

Study on the Synthesis, Characterization, and Sorption of Some Metal Ions on Gelatin- and Acrylamide-Based Hydrogels

Ghanshyam S. Chauhan, Suresh Kumar, Anita Kumari, Rakesh Sharma

Department of Chemistry, Himachal Pradesh University, Shimla 171 005, India

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ABSTRACT: Graft copolymers and networks of gelatin were synthesized with three acrylamides (acrylamide, 2-acrylamido-2-methyl-1-propanesulfonic acid, and *N*-iso-propylacrylamide) by using a redox initiator system consisting of ammonium peroxydisulfate–ferrous ammonium sulfate in either the absence or the presence of a crosslinker (*N,N*-methylene bisacrylamide) at two temperatures. Characterization of synthesized polymers was studied by FTIR and thermal studies to investigate evidence of grafting or interpenetrating network formation and to investigate the effect of reaction conditions and crosslinker concentration on the properties of synthesized polymers. Detailed investigation into water-uptake properties of these hydrogels was carried out as a function of time, temperature, and pH. The inherent

properties of the monomer incorporated onto gelatin collectively act as determinant of the water-absorption behavior of the hydrogels. Sorption of Fe^{+2} , Cr^{+6} , and Cu^{+2} ions from their aqueous solutions was also studied on select hydrogels, where it was observed that metal ions are sorbed by effective partitioning between hydrogels and solution phase and apart from the nature of metal ions, and structural aspects of hydrogels also determine the quantum of metal ion uptake. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3856–3871, 2003

Key words: gelation; graft copolymers; hydrogels; networks; water uptake

INTRODUCTION

Gelatin has been modified through grafting or crosslinking reactions with single or binary monomers by many investigators to obtain hydrogels for various applications including drug delivery.¹ Use of a persulfate redox system has been reported for grafting of hydrophobic monomers as methyl and ethyl acrylate^{2,3} and methyl methacrylate⁴ onto gelatin. Misra et al.^{5,6} reported grafting of methyl acrylate and methyl and ethyl acrylate onto gelatin in the presence of Ce^{4+} ions. Otani et al.⁷ reported crosslinking of gelatin with various polycarboxylic acids by the use of water-soluble carbodiimide and adhesion properties of resulting hydrogels to mouse skin were evaluated. Hydrogels have also been prepared by the graft copolymerization of 2-hydroxyethyl methacrylate/butyl methacrylate mixtures onto gelatin using Ce^{4+} ions as initiator simultaneously with ethylene glycol dimethacrylate as crosslinker. The equilibrium water content of these hydrogels was reported to increase

with pH and the percentage of hydrophilic monomer component of the hydrogel.⁸ Hydrogels of gelatin with acrylamide (AAm) and methacrylamide and crosslinked with 1,4-diacryloyl piperazine or 1,13-diacryloyl-4,7,10-trioxa-1,13-decandiamine by radical polymerization have been reported as strong glassy hydrogels termed as hydroglasses.⁹ *In situ* polymerization of AAm with methyl acrylate and methyl methacrylate in an aqueous system solution followed by subsequent crosslinking with glutaraldehyde yields interpenetrating hydrogel networks with high mechanical strength, elasticity, and thermal stability where the swelling characteristics of hydrogels could be manipulated by variation of the gelatin and AAm molar ratio in the feed.¹⁰ Chun and Kim¹¹ reported the use of gelatin and *N*-iso-propylacrylamide (*N*-i-PAAm)-based composite membrane for the thermally actuated permeation of 4-acetamidophen. However, there is only scanty information on use of gelatin hydrogels for metal ion sorption.

In the present study graft copolymers and hydrogels of gelatin were synthesized with monomers bearing amide or modified amide functionalities by graft copolymerization and network formation. Hydrogels were synthesized by using a redox system consisting of ammonium peroxydisulfate–ferrous ammonium sulfate (APS–FAS) in either the presence or the absence of crosslinker, *N,N*-methylene bisacrylamide (*N,N*-

Correspondence to: G. Chauhan (ghanshyam_in2000@yahoo.com).

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TABLE I
Effect of Reaction Temperature on $P_{\text{add-on}}$ of Different Acrylamides

Reaction temperature (°C)	$\%P_{\text{add-on}}$
Grafting of AAm	
25	106.55
50	56.95
60	107.35
70	88.25
80	55.70
Grafting of AAmPSA ^a	
25	267.70
60	258.50
Grafting of N-i-PAAm ^a	
25	60.80
60	81.50

^a Backbone = 2.0 g, APS:FAS (2.185:0.255 mM), monomers (28.137 mM), water = 10 mL, and time = 0.5 h.

MBAAm). The monomers incorporated onto gelatin are amenable to further functionalization by simple polymer analogous reactions. These also possess a wide spectrum of physical properties, ranging on the one hand from a polyelectrolyte nature to the highly hydrophilic nature of 2-acrylamido-2-methyl-1-propanesulfonic acid (AAmPSA) and thermosensitivity of the less hydrophilic N-i-PAAm. Such a wide range of properties is expected to result in a broad spectrum of end uses of these hydrogels. In continuation of our earlier work on the use of hydrogels for remediation of metal ions, select hydrogels were used as metal ion sorbents to explore and define their uses in pollution control, metal ion sorption, and enrichment technologies. The possible use of candidate hydrogels will also be explored for use as detoxifying agents and also in loading of some metal ions of medicinal importance. Apart from the activity of acrylamides to interact with metal ions, the potential of the present work also arises from the fact that the amino acids of gelatin have active groups that can also interact with metal ions. No such applications of gelatin- and acrylamide-based hydrogels have been reported to date. To investigate the effect of synthetic conditions and crosslinker concentration on the properties of hydrogels, characterization was determined by FTIR and both thermal and water-uptake studies to obtain evidence of grafting or interpenetrating network (IPN) formation.

EXPERIMENTAL

Materials and methods

Acrylamide (AAm; S. D. Fine Chemicals, Mumbai, India), 2-acrylamido-2-methyl-1-propanesulfonic acid (AAmPSA; Aldrich Chemical, Milwaukee, WI), *N*-isopropylacrylamide (N-i-PAAm; Aldrich Chemical),

N,N-methylene bisacrylamide (*N,N*-MBAAm; CDH, Mumbai, India), gelatin (Qualigens, Mumbai, India), ammonium persulfate (APS; Glaxo, Mumbai, India), and ferrous ammonium sulfate (FAS; Sarabhai M. Chemicals, Vadodara, India) were used as received.

Synthesis of hydrogels by graft copolymerization

Graft copolymers were synthesized by variations of different reaction conditions following the reaction scheme as detailed for a set of reactions. Gelatin (2.0 g) was dissolved in distilled water (20.0 mL) along with a known concentration of initiator APS : FAS (2.185 : 0.255 mM) and AAm (28.137 mM) and these were reacted for 0.5 h at room temperature. Using these reaction conditions graft copolymers were also synthesized at 50, 60, 70, and 80°C to study the effect of homogenization of reaction mixtures and energy requirements of dissociation of initiator. Graft copolymers of gelatin with

TABLE II
Effect of Crosslinker on $\%P_{\text{add-on}}$ of Gelatin and Different Acrylamides^a

Sample no.	Crosslinker (mM)	$\%P_{\text{add-on}}$
Crosslinking reactions of gelatin and AAm ^a		
Reaction temperature = 25°C		
1	0.324	64.00
2	0.434	88.60
3	0.648	139.20
4	1.297	126.65
Reaction temperature = 60°C		
1	0.324	102.95
2	0.434	73.55
3	0.648	94.03
4	1.297	108.25
Crosslinking reactions of gelatin and AAmPSA ^a		
Reaction temperature = 25°C		
1	1.297	229.80
2	1.945	339.45
3	2.594	367.80
4	3.243	365.15
Reaction temperature = 60°C		
1	1.297	170.00
2	1.945	195.50
3	2.594	190.60
4	3.243	191.00
Crosslinking reactions of gelatin and N-i-PAAm ^a		
Reaction temperature = 25°C		
1	0.324	157.10
2	0.434	172.10
3	0.648	168.80
4	1.297	177.20
Reaction temperature = 60°C		
1	0.324	174.40
2	0.434	158.00
3	0.648	169.00
4	1.297	187.00

^a Backbone = 2.0 g, APS:FAS (2.185:0.255 mM), monomers (28.137 mM), water = 10 mL, and time = 0.5 h.

TABLE III
Analysis of FTIR Spectra of Networks

Polymer	[<i>N,N</i> -MBAAm] (mM)	Reaction temperature (°C)	Characteristic peaks		Remarks
			(cm ⁻¹)	% absorbance	
Gelatin			2926.5	77.94	C—H stretching
			1654.5	88.16	CO stretching of CONH ₂
			1402.8	65.12	C—N stretching
Gelatin- <i>cl</i> -poly(AAm)	0.648	60	1654.5	87.12	CO stretching of CONH ₂
Gelatin- <i>cl</i> -poly(AAm)	0.324	25	1654.5	77.82	CO stretching of CONH ₂
Gelatin- <i>cl</i> -poly(AAmPSA)	1.945	60	3437.7	88.28	—NH stretching
			1650.5	84.67	CO stretching of CONH ₂
			1300.7	58.88	S=O stretching in SO ₃ H
			1399.3	75.49	C—N stretching
			3263.5	83.17	—NH polymeric association
Gelatin- <i>cl</i> -poly(N- <i>i</i> -PAAm)	0.324	60	2976.2	73.25	C—H stretching
			1643.5	86.56	CO stretching of CONH ₂
			1401.0	75.18	C—N stretching
			1129.8	85.25	Skeletal isopropyl group
			3242.2	82.54	—NH stretching
Gelatin- <i>cl</i> -poly(N- <i>i</i> -PAAm)	0.648	60	2977.4	73.45	C—H stretching
			1659.5	83.34	CO stretching of CONH ₂
			1399.8	73.44	C—N stretching
			1129.9	81.21	Skeletal isopropyl group

AAmPSA and N-*i*-PAAm were also synthesized following the same scheme. A detailed reaction outline and results are presented in Table I.

