

# Functionalization of Poly(4-vinyl pyridine) Grafted Cellulose by Quaternization Reactions and a Study on the Properties of Postquaternized Copolymers

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**ABSTRACT:** Graft copolymers of 4-vinyl pyridine (4-VP) synthesized by using simultaneous gamma irradiation method were further functionalized by post polymer quaternization reactions at N: of the pyridine ring of the graft copolymers. Using the optimum grafting conditions reported earlier for the grafting of 4-VP onto extracted cellulose, graft copolymer was synthesized in bulk and was further functionalized by quaternization with hexyl bromide ( $C_6H_{13}Br$ ), benzyl chloride ( $C_6H_5CH_2Cl$ ), *n*-butyl bromide ( $C_4H_9Br$ ), and maleic anhydride (MAh). The quaternized polymers were studied for treatment of hardness of water, antibacterial action, emulsification properties, metal ion uptake and stability toward thermal degradation, and enzy-

matic and alkaline hydrolysis to evaluate the suitability of these polymers in harsh chemical, microbial, and thermal environments. The functionalized polymers were also characterized for surface morphology (SEM), elemental analysis and FTIR for investigations of structural aspects, and to obtain evidence for quaternization. The functionalized copolymers exhibit a range of properties that can be used in many fields of water purification technologies including antibacterial agents and ion exchangers. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2454–2464, 2004

**Key words:** functionalization of polymers; graft copolymers; swelling; thermal properties; poly(4-vinyl pyridine)

## INTRODUCTION

The membranes of cellulose and cellulose acetate have been reported to be strong virus filters.<sup>1,2</sup> Quaternary nitrogen containing polymers are reported to be antimicrobial in nature.<sup>3–6</sup> The quaternized 4-vinyl pyridine (4-VP) moieties not only have the potential to act as catalysts but are also known biocides. There are early reports on the development of quaternized poly(4-VP) and its uses in various fields like ion-exchange membranes as a virus filter and as polyelectrolyte. Hegazy and coworkers<sup>7</sup> reported the use of LDPE-g-poly(AAc-co-4VP) membranes for wastewater treatment and reported metal ion uptake using atomic absorption and X-ray fluorescence. Kawabata et al.<sup>8</sup> reported use of cellulose-coated crosslinked poly(*N*-benzyl-4-VP-co-styrene) chloride as a virus filter. The solution properties of poly(4-VP)-*N*-alkyl halides having small chains at low concentrations behave as polyelectrolytes and these include poly(4-VP) hydrochloride. On the other hand, long-chain derivatives behave

differently and act as polysoaps, given that alkyl groups, hydrophobic in nature, form aggregates in solutions casting soap properties. In the present study we report some properties of the quaternized copolymers, characterized by different physical methods.

## EXPERIMENTAL

### Materials

Maleic anhydride, hexyl bromide, butyl bromide, and benzyl chloride (SRL, Mumbai, India) were used as received.

### Quaternization of graft copolymers

Synthesis of graft copolymers by a simultaneous method was carried out under optimum reaction conditions using 1.0 g of cellulose extracted from pine needles,  $234.2 \times 10^{-2}$  mol/L of 4-vinyl pyridine in 10.0 mL of water, and at total dose of irradiation of 11.5 kGy, evaluated and reported in an earlier communication.<sup>9</sup> Using these conditions, in the present study grafting was performed in bulk with 10.0 g of cellulose and corresponding amounts of monomer and water were taken to synthesize stock material by simultaneous gamma-ray initiation. The known amount of the above graft copolymer was treated three times with hexyl bromide, butyl bromide, and benzyl bromide and was refluxed for appropriate time

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periods ranging, respectively, from 4, 8, to 2 h. Maleic anhydride was taken in 1 : 1 ratio of the graft copolymer and refluxed in 50.0 mL of cyclohexane for 1 h. The quaternized products were isolated by filtration and dried in an air oven at 50°C. The degree of quaternization was calculated as follows:

Degree of quaternization

$$= \frac{\text{Quaternization agent(moles)}}{\text{Total poly(4-VP)in the graft copolymer (moles)}}$$

### Characterization by FTIR, SEM, elemental analysis, and TGA

Characterization of functionalized polymers was performed by elemental analysis, scanning electron microscopy (SEM), FTIR, and TGA. FTIR spectra were recorded on Perkin-Elmer FTIR (Perkin Elmer Cetus Instruments, Norwalk, CT) in KBr pellets. Elemental analysis was carried out on a Carlo Erba-1150 instrument. Scanning electron micrographs (SEM) were studied on a Cambridge Stereoscan 150. Thermogravimetric analysis was performed on a Shimadzu TG/DT simultaneous analyzer Shimadzu, Kyoto, Japan) in nitrogen at a heating rate of 20°C/min.

### Study of physical properties

#### Water uptake behavior

Water uptake studies were carried out in distilled water at room temperature by an equilibration method as a polymer of known weight was immersed and kept undisturbed for 24 h in 50 mL of distilled water.<sup>10</sup> Percentage water uptake ( $P_u$ ) was calculated as follows:

$$P_u (\%) = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}} \times 100$$

#### Solubility studies

Solubility studies of the functionalized polymers were carried out in water at 25°C by immersion of polymer (1 g) in 100 mL of distilled water. The polymers were swollen in water for 15 h and then stirred for 25 h, after which solubility was determined by subtracting the weight of the undissolved fraction from the gross weight of the functionalized graft copolymer.

#### Surface tension, water-softening, and emulsification properties

All the functionalized polymers were solubilized to the maximum by dissolving in distilled water. Surface

tension of the solution was determined by the drop count method. Emulsification value ( $V_2 - V_1$ ) of the samples was determined by charging an aqueous solution of the polymers (70.0 mL) to a conical flask with 30.0 mL of toluene ( $V_1$ ). The solution was shaken vigorously for 15 min and kept undisturbed for 24 h, after which volume was again measured ( $V_2$ ). The emulsification value (EV) was determined from the changes in volume as

$$EV = \frac{V_2 - V_1}{V_1} \times 100$$

Hardness of water was studied by treating the sample from Shimla Municipal Corp. drinking water supply by stirring polymers for specified time and then the resultant solution was titrated with ethylenediaminetetraacetic acid (EDTA) for complexation of the specific ions.

