

Synthesis, Characterization, and Swelling Responses of Poly(*N*-Isopropylacrylamide)- and Hydroxypropyl Cellulose-Based Environmentally Sensitive Biphasic Hydrogels

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ABSTRACT: Thermosensitive networks based on hydroxypropyl cellulose and *N*-isopropylacrylamide cross-linked with *N,N*-methylene bisacrylamide were synthesized by a simultaneous gamma radiation technique. The network yield was optimized by the variation of reaction parameters such as the total radiation dose, concentration of crosslinker and monomer, and amount of water. The hydrogels had a biphasic structure and good mechanical strength, even in the fully swollen state, and could be synthesized in any shape and size. Volume transitions as a function of time and temperature were studied for these hydrogels in water, and the effects on swelling in different media such as 0.5*N* NaOH, 0.5*N* HCl, and 5% NaCl at the optimum time and temperature were also studied. The response of the hydrogels to

these diverse changes in the swelling media was observed, and the volume transitions due to environmental changes in the hydrogels were not sharp and discontinuous as a maximum volume collapse occurred at a temperature higher than the reported lower critical solution temperature of 32.5°C for *N*-isopropylacrylamide. These hydrogels were environmentally sensitive and responded to changes in their thermal and ionic environment and have potential applications in diverse fields such as drug delivery, enzyme technology, and environmental management. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 479–488, 2004

Key words: hydrogels; networks; radiation; swelling

INTRODUCTION

The synthesis of hydrogels by gamma radiation is a convenient method of polymer synthesis as the degree of crosslinking and the swellability of these hydrogels can be regulated by the variation of the total radiation dose. Many studies have been reported on the use of such gels in controlled drug delivery,^{1,2} thermocontrolled chromatography,³ regulation of activity of enzymes,^{4,5} and solute separation technologies.^{6,7} The influence of temperature as an external response on hydrogel swelling with poly(*N*-isopropylacrylamide) [poly(*N*-*i*-PAAm)] gels is perhaps the most well-investigated study of thermosensitive hydrogels. Nagaoka et al.⁸ reported the synthesis of poly(*N*-*i*-PAAm) hydrogels by a radiation technique. Fast-responding thermoreversible hydrogels based on poly(vinyl methyl ether) were prepared by gamma radiation and were used in controlled release applications.⁹ Important characteristics of the thermosensitive hydrogels such as the lower critical solution temperature (LCST), rates of shrinking, and swelling and permeation rates

of substances within these gels can be controlled by compositional changes as controlled hydrophilicity or more hydrophobicity of the constituent monomers,¹⁰ variation of crosslinking density, and a change in the ionic strength or nature of the swelling medium.¹¹

First-order thermoreversible volume transitions have been reported in nonionic polymeric gels such as crosslinked poly(*N*-*i*-PAAm) near its LCST because it undergoes a sharp volume phase transition (gel collapse) at a temperature close to 32.5°C. Grafted poly(*N*-*i*-PAAm) chains with free mobile ends in a network respond dramatically to changes in the thermal environment as compared to uncrosslinked poly(*N*-*i*-PAAm).¹² Due to a low mechanical strength, poly(*N*-*i*-PAAm) gel in its highly swollen state cannot be used in many applications. Modification with hydrophobic components through copolymerization or interpenetrating network formation improves its mechanical properties. Cellulosics are also well-known reinforcing agents and, due to their linear structure, provide desired mechanical strength to the networks.¹³ However, modification with hydrophobic components via an interpenetrating network formation affects only the equilibrium swelling levels without affecting the gel collapse temperature.¹⁴

To synthesize environmentally sensitive smart polymeric materials for use in separation and enrichment

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technologies, those that can undergo temperature-induced sorption and desorption with repeatability and reusability, we synthesized a large range of hydrogels based on acrylamide and celluloses.^{15,16} In this article, we report the synthesis and characterization of hydrogels based on hydroxypropyl cellulose (HPC) and poly(*N*-*i*-PAAm). The effect of structural aspects of the hydrogels on the LCST of poly(*N*-*i*-PAAm) was studied as a function of the nature of the swelling medium. The networks were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and thermal studies to investigate effects of synthetic conditions on some structural aspects of the networks.

EXPERIMENTAL

Materials

N-isopropylacrylamide (*N*-*i*-PAAm; Sigma, St. Louis, MO), propylene oxide (BDH, Poole, England), and *N,N*-methylene bisacrylamide (*N,N*-MBAAm; CDH, Delhi, India) were used as received. The extraction of cellulose and the synthesis of HPC was discussed elsewhere.¹⁷ Cellulose was extracted from pine needles by an ammonia extraction method. HPC was synthesized from 1,2-propylene oxide and alkali cellulose as a known amount of cellulose was stirred with 18% sodium hydroxide solution for 2 h. Alkali cellulose thus produced was mixed with an excess of isopropanol and was filtered. The residue was then treated with 1,2-propylene oxide in isopropanol in the presence of a small amount of water at 70°C for 3 h; the product was dissolved in water, reprecipitated by the addition of isopropanol, filtered, washed with methanol and acetone, and dried. Cellulose (1.0 g) yielded 1.15 g of HPC, and the calculated molar degree of substitution for HPC was 0.42, and it was 32% soluble in water.

