Preparation and Characterization of a Novel pH-, Thermo-, and Ionic Strength-Responsive Hydrogels Based on Xanthan Gum–Poly(aspartic acid)

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ABSTRACT: A series of interpenetrating polymer networks (IPN) hydrogels with different compositions that based on xanthan gum (XG) and poly(aspartic acid) (PASP) were synthesized. The effects of various external surrounding stimuli, including pH, temperature, and ionic strength on XG–PASP hydrogels swelling properties were investigated. Chemical structural changes of the IPN hydrogels were characterized by Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), transmission electron microscopy (TEM), and swelling ratio measurement. The swelling process was found to be a Fickian diffusion and reached swelling equilibrium quickly. It was found that the feed composition of PASP was an important factor that affected the properties of IPN hydrogels. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 539–546, 2007

Key words: hydrogels; poly(aspartic acid); xanthan gum; stimuli-sensitive polymers; swelling

INTRODUCTION

Polymer blending of two or more constituents is an important method to obtain unusual and superior properties compared with those of homopolymers. Polymer blending can be achieved by physical, chemical, and radiant methods. Many researches focusing on multi-component polymers have been extensively carried out. Among them, blends between natural and chemical synthetic polymers have received particular attention because they can be applied as biomedical and biodegradable materials.[1–3]

The application of natural polymers such as proteins and polysaccharides for biocompatibility has also drawn many studies. Chemical or physical alteration methods have been carried out to overcome limitations that these materials exhibit, such as reactivity and process-ability. Particularly, interpenetrating polymer networks (IPN) attract much attention.[4,5] IPN is defined as a combination of two polymers that has the two following characteristics: first, one of the polymers must be synthesized or crosslinked in the immediate presence of the other, and second, the combination must provide the possibility of effectively producing advanced multi-component polymeric system with new property profiles.[6]

Poly(aspartic acid) (PASP) is a kind of biodegradable polyamino acid resin which contains many amide linkages as well as peptides. The PASP hydrogels are extensively used as scale inhibitors, corrosion inhibitors, pesticides, horticulture fertilizer, water-blocking tapes, absorbent pads, and numerous other applications because of their moisture absorption, antievaporation, water-holding, and biodegradability properties.[7,8]

Xanthan gum (XG) is a natural polysaccharide and an important industrial biopolymer. The high molecular weight polysaccharide has been extensively researched because of its property that allows it to be used as supplement of other natural and synthetic water-soluble gums.[9,10] The viscidity of the XG solution does not change much because of environmental condition changes such as pH, ionic strength, temperature, and the presence of enzyme. This unique property of XG is attributed to its particular molecular structure. The primary structure of this polysaccharide comprises cellulosic backbone (β-D-glucose residues) and a trisaccharide side chain of β-D-mannose–

β-D-glucuronic acid–α-D-mannose attached with alternate glucose residues of the main chain. The anionic character of this polymer is due to the presence of both glucuronic acid and pyruvic acid groups on the side chain and this trisaccharide side chain plays an important role in stabilizing the rigid structure of the XG molecule.[11] Because of its property in thickening aqueous solutions, as a dispersing agent, and as a stabilizer of emulsions and suspensions, XG is extensively used in pharmaceutical formulations, cosmetics, and agricultural products.[12,13]

IPN hydrogels, composed of XG and PASP by chemical crosslinking agent (1,6-hexamethylene diamine) using deionized water as dispersant in aqueous solution, were synthesized in this research (Fig. 1). A novel approach to form the IPN hydrogels presented here is the combination of stimuli responsive hydrolysable networks of the XG with the PASP. XG exhibits a stimuli-responsive behavior due to the large quantities of hydrophilic hydroxyl groups (—OH) on its chain. As far as we know, the XG–PASP IPN hydrogels have not been studied and reported so far.

In this research, our aim was to synthesize a series of XG–PASP IPN hydrogels by copolymerization through chemical crosslinking method. The swelling behavior and the stimuli-responsive properties in various pH, ionic strength, and temperature conditions were studied. In addition, the thermal property, copolymerization mechanism, and microorganism were also studied.

