Synthesis and Characterization of Cellulose Ion Exchangers. I. Polymerization of Glycidyl Methacrylate, Dimethylaminoethyl Methacrylate, and Acrylic Acid with Cotton Cellulose Using Thiocarbonate–H_2O_2 Redox System

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ABSTRACT: Polymerization of glycidyl methacrylate (GMA), dimethylaminoethyl methacrylate (DMAEMA) and acrylic acid (AA) with cotton fabric using a cellulose thiocarbonate–hydrogen peroxide redox system as an initiator was investigated under different conditions. This includes the nature and concentration of the initiator and monomer, polymerization time and temperature, and liquor ratio. The percent of polymer add-on is generally favored by increasing monomer and H_2O_2 concentration, as well as duration and temperature of the polymerization, but with the certainty that the percent of polymer add-on follows the following order: GMA > DMAEMA > AA. On the other hand, the percent of polymer add-on increases by decreasing the liquor ratio. Incorporation of Fe^{2+} or Cu^{2+} ion in the polymerization system enhances the percent of polymer add-on significantly. Replacing the H_2O_2 by other oxidants such as Cr^{6+} or Mn^{4+} is made, and the capability of such cations to expedite polymerization of the said monomers with cotton cellulose is studied. Also studied is the synthesis of cation exchanger via reaction of poly(GMA)–cellulose copolymer with hexamethylene tetramine. Furthermore, the ion exchange characteristics of the cellulosic copolymers obtained with this as well as with other monomers are reported. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66**: 1029–1037, 1997

INTRODUCTION

Vinyl graft copolymerization onto cellulose and modified celluloses has been the subject of several publications.[1–18] Recently, we have reported on the grafting of different vinyl monomers onto cotton fabric using cellulose thiocarbonate and different oxidants.[19–20] Previous reports have also dealt with graft polymerization of vinyl monomers onto cellulose using different initiators, such as the ions of vanadate (V^{5+}),[21] manganese (Mn^{4+}),[22] or chromium (Cr^{6+}),[23] or the redox system of Fe^{2+}-hydrogen peroxide.[24]

This work aims at preparing ion-exchange cotton fabrics containing amino and carboxylic groups via polymerization of glycidyl methacrylate (GMA), dimethylaminoethyl methacrylate (DMAEMA), and acrylic acid (AA) with cotton fabric using cellulose thiocarbonate along with different oxidants, namely Cr^{6+}, V^{5+}, Mn^{4+}, and Cu^{2+} ion, as well as a ferrous–hydrogen peroxide redox system. Major factors affecting the polymerization reactions are examined. The work is further extended to include characterization of the prepared ion exchangers.

EXPERIMENTAL

Materials

Cotton fabric (400 g m²; 21 picks × 61 ends/cm) kindly supplied by Misr Spinning and Weaving

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Co., Mehalla El-Kubra, was used after purification by scouring for 2 h at the boil using aqueous solution containing 1% sodium hydroxide. It was then thoroughly washed and air-dried at room temperature.

GMA, DMAEMA, and AA were of laboratory grade chemicals. Carbon disulphide, sodium hydroxide, ferrous sulphate, ammonium vanadate, potassium permanganate, potassium dichromate, copper sulphate, and ethylene diamine were also of laboratory grade chemicals.

Thiocarbonation of Cotton Fabric

The cotton fabric was placed in a 500 mL stoppered glass vessel containing the thiocarbonation solution (1% NaOH w/v; 1% CS_2 v/v) and suitable wetting agent to increase the efficiency of the thiocarbonation reaction. The material to liquor ratio was 1 : 25, and the temperature of this solution was kept at 30°C. The contents of the vessel were continuously shaken throughout the thiocarbonation reaction. After 2 h, the solution was drained, and the fabric was thoroughly washed with cold distilled water until the washing liquor acquired pH 7. The cotton fabric in this form will be referred to as cellulose thiocarbonate.

Grafting Procedure[6,7,9]

Unless otherwise indicated, the thiocarbonated cotton fabric sample was pretreated by immersing in 0.1% ferrous sulphate solution in a bottle kept at room temperature for 30 min with continuous shaking to avoid the heterogenity deposition all over the sample surface. After impregnation, the sample was washed repeatedly with distilled water and squeezed between two filter papers before introducing it into the polymerization solution.

The sample was placed in a glass vessel containing the polymerization solution consisting of specific concentration of both H_2O_2 (initiator) and the monomer at pH 2. The material to liquor ratio was 1 : 25. The glass vessel was kept in a thermostate water bath at a definite temperature and time. The sample was under continuous shaking during the polymerization reaction. At this end, the so-treated sample was quickly removed from the polymerization solution, thoroughly washed with distilled water, and repeatedly extracted with a proper solvent, depending upon the nature of the homopolymer to be removed.