Synthesis of the networks

Networks were obtained as insolubilized products from an aqueous medium after reactions with a γ -ray simultaneous irradiation method with method and a reaction scheme discussed elsewhere.¹⁵ HPC (1.0 g.), a known amount of *N*-*i*-PAAm, and *N,N*-MBAAm in an aqueous system were irradiated for different time intervals in a Gamma Chamber-900 with a Co⁶⁰ γ -ray source (Bhabha Atomic Research Centre, Mumbai, India). We separated the insolubilized product from each reaction and treated it for the removal of any sol fraction by stirring with water and methanol for solvent polarity gradient treatment separately and dried it in an air oven at 40°C. The polymers thus obtained were termed *xerogels*. Network formation efficiency (%*E*) was defined by the following relationship:

TABLE I
%*E* as a Function of the Synthetic Reaction Conditions

Total radiation dose (Gy) $\times 10^{-4}$	<i>N</i> - <i>i</i> -PAAm (mol/L) $\times 10^4$	<i>N,N</i> -MBAAm (mol/L) $\times 10^4$	Volume of water (mL)	% <i>E</i>
12.36	88.49	12.98	5.0	80.11
37.10	88.49	12.98	5.0	81.31
49.46	88.49	12.98	5.0	80.69
61.80	88.49	12.98	5.0	79.77
98.92	88.49	12.98	5.0	80.45
148.39	88.49	12.98	5.0	81.3
37.10	88.49	0.00	5.0	85.29
37.10	88.49	3.25	5.0	81.88
37.10	88.49	6.49	5.0	79.11
37.10	88.49	9.74	5.0	76.17
37.10	88.49	12.98	5.0	81.31
37.10	88.49	16.23	5.0	80.25
37.10	88.49	3.25	5.0	81.88
37.10	88.49	3.25	10.0	94.86
37.10	88.49	3.25	15.0	98.29
37.10	88.49	3.25	20.0	98.10
37.10	88.49	3.25	25.0	98.13
37.10	44.25	3.25	25.0	60.91
37.10	88.49	3.25	25.0	98.43
37.10	132.74	3.25	25.0	98.51
37.10	176.99	3.25	25.0	98.75
37.10	221.24	3.25	25.0	99.29

HPC = 1 g.

%*E*

$$\%E = \frac{\text{Weight of xerogel}}{\text{Total weight of monomer, HPC, and crosslinker}} \times 100$$

The effect of synthetic reaction conditions on %*E* was studied per the reaction scheme given in Table I.

FTIR, SEM, and swelling and thermal studies

FTIR spectra (PerkinElmer, in KBr pellets), scanning electron micrographs (Jeol JSM-6100 scanning microscope), and wide-angle X-ray diffractions (WAXDs) of the networks were recorded. Thermal degradation behavior was studied on a Shimadzu simultaneous thermogravimetric (TG)/differential thermal (DT) analyzer in air at a heating rate of 20°C/min. Swelling studies were carried as a function of various synthetic reaction conditions, swelling time, and temperature by the immersion of a known weight of xerogel in water and a different media.¹⁵

RESULTS AND DISCUSSION

HPC had 0.42 degrees of substitution and was 32% soluble in water.¹⁷ As shown by the WAXD studies of extracted cellulose, the extracted cellulose was low in

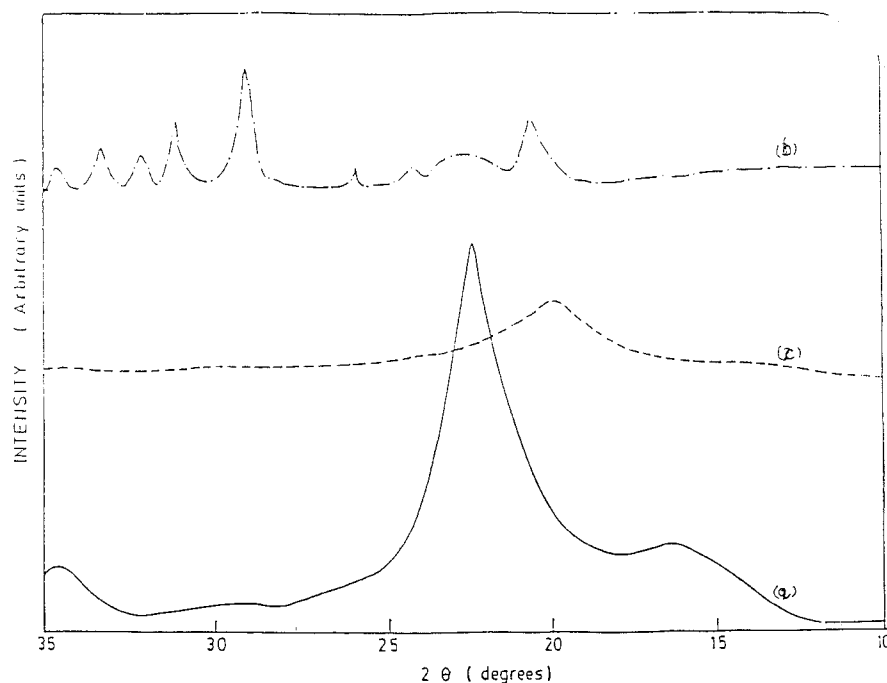


Figure 1 WAXD pattern of (a) commercial cellulose, (b) extracted cellulose, and (c) HPC.

molecular weight and had a far lower degree of crystallinity (31.00%) compared to a commercial cellulose sample (59%). On hydroxypropylation, this was further reduced to 15.54% due to lesser interpolymer chain interactions and the hydrophobic contribution of the hydroxypropyl units in case of HPC compared to the native cellulose (Fig. 1). Such low crystallinity was desirable in the direction of maximum homogenization of linear chains of HPC for network formation, and the surface-active nature of HPC should have further contributed to facilitate uniform network formation. Evidence of network formation was provided by elemental analysis of different hydrogels, and data on the percentage nitrogen showed that a good amount of monomer was incorporated on the backbone polymer. Two networks with %*E* values of 98.13 and 99.29 were analyzed for the presence of N, and we found 11.11 and 8.19% N, the values of which were very near the calculated values of 11.12 and 8.19 with very small deviations.

