Structural Aspects and Nature of Swelling Medium As Equilibrium Swelling Determinants of Acrylamide and Cellulosic-Based Smart Hydrogels

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ABSTRACT: Hydroxypropylcellulose (HPC)-based interpenetrating networks (IPN) with acrylamide (AAm) were synthesized in aqueous medium by simultaneous γ-ray initiation in the presence of N,N-methylenebisacrylamide (N,N-MBAAm). The effect of the synthetic reaction conditions was evaluated for optimum network yield and networks of cellulose and some of its derivatives were obtained with AAm by using these conditions. FTIR, elemental analysis, and scanning electron micrography (SEM) for various structural aspects have characterized networks. Apart from kinetics of IPN formation, this article discusses swelling response of these novel hydrogels in different swelling media. Swelling behavior was studied as a function of synthetic reaction conditions, structure of cellulosics used, and nature of swelling medium (water, 0.5N NaOH, 0.5N HCl, and 5% NaCl). Equilibrium swelling was observed to depend on both structural and environmental factors. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1161–1169, 2002

Key words: cellulosic; hydroxypropyl cellulose; equilibrium swelling; interpenetrating networks; smart hydrogels

INTRODUCTION

Hydrogels are crosslinked hydrophilic polymer networks that swell to equilibrium without dissolving and their shape is preserved even in swollen state.[1] Grafting of vinyl monomers onto various surfaces is a convenient method for preparing hydrogels of various substrates,[2–4] and during recent years, radiation was extensively used as a method in network formation and inducing surface grafting.[5–9] Synthetic conditions have tremendous influence on different structural aspects of polymeric network. Thus, a desired polymer can be obtained by a tailor-made combination of properties of the constituents. In the present study, hydroxypropylcellulose (HPC)-surface active and water-soluble cellulose ether, was used as a model polymeric matrix with acrylamide (AAm) to get interpenetrating networks (IPN). Polyacrylamide yields stable, clear, and homogeneous gels by crosslinking, which swell extensively in water but are poor in hydrolytic stability and tensile strength, whereas cellulose derivatives have good tensile strength but poor hydrophilicity compared to PAAm. Hydrogels via IPN formation can be obtained with more diversified properties by use of linear cellulosics as reinforcing agents with high swelling monomers such as 2-hydroxymethyl methacrylate, N-vinylpyrrolidone, and N,N-dimethylacrylamide.[10–12]

The present work is, hence, an attempt to develop smart hydrogels for environmental manage-

Table I   Kinetics of IPN Formation[a]

Cellulosic Matrix	Total Radiation Dose $\times 10^{-4}$ (Gy)	AAm $\times 10^4$ (mol)	N,N-MBAAm $\times 10^4$ (mol)	Volume of Water (mL)	$P_{\text{add-on}}$
HPC	13.57	140.68	12.98	5.0	57.0
—do—	27.14	140.68	12.98	5.0	109.0
—do—	40.71	140.68	12.98	5.0	105.0
—do—	54.27	140.68	12.98	5.0	111.0
—do—	81.41	140.68	12.98	5.0	123.0
—do—	108.54	140.68	12.98	5.0	105.0
—do—	26.94	140.68	0.00	5.0	—
—do—	26.94	140.68	3.25	5.0	68.0
—do—	26.94	140.68	6.49	5.0	81.0
—do—	26.94	140.68	9.74	5.0	85.0
—do—	26.94	140.68	12.98	5.0	109.0
—do—	26.94	140.68	16.23	5.0	121.0
—do—	26.75	0.00	3.25	5.0	—
—do—	26.75	70.34	3.25	5.0	—
—do—	26.75	140.68	3.25	5.0	95.0
—do—	26.75	211.82	3.25	5.0	122.0
—do—	26.75	281.37	3.25	5.0	202.0
—do—	26.75	351.71	3.25	5.0	208.0
—do—	26.55	351.71	3.25	5.0	208.0
—do—	26.55	351.71	3.25	10.0	223.0
—do—	26.55	351.71	3.25	15.0	211.0
—do—	26.55	351.71	3.25	20.0	210.0
—do—	26.55	351.71	3.25	25.0	220.0
Cellulose	26.55	351.71	3.25	10.0	239.0
Cell-NHNH$_2$	26.55	351.71	3.25	10.0	298.0
Cell-CN	26.55	351.71	3.25	10.0	170.0
Cell-PO$_4$	26.55	351.71	3.25	10.0	204.9
HEC	26.55	351.71	3.25	10.0	213.5