Synthesis of hydrogels by crosslinking reactions

Crosslinked hydrogels of gelatin with all three monomers in different experiments were synthesized under the same reaction conditions of concentrations of initiator and monomer, and reaction time; the volume of water and gelatin at two temperatures as described above and only the concentration of crosslinker (*N,N*-MBAAm) were varied over a range of four concentrations.

Separation of hydrogels

In the case of hydrogels synthesized in the absence of crosslinker, homopolymer was separated from the reaction mixture by precipitation with acetone and dried under vacuum. Xerogels (dried gels) were resolubilized in water, lyophilized with acetone, and dried again. Xerogels were repeatedly treated with water and stirred for 1 h and also stirred in methanol to remove any sol fraction, whereas in the case of hydrogels synthesized with crosslinker, the product self-insolubilized in the process of crosslinking was separated by filtration and, then without drying, was treated with water and methanol as detailed above to obtain a constant weight. These gels were treated with acetone and then dried under vacuum. Incorporation of monomer (and crosslinker) onto gelatin has been

defined as percentage add-on ($\%P_{\text{add-on}}$) and is expressed as

$$\%P_{\text{add-on}} = \frac{\text{Weight of xerogel} - \text{weight of polymer backbone}}{\text{Weight of polymer backbone}} \times 100$$

FTIR and thermogravimetric studies

FTIR spectra of gelatin and its hydrogels were recorded on KBr pellets on a Perkin–Elmer apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were studied on a TG–DT simultaneous analyzer (Shimadzu, Kyoto, Japan) in air after flushing with N₂ stream at a heating rate of 10°C/min.

Water uptake by hydrogels

All graft copolymers and networks synthesized were subjected to water-uptake studies. A known weight of polymer (0.1 g) was swollen in water and the percentage water uptake (P_u) was measured at intervals of 2, 4, 5, 8, and 24 h at 25°C temperature in a controlled water bath. The above process was repeated to study the effect of temperature on swelling at 32, 37, and 42°C. Swelling was also studied as a function of pH (4.0 and 9.2) and the effect of

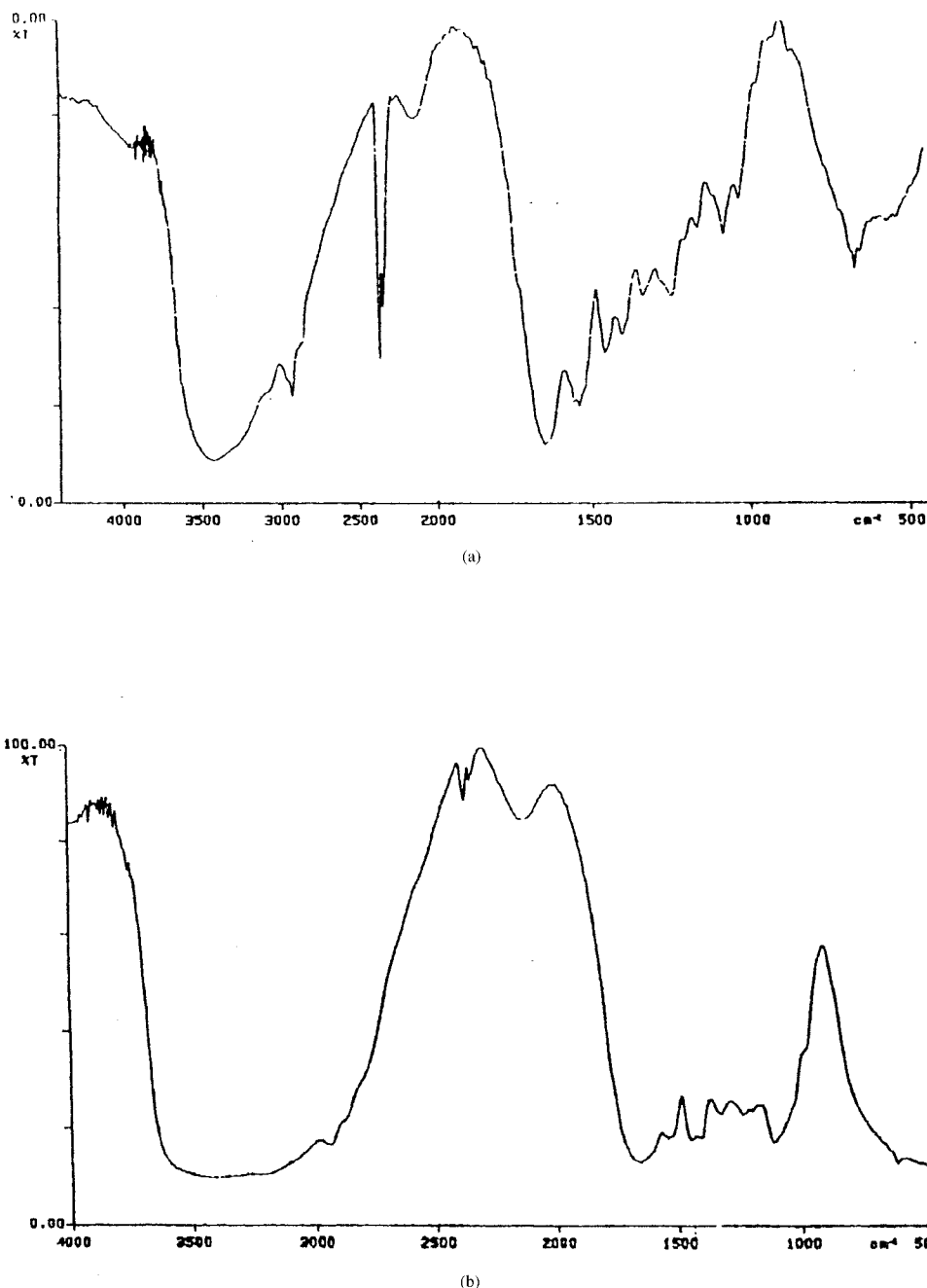


Figure 1 (a) FTIR spectrum of pure gelatin; (b) FTIR spectrum of gelatin-*cl*-poly(AAm) synthesized at 25°C. Concentration of crosslinker, 0.648 mM; (c) FTIR spectrum of gelatin-*cl*-poly(AAmPSA) synthesized at 25°C. Concentration of crosslinker, 2.594 mM; (d) FTIR spectrum of gelatin-*cl*-poly(N-*i*-PAAm) synthesized at 25°C. Concentration of crosslinker, 0.434 mM.

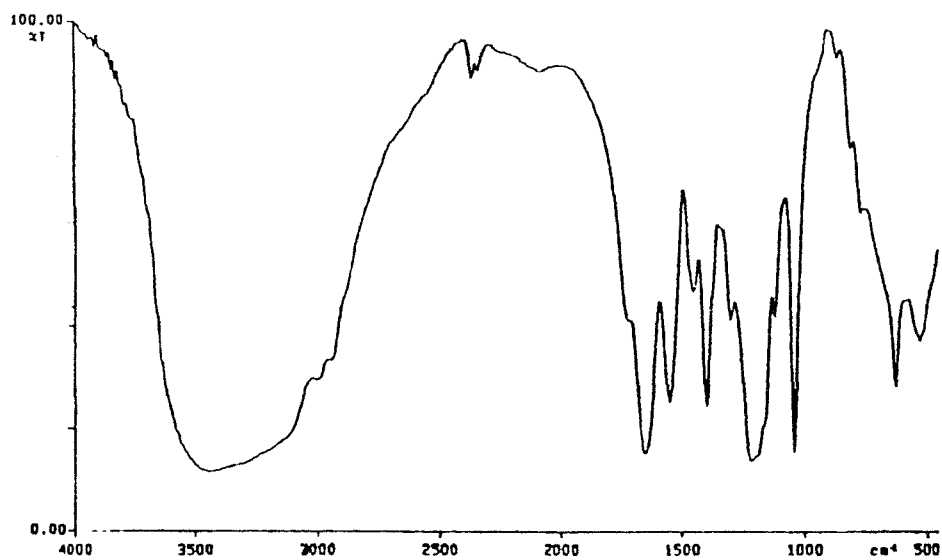
partial hydrolysis of hydrogels with 0.5N NaOH at 25°C for 24 h. Percentage water uptake (P_u) was calculated as