SEM of HPC and its hydrogels

Scanning electron micrographs of HPC and its networks at various resolutions are presented in Figure 2. SEM of different hydrogels was studied to investigate their morphological features. Figure 2i(a,b) reveals the contrasted surface morphology of the networks of HPC and poly(*N-i*-PAAm) crosslinked with *N,N*-MBAAm. SEM of the HPC-*cl*-poly(*N-i*-PAAm) hydrogels provided evidence that network formation had

taken place [Fig. 2ii(a,b)]. The biphasic nature of the networks was evident in the dorsal view (with respect to the reaction vessel at the time of synthesis), which was quite different from the ventral view, and the contrast of the two sides was very sharp. The hydrogel so formed had a more smooth and homogeneous dorsal side, and the ventral side had a heterogeneous nature. Furthermore, the heterogeneity of the two phases of the hydrogels was more contrasting due to the fact that while these mixtures were irradiated, the insoluble fraction of the backbone settled down where the monomer and crosslinker also diffused and polymerized. The soluble part of the backbone, along with the monomer, polymerized and crosslinked to form the upper phase. The porosity of these two sides was obviously going to be different, and such structural features of the networks rendered better membrane workability for selective sorption of the effluents in environmental management technologies.

FTIR of the networks

HPC showed prominent bands at 3412.5 cm^{-1} (O—H stretching), 2926.9 cm^{-1} (C—H stretching), and 1058.0 cm^{-1} (C—O—C stretching; Fig. 3).¹⁷ IR absorption bands due to amide C=O stretching were prominent at 1655.5 cm^{-1} , and a prominent peak due to the $-\text{CH}(\text{CH}_3)_2$ group of *N-i*-AAM was observed at 1379.2 cm^{-1} in poly(*N-i*-PAAm) hydrogels apart from the previously listed bands.

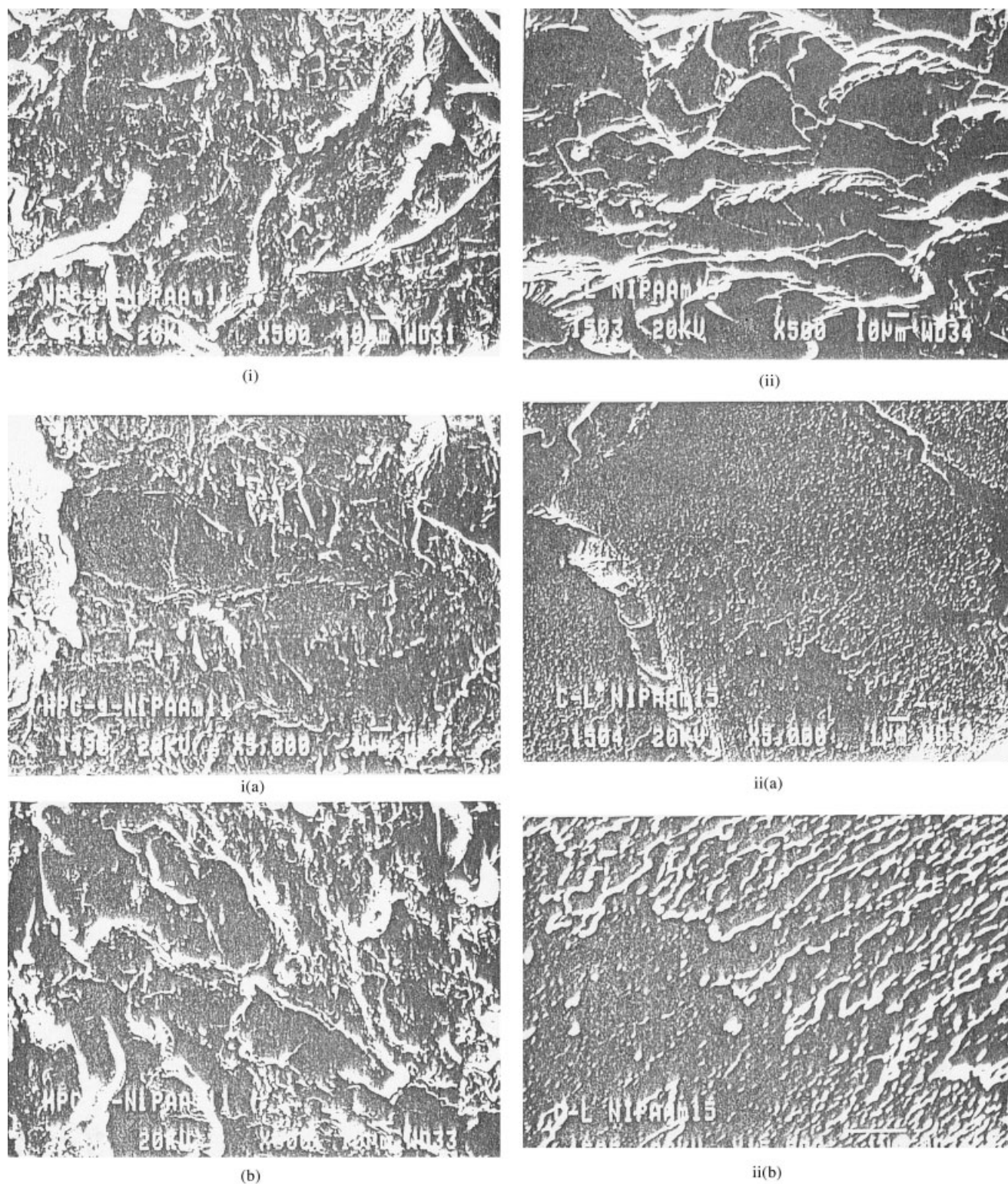


Figure 2 Scanning electron micrographs of (i) HPC-cl-poly(*N-i*-PAAm): (a) dorsal and (b) ventral views and (ii) *cl-N-i*-PAAm (magnifications are given in the micrographs).