#### Antibacterial activity

Antibacterial activity of cellulose, cellulose-g-poly(4-VP) ( $P_g = 113.0$ ), and its quaternized polymers was studied at different dilutions of municipal water that contained *Salomonella* and different *Bacillus* species. Bacteria colonies were compared by direct count method and high-resolution photographs were taken.

#### Alkaline hydrolysis

To study stability of the quaternized copolymers under chemical and biochemical environments these were subjected to alkaline and enzymatic hydrolysis. A known amount of polymer (0.5) was stirred with 50.0 mL of 10% of sodium hydroxide solution at 40°C in a water bath. Three fractions were isolated from each sample, one dissolved, one undissolved, and a third precipitated by applying common ion effect with NaBr for polymers that had bromide ions and NaCl for polymer functionalized with benzyl chloride, thereby excluding maleic anhydride derivative from this study. The third fraction was precipitated by methanol and this fraction was ungrafted cellulose as sodium salt.

#### Enzymatic hydrolysis

Cellulose and its graft copolymer and functionalized graft copolymers (100 mg) were taken in M/15 phosphate buffer (10.0 mL) and were incubated under shaking with cellulase (4 mg) at 30°C for 1–4 weeks in a neutral medium (10.0 mL phosphate buffer) containing M/15 solution of  $\text{Na}_2\text{HPO}_4$  (pH = 9.5) and  $\text{NaH}_2\text{PO}_4$  (pH = 5.5), prepared in distilled water. The reagent to test for release of sugars was prepared by

TABLE I  
Degree of Quaternization

Series	Polymer	Yield (g)	Quaternizing agent × 10 <sup>2</sup> (mol)	Degree of quaternization
1	Cell-g-poly( <i>N</i> -benzyl-4-vinyl pyridinium chloride)	14.426	3.4	0.69
2	Cell-g-poly( <i>N</i> -butyl-4-vinyl pyridinium bromide)	14.2	3.1	0.60
3	Cell-g-poly( <i>N</i> -hexyl-4-vinyl pyridinium bromide)	17.40	4.4	0.86
4	Cell-g-poly(4-vinylpyridine- <i>N</i> -maleate)	14.63	4.7	0.92

dissolving 1.0 g dinitro salicylic acid, 0.2 g phenol, 1.0 g NaOH, 0.05 g sodium sulfite, and 2.0 g of sodium potassium tartrate in 100 mL of distilled water. Each sample after the incubation period was filtered and the filtrates of the samples were analyzed, to test for the release of sugars, with reagent that was prepared by dissolving 1.0 g dinitro salicylic acid, 0.2 g phenol, 1.0 g NaOH, 0.05 g sodium sulfite, and 2.0 g of sodium potassium tartrate in 100 mL of distilled water. None of the solutions gave a brown color with DNSA reagent, indicating that samples were not degradable under the said enzymatic action. Observations on weight loss of the polymers after every week were also recorded.

#### Metal ion sorption study by quaternized copolymers

Cu<sup>+2</sup> and Fe<sup>+2</sup> ions were sorbed on different functionalized polymers by a previously reported method, and percentage ion uptake ( $P_u$ ) was expressed as<sup>10</sup>

$$P_u (\%) = \frac{\text{Amount of ion sorbed}}{\text{Total amount of ions in feed}} \times 100$$

## RESULTS AND DISCUSSION

Grafting of 4-VP results in reactive polymers because the N: of the pyridine moiety is free and functional and can react further to give polymers with useful properties. This amenability of the pyridine moiety to change also changes the resultant properties of the polymer in dramatic ways. Quaternization of poly(4-VP) graft copolymers was successfully carried out and the quantum of reaction was satisfactorily high in all cases, although it was extremely high in the case of maleic acid as a result of its direct acid–base interactions with 4-VP (Table I). The quaternization of 4-VP cannot be carried out beyond a certain extent because of the steric and electrostatic considerations, given that generation of one charge unit on nitrogen retards the activity of another nitrogen for quaternization by three times. However, functionalization affected by these postreactions on 4-VP moieties was enough to influence important properties of the graft copolymers including interaction with water, polysoap behavior,

emulsification, and bactericidal action. Some structural and functional attributes of these polymers are discussed below.

