Graft Copolymerization of Vinyl Monomers on Modified Cottons. XVIII. Grafting of Methyl Methacrylate and Acrylonitrile on Cotton Treated with N-Methylol Crosslinking Agents using Tetravalent Cerium as Initiator

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Synopsis

Ce^{IV}-induced grafting of methyl methacrylate and acrylonitrile on cotton fibers crosslinked with dimethylol ethylene urea, dimethylol dihydroxyethylene urea, and dimethylol carbamate was investigated. The graft yields obtained with crosslinked cotton were signifcantly lower than the untreated cotton, irrespective of the crosslinking agent and the monomer used. However, the extent and rate of grafting depended upon the degree of crosslinking and the nature of monomer. Based on the magnitude of grafting and Ce^{IV} consumption during grafting and oxidation of the untreated and crosslinked cottons, the different reactions occurring during grafting of vinyl monomers on these modified cottons were elucidated.

INTRODUCTION

Various vinyl monomers such as acrylonitrile, acrylamide, and certain esters of acrylic and methacrylic acids have been successfully grafted on cellulosic materials using the ceric ion type, Ce(IV), catalyst.[1-8] Studies on the oxidation of alcohols, such as poly(vinyl alcohol)[9] and Pinacol,[10] and of the model compounds such as 1,2-cyclohexane-diol[6] with Ce(IV) as well as ESR studies[8] on Ce(IV)-oxidized cellulose revealed that oxidation occurred mainly at the secondary hydroxyl groups of the anhydroglucose unit with cleavage of the C_2—C_3 bond. In addition to the glycol bond cleavage, oxidation of cellulose with Ce(IV) involved the hemiacetal group in the cellulose chain.[3,11,12] The ceric ion method has been also used for vinyl graft copolymerization onto modified celluloses.[6,13-32]

This work presents a study concerning with graft polymerization of methyl methacrylate and acrylanitrile on cotton crosslinked to different degrees with dimethylol ethylene urea, dimethylol dihydroxy ethylene urea, and dimethylol carbamate. The grafting reaction was studied with respect to graft yield and ceric consumption.

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EXPERIMENTAL

Materials

Cotton Fibers

Monofi Egyptian cotton was purified by a mild alkaline scouring (2% sodium hydroxide and 0.2 wetting agent, based on the weight of material) for about 5 h at 110°C and 6–10/in.^{2} using a material to liquor ratio of 1:10.

Reagents

Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), reagent grade A.R. chemicals, was used as a catalyst for crosslinking. Dimethylolethylene urea (DMEU), dimethyloldihydroxyethylene urea (DMDEU), and dimethylol carbamate (DMC), were technical grade chemicals. They were kindly supplied by Höechst, W. Germany, as a 50% solution under the commercial names cassurit RI, Arkofix NG, and Arkofix CA, respectively.

Methyl methacrylate and acrylonitrile were used as vinyl monomers. They were freshly distilled before used. Ceric ammonium nitrate (CAN) and ceric ammonium sulphate (CAS), B.D.H. reagent, was used as initiator after standardization with ferrous sulphate.
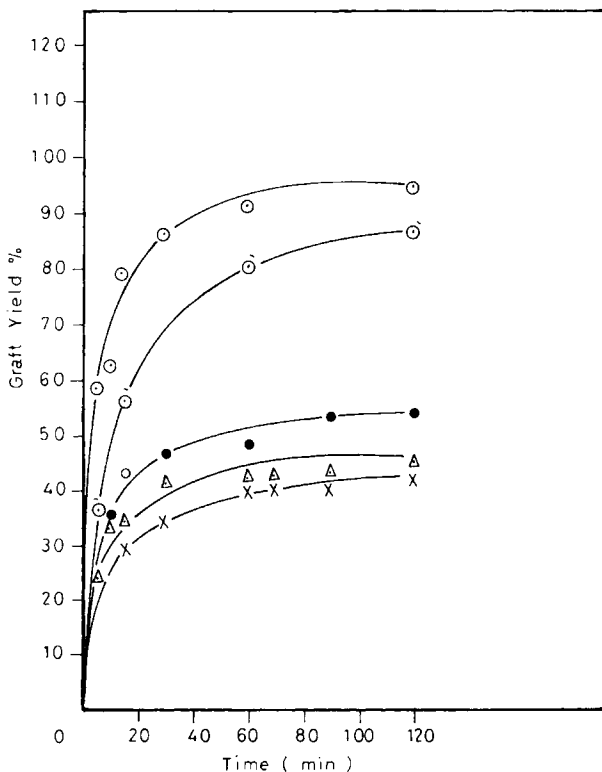

Fig. 1. Rates of grafting of methyl methacrylate on cotton cellulose treated with DMEU. Temperature, 70°C; MMA concentration, 2%; (⊙) magnesium-chloride-treated cotton; (⊙) untreated cotton; cotton samples treated with DMEU: (●) 0.422% N; (▲) 0.96% N; (✕) 1.62% N.
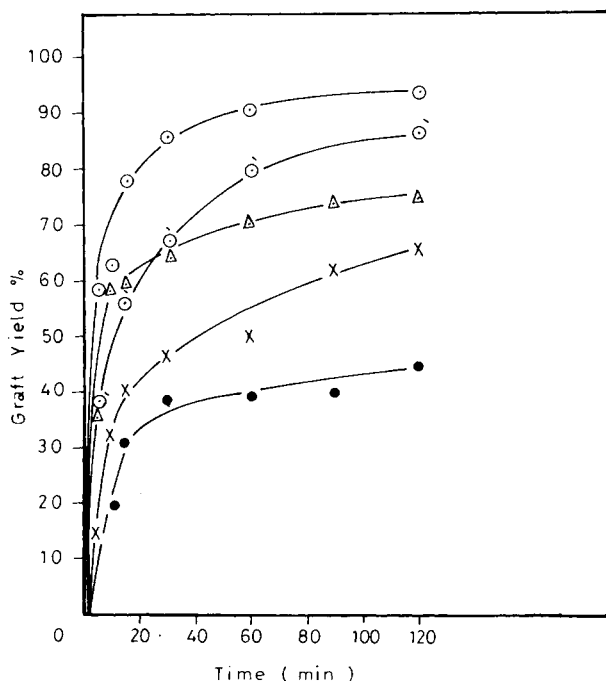
Fig. 2. Rates of grafting of methyl methacrylate on cotton cellulose treated with DMDEU. Temperaure, 70°C; MMA concentration, 2%; (o), magnesium-chloride-treated cotton; (ō) untreated cellulose; cotton samples treated with DMDEU: (▲) 0.108% N; (×) 0.472% N; (●) 1.3% N.

Preparation of Crosslinked Cotton

Cotton fibers were first impregnated in a solution containing the N-methylol finishing agent and magnesium chloride hexahydrate (10 g/L) for 5 min at room temperature followed by squeezing to a wet pickup of ca. 100%, drying at 70°C for 5 min and then curing at 160°C for another 5 minutes. After curing, the fibers were thoroughly washed in a solution containing 2 g/L soap and dried at ambient conditions. Different extents of crosslinking (expressed as % N) were obtained by changing the finishing agent concentration from 50 to 200 g/L. A control sample was prepared by treating cotton with magnesium chloride in absence of the finishing agent.

Grafting Procedure

Unless otherwise stated, the graft polymerization reaction was carried as follows: a 0.5-g cellulosic sample was introduced in a 70-ml glass-stoppered Erlenmyer flask containing 50 mL of an acidified solution consisting of ceric ammonium nitrate (CAN) and the vinyl monomer. Acidification of the CAN solution was carried out by adding 1 mL of concentrated nitric acid per 100 mL of CAN solution. The flask was stoppered and kept in a thermostate, and the contents were occasionally shaken. At the end of the desired reaction time, the fibers were removed, thoroughly washed, and repeatedly soxhlet-extracted with either DMF or acetone in case of acrylonitrile and methylmethacrylate respectively.

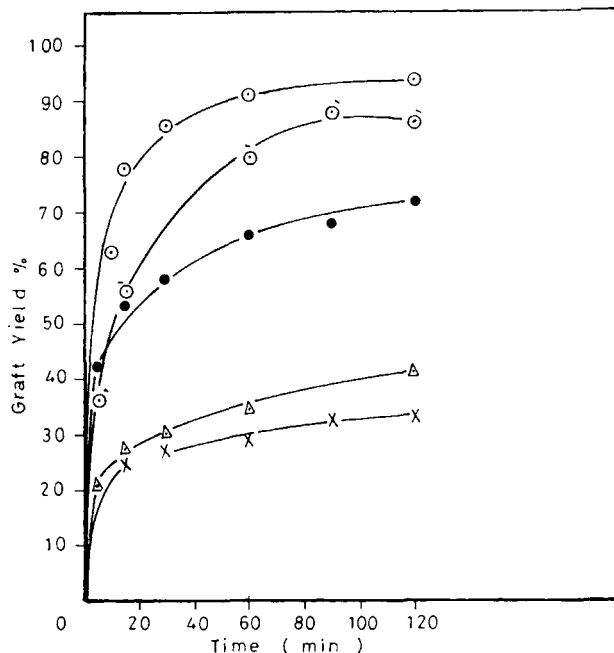The percentage graft yield was calculated as follows:

Fig. 3. Rates of grafting of methyl methacrylate on cotton cellulose treated with DMC. Temperature, 70°C; MMA concentration, 2%; (⊙) magnesium-chloride-treated cotton; (⊖) untreated cellulose; cotton samples treated with DMC: (●) 0.318% N; (▲) 0.502% N; (×) 0.92% N.

$$\% \text{ graft yield} = \frac{\text{wt of grafted polymer} - \text{wt of original sample}}{\text{dry wt of original sample}} \times 100$$

Oxidation Procedure

Oxidation of cellulosic samples with CAN and CAS was carried out under conditions identical with those described above, except that the monomer was omitted.

Acid Hydrolysis

The grafted samples were treated with 1 N HCl at 65°C for 1 hr. The samples were then thoroughly washed with distilled water and dried at ambient conditions.

Analysis

The Nitrogen content of the modified cotton was determined according to the microkjeldahl method. The ceric consumption during grafting and oxidation was determined by a method described by Mino et al.[10]

RESULTS AND DISCUSSION

Resin finishing, more correctly crosslinking, of cotton textiles with N-Methylol finishing agents are popular because they impart easy-care and durable press properties to the cotton fabric.[33–36] Such treatments causes a considerable changes in the physical as well as chemical structure of cotton.[35,36] The effects of these changes are reflected on the behavior of cotton towards grafting as can be seen under.

Graft Yields

Figure 1, 2, and 3 show the graft yield as a function of the reaction time when MMA was grafted onto cotton crosslinked with DMEU, DMDEU, and DMC, respectively, whereas Figures 4, 5, and 6 show similar relation when MMA was replaced by AN. Grafting rate curves for untreated cotton and cotton treated with $MgCl_2 \cdot 6H_2O$ are included in each of these figures for comparison.

The data (Figs. 1–6) indicate:

(a) that crosslinking of cotton cellulose with N-methylol finishing agents reduces significantly the susceptibility of cellulose towards grafting;

(b) that the nature of N-methylol finishing agents affects the magnitude of grafting;

(c) that the extent and rate of grafting depend upon the extent of crosslinking reaction, expressed as % N;