It must be noted that when ammonium metavanadate, potassium permanganate, or potas-

sium dichromate were used as initiators, H_2O_2 was omitted from the polymerization medium.

Aminization[25,26]

The poly(GMA)–cellulose copolymer was reacted with aqueous solution of ethylene diamine in a 150 mL stoppered glass bottle. The reaction was carried out at 80°C for 1 h. The sample was then thoroughly washed with water and dried at 50°C, then further dried over P_2O_5 for 24 h before analysis.

Analysis and Test Methods

The percent of polymer add-on was calculated as follows:

$$\text{polymer add-on \%} = \frac{W_2 - W_1}{W_1} \times 100,$$

where W_1 is the dry weight of original sample, and W_2 is the dry weight of grafted sample.
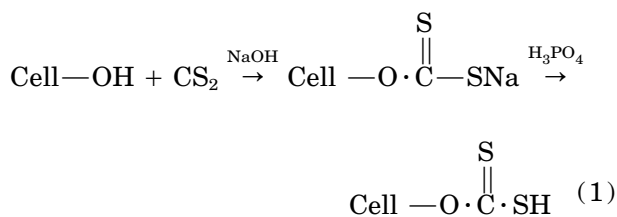
The extent of grafting with DMAEMA and the extent of the aminization of fabrics grafted with GMA was monitored through the nitrogen content (N%) using the Keljdahl method.[27]

For estimation of free epoxy rings in poly(GMA) containing cotton, a procedure was adopted which, in essence, is based on methods described elsewhere.[28,29] The carboxyl content was determined as per the alkalimetric method as described in Daul et al.[30] The total ion-exchange capacity was determined by a method reported by Kunin.[31]
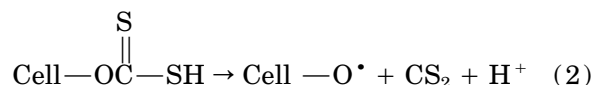
RESULTS AND DISCUSSION

Tentative Mechanism

Cellulose reacts with carbon disulphide to yield cellulose thiocarbonate as shown by the mechanism suggested by eq. (1), as follows:

$$\text{Cell—OH} + CS_2 \xrightarrow{\text{NaOH}} \text{Cell} - O \cdot \overset{\overset{\displaystyle S}{\|}}{C} - SNa \xrightarrow{H_3PO_4}$$

$$\text{Cell} - O \cdot \overset{\overset{\displaystyle S}{\|}}{C} \cdot SH \quad (1)$$
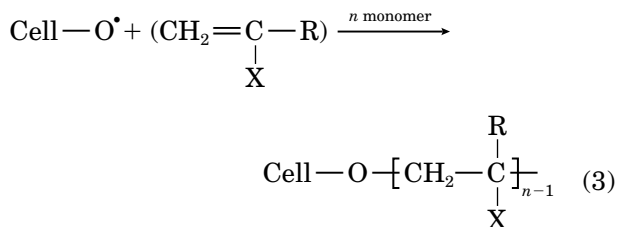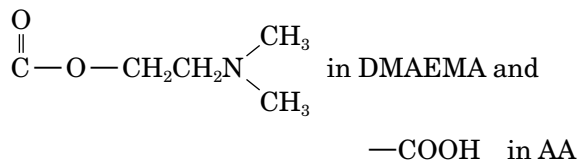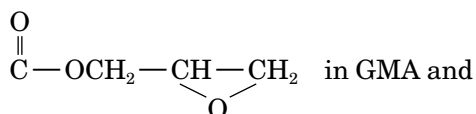
Disintegration of the thiocarbonate groups and/

or its involvement in a redox reaction with an oxidant lead ultimately to cellulose macroradical, as shown in eq. (2), as follows:

$$\underset{\text{Cell}-\text{OC}-\text{SH}}{\overset{\overset{\text{S}}{\|}}{}} \rightarrow \text{Cell}-\text{O}^{\bullet} + \text{CS}_2 + \text{H}^+ \quad (2)$$