Thermal degradation behavior

TG curves of crosslinked HPC and HPC-cl-poly(*N-i*-PAAm) revealed that the former decomposed in three stages; the latter did so in two stages after the loss of

moisture was discounted (Fig. 4). The crosslinked HPC lost 24.50 wt % mostly due to moisture starting at 33.32–269.96°C in the first stage of decomposition as the TG was flattened around 80–100°C after a sharp

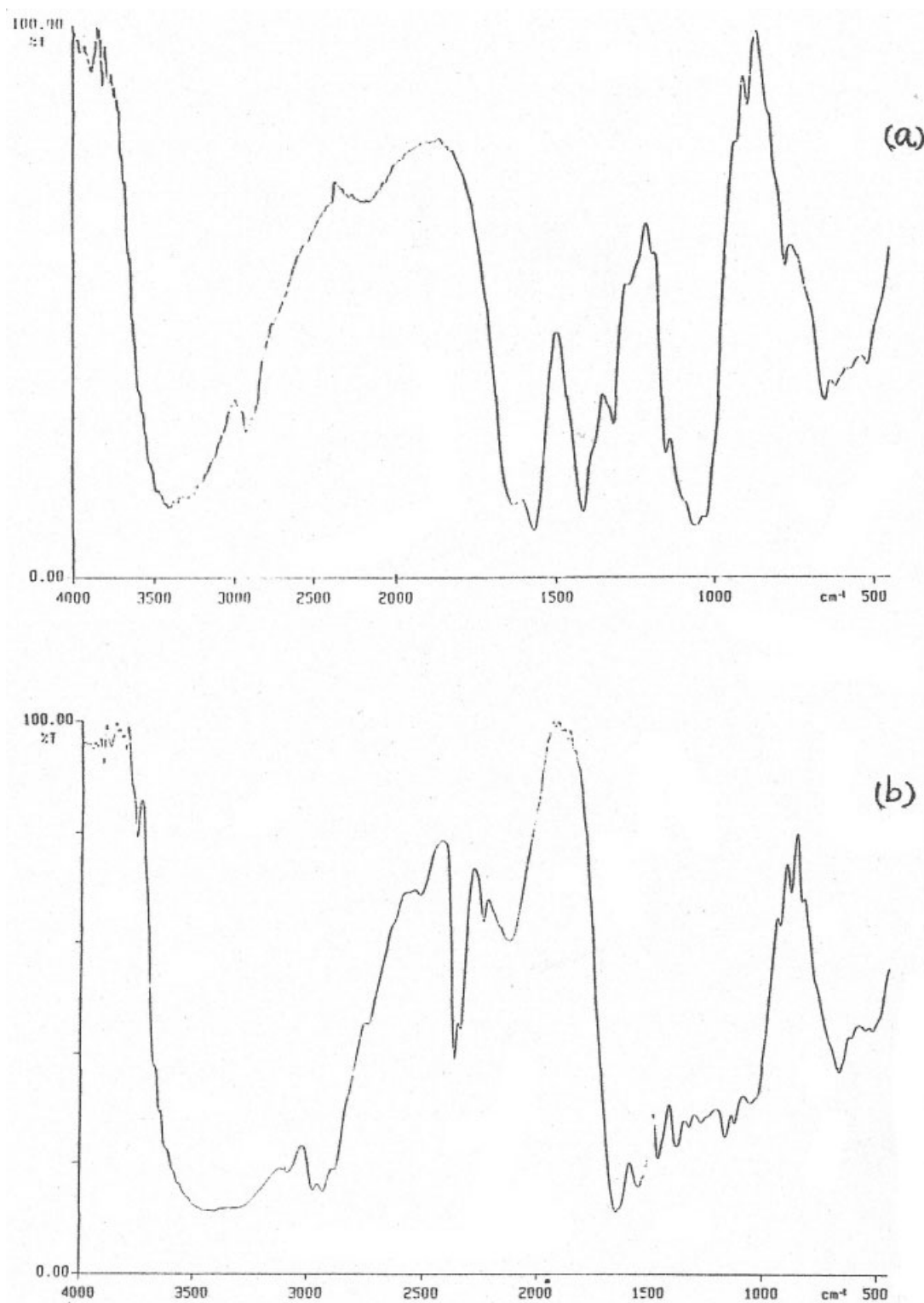


Figure 3 FTIR of (a) HPC and (b) HPC-cl-poly(*N-i*-PAAm).

weight loss at the lower temperature. Some loss in weight was also attributed to the loss of hydroxypropyl groups. Actual decomposition started at 269.96–346.62°C with a sharp weight loss (44.84%) over a small range of temperature; most of this weight loss

was attributed to the loss of hydroxypropyl groups and dehydration of the anhydroglucose units of the cellulose. In the next stage of decomposition (346.62–523.25°C), 40.71 wt % was lost due to the volatilization of smaller components, and no residue was left. Suc-