MATERIALS AND METHODS

Materials

XG with average molecular weight of 2×10^6 was purchased from Beijing Chemical Reagent Co. (China). All other materials were as described previously.[8]

Synthesis of XG–PASP hydrogels

The XG–PASP hydrogels were synthesized as described before,[8] with the exception that the XG was dissolved in deionized water and was added into beaker before PSI was crosslinked by 1,6-hexamethylene diamine. The specific composition of XG–PASP IPN hydrogels is showed in Table I.
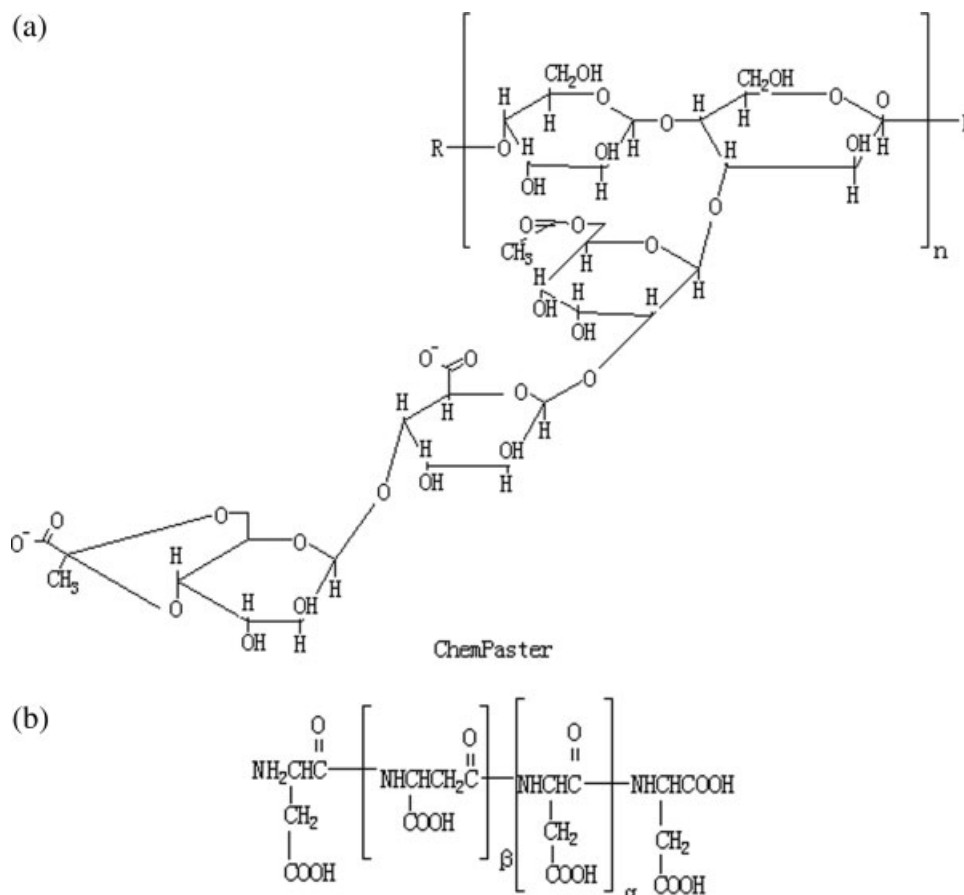

Figure 1   Chemical structure of XG (a) and (b) PASP.

TABLE I
Feed Composition of the XG–PASP Hydrogels[a]

Sample code	XG (wt %)	PASP (wt %)	Molar ratio of XG/PASP
IPN28	20	80	1/80
IPN46	40	60	1/30
IPN64	60	40	3/20
IPN82	80	20	2/5

[a] Concentration of cross-linker was 0.0333 mol/L.

Characterization of XG–PASP hydrogels

Swelling measurement

To measure the swelling ratio of the hydrogels, the dried sample was weighted and placed in a fabric bag. Then it was immersed in water or in various solutions with certain pH, temperature, and ionic strength. After the fabric bag was withdrawn from water or solution and the excessive solution was removed, the swollen sample was weighted at certain time intervals. Measurements were continued until the weight of hydrogels attained a constant value. The swelling ratio was calculated by the following equation:

$$\text{Swelling ratio} = \frac{W_s - W_d}{W_d} \qquad (1)$$

where W_s was the weight of the swollen hydrogel and W_d was the weight of the dried hydrogel, respectively. Triplicate data were recorded for each sample and an average value was calculated.

DSC analysis

Dynamic thermogravimetric analysis of the thermal behavior and melting point of sample (5 mg) was carried out using Perkin–Elmer Model Pyris-1 differential scanning calorimetry (DSC). The sample was cut into small pieces and put into an aluminum vessel. The experiment was performed at a heating rate of 10°C/min of nitrogen gas flow from room temperature to 300°C.

TEM analysis

The micrograph of hydrogels was studied using transmission electron microscopy (TEM) to characterize the physical crosslinked density and the connected channels. The sample was vacuum-dried, then coated with gold-palladium, and examined by the TEM (HITACHI H800).

