SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS OF 2-HYDROXYETHYL METHACRYLATE AND SOME COMONOMERS ONTO EXTRACTED CELLULOSE FOR USE IN SEPARATION TECHNOLOGIES

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To develop low-cost and environmentally friendly polymeric materials for enrichment, separation, and remediation of metal ions from water, graft copolymers based on cellulose extracted from pine needles were synthesized by grafting of 2-hydroxy methacrylate (HEMA) alone and with comonomers acrylic acid, acrylamide, and acrylonitrile by benzoyl peroxide initiation. The effects of change in concentrations of monomer and initiator, reaction time and temperature; and nature and composition of solvent system on graft yield and grafting efficiency were evaluated. At the optimum reaction conditions evaluated for the grafting of HEMA alone, comonomers as acrylamide, acrylic acid, and acrylonitrile at their five different concentrations were also co-grafted along with HEMA onto cellulose backbone polymer. Graft copolymers were further functionalized by partial hydrolysis, and were characterized by water uptake, FTIR, and elemental analysis**.** Sorption of Fe^{2+}, Cu^{2+} and Cr^{6+} ions on graft copolymers were investigated to define their end-uses in separation technologies.

Keywords: Graft copolymers; Comonomers; Metal ion sorption; FTIR

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INTRODUCTION

In order to develop renewable resource-based functional polymers with well-defined structures for use in separation and enrichment technologies, Chauhan et al. have reported grafting of vinyl monomers as a single monomer or as binary monomer mixtures onto the cellulose extracted from pine needles and its derivatives (Chauhan et al. 2000, 2002, 2003, 2002, 1999, 2005). Cellulose is a suitable candidate for the preparation of hydrogels by grafting or crosslinking reactions, as its linear structure provides good reinforcing properties to the networks. Grafting of acrylamide onto cellulose was reported by using ceric ammonium nitrate as initiator, and this grafted cellulose was investigated for sorption of Cu, Cr, Ni and Pb ions (Nada et al. 2007). 2-Hydroxyethyl methacrylate (HEMA) is a monomer of gelling nature (Chu et al. 1995; Karlsson and Gatenholm 1996) and its hydrogels find uses in biomedical applications such as drug release (Ende and Peppas 1997; Sassi et al. 1996) and artificial organs (Singh and Agarwal 1992; Tighe et al. 1987). Grafting of HEMA has been reported onto cellulosic backbones. Shukla and Athalye (1995) reported that the intensity and incident wavelength of radiation played an important role in photo-induced graft-copolymerization of HEMA onto cotton cellulose in the presence of uranyl nitrate as photo-initiator. Photo-induced grafting of HEMA onto cotton cellulose in the presence of triethylene glycol dimethacrylate (TEGDMA) results in structural changes along with changes in properties of the substrate such as, moisture regain, water uptake, and dyeability with a direct and a reactive dye in accordance with the graft level (Shukla and Athalye 1994). High spatio-resolved micro-architecture surfaces for microprocessing of biomedical devices have been prepared by photo-induced grafting of HEMA onto cellulose in the presence of benzyl N,N-diethyl dithiocarbamate by Higashi and coworkers (1999). Karlsson and Gatenholm (1997) prepared hydrogels of HEMA and cellulose fiber by means of an ozone-induced graft polymerization process. Graft copolymers of HEMA also been reported relative to their biomedical properties. Collagen-poly-HEMA hydrogels (Rao 1998) had been prepared as an implant for delivering anticancer drugs such as 5-fluorouracil, mitomycin and bleomycin for solid fibrosarcoma in rat model. Sefton et al. (Sefton et al. 2000; Dawson et al. 1987; Roberts et al. 1996) have used the poly(hydroxyethyl methacrylate-co-methyl methacrylate) (HEMA–MMA) for encapsula-tion of various live cells. It is thus apparent from the review of literature that grafting of HEMA, especially its binary monomer mixture onto cellulose, can be used for the preparation of hydrogels with diversified structural and functional properties for applications in separation and enrichment technologies.

The present paper deals with the study of effect of grafting conditions on grafting HEMA onto cellulose. The effect of change in the concentrations of monomer and initiator, reaction time and temperature; and nature, amount and composition of solvent system was evaluated. At the optimum reaction conditions evaluated for the grafting of HEMA alone, acrylamide (AAm), acrylic acid (AAc), and acrylonitrile (AN) were co-grafted along with HEMA onto cellulose backbone to generate a wide spectrum of useful properties. The graft copolymers were further functionalized by partial hydrolysis. These were characterized by various chemical and physical methods. There is scant information on the grafting of HEMA with other monomers as binary monomer mixtures. This study is an attempt to investigate the grafting behaviour of HEMA with other monomers, to study the effect of comonomer presence on the properties and use profile in separation and purification technologies. However, in the present article, the use of candidate graft copolymers was limited to the uptake of some common metal ions present as effluents in the industrial waste water.

EXPERIMENTAL

Materials

Extraction of cellulose from the dried pine needles of *Pinus roxbughii* was reported in an earlier communication (Chauhan et al. 2000). Ammonium persulfate (S.D. Fine, Mumbai), acrylic acid, acrylonitrile, acrylamide, and 2-hydroxy ethyl methacrylate (Merck, Germany) were used as received.

Grafting of HEMA and Binary Monomer Systems

The optimum reaction conditions for grafting of HEMA were obtained by changing one reaction parameter at a time, as per the details given in Table 1. At the optimum reaction conditions worked out for the grafting of unitary monomer system (HEMA) onto cellulose, binary monomer mixtures of HEMA were co-grafted with HEMA at five different concentrations of the comonomers (CM) AAc, AAm, and AN.

Separation of Homopolymers/Copolymers

Graft copolymers and homopolymer of poly(HEMA) were separated by solvent extraction method in methanol. Extraction was carried until a constant weight of graft copolymer was obtained. The homopolymer poly(HEMA) or ungrafted copolymers of poly(HEMA-*co*-CM) was removed from the graft copolymers by using different solvent systems of equal solvent compositions viz.: methanol-water for poly(HEMA-*co*-AAc), poly(HEMA-*co*-AAm), poly(AAm), and poly(AAc), and methanol-DMF for poly (HEMA-*co*-AN). The graft copolymers were dried in air oven at 50 ºC and percent grafting (P_g) and grafting efficiency (%GE) are expressed as:

$$P_g = \frac{\text{Weight of graft copolymer - weight of polymer backbone}}{\text{Weight of polymer backbone}} \times 100$$

$$\%GE = \frac{\text{Weight of graft copolymer - weight of polymer backbone}}{\text{Weight of monomer charged}} \times 100$$

FTIR, Elemental Analysis and Solvent Uptake Studies

Graft copolymers were characterized by FTIR (Perkin Elmer in KBr pellets) and nitrogen analysis was carried on an elemental analyzer (Carlo Erba). The characterization results were compared with those of the native cellulose. Graft copolymers were swollen in water and dimethylformamide (DMF) by immersion in the respective solvent for 2h and solvent uptake in per cent (P_s) was measured by the following relationship:

$$P_s = \frac{\text{Weight of the swollen polymer - weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

Graft copolymers were partially hydrolyzed by 0.5N NaOH for 48 h at 50 ºC.