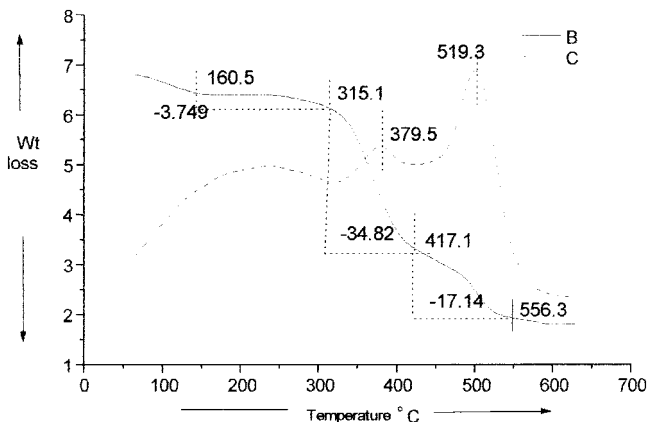


Figure 4 TG/DT analysis curves of HPC-*cl*-poly(*N-i*-PAAm).

cessive 10% weight losses at corresponding temperatures of 49.95°C (10%), 226.6°C (20%), 293.2°C (30%), 313.32°C (50%), 336.63°C (60%), 359.94°C (70%), 409.96°C (80%), 465.65°C (90%), and 532.16°C (100%) supported the previously explained degradation patterns in which the network was stable as the initial decomposition temperature (IDT) was quite high and more sharp weight losses occurred at later stages.

The IDT was very high for the amide-containing network (315.1°C) compared to *cl*-HPC (269.96°C). The high stability of the network was due to the fact that unlike poly(acrylamide), which degrades earlier due to the dehydration of $-\text{CONH}_2$ groups, such a possibility did not exist due to substitution of the amide group in case of poly(*N-i*-PAAm). This argument was further supported by a low weight loss and the flattening of the TG in the earlier stages up to 280°C, where the dehydration of cellulose to anhydroglucose occurred. Furthermore, it was supported by the successive 10% weight losses at 316.94°C (10%), 372.38°C (20%), 385.42°C (30%), 408.26°C (40%), 496.3°C (50%), and 556.5°C (60%). Moisture loss, starting 60°C (8.806%), was followed by the first stage of degradation at 315–417.10°C with a weight loss of 34.82%, and the second stage started at 417.10–556.3°C with a weight loss of 17.14%, leaving a 38.93% residue. DT analysis showed only 346.62, 459.98, and 379.5 and 519.3°C, respectively, for the HPC- and amide-containing networks. It was evident that most of the processes in the degradation were exothermic, and no significant endothermic peaks were observed; hence, these networks were high-energy materials.

Kinetics of network formation

Network formation in a cellulosic matrix is affected by multiple factors. Free-radical abstraction from different $-\text{OH}$ or $-\text{CH}$ groups of cellulose creates active sites for crosslinker attachments and the formation of

networks. Strength, porosity, and the yield of the network are also determined by the structure of the matrix. Synthetic conditions play an important role in governing the swellability of these networks as the length of polymeric chains, the texture of network formed, and the orientation of various groups in networks are also affected in a big way by the variation of the reaction conditions.

As shown in Table I, %*E* was not much affected by the increase in the total dose of radiation. It did not change appreciably, as a maximum %*E* of 81.31 was obtained at 37.09×10^4 Gy, and it decreased to 79.77 with increasing radiation dose to 61.83×10^4 Gy and tended to be constant, that is, 80.45 and 81.31 as the total radiation dose was increased to 98.92×10^4 and 148.39×10^4 Gy. A marginal increase in %*E* from 85.29 (in the absence of crosslinker) was observed when the crosslinker concentration was varied at 37.09×10^4 Gy. %*E* increased marginally from 76.17 (at 9.74×10^{-4} mol of *N,N*-MBAAm) to 81.31 (at 12.98×10^{-4} mol) and finally to 70.6 with 16.23×10^{-4} mol of the crosslinker. The total radiation dose and concentration of crosslinker did not affect %*E*.¹⁵ The effect of the amount of water is again presented in Table I. An increase in the amount of water facilitated network formation as %*E* increased with increase in the amount of water from 5.00 mL (81.88) to 25.00 mL (98.13). At optimum conditions worked out for maximum dose rate, crosslinker, and monomer concentration, a maximum %*E* was obtained in 25.00 mL of water. An increase in the monomer concentration from 44.25×10^{-4} to 221.24×10^{-4} mol increased %*E* in a linear fashion from 60.91 to 99.29 at 221.24×10^{-4} mol of the monomer.

Swelling capacity of the networks

Synthetic reaction conditions apart from the extent of compositional changes also affected other structural features of the network such as pore size and pore size distribution. Swelling studies of hydrogels were carried out to investigate the effects of different synthetic conditions on water uptake by the network as a function of changes in the thermal and ionic environment of the networks. The effect of network formation on the LCST of poly(*N-i*-PAAm) incorporated into networks with HPC was also studied.