FTIR analysis

The chemical structure of hydrogels was investigated using Fourier transform infrared spectroscopy (FT-IR). The sample was vacuum-dried and dispersed in

KBr. The spectra of the sample were taken at 4000–500 cm^{-1} wavelength by FTIR-60SXB spectrometer.

pH-sensitivity of hydrogels

The dried hydrogels sample was immersed in desired solutions with various pH values (2–13, ionic strength = 0.02 mol/L) at 25°C. The swelling measurement was carried out at certain time intervals until a constant weight was reached for each sample. The swelling ratio was determined using eq. (1).

Ionic-strength-sensitivity of hydrogels

The effect of ionic strength on swelling behavior of the IPN samples was investigated in solution with a total ionic strength ranging from 0.005 to 0.1 mol/L (0.005, 0.01, 0.02, 0.05, and 0.1 mol/L, respectively) at pH of 7.2. The calculated amount of NaCl was added to maintain the ion strength.

RESULTS AND DISCUSSION

Swelling kinetics

To study the swelling kinetics of the IPN hydrogels, three representative pH of 2.3, 7.8, and 12.4 were chosen. The pH of the solution was adjusted by hydrochloric acid and ammonia solution of 0.1 mol/L at 25°C. The ionic strength of the three solutions was maintained at 0.01 mol/L by adding a certain amount of NaCl. The swelling ratios were measured at time intervals.

The swelling ratio of four IPN hydrogels is shown in the Figure 2. The swelling ratio increases fast at early stage; then the swelling ratio no longer changes and approaches the swelling equilibrium. In addition, the pH has an evident influence on swelling ratio: when the pH was too low or too high, the swelling ratio is smaller compared with that at a pH of 7.8. The reason is that when the pH moves away from 7, the ionization of hydrogels becomes the limiting step. When a gel is initially at dry state, the swelling process occurs after the solvent penetrates into the network of gel. For an ionizable gel, the ionization rate of charge groups is blocked by charges in solvent. So if the pH is higher or lower than 7, the swelling ratio of the hydrogels tends to decrease.

The method of Franson and Peppas[14] to research the kinetics of hydrogels swelling ratio is employed here. A parameter R is used here to define the swelling ratio:

$$R = \frac{W_s}{W_d}, \qquad (2)$$

where W_s is the weight of swollen gel and W_d is the weight of the dry gel. The analysis of swelling process fits the following empirical equation:
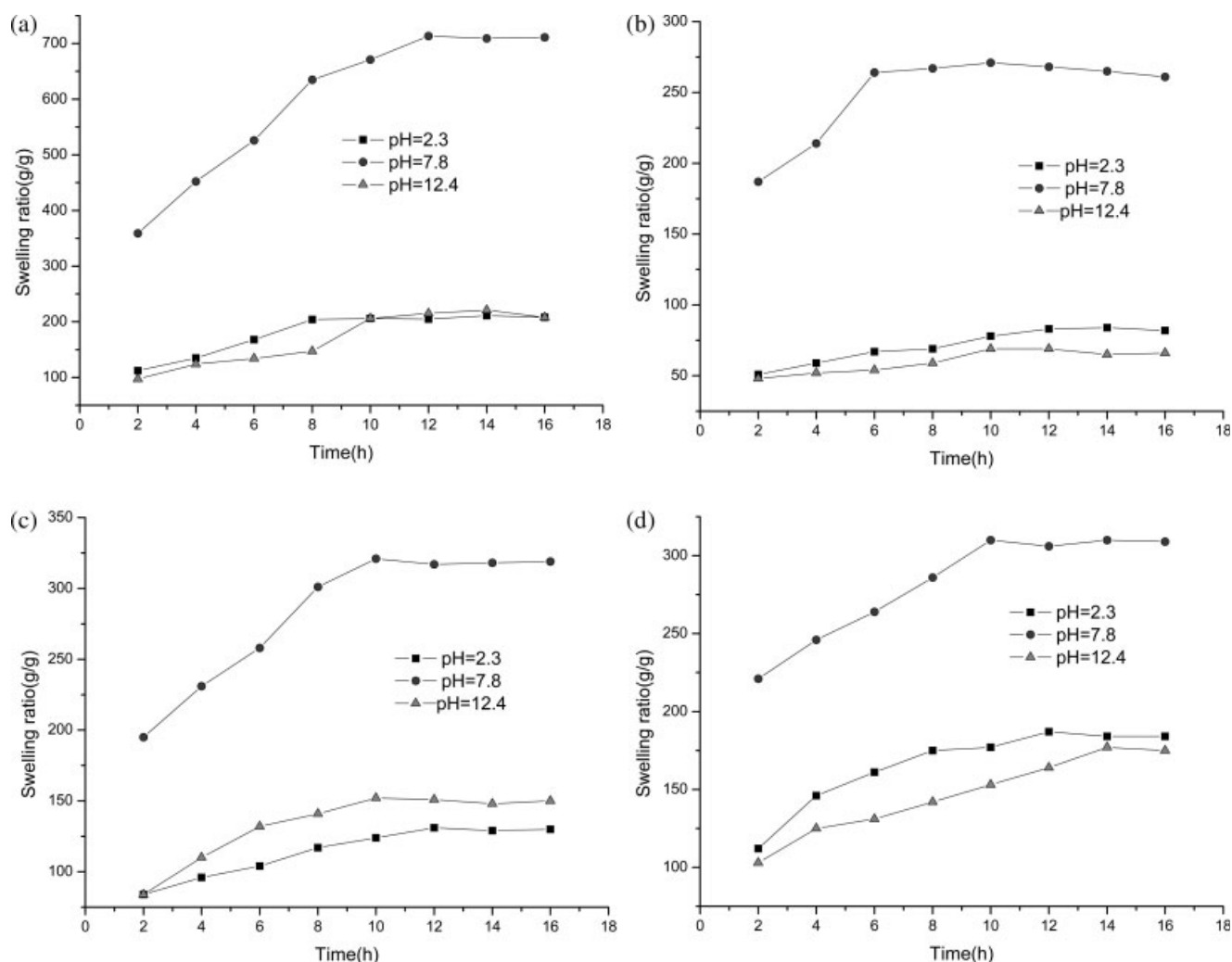
Figure 2 The swelling kinetic of IPN hydrogels at ionic strength 0.01 mol/L at 25°C (a) IPN28, (b) IPN46, (c) IPN64, and (d) IPN82.

