dissociate to form carboxylate ions which lead to the breakage of the hydrogen bond, meanwhile, the charge repulsion increase, all of this conduce rather extended conformation, and a rather higher swelling degree.

3.6. The reversibility behaviour of pH-responsive

Based on the consideration of hydrogen bond which can be made or broken when the surroundings change, we investigated the pH dependent swelling reversibility of the semi-IPN6 hydrogel at different pH. The typical pulsate reversible swelling behaviour is reported in Fig. 8. The curve in this figure shows that the semi-IPN hydrogel swells in buffer solution of pH 7.03 and then shrinks in buffer solution of pH 3.01 or vice versa, and the process can be repeated many times. This result demonstrates that the semi-IPN hydrogel has obvious pH dependent swelling reversibility, furthermore, the reversibility behaviour has excellent reproducibility.

3.7. Swelling behaviour of the samples in NaCl aqueous solutions with different concentrations

To investigate whether the semi-IPN hydrogel with pH-sensitive has ionic strength-sensitivity, the swelling experiment



Scheme 3.

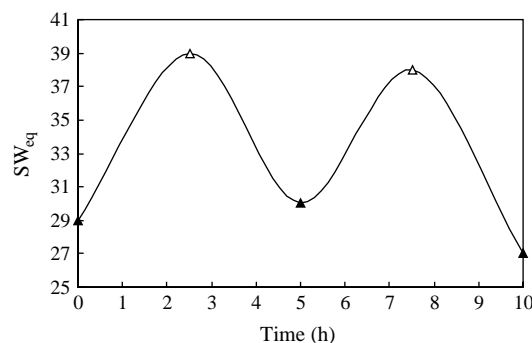


Fig. 8. Trend of the equilibrium swelling degree (SW_{eq}) versus swelling time (h) for sample of the semi-IPN6 hydrogel measured in varying pH buffer solutions between 3.01 (▲) and 7.03 (Δ) at intervals of 150 min at 37°C .

was performed in aqueous salt solutions (Fig. 9) and the result shows that the swelling capacity of PVP4 hydrogel is independent on the ionic strength and the equilibrium swelling degree of the semi-IPN4 hydrogel would drops only when ionic strength is very high ($I \geq 2.0\text{ M}$). Additionally, the experiment of ionic strength dependent swelling reversibility demonstrates that the semi-IPN4 hydrogel swollen in NaCl aqueous solution of $I = 0.2\text{ M}$ does not deswell in NaCl aqueous solution of $I = 4.0\text{ M}$ and vice versa. All of these mean that the semi-IPN hydrogel has no ionic strength-sensitivity. The reason is that the hydrogen bonds (between polymer and polymer as well as polymer and water) in the hydrogel are found to be not influenced by the small molecule salt as we have reported [17]. In other words, the presence of weak hydrated cation and weak hydrated anion would not influence hydrogen bond in the hydrogel [21]. Only when the concentration of NaCl (C_{NaCl}) is large enough, the dramatic increasing of osmotic pressure would inhibit the diffusion of water from the outer region to the inner of the hydrogel. Furthermore, the amount of non-freezable water in the hydrogel estimated by DSC measurement is enhanced for swollen hydrogel, this suggests that water molecule with stronger hydrogen bond in the hydrogel, which serve as non-freezable water [24–26], difficult diffuse to outer even upon the large osmotic pressure.

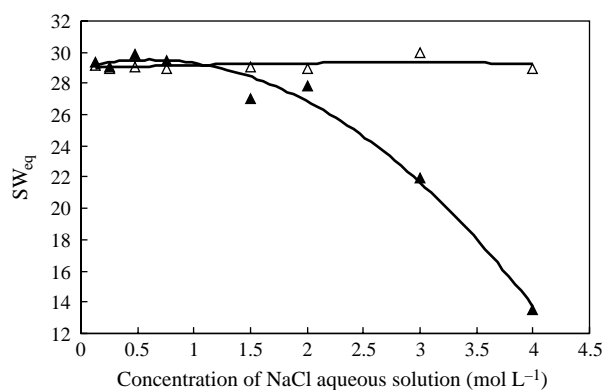


Fig. 9. Equilibrium swelling degree (SW_{eq}) versus concentration of NaCl aqueous solutions (C_{NaCl}) for the samples at 37°C . (▲) the semi-IPN4 ($R = n_{\text{PAA}}/n_{\text{PVP}} = 2:1$); (Δ) the PVP4 hydrogel.

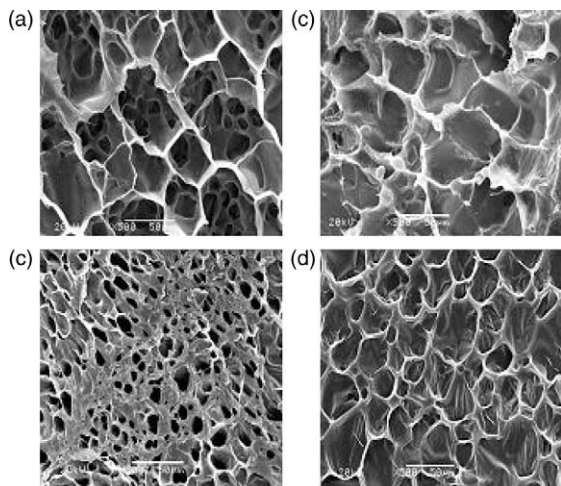


Fig. 10. The SEM micrographs of the hydrogels. (a) The PVP6 hydrogel swelled in buffer solutions of pH 2.07; (b) the PVP6 hydrogel swelled in buffer solutions of pH 10.98; (c) the semi-IPN6 hydrogel swelled in buffer solutions of pH 2.07; (d) the semi-IPN6 hydrogel swelled in buffer solutions of pH 10.98.

Our experiments demonstrate that the difference of molecular weight of PAA has little influence on the swelling properties of the semi-IPN hydrogel made of PVP4 bead and PAA with different molecular weight, respectively.

3.8. Morphology

Cross sectional morphology of dried PVP6 gels swollen completely in two buffer solutions of pH 2.07 and 10.98 are shown in Fig. 10(a) and (b), respectively. From these we can see that the two hydrogels have similar surface morphology with the larger three-dimensional pores corresponding to similar swelling capacity and very thin pores wall. Fig. 10(c) and (d) show the different morphologies of the semi-IPN6 hydrogels swollen completely in buffer solutions of pH 2.07 and 10.98, respectively. By comparison with the morphologies of PVP6 hydrogels, the semi-IPN hydrogel has two peculiar features: one is the difference of diameter of the macro pores of the semi-IPN hydrogels swollen in two type solutions. Fig. 10(c) shows the smaller three-dimensional net-hole due to the rather compact structure of the semi-IPN6 hydrogel swollen in buffer solution of pH 2.07; Fig. 10(d) shows the larger three-dimensional net-hole of the semi-IPN6 hydrogel swollen in buffer solution of pH 10.98. From these we would easy to understand why the semi-IPN6 hydrogel has different swelling capacities in two type solutions. The other feature is the stronger wall due to the rather orderly aggregates of polymer chain segments in the inner of the semi-IPN hydrogel, this is contrast to the results shown in Fig. 10(a) and (b).

4. Conclusions

Sequential novel spherically shaped pH-sensitivity semi-IPN hydrogels were synthesized by the combination with chemical crosslink and physical crosslink in this work. FTIR

and DSC measurements testify that the semi-IPN hydrogel is based on the formation of the hydrogen bond between the carbonyl group in the PVP network and the carboxylic acid group on the PAA chain. The swelling studies show that (1) the semi-IPN hydrogel has the stronger swelling capability in distilled water at 37 °C than neat PVP hydrogels due to the more hydrophilic component of PAA. (2) The semi-IPN hydrogel has outstanding pH-sensitivity property in the range of pH from 2.25 to 4.00 at 37 °C, this behavior is attributed to the formation of hydrogen bond between PVP and PAA which can be made or broken when the pH of surrounding changes. (3) The semi-IPN hydrogel is non-responsive to ionic strength over the range of concentration of inorganic salt investigated. This peculiar property is unlike the hydrogel based on the ionic interaction [27].

Acknowledgements

The financial support of Special Doctorial Program Funds of the Ministry of Education of China (contract grant number: 20030730013) is gratefully acknowledged.

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