Effect of synthetic reaction conditions, swelling time, and temperature on hydrogel swelling

The effect of swelling time at 22°C was studied, and it was observed that almost all of the hydrogels synthesized as a function of the concentration of crosslinker and the amount of water showed optimum swelling at 8 h in the hydrogels synthesized in the absence of crosslinker. For different swelling times, with the vari-

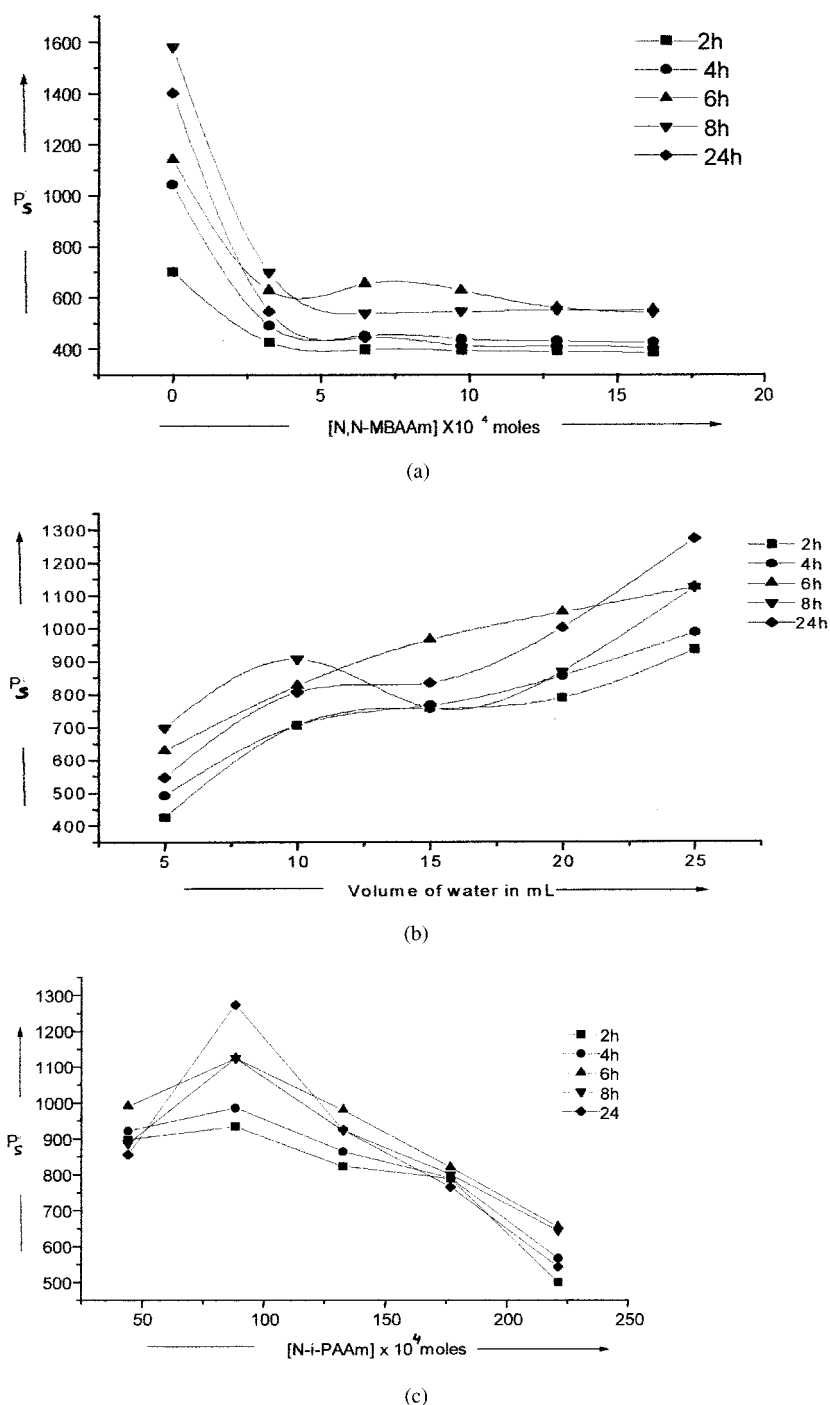


Figure 5 Effect of time on the percentage swelling as a function of (a) *N,N*-MBAAm, (b) volume of water, and (c) *N-i*-PAAm in the synthetic medium.

ation of swelling time, the order was worked out as $2 < 4 < 6 < 24 < 8$ h, with a maximum in those networks synthesized in the absence of *N,N*-MBAAm. For the networks synthesized with a higher amount of crosslinker, percent swelling (P_s) decreased sharply and tended to be independent of crosslinker concentration; a linear relationship in the decrease of P_s was observed with increasing crosslinker concentration,

and a maximum P_s was observed at 6 h and not at 8 h. Thus, the equilibrium swelling was affected by a shortening of the swelling period in networks synthesized in the presence of crosslinker. P_s decreased from 1142.0 to 553.0 as the amount of crosslinker increased [from no crosslinker to 16.23×10^{-4} mol of *N,N*-MBAAm; Fig. 5(a)] as a manifestation of increase in the crosslinking density. However, as the amount of