Metal Ion Sorption Studies

Cu^{2+}, Fe^{2+}, and Cr^{6+} ions were sorbed from their aqueous solutions and were analyzed for concentration of the rejected ions on a DR 2010 Spectrophotometer (Hach Co., USA) by using its standard pillow reagents that have high sensitivity with maximum limits of 5.0, 3.0, and 0.6 mg/l, respectively, of Cu^{2+}, Fe^{2+}, and Cr^{6+} ions. All weights were taken on a Denver TR-203 Balance having a minimum readability of 1.0 mg. Ion sorption studies of cellulose, its derivatives and graft copolymers of cellulose with poly(HEMA), and binary comonomer systems synthesized at optimum reaction conditions and partially hydrolyzed polymers were carried by immersion of the sample for 2 h in 20.00 mL solutions of metal ions of known concentration. The pH of the solution was raised to 7.0 pH by using buffer solutions. Metal ion uptake is expressed as follows:

$$\text{Percent uptake } (P_u) = \frac{\text{amount of metal ions sorbed}}{\text{total amount of metal ions present}} \times 100$$

RESULTS AND DISCUSSION

It is of interest to see the effect of the presence of comonomer on the reactivity of HEMA in the grafting reactions. HEMA is a water-soluble monomer and so are AAc and AAm, but another comonomer AN has hydrophobic nature. Hence, one of the factors that should affect grafting efficiency in the present study is the viscosity and accessibility of the growing macroradicals of HEMA and comonomers in an aqueous medium.

Effects of Reaction Parameters on Grafting of HEMA onto Cellulose

Effect of nature and amount of solvent

The solvent effect on P_g and %GE was studied in 10.00 mL of acetone, benzene, dioxane, methanol, and water, while other reaction conditions were kept constant (Table1). Benzoyl (BPO) was dissolved separately in a known quantity (2.00 mL) of acetone in order to distribute it uniformly to the monomer and backbone polymer. Under these reaction conditions, the maximum P_g and %GE was recorded in the water-acetone solvent system, and at 10: 2 solvent composition, 21.1 P_g and 19.72 %GE were observed. P_g and %GE values were smaller in other solvent systems, and an order for P_g and %GE in different solvent-acetone compositions can be put as: benzene-acetone < methanol-acetone < dioxane-acetone < acetone < water-acetone. Water as solvent affected graft yield in a positive manner by uniform diffusion of the monomer and also by swelling the backbone polymer. It also had a negligible chain transfer constant; hence wastage of the monomer was minimal. An increase in the amount of water from 5.00 mL to 25.00 mL (in the water:acetone solvent system) in the reaction system decreased P_g from 31.0 to 6.7 (Table 1). %GE also decreased with an increase in the amount of water from 5.00 mL to 25.00 mL. An optimum value %GE, 28.97 was observed at 5.00 mL amount of water. The decrease in P_g and %GE as a consequence of the increase in the amount of solvent resulted from the low accessibility of the reacting species to both monomer and backbone polymer. Thus, overall polymerization processes were adversely affected. The effect of amount of acetone (solvent for initiator) on P_g and %GE was studied by its variation from 1.00 to 5.00 mL in 5.0 mL of water. P_g and %GE decreased on increase of acetone, which can be attributed to its high chain transfer constant. Thus, the optimum P_g (56.3) and %GE (52.62) was observed in water:acetone (5.00: 1.00mL) solvent composition (Table

1). These results make it clear that optimum amount of solvents is required for the solubilization of initiator and also the growing HEMA macroradicals, and swelling of the cellulose also promote grafting by allowing access to the active sites on the backbone.

Effect of initiator and monomer concentrations

A gradual decrease in P_g was observed as (BPO) was progressively increased. The optimum 56.3 P_g and 52.62 %GE were observed at (BPO) = 6.89×10^{-2} mol/L, when concentration of BPO was increased from 6.89×10^{-2} mol/L to 34.44×10^{-2} mol/L (Table 2). Further increase in the initiator concentration up to 34.44×10^{-2} mol/L decreased P_g (17.9) and %GE (16.73). At the higher initiator concentrations P_g decreased because of the higher mutual termination of the growing HEMA macroradicals, leading to more homopolymer formation. On the variation of concentration of HEMA from 68.59×10^{-2} mol/L to 342.95×10^{-2} mol/L at the optimum solvent composition and optimum concentration of BPO, an increase in P_g was observed with the optimum P_g of 125.6 at 342.95×10^{-2} mol/L of HEMA, and %GE increased from 6.17 to 58.38 (Table 2). Further increase in the monomer concentration resulted in reduced graft yield due to the preferential homopolymer formation.

Effect of reaction time and temperature

At the optimum conditions obtained for the solvent, monomer, and initiator concentrations, the effect of variation of reaction time on P_g and %GE was studied (Table 3). Both P_g (172.9) and %GE (64.64) were found to increase with the reaction time affording the maximum values after 3 h. Temperature was varied form 60 to 100 ^{o}C at the optimum reaction parameters evaluated for different reaction parameters. There existed an optimum temperature (90 ^{o}C) to afford a maximum of 245.1 and %GE of 91.63, below which there was decomposition of initiator to generate free radicals adequate to efficiently utilize the monomer (Table 3).

Table 1. Effect of Nature and Amount of Solvent on Grafting Parameters[a]

Sr. No.	Solvent in mL.			BPO × 10^{-2} mol/L	HEMA × 10^{-2} mol/L	P_g	%GE
	Sol A		Sol B (acetone)				
1.	**Acetone**	10.00	2.00	3.443	68.59	9.2	8.59
2.	Benzene	,,	,,	,,	,,	0.2	0.19
3.	Dioxane	,,	,,	,,	,,	8.0	7.48
4.	Methanol	,,	,,	,,	,,	2.8	2.62
5.	**Water**	,,	,,	,,	,,	**21.1**	**19.72**
6.	,,	**5.00**	**,,**	**5.90**	**117.58**	**31.0**	**28.97**
7.		10.00	,,	3.443	68.59	21.1	19.72
8.	,,	15.00	,,	2.43	48.42	19.6	18.32
9.	,,	20.00	,,	1.88	37.41	15.5	14.49
10.	,,	25.00	,,	1.53	30.48	6.7	6.26
11.	,,	**5.00**	**1.00**	**6.89**	**137.18**	**56.3**	**52.62**
12.	,,	,,	2.00	5.90	117.58	31.0	28.97
13.	,,	,,	3.00	5.17	102.88	26.10	24.39
14.	,,	,,	4.00	4.59	91.45	18.6	17.38
13.	,,	,,	5.00	4.13	82.30	4.2	3.93

[a] Cellulose = 1.0 g, time = 2.0 h, temperature = 70 ºC

Table 2. Effect of Monomer and Initiator Concentrations on Grafting Parameters[a]

Sr. No.	BPO × 10^{-2} mol/L	HEMA × 10^{-2} mol/L	P_g	%GE
1.	13.77	137.18	35.4	33.08
2.	20.66	,,	27.8	25.98
3.	27.55	,,	27.0	25.23
4.	34.44	,,	17.9	16.73
5.	6.89	68.59	3.3	6.17
6.	,,	205.77	93.7	58.38
7.	,,	274.36	112.6	52.62
8.	,,	**342.95**	**125.6**	**46.95**

[a] Cellulose = 1.0 g, time = 2.0 h, temperature = 70 ºC, water + acetone = (5: 1) mL

Table 3. Effect of Reaction Time and Temperature on Grafting Parameters[a]

Sr. No.	Time (h)	Temperature (°C)	P_g	%GE
1.	1.0	70	98.5	36.82
2.	1.5	,,	108.3	40.49
3.	2.5	,,	159.8	59.74
4.	**3.0**	**,,**	**172.9**	**64.64**
5.	,,	60	148.7	55.59
6.	,,	80	230.8	86.28
7.	,,	**90**	**245.1**	**91.63**
8.	,,	100	225.8	84.41

[a] Cellulose = 1.0 g, (BPO) = 6.89 × 10^{-2} mol/L, (HEMA) = 342.95 × 10^{-2} mol/L,, water + acetone = (5: 1) mL

