

Synthesis and Characterization of *N*-Vinyl Pyrrolidone and Cellulosics Based Functional Graft Copolymers for Use as Metal Ions and Iodine Sorbents

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ABSTRACT: To develop cost effective and eco friendly polymeric materials for enrichment and separation technologies, 1-vinyl-2-pyrrolidone (*N*-VP) was graft copolymerized onto cellulose, extracted from pine needles. Optimum conditions have been evaluated for the grafting of *N*-VP onto cellulose and at these conditions it was also grafted onto cellulose phosphate, hydroxypropyl cellulose, cyanoethyl cellulose, and deoxyhydrazino cellulose. At the optimum grafting conditions for *N*-VP, it was also cografted with maleic anhydride. Kinetics of radiochemical graft copolymerization has been studied and evaluation of the polymerization and grafting parameters as percent grafting, percent grafting efficiency, rate of polymerization, homopo-

lymerization, and graft copolymerization have been evaluated. Graft copolymers have been characterized by elemental analysis, FTIR, and swelling studies. An attempt has been made to study sorption of some metal ions such as Fe^{2+} and Cu^{2+} and iodine on select graft copolymers to investigate selectivity in metal ion sorption and iodine sorption as a function of structural aspects of the functionalized graft copolymers to find their end uses in separation and enrichment technologies. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 373–382, 2005

Key words: cografting; graft copolymers; hydrogels; irradiation; metal ions sorption; vinyl pyrrolidone

INTRODUCTION

N-vinyl pyrrolidone (*N*-VP) has a high gelling nature and also possesses good complexing ability. In the crosslinked form, poly(*N*-VP) forms three-dimensional high water absorbing hydrogels but these are poor in mechanical strength. To improve upon this limitation of poly(*N*-VP), in the present study it has been fixed onto cellulose and different cellulosics by radiation grafting to get high water absorbing graft copolymers for use in metal ion enrichment, separation, and effluent remediation technologies. Not much work has been reported on the grafting of *N*-VP onto cellulose or its derivatives (cellulosics). Its graft copolymers with cellophane have been reported to have good diffusional efficiency.^{1,2} Bojanic et al.³ have reported use of graft copolymers of cellulose and *N*-VP for metal ion enrichment. Dengre et al.⁴ have used hydrogels of poly(*N*-VP-*cl*-AAm) crosslinked for the release of vitamin B₁₂. We have prepared a large variety of functional polymers for water technologies by radiation grafting of a single monomer or cografting of two monomers onto cellulosics from the binary monomer mixtures.^{5–7} Some of the copolymers and net-

works prepared from the cellulosics and functionalized with various acrylamides were used for the metal ion sorption.^{8–10} One of the most significant observations from this work is that affecting structural changes, such as creation of charged groups by simple post reactions, as hydrolysis results in the increase of partition coefficients and retention capacity of the hydrogels. In the present article, we report grafting of *N*-VP onto cellulose extracted from pine needles and also onto cellulose derivatives as cellulose phosphate (Cell-PO₄), hydroxypropyl cellulose (HPC), cyanoethyl cellulose (CEC), and deoxyhydrazino cellulose (Cell-NHNH₂) by simultaneous irradiation method. *N*-VP has also been cografted with maleic anhydride (MAH) at the optimum grafting conditions evaluated for the former. The kinetics of grafting has been investigated and the graft copolymers have been characterized by FTIR, elemental analysis, and swelling studies. The sorption of model metal ions as Fe^{2+} , Cu^{2+} , and iodine has been studied as function of graft yield. An attempt has been made to correlate the structure and properties of the graft copolymers.

EXPERIMENTAL

Materials and methods

Vinyl pyrrolidone (Merck, Schuchardt, Germany) was distilled under reduced pressure. All solvents used

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were distilled under normal conditions. Cellulose was separated from the pine needles by the improved ammonia digestion method reported earlier.⁵ Cellulose powder was then dried in an air oven at 40°C.

Preparation of cellulose phosphate

Cellulose (1.0 g) was treated with a mixture of 18% phosphoric acid, 50% urea, and 32 mL water at 160°C until ammonia was evolved. The mixture was squeezed, filtered, and washed with excess of water. Water-insoluble cellulose phosphate was then dried in an air oven at 40°C.

Preparation of deoxyhydrazino cellulose

Sulfonylation

Cellulose (1.0 g) was refluxed with benzene sulfonyl chloride (10.0 mL) at 50°C for 30.0 min in methanol (20.0 mL). Clear white sulfonylated cellulose was then filtered, washed with methanol, and dried in an air oven at 40°C.

Reaction with cellulose hydrazine hydrate

Sulfonylated cellulose (1.0 g) was refluxed with hydrazine hydrate (10.0 mL) at 130°C for 24 h in methanol. Water-insoluble deoxyhydrazino derivative was filtered and dried.

Preparation of cyanoethyl cellulose

Cellulose (1 g) was treated with a mixture of acrylonitrile (5.0 mL) in distilled water (40.0 mL) and 5% NaOH (5.0 mL) for 3 h at 50°C to get the cyanoethyl cellulose.

Synthesis of hydroxypropyl cellulose

Hydroxypropyl cellulose was prepared by reaction of alkali cellulose and 1,2-propylene oxide in isopropanol as reported elsewhere.¹¹

Graft copolymerization

Graft copolymerization of *N*-vinyl pyrrolidone onto cellulose

Cellulose (1.0 g) and monomer (0.5 mL) were taken in 10.0 mL of distilled water in a reaction vessel and irradiated for different time intervals in a Gamma Chamber 900 (BARC Trombay, India). After irradiation, samples were extracted in water by stirring for 24 h to ensure complete removal of the homopolymer and dried at 40°C in an air oven. The extraction process was repeated to achieve constant weight. Extracted poly(*N*-VP) from each extraction step was pre-

cipitated from water by adding acetone, was filtered and dried in an oven at 40°C, and was weighed. At the optimum radiation dose (1.8×10^4 Gy) and keeping the amount of water and cellulose constant, the amount of monomer was changed next to find the optimum monomer concentration. Similarly, the effect of water-methanol system was studied at five different water : methanol compositions, e.g., 80 : 20, 60 : 40, 40 : 60, 20 : 80, and 0 : 100 (keeping total volume at 10.0 mL). The effect of the nature of solvent on grafting parameters was studied by changing the reaction medium from water and methanol to acetone, dioxane, and benzene.