$$R = kt^n, \qquad (3)$$

where k is an empirical swelling rate constant and n is an empirical number called kinetic exponent. Equation (3) is a phenomenological law in which n is related to the type of sorption of the gels. The n and k values are determined from the initial portion of log–log plots of R versus log time (values of t to be expressed in seconds), the slope being the value of n. If $n \leq 0.5$ it is a case of Fickian diffusion where diffusion is rate-limiting step, whereas $0.5 < n < 1$ it is a case of non-Fickian diffusion. From the linear fit results in Table II, the IPN hydrogels swelling process is a Fickian diffusion because $n < 0.5$.

Particularly, a simple mathematical model is expressed to simulate swelling kinetics of hydrogels (pH $= 7.8$) on basis of Michaelis–Menten (M–M) equation:

$$S = \frac{S_{max}T}{K_m + T}, \qquad (4)$$

where S_{max} is the maximum swelling ratio of hydrogels, T is the time swelling ratio is measured, and K_m is the Michaelis–Menten constant for the hydrogels swel-

TABLE II
Estimated Values of k, n, and Regression Coefficient for the Swelling Ratio of IPN Hydrogels at Different pH from Eq. (2)

Sample code	pH	n	k	r^2
IPN28	2.3	0.3369	0.9791	0.8875
	7.8	0.2474	1.7776	0.9474
	12.4	0.1802	1.5371	0.9077
IPN46	2.3	0.2539	0.7988	0.9711
	7.8	0.1829	1.6406	0.8380
	12.4	0.1835	1.0181	0.8571
IPN64	2.3	0.2311	1.0986	0.9718
	7.8	0.2593	1.3732	0.9435
	12.4	0.2854	0.9385	0.9132
IPN82	2.3	0.2391	1.2261	0.9296
	7.8	0.1784	1.7903	0.9592
	12.4	0.2169	1.0765	0.9792

TABLE III
Estimated Value of S_{max}, K_m, and Regression Coefficient for the Swelling Ratio of IPN Hydrogels at pH of 7.8 from Eq. (5)

Sample code	S_{max}	K_m	r^2	S'_{max}
IPN28	833	1.8331	0.9945	782
IPN46	294	1.2054	0.9307	271
IPN64	357	1.7493	0.9445	321
IPN82	323	1.0336	0.9201	310

ling process. To determine the kinetics parameters of K_m and S_{max}, eq. (4) is rearranged to obtain Lineweaver–Burk equation as follows:

$$\frac{1}{S} = \frac{K_m}{S_{max}}\frac{1}{T} + \frac{1}{S_{max}} \quad (5)$$

A straight line may be obtained on Lineweaver–Burk plot and from intercepts on both the axis, S_{max} and K_m are determined.