$$\% \text{ Water uptake } (P_u) = \frac{W_w - W_d}{W_d} \times 100$$

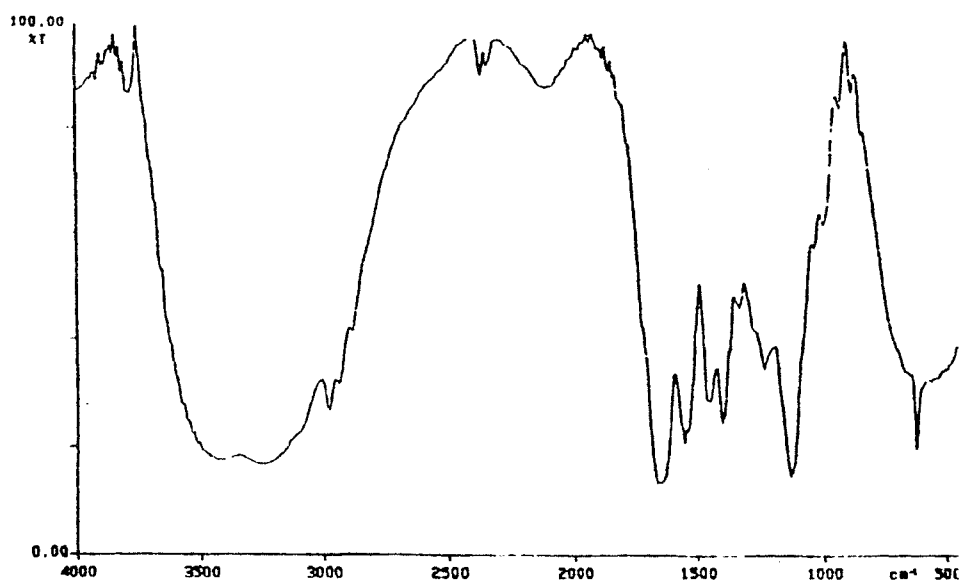
where W_w and W_d are the weights of swollen hydrogels and xerogels, respectively.

Metal ion sorption studies

Following a method reported earlier, sorption of some metal ions on select hydrogels was carried out.^{12,13} Polymers were immersed in 20.00 mL metal ion solutions of known strength for 24 h. Filtrates of the solutions were analyzed for concentration of rejected ions on a DR 2010 spectrophotometer (Hach Co., Loveland, CO) with maximum limit of ion strength of 5.0, 3.0, and 0.6 mg/L of solution, re-



(c)



(d)

Figure 1 (Continued from the previous page)

spectively, of Cu^{+2} , Fe^{+2} , and Cr^{+6} by using its standard pillow reagents.

RESULTS AND DISCUSSION

Kinetics of grafting reactions

Kinetics of grafting reactions of AAm onto gelatin in the absence of crosslinker was studied at constant conditions of initiator and monomer concentrations, reaction time, and amount of water, whereas only the

temperature was varied in the range 25, 50, 60, 70, and 80°C (Table I). A maximum graft yield of 107.35 was observed at 60°C and $P_{\text{add-on}}$ values of 22.40, 56.95, 107.35, 88.25, and 55.70 were recorded for the whole range of temperature, which decreased after 60°C because of the predominance of homopolymerization and side reactions leading to wastage of monomer. At higher temperatures denaturation of gelatin may also affect the graft yield. In the case of AAmPSA the $P_{\text{add-on}}$ value is higher at lower reaction temperature

TABLE IV
Thermal Behavior of Gelatin and Its Networks

Sample no.	Polymer	Crosslinker (mM)	Reaction temperature	Degradation stage (°C)	Thermogravimetric data			
					Wt. loss (%)	Residue (%)	IDT (°C)	FDT (°C)
1	Gelatin	—	—	251.8–456.7 456.7–592.6	53.57 31.42	0.73	251.8	592.6
2	Gelatin-g-poly(AAmPSA)	—	25	193.6–429.9	70.31	18.75	193.6	429.9
3	Gelatin-cl-poly(AAmPSA)	2.594	25	137.2–197.2 197.2–432.6	37.00 30.00	33.00	197.2	432.6

and there is some decrease at higher temperature. Such high graft yield can be ascribed to the higher solubility of monomer even at lower temperature and

its polyelectrolyte behavior, which retard grafting at higher temperature. Trends in graft yield for N-i-PAAm are different, given that higher yield has been

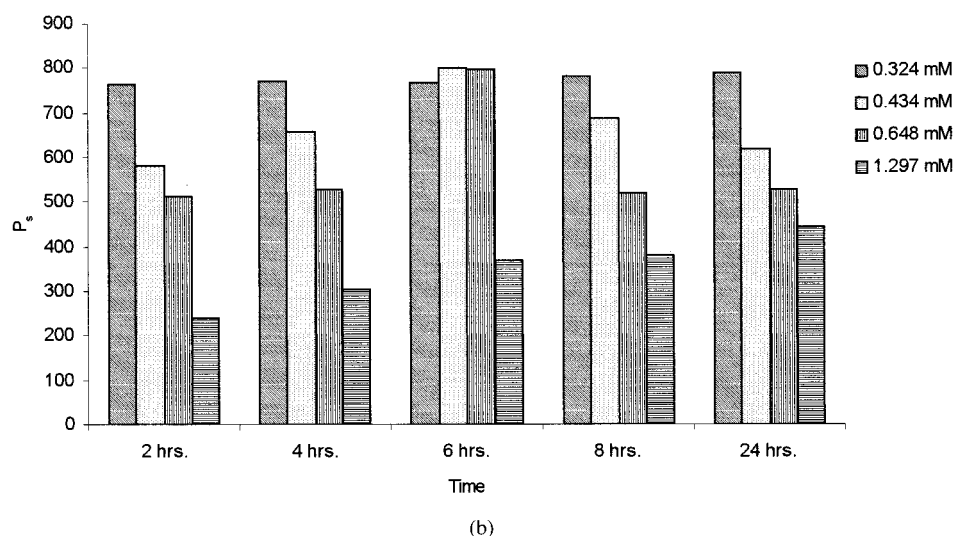
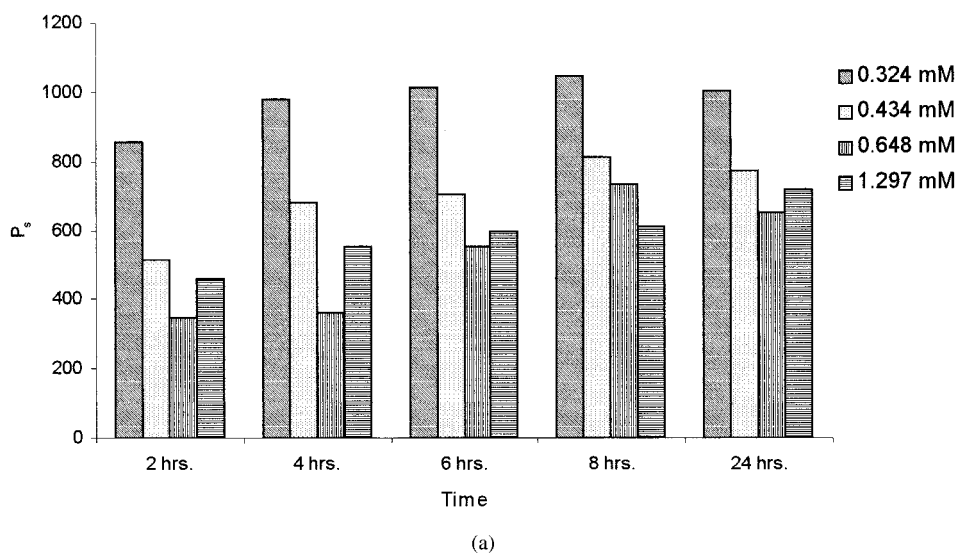


Figure 2 (a) Effect of crosslinker concentration on P_u of gelatin-cl-poly(AAm) prepared at 25°C with respect to time at 25°C and pH 7.0; (b) effect of crosslinker concentration on P_u of gelatin-cl-poly(AAm) prepared at 60°C with respect to time at 25°C and pH 7.0.