Graft copolymerization of *N*-vinyl pyrrolidone onto cellulose

At the optimum reaction conditions of grafting worked out for the grafting of *N*-VP onto cellulose, it was graft copolymerized onto cellulose derivatives viz. cellulose phosphate, deoxyhydrazino cellulose cyanoethyl cellulose, and HPC following the same reaction scheme as outlined above for the grafting of *N*-VP onto cellulose.

Cografting of *N*-vinyl pyrrolidone and maleic anhydride

At the optimum conditions worked out for the grafting of *N*-VP onto cellulose, its binary mixture with maleic anhydride was graft copolymerized onto cellulose at constant [*N*-VP]. Only the concentration of maleic anhydride was varied in the molar ratio 0.25 : 1, 0.5 : 1, 1 : 1, 1.5 : 1, and 2 : 1. The homopolymer was separated by extraction with water as discussed above. Grafting parameters were calculated by applying the following relationships.

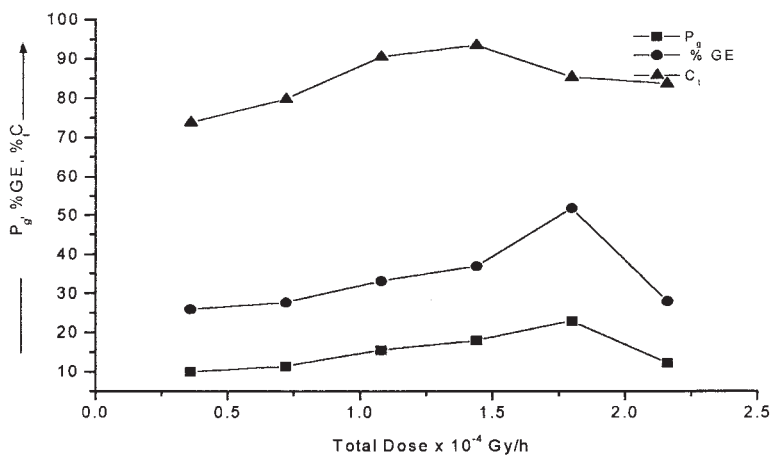
Different grafting parameters like percent grafting (P_g), percent total conversion ($\%C_v$), percent grafting efficiency ($\%GE$), rate of polymerization (R_p), rate of homopolymerization (R_h), and rate of grafting (R_g) were evaluated from the expressions reported earlier.⁵

Characterization of polymers

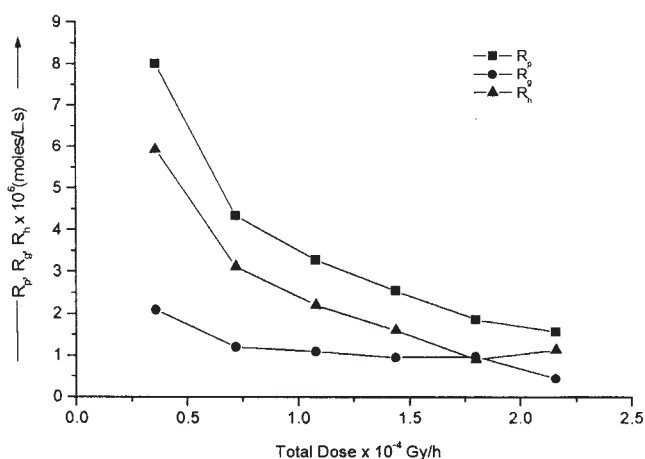
FTIR spectra of various polymers were recorded on KBr pellets on Perkin-Elmer equipment. Nitrogen analysis was recorded on a Carlo Erba EA-1108.

Swelling studies

A known weight of various graft copolymers was swollen by immersion in 50.0 mL of distilled water at room temperature. After a certain time the swollen hydrogels were removed and wiped off with tissue paper to remove any superficial water and weighed immediately to determine the water uptake. The cel-



(a)



(b)

Figure 1 (a) Variation of P_g , %GE, and %C_t with total dose radiation (water = 10 mL, [N-VP] = 0.468×10^{-3} mol/L, and cellulose = 1 g). (b) Variation of R_p , R_g , and R_h with total dose of radiation (water = 10 mL, [N-VP] = 0.468×10^{-3} mol/L, and cellulose = 1 g).

lulose based graft copolymers were studied at room temperature for 24 h. Percent swelling (P_s) was calculated as

$$P_s = \frac{(W_s - W_d)}{W_d} \times 100$$

W_s and W_d are weights of swollen and dried hydrogels (xerogels), respectively.

Metal ion sorption studies

Sorption studies were carried as reported earlier.⁵ Iodine, copper sulfate, and ferrous sulfate (analytical grade, CDH, Mumbai, India) were used as received. Filtrates of the solutions were analyzed for concentration of rejected ions on a DR 2010 Spectrophotometer (Hach Co., Loveland, CO) by using its standard pillow

reagents. All weights were taken on a Denver TR-203 balance having a minimum readability of 1.0 mg.⁸

Percent uptake (P_u)

$$= \frac{\text{amount of metal taken by the polymer}}{\text{total amount of metal ions in the feed}} \times 100$$

RESULTS AND DISCUSSION

Effect of total dose of radiation

Effect of total radiation dose on P_g and other grafting parameters has been studied. P_g increases from 10.0 at 0.36×10^4 Gy with an increase in total dose of radiation to the maximum (23.0) at 1.8×10^4 Gy [Figure 1(a)]. Further, an increase in the total dose of radiation decreases it to 12.2 at 2.16×10^4 Gy. %GE increases