In the presence of a vinyl monomer, the cellulose macroradical may induce graft polymerization of the vinyl monomer on the cellulose backbone, as represented by eq. (3):

$$\text{Cell}-\text{O}^{\bullet} + (\text{CH}_2{=}\underset{\underset{\text{X}}{|}}{\text{C}}-\text{R}) \xrightarrow{n \text{ monomer}}$$

$$\text{Cell}-\text{O}\left[\text{CH}_2-\underset{\underset{\text{X}}{|}}{\overset{\overset{\text{R}}{|}}{\text{C}}}\right]_{n-1} \quad (3)$$

where X is CH_3 in GMA, and DMAEMA and H in AA; and R is

$$\underset{\text{C}-\text{OCH}_2-\text{CH}-\text{CH}_2}{\overset{\overset{\text{O}}{\|}}{}} \quad \text{in GMA and}$$
$$\qquad\qquad\qquad \underset{\text{O}}{\diagdown\diagup}$$

$$\underset{\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{N}}{\overset{\overset{\text{O}}{\|}}{}}\overset{\diagup\text{CH}_3}{\underset{\diagdown\text{CH}_3}{}} \quad \text{in DMAEMA and}$$

$$-\text{COOH} \quad \text{in AA}$$

With the above mechanism in mind, major factors affecting polymerization of GMA, DMAEMA, and AA with cotton cellulose using a cellulose thiocarbonate–H_2O_2 redox system are studied. Results obtained, along with the appropriate discussion, are given below.

Polymerization Temperature

Figure 1 shows the effect of temperature on the percent polymer add-on obtained upon polymerization of GMA, DMAEMA, and AA with cotton cellulose. Obviously, the trend representing the temperature–percent polymer add-on relationship is governed by the nature of the monomer. While the percent of polymer add-on increases marginally by raising the temperature from 40 to 70°C in the case of DMAEMA, it only commences at temperatures above 50°C in the case of AA.
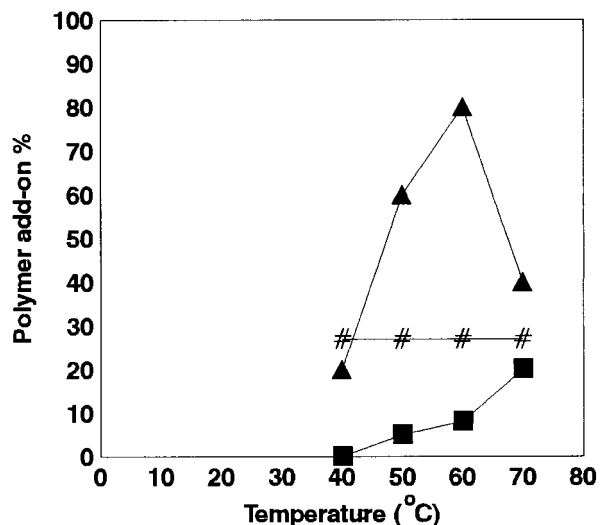

Figure 1 Variation of the polymer add-on with polymerization temperature (monomer, 200%; H_2O_2, 0.1%; material-to-liquor ratio, 1 : 25; pH, 2; time, 2 h): (▲) GMA; (#) DMAEMA; (■) AA.

With GMA, on the other hand, the percent of polymer add-on exhibits a maximum at 60°C; below or above this particular temperature, the percent of polymer add-ons are much lower.

That the temperature acts in favor of polymerization is rather logical and is in accordance with previous reports,[6] which ascribed this to the following:

1. speedy disintegration of the thiocarbonate groups;
2. greater activation energy;
3. enhanced oxidant efficiency;
4. enhancement of the solubility of the monomer and its diffusion from the solution phase to the fibre phase; and
5. a higher rate of initiation and propagation of the graft.

On the other hand, the adverse effect of temperature on the percent polymer add-on at higher temperature (i.e., 70°C) in the case of GMA could be interpreted in terms of faster termination rates of growing poly(GMA) chain radicals. Faster rate of termination leads to poly(GMA) of lower molecular weight and, therefore, of a lower percent of polymer add-on. However, the role of raising the temperature in enhancing homopolymer formation rather than grafting cannot be ruled out.

Duration of Polymerization

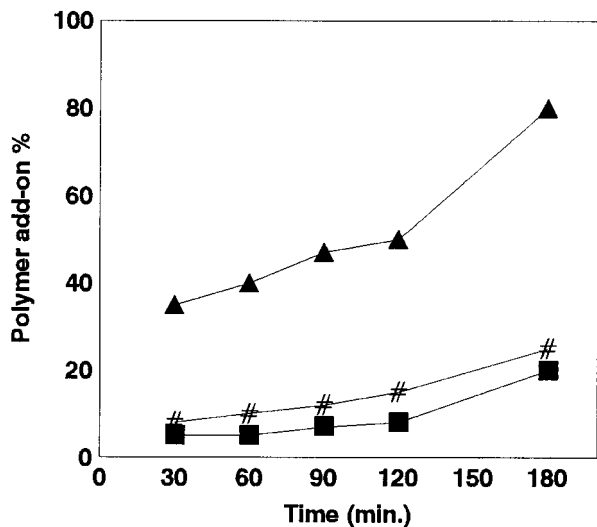Figure 2 shows the effect of duration of polymerization on the percent of polymer add-on for GMA,

Figure 2 Variation of the polymer add-on with time (monomer, 200%; H_2O_2, 0.1%; material-to-liquor ratio, 1 : 25; pH, 2): (▲) GMA; (#) DMAEMA; (■) AA.