#### Characterization of polymers

##### Scanning electron microscopy

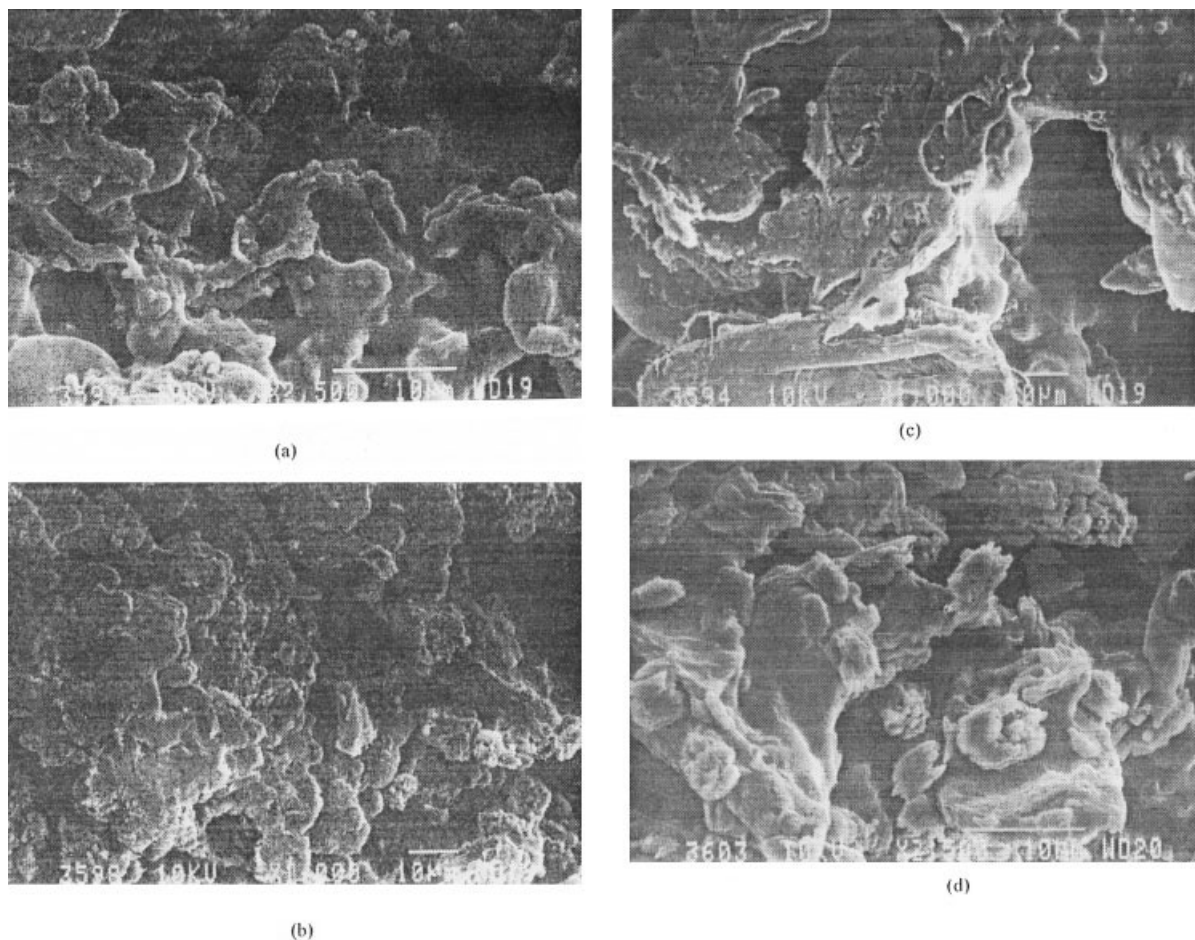
SEM micrographs of the cellulose-g-poly(4-VP) were examined for changes in the surface morphology after functionalization. These micrographs reveal that texture and surface morphology of the functionalized graft copolymer are different from those of the cellulose graft poly(4-VP) copolymers. In the case of benzyl derivative larger voids are seen at significant distance. The voids are also clear over the surface of butyl and hexyl derivatives but they are closer than the benzyl derivative, whereas significant cluster formation is visible in maleate derivative because of the more prominent associations (Fig. 1).

##### Elemental analysis

We reported earlier that the elemental analysis of cellulose contains different elements as carbon (43.4%), hydrogen (4.16%), and nitrogen (1.55%), and its graft copolymer ( $P_g = 68.0$ ) contains carbon (57.86%), hydrogen (6.1%), and nitrogen (7.26%).<sup>9</sup> The presence of these elements corresponds to 68% incorporation of poly(4-VP) onto the cellulose backbone (i.e., equal to the gravimetric value of the incorporated polymer). The functionalized samples show the presence of the corresponding halogen attached in elemental analysis and there is also an increase in the percentages of C, H, and O, revealing functionalization of the grafted polymers. Percentage values of different constituent elements are given in Table II.

##### Analysis of FTIR spectral data

Cellulose and its graft copolymers with varying  $P_g$  values were analyzed by FTIR spectroscopy. The FTIR spectrum of cellulose shows prominent peaks at 3471.89, 2927.66, 1323.16, 1165, 1016.8, and 871.67 cm<sup>-1</sup> (Fig. 1).<sup>9</sup> These peaks correspond to O—H,



**Figure 1** SEM micrographs of (a) cellulose-g-poly(*N*-butyl vinyl pyridinium bromide); (b) cellulose-g-poly(*N*-hexyl vinyl pyridinium bromide); (c) cellulose-g-poly(*N*-benzyl vinyl pyridinium bromide); and (d) cellulose-g-poly(*N*-maleate vinyl pyridinium) (magnifications: a, b, d:  $\times 2500$ ; c:  $\times 1000$ ).

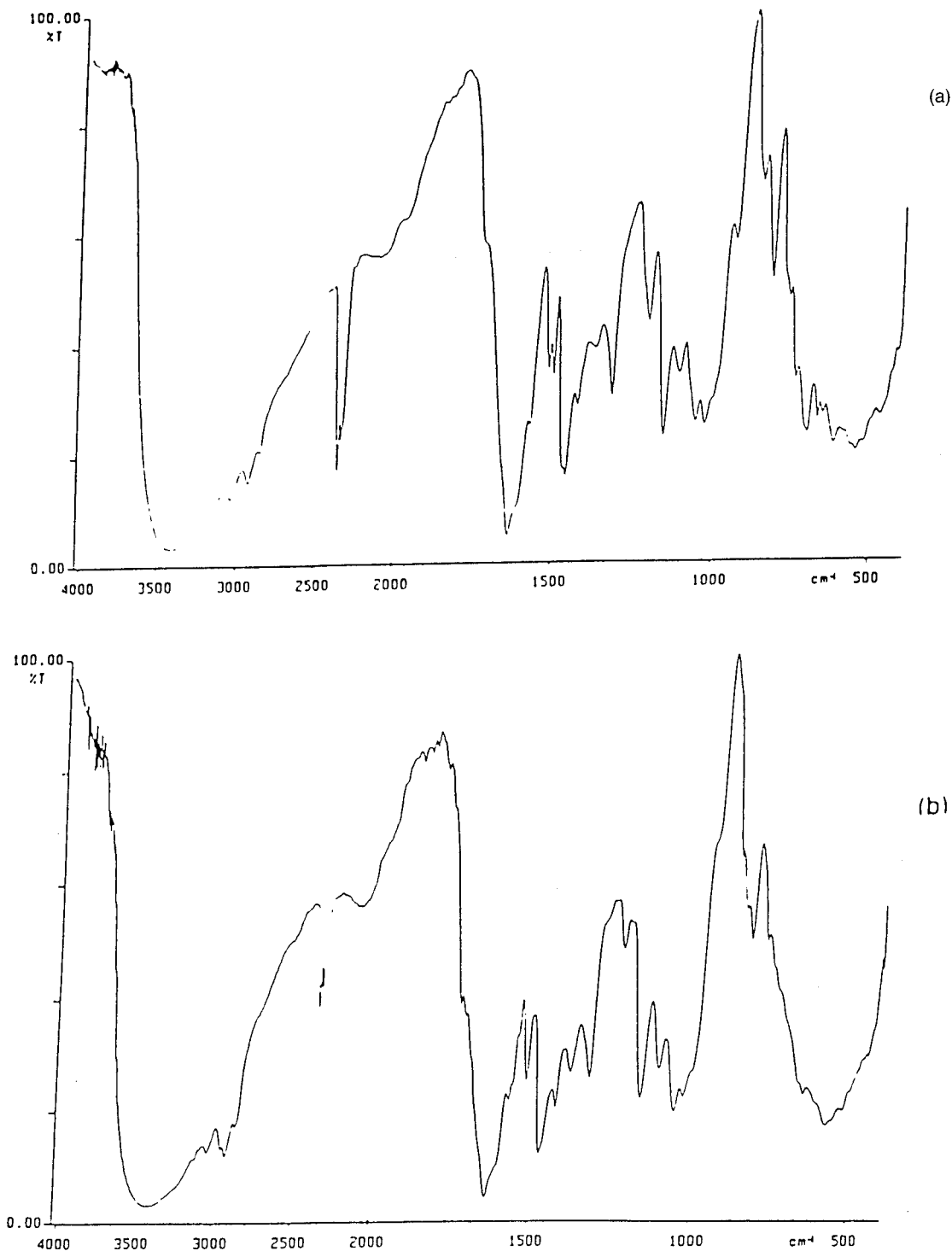
C—H, C—O—C stretching, and —OH bending, respectively, and a peak at  $1645.69\text{ cm}^{-1}$ . FTIR spectra of the graft copolymers show prominent additional peaks at  $1623\text{--}1597\text{ cm}^{-1}$  and doublets at  $1416$  and  $1552\text{ cm}^{-1}$  attributed to stretching of the —C=N and —C=C bonds. The absorption peak attributed to the —OH stretching is sharper and shifts downfield from  $3471\text{ cm}^{-1}$  in pure cellulose to  $3185\text{ cm}^{-1}$  in different quaternized copolymers (Fig. 2). This indicates formation of a new yet weak association that comes