Grafting of binary monomer mixtures

The binary monomer mixtures of HEMA with AAm, AAc, and AN were separately grafted onto cellulose at the optimum grafting conditions evaluated for HEMA (BPO (6.89 × 10^{-2} mol/L), HEMA (342.95 × 10^{-2} mol/L), reaction time (3h), reaction temperature (90 °C), and water: acetone (5.00: 1.00) mL). In the case of co-grafting of AAm, P_g increased from 255.6 to 383.6 and %GE decreased continuously from 81.79 to 77.89 with the increase of AAm concentration from 105.63 × 10^{-2} to 528.19 × 10^{-2} mol/L (Fig. 1). When the concentration of AAc was varied from 121.52 × 10^{-2} mol/L to 607.64 × 10^{-2} moles/L, P_g increased with a maximum of 330.9, and %GE decreased from 71.16 to 62.43 (Fig. 2). In the binary monomer system of HEMA and AN, on change of the concentration of AN from 126.72 × 10^{-2} to 633.60 × 10^{-2} mol/L, P_g increased uniformly from 285.5 to 404.9 (Fig. 3), and %GE decreased from 92.76 to 86.33. Thus, very high graft yields were obtained with the comonomers. High values of P_g and %GE were obtained as a consequence of grafting of all the three comonomer systems. While the high P_g means a high amount of the polymers attached to the cellulose backbone, high %GE means that most of the monomer/s charged was used in grafting and was not wasted in side reactions and homopolymer formation. The result is availability of a high level of functional groups on the cellulose backbone.

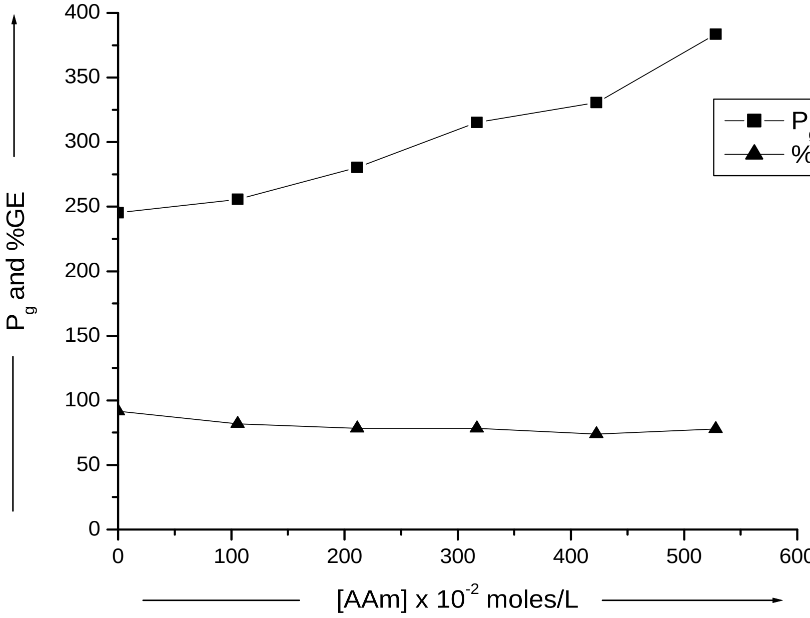

Fig. 1. Effect of (AAm) on percent grafting and grafting efficiency (HEMA = 342.95 × 10^{-2} mol/L, BPO = 6.887 × 10^{-2} mol/L, water: acetone = 5.00: 1.00 mL, time = 3h, temperature = 90°C)

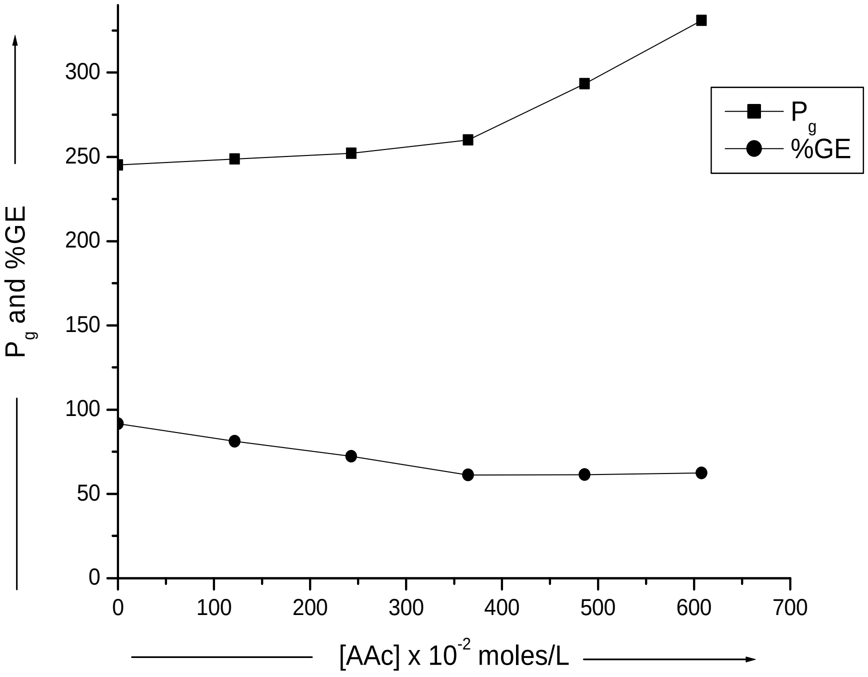

Fig. 2. Effect of (AAc) on percent grafting and grafting efficiency (HEMA = 342.95 × 10^{-2} mol/L, BPO = 6.887 × 10^{-2} mol/L, water: acetone = 5.00: 1.00 mL, time = 3h, temperature = 90°C)

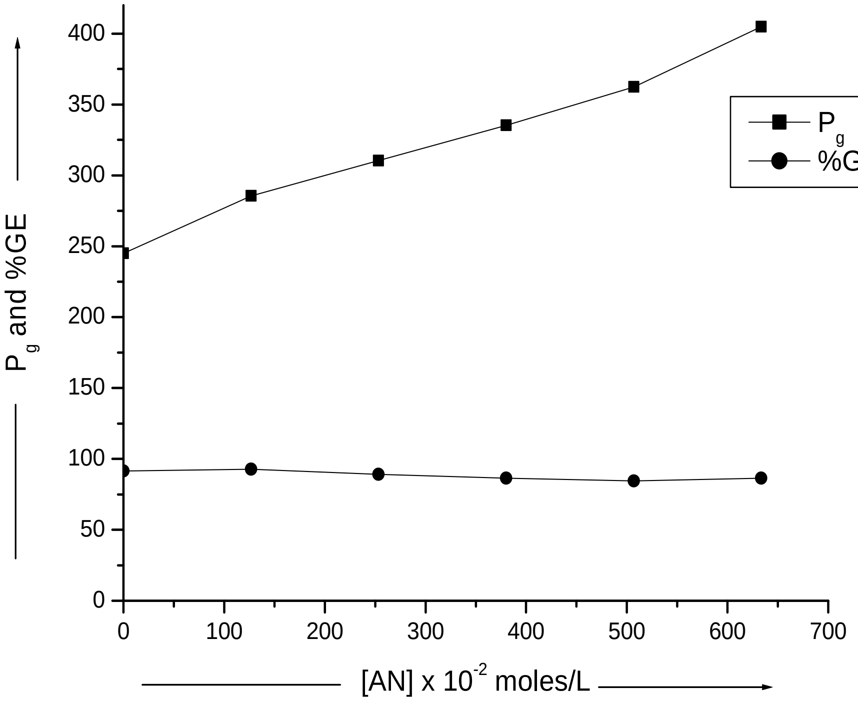

Fig. 3: Effect of (AN) on percent grafting and grafting efficiency (HEMA = 342.95 × 10^{-2} mol/L, BPO = 6.887 × 10^{-2} mol/L, water: acetone = 5.00: 1.00 mL, time = 3h, temperature = 90°C).