From the simulative results in Table III, the value of S_{max} is close to the S'_{max} (measured by experiment), which indicates that the M–M kinetic equation can be used to model the swelling process of the IPN hydrogels.

pH-sensitivity of IPN hydrogels

A number of factors that influence the swelling ratio of ionic hydrogels including the property of gels and swelling medium. The results of pH-dependent equilibrium swelling ratio in the solution between 2 and 10 at the ionic strength of 0.02 mol/L are shown in the Figure 3. The 0.1 moL/L hydrochloric acid and ammonia solutions were used to adjust the pH and certain amount of NaCl was added to maintain ionic strength. As can be seen from the Figure 3, the maxi-
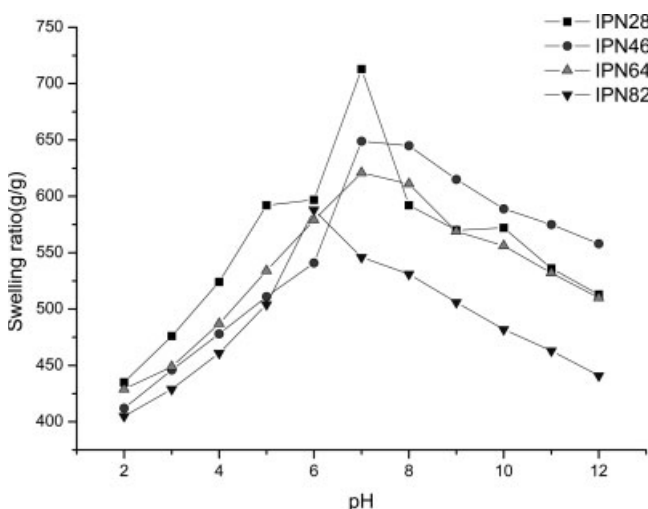
mum swelling ratio is attained when the solution pH is 7 except for IPN82. There are three factors that influence swelling equilibrium of electrolyte networks (1): the net osmotic pressure of the network followed by mobile counter ions surrounding fixed charge groups (2); free energy of mixing of network chains with solvent, and (3) elastic retractile response of the network.[15] The equilibrium swelling ratio is obtained when the three factors reach equilibrium. The maximal swelling ratio from IPN28 to IPN82 decreases from 713 to 518 g/g, so the swelling capacity decreases with the XG component increasing.

Effect of ionic strength on swelling ratio

The ionic strength characteristics of the IPN hydrogels were investigated by measuring swelling ratio over ionic strength ranging from 0.0025 to 0.1 mol/L at pH of 7.2. Considering that the hydrogel is a polyelectrolyte, it means the swelling ratio would decrease as ionic strength increases. As shown in Figure 4, the swelling ratio increases with increasing ionic strength up to 0.005 mol/L for IPN28, 0.01 mol/L for IPN46 and IPN 82, and 0.02 mol/L for IPN64, whereas above this value it decreases with further increase in ionic strength. The result demonstrates that the hydrogel changes its swelling property when the ionic strength is changed. During the swelling process, the anion charge groups on hydrogels are first ionized. Then the surface swells due to the electrostatic repulsion between adjacent ionized groups. The dissociation of hydrolgel networks may be enhanced as ionic strength increases up to a fixed value; however, with ionic strength continuously increasing, the anionic groups on the hydrogels are screened by Na$^+$ ions. So the swelling ratio decreases

Figure 3 Influence of pH on the swelling ratio of IPN hydrogels under 0.02 mol/L ionic strength at 25°C.
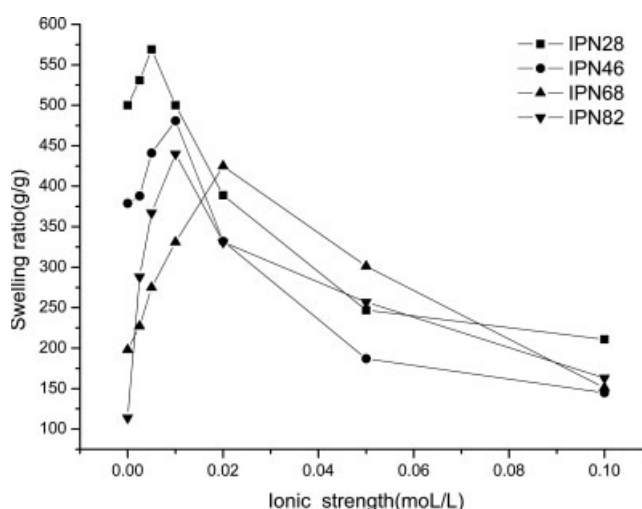

Figure 4 Effect of ionic of strength on the swelling ratio of IPN hydrogels at temperature of 25°C, pH of 7.2.

with the further increase in ionic strength. Another possible contribution to this phenomenon is that Cl⁻ presenting in outside solution swamps the negatively charged carboxylic groups.