[a] Weight of cellulosic used, 1.0 g.

ment, such as separation and enrichment technologies, enzyme immobilization, and drug delivery matrices. A combination of different constituents of hydrogels, synthetic conditions, and nature of swelling environment has tremendous influence on properties of hydrogels. Hence, investigation into the kinetics of synthesis, structure of novel hydrogels, and effect of the nature of swelling environment on swellability was attempted. Apart from HPC, cellulose derivatives used in this study were hydroxy ethyl cellulose (HEC); hydrazinodeoxycellulose (Cell-NHNH$_2$); cellulose phosphate (Cell-PO$_4$); and cyanoethylcellulose (Cell-CN), including cellulose itself.

EXPERIMENTAL

Materials

AAm (CDH, New Delhi, India), propylene oxide (BDH, Poole, England), and N,N-methylenebisac-

rylamide (N,N-MBAAm; CDH) were used as received.

Synthesis of HPC, Cellulose Derivatives, and IPN Formation

HPC was synthesized from extracted cellulose[13] by an improvised method using 1,2-propylene oxide and alkali cellulose in isopropanol.[14] Cellulosics other than HPC (cellulose, HEC, Cell-CN, Cell-PO$_4$, and Cell-NHNH$_2$) were synthesized by known methods.[15] IPNs were synthesized by simultaneous irradiation method using γ-rays as initiator and a known amount of HPC, monomer, and N,N-MBAAm in an aqueous system by following the reaction scheme detailed in Table I.

Separation of Gel and Sol Fractions

Insolubilized product was separated from each reaction and any sol fraction was removed by

stirring for 1 h in distilled water. Depending upon the consistency of weight of xerogels after every wash and dry cycle, more stirrings of equivalent time (usually three to five per sample) were carried for recording constant weight and dried in an air oven at 40°C. These were then subjected to solvent polarity gradient treatment with methanol and stirred for 2 h for removal of any sol fraction left. IPN yield is defined as percentage add-on (P_{add-on}) and calculated as a function of weight increase of HPC or other backbone:

$$\%P_{add-on} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_2 and W_1 are weights of IPN and cellulosics, respectively.

FTIR, SEM, Elemental Analysis, and Swelling Studies

Elemental analysis was carried out on Carlo Erba elemental analyzer EA1108; FTIR spectra of cellulosics and their IPNs were recorded on Perkin–Elmer FTIR spectrometer in KBr pellets, and SEM was taken on a JEOL JSM-6100 scanning microscope.

Swelling Studies

Equilibrium swelling was studied by immersing 0.100 g of each polymer (xerogel) in water for 24 h at room temperature (22°C) and an amount of sorbed water was measured by a screening method. Hydrogels were partially hydrolyzed by 0.5N NaOH, washed, and swollen in distilled water for 24 h. Swelling of hydrolyzed hydrogels was also studied in 0.5N HCl and 5.0% NaCl solutions. Equilibrium percentage swelling (P_s) was calculated as:

$$P_s = [(W_s - W_d)/W_d \times 100]$$

where W_s and W_d are weights of swollen and dried polymers, respectively.

RESULTS AND DISCUSSION

IPN formation in a cellulosic matrix as one component via free-radical abstraction from its different —OH or —CH groups act as active sites for crosslinker attachments. In the present study,

partial solubility of HPC (32%) and high solubility of other components of the proposed IPN in aqueous medium resulting in the formation of biphasic networks should be of special interest in membrane applications. Because synthetic conditions affect structural aspects, and therefore, swelling characteristics of hydrogels, the kinetics of IPN formation is discussed in detail.

Effect of Total Radiation Dose on P_{add-on}

Radiation dose affects the polymerization processes by affecting abstraction of atoms, chain scission, and formation of crosslinks. Percentage add-on (P_{add-on}) as a function of total radiation dose is presented in Table I. Total dose of radiation was varied at a constant monomer (140.68 $\times 10^{-4}$ mol) and crosslinker concentrations (12.98 $\times 10^{-4}$ mol). It is observed that with variation of total radiation dose from 13.57×10^4 Gy to 108.0 $\times 10^4$ Gy, P_{add-on} increases in a linear fashion, giving maximum P_{add-on} (123.0%) at an optimum total radiation dose of 81.41×10^4 Gy. After that, it decreases to 105% with a further increase of radiation dose to 108.54×10^4 Gy. An increase in P_{add-on} with increasing radiation dose is due to facilitated generation of active sites on backbone where AAm is incorporated. Further increase in radiation dose results in depolymerization and chain scission reactions.