DMAEMA, and AA. As is evident, the percent of polymer add-on increases by increasing the duration of polymerization within the range studied though the increment is more significant upon prolonging the duration from 120 to 180 min. This is observed irrespective of the nature of monomer used but with the certainty that GMA exhibits the highest percentage of polymer add-on, whereas AA exhibits the least.

The favorable effect of duration on the percent of polymer add-on is rather expected. Time is a
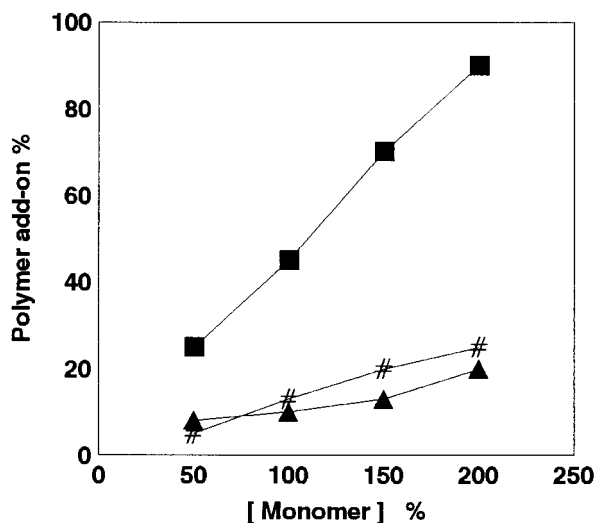
Figure 3 Variation of the polymer add-on with monomer concentration (material-to-liquor ratio, 1 : 25; pH, 2; time, 3 h; H_2O_4, 0.1%): (▲) GMA; (#) DMAEMA; (■) AA.
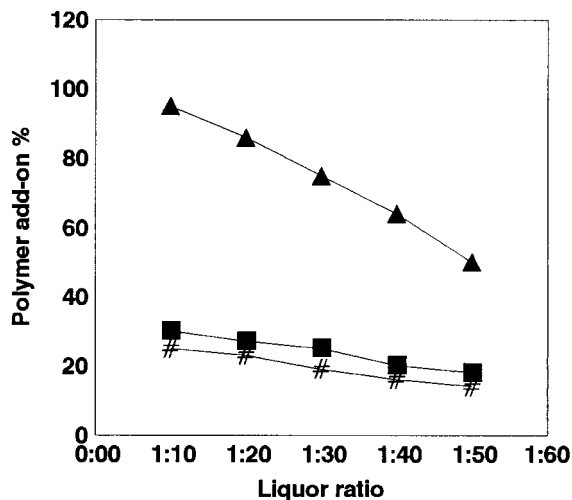

Figure 4 Variation of the polymer add-on with the liquor ratio (monomer, 200%; H_2O_2, 0.1%; pH, 2; time, 3 h): (▲) GMA; (#) DMAEMA; (■) AA.

must (1) for cellulose to undergo swelling, (2) for solubility of the monomer and its diffusion from the aqueous phase to the fiber phase, (3) for reaction of the redox initiator and subsequent decomposition to give rise to free radical species, (4) for contact and adsorption of the ingredients of polymerization system, and (5) for conversion of monomer to polymer grafted and/or homopolymerized with intimate association with cellulose via initiation and propagation steps.

Monomer Concentration

Figure 3 shows the effect of monomer concentration on the percent of polymer add-on when GMA,
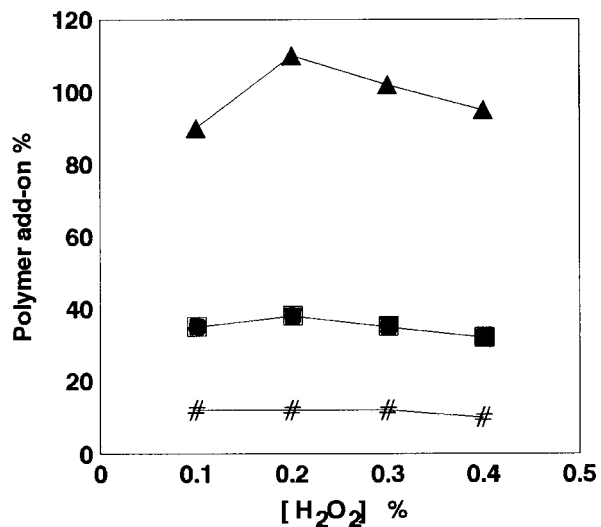

Figure 5 Variation of the polymer add-on with H_2O_2 concentration (monomer, 200%; pH, 2; time, 3 h): (▲) GMA; (#) DMAEMA; (■) AA.