into play as a result of the loosening of cellulose structure and possible interactions of the unmodified —OH groups with N: of the pendant pyridine rings. In the absorption peaks of functionalized polymers, overtones and combination bands attributed to the quaternary ammonium salts are also observed in benzyl, butyl, hexyl, and maleate derivatives at  $2360.8$ ,  $2362.0$ ,  $2343.4$ , and  $2341.4\text{ cm}^{-1}$  with absorbance of 83, 62, 66, and 36%, respectively, each corresponding to the quantum of quaternization,

**TABLE II**  
Elemental Analysis of Graft and Quaternized Copolymers

Series	Polymer	%C	%H	%N	%O	%Br/Cl	Yield (%)
1	Cellulose	43.4	4.16	1.55	—	—	—
2	Cell-g-poly(vinylpyridine)	57.86	6.1	7.26	—	—	113 <sup>a</sup>
3	Cell-g-poly( <i>N</i> -benzyl-4-vinyl pyridinium chloride)	64.15	6.1	4.46	—	10.41	59.06
4	Cell-g-poly( <i>N</i> -butyl-4-vinyl pyridinium bromide)	54.78	6.46	4.95	—	17.3	42.4
5	Cell-g-poly( <i>N</i> -hexyl-4-vinyl pyridinium bromide)	47.41	7.03	3.93	—	19.74	74.08
6	Cell-g-poly( <i>N</i> -maleate-4-vinyl pyridine)	50.0	5.62	3.78	39.7	—	46.3

<sup>a</sup>  $P_g$ .



**Figure 2** FTIR spectra of functionalized cellulose-g-poly(*N*-halo aryl/alkyl vinyl pyridinium halide): (a) benzyl chloride derivative; (b) butyl bromide derivative; (c) hexyl bromide derivative; (d) maleic anhydride derivative.

which is maximum in the benzyl derivative and minimum in the maleate derivative. There is also a shift to higher  $\nu$  in the absorption of the  $-\text{C}=\text{N}-$  moiety observed at  $1638\text{--}1641\text{ cm}^{-1}$ . Additional peaks at  $1513$  and  $1455\text{ cm}^{-1}$  are also observed in the benzyl derivative attributed to the presence of phe-

nyl ring. The absorption peak attributed to the stretching of  $\text{C}=\text{O}$  of the five-member anhydride ring shows a doublet at  $1751$  and  $1719\text{ cm}^{-1}$  that is far lower than the usual value because of the reaction at nitrogen of poly(4-VP) and possible hydrolysis of some of the anhydride moiety to maleic acid.