Effect of Crosslinker Concentration on P_{add-on}

In the absence of crosslinker, only a small amount of monomer was incorporated onto the backbone at optimum values of radiation dose. In the presence of crosslinker (3.13×10^{-4}-16.23×10^{-4} mol), P_{add-on} increases from to 54.0 to 105.0 (Table I). Thus, in the presence of crosslinker, a maximum amount of monomer gets incorporated at 12.98×10^{-4} mol of N,N-MBAAm. Because the presence of N,N-MBAAm results in enhanced chemical crosslinking processes leading to insolubilization of product, then the loss of HPC and AAm reacted in the system because solubility was minimized. Lower crosslinker concentration was used in further studies because crosslinker concentration increases crosslinking density, and hence, reduces the pore size of hydrogels.

Effect of AAm Concentration on P_{add-on}

P_{add-on} was studied as a function of AAm concentration at a dose rate of 26.75×10^4 Gy; it was

Table II   Swelling Behavior of Poly(AAm) Networks of Other Cellulosics

Backbone	$P_{\text{add-on}}$	P_s	P_s After Hydrolysis with 0.5N NaOH	P_s in 0.5N HCl of Hydrolyzed Sample (with 0.5N NaOH)	P_s in 5% NaCl of Hydrolyzed Sample (with 0.5N NaOH)
HPC	220.00	562.00	2919.00	403.00	1578.00
Cellulose	239.00	631.00	4919.00	291.50	1810.00
RCell-NHNH$_2$	298.00	557.00	4026.00	264.00	1402.00
RCell-CN	170.00	579.00	4156.00	203.00	1517.00
RCell-PO$_4$	304.90	313.00	3233.00	240.00	1178.00
HEC	313.50	442.00	3500.00	290.00	1325.00

observed that increasing monomer concentration from 70.34×10^{-4} to 351.71×10^{-4} mol increases $P_{\text{add-on}}$ to a maximum of 208.0% at 351.71×10^{-4} mol of AAm (Table I). No $P_{\text{add-on}}$ was observed in the absence of AAm when only N,N-MBAAm (3.246×10^{-4} mol) was present, despite the fact that N,N-MBAAm is a bifunctional monomer, but is reacted only in the presence of AAm. Increase in $P_{\text{add-on}}$ with increasing [AAm] is attributed to greater availability of monomer for chain initiation.

Effect of Amount of Water on $P_{\text{add-on}}$

Solvent amount does not only control polymerization processes, hence, polymer yield, but also plays an important role in controlling the porosity of the network formed. The effect of the amount of water on $P_{\text{add-on}}$ is presented in Table I. At the conditions worked out for maximum total radiation dose and monomer concentration, maximum $P_{\text{add-on}}$ was obtained in 10.00 mL of water. $P_{\text{add-on}}$ increases initially when the amount of water varied from 5.00 (208.0%) to 10.00 mL (223.0%), and then, decreases to 211.0% at 15.00 mL, 210.0% at 20.00 mL, and 220.0% at 25.00 mL of water. Higher solubility and accessibility of AAm and growing macroradicals in aqueous system leads to more incorporation of AAm with an increase of water, which gets reversed with increased dilution.

Effect of Nature of Backbones on $P_{\text{add-on}}$ of AAm Hydrogels

Variation of backbone affects $P_{\text{add-on}}$ in a pronounced way. The order of $P_{\text{add-on}}$ for various backbones is Cell-NHNH$_2$ (298.0%) > cellulose (239.0%) > HPC (223.0%) > HEC (213.5%) > Cell-PO$_4$ (204.0%) > Cell-CN (170.0%). The

extent of $P_{\text{add-on}}$ is not affected much by etherification, as is evident from the values of $P_{\text{add-on}}$ of cellulose, HPC, and HEC. It appears that water-soluble backbones such as HPC and HEC undergo homogenous polymerization processes with cross-linker and AAm but total backbone is not cross-linked, resulting in lower $P_{\text{add-on}}$ that manifested only in the extent of insolubilization of the product.