DMAEMA, and AA were independently polymerized with the cotton fabric. It is seen that the percent of polymer add-on increases significantly as the monomer concentration increases within the range studied regardless of the monomer used. Here too, GMA is far superior to DMAEMA and AA for reasons to be cited later.

The significant increment in the percent of polymer add-on by increasing monomer concentration could be attributed to the greater availability of monomer molecules in the vicinity of the cellulose at a higher monomer concentration. It is well known that the cellulose monoradicals are immobile and their addition reaction to the double bond of the monomer molecules depends solely on availability of these molecules in the proximity of the cellulose macroradicals. In combination with this is the gel effect.[32] The later occurs when the polymer is soluble in its own monomer. This create a viscous environment which impedes termination, thereby increasing the molecular weight of the formed polymer and, therefore, the percent of polymer add-on.

Liquor Ratio

Figure 4 depicts the dependence of the percent of polymer add-on on the liquor ratio of the polymerization system. Evidently, the percent of polymer add-on decreases as the liquor ratio increases. This is rather a direct consequence of dilution of and lower molecular collision among the polymerization ingredients (reactants).

H_2O_2 Concentration

Figure 5 shows the percent of polymer add-on as a function of H_2O_2 concentration when GMA,
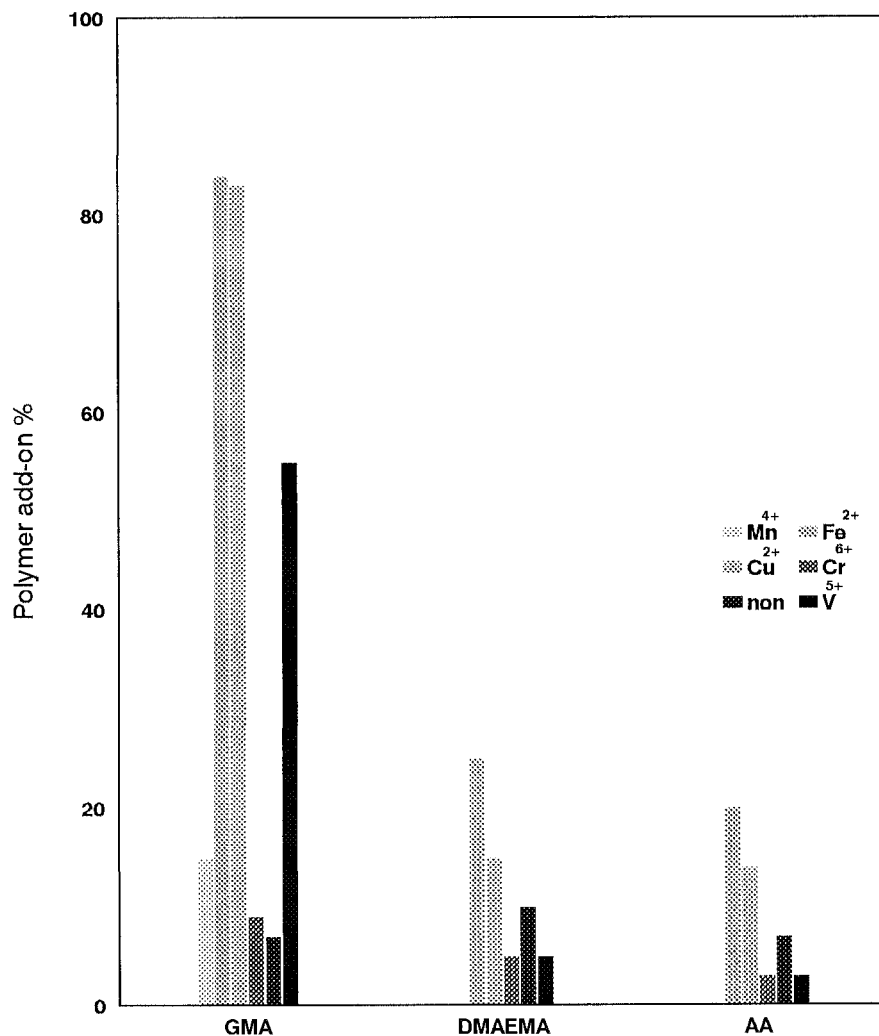

Figure 6 Polymer add-on as a function of the initiator (monomer, 200%; H_2O_2, 0.1% in using Fe^{2+} & Cu^{2+} as initiators; material-to-liquor ratio, 1 : 25; pH, 2; time, 3 h).