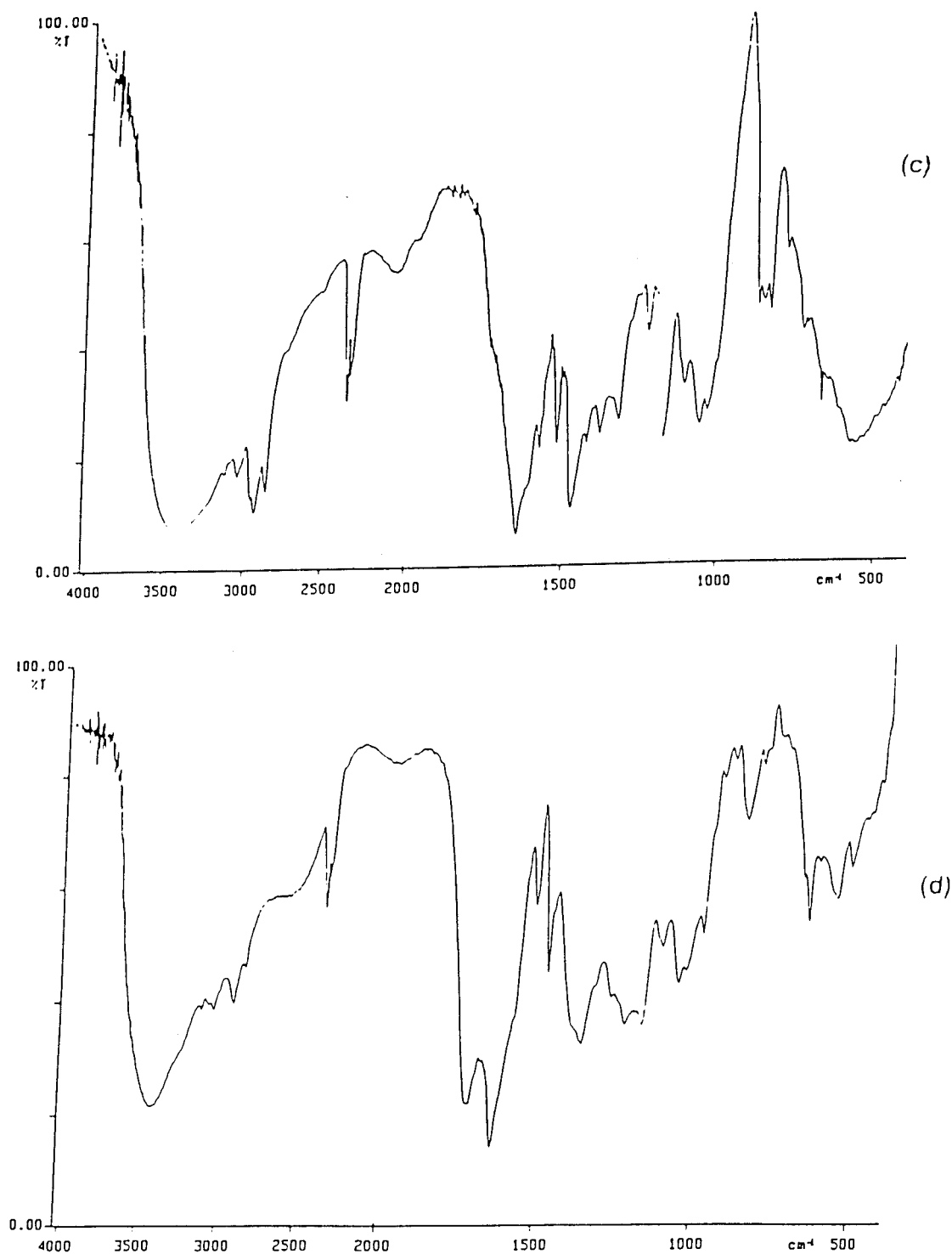
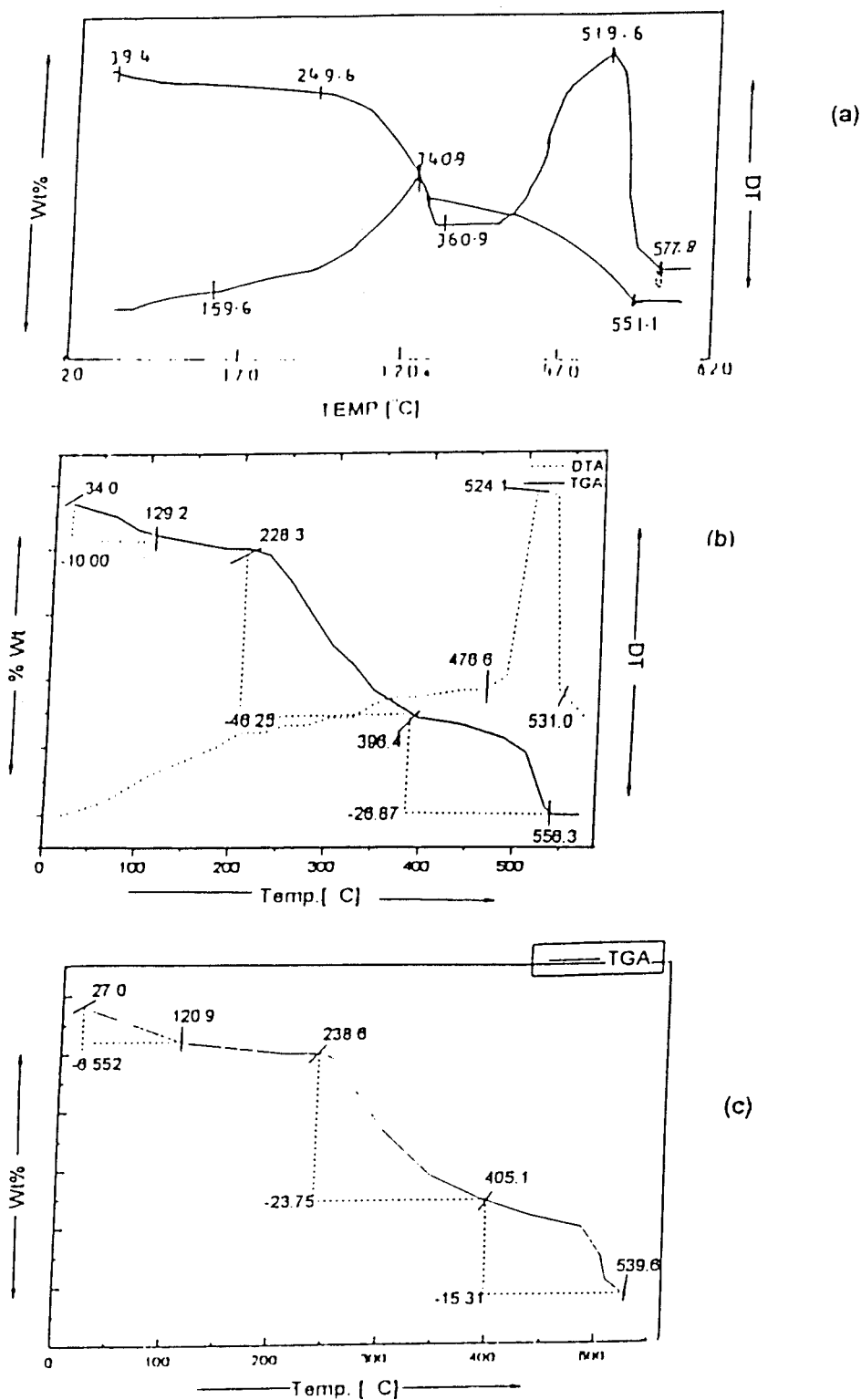


Figure 2 (Continued from the previous page)