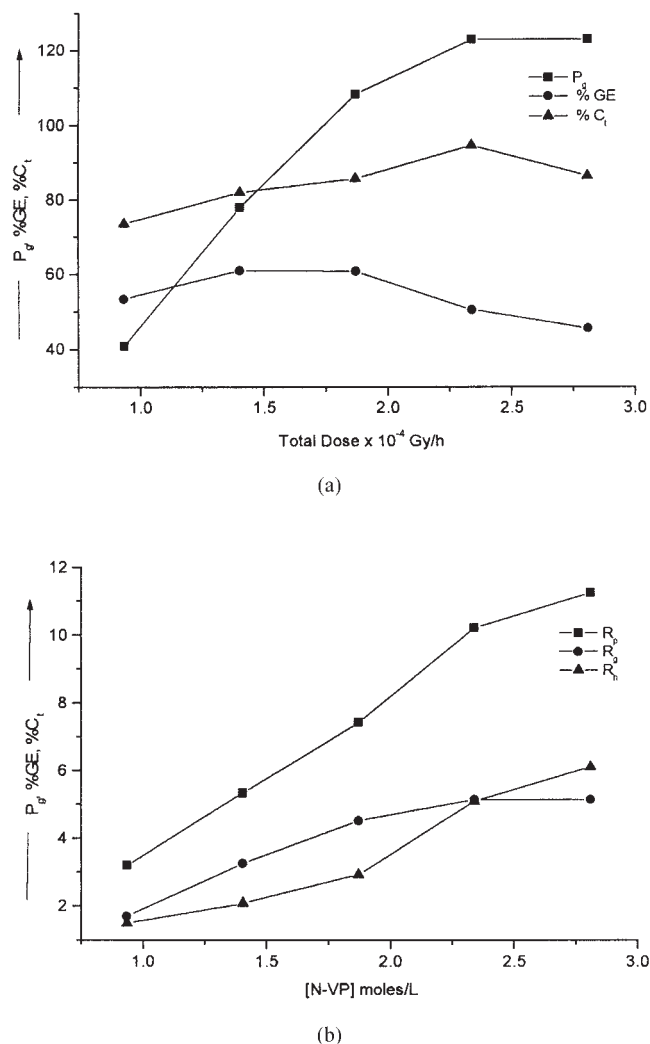


Figure 2 (a) Effect of [N-VP] on P_g , %GE, and %C_t (total dose = 1.8×10^4 Gy, H₂O = 10 mL, and cellulose = 1.0 g). (b) Effect of [N-VP] on R_p , R_g , and R_h (total dose = 1.8×10^4 Gy, H₂O = 10 mL, and cellulose = 1.0 g).

from 26.0 to 51.8 and then decreases to 28.0 for the same range of total dose of radiation. On increasing total radiation dose from 0.36×10^4 to 1.44×10^4 Gy, %C_t increases from 73.85 to 93.46 and thereafter it decreases to 85.38 with progressive increase in radiation dose. On the other hand, different rates of polymerization (R_p , R_h , and R_g) decrease uniformly with the increase in total dose of radiation [Figure 1(b)]. At the higher radiation doses, the decrease in P_g and R_g is due to the preferential homopolymerization and wastage of monomer in some side reactions via chain transfer reactions.

Effect of monomer concentration

Variation of P_g as a function of [N-VP] at the optimum total dose (1.8×10^4 Gy) is represented in Figure 2(a). At the lower monomer concentration (0.468 mol/L),

the maximum P_g obtained was 23.0. With the increase in monomer concentration from 0.468 to 2.81 mol/L, P_g increases regularly from 23.0 to 123.0 at 2.342 mol/L and it tends to be constant with the further increase in [N-VP] to 2.811 mol/L. Thus, 2.342 mol/L of N-VP is evaluated as the optimum monomer concentration. %GE increases to a maximum (60.9) and then tends to be constant before decreasing at the highest monomer concentration studied. %C_t increases to a maximum of 94.57 and then again decreases to 86.31 with the increase of [N-VP]. It is obvious that, at the higher monomer concentrations, the monomer is consumed either in homopolymer formation or wasted in side reactions as the grafting processes become constant. [N-VP] has a high gelling tendency, hence at higher monomer concentrations the viscosity of the monomer system increases and accessibility to the backbone polymer is restricted. It results in the increased mutual termination of the growing macroradicals and more homopolymer is formed. This argument is also supported by the proportionate increase of R_p from 1.85×10^{-6} to 11.23×10^{-6} mol/L·s and the R_h increase from 0.892×10^{-6} to 6.1×10^{-6} mol/L·s, as [N-VP] is increased to 2.811 mol/L. However, R_g tends to be constant even at the higher [N-VP] [Figure 2(b)].

Effect of the amount of water and nature of solvent

At the optimum conditions of total dose and [N-VP], effect of variation of water (from 5.0 to 25.0 mL) on grafting parameters was studied and it has been observed that maximum P_g (230.0), %GE (95.63), %C_t (92.50), R_p (20.06×10^{-6} mol/L·s), and R_g (19.19×10^{-6} mol/L·s) were observed in 5.0 mL of water [Figure 3(a and b)]. An increase in the amount of water up to 25.0 mL uniformly decreases P_g (67.60), %GE (28.58), R_p (3.95×10^{-6} mol/L·s), and R_g (1.12×10^{-6} mol/L·s) but there is a relative increase in R_h from 0.87×10^{-6} to 2.82×10^{-6} mol/L·s in 5.0 mL of water. Thus, the homopolymerization processes become predominant due to the decreased accessibility of the growing macroradicals to the active sites on the backbone polymer resulting in their enhanced mutual termination. In the present case, the nature of solvents has been observed to affect P_g . The highest P_g (123.0) has been observed in water (%GE = 45.8 and %C_t = 86.31) that has the lowest chain transfer constant and the lowest P_g (5.5) has been obtained in dioxane (%GE = 3.53 and %C_t = 59.8). The order of P_g in these solvents is dioxane < acetone < MeOH < benzene < water and that of %C_t is water > MeOH > dioxane > benzene > acetone (Table I). These trends manifest the importance of the solubility of the monomer as the prime factor in determining the extent of graft level.