Effect of temperature on swelling ratio

Stepwise swelling ratio was measured in water with temperature alternating between 25 and 40°C as shown in the Figure 5. The swelling ratio was measured every 1 h, as temperature was switched every 2 h. The swelling process is repeatable as temperature changes. IPN28 hydrogel responds to temperature changes more rapidly than other IPN hydrogels.

FTIR characterization of IPN hydrogel

The FTIR spectra of PASP, XG, and IPN28 are shown in the Figure 6. The peaks at around 1715 and 1658 cm^{-1} in the PASP are assigned to the terminal ester carbonyl bond and imine bond, respectively. In the case of the XG, new peaks appear at around 3432 and 1054 cm^{-1}, which could be attributed to the terminal hydroxyl group on trisaccharide chain and ether group that combined to saccharide chain. The successful incorporation of carboxyl group onto the XG molecules is demonstrated by the presence of a carboxylic band from the carbonyl stretching of XG–PASP at around 1719 cm^{-1}, indicating the activated carboxyl groups could react with hydroxyl groups to form ester linkages.
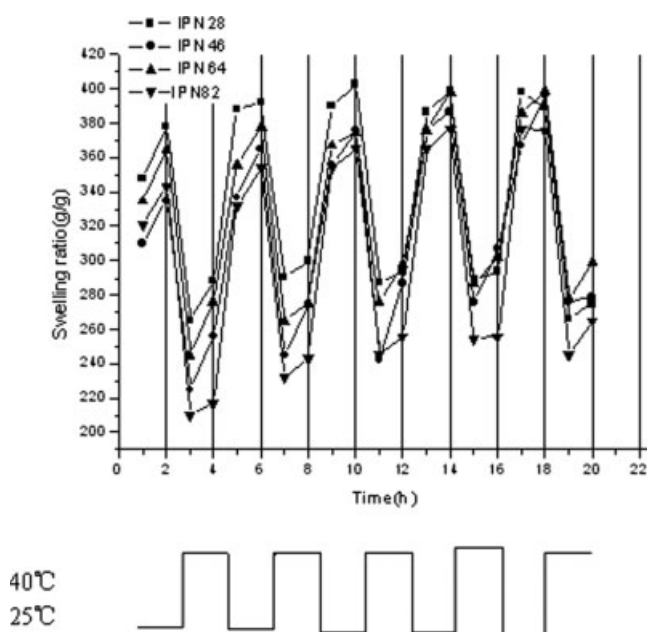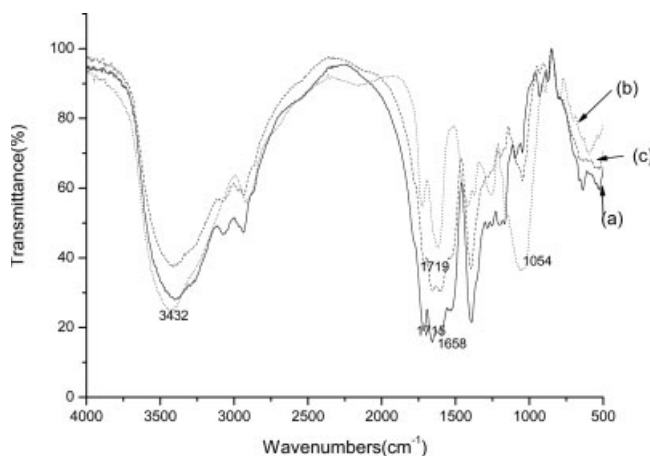

Figure 6 FTIR spectra of (a) PASP, (b) XG, and (c) IPN28.