#### Thermal analysis

Cellulose-*g*-poly(4-VP) degrades in two stages.<sup>9</sup> All three functionalized derivatives (*N*-benzyl chloride, *N*-butyl bromide, *N*-hexyl bromide) show two-stage decomposition with initial weight loss in the range 6.55–10.0% because of the presence of moisture. The real thermal decomposition stage starts with initial

decomposition temperature (IDT) in the range 228.3–232.8°C. The benzyl derivative degrades in two stages from 228.3–396.4 and 396.4–556.3°C (with respective weight loss of 46.25 and 26.87%); the butyl derivative degrades from 238.6–405.1 and 405.1–539.6°C (with respective weight loss of 23.75% and 15.31%); and the hexyl derivative degrades



**Figure 3** TGA and DTA curves of (a) cellulose-g-poly(4-VP); (b) cellulose-g-poly(4-vinyl-*N*-benzyl pyridinium chloride) (in air, heating rate = 20°C/min, wt of polymer a = 8.4 mg, weight of polymer b = 5.0 mg); (c) cellulose-g-poly(4-vinyl-*N*-butyl pyridinium bromide); (d) cellulose-g-poly(4-vinyl-*N*-hexyl pyridinium bromide) (in air, heating rate = 20°C/min, weight of polymers c and d = 5.0 mg); (e) cellulose-g-poly(*N*-maleate-4-vinyl pyridine) (in air, heating rate = 20°C/min, weight of polymer = 5.0 mg).

from 232.8–394.2 and 394.2–629.8°C with respective weight losses of 26.68 and 21.43% (Fig. 3). However, thermal degradation behavior is quite different in

the case of *N*-maleate derivative because after the initial 6.25% weight loss resulting from the presence of moisture, it shows multistage decomposition

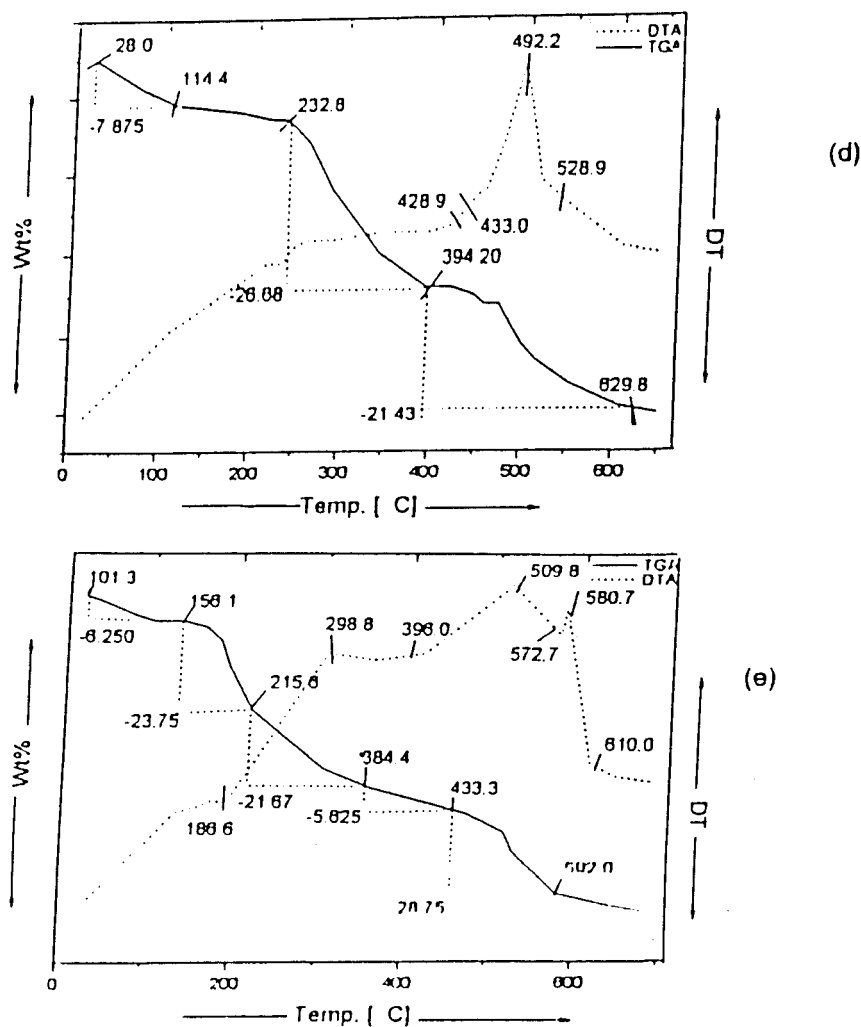


Figure 3 (Continued from the previous page)

with lowered IDT of 156.1°C and degrades in four stages at 156.1–215.6, 215.6–384.4, 384.4–433.3, and 433.3–592.0°C with respective weight losses of 23.75, 21.87, 5.63, and 28.75%. Thus, thermal stability of the three derivatives increases, whereas it decreases sharply in the case of maleate. Such behavior is explained as being attributed not only to the rather facile dehydration and decarboxylation of the maleic anhydride moieties but also to the internal reactions analogous to the Hoffman exhaustive degradation.

Compared to cellulose and cellulose-g-poly(4-VP), differential thermal analysis (DTA) curves of these polymers are different. This indicates that the energy-exchange processes in the degradation of these polymers are different and most of the processes are exothermic. On analogy of similarities in the thermograms of hexyl, benzyl, and butyl derivatives, DTA curves of these three derivatives show many similarities, whereas the DTA curve of the maleate derivative is different because more exothermic peaks indicate the multiplicity of the degradation processes.

