

# Synthesis and Characterization of Acrylamide and 2-Hydroxypropyl Methacrylate Hydrogels for Specialty Applications

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**ABSTRACT:** To modify acrylamide (AAm) hydrogels for specialty applications, it was copolymerized with 2-Hydroxypropyl methacrylate (HPMA) in different molar ratio at 25°C in 1:1 water–acetone solvent system, using ammonium persulphate (APS) and *N,N,N,N*-tetramethyl ethylene diamine (TEMED) initiator–accelerator system. Two series of hydrogels were thus prepared using two different crosslinkers—ethylene glycol dimethacrylate (EGDMA) and *N,N*-methylene bisacrylamide (*N,N*-MBAAm). To affect property profile of the hydrogels, concentration of HPMA was varied over a range of five concentrations from 3.5 to 28 mM. Hydrogels were further functionalized by partial hy-

drolysis with NaOH and Hofmann amide degradation reaction. FTIR, Nitrogen analysis, and SEM were used to establish monomer reactivity and structure relationship of the hydrogels. Metal ion uptake was studied as a function of various structural aspects of the hydrogels. Water uptake behavior of the hydrogels was studied at constant time, temperature, and pH, both pre and post metal loading. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3040–3049, 2006

**Key words:** acrylamide; hydrogels; 2-hydroxypropyl methacrylate; metal ion uptake; network efficiency; water uptake

## INTRODUCTION

Selective and effective metal ions uptake has been widely reported on polyacrylamide [poly(AAm)] whether as chains of a graft copolymer or as its crosslinked homopolymer. We have earlier reported use of functionalized poly(AAm) in different forms for the uptake of some transition metal ions.<sup>1–2</sup> Apart from their applications in environmental technologies, polymers sensitive to metal ions are also finding increased use in electronic and allied applications. Polyfunctional complexing agents and many auxiliary chemicals are required to prepare active support to the targeted species. Maleic acid, itaconic acid, and ethylenediaminetetraacetic acid are such active agents that are frequently introduced onto poly(AAm) hydrogel to make it an effective chelating agent. Kantoglu *et al.*<sup>3</sup> modified poly(AAm) by grafting ethylenediaminetetraacetic acid and used the resultant support for the selective absorption of uranyl ions, in the presence of cadmium and lead ions. Poly(acrylamide-*co*-maleic acid) hydrogels were used for monovalent cationic dye adsorption,<sup>4</sup> uptake of  $\text{UO}_2^{+2}$  ions,<sup>5</sup> and for the competitive removal of  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Zn}^{2+}$ .<sup>6</sup> On

the other hand, spectrum of applications of poly(AAm) hydrogels in advanced technologies can be improved by way of modification of its amide groups by alkylation<sup>7</sup> or even by way of metal ions uptake.<sup>8</sup> Partial hydrolysis, which is usually partial under operating conditions,<sup>9,10</sup> is a simple reaction that results in generation of carboxylate groups on the polymer. The result is significant changes in the water and metal uptake properties of the hydrogels.<sup>1</sup> Functionalization of polymeric supports such as hydrogels by the simple post polymer reactions is an efficient and clean operation.

Poly(AAm) hydrogels absorb large amount of water because of the presence of hydrophilic amide groups. Large water uptake results in the lack of hydrolytic stability and low tensile strength of these hydrogels and this ultimately restricts its uses in many applications where high mechanical strength and elasticity are desired properties of materials. The mechanical performance of poly(AAm) hydrogels can be improved by formation of its interpenetrating networks. Further, hydrophobicity of a hydrogel can be increased by its polymerization with a comonomer such as methacrylates. Such modification of poly(AAm) hydrogels results in the lower water uptake, but improves its strength. However, a proper balance of hydrogen bonding and hydrophobic interactions results in sharp volume phase changes of hydrogel.<sup>11,12</sup> Functional groups like amide those interact with wa-

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ter are also essential for metal ion uptake.<sup>13,14</sup> Hence, lower water uptake and improved strength results when hydrogels are loaded with metal ions. This aspect is catching the attention of researchers, and studies on networks containing metal–ligand interactions are reported. Gels containing metal–ligand interactions show better thermo-mechanical properties including increased  $T_g$  and higher degradation temperature than those of the original gels.<sup>15,16</sup>

In this article, we report preparation and characterization of AAm and HPMA based hydrogels for use as active polymeric supports for separation and removal of ionic species from the water systems. The work reported in this article attempts to investigate the effect of functionalization of networks by polymer analogous reactions such as saponification and Hofmann amide degradation, and correlation of the metal uptake and water uptake levels of the hydrogels before and after metal ions sorption.

## EXPERIMENTAL

### Materials

Acrylamide, *N,N,N,N*-tetramethyl ethylene diamine (S.D. Fine, Mumbai, India), *N,N*-methylene bisacrylamide (Qualigens Fine Chemicals, Mumbai, India), ammonium per sulfate (Sarabhai Chemicals, Vadodra, India), 2-Hydroxyl propyl Methacrylate, and ethylene glycol dimethacrylate (Merck, Goa, India) have been used as received.

### Synthesis and separation of networks

A model reaction is described as follows. 2-Hydroxypropyl methacrylate along with the fixed amounts of acrylamide (28 mM), ammonium per sulfate (1 mM) and ethylene glycol dimethacrylate (2.8 mM) and 0.5 mM of *N,N,N,N*-tetramethyl ethylene diamine was taken in 10.0 mL solvent system comprising of equal volumes of acetone and water. The reaction system was allowed to stand at 25°C for half an hour. Only the concentration of 2-hydroxypropyl methacrylate was varied in four other sets of reactions. Preparation of networks using *N,N*-MBAAm as crosslinker was also carried by the same reaction scheme.

Insolubilized polymers were separated from the reaction system by simple filtration, and sol fraction was separated from the networks by treating these repeatedly with water, methanol, and acetone, separately, in the order of decreasing polarity. The process was repeated till a constant weight was obtained and the hydrogels were dried in the vacuum oven till a constant weight was obtained to obtain *xerogel*. Percent formation efficiency (%E) of the network formed was calculated as:

$$\%E = \frac{\text{Weight of xerogel}}{\text{Weight of the monomers (MMA + AAm + crosslinker)}} \times 100$$

### Saponification and Hofmann degradation of amide

Partial hydrolysis was carried out by immersion of the known weight of each network in 50 mL of 0.5M NaOH solutions at 25°C. The functionalized networks were then washed, dried, and weighed. In case of Hofmann amide degradation reaction, 0.5 g of each network was immersed in 10.0 mL of water and kept in ice bath. 2.0 mL of 1% aqueous KOH solution was added gradually with constant stirring, to the pre-cooled reaction system. Bromine (2.0 mL) was added dropwise with constant stirring and temperature of the bath was not allowed to rise above 5°C. The mixture was stirred for half an hour and the product was separated by filtration. It was neutralized with 0.5M HCl, followed by filtration, and dried in vacuum oven at 40°C and weighed.

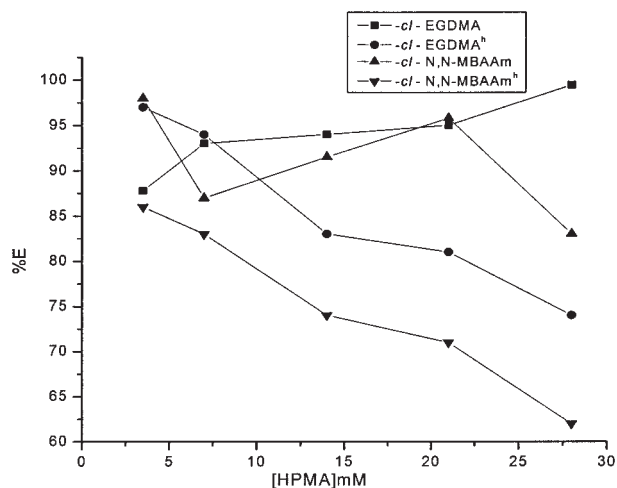
### Swelling ratio

The swelling behavior of all the networks was studied in water as a function of time and temperature. The networks show equilibrium swelling at 120 min and 45°C. The swelling ratio was studied as function of [HPMA], nature of crosslinker on the unfunctionalized and networks that were functionalized by post reactions. All the networks (0.1 g) were immersed in water for 120 min and temperature was 45°C in a temperature-controlled bath (accuracy  $\pm 0.1^\circ\text{C}$ ). The surface water from the networks was wiped off with a tissue paper and swelling ratio ( $S_r$ ) has been expressed by the following relationship:

$$\text{Swelling ratio } (S_r) = \frac{\text{Weight of the swollen hydrogel}}{\text{weight of the xerogel}}$$

### Metal ions uptake studies

Metal ions sorption was studied as reported earlier.<sup>1</sup> Networks from each monomer series were separately immersed for known time in the aqueous solutions of copper sulfate, ferrous sulfate, and chromium oxide of known concentrations. All weights were taken on Denver TR-203 Balance having minimum readability of 1.0 mg. Filtrates of the solutions were analyzed for concentration of rejected ions on DR 2010 Spectrophotometer (Hach Co., US) by using its standard pillow reagents. Using this method, maximum limit of ion strength that can be studied on this instrument is 5.0, 3.0, and 0.6 mg/L of solution, respectively, of Cu+2, Fe+2, and Cr+6. Results of analysis have been presented as:



**Figure 1** Effect of [HPMA] on percent yield of networks (<sup>h</sup> indicates partially hydrolyzed).

Percent ion uptake ( $P_u$ )

$$= \frac{\text{Total metal ions in the feed} - \text{Amount of metal ions rejected}}{\text{Total metal ions in the feed}}$$

#### SEM, nitrogen analysis and FTIR studies

SEMs of the networks were recorded on Joel JSM 6100 and FTIR spectra were recorded in KBr pellets on Perkin-Elmer. Elemental analysis (Nitrogen contents only) was recorded on Carlo Erba EA-1108.

### RESULTS AND DISCUSSION

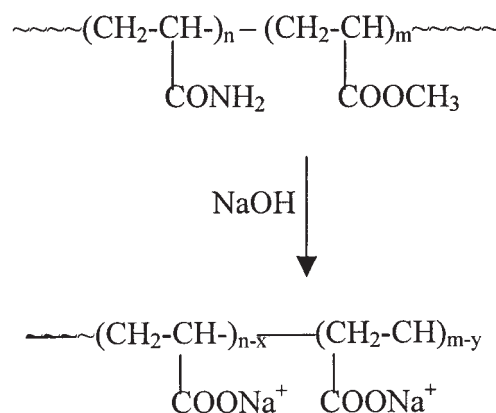
Properties of the networks prepared have been investigated as a function of variation of mole ratio of the monomers in the feed, nature of the crosslinker, and effect of post reactions on the networks.

#### Effect of methacrylate concentration and nature of crosslinker on network yield

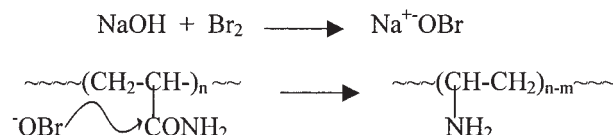
In the present study, since the [AAm] was kept constant (28 mM) throughout the reaction scheme to prepare both the series of the networks, only [HPMA] was varied. When EGDMA was used as crosslinker, it has been observed that %E increased linearly from 87.8 to 99.45 on increase of [HPMA] in the feed from 3.5 mM to 28.0 mM. (Fig. 1). When *N,N*-MBAAm was used as crosslinker, %E decreased linearly from 98.0 to 83.0 with the increase of [HPMA]. Such trends in results are manifestations not only of monomer reactivity ratio of the AAm with the methacrylate, but also are consequences of increase in the hydrophobicity of the contents of the reaction system as comonomer

(HPMA) and crosslinker are both of hydrophobic nature. On the other hand, on use of *N,N*-MBAAm as crosslinker the higher %E was observed at lower [HPMA], which decreased with the increase in [HPMA]. It also follows that the monomer wastage in crosslinking reactions is very low as most of the constituents of the reaction system are incorporated into the networks. Further, the network formation process is also facile and not energy intensive, as the networks were prepared at low temperature (25°C). Almost negligible wastage of the reactant system and low energy requirement in polymerization processes are in line with the requirements of green chemistry.

On saponification with 0.5M NaOH, some of the amide and ester groups get partially hydrolyzed to carboxylate groups, which were later converted to carboxylic groups by treatment with HCl. While in Hoffmann amide degradation reaction, only the amide moiety is changed to amine groups. Weight loss of the polymers has been observed in both the cases (Fig. 1). Structure of the Hofmann product (I) is presented later:



Where  $n-x$  and  $m-y$  are degree of hydrolysis of amide and ester groups. I can be converted to carboxylic functions by treatment with HCl. Hofmann amide degradation scheme is given as:



where  $n-m$  is degree of Hofmann amide degradation.

#### Characterization of hydrogels

SEM, nitrogen analysis and FTIR analysis were used to get evidence of incorporation of both the monomers and to analyze other structural aspects of the net-



TABLE I  
Elemental (Nitrogen) Analysis of Networks

| Networks  | Wt. (g) | N (%) | Wt. N (g) | AAm (g) | MMA (g) | Ratio of MMA/AAm |
|---|---------|-------|-----------|---------|---------|------------------|
| Poly(AAm-co-HPMA)- <i>cl</i> -EGDMA <sup>a</sup>              | 3.052   | 10.42 | 0.318     | 1.610   | 1.442   | 1.81             |
| Poly(AAm-co-HPMA)- <i>cl</i> -EGDMA <sup>b</sup>              | 2.467   | 5.48  | 0.135     | 0.685   | 1.782   | 5.25             |
| Poly(AAm-co-HPMA)- <i>cl</i> - <i>N,N</i> -MBAAm <sup>b</sup> | 2.090   | 2.89  | 0.060     | 0.306   | 1.784   | 11.77            |
| Poly(AAm-co-HPMA)- <i>cl</i> -EGDMA <sup>c</sup>              | 3.504   | 5.02  | 0.175     | 0.891   | 2.613   | 5.92             |

<sup>a,b</sup> Networks prepared, respectively, with 3.5 mM and 28 mM of MMA in the feed.

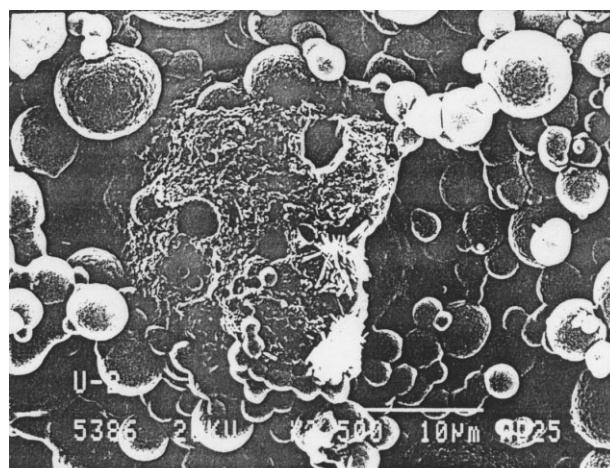
<sup>c</sup> Partially hydrolyzed network.

works. The increase in the weight of the network is the obvious evidence of the incorporation of monomers in the network. Further, nitrogen analysis does not only provide the evidence of incorporation of monomers, but also the relative percentage of both the monomers in the networks. In case of the networks crosslinked with EGDMA, the composition of the networks from the ratio of AAm to that of the HPMA has been calculated from the N analysis. The ratio of HPMA to AAm in the network has been observed to increase with the increase of [HPMA] in the feed, and it is supported by the fact that % N decreases in these networks with the increase in [HPMA] in the feed (Table I). Since in this case, %E also increases with the increase of [HPMA], it can be concluded that more of HPMA was incorporated in the networks as its concentration increased in the feed at the constant feed of AAm. It is clear that the incorporation of the methacrylate increases with its availability in the feed and it is also dictated by the reactivity ratio of the monomers.<sup>17</sup>

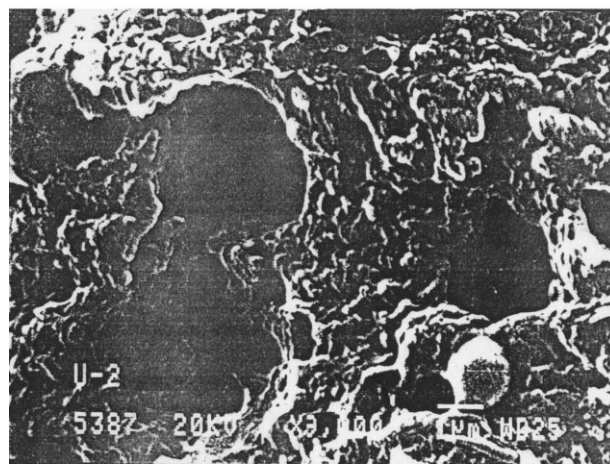
SEM of EGDMA crosslinked network prepared at the highest [HPMA] reveals formation of well-defined pores and crosslinks. Because of the interactions of the hydrophobic and hydrophilic nature of the network components, its surface has also some globular shapes due to coiling of the polymer chains. On partial hydrolysis, many crosslinks are disrupted and the pore size increases by many times (Fig. 2(a)). On the other hand, surface morphology of the *N,N*-MBAAm crosslinked network prepared at the same feed concentration of HPMA, as in case of the EGDMA, reveals a sharp contrast in the surface morphology. It is observed that the surface is highly uniform and appears as film in the amide crosslinked network (Fig. 2(b)). Thus, it follows that not only does the nature of the crosslinker affect the surface morphology of the network; it also implies that the properties of the network are expected to be distinctly different.

FTIR spectrum of poly(AAm-co-HPMA)-*cl*-EGDMA synthesized at 3.5 mM of HPMA shows characteristic absorption peaks both for AAm and ester groups. Absorption peaks at 3491.9 (% A

= 96.67), 2925.0 (% A = 96.41), 1700.0 (% A = 90.0), and 1669.0 cm<sup>-1</sup> (% A = 96.84), respectively, correspond to the stretching vibrations of —NH<sub>2</sub>, —CH, ester —C=O of HPMA and EGDMA, and amide

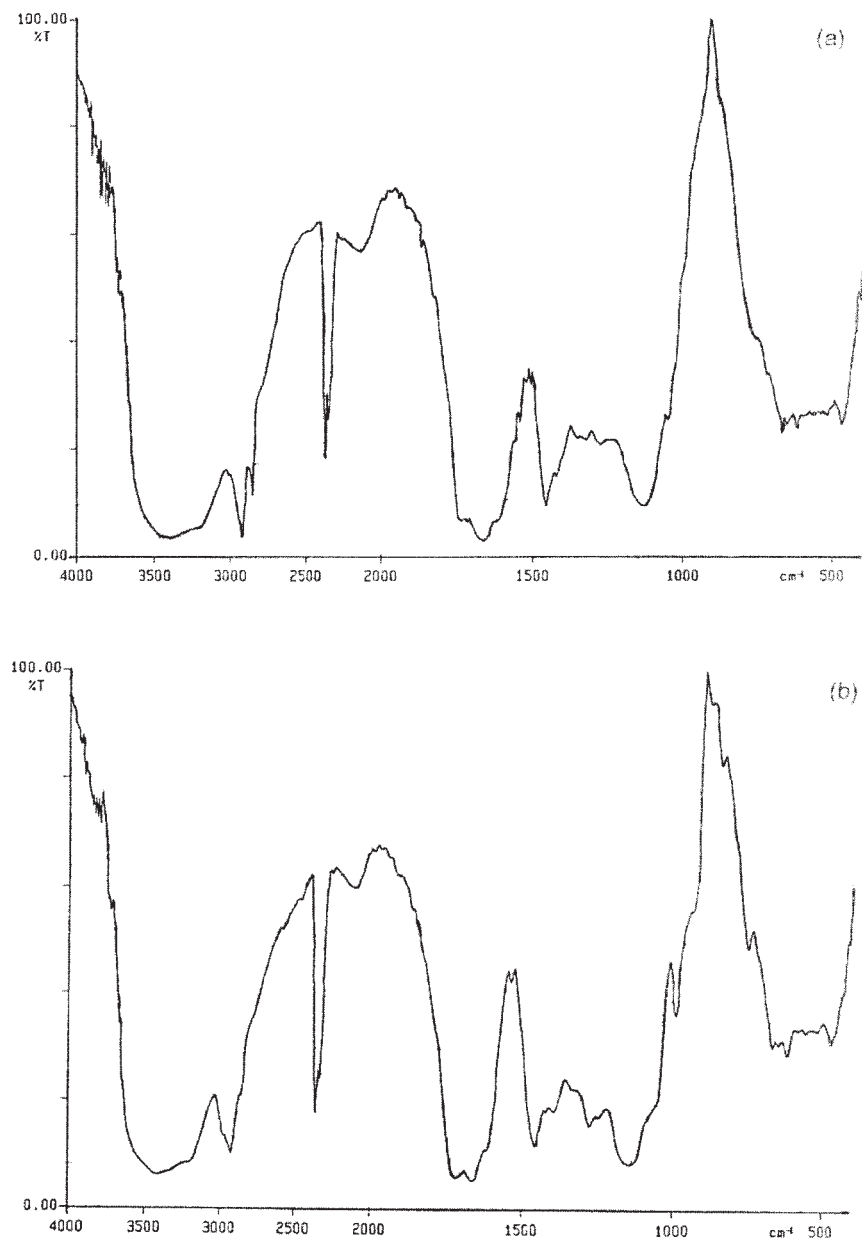


(a)



(b)

Figure 2 SEM (a) Poly(AAm-co-HPMA)-*cl*-EGDMA and Poly(AAm-co-HPMA)-*cl*-*N,N*-MBAAm (magnification given in the micrographs).



**Figure 3** FTIR spectrum of Poly(AAm-co-HPMA) crosslinked with EGDMA at (a) low (b) high HPMA concentrations. FTIR spectrum of Poly(AAm-co-HPMA) (c) crosslinked with *N,N*-MBAAm at high [HPMA] and (d) partially hydrolyzed Poly(AAm-co-HPMA) crosslinked with EGDMA.

$\text{—C=O}$  of AAm (Fig. 3(a)). FTIR spectrum of the network synthesized with 28 mM of the HPMA in feed, shows absorption bands at 3422.1 (% A = 93.63), 2928.1 (% A = 89.7), 1700.0 (% A = 91.0), and  $1671.3\text{ cm}^{-1}$  (% A = 94.49), respectively, because of the stretching vibrations of  $\text{—NH}_2$ ,  $\text{—CH}$ ,  $\text{—C=O}$  of  $\text{—COOR}$ , and  $\text{—CONH}_2$  (Fig. 3(b)). The lower %A of  $\text{—NH}_2$  group (93.63%) in this network suggest higher incorporation of HPMA. Such conclusion is also supported by the N analysis results. The FTIR spectrum of poly(AAm-co-HPMA) prepared with crosslinker *N,N*-MBAAm and with the highest [HPMA] shows characteristic absorption

peaks at 3401.0 (% A = 94.15), 2926.6 (% A = 93.07), 1700.0 (% A = 92.0), and  $1672.3\text{ cm}^{-1}$  (% A = 95.53), respectively, ascribed to the stretching vibrations of afore-mentioned groups. The higher % A due to the  $\text{—NH}_2$  group was observed that implies increase in the number of  $\text{—NH}$  groups in the network because of the presence of *N,N*-MBAAm (Fig. 3(c)). Apart from the usual peaks, FTIR spectrum of partial hydrolyzed poly(AAm-co-HPMA)-*cl*-EDGMA and with the highest [HPMA] shows characteristic absorption peaks at 3446.1 (% A = 91.09), 1700.0 (% A = 57.14), and  $1654.2\text{ cm}^{-1}$  (% A = 68.0), respectively, for stretching vibrations of  $\text{—NH}_2$ ,  $\text{—C=O}$  of

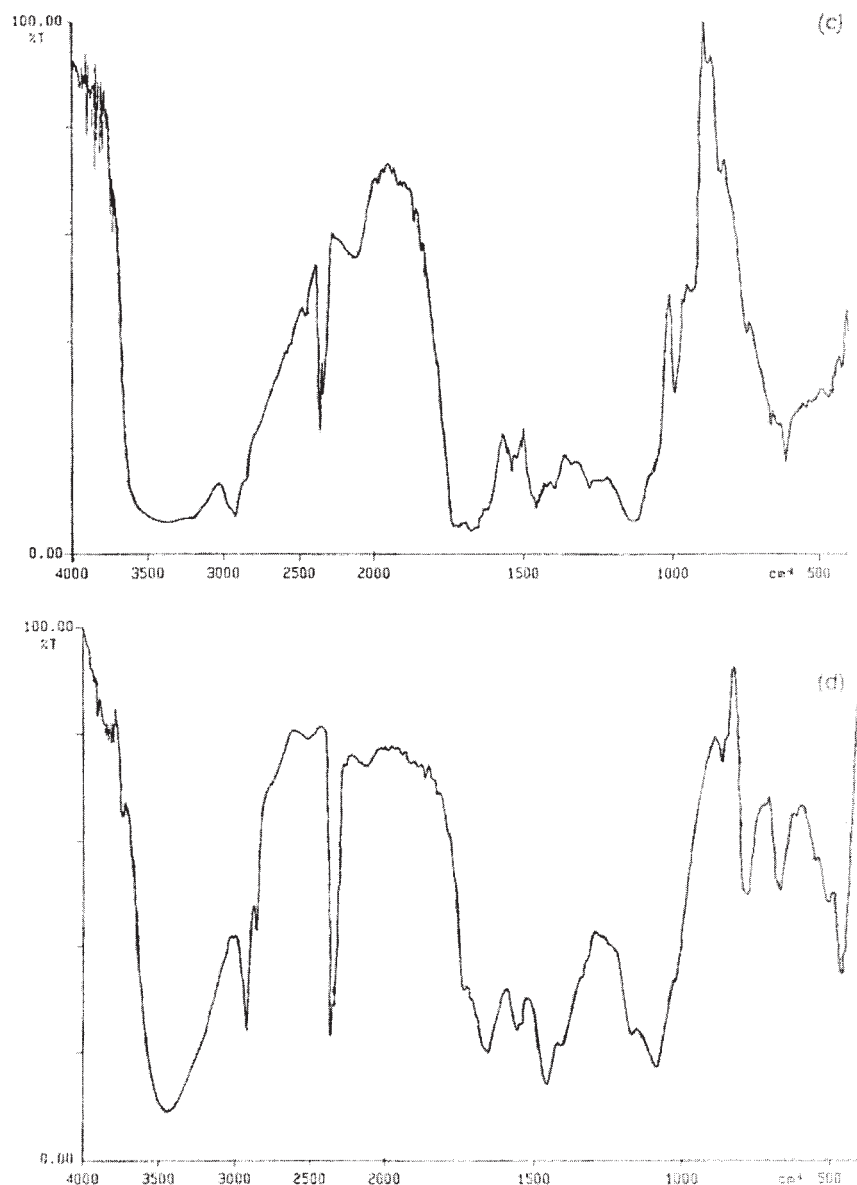


Figure 3 (Continued from the previous page)

—COOR, and —CONH<sub>2</sub> (Fig. 3, days). The lower characteristic % A values of the —C=O stretching of the ester and amide groups means loss of these groups on partial hydrolysis.

#### Metal ions uptake studies

Apart from the ion exchange or adsorption of ions on the active groups, sorption of ions also takes place in the bulk of the network by way of the effective partitioning of ions between solution and the polymer phases. In the present case, since the networks have adsorbent groups like —CONH<sub>2</sub> in the parent network, ion exchange groups (—COO<sup>−</sup>Na<sup>+</sup>) are generated after partial hydrolysis and metal ion complexing basic groups like —NH<sub>2</sub> are generated by Hofmann

amide degradation reaction, different processes contribute for the overall metal ion uptake.<sup>1</sup> Metal uptake behavior of the networks has been studied as a function of [HPMA], nature of crosslinker, and effect of the post reactions.

#### Sorption behavior of Cr<sup>6+</sup>

In case of the hydrogels crosslinked with EGDMA, it was observed that as the amount of HPMA increases in the networks,  $P_u$  decreases from 15 to 6. The trend in these results is just reverse for the hydrogels based on *N,N*-MBAAm, where the lowest and the highest values for  $P_u$  are 3.0 and 18.75. The difference in the metal uptake levels by these two series of networks is related to the structure of the hydrogels. From the

SEM of these networks, it is evident that in the EGDMA series well-defined pores are visible, crosslinking density is lower, and hence, pore size is more. Result is a higher uptake in the bulk of the network. But in case of *N,N*-MBAAm, the networks have film like smooth surface due to higher crosslinking density and result is smaller pores and lower metal ions uptake in the bulk of the networks. In case of *N,N*-MBAAm, the dominant factor is adsorption on the surface. These structural differences, as revealed by the surface morphology of the networks, are manifested in different metal ion uptake behavior by way these two series of networks.

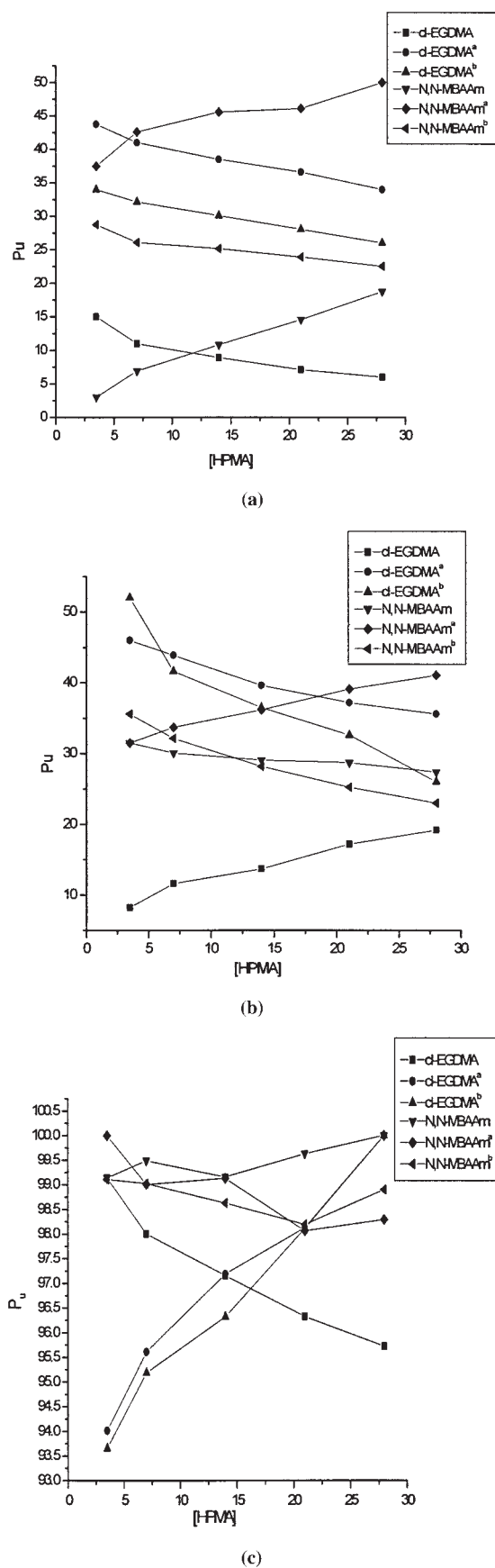
$P_u$  increases many a time in both the series of networks functionalized by polymer analogous reactions (Fig. 4(a)). Such trends in the results are ascribed to the opening up of these networks by functionalization as compared with the unfunctionalized network that has film like smooth surface, especially, in *N,N*-MBAAm crosslinked networks. Other contributory factor is generation of more active groups like  $\text{—COO}^-$  and  $\text{—NH}_2$ . Functionalization results in the higher sorption of metal ions in the bulk rather on the surface of the network. While in case of Hofmann products the trends in results are similar in both the series of networks, these are different in case of partially hydrolyzed networks.

### Sorption behavior of $\text{Cu}^{2+}$ ions

Sorption behavior of  $\text{Cu}^{2+}$  ions by both the hydrogel series is presented in (Fig. 4(b)). In case of the unfunctionalized networks, the trends in the results are just reverse to those observed in case of  $\text{Cr}^{6+}$  ions. The unfunctionalized *N,N*-MBAAm based networks sorb far more  $\text{Cu}^{2+}$  than the other series of networks. With the increase in [HPMA],  $P_u$  increases for EGDMA based hydrogels, but decreases in *N,N*-MBAAm based hydrogels. On functionalization, the trends in the results are same as observed for  $\text{Cr}^{6+}$ , and  $P_u$  was observed to increase for both the series of hydrogels.

### Sorption behavior of $\text{Fe}^{2+}$ ions

Sorption behavior of  $\text{Fe}^{2+}$  ions is presented in Figure 4(c). When compared with that of  $\text{Cr}^{6+}$  and



**Figure 4** (a) Percent uptake of  $\text{Cr}^{6+}$  ions in poly(AAm-co-HPMA) as a concentration of HPMA (<sup>a</sup> indicates partially hydrolyzed, <sup>b</sup> indicates Hofmann degraded). (b) Percent uptake of  $\text{Cu}^{2+}$  ions in poly(AAm-co-HPMA) as a function of concentration of HPMA (<sup>a</sup> indicates partially hydrolyzed, <sup>b</sup> Hofmann degraded). (c) Percent uptake of  $\text{Fe}^{2+}$  ions in poly(AAm-co-HPMA) as a function of concentration of HPMA (<sup>a</sup> indicates partially hydrolyzed; <sup>b</sup> indicates Hofmann degraded).

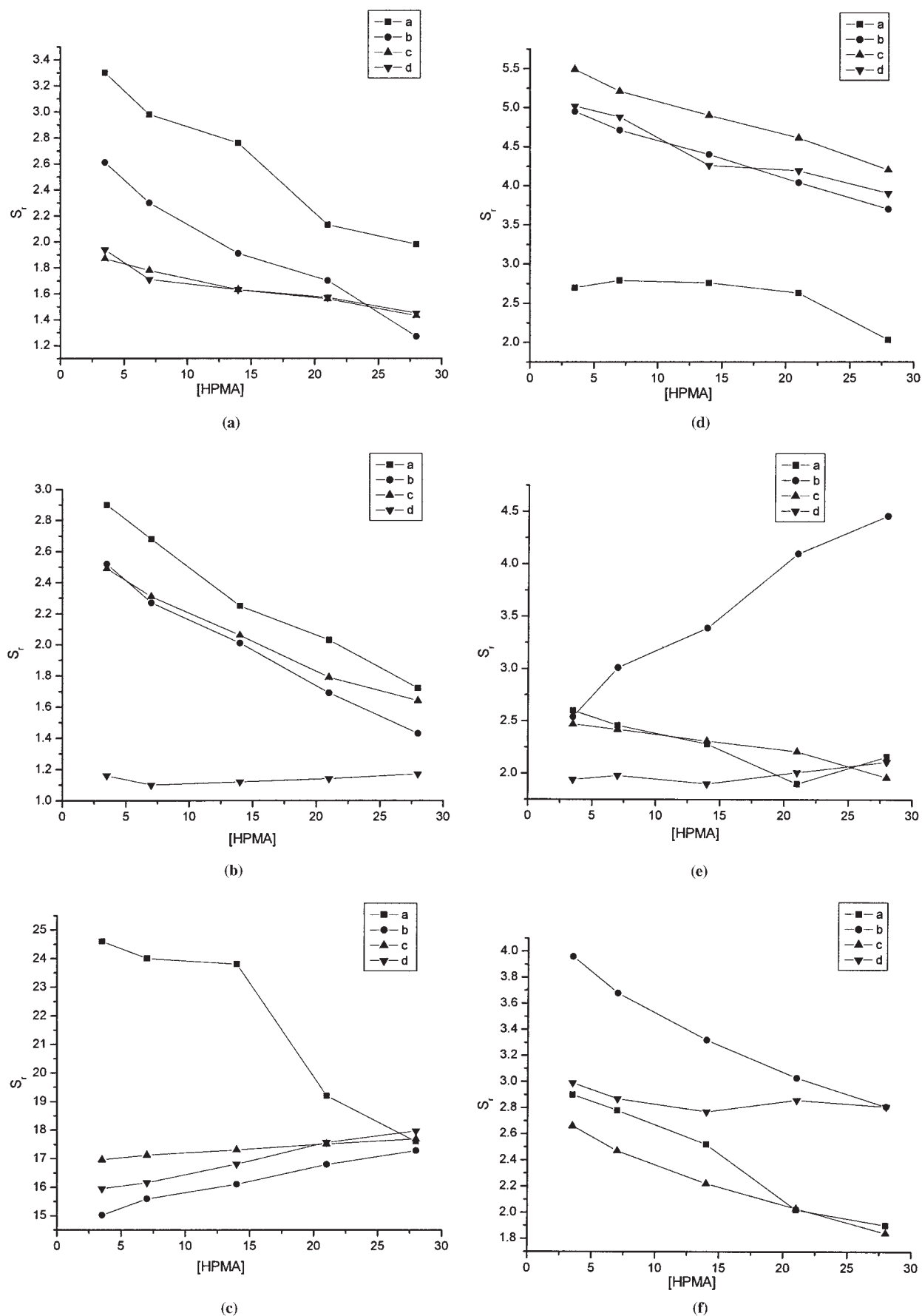


Figure 4 (Continued from previous page)



$\text{Cu}^{2+}$ , there is a major shift in the uptake behavior in this case as  $P_u$  up to 100% has been observed even by the unfunctionalized networks. On partial hydrolysis,  $P_u$  increases to 100%. Such high affinity for  $\text{Fe}^{+2}$  ions by the functionalized hydrogels has been earlier reported in case of hydroxypropyl cellulose and poly(methacrylamide) based hydrogels.<sup>1</sup> Hydrolysis enhances metal ion uptake as it effectively increases metal ion partitioning between the solution and polymer phase.

### Swelling behavior of the hydrogels

Water uptake and swelling properties of hydrogels are affected by many factors, including structural aspects of the hydrogels as well as the environmental factors like pH, temperature, and time.

### Effect of [HPMA] and nature of crosslinker and functionalization on the swelling ratio

In the present study, swelling ratio of the networks has been studied as a function of [HPMA] in the networks, nature of crosslinker, and effect of functionalization at the time and temperature evaluated for equilibrium swelling. The shape of the hydrogels does get distorted on water uptake. The presence of hydrophobic component (HPMA) in the network adversely affects the quantum of water uptake and contributes to the improvement in its mechanical stability by way of lower affinity for water. It has been observed that  $S_r$  of the hydrogels decreases with the increase of [HPMA] in both the network series (Figs. 5(a) and 5(b)). From the swelling behavior of these networks, it is observed that though the quantum of water uptake is affected by the nature of crosslinker, it does not affect the swelling behavior of the networks. Despite the hydrophilic nature of the *N, N*-MBAAm, the higher crosslinking density in *N, N*-MBAAm based network series results in lower water uptake. The water uptake was observed to decrease with the increase of [HPMA] contents of the networks suggesting increase in hydrophobicity of the networks. On functionalization,  $S_r$  increased many times on partial hydrolysis, but decreases in Hoffman degradation reaction products. The higher

water uptake in case of the former is attributed to the charge separation because of the generation of carboxylate groups and consequent enhanced interactions with water, while in case of the latter, the lower water uptake by the networks is attributed to the presence of amino groups.

### Swelling ratio of the metal ion loaded network

A comparative study of  $S_r$  without metal ions uptake and after metal ion uptake has been shown in Figure 5(c)–5(f). It is evident from the results that the nature and quantum of the metal ion affects  $S_r$  in a significant manner. Water uptake in EGDMA based network series loaded with metal ions follows the trend:  $\text{Fe}^{2+} \approx \text{Cu}^{2+} \ll \text{Cr}^{6+}$ . Whereas it is clearly demarcated in case of *N,N*-MBAAm based hydrogel series as the trend for  $S_r$  follows  $\text{Fe}^{2+} \ll \text{Cu}^{2+} < \text{Cr}^{6+}$ . In case of functionalized networks, it is evident that the effect of the nature of crosslinker is a major contributory factor than the nature of metal ions to affect the  $S_r$ . For all the three metal ions,  $S_r$  increases in *N,N*-MBAAm based networks after metal ions loading, the trends are just reverse for the other series of networks. In case of Hofmann based series crosslinked with EGDMA,  $S_r$  is more a manifestation of the nature of metal ions, as  $\text{Cr}^{+6}$  loaded networks swell more than the unloaded networks. Such behavior results from the preferential interactions of  $\text{Cr}^{6+}$  with amino groups, and consequently, the attached metal ions are hydrated more. While in case of the  $\text{Fe}^{2+}$  loaded networks the decrease in the  $S_r$  values after metal ions loading is related to the quantum of metal ions uptake. Such behavior is more sharply manifested in  $\text{Fe}^{2+}$  loaded networks where the quantum of the loaded ions is also very high. It implies that metal ions are sorbed in the bulk of the networks by making linkages to the adsorbent pendant groups like amide, amino, ester, or carboxylate groups. Such occupancy by the metal ions in the interior of the gels constricts the space for water to reach the interior of the network.

**Figure 5** (a) Percent Swelling of Poly(AAm-co-HPMA)-cl-EGDMA as a function of [HPMA]. a, Before metal ion uptake; b, after  $\text{Cr}^{+6}$  sorption; c, after  $\text{Cu}^{+2}$  sorption; d, after  $\text{Fe}^{+2}$  sorption. (b) Percent swelling of Poly(AAm-co-HPMA)-cl-*N,N*-MBAAm as a function of [HPMA]. a, Before metal ion uptake; b, after  $\text{Cr}^{+6}$  sorption; c, after  $\text{Cu}^{+2}$  sorption; d, after  $\text{Fe}^{+2}$  sorption. (c) Percent Swelling of partially hydrolyzed Poly(AAm-co-HPMA)-cl-EGDMA as a function of [HPMA]. a, Before metal ion uptake; b, after  $\text{Cr}^{+6}$  sorption; c, after  $\text{Cu}^{+2}$  sorption; d, after  $\text{Fe}^{+2}$  sorption. (d) Percent Swelling of partially hydrolyzed Poly(AAm-co-HPMA)-cl-*N,N*-MBAAm as a function of [HPMA]. a, Before metal ion uptake; b, after  $\text{Cr}^{+6}$  sorption; c, after  $\text{Cu}^{+2}$  sorption; d, after  $\text{Fe}^{+2}$  sorption. (e) Percent Swelling of Hofmann degraded Poly(AAm-co-HPMA)-cl-EGDMA as a function of [HPMA]. a, Before metal ion uptake; b, after  $\text{Cr}^{+6}$  sorption; c, after  $\text{Cu}^{+2}$  sorption; d, after  $\text{Fe}^{+2}$  sorption; (f) Percent Swelling of Hofmann degraded Poly(AAm-co-HPMA)-cl-*N,N*-MBAAm as a function of [HPMA]. a, Before metal ion uptake; b, after  $\text{Cr}^{+6}$  sorption; c, after  $\text{Cu}^{+2}$  sorption; d, after  $\text{Fe}^{+2}$  sorption.

## CONCLUSIONS

From the metal ion sorption studies, it can be concluded that without functionalization, both the hydrogel series show selectivity in the sorption of  $\text{Cu}^{2+}$  and  $\text{Cr}^{6+}$  ions as the quantum of metal ion uptake increases only after functionalization. The amount of water uptake is usually directly related to the metal ion uptake. It has also been observed that higher the water uptake, higher is the metal ion uptake by the hydrogels. The size of metal ions after hydration affects the level of metal ion uptake, and barring a few exceptions, it is concluded that both the networks series have preference for metal ions in the order  $\text{Fe}^{+2} \gg \text{Cu}^{+2} > \text{Cr}^{+6}$ . Mechanism, quantum, and selectivity in metal ions sorption are functions of the nature of the crosslinker and nature of the post reactions. Water-uptake studies reveal that metal ions are sorbed into the bulk of the networks by making linkages to the adsorbent pendant groups. Hence, lowering of the water uptake by the presence of methacrylate and metal ions results in the improved mechanical strength or reduced hydrolytic stability of the poly(AAm) hydrogels by way of improved hydrophobicity and lower water uptake. Hence, from these results it follows that these networks can be suitably tailored for the effective and specific separation and enrichment of different multivalent metal ions.

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