Evidence of IPN Formation by SEM, Elemental Analysis, and FTIR

From the wide-angle X-ray diffraction (WAXD) of extracted cellulose and HPC, it comes out that extracted cellulose has a far smaller degree of crystallinity (31.00%) than commercial cellulose (59.0%) and it gets further reduced on hydroxypropylation (15.54%) in the case of HPC.[16] SEMs of HPC and different IPNs were studied to evaluate the effect of synthetic conditions on structure morphologies of IPNs (Fig. 1). Differences in surface morphologies of crosslinked HPC and crosslinked poly(AAm) are evident from their SEMs and so are those of these polymers with HPC-cl-poly(AAm) hydrogels. However, from the SEM of the latter it is of interest that its two sides have different morphology, hence, discernible differences in the pore-size formation and pore distribution. This biphasic nature of the hydrogels where the dorsal side is more smooth and homogeneous and the ventral side with heterogeneous nature results from inhomogeneities in the HPC matrix in aqueous medium. This structural aspect of the networks has special potential for use of these materials in membrane applications.

IR absorption bands due to amide C=O stretching of AAm appear prominently at 1654.6 cm^{-1} in its poly(AAm) IPN apart from the absorp-
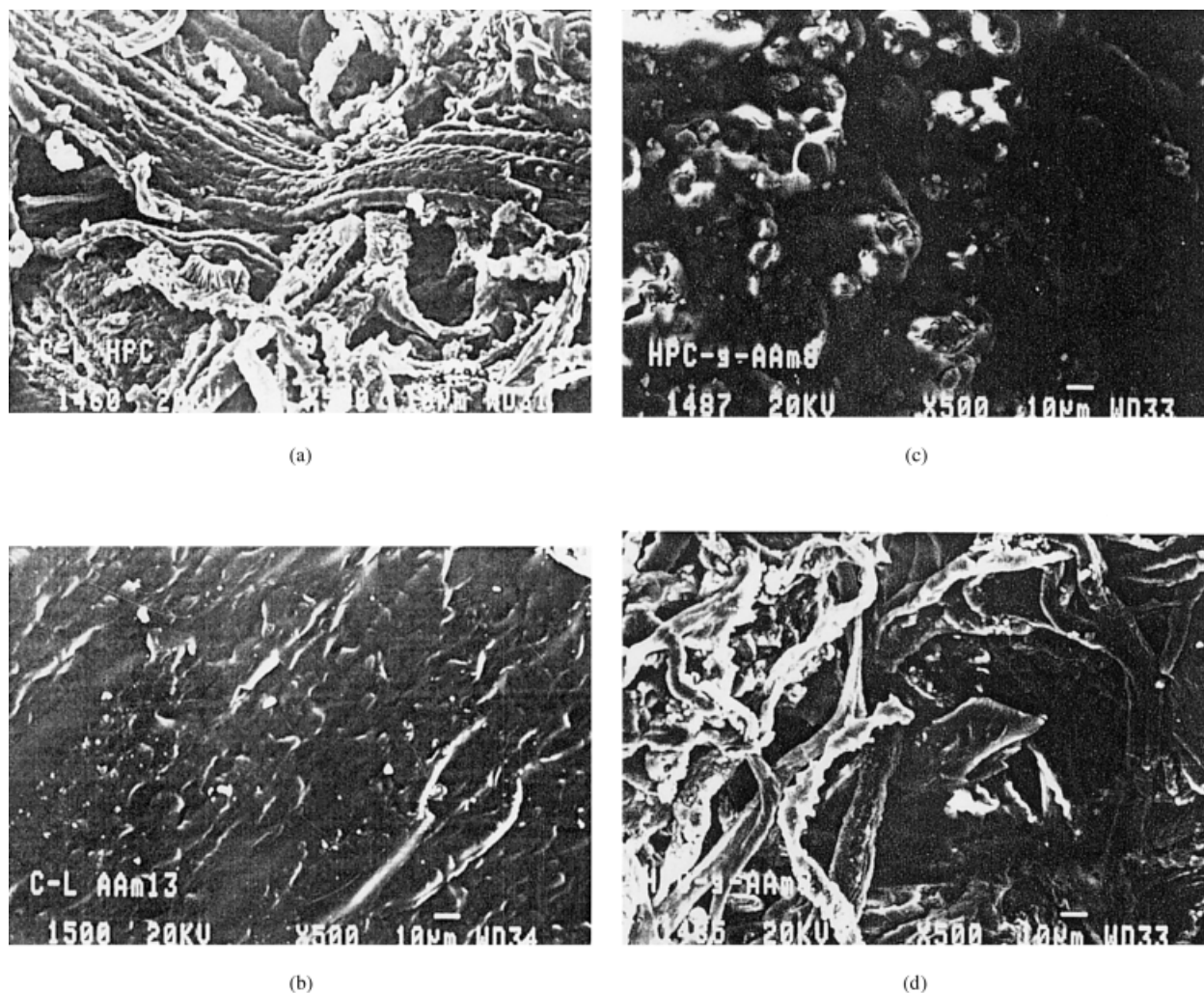
Figure 1 Scanning electron micrographs of (a) *cl*-HPC, (b) *cl*-poly(AAm), (c) HPC-*cl*-poly(AAm) dorsal view, and (d) HPC-*cl*-poly(AAm) ventral view (magnifications given in the micrographs).