Characterization of Graft Copolymers

The evidence of monomer incorporation and the differences in the structure of graft copolymers were obtained from FTIR, elemental analysis, and swelling behaviour of the graft copolymers**.**

Elemental analysis

The incorporation of both poly(AAm) and poly(AN) was established from the elemental (N) analysis of cell-g-poly(HEMA-co-CM), and % N was found to increase with the P_g and with the increase of CM concentration (AAm and AN) in the feed. The amount of N has been observed to decrease after partial hydrolysis as $–CONH_2$, and –CN groups were partially converted to carboxylate groups $–COO^-Na^+$ (Table 4). The presence of N in the partially hydrolyzed graft copolymers suggests that the hydrolysis under the conditions employed was partial.

FTIR study of cellulose and its graft copolymers

FTIR spectra of cell-*g*-poly(HEMA) (optimum P_g), and cell-*g*-poly(HEMA-*co*-CM) and the effect of hydrolysis on FTIR absorption peaks in case of cell-*g*-poly(HEMA-*co*-CM) have also been studied (Figs. 4-6). A prominent band at or around 1735 cm^{-1} in the cell-*g*-poly(HEMA) provides evidence that poly(HEMA) was incorporated on the cellulose backbone (Fig. 4b).

Table 4: Elemental Analysis of Graft Copolymers With Respect to AAm and AN

Sr. No.	Polymer	P_g	% N	N (g)	CM (AAm /AN)	HEMA (g)	Ratio of CM/ HEMA (g/g)
1.	Cellulose						
2.	Cell-*g*-poly (HEMA-*co*-AAm)	255.6	2.16	0.0432	0.389	2.167	0.1795
3.	,,	280.6	3.05	0.0677	0.589	2.217	0.2656
4.	,,	315.1	4.03	0.0781	0.849	2.302	0.3688
5.	,,	330.4	4.25	0.0827	0.934	2.370	0.3991
6.	,,	383.6	5.33	0.0954	1.309	2.527	0.5180
7.	Cell-*g*-poly (HEMA-*co*-AN)	285.5	2.86	0.0640	0.418	2.437	0.1715
8.	,,	310.4	2.76	0.0494	0.429	2.675	0.1604
9.	,,	335.3	4.48	0.0831	0.739	2.614	0.2827
10.	,,	362.3	6.56	0.1429	1.151	2.472	0.4656
11.	,,	**404.9**	**6.95**	**0.1665**	**1.329**	**2.720**	**0.4886**
12.	Cell-*g*-poly(HEMA-*co*-AN)^h	**404.9**	**5.81**	**0.1136**	**1.112**	**2.937**	**0.3786**

^{h} = hydrolyzed polymer.

In the case cell-*g*-poly(HEMA-*co*-CM), apart from the characteristic peaks attributed to cellulose and HEMA, the grafting of the CMs in the graft copolymers was marked by the presence of the characteristic peaks due to the stretching of C=O of HEMA (around 1735 cm^{-1}), AAm (around 1670 cm^{-1}) in Fig. 4c and AAc (1617 cm^{-1}) in Fig. 5a and stretching due to -CN of AN (2241 cm^{-1}) in Fig. 5b. To analyze the structure of the graft chain using FTIR data as a tool, the ratio of absorbances were studied in the region of stretching frequency of cyclic ether of cellulose backbone to stretching frequency of >C=O group of methacrylate (≈1060 cm^{-1}/1735 cm^{-1}). Similarly, the ratio of absorbances were studied for stretching frequency of >C=O HEMA to stretching frequency of characteristic group of comonomers (≈1735 cm^{-1}/A cm^{-1}, where A ≈ 1670 cm^{-1}, 1730 cm^{-1}, 2240 cm^{-1}), respectively, for >C=O of AAm and AAc and C≡N of AN. It was concluded therefrom that the ratio of cellulose/HEMA and HEMA/CM decreased almost linearly with the increase in P_g. This implies a progressive increase of poly(HEMA) in the cell-*g*-poly(HEMA) with respect to cellulose, and increase of CM with respect to poly(HEMA) in cell-*g*-poly(HEMA-*co*-AAm). In the case of cell-*g*-poly(HEMA-*co*-AN) the reactivity of the monomer system was low, as reflected in the low P_g values. The absorbance ratio of HEMA with respect to AN was high, as the amount of HEMA was very high with respect to AN, and it was in consonance with their reactivity ratio. The hydrolysis of graft copolymers (cell-*g*-poly(HEMA-*co*-CM) having the maximum P_g revealed that the absorbance due to >C=O of HEMA was reduced from that in the precursor (Fig. 6). This indicated hydrolysis of HEMA, along with that of -CONH$_2$.

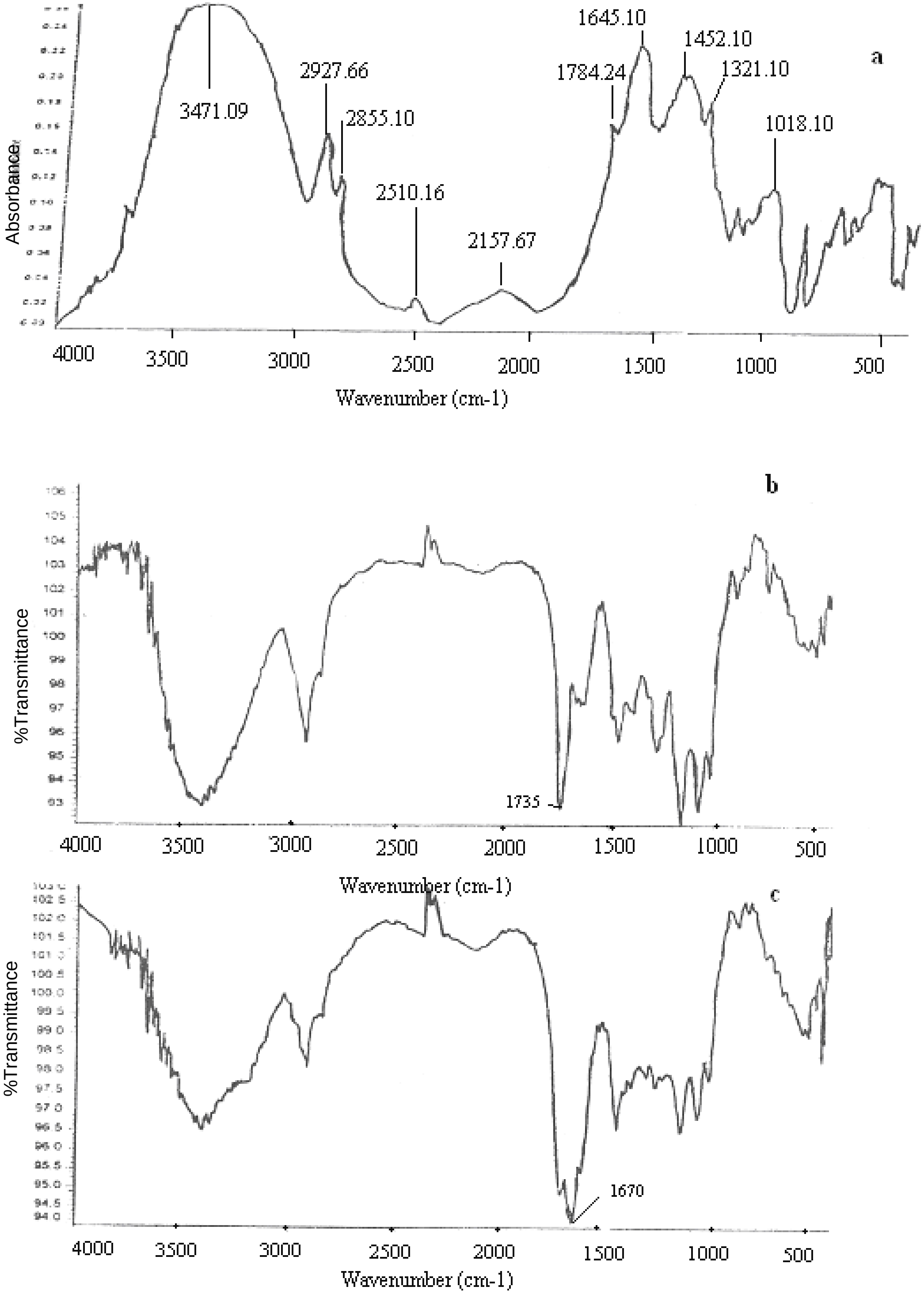

Fig. 4. FTIR Spectra of
a. Cellulose
b. Cell-g-Poly(HEMA)
c. Cell-g-Poly(HEMA -*co*-AAm)