Table I   Effect of the Epoxy Content of the Copolymer on the Ion Exchange Capacity of Aminized Poly(GMA)–Cotton Copolymer

Epoxy Content (meq 100 g sample)	Nitrogen Content (N%)	Ion Exchange Capacity (meq 100 g sample)
61	0.8	61
81	0.9	64
93	1.2	90
126	1.6	114

Aminization with ethylene diamine.

DMAEMA, and AA were independently polymerized with cotton cellulose. The results reveal that the percent of polymer add-on increases slightly by increasing H_2O_2 concentration, reaches maximum at 0.2%, then decreases thereafter. This is observed, irrespective of the monomer used, but with the existence of the order GMA > DMAEMA > AA, as noticed before.

Enhancement in the percent of polymer add-on, though little, by increasing H_2O_2 concentration up to a certain concentration suggests that the most appropriate amount of free radical species for vinyl polymerization to the cotton cellulose occurs at this particular H_2O_2 concentration. Above the latter, there will be abundance of free radicals, which contributes largely in the termination of growing chains and/or by self-coupling; thus, the percent polymer of add-on decreases.
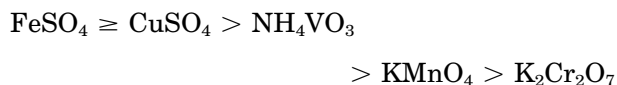
Nature of the Monomer

In the foregoing sections (see Figs. 1–5), it has been shown that, regardless of all factors governing the polymerization reaction, the percent of polymer add-on follows the following order: GMA > DMAEMA > AA. This order could be associated with differences among these monomers with respect to[33] (1) molecular size and solubility of the monomer, (2) diffusion of the monomer molecule and/or its radical from the aqueous phase to the fiber phase, (3) relative tendency to activation, (4) the ability of the monomer molecule to initiate a chain on the cellulose, and (5) ability of the monomer to convert to grafting face-to-face with homopolymerization.

Nature of Coinitiator Cations

Previous reports[34–35] have disclosed that the presence of cations, such as Cu^{2+} and Fe^{2+} ions, during free radical graft polymerization of vinyl monomers onto cellulose enhances grafting significantly. It appears, therefore, of interest to establish the influence of different cations on the polymerization systems under investigation.

Figure 6 shows the dependence of the percent of polymer add-on on the nature of the cations incorporated in the polymerization system to act as a coinitiators. Obviously, the percent of polymer add-on is higher in the presence of rather than in the absence of, the cations. Furthermore, the percent of polymer add-on follows the following order:

$$FeSO_4 \geqq CuSO_4 > NH_4VO_3$$
$$> KMnO_4 > K_2Cr_2O_7$$

This order is valid, irrespective of the nature of the monomer used.

Table II   Dependence of the Ion Exchange Capacity of Poly(DMAEMA)–Cotton Copolymer on Its Nitrogen Content

Polymer Add-on (%)	Nitrogen Content (N%)	Ion Exchange Capacity (mmol 100 g sample)
10.2	0.78	55
13.0	0.90	64
20.0	1.30	91
24.0	1.53	108

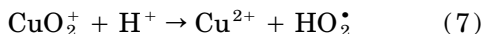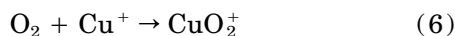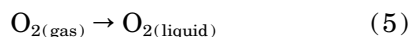**Table III   Dependence of the Ion Exchange Capacity of Poly(AA) Cotton Copolymer on its Polymer Add-on**

Polymer Add-on (%)	Ion Exchange Capacity (meq 100 g sample)
5	66
15	185
20	230
36	365
50	460

The outstanding enhancement in the percent of polymer add-on in the presence of rather than in the absence of Fe^{2+} ion could be associated with creation of $HO^{\bullet}$ free radical species according to the reaction suggested by eq. (4), as follows:

$$H_2O_2 + Fe^{2+} \rightarrow HO^- + HO^{\bullet} + Fe^{3+} \quad (4)$$
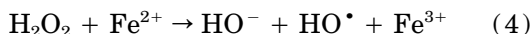
Reaction of the $HO^{\bullet}$ radical with cellulose gives rise to cellulose macroradical, which is capable of initiating grafting.[36]