tion bands of HPC (Fig. 2). These bands were also observed for other cellulose derivatives used, as a broad band appears at 3363.8 cm^{-1} because of overlapping of —NH and —OH group stretching, at 1653.9 cm^{-1} due to —NH bending in hydrazinodeoxycellulose, at 3410.3 cm^{-1} (—OH stretching) in HEC, and at 2253.7 cm^{-1} due to —CN stretching of cyanoethyl cellulose. FTIR also provides evidence of partial hydrolysis as a shift in absorbance of C=O from 1654.6 to 1670 cm^{-1} (%T = 3.33) and prominent peak due to carboxylate anion stretching at 1560.2 cm^{-1} (%T = 6.70) was observed. Further evidence to network formation is provided by elemental analysis of different IPNs that could not be quantified and correlated with gravimetric values of

AAm incorporated for obvious reasons as the presence of N in crosslinker.

## Synthetic Conditions and Swelling Behavior of Hydrogels

The nature and extent of interactions between solvent and polymer chains are affected by polymer structure because of the porosity and the nature of the groups on the polymer, which in turn are determined by the synthetic conditions. With an increase of total radiation dose, P_s changes appreciably, but decreases with its further increase (Fig. 3). Swellability of hydrogels decreases with an increase in [N,N-MBAAm] in
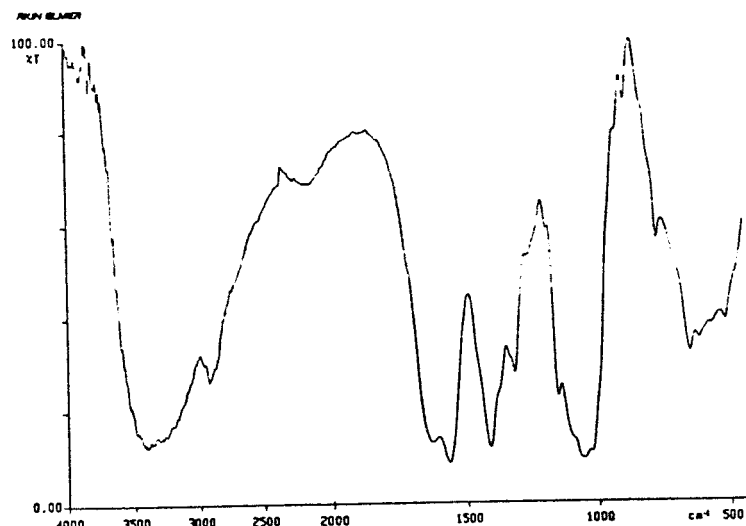
(a)
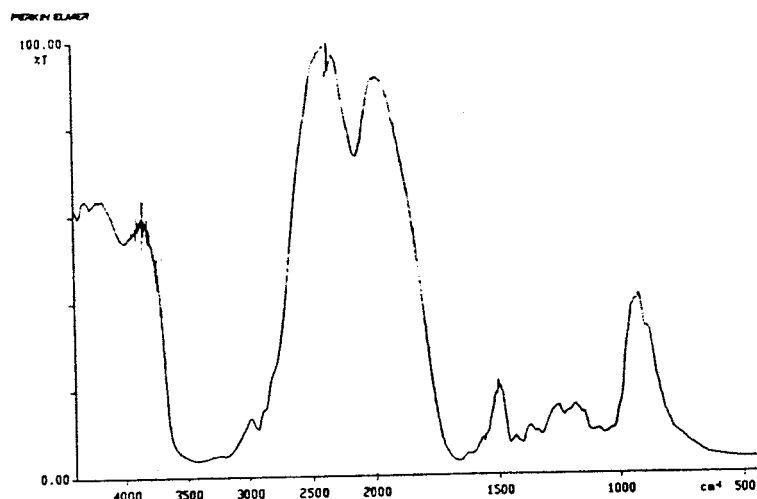
(b)
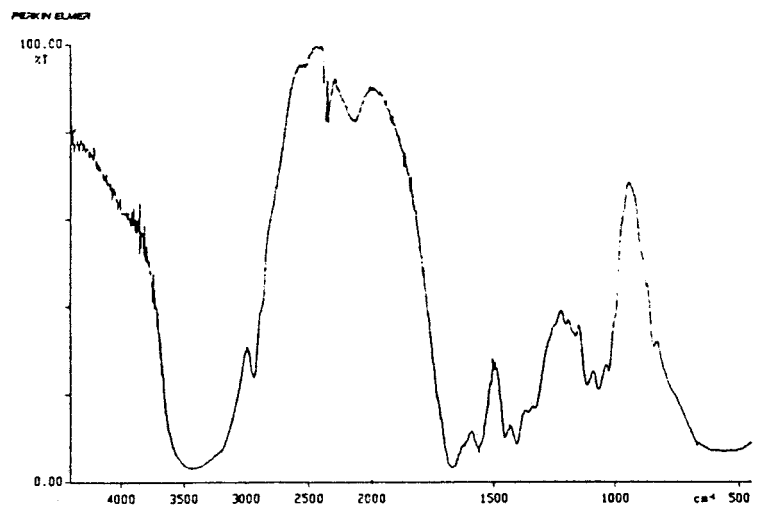
(c)