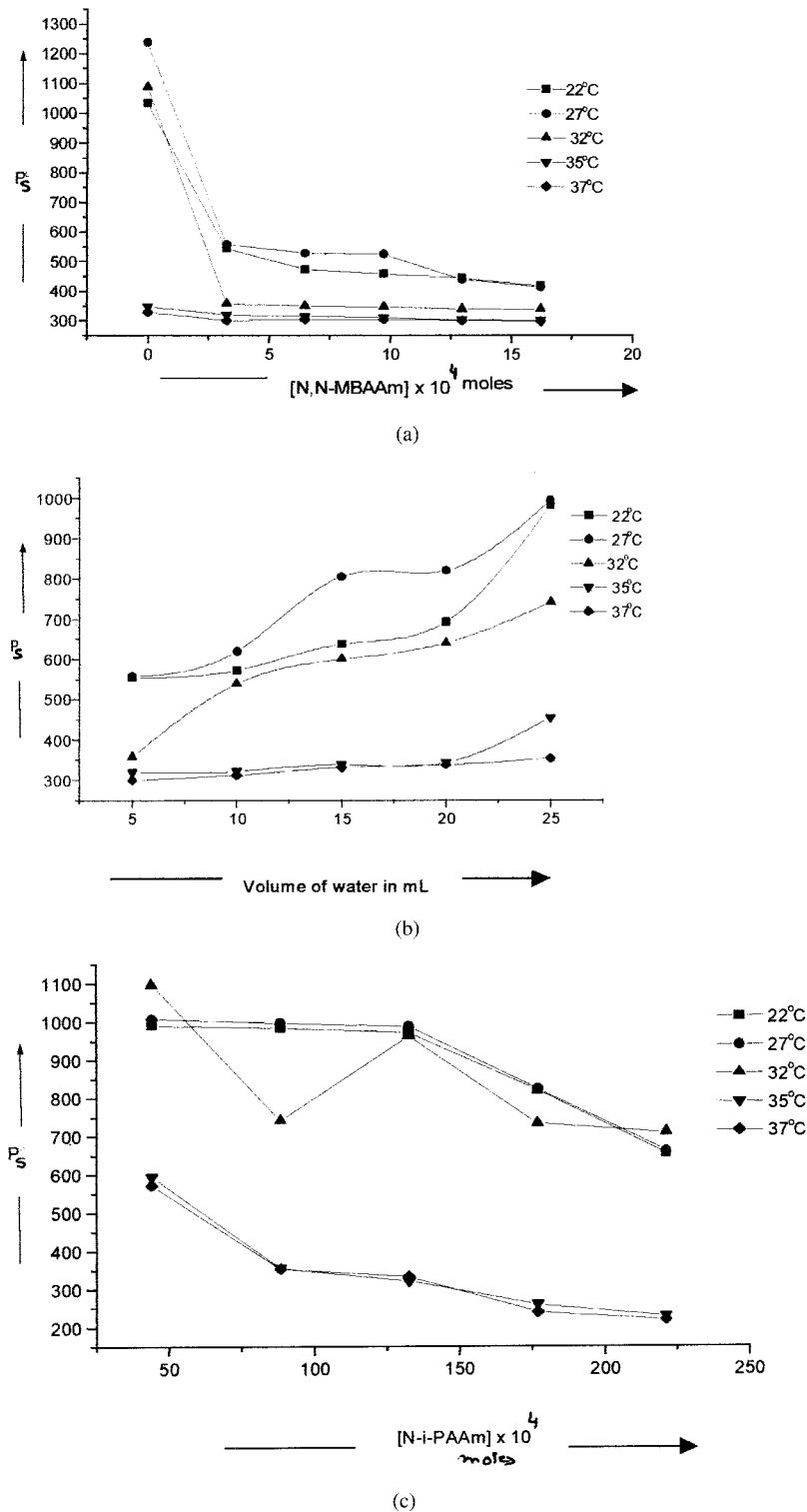


Figure 6 Effect of temperature on the percentage swelling as a function of (a) N,N -MBAAm, (b) volume of water, and (c) N - i -PAAm in the synthetic medium.

water in the synthetic medium was increased at the lowest $[N,N$ -MBAAm], water uptake also increased due to the presence of a larger amount of water in the reaction medium, which acted as a diluent, and the porosity of the network was affected, as reflected in a

uniform increase in P_s from 553.0 to 1125.0 with the variation in the amount of water from 5.00 to 25.00 mL [Fig. 5(b)]. The order for the effect of the amount of water for the network synthesized in the minimum amount of water was same as observed earlier for the