On the other hand, the outstanding increase in the percent of polymer add-on by the presence of Cu^{2+} ions could be ascribed to a variety of reasons. First, Cu^{2+} ion accelerates the decomposition of H_2O_2. Decomposition of peroxides by metallic ions is well established.[37,38] Second, cellulose thiocarbonate and/or the vinyl monomer form, perhaps, a redox system. As a result, Cu^{2+} is converted to Cu^+ ion. Third, the cuprous ion so obtained would be oxidized back to the cupric state by atmospheric oxygen and/or by H_2O_2; this conversion must presumably entail radical intermediate, as suggested by eqs. (5)–(7).[39]

$$O_{2(gas)} \rightarrow O_{2(liquid)} \quad (5)$$

$$O_2 + Cu^+ \rightarrow CuO_2^+ \quad (6)$$

$$CuO_2^+ + H^+ \rightarrow Cu^{2+} + HO_2^{\bullet} \quad (7)$$

The $HO_2^{\bullet}$ radical may be involved presumably in the initiation of graft polymerization or can undergo a reaction leading to the formation of hydrogen peroxide as well as a hydroxyl radical. As already indicated, the formation of the $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals by the decomposition of hydrogen peroxide under the influence of metallic ion has been reported.[37,38]

Figure 6 shows that when Cr^{6+} ion was used as an initiator for polymerization of GMA, DMAEMA, or AA with cotton cellulose, a noticeable add-on could only be achieved with GMA.

Moreover, the magnitude of the add-on is much lower than its mates observed with Fe^{2+}—H_2O_2 or Cu^{2+}—H_2O_2 initiation system. This could be interpreted in terms of differences in the ability of the initiation system to create free radical species capable of initiating polymerization.

It is understandable that the use of Cr^{6+} as an initiator for vinyl graft polymerization onto cellulose is based on the ability of its δ-outer atomic orbitals to accomodate transferring electrons from the substrate to form substrate radicals and chromium ion with a lower valency state.[40] The most probable mechanism for generation of cellulose macroradicals may be written, as shown in reactions suggested by the following.
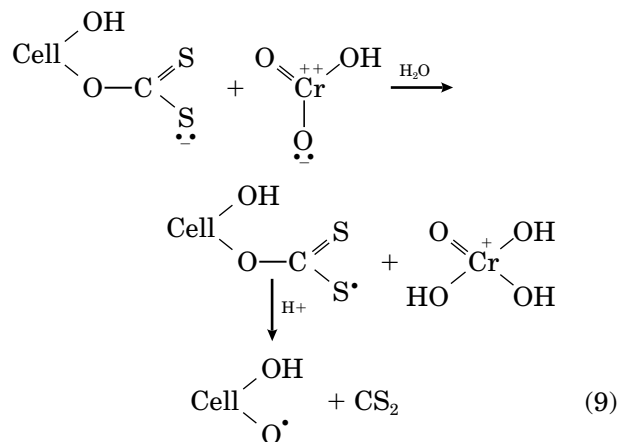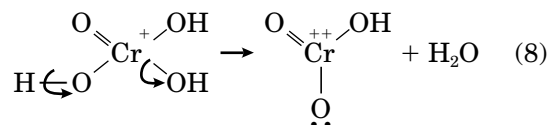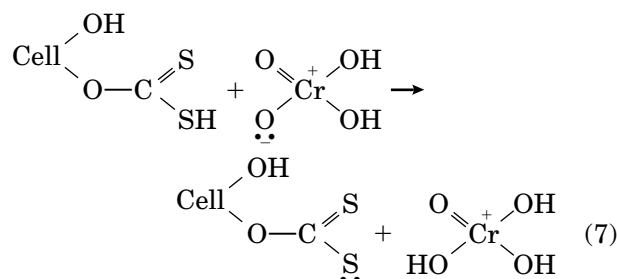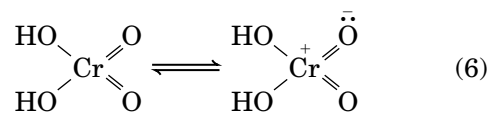

Figure 6 shows the percent of polymer add-on when initiation of polymerization was induced by the cellulose thiocarbonate–V^{5+} ion redox system. Obviously, significant formation of the poly-

mer add-on occurs only when GMA is used as the monomer. On the contrary, the other two monomers, namely DMAEMA and AA, display very low magnitudes of polymer add-on.