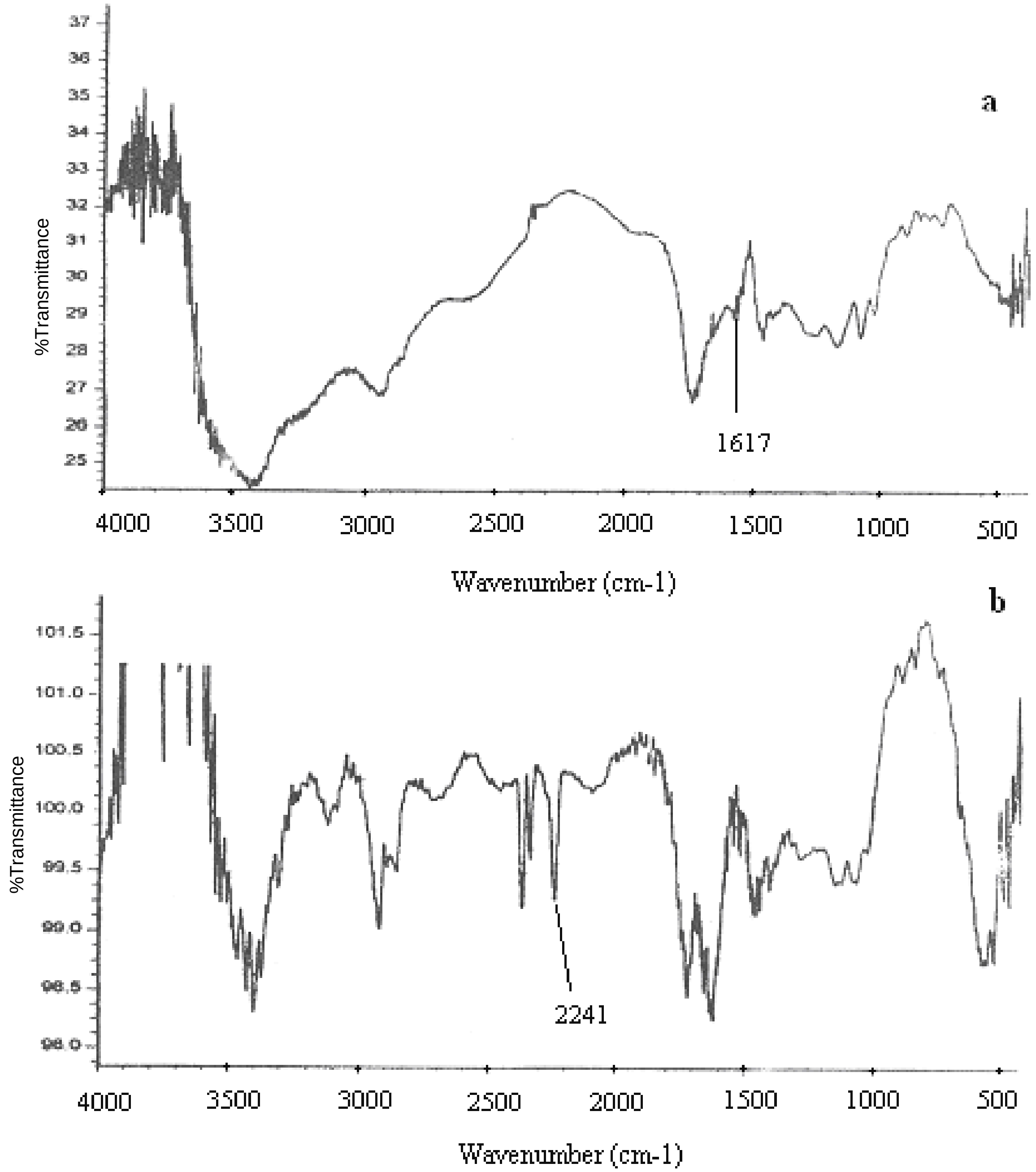

Fig. 5. FTIR spectra of
a Cell-g-Poly(HEMA-*co*-AAc)
b Cell-g-Poly(HEMA-*co*-AN)

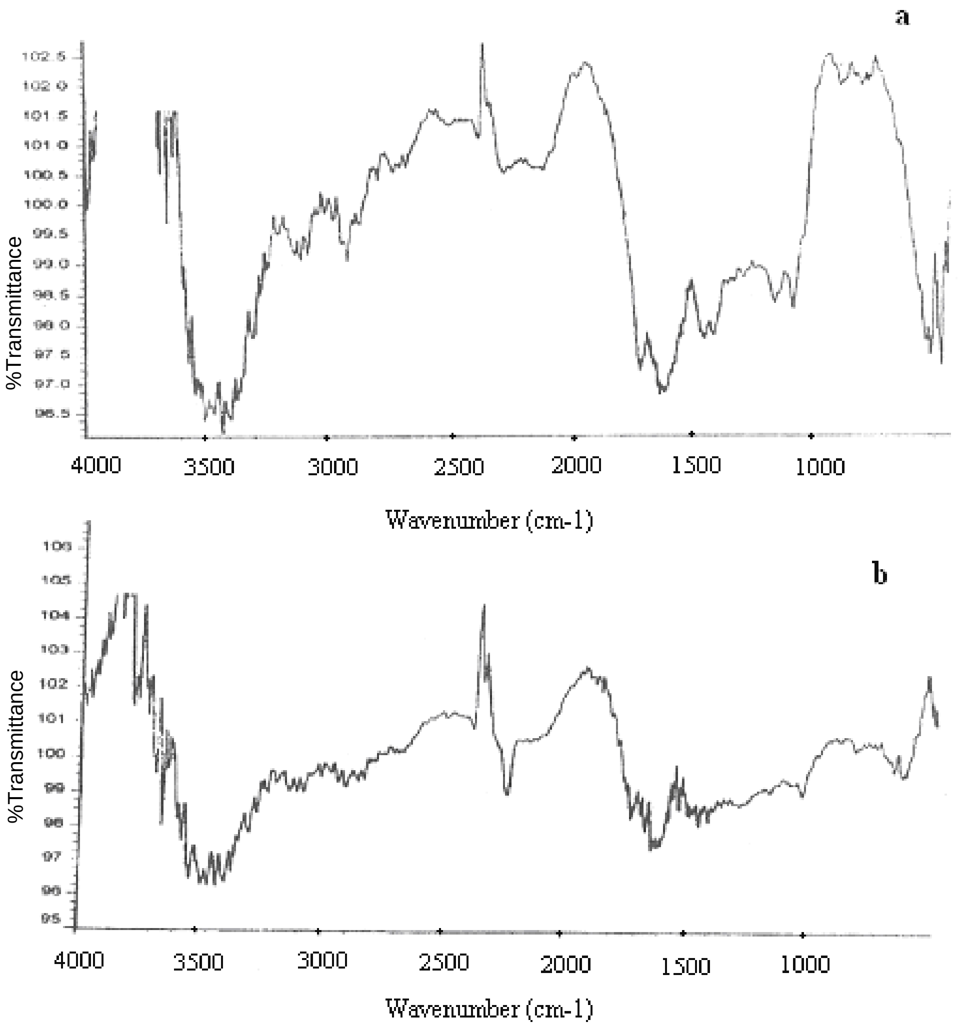

Fig. 6. FTIR spectra of
a Hydrolyzed Cell-g-Poly(HEMA-*co*-AAm)
b Hydrolyzed Cell-g-Poly(HEMA-*co*-AN)