### Physical properties of the functionalized copolymers

#### Solubility of functionalized copolymers

The benzyl derivative was found to be more soluble out of all the quaternized polymers (260 mg is soluble in 100 mL) of water and the maleate derivative shows minimum solubility (92 mg/100 mL) (Table III). Being totally insoluble, cellulose-g-poly(4-VP) is solubilized on quaternization as the quaternary nitrogen in the long chain of grafted polymer becomes hydrophilic as supported by the enhanced water uptake, implying enhanced water interactions. The high solubility of the benzyl derivative is attributed to the fact that yield of quaternization was very high leading to an increase in polar character of the pendent moieties of poly(4-VP) and also opening up of the cellulose chains by disruption of the intermolecular association. The trend in solubility was found to be benzyl > butyl > hexyl > maleate. The butyl as well as hexyl derivatives are less soluble in water because of the long hydrophobic alkyl chains and this also explains the least solubility

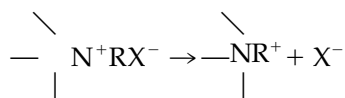
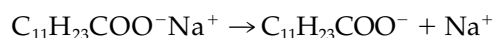


TABLE III  
Water Uptake, Surface Tension, Water Softening, and Emulsification Properties

Series	Polymer	Density	Solubility (g/100 mL)	Water uptake ( $P_u$ )	Surface tension (dyne/cm)	Emulsification value	Hardness of water (ppm)
1	Cell-g-poly(4-vinyl pyridine)	—	—	—	—	—	455.7
2	Cell-g-poly( <i>N</i> -benzyl-4-vinyl pyridinium chloride)	1.0219	0.260	628.0	62.87	0.3	0.0
3	Cell-g-poly( <i>N</i> -butyl-4-vinyl pyridinium bromide)	1.0221	0.190	538.0	—	1.3	0.0
4	Cell-g-poly( <i>N</i> -hexyl-4-vinyl pyridinium bromide)	1.0206	0.125	58.0	—	0.0	386.88
5	Cell-g-poly(4-vinyl pyridine- <i>N</i> -maleate)	1.0207	0.92	76.0	72.35	0.0	511.5

of the hexyl derivative among all three. On the other hand, the maleate derivative is found to be the least soluble because the counter ion in this case is not free as are the chloride and the bromide ions in the other three cases. The partial solubility of these polymers is attributed to the nonuniform quaternization, given that more quaternized cellulose chains dissolve in water, whereas others do not. This argument is further supported by the fact that the trend in solubility and degree of quaternization of the alkylated/benzylated copolymers are the same because the copolymer with higher degree of quaternization is also maximally soluble. It can also be attributed to the nonuniformity in grafting, especially differences in the grafting frequency in the crystalline and amorphous regions of cellulose that affect the quaternization efficiency.

The soluble fraction of these polymers in aqueous solutions is sufficient to show some soap properties because they give foam in the solution. They behave as invert soaps because compared to the sodium derivative of fatty acid, in this case the cation more than the anion is responsible for the soapy action (as shown).



It was also observed that the bromide and chloride derivatives become hydrolyzed as the resultant solu-

tion develops a dark green color as a result of the formation of charge transfer complexes.

#### Water uptake behavior

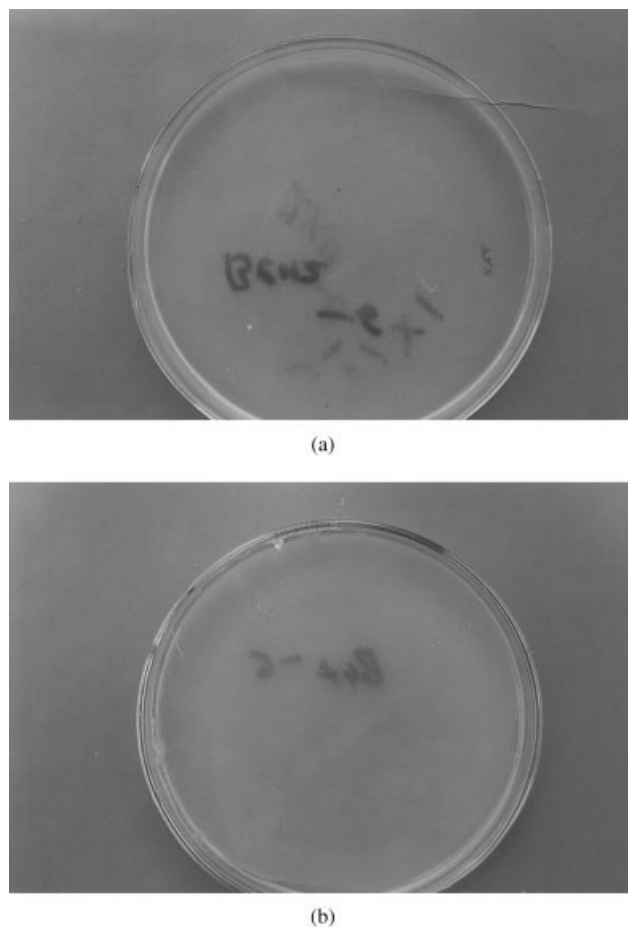
There is an increase in the water-retention property of the functionalized graft copolymer, compared to that of cellulose-g-poly(4-VP), resulting from the generation of charged groups on poly(4-VP) moieties. The benzyl and butyl derivatives show 628 and 538% water uptake, respectively (Table III). These high values are attributed to the solubilization of the cationic end of the polymer in aqueous media resulting in the easy approach of water moieties to the inner region of cellulose backbone. Higher water uptake by benzyl derivative is the result of higher quaternization efficiency. On the other hand, hexyl and maleate derivatives show a low water retention property because observed  $P_u$  values (58 and 76%, respectively) are even lower than that observed for the graft copolymer. These results are self-explanatory, given that incorporation of nonpolar pendant chains of hydrophobic nature and the formation of a closed ring complex by maleic acid blocks the entry of the water moieties.