Thermal characterization

The results of DSC analyses of the IPN hydrogels are shown in Figure 7. XG reveals a relative sharp melting endothermic peak at 93°C, whereas weaker and broader melting peaks for other IPN hydrogels are observed. The depression of the melting temperature and the peak broadening indicate the ordered association of the XG molecules is decreased by the presence of PASP. When the chemical crosslinking reaction took place in the solution, the reorientation of XG segments was limited, resulting in a further decrease in the crystallinity of IPN hydrogels compared with the XG. Subsequently, the melting temperature of the XG segments in the IPN hydrogels is lower than that of the linear XG. It is well known that the melting temperature depression is caused by morphological and chemical modifications. The morphological changes involve the thickness of crys-
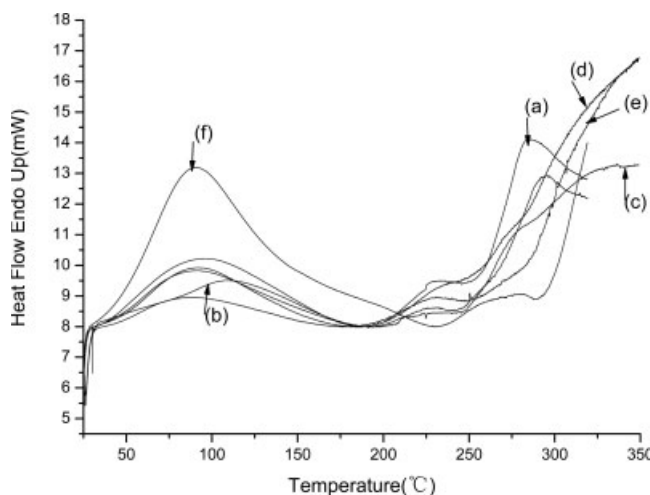

Figure 5 Temperature-responsiveness swelling ratio of the IPN hydrogels at pH of 7.0.

Figure 7 DSC melting endotherms of dry products: (a) PASP, (b) IPN28, (c) IPN46, (d) IPN64, (e) IPN82, and (f) XG.
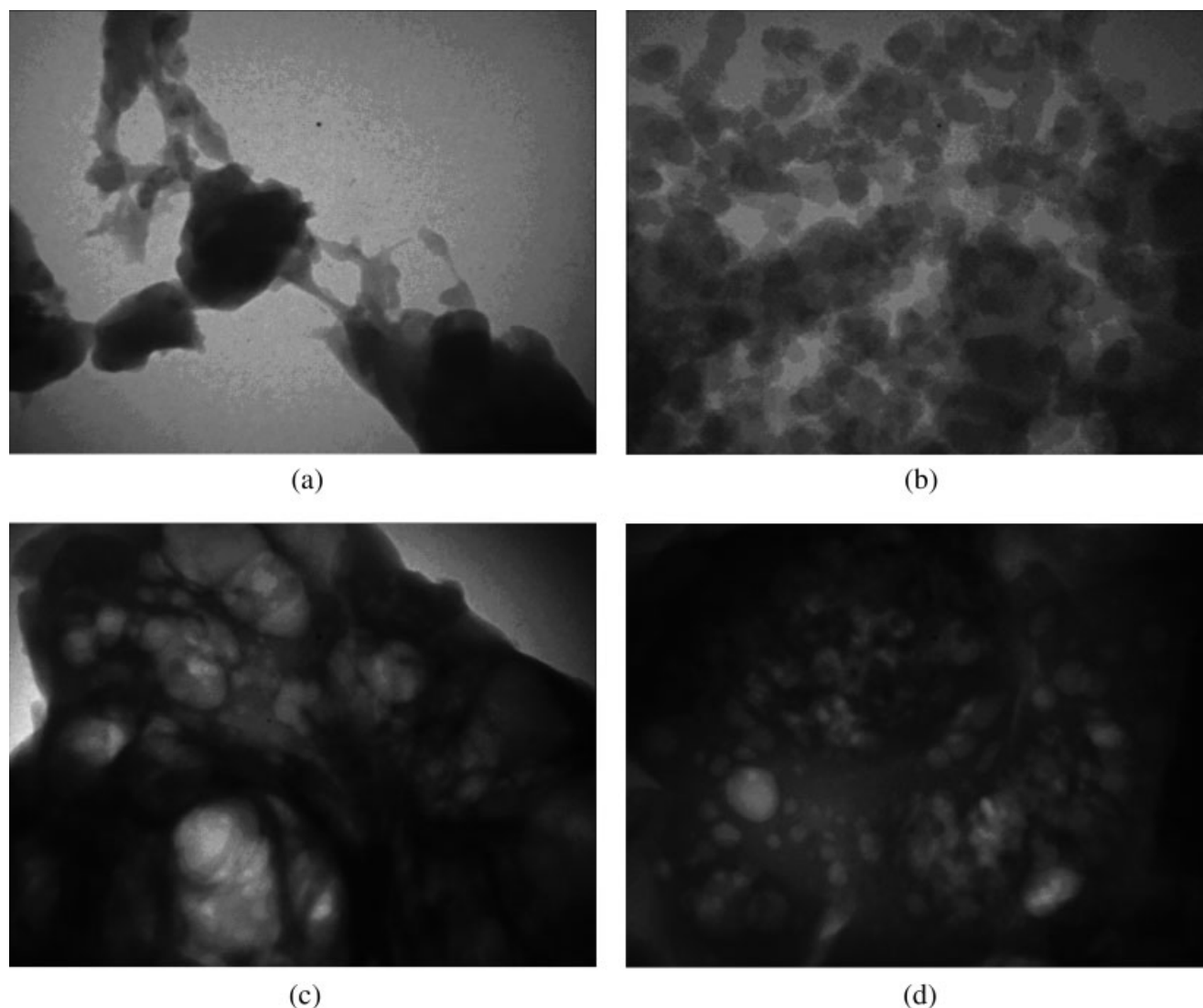
Figure 8 The TEM micrographs of hydrogels: (a) XG, (b) PASP, (c) IPN28, and (d) IPN46; (scale bar = 250 nm).