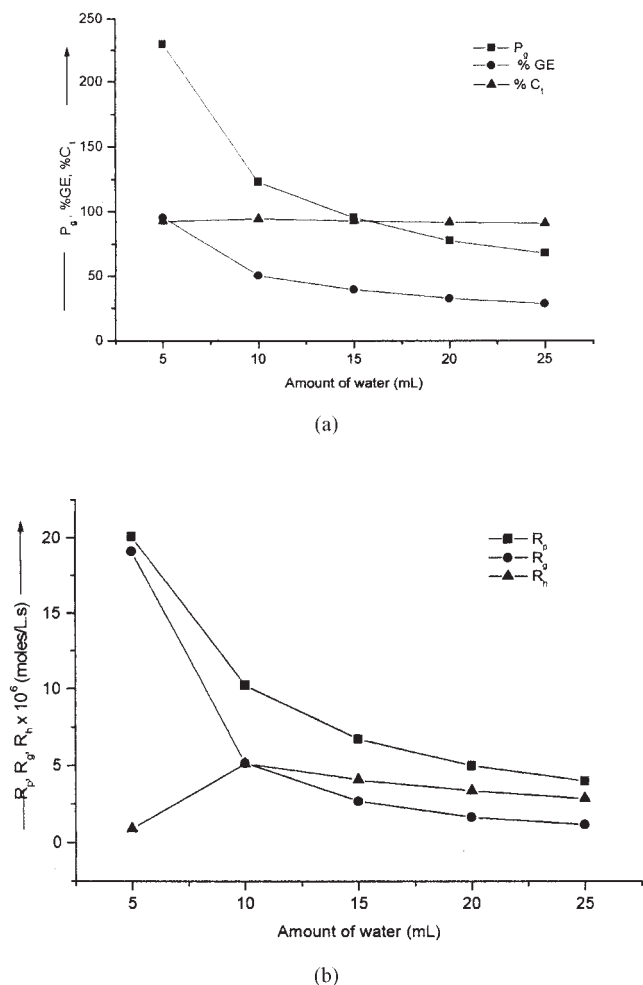


Figure 3 (a) Effect of amount of water on P_g , %GE, and % C_t (total dose = 1.8×10^4 Gy and cellulose = 1.0 g). (b) Effect of amount of water on R_p , R_g , and R_h (total dose = 1.8×10^4 Gy and cellulose = 1.0 g).

Effect of the water-methanol system

Methanol addition to the reaction system decreases P_g uniformly [Figure 4(a)]. As the solvent composition was varied from 100% water to 100% methanol, P_g decreased from 230.0 to 8.0 and %GE also decreased significantly from 95.63 (in water) to 5.6 (in 100% MeOH). It has been observed that, with the increase in methanol composition, % C_t decreases in a drastic

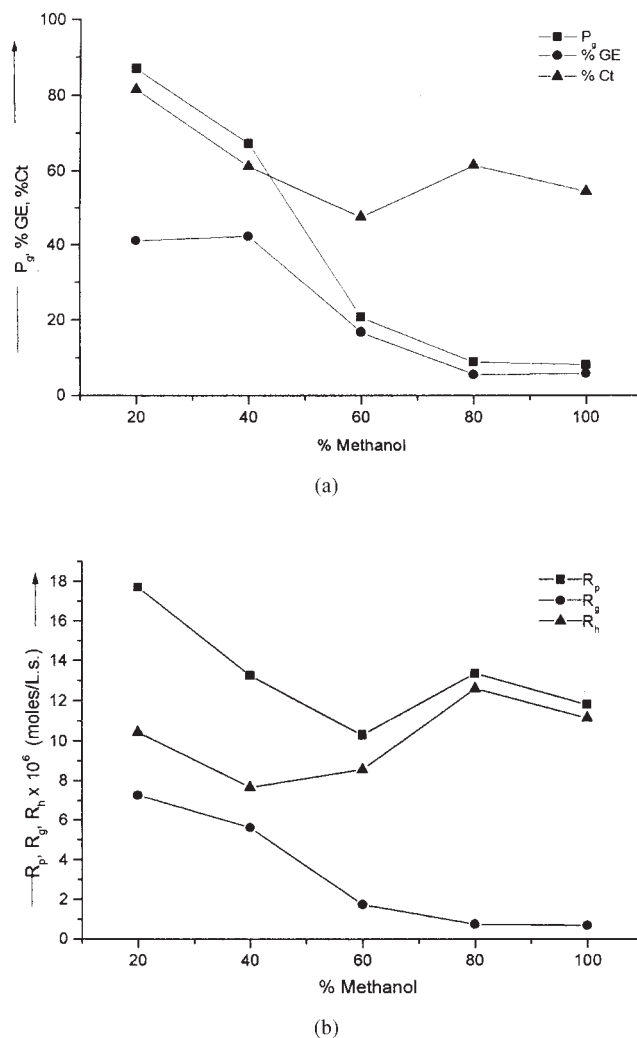


Figure 4 (a) Effect of methanol in binary mixture of methanol-water on P_g , %GE, and % C_t ([N-VP] = 4.684 mol/L, total dose = 1.80×10^4 Gy, and cellulose = 1.0 g). (b) Effect of methanol in binary mixture of methanol-water on R_p , R_g , and R_h ([N-VP] = 4.684 mol/L, total dose = 1.80×10^4 Gy, and cellulose = 1.0 g).

manner to 54.38 in 100% methanol. R_p decreases from 20.06×10^{-6} mol/L.s in the absence of methanol to 10.29×10^{-6} mol/L.s in 60% methanol with the exception at 80 : 20 water-methanol composition where it is higher at 13.34×10^{-6} mol/L.s. Similar trends

TABLE I
Solvent Effect on Grafting of Poly(N-VP) onto Cellulose^a

Sr. no.	Solvent (mL)	[M] (mol/L)	Total dose ($\times 10^{-4}$ Gy)	P_g	% GE	% C_t	$R_p (\times 10^6)$ moles/L · s	$R_g (\times 10^6)$ mol/L · s	$R_h (\times 10^6)$ mol/L · s
1	MeOH	2.32	1.80	8.00	5.66	54.38	5.9	0.3	5.56
2	Acetone	2.342	1.80	7.00	8.66	31.08	3.37	0.29	3.07
3	Benzene	2.342	1.80	5.50	3.53	59.8	6.49	0.22	6.26
4	Dioxane	2.342	1.80	38.9	38.36	39.0	4.23	1.622	2.61

^a Cellulose = 1.0 g.