The use of ammonium metavanadate in vinyl graft polymerization is based on the formation of the active species $V(OH)_3^{2+}$ ions, which attack the cellulose backbone, creating free radicals capable of initiating the polymerization.[31] The most probable mechanism for generation of cellulose macroradicals may be written as shown in the reactions suggested by eqs. (10)–(12).
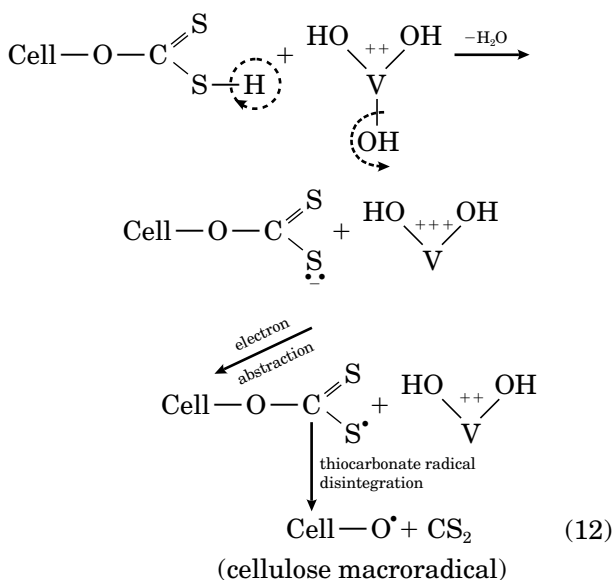
$$NH_4VO_3 + 3H^+ \rightarrow NH_4^+ + VO_2^+ + 3H_3O^+ \quad (10)$$

$$VO_2^+ + H_3O^+ \rightarrow V(OH)_3^{2+} \quad (11)$$
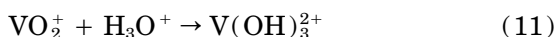

$$(12)$$
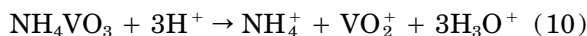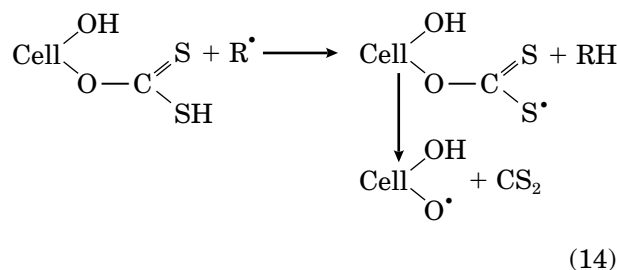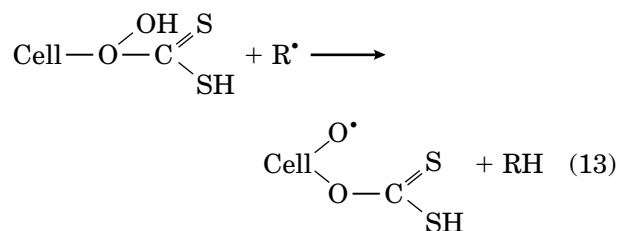(cellulose macroradical)

Figure 6 shows the percent of of polymer add-on obtained with the three monomers under investigation when the cellulose thiocarbonate–Mn^{4+} redox system was used to expedite polymerization. It is seen that substantial polymer add-ons are attained with this initiation system regardless of the monomer used, in accordance with previous reports.[41] The latter disclose that in presence of an acid, formation of primary radical species occurs, as a result of the action of the acid on the deposited MnO_2.

$$Mn^{+4} + H_2SO_4 \rightarrow SO_4^{\bullet} + Mn^{+3} + 2H^+$$

Once the free radical species are created, they produce cellulose macroradicals via direct abstraction of hydrogen atom from the hydroxyl groups of the cellulose molecules or through disintegra-

tion of cellulose thiocarbonate, or both, as shown in the following:

$$(13)$$

$$(14)$$

Cellulose macroradicals may also be formed upon direct attack of Mn^{4+} or Mn^{3+} ions on the cellulose molecule, via abstraction of hydrogen atoms.

Based on the foregoing, it is probably correct to conclude that differences in the ability of the add-ons observed upon using the different initiation systems are a manifestation of their mechanisms of producing cellulose macroradicals capable of initiating graft polymerization. This, in turn, is governed by the mode and routes involved in the reaction of the oxidant with the cellulose as outlined above, as well as the response of the monomer for the cellulose macroradical.

Characterization of the Prepared Ion Exchangers

Aminization of poly(GMA) cellulose graft copolymers was affected via reaction with ethylene diamine. The extent of aminization is expressed as %N, and the results obtained are set out in Table I. It is seen (Table I) that the extent of aminization is directly related to the epoxy content of the copolymer. It is also seen that the ion exchange capacity is directly related to the extent of aminization.

Tables II and III show that the ion exchange capacity values for exchangers based on poly(DMAEMA) and poly(AA) cotton copolymers, respectively. Here too, the capacity of the ion exchanger is directly related to the polymer add-on; the capacity increases by increasing the polymer

add-on percent irrespective of the nature of the polymer.

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