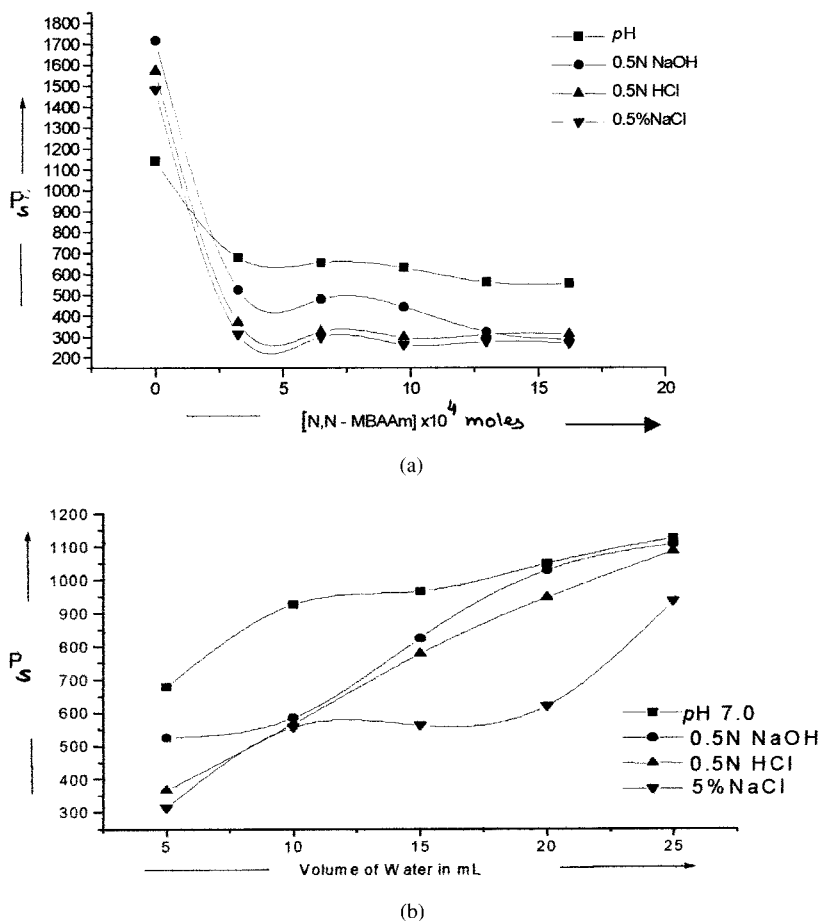


Figure 7 Effect of the nature of the swelling media on the percentage swelling as a function of (a) *N,N*-MBAAm and (b) volume of water in the synthetic medium.

effect of crosslinker concentration, that is, $2 < 4 < 24 < 6 < 8$ h, and with the increase in the amount of water in the reaction medium, a maximum P_s was observed at 6 h. With the variation of monomer concentration (from 44.25×10^{-4} to 88.49×10^{-4} mol) at the lowest $[N,N\text{-MBAAm}]$ and with 25.00 mL of water, P_s increased from 990.0 to 1125.0, but it decreased with a further increase in monomer concentration from 132.74×10^{-4} to 221.24×10^{-4} mol [Fig. 5(c)] with the trend in swelling time $24 < 8 \approx 2 < 4 < 6$ h; hence, 6 h was taken as the optimum swelling time for further studies.

The effect of swelling temperature was also studied on the hydrogels synthesized by the variation of different reaction conditions. For the hydrogels synthesized by the variation of crosslinker concentration [Fig. 6(a)] and also by the variation of the amount of water [Fig. 6(b)], the variation of swelling temperature had a pronounced effect on the swelling extent of these networks. An increase in P_s was observed up to 200% on increasing the temperature in the range 22–27°C [Fig. 6(a)]. With further increases in the temperature to 32°C (almost the LCST of the incorporated monomer), P_s decreased by a magnitude of 80–200 in

hydrogels synthesized by the variation of crosslinker and the amount of water. The order for different temperatures was observed as $37 \approx 35 < 22 < 32 < 27^\circ\text{C}$, and a decrease in P_s with an increase in swelling temperature was more pronounced. P_s increased progressively with increasing amount of water, but the trend of the effect of temperature was slightly different: $37 \approx 35 < 32 < 22 < 27^\circ\text{C}$ [Fig. 6(b)]. P_s in the networks synthesized by the variation of monomer was observed to decrease uniformly and more sharply with increasing monomer [Fig. 6(c)]. Further increases in temperature to 35°C resulted in a more sharp decrease in P_s of the hydrogels, and volume collapse was significant up to threefold in some hydrogels. Increases in the swelling temperature to 37°C resulted only in a small volume change, but there was a sharp volume collapse in one hydrogel synthesized with 13.27 mM of monomer. This change in the volume of hydrogels near the physiological temperature of the human body makes these hydrogels possible candidates as drug-delivery systems. P_s did not vary significantly and tended to remain almost same at the swelling temperatures higher than the known LCST of poly(*N-i*-PAAm). It appeared that HPC as a reinforce-

ing agent contributed to the stabilization of the LCST of poly(*N-i*-PAAm) above its known LCST of 32.5°C. Thus, these hydrogels showed responsiveness to their thermal environment and could thus be termed *smart thermosensitive hydrogels*. Although 35°C could be taken as the LCST of these hydrogels, it is important to note that volume collapse was continuous and not so drastic as reported for poly(*N-i*-PAAm) hydrogels. Such observations are important and are due to the surface-active nature of HPC itself.

Effect of the nature of the medium on the swelling behavior of the hydrogels

Apart from the thermal environment, these hydrogels were also sensitive to their ionic and pH environment as they were able to respond to environmental changes. P_s was again studied as a function of synthetic variables such as the crosslinker concentration and amount of water in different swelling media. The effect of crosslinker concentration was both quantitative and qualitative as the network synthesized at the lowest crosslinker concentration swelled on the order of 0.5N NaOH > 0.5N HCl > 5% NaCl > pH 7.0. However, the networks synthesized at higher crosslinker concentrations showed different patterns of swelling: pH 7.0 > 0.5N NaOH > 0.5N HCl > 5% NaCl, thus making it evident that a higher crosslinking density in the network affected hydrogel responses to environmental changes. In the presence 0.5N NaOH, hydrogels synthesized at various crosslinker concentrations deswelled as compared to the water uptake in normal water at pH 7.0, although the changes in P_s values were not very sharp [Fig. 7(a)]. Hydrogels synthesized by the variation in the amount of water also show a decreased in P_s [Fig. 7(b)]. Hydrogels swollen in 0.5N HCl again showed a change of volume as P_s decreased more in all of the hydrogels compared to that observed for those swollen

in 0.5N NaOH. Further volume change was affected when these hydrogels were swollen in 5% NaCl as P_s values decreased far below those observed in pure water. However, hydrogels synthesized without crosslinker showed higher P_s values in all of the media than in pure water. However, for the previously noted exceptions, the trends for P_s in different swelling environments could be put in the descending order: pH 7.0 > 0.5N NaOH > > 0.5N HCl > 5% NaCl. The pronounced change in the volume of hydrogels in 0.5N HCl and 5% NaCl solutions make these hydrogels possible candidates for use in drug-delivery systems and environmental management technologies.

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