Figure 2 FTIR of (a) HPC, (b) HPC-*cl*-poly(AAm), and (c) hydrolyzed HPC-*cl*-poly(AAm).
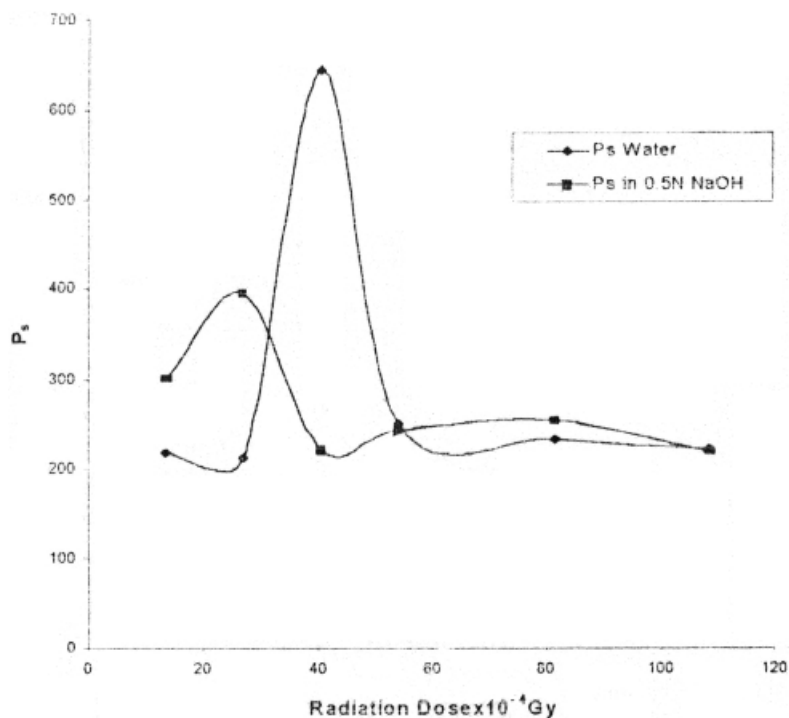
Figure 3 Effect of total radiation dose on P_s of HPC-*cl*-poly(AAm).