TABLE II
Grafting of Poly(*N*-VP) onto Cellulosics^a

Backbone	P_g	% GE	%C _t	$R_p (\times 10^6$ mol/L · s)	$R_g (\times 10^6$ mol/L · s)	$R_h (\times 10^6$ mol/L · s)
Poly(<i>N</i> -VP) ^b						
Cell-PO ₄	239.0	95.6	96.15	20.85	19.94	0.91
Cell-NH ₂	183.0	77.70	90.57	19.64	15.26	4.38
HPC	224.0	89.60	96.15	16.88	14.76	2.12
CEC	177.0	87.45	77.85	20.85	18.69	2.16

^a Cellulosics = 1.0 g.

^b Solvent = 5.0 mL.

have been observed for R_g and R_h [Figure 4(b)]. The effect of methanol can be explained by its failure to swell cellulose backbone compared to water and methanol being a good chain transfer agent initiates wasteful side reactions by chain transfer both from the backbone radical (Cell⁻) and also from the M⁻ radical.⁷

Effect of the nature of backbone

Grafting of *N*-VP on different backbones synthesized by derivatization of cellulose, viz. Cell-PO₄, Cell-NH₂, HPC, and CEC at optimum grafting conditions evaluated for cellulose, afforded P_g s of 239.0, 183.0, 224.0, and 177.0 (cellulose = 230.0) and %GEs of 95.6, 77.7, 89.60, and 87.45 (cellulose = 95.63), respectively (Table II). The maximum %C_t was observed with Cell-PO₄ and HPC (96.15) and was lower at 90.57 and 77.85, respectively, for Cell-NH₂ and CEC compared to 95.63 for cellulose. It is clear that the nature of backbone does not only affect grafting yield but also significantly affects different polymerization processes. The same value of R_p (20.85×10^{-6} mol/L · s) was observed in Cell-PO₄ and CEC but far different results observed for R_g are manifested in the higher %GE and P_g . It means that more homopolymerization processes are observed in the presence of the CEC. Quantitatively speaking, such results with Cell-PO₄ are perhaps the result of better interaction of

a tertiary amide (the monomer) with an acidic function (backbone) increases partitioning of the monomer to the backbone. Such partitioning of the monomer and its interactions with backbones is lesser in other cases; hence, the result is more homopolymer formation. Further, CEC is hydrophobic in nature and the interactions of monomer and backbone are not favorable. In the case of HPC, it being partially water soluble, better interaction with the monomer is obvious. The order of reactivity on the basis of R_g is Cell-PO₄ > cellulose > HPC > Cell-NH₂ > CEC.

Cografting of *N*-VP and MAH

At the optimum conditions worked out for the grafting of *N*-VP onto cellulose, its binary mixture with MAH was graft copolymerized onto cellulose. Keeping the [*N*-VP] constant, only [MAH] was varied in the molar ratio 0.25 : 1, 0.5 : 1, 1 : 1, 1.5 : 1, and 2 : 1. It has been observed that initially the addition of MAH affects P_g adversely. However, it increases with the increase in [MAH] from 9.0 to 17.0. Thereafter, it decreases to 9.3 with the increase in the monomer molar ratio from 0.25 : 1, 0.5 : 1, 1 : 1, 1.5 : 1, and 2 : 1. It is stated that these two monomers form a complex and that is grafted onto cellulose. Mole fractions of the *N*-VP and MAH in the graft copolymers calculated on the basis of percent nitrogen have been found to be

TABLE III
Elemental Analysis of Cell-g-poly(*N*-VP)

S. no	Polymer	P_g	% N		% C		% H	
			Observed	Calculated	Observed	Calculated	Observed	Calculated
Graft copolymers of cellulose								
1	Cell-g-poly(<i>N</i> -VP)	67.2	5.07	5.069	46.56	52.02	5.9	5.75
2	Cell-g-poly(<i>N</i> -VP)	77.5	5.51	5.50	46.43	52.77	6.28	5.88
3	Cell-g-poly(<i>N</i> -VP)	123.0	6.99	6.96	49.06	55.23	6.74	6.33
4	Cell-g-poly(<i>N</i> -VP)	230.0	8.86	8.80	53.42	58.36	6.77	6.91
Graft copolymers of cellulosics								
1	CEC-g-poly(<i>N</i> -VP)	177.0	8.51	8.48	37.44	58.15	6.12	7.31
2	HPC-g-poly(<i>N</i> -VP)	224.0	8.72	8.719	43.51	56.57	6.48	7.08
3	Cell-NH ₂ -g-poly(<i>N</i> -VP)	183.0	8.56	8.56	49.1	58.00	6.41	7.27
4	Cell-PO ₄ -g-poly(<i>N</i> -VP)	239.0	9.95	9.4	70.05	60.33	7.42	7.5

TABLE IV
Elemental Analysis of Cell-g-poly(*N*-VP-co-MAH)

Sr. no	NVP (g)	MAH (g)	<i>N</i> -VP (mol)	MAH (mol)	P_g	%N	<i>N</i> -VP (g)	MAH (g)	Molar ratio <i>N</i> -VP/MAH
1	2.6	2.29	1.0	1.0	17	0.98	0.09	0.08	1.17
2	2.6	3.44	1.0	1.5	15	0.87	0.079	0.071	1.16
3	2.6	4.59	1.0	2.0	9.3	0.55	0.0469	0.046	1.07

0.501 : 0.499 ($P_g = 9.3$), 0.505 : 0.496 ($P_g = 15.0$), and 0.490 : 0.506 ($P_g = 17.0$), respectively, implying that these monomers are grafted in a 1 : 1 mol fraction ratio in an alternate fashion. We have earlier also reported such results for the grafting of MAH and styrene onto this backbone.⁶ In the present case lower graft yield and the reactivity behavior of MAH and *N*-VP can be explained by understanding their reported reactivity ratio. *N*-VP has a very low tendency to react with itself in the presence of MAH as the r_1 (-0.027 at 30°C) is very low, while the tendency to react with MAH is better ($r_2 = 0.074$ at 30°C).¹²

Characterization of graft copolymers

Elemental analysis

P_g was quantitatively determined on the basis of %N found in the analysis of graft copolymers, which was found to be in consonance with the observed gravimetric values (Table III). Cellulose contains C = 43.4%, H = 4.16%, and N = 1.55%.⁵ The nitrogen in cellulose is due to the ammoniation in the extraction process that gets detrapped from the cellulose matrix in the long grafting process. Four different graft levels ($P_g = 67.2, 77.5, 123.0,$ and 230.0) were studied and the theoretically calculated percentage of elements for these graft levels reveal that the nitrogen present in these copolymers is in close agreement with the gravimetric P_g . Graft copolymers of cellulose derivatives such as Cell- PO_4 , CEC, HPC, and Cell-NHNH₂, were also analyzed for elemental analysis (C, H, N). Again the theoretical and observed percent of elements are in close agreement with each other. Cell-g-(MAH-co-*N*-VP) with a P_g of 17.0 was found to contain N = 0.98%, C = 44.28%, and H = 5.27%, which reveals 0.09 g incorporation of *N*-VP and 0.08 g of MAH. Theoretical

values of these elements are in close agreement with the experimental value and it can be concluded that MAH and *N*-VP have been incorporated in a 1 : 1M ratio (Tables IV and V).