Scanning electron microscopy of cellulose and its graft copolymers

Scanning electron micrographs (SEM) of cellulose and different graft copolymers are presented in Figs. 7a–7d. SEM of cell-*g*-poly(HEMA) taken at different magnifications are presented in Fig 7b. Grafting of vinyl monomers on a backbone considerably opens up its matrix. SEM of the cell-*g*-poly(HEMA) revealed that grafting was uniform in the cellulose, as deposits of the graft copolymers were seen both in amorphous and crystalline regions. SEM of graft copolymers of HEMA and comonomers (maximum P_g) at different magnifications are presented in Figs. 7c – 7e. It appears that grafting of comonomers and HEMA led to physical and chemical crosslinking, as well-defined pores are visible in these micrographs.

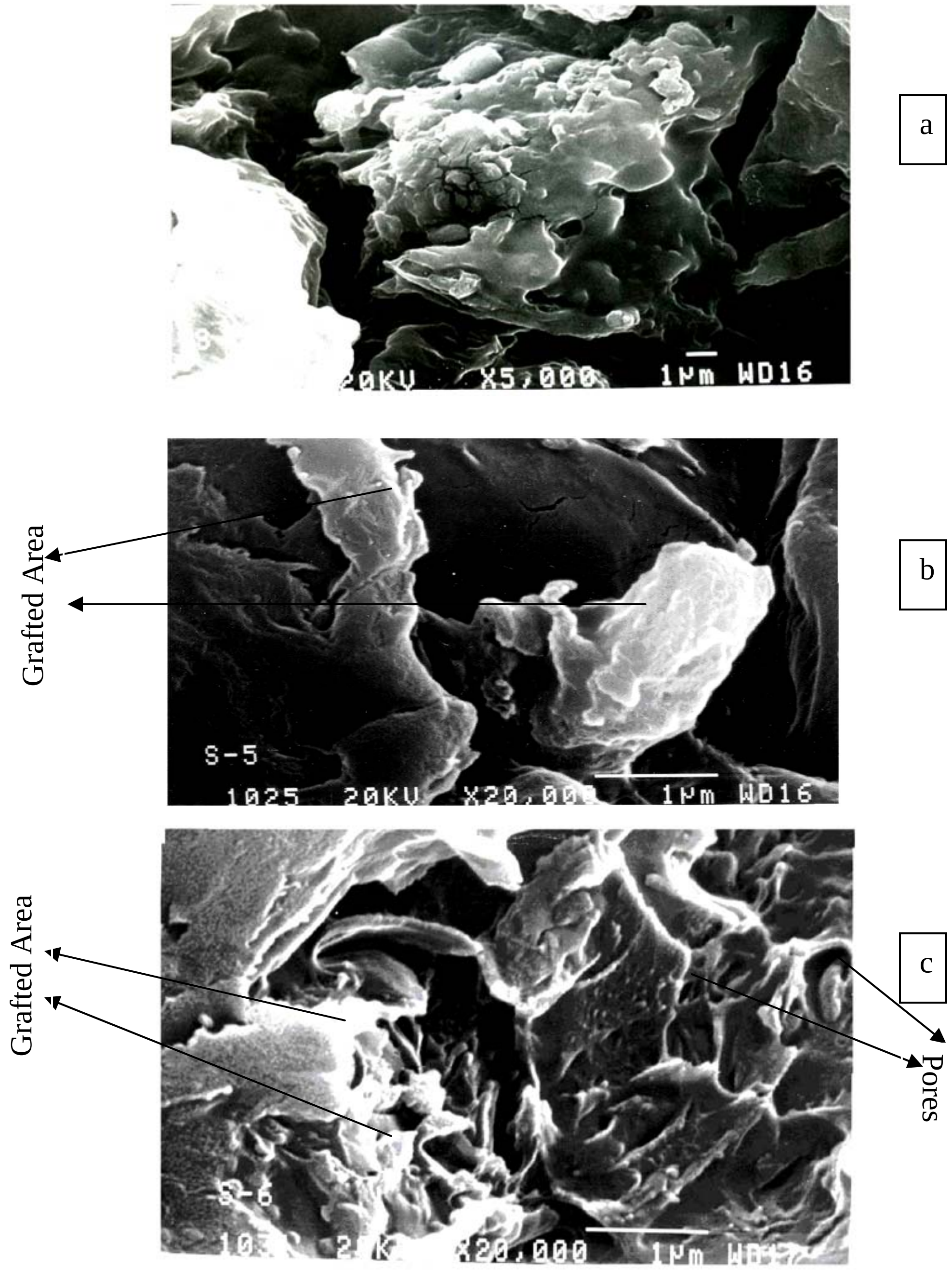

Fig. 7. SEM of
a. Cellulose
b. Cell-g-Poly(HEMA)
c. Cell-g-Poly(HEMA-*co*-AAm)

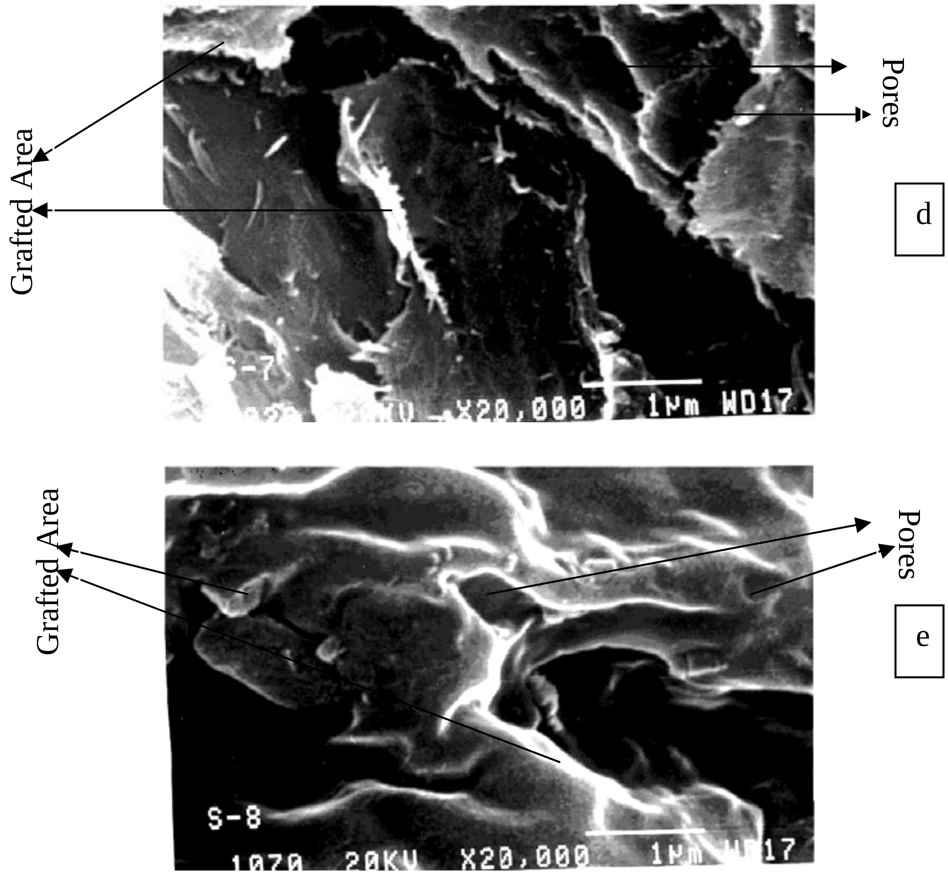

Fig. 7. SEM of
d. Cell-g-Poly(HEMA-*co*-AAm)
e. Cell-g-Poly(HEMA-*co*-AN)