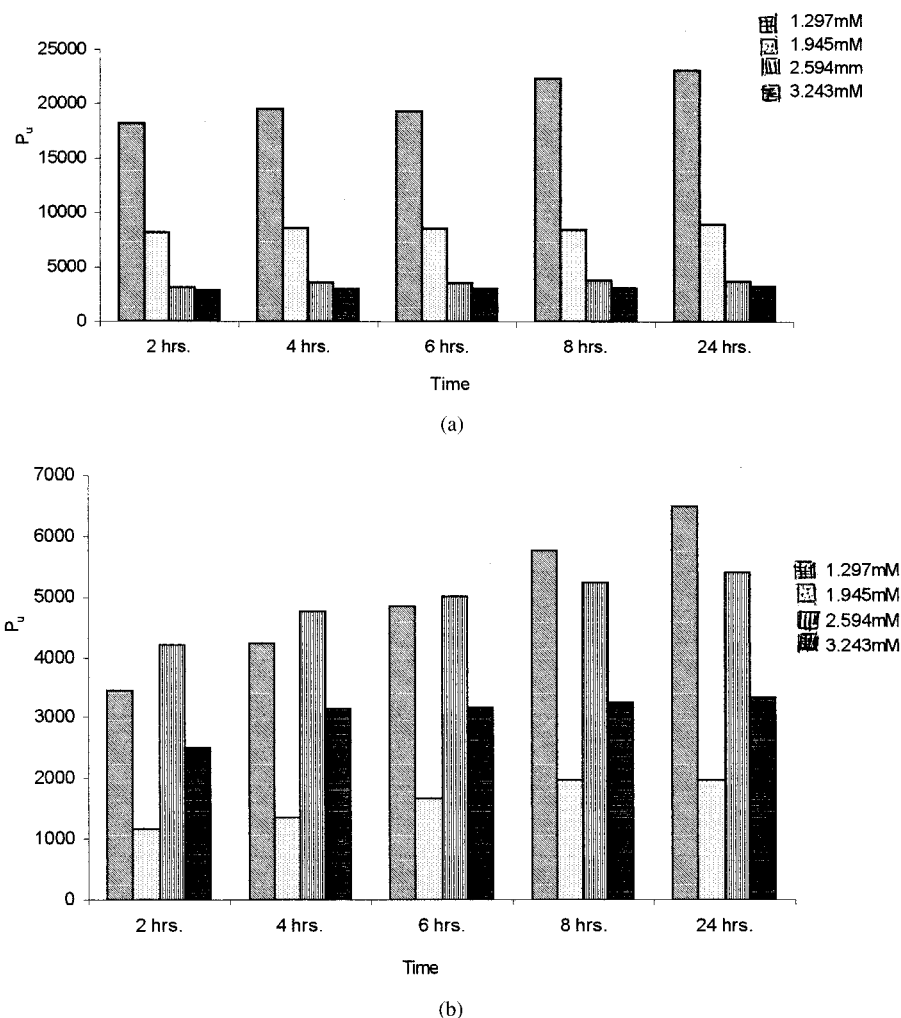


Figure 3 (a) Effect of crosslinker concentration on P_u of gelatin-cl-poly(AAmPSA) prepared at 25°C with respect to time at 25°C and pH 7.0; (b) effect of crosslinker concentration on P_u of gelatin-cl-poly(AAmPSA) prepared at 60°C with respect to time at 25°C and pH 7.0.

obtained at higher temperatures, a trend that can be ascribed to the poor solubility of the monomer at low temperature because of its hydrophobic nature.

Effect of crosslinker concentration on kinetics of network formation

Networks were synthesized at two temperatures (i.e., 25 and 60°C) by variation of crosslinker concentration. $P_{\text{add-on}}$ increases with increase of crosslinker concentration after an initial increase at both temperatures. The crosslinker concentration was varied from 1.297 to 3.243 mM in the case of AAmPSA because lower concentrations of crosslinker failed to yield self-insolubilized products and the rest of the conditions were the same as discussed for AAm (Table II). $\%P_{\text{add-on}}$ initially increases from 229.8 to 339.45 and then tends to be constant at 367.80, as shown in Table II, and 365.15 at higher crosslinker concentrations at 25°C; this trend is more sharply defined when net-

works were synthesized at 60°C as the network yield increases from 170.00 to 195.50, 190.60, and 191.00 with increase of crosslinker concentration. In the case of N-i-PAAm-based networks it has been observed that $\%P_{\text{add-on}}$ is scarcely affected by the $[N,N\text{-MBAAm}]$ and tends to be constant as it varies from 157.10 to 177.20 at 25°C and from 174.40 to 187.00 at 60°C (Table II).

Analysis of FTIR spectra of gelatin and its crosslinked networks

Important peaks and percentage absorbance values of the FTIR spectrum of gelatin-cl-poly(AAm) are presented in Table III. The FTIR spectrum of gelatin shows prominent peaks for $-\text{NH}$, $-\text{CH}$, and $\text{C}=\text{O}$, the latter of which is prominent in the parent spectra attributed to the commonality of the stretching $\text{C}=\text{O}$ group of amide with absorbance of 88.16% at 1654.5 cm^{-1} [Fig. 1(a)]. FTIR spectra of its networks with

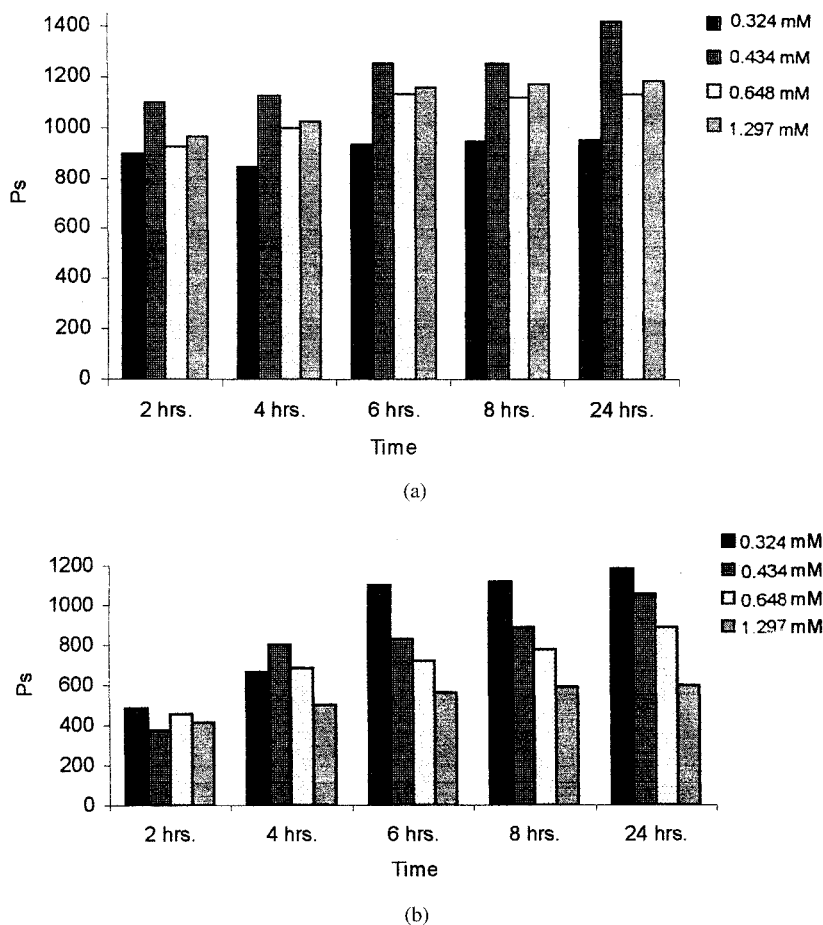


Figure 4 (a) Effect of crosslinker concentration on P_u of gelatin-cl-poly(N-i-AAm) prepared at 25°C with respect to time at 25°C and pH 7.0; (b) effect of crosslinker concentration on P_u of gelatin-cl-poly(N-i-AAm) prepared at 60°C with respect to time at 25°C and pH 7.0.

AAM are scarcely distinguishable because of the close community of distinguishing groups like amide [Table III and Fig. 1(b)]. The FTIR spectrum of gelatin-cl-poly(AAmPSA) shows a characteristic peak attributed to S=O stretching at 1300.7 cm^{-1} (%absorbance = 58.88) [Table III and Fig. 1(c)]. Characteristic absorption peaks of poly(N-i-PAAm) attributed to isopropyl and amide group stretching appear in the spectrum of gelatin-cl-poly(N-i-PAAm) networks synthesized, respectively, at 60 and 25°C; these peaks appear at 1129.9 cm^{-1} (%absorbance = 81.21), 1659.5 cm^{-1} (%absorbance = 83.34), 1129.8 cm^{-1} (%absorbance = 85.25), and 1643.5 cm^{-1} (%absorbance = 86.56) [Table III and Fig. 1(d)].

Thermogravimetric analysis

The thermal behavior of different polymers was studied to account for the effect of grafting of AAM and AAmPSA onto gelatin and also for the effect of reaction conditions. After discounting a 14.0% moisture loss, gelatin degrades in two stages from 251.8 to

456.7°C and 456.7 to 592.6°C with respective losses of 53.57 and 31.42%, with only a small amount of residue (0.73%) remaining (Table IV). Gelatin-g-poly(AAmPSA) synthesized at 25°C degrades in one stage from 193.6 to 429.9°C, losing 70.31% weight. The loss of weight attributed to absorbed moisture is 10.94, and 18.75% residue remains. The crosslinked network degrades in two stages from 137.2 to 197.2°C and 197.2 to 432.6°C, leaving behind a moderate amount of residue (33.0%). Thus it follows that grafting and network formation of AAmPSA and gelatin adversely affect thermal stability of gelatin and provide evidence of grafting and network formation (Table IV).

Water-uptake studies

All the hydrogels prepared by variations of crosslinker concentration as well as those prepared in the absence of crosslinker by grafting were investigated for water-uptake behavior with respect to variation of time, temperature, and change of pH (4.0–9.2 and in 0.5N NaOH solution).