FTIR spectrum analysis

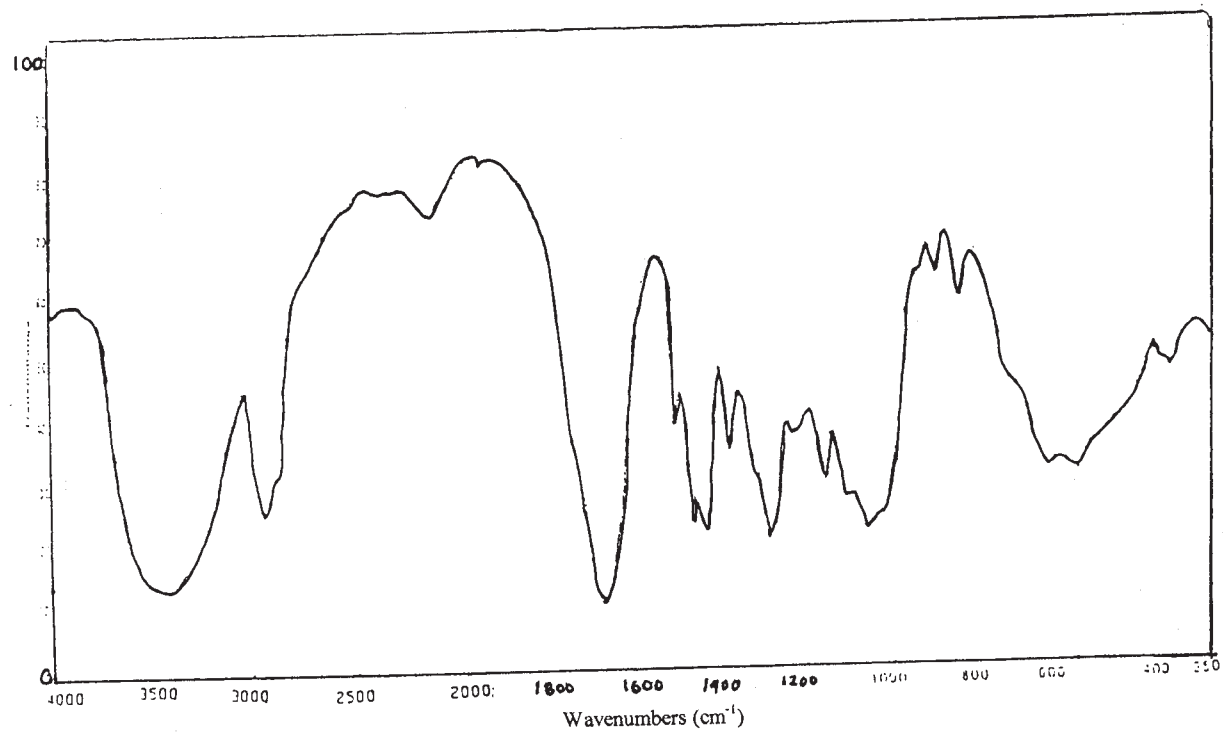
Apart from the IR bands shown by native cellulose, some prominent peaks around 1650–660 and 1280 cm^{-1} due to the C=O stretching and C–N stretching of the cyclic tertiary amide have been observed in the FTIR spectrum of Cell-g-poly(*N*-VP) [Figure 5(a)]. The ratio of absorbance of C=O stretching of amide and C–O–C stretching of the anhydroglucose unit of cellulose increases with P_g , providing direct evidence of quantitative incorporation of *N*-VP onto cellulose. FTIR spectra of graft copolymers of cellulose derivatives show additional characteristic peaks due to the C=O stretching of the tertiary amide, –NHNH₂, and PO_4 groups. Cell-g-poly(MANh-co-*N*-VP) spectra has a peak at 1735 cm^{-1} due to C=O stretching of maleic acid that is obtained *in situ* due to the hydrolysis of MAH in the reaction medium. Another peak at 1660 cm^{-1} is ascribed due to the C=O stretching of amide function [Figure 5(b)]. Ratio of absorbance of C=O of amide to C=O of acid was found to be nearly 1 : 1, confirming grafting of both the monomers in a 1 : 1M ratio.