#### Surface tension, emulsification, and water-softening properties

Surface tension of water was reduced by 10 dyn/cm by the benzyl derivative but not by the others to any significant extent and it seems that the interaction of this derivative with water is maximum, as discussed in the preceding section. Emulsification values shown

TABLE IV  
Enzymatic and Alkaline Hydrolysis of Functionalized Polymers

Series	Polymer	Enzymatic hydrolysis	Alkaline hydrolysis		
			$F_1$	$F_2$	$F_3$
1	Cellulose	—	0.609	0.285	0.0
2	Cell-g-poly(4-VP)	—	0.515	0.038	0.0
3	Cell-g-poly( <i>N</i> -benzyl-4-vinyl pyridinium chloride)	—	0.38	0.358	0.078
4	Cell-g-poly( <i>N</i> -butyl-4-vinyl pyridinium bromide)	—	0.614	0.0	0.38
5	Cell-g-poly( <i>N</i> -hexyl-4-vinyl pyridinium bromide)	—	0.597	0.12	0.0
6	Cell-g-poly(4-VP)- <i>N</i> -maleate	—	0.491	0.36	0.0



**Figure 4** High-resolution photographs of bacteria post-treated with fictionalized graft copolymers: (a) benzyl derivative; (b) butyl derivative. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

by different polymers are not significant (Table III). The solubility determines the emulsification behavior because lesser solvent interaction does not significantly increase volume on mixing. Softening of water is also attributed to the quaternary ammonium character of the polymers, as is the case with ion exchangers or synthetic resins. These properties can be useful in textile industries and wastewater purification tech-

nologies. The metal ion uptake property of the developed material has been used to reduce the  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  ions concentration (water hardening ions) from tap water and the results are positive except for the native cellulose and maleated polymer, which occurs because in the native cellulose  $\text{Ca}^{+2}$  ions get entrapped within the cellulose matrix in the bleaching process. No hardness was observed in water treated with the benzyl and butyl derivatives. The same trends were observed in the emulsification properties of these polymers.

#### Stability of quaternized copolymers to alkaline and enzymatic hydrolysis

The bromide and chloride derivatives on alkaline hydrolysis impart a dark green color to the solution. The development of color is attributed to formation of the charge transfer complex between the nitrogen bearing positive and oxygen of the hydroxyl ion. The hexyl and the butyl derivatives show the same coloration on stirring in distilled water for 24 h, although if the stirred solution is left undisturbed then it loses the color. This can be explained on the basis that the unstable charge transfer complex is formed on stirring and because of the complex (because water will not be able to hydrolyze the sample as the alkali do) it loses the color (Table IV).

It has been observed that despite exposure to the enzymatic environment no biodegradation occurred as observed from the gravimetric results of the polymers and nondetection of sugar after subjecting to hydrolysis for 4 weeks. Cellulose degrades slowly on exposure to hostile conditions including microbial attack. However, in the present case even cellulose does not degrade and such stability can be attributed to the extraction process of the cellulose from pine needles. In graft and functionalized copolymers such stability to biodegradation can be attributed to the antibacterial action of the pyridine, quaternary pyridinium ions, halides, and—more important—the nonaccessibility of enzyme molecules to the 1,4-linkage of the anhydroglucose units of cellulose resulting from the hindrance presented by the graft chains of the comb-shape graft copolymers (Table IV).

**TABLE V**  
Sorption of  $\text{Cu}^{+2}$  and  $\text{Fe}^{+2}$  Ions on Cell-g-Poly(4-VP)<sup>a</sup>

Series	Polymer	$P_g$	$P_u$	
			$\text{Cu}^{+2}$	$\text{Fe}^{+2}$
1	Cell-g-poly(4-VP)	113.0	67.50	100.00
2	Cell-g-(N-benzyl pyridinium chloride)	—	56.50	98.60
3	Cell-g-(N-butyl pyridinium bromide)	—	46.24	97.50
4	Cell-g-(N-hexyl pyridinium bromide)	—	83.79	99.80
5	Cell-g-(N-pyridinium maleate)	—	76.20	45.70

<sup>a</sup> Feed = 10.0 mg/L.

### Antibacterial action

In the present study it has been observed that the extracted cellulose and its graft and functionalized copolymers are very stable to enzymatic degradation, given that no reducing sugar has been observed in the present case after enzymatic hydrolysis. On the contrary, the quaternized polymers are strongly antibacterial and thus block the enzyme activity. Interaction of the bactericidal agent with the cell wall of the microorganisms interferes with the metabolic process of the microorganism and this causes bactericidal or microbial-inhibiting action. These polymers have the advantage over the phenolics or chlorine bactericides because they are nonirritating and odor free, and because of their long activity and nature of the fixed active groups on the polymer chains. Although a variety of mechanisms have been proposed for the bactericidal activity of the quaternary ammonium type compounds, it is mainly attributed to their ability to release cell content into the surrounding medium. The antibacterial action is a consequence of the inhibition of certain bacterial enzymes, especially those involved in respiration and glycolysis. It was observed that when the municipal water supply was treated with these polymers, they showed very strong antibacterial activity, which was observed only very slightly in the case of native cellulose and graft copolymers. In the quaternized cellulose the order of activity is given as: benzyl > butyl > hexyl > maleate. High-resolution photographs of the treated water depicting resultant bacterial colonies in treated water are given in Figure 4.

### Metal ion sorption studies

Cellulose itself is a good metal binder but modified cellulose by grafting with poly(4-VP) enhances the metal-binding property of cellulose. It is evident from Table V that in the case of  $\text{Cu}^{+2}$  ions, cellulose-g-poly(4-VP) sorbs 67.5% from a feed of 10.0 mg/L and it varies with the nature of functionalized polymers. Sorption of  $\text{Fe}^{+2}$  ions is 100% in the graft copolymer; however, the extent of sorption is significantly af-

ected in quaternized polymers that show decreased sorption capacity, probably because of the anion exchange at the quaternary nitrogen. Such an exchange is not possible in nonquaternized polymers. The explanation for the observed results is obvious: quaternization of nitrogen atom in the pyridine nucleus reduces the retention capacity of polymeric material attributed to the consumption of the lone pair of electrons on **N:** and charge separation on pyridine moieties. These results also explain that sorption of metal ions has nothing in common with the ion-exchange process. However, in the case of  $\text{Fe}^{+2}$  even the quaternized polymers are as good sorbents as nonfunctionalized graft copolymers. This may be explained as selective binding of  $\text{Cu}^{+2}$  with **N:** compared to  $\text{Fe}^{+2}$  ions, and better sorption of  $\text{Fe}^{+2}$  may be explained as a function of efficient partitioning of the later ions between polymer and the solution phase compared to the  $\text{Cu}^{+2}$  ions. However, cellulose-g-poly(*N*-maleate-4-vinyl pyridinium) sorbs almost half the amount of  $\text{Fe}^{+2}$  less than other quaternized polymers and this pronounced effect may be attributed to the hindered approach of metal ions to the active site and bulk of the polymer as also suggested by the water interaction/uptake of this salt.

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