regular fashion because of the increase in crosslinking density and the decrease in pore size of the network[17,18] (Fig. 4). An increase in [AAm] increases swelling capacity of hydrogel because of an increase in the number of hydrophilic groups on polymer chain, hence, enhanced dipole–dipole interactions between amide group and water. However, P_s tends to be constant at higher monomer concentrations (Fig. 5). An increase in the amount of water in the reaction system initially
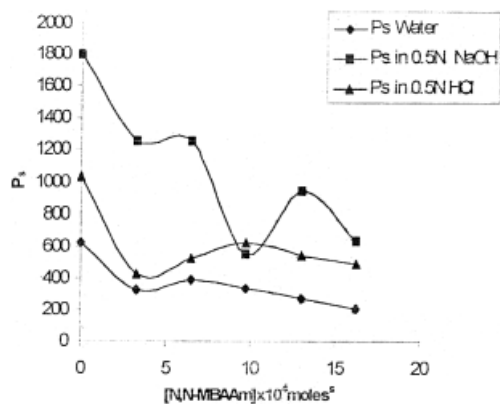

Figure 4 Effect of crosslinker on P_s of HPC-*cl*-poly(AAm).

increases P_s because of the well-defined network structure formed with increased polymerization processes[19] (Fig. 6). It was observed that out of the cellulosics studied, cellulose-based IPN is swollen most in water and the others follow the order: cellulose-*cl*-poly(AAm) (631.0) > cyanoethyl cellulose-*cl*-poly(AAm) (579.0) > HPC-*cl*-poly(AAm) (562.0) > hydrazinodeoxycellulose-*cl*-poly(AAm) (557.0) > HEC-*cl*-poly(AAm) (442.0) > cellulose phosphate-*cl*-poly(AAm) (313.0). In case of cellulose derivatives apart from HPC and HEC, lesser hydrophilic groups are incorporated, hence, observed results. Further, apart from the introduction of polar groups, well-structured polymer matrices in both these cases are expected because of the homogeneity of the reaction system; hence, higher P_s can be expected on the basis of more defined network structure. However, lower P_s observed in HEC and HPC-based matrices may not be gravimetrically true because of the solubility of backbone polymer itself and the consequent failure to get any part of it crosslinked.