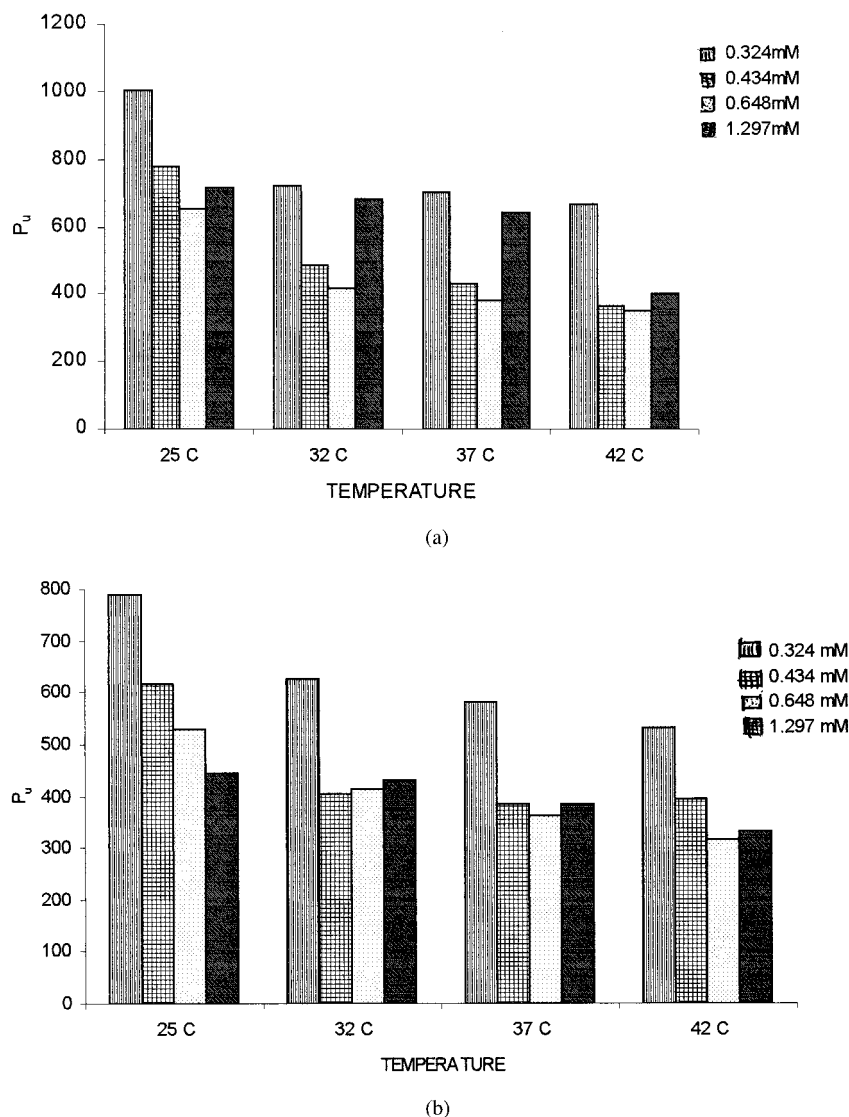


Figure 5 (a) Effect of crosslinker concentration on P_u of gelatin-cl-poly(AAm) prepared at 25°C with respect to temperature at pH 7.0; (b) effect of crosslinker concentration on P_u of gelatin-cl-poly(AAm) prepared at 60°C with respect to temperature at pH 7.0.

Effect of time on water-uptake behavior

Gelatin-g-poly(AAm) hydrogel prepared without crosslinker at 25°C ($P_{\text{add-on}} = 106.55$) was subjected to water uptake and it was observed that P_u increases in a linear fashion from 773.5 to 1065.0 as time increases from 2 to 24 h. In the case of hydrogels prepared at 60°C without crosslinker ($P_{\text{add-on}} = 41.75$) it was observed that P_u increases in a linear fashion from 1289.5 to 1510.4; thus hydrogels synthesized without crosslinker at higher temperature show better swellability than those prepared at 25°C. In the case of gelatin-cl-poly(AAm) it was observed that at 2 h, P_u decreases with the increase in the crosslinker density but increases in a linear fashion with increase in time for the same hydrogel, after which it tends to be constant from 6 h onward, especially at lower

crosslinker concentration; such behavior is more sharply defined in the case of hydrogels synthesized at higher temperature. Thus it appears that at higher temperature, because of increased homogenization of the reaction system, the structural aspects of hydrogels are affected in a different manner compared to the hydrogels synthesized at lower reaction temperature [Fig. 2(a)]. It is more understandable from the fact that, despite the high $P_{\text{add-on}}$ and consequent far higher number of water-interacting groups, the hydrogel synthesized at higher temperature (60°C) even at the lowest crosslinker concentration takes up comparatively less water [Fig. 2(b)]. Thus it is understandable that pore size attributed to the higher crosslinking density in hydrogels synthesized at higher temperature is considerably less and it follows that the reaction temper-

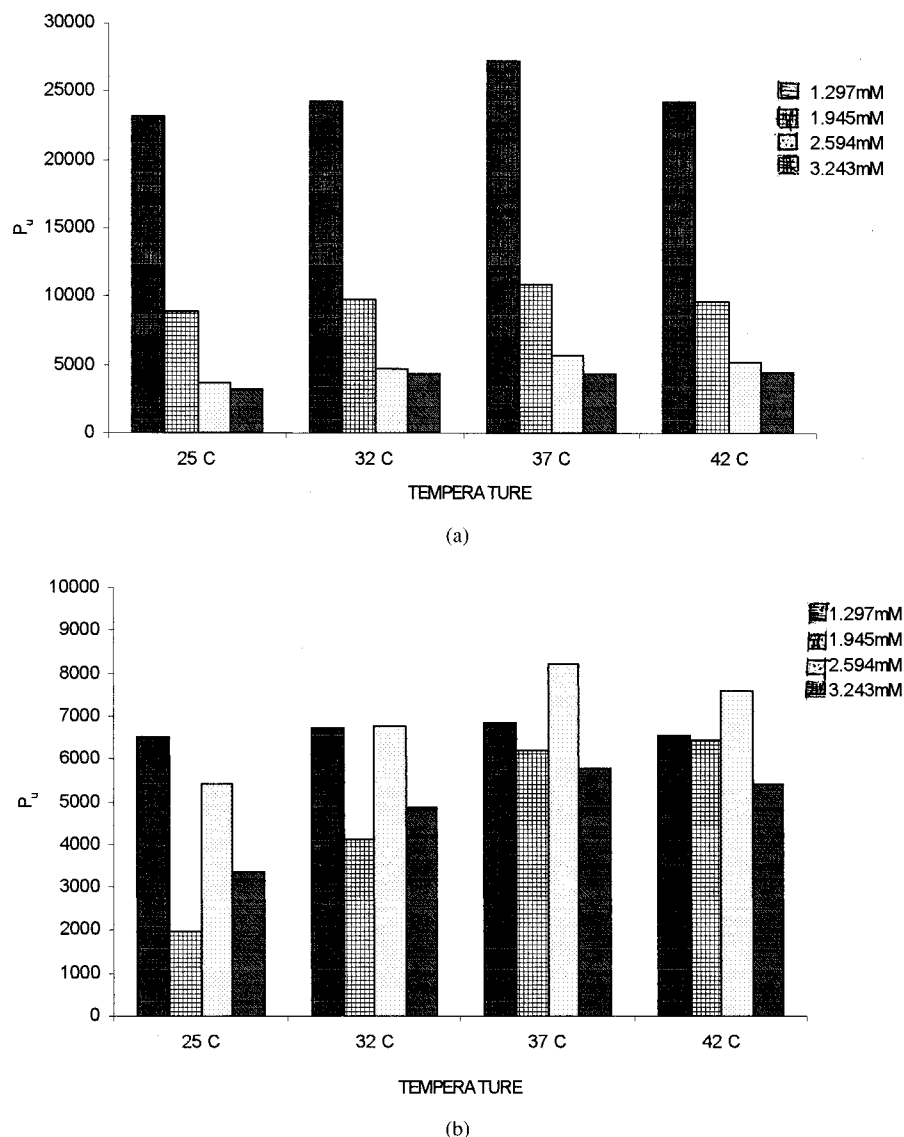


Figure 6 (a) Effect of crosslinker concentration on P_u of gelatin-*cl*-poly(AAmPSA) prepared at 25°C with respect to temperature at pH 7.0; (b) effect of crosslinker concentration on P_u of gelatin-*cl*-poly(AAmPSA) prepared at 60°C with respect to temperature at pH 7.0.

ature has a marked effect on the structural aspects of hydrogels without crosslinker or in its presence.

In the case of gelatin-*cl*-poly(AAmPSA) prepared again at both temperatures and different crosslinker concentrations it was observed that P_u increases with time for the same crosslinker concentration; however, for a particular time P_u decreases as the crosslinker concentration increases for hydrogels prepared at both high and low temperatures [Fig. 3(a), (b)]. It was observed that hydrogels synthesized at low temperature (25°C) have higher P_u values compared to those of hydrogels synthesized at higher temperature. Graft copolymers prepared at both 25 and 60°C without crosslinker did not swell but changed into sol. In the case of gelatin-*cl*-poly(N-i-PAAm) it was observed that P_u increased

in a linear fashion with time for each hydrogel. However, the P_u value was higher for the hydrogel synthesized at crosslinker concentration of 0.434 mM ($P_{\text{add-on}} = 172.1$). On the other hand, the P_u value for the hydrogel synthesized at crosslinker concentration of 0.324 mM was low and it appears that low crosslinker concentration failed to form an effective network in this case. P_u decreased for every swelling time [Fig. 4(a), (b)]. Hydrogels prepared at low temperature without crosslinker ($P_{\text{add-on}} = 60.80$) swelled in a linear fashion from 800.9 to 1536.4 as the time was varied. In the case of hydrogels prepared at higher temperature without crosslinker ($P_{\text{add-on}} = 81.50$), P_u increased up to 370.3 and then started to deswell, although not in a sharp manner. This observation reflects not only the