Swelling behavior

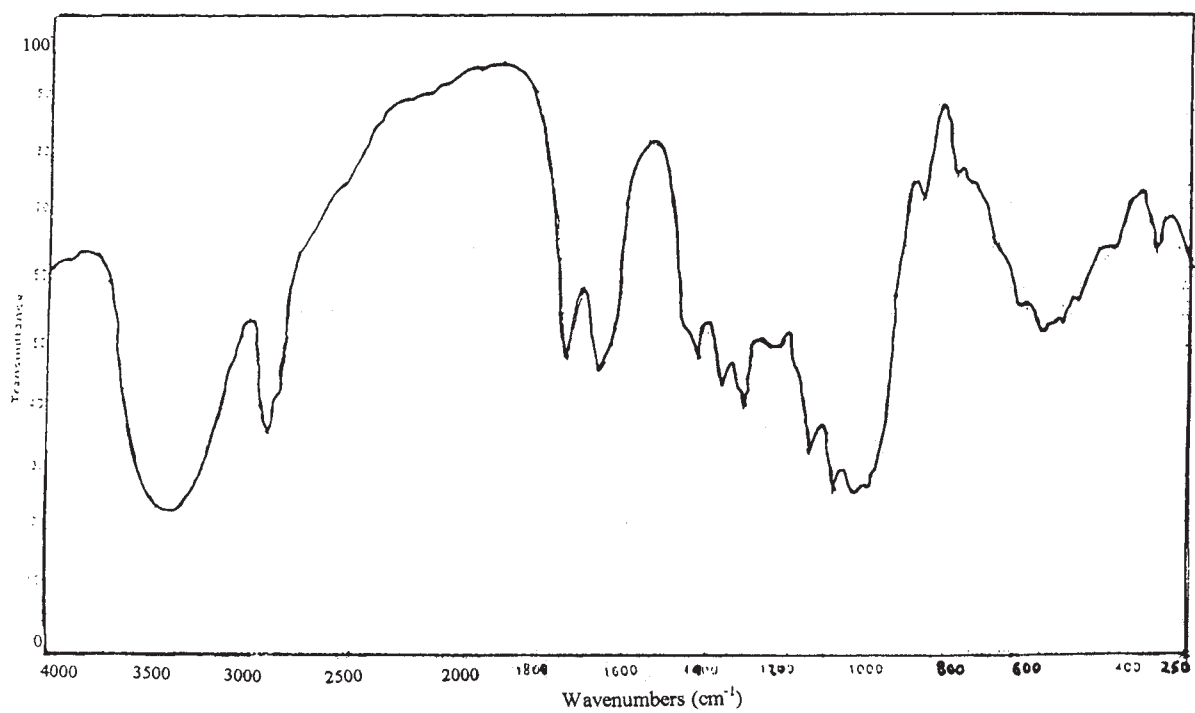
The result of swelling behavior of cellulose graft polymers is presented in Figure 6. Compared to cellulose ($P_s = 390.0$), P_s increases with the increase in P_g to 1160.0, 1480.0, 1660.0, and 1750.0 as P_g increases from 67.7 to 230.0. Such trends in results are expected as

TABLE V
Nitrogen Analysis of (MAH-co-*N*-VP) Chains

Molar ratio (MA/ <i>N</i> -VP)	P_g	% Nitrogen	Amount of <i>N</i> -VP (g)	Amount of MAH (g)	Mole fractions MAH in feed (f_1)	<i>N</i> -VP in feed (f_2)	MAH in graft copolymer (F_1)	<i>N</i> -VP graft copolymer (F_2)	Ratio (F_2/F_1)
2:1	9.3	0.55	0.0456	0.0474	0.667	0.333	0.499	0.501	1.004
1.5:1	15.0	0.87	0.074	0.076	0.60	0.40	0.496	0.505	1.018
1:1	17.0	0.98	0.0843	0.0857	0.50	0.50	0.490	0.506	1.032



(a)



(b)

Figure 5 (a) FTIR spectra of Cell-g-poly(N-VP). (b) FTIR spectra of Cell-g-poly(N-VP-co-MAH).

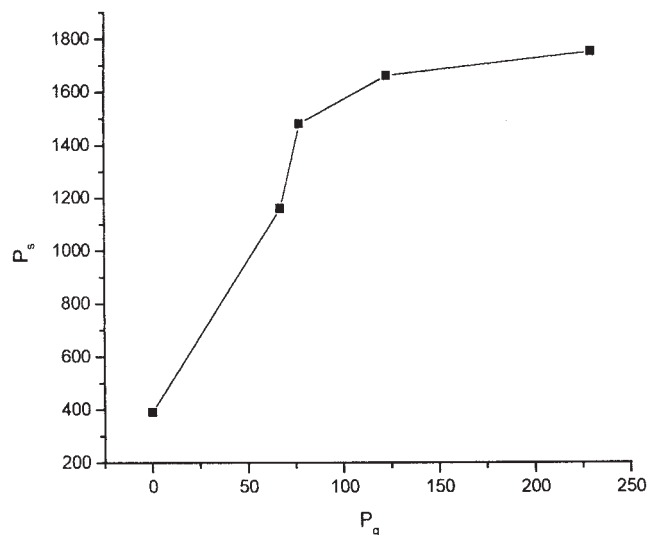


Figure 6 Percent swelling in water as a function of P_g .

poly(*N*-VP) is a hydrophilic and gelling polymer having polar groups. Derivatization of cellulose to its derivatives such as Cell-PO₄, Cell-NHNH₂, CEC, and HPC results in an increase in the water uptake, which supports the fact that derivatization opens up the cellulose structure that increases the water interactions by exposing the otherwise masked hydrophilic groups to water. The sequence of P_s in these derivatives is as follows: Cellulose < Cell-NHNH₂ < CEC < Cell-PO₄ < HPC (Table VI). Among the cellulose derivatives and their graft copolymers, the highest P_s was observed in Cell-PO₄ (1660.0) and its graft copolymer ($P_s = 2370.0$, $P_g = 239.0$).

Metal ions and iodine sorption study

Sorption is the common term used to convey the nature of uptake of metal ions or iodine species by adsorption on anchor groups, ion exchange (as in case

TABLE VI
Swelling Behavior of Poly(*N*-VP)

S no.	RCell-g-poly(<i>N</i> -VP)	
	Polymer	P_s
1	Cellulose	390.0
2 ^a	Cell-g-poly(<i>N</i> -VP)	1750.0
3	Cell-PO ₄	1660.0
4 ^a	Cell-PO ₄ -g-poly(<i>N</i> -VP)	2370.0
5	Cell-NHNH ₂	500.0
6 ^a	Cell-NHNH ₂ -g-poly (<i>N</i> -VP)	1240.0
7	CEC	830.0
8 ^a	CEC-g-poly(<i>N</i> -VP)	1620.0
9	HPC	1530.0
10 ^a	HPC-g-poly(<i>N</i> -VP)	1620.0

^a Maximum P_g .