Effect of Hydrolysis and Nature of Medium on Swelling Behavior of IPNs

Partial hydrolysis of hydrogels improves water retention capacity of hydrogels many times.[20] In
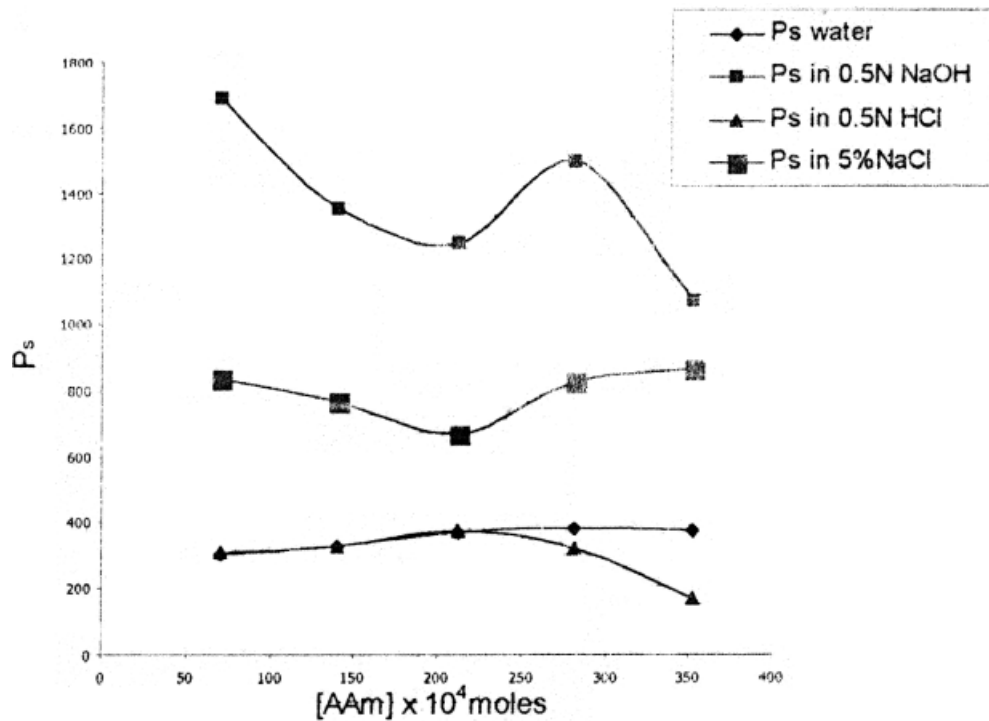
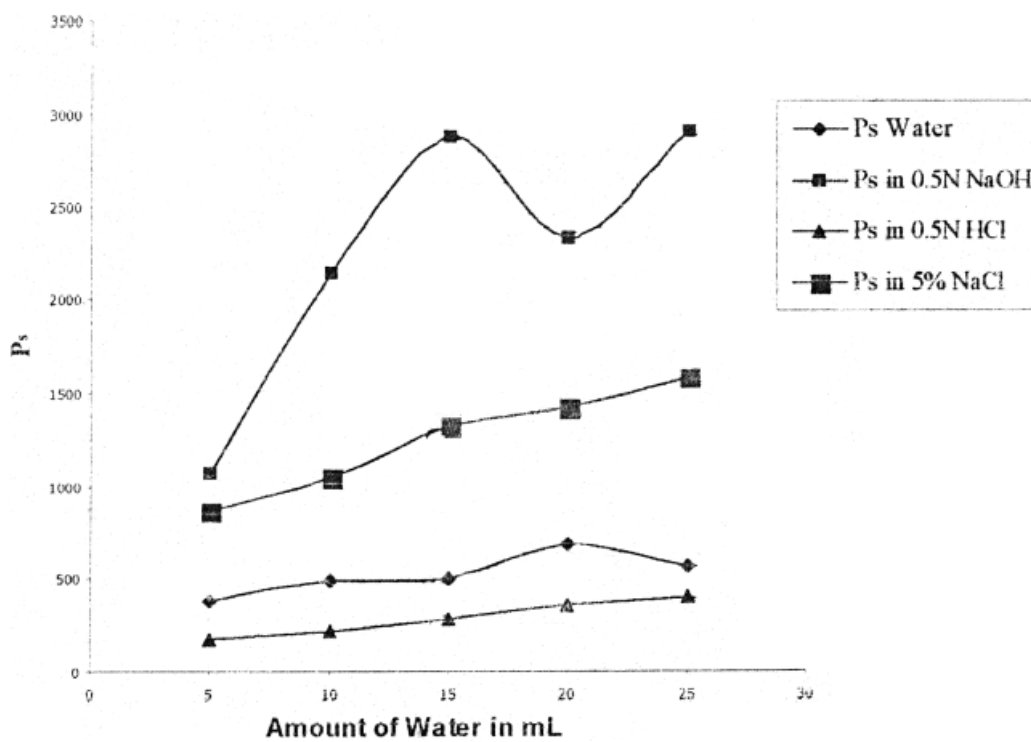**Figure 5**   Effect of [AAm] on P_s of HPC-*cl*-poly(AAm).

Figure 6   Effect of amount of water on P_s of HPC-*cl*-poly(AAm).

the present study also, partial hydrolysis of hydrogels with 0.5 NaOH increases swelling almost as many folds because of an increase in ion–dipole interactions of COO^- and $CONH_2$ and a balancing of ion–dipole forces. A shift in P_s becomes less pronounced with an increase in crosslinker concentration by affecting structural features of hydrogels such as pore size. An increase of AAm concentration increases P_s but subsequently decreases with monomer concentration due to less availability of NaOH per amide group. A more significant shift in P_s (up to six times) was observed in IPNs synthesized by variation of the amount of water as reaction medium. The effect of hydrolysis on swelling behavior of IPNs of cellulose and its other derivatives is significant as almost 8–10 times enhancement in P_s was observed. For obvious reasons, it is maximum in hydrolyzed hydrogels of cellulose phosphate. Hydrogels hydrolyzed in 0.5 NaOH and reswollen in 0.5N HCl show dramatic volume collapse due to reprotonation of the hydrolyzed group manifested in reduction in ion–dipole interaction. These results are important and support the role of partial hydrolysis in enhancing swelling of IPNs. Volume collapse of preswollen and partially hydrolyzed hydrogels was also observed in 5.0% NaCl solution, although this effect is not so dramatic as in the case of acid. The effect of brine environment on swelling behavior of hydrogels of cellulose and its derivatives is similar to that observed for those of HPC as for partially hydrolyzed hydrogel swell maximum in water, whereas there is dramatic volume collapse in 0.5 HCl.

It can be concluded that both volume–phase transitions of these hydrogels are affected both by the structural and by the nature of swelling medium. These hydrogels are environmentally sensitive, smart (or intelligent gels), and hence, can be used in many applications as per their response to environmental changes.

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