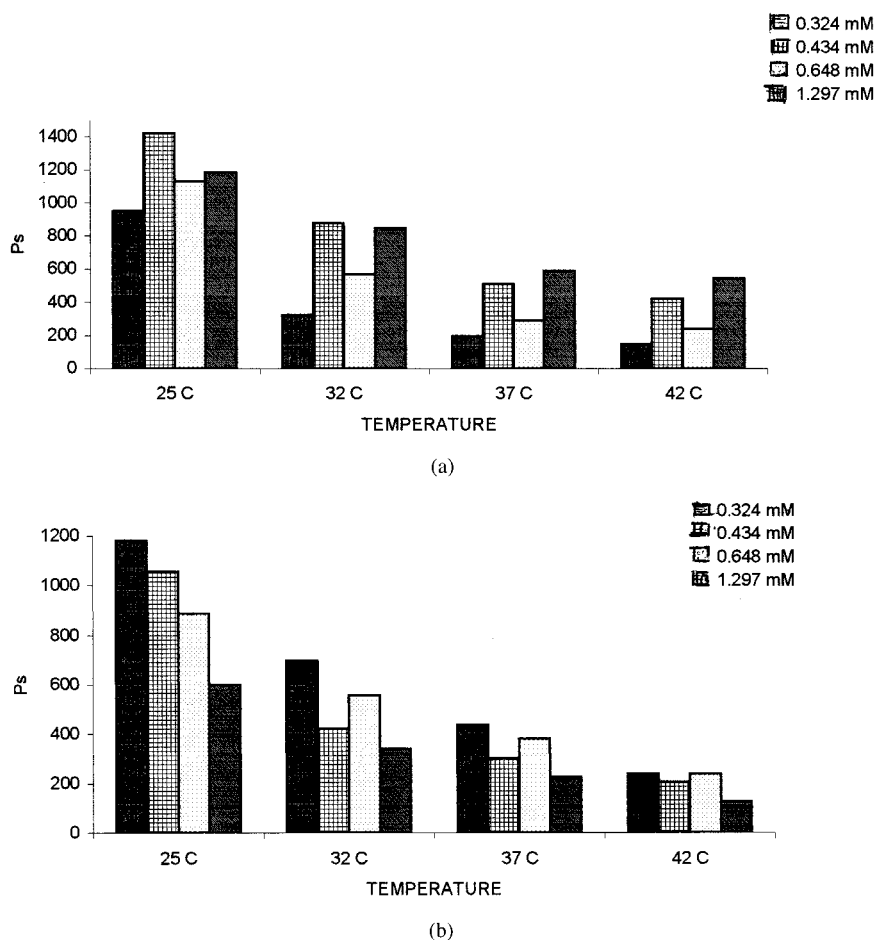


Figure 7 (a) Effect of crosslinker concentration on P_u of gelatin-cl-poly(N-i-AAm) prepared at 25°C with respect to temperature at pH 7.0; (b) effect of crosslinker concentration on P_u of gelatin-cl-poly(N-i-AAm) prepared at 60°C with respect to temperature at pH 7.0.

significance of temperature in affecting the structural aspects of the hydrogels but also that the $\%P_{\text{add-on}}$ is an important factor.

Effect of temperature on water-uptake behavior of hydrogels

Swelling temperature has a significant effect on the swelling and deswelling kinetics of hydrogels. One of the most significant classes of hydrogels is known as thermoresponsive hydrogels, which respond intelligently/smarty to changes in their thermal environment: poly(N-i-PAAm) is one of the most investigated polymers of this class. In the case of gelatin-cl-poly(AAm) prepared at both temperatures P_u decreases with both the increase in temperature and the increase in crosslinker concentration. For hydrogels synthesized at high temperature (60°C) an almost similar behavior is exhibited except for the fact that P_u tends to be constant with increasing crosslinker concentration, especially at higher temperature. Thus these gels are sensitive to their thermal environment

and changes in the volume of the gels are continuous and not drastic [Fig. 5(a), (b)]. In the case of gelatin-cl-poly(AAmPSA) prepared at the lowest crosslinker concentration, an increase in the swelling temperature led to a P_u increase with temperature up to 37°C, after which it decreased in almost all the hydrogels prepared at 25 and 60°C [Fig. 6(a), (b)]. However, in the case of the hydrogels synthesized at higher crosslinker concentrations the trends in P_u are the same, although water uptake is very low compared to that of the hydrogel synthesized at the lowest concentration and at 25°C.

Because poly(N-i-PAAm) is a thermoresponsive polymer its volume transition on swelling in water should be of interest. Its lower critical solution temperature (LCST) is 32.5°C; thus any increase of swelling temperature above this usually results in a sharp volume collapse. Moreover, in the present study the thermosensitivity is obvious in the hydrogels of gelatin-cl-poly(N-i-PAAm), given that at 32°C the gels shrank to almost about half of the P_u at lower temperature for both hydrogel series prepared at 25 and

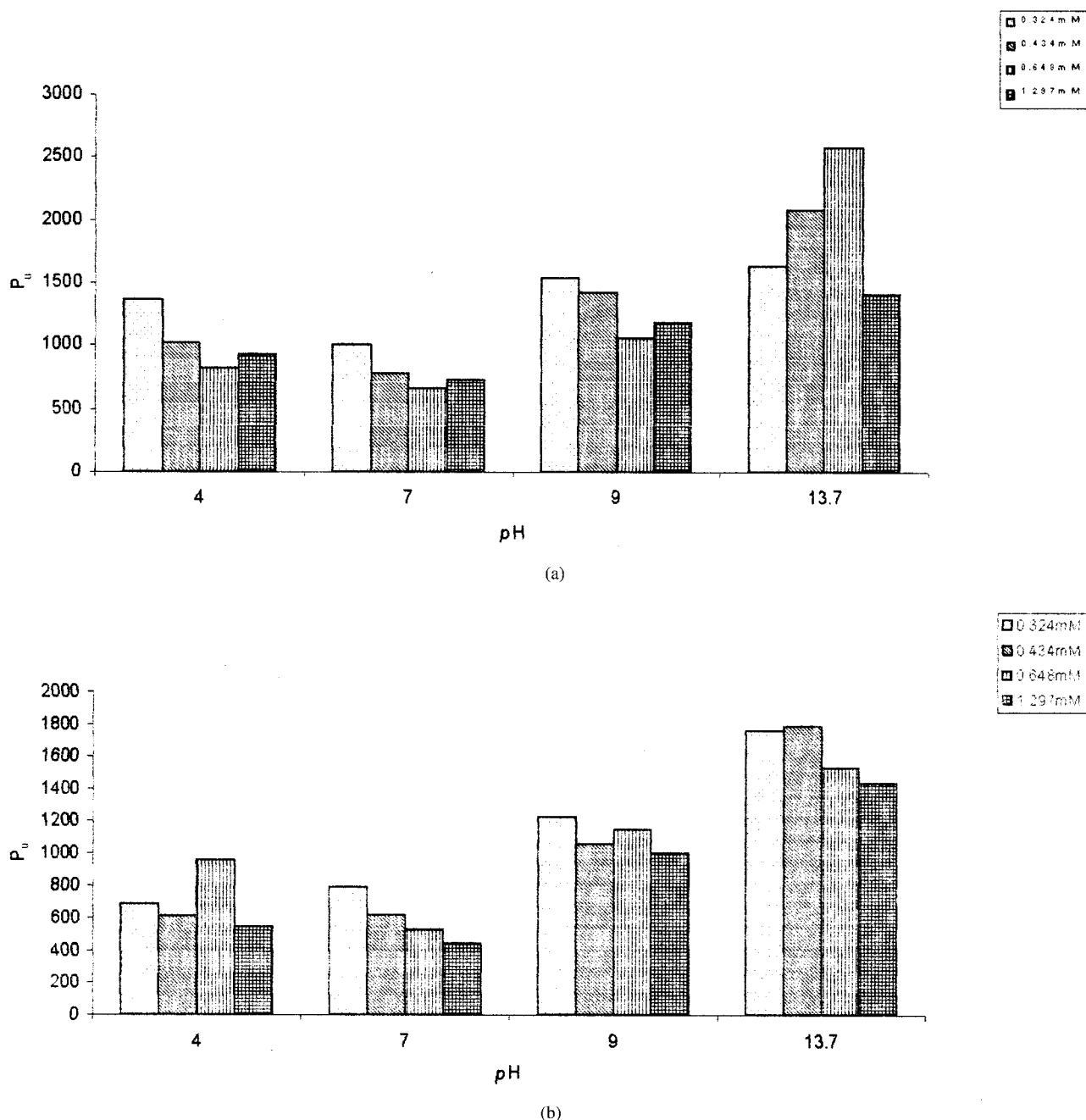


Figure 8 Effect of pH on P_u of gelatin-cl-poly(AAm) prepared at 25°C; (b) effect of pH on P_u of gelatin-cl-poly(AAm) prepared at 60°C.

60°C, although it is more marked in the latter case. Thus there is no effect of grafting or network formation on the LCST of poly(N-i-PAAm) [Fig. 7(a), (b)].