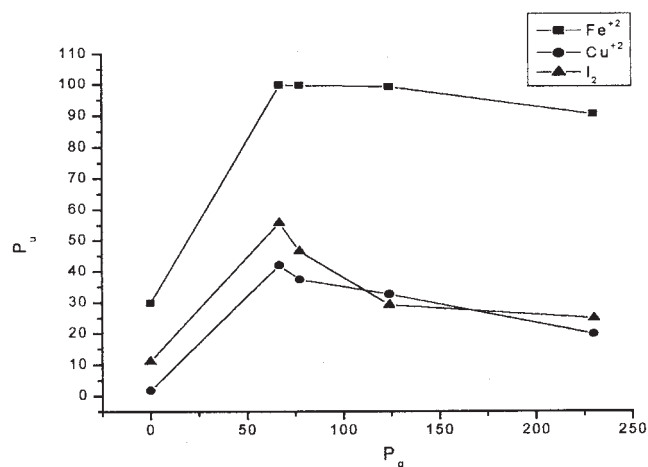


Figure 7 Comparative percent uptake of Fe²⁺, Cu²⁺, and I₂ onto Cell-g-poly(*N*-VP) as a function of P_g .

of Cell-PO₄ and its graft copolymers), and in the bulk of the hydrogel.

Sorption of metal ions by graft copolymers

Sorption of metal ions was studied as function of P_g . In Cell-g-poly(*N*-VP), both Cu²⁺ and Fe²⁺ have been sorbed in a good amount even at low P_g , but P_u decreases initially and then tends to remain independent of the P_g (Figure 7). Graft copolymerization onto cellulose derivatives such as Cell-PO₄, Cell-NHNH₂, and CEC results in an increase in the metal ion sorption (both Cu²⁺ and Fe²⁺ ions) compared to the native cellulose with maximum P_g , as these have extra active groups for the attachment of metal ions (Table VII). The Fe²⁺ uptake is far higher than that of Cu²⁺ ions. Graft copolymers of poly(MAH-co(*N*-VP)) also show high metal ion sorption, which was also observed to decrease with the increase in P_g (Figure 8). Metal ion sorption on the hydrogels is due to the partitioning of the metal ions between the polymer and solution phases; therefore, the higher water uptake should result in higher partition coefficient. However, in the present case it is appropriate to state that, at the higher P_g due to the gelling of poly(*N*-VP), its different groups associate and block the entry of metal ions to the inner core. Hence, there is decreased uptake of metal ions at the higher P_g .

Iodine sorption study by graft copolymers

Iodine, polyiodide anion, azo dyes, sodium dodecyl sulfate, and methyl orange have been adsorbed by poly(*N*-VP) in a substantial amount. In the present study it has been observed that the extent of I₂ adsorption is not significant. Iodine absorption follows almost the same pattern and extent as has been ob-

TABLE VII
Sorption of Fe^{2+} , Cu^{2+} , and I_2 by Poly(*N*-VP) Based Polymers

Polymer	P_g	P_u		
		Fe^{2+}	Cu^{2+}	$^3\text{I}_2$
Cell- PO_4	0.0	54.2	2.2	22.22
Cell- PO_4 -g-poly(<i>N</i> -VP)	239.0	73.5	24	33.33
Cell-NHNH ₂	0.0	70.4	4.92	13.88
Cell-NHNH ₂ -g-poly(<i>N</i> -VP)	183.0	75.1	27.8	20.0
CEC	0.0	44.6	3.0	24.44
CEC-g-poly(<i>N</i> -VP)	177.0	78.5	8.4	28.88
HPC	0.0	43.2	6.8	13.33
HPC-g-poly(<i>N</i> -VP)	224.0	99.9	12.4	24.75
Cellulose	0.0	29.8	1.85	11.11
Cell-g-poly(<i>N</i> -VP)	230.0	90.4	19.8	24.71

^a Weight of the dry polymer = 50 mg; Cu^{2+} and Fe^{2+} feed = 10 mg/L; iodine feed = 11.25 mg/L.

served for the sorption of C^{2+} ions (Figure 8). Adsorption of I_2 is explained as follows. The lactum form of poly(*N*-VP) forms a charge transfer complex with I_2 since the lactim form is unstable and it can be converted to lactum by a desorption process, which means adsorption is a reversible process. Since the lactim form is susceptible to hydrogen bonding as well as hydrolysis, with the increase in P_g , polymeric association increases and binding sites are blocked. Cellulose is expected to form an adsorption complex with I_2 in analogy of a starch- I_2 complex. In the derivatization process the structure of cellulose becomes more open and surface area for sorption increases, resulting in higher iodine adsorption capacity of cellulose derivatives compared to cellulose (Table VII).

CONCLUSIONS

From the discussion it can be concluded that the nature of backbone does not only affect graft yields, but

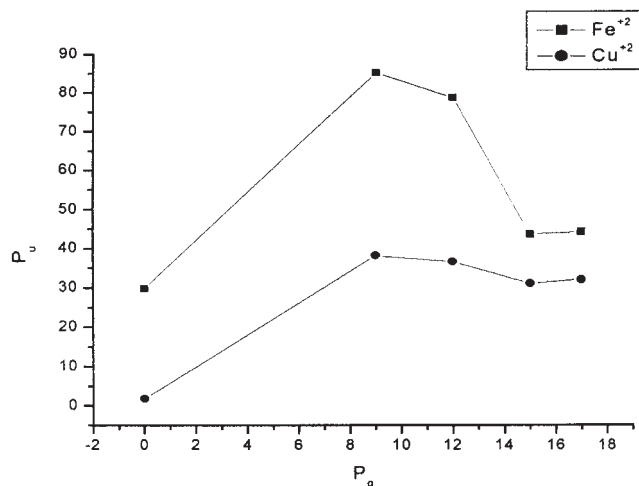


Figure 8 Comparative percent uptake of Fe^{2+} and Cu^{2+} onto Cell-g-poly(MAH-co-*N*-VP).

also significantly affects different polymerization processes. The order of reactivity for all the backbones on the basis of R_g is Cell- PO_4 > cellulose > HPC > Cell-NHNH₂ > CEC. Derivatization of cellulose results in the increase in water uptake, which supports the fact that derivatization opens up the cellulose structure that exposes to water the otherwise masked hydrophilic groups. The sequence of P_s in these derivatives can be expressed as cellulose < Cell-NHNH₂ < CEC < Cell- PO_4 < HPC. Metal ions and iodine uptake is appreciable on most of these graft copolymers. The grafting improves both the metal ions and iodine sorption and better results have been observed at lower P_g values. Fe^{2+} uptake is higher on all of the supports used. The cograftering of maleic anhydride and derivatization of cellulose and consequent grafting on these cellulotics does not enhance metal ions or iodine uptake.

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