tallites and degree of crystallinity. Chemical changes are results of the crosslinking and of branching due to the grafting of the crosslinking agent.[16] Thus, it would be seen that PASP influences the thermal behavior of XG and it could be regarded that the XG is grafted to crosslinked PASP. Figure 7 shows the endothermic peak decreases rapidly for samples containing over 20 wt % PASP. The melting temperature depression and the peak broadening indicate that the XG molecules are constrained by the entanglement of the two polymers.

TEM morphological observation

Figure 8(a–d) show the network morphology of the dried IPN hydrogels synthesized in this study. The different feed compositions would evidently affect the inner structure especially for network size and number. It could be seen that the ordered micro-

structure is constrained by the including of PASP. The crosslinking sections of hydrogels are with more channel density and lead the XG molecules reorientation, which induce the depression of melting temperature and broadening peak [Fig. 7(c,d)].

CONCLUSIONS

A series of IPN hydrogels composed of the XG and PASP with various feed compositions by crosslinking agent 1,6-hexamethylene diamine were synthesized and their response to temperature, ionic strength, and pH was characterized. The swelling process kinetics of hydrogels tended to be a Fickian diffusion. IPN hydrogels had maximum swelling ratio when the pH of solution was $\sim$ 7; ionic strength and temperature also had influence on the swelling ratio. The spectra of FT-IR confirmed the copolymerization of XG–PASP. DSC revealed the melting tem-

perature of hydrogels decreased with increasing component of the PASP. TEM indicated that the feed composition influenced the network size and density. The IPN28 sample showed the highest thermo-, ionic strength-, and pH-sensitivity and swelling property.

References

1. Park, J. S.; Park, J. W.; Ruckenstein, E. Polymer 2001, 42, 4271.
2. Carenza, M. Radiat Phys Chem 1992, 39, 485.
3. Cascone, M. G.; Barbani, N.; Cristallini, C.; Giusti, P.; Ciardelli, G.; Lazzeri, L. J Biomater Sci Polym Ed 2001, 12, 267.
4. Seung, J. L.; Seong, S. K.; Young, M. L. Carbohydr Polym 2000, 41, 197.
5. Hee, K. J.; So, Y. K.; Young, M. L. Polymer 2001, 42, 6851.
6. Sperling, L. H. Interpenetrating Polymer Networks and Related Materials; Plenum: New York, 1981.
7. Tomida, M.; Yabe, M.; Arakawa, Y. Polymer 1997, 38, 2791.
8. Jun, Y.; Li, F.; Tianwei, T. J Appl Polym Sci 2006, 102, 550.
9. Bryant, C. M.; McClements, D. J. Food Hydrocolloids 2000, 14, 383.
10. Veiga-Santosa, P.; Oliveirab, L. M.; Ceredac, M. P.; Alvesd, A. J.; Scamparini, A. R. P. Food Hydrocolloids 2005, 19, 341.
11. Barbara, K. Polym Degrad Stab 1998, 59, 81.
12. Montri, C.; Manop, S. Carbohydr Polym 2005, 61, 288.
13. Miladinov, V. D.; Hanna, M. A. Ind Crop Prod 1996, 5, 183.
14. Franson, N. M.; Peppas, N. A. J Appl Polym Sci 1983, 28, 1299.
15. Siegel, R.; Firestone, B. Macromolecules 1998, 21, 3254.
16. Choong-Kyun, Y.; Kew-Ho, L. J Membr Sci 1996, 109, 257.