Effect of pH on water-uptake behavior

As an environmental controlling factor, pH has a significant effect on the water-uptake capacities of hydrogels, and immersion of hydrogels in 0.5N NaOH for 24 h may result in generation of new water interaction

centers on the polymer chains resulting in significant changes in water uptake attributed to partial hydrolysis of $-CONH_2$ to $-CO_2Na^+$ groups. In the case of gelatin-cl-poly(PAAm), hydrogels showed a linear increase in P_u for every crosslinker concentration in pH 4.0 and 9.0, in a 0.5N NaOH solution, and there is an obvious partial hydrolysis of the amide group of poly(AAm) that leads to higher water uptake in 0.5N NaOH solution [Fig. 8(a), (b)]; this factor is of lesser significance in the case of AAmPSA- and N-i-PAAm-

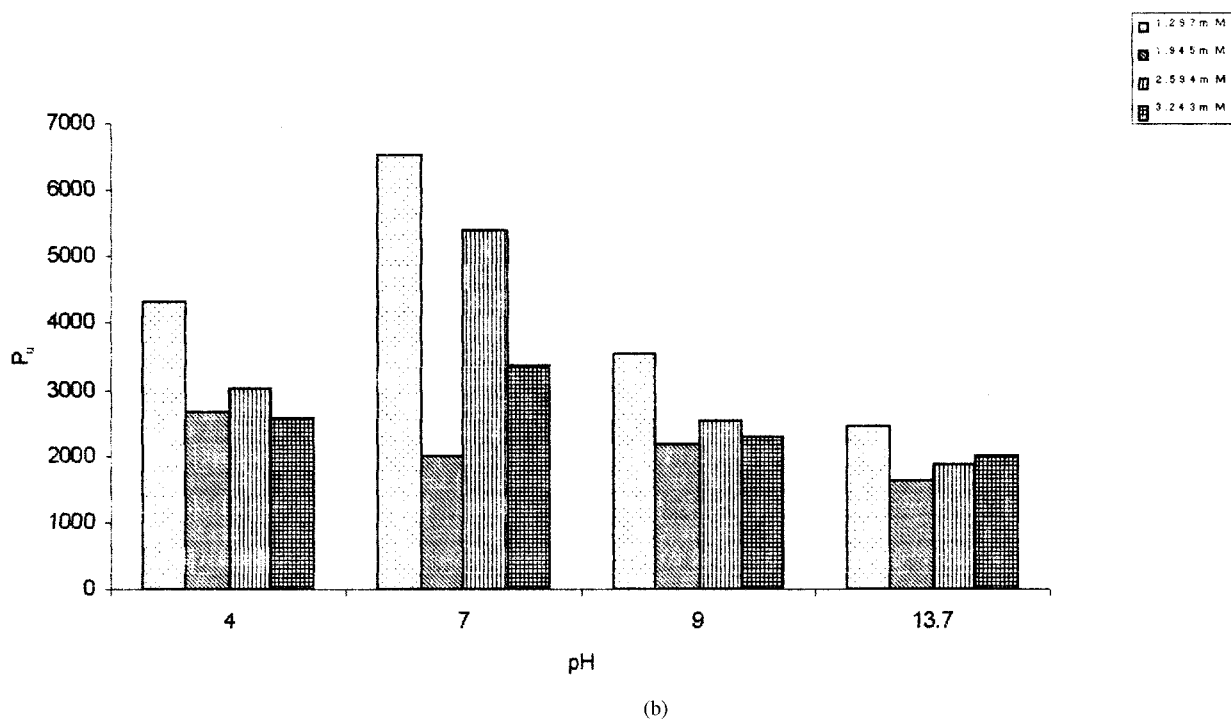
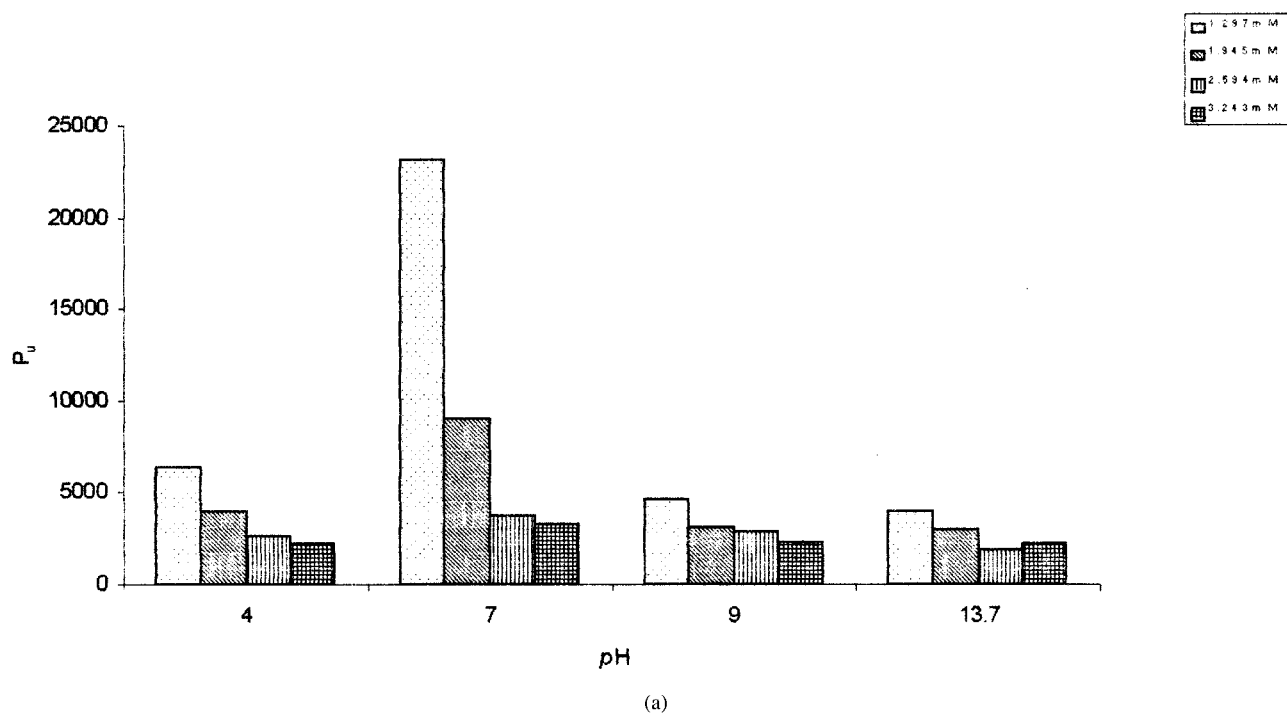


Figure 9 Effect of pH on P_u of gelatin-cl-poly(AAmPSA) prepared at 25°C; (b) effect of pH on P_u of gelatin-cl-poly(AAmPSA) prepared at 60°C.

based hydrogels because of the inherent structure of the amide group of these polymers. Hydrogels of poly(AAmPSA) absorb water in media of different pH values, following the order $4.0 > 9.0 > 0.5N \text{ NaOH} > 7.0$ [Fig. 9(a), (b)]. Poly(N-i-PAAm)-based hydrogels scarcely distinguish between pH 4.0 or 9.0 and pH

7.0 but do deswell considerably in 0.5N NaOH [Fig. 10(a), (b)]. The water-uptake behavior of hydrogels is affected by the heterogeneous nature of functional groups of amino acids of gelatin that are protonated/hydrolyzed on interaction with the swelling medium.

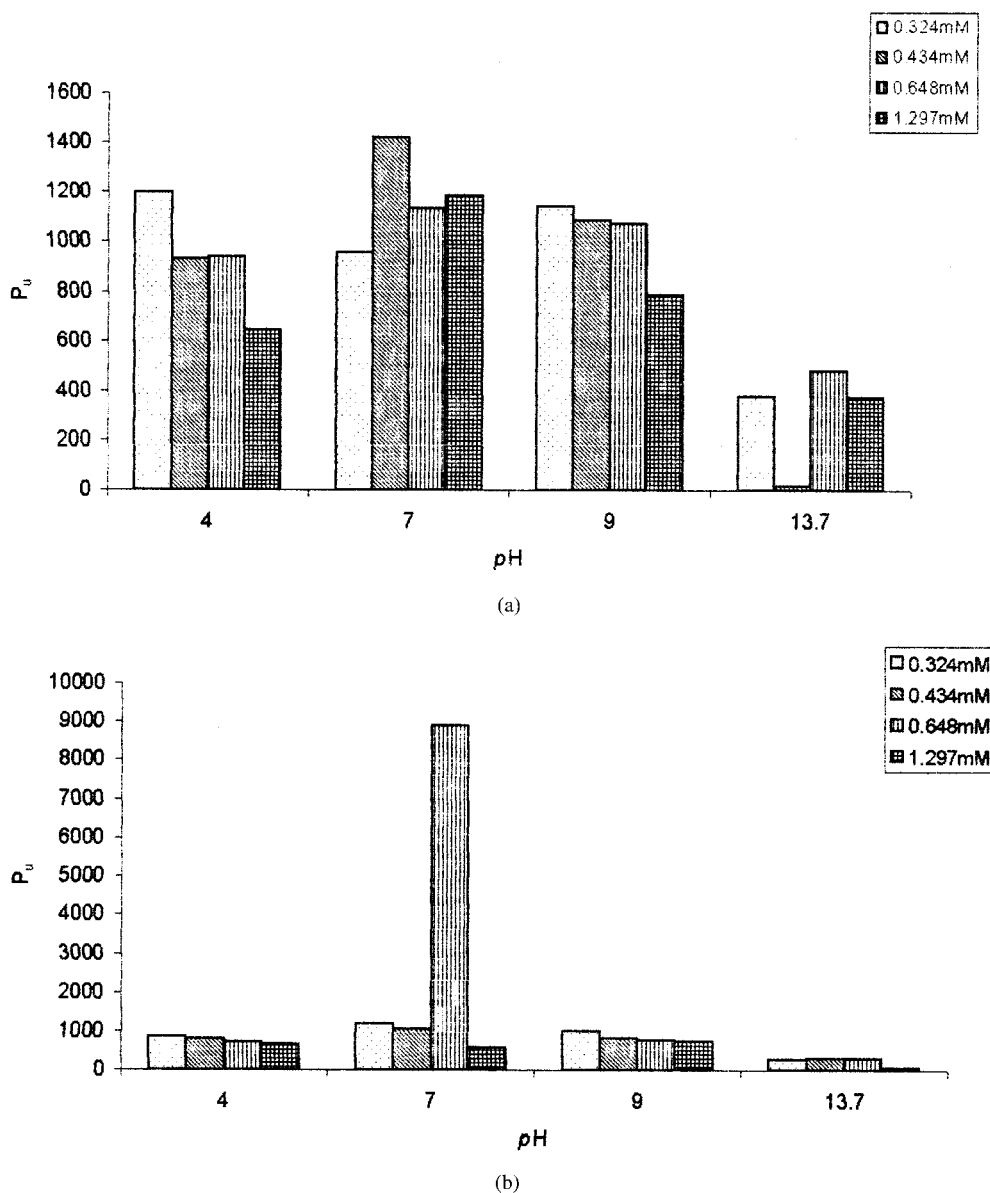


Figure 10 Effect of pH on P_u of gelatin-cl-poly(N-i-AAm) prepared at 25°C; (b) effect of pH on P_u of gelatin-cl-poly(N-i-AAm) prepared at 60°C.