Water uptake behavior of graft copolymers

Water uptake studies of the graft copolymers were carried in water and DMF at room temperature. Cell-*g*-poly(HEMA) synthesized at different reaction conditions having P_g of 98.5, 125.6, 172.9, and 245.1 were subjected to swelling studies. P_s values were significantly high at 454.8, 480.8, 422.4, and 394.0 in water and 872.8, 1284.0, 1330.0,and 1062.8 in DMF, respectively (Fig. 8a). It was deduced from these results that as the grafting increased, the P_s in water as well as DMF decreased after reaching a maximum. In DMF the P_s was high due to the solvation of poly(HEMA) chains. The decrease in P_s after reaching the maximum is a manifestation of long graft chains, as the solvent cannot easily access all the groups of the grafted polymer. In the partially hydrolyzed graft copolymers, P_s in water increased many times relative to its value in DMF due to the presence of ionic groups.

In the case of cell-g-poly(HEMA-co-AAm), P_s increased both in water and DMF in a linear fashion with the increase in the concentration of AAm in the feed. In the case of partially hydrolyzed cell-g-poly(HEMA-co-AAm), which changed to a grafted terpolymer having poly(AAm), poly(COO^-) and poly(HEMA) on the cellulose backbone, a regular increase in P_s was observed in both water and DMF (Fig. 8b). P_s showed similar behavior in Cell-g-poly(HEMA-co-AAc) graft copolymers with continuous increase in P_s with P_g (Fig. 8c). In the case of cell-g-poly(HEMA-co-AN), P_s decreased appreciably with the increase in P_g as a consequence of an increase in the hydrophobicity of the graft copolymers (Fig. 8d). From the foregoing discussion, it can be concluded that these graft copolymers swelled appreciably in both the solvents within a short period of 2hrs.

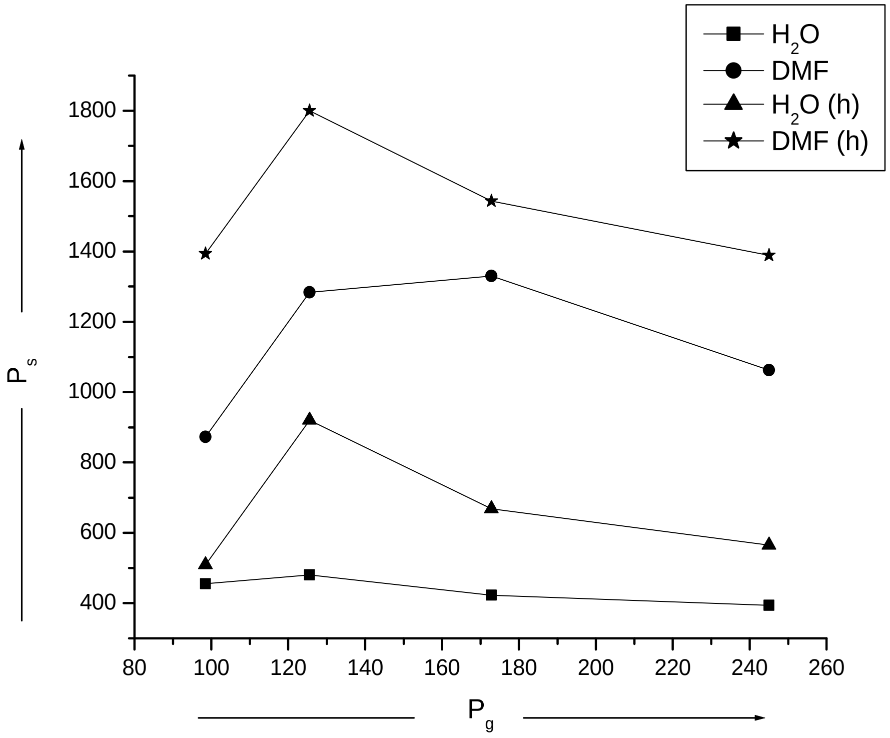

Fig. 8a. Percentage swelling of cell-*g*-poly(HEMA) as a function of percent grafting (equilibrium time = 24h, solvent = 20.00 mL, graft copolymer = 0.25 g) where (h) is hydrolyzed graft copolymer

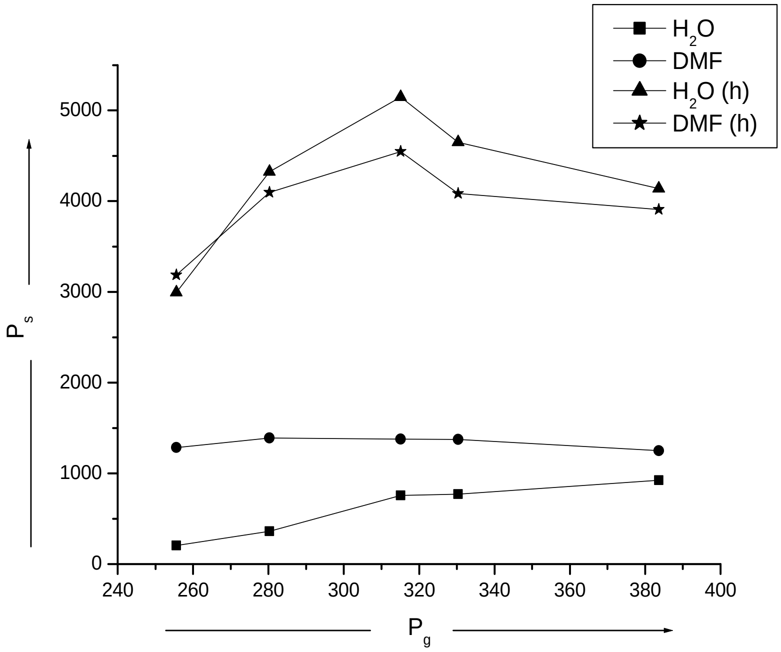

Fig. 8b. Percentage swelling of cell-*g*-poly(HEMA-*co*-AAm) as a function of percent grafting (equilibrium time = 24h, solvent = 20.00 mL, graft copolymer = 0.25 g) where (h) is hydrolyzed graft copolymer

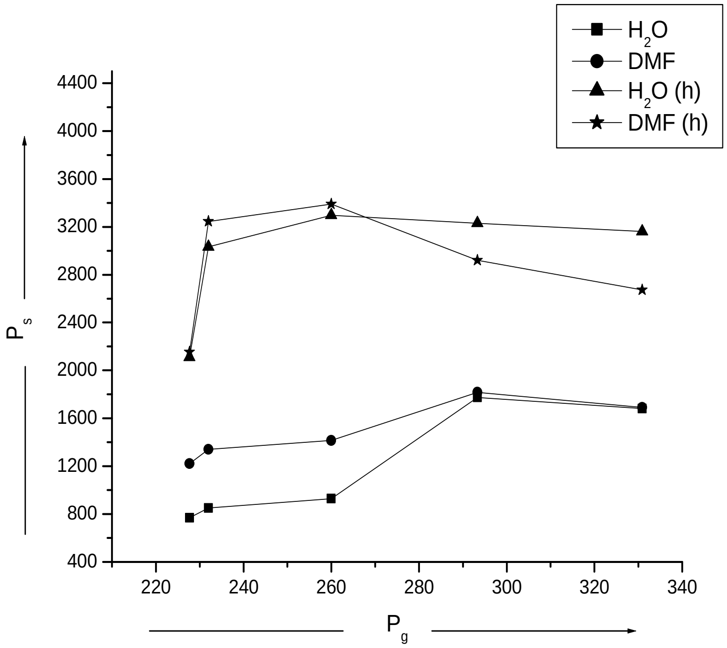

Fig. 8c. Percentage swelling of cell-*g*-poly(HEMA-*co*-AAc) as a function of percent grafting (equilibrium time = 24h, solvent = 20.00 mL, graft copolymer = 0.25 g) where (h) is hydrolyzed graft copolymer

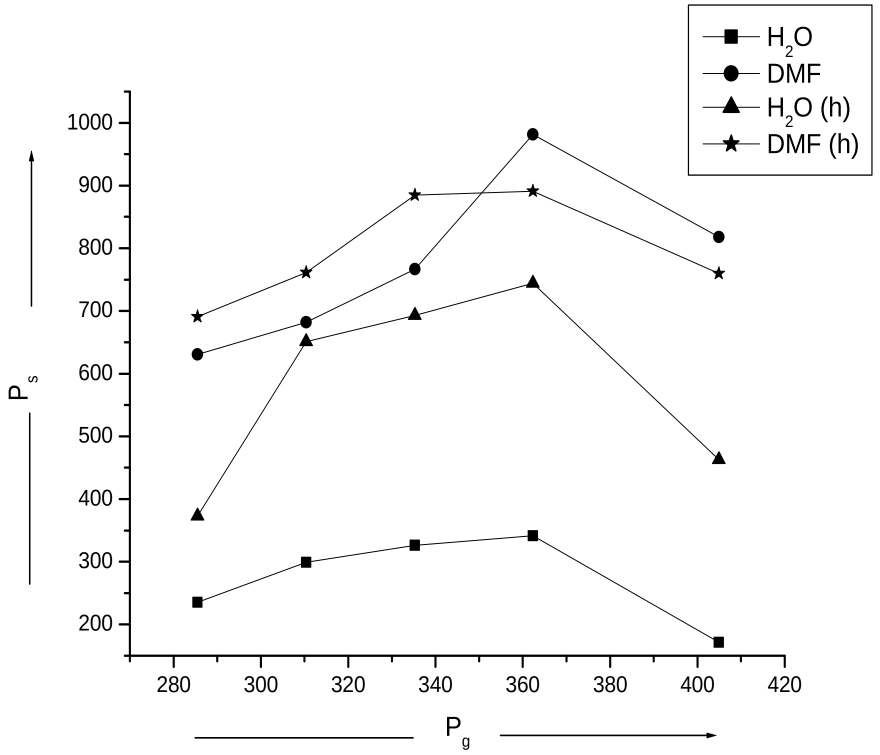

Fig. 8d. Percentage swelling of cell-*g*-poly(HEMA-*co*-AN) as a function of percent grafting (equilibrium time = 24h, solvent = 20.00 mL, graft copolymer = 0.25 g) where (h) is hydrolyzed graft copolymer

Metal Ions Uptake Behaviour of Cellulose, its Derivatives and Graft Copolymers

The ionic species effectively sorbed by functionalized cellulose graft copolymers from the solution phase. The sorption of these species should have a direct relationship to the capacity of the graft copolymers to swell in water. The results for the sorption of some common ions like Cr^{6+}, Cu^{2+}, and Fe^{2+} are presented in Table 5. It is evident therefrom that apart from the nature of metal ions, structure of the grafted polymer, and especially the nature of CM played an important role in the uptake of these ions. Sorption of Cr^{6+} was not appreciable when compared to that of Cu^{2+} and Fe^{2+} for the same series of polymers. The extent of the metal ion sorption for the latter two was almost the same. It is also evident that the functionalization of cellulose by grafting enhanced its capacity to sorb these ions. Such advantage was not there on derivatization to its phosphate form, which has an ionizable proton, and oxidized forms. Poly(AAc)-grafted copolymers afforded good results, as it can exchange ions apart from adsorption and uptake of metal ions in the bulk of the polymer.

Table 5. Sorption of Metal Ions*

Sr. No.	**Polymer**	P_g	P_u (before hydrolysis)	P_u (after hydrolysis)
	Sorption of Cr^{6+}			
1.	*Cellulose*	--	11.93	--
2.	Cell-*g*-poly(HEMA)	245.1	9.84	6.56
3.	**Cell-*g*-poly(HEMA-*co-AAm)***	383.6	**19.67**	6.56
4.	Cell-*g*-poly(HEMA-*co*-AAc)	330.9	13.12	4.92
5.	Cell-*g*-poly(HEMA-*co*-AN)	404.9	16.39	11.48
6.	Cellullose phosphate	--	6.43	--
7.	Oxycellulose	--	3.02	--
	Sorption of Cu^{2+}			
1.	Cellulose	--	4.49	--
2.	Cell-*g*-poly(HEMA)	245.1	8.5	4.09
3.	Cell-*g*-poly(HEMA-*co*-AAm)	383.6	16.26	32.21
4.	**Cell-*g*-poly(HEMA-*co*-AAc)**	330.9	**32.10**	**44.00**
5.	Cell-*g*-poly(HEMA-*co*-AN)	404.9	14.56	16.72
6.	Cellullose phosphate	--	5.09	--
7.	Oxycellulose	--	3.91	--
	Sorption of Fe^{2+}			
1.	Cellulose	--	6.02	--
2.	Cell-*g*-poly(HEMA)	245.1	24.03	34.91
3.	**Cell-*g*-poly(HEMA-*co*-AAm)**	383.6	**20.14**	**100.000**
4.	**Cell-*g*-poly(HEMA-*co*-AAc)**	330.9	**32.16**	**100.000**
5.	Cell-*g*-poly(HEMA-*co*-AN)	404.9	3.53	16.57
6.	Cellullose phosphate	--	10.53	--
7.	Oxycellulose	--	11.62	--

*Feed solution = 20.00 mL **of mg/L**, polymer = 0.1 g.

Effect of partial hydrolysis on metal ions uptake

Functionalization of the graft copolymers by partial hydrolysis showed far better metal ion sorption, leading even up to 100% in case of Fe^{2+}, but the sorption of Cu^{2+} was not affected much. The effect was rather adverse in the case of sorption of Cr^{6+}, and these results are in agreement with our earlier work (Chauhan et al. 2005, 2006). Partial hydrolysis generated ionic groups on the graft copolymers, absorbed higher amounts of water, thus, better portioning of the metal ions between polymer and solution phase resulted in higher metal ions uptake. Such effect is significant both in poly(AAc) and poly(AAm) based graft copolymers due to the relative ease of hydrolysis of $-CO_2H$ and $-CONH_2$ groups, along with those of the esters moiety of the graft copolymer as compared to –CN of the poly(AN)-based graft copolymer.

CONCLUSIONS

1. Reaction conditions were established for optimum grafting of HEMA and used to co-graft with it co-monomers such as acrylamide, acrylic acid, and acrylonitrile. Graft copolymers were characterized by elemental analysis, FTIR, and swelling studies.

2. The sorption of Fe^{2+} ions was greater than that of Cu^{2+} or Cr^{6+}. The observed selectivity was further improved by the functionalization of the graft copolymers by partial hydrolysis.
3. It can be concluded that grafting has an advantage over simple derivatization of cellulose and simple polymer analogous reactions to affect the extent of metal ion sorption. The effect of the grafted comonomer on metal ion sorption behaviour can be put in the order: poly(AAc) > poly(AAm) >> poly(AN).

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Article submitted: March 4, 2009; Peer review completed: April 8, 2009; Revised version received and accepted: May 30, 2009; Published June 2, 2009.