Metal ion sorption studies

An attempt has been made to study sorption of Fe^{+2} , Cu^{+2} , and Cr^{+6} on select hydrogels to investigate quantum and selectivity in metal ion sorption and relationship between structural aspects of the hydrogels. It is expected that the structural aspects of the hydrogels depend on the structural differences in the nature of amide group and consequent capacity to take up water, which affect partitioning of metal ions between the polymer and solution phase. Given the structural aspects of these hydrogels it has been reported by us that metal ion uptake on hydrogels is a function of ion exchange, adsorption, and simple sorption in the bulk of hydrogels.¹³

Trends in sorption behavior of hydrogels

Results of sorption of Cr^{+6} ions on different hydrogels of poly(AAm) are given in Table V. Polymeric matrices with the lowest crosslinker concentration sorb more ions than those synthesized with the highest crosslinker concentration, which means that metal ion sorption is more a bulk phenomenon and is affected by pore size as a function of crosslinking density, which in turn affects water uptake, thus resulting in less effective metal ion partitioning of the metal ion between solution and polymer phase. Similar trends have been observed with poly(AAmPSA)- and poly(N-i-PAAm)-based hydrogels. Sorption behavior of Cu^{+2} ions by the same series of polymers is presented in Table V. An increase in metal

TABLE V
Sorption Studies of Metal Ions on Hydrogels

Sample no.	Polymer matrix	Crosslinker (mM)	M ^{+z} ions uptake (mg)	M ^{+z} rejected (mg)	%Uptake
Sorption of Cr ⁺⁶ (ions in feed = 16.80 mg/L)					
1	Gel-cl-poly(AAm)	0.324	3.6	13.2	21.42
2	Gel-cl-poly(AAm)	1.297	3.6	13.2	21.42
3	Gel-cl-poly(N-i-PAAm)	0.324	7.8	9.0	46.42
4	Gel-cl-poly(N-i-PAAm)	1.297	2.1	14.7	12.50
5	Gel-cl-poly(AAmPSA)	1.297	4.5	12.3	26.78
6	Gel-cl-poly(AAmPSA)	3.243	0.0	16.80	0.0
Sorption of Cu ⁺² (ions in feed = 5.6 mg/L)					
1	Gel-cl-poly(AAm)	0.324	1.12	4.48	20.00
2	Gel-cl-poly(AAm)	1.297	1.84	3.76	32.85
3	Gel-cl-poly(N-i-PAAm)	0.324	2.36	3.24	42.14
4	Gel-cl-poly(N-i-PAAm)	1.297	1.72	3.88	30.71
5	Gel-cl-poly(AAmPSA)	1.297	4.36	1.24	77.85
6	Gel-cl-poly(AAmPSA)	3.243	5.12	0.48	91.42
Sorption of Fe ⁺² (ions in feed = 16.45 mg/L)					
1	Gel-cl-poly(AAm)	0.324	01.26	15.19	07.65
2	Gel-cl-poly(AAm)	1.297	00.63	15.82	03.82
3	Gel-cl-poly(N-i-PAAm)	0.324	03.43	13.02	20.85
4	Gel-cl-poly(N-i-PAAm)	1.297	03.71	12.74	22.55
5	Gel-cl-poly(AAmPSA)	1.297	13.30	03.15	80.85
6	Gel-cl-poly(AAmPSA)	3.243	15.33	01.12	93.19
Effect of partial hydrolysis on Cr ⁺⁶ uptake					
		Crosslinker (mM)		%Uptake before hydrolysis	
1	Gel-cl-poly(AAm)	0.324		21.42	0.0
2	Gel-cl-poly(N-i-PAAm)	0.324		46.42	40.54
3	Gel-cl-poly(AAmPSA)	3.243		0.0	0.0
Effect of partial hydrolysis on Cu ⁺² uptake					
1	Gel-cl-poly(AAm)	1.297		32.85	56.75
2	Gel-cl-poly(N-i-PAAm)	0.324		42.14	40.54
3	Gel-cl-poly(AAmPSA)	3.243		91.42	0.0
Effect of partial hydrolysis on Fe ⁺² uptake					
1	Gel-cl-poly(AAm)	0.324		7.65	89.54
2	Gel-cl-poly(N-i-PAAm)	0.324		20.85	4.39
3	Gel-cl-poly(AAmPSA)	3.243		93.19	93.65

ion sorption has been observed compared to that of Cr⁺⁶ ions and it is of interest that in all three series of monomers, but especially for poly(AAmPSA)-based hydrogels, the ion uptake is higher in those matrices synthesized at highest crosslinker concentration. It can be argued that in this case the ion exchange at -SO₃H contributes considerably to the total percentage uptake. AAmPSA-based hydrogels absorb far more Cu⁺² ions compared to other hydrogels based on AAm and N-i-PAAm. Similar trends have also been observed for Fe⁺² ions.

Effect of partial hydrolysis on metal ion sorption behavior of hydrogels

Polymeric networks that showed comparatively better metal ion sorption were subjected to partial hydrolysis with 0.5N NaOH for 48 h, after which metal ions were

sorbed on the hydrolyzed matrices. Hydrolysis enhances metal ion uptake as it increases ion-ion interactions and also swellability of the hydrogels. From Table V it may be observed that most of hydrolyzed hydrogels do not absorb any Cr⁺⁶ ions and instead become oxidized; breakdown of the networks is also observed in some cases. Cr⁺⁶ ions are not well sorbed and these results may also be attributed to their oxidizing nature. However, in the cases of Cu⁺² and Fe⁺² ions an increase in ion uptake is substantial, often observed in the unhydrolyzed hydrogels, although the results are more obvious for the latter. Further, because of the facile hydrolysis of amide groups of AAm compared to that of the secondary amide groups of N-i-PAAm, a far higher amount of these two ions has been observed in almost all the hydrogels of poly(AAm), although the amount is far less in

AAmPSA-containing hydrogels, again because of the intrinsic structural effects.

CONCLUSIONS

From the preceding discussion it may be concluded that reaction conditions and the nature of monomer play important roles in determining the properties of networks of gelatin and acrylamides. It can be concluded that preparation of hydrogels at higher temperature involves more uniform reactions, resulting in higher crosslinking density and thus lower water uptake. Moreover, the % $P_{\text{add-on}}$ is also an important factor that significantly affects properties of the hydrogels. Metal ion sorption is dependent on the structural aspects of the hydrogels in that the quantum of metal ion sorption is affected by the crosslinker concentration as well as by the partial hydrolysis of the hydrogels. The increase in metal ion sorption in all three series of monomers, but especially in poly(AAmPSA)-based hydrogels, has contributed considerably to the total percentage uptake by the ion-exchange processes that occur at $-\text{SO}_3\text{H}$ groups. The role of pH and partial hydrolysis in affecting water uptake and the observation that partial hydrolysis affects the uptake of metal

ions in a selective manner can be used for technological advantages.

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References

1. Lim, F., Ed. *Biomedical Applications of Microencapsulation*; CRC Press: Boca Raton, FL, 1984.
2. Nagabhushnam, T.; Santappa, M. *J Polym Sci Polym Chem Ed* 1976, 14, 507.
3. Nagabhushnam, T.; Santappa, M. *J Polym Sci Polym Chem Ed* 1976, 16, 3287.
4. Kuwajima, T.; Yoshida, H.; Hayashi, K. *J Appl Polym Sci* 1976, 20, 976.
5. Misra, B. N.; Mehta, I. K.; Sood, D. S. *J Macromol Sci Chem* 1981, 15, 457.
6. Khetrapal, R. C.; Gill, K. D.; Mehta, I. K.; Misra, B. N. *J Macromol Sci Chem A* 1982, 18, 445.
7. Otani, Y.; Tabata, Y.; Ikada, Y. *Macromol Symp* 1998, 130, 169.
8. Vazquez, B.; Grurruchaga, M.; Goni, I. *Polymer* 1995, 36, 2311.
9. Wiersma, A. J.; Bos, M.; Pennings, A. J. *Polymer Bull* 1994, 33, 613.
10. Chatterji, P. R. *J Appl Polym Sci* 1990, 40, 401.
11. Chun, S. W.; Kim, J. D. *J Controlled Release* 1996, 38, 39.
12. Chauhan, G. S.; Mahajan, S. *J Appl Polym Sci*, to appear.
13. Chauhan, G. S.; Mahajan, S. *J Appl Polym Sci* 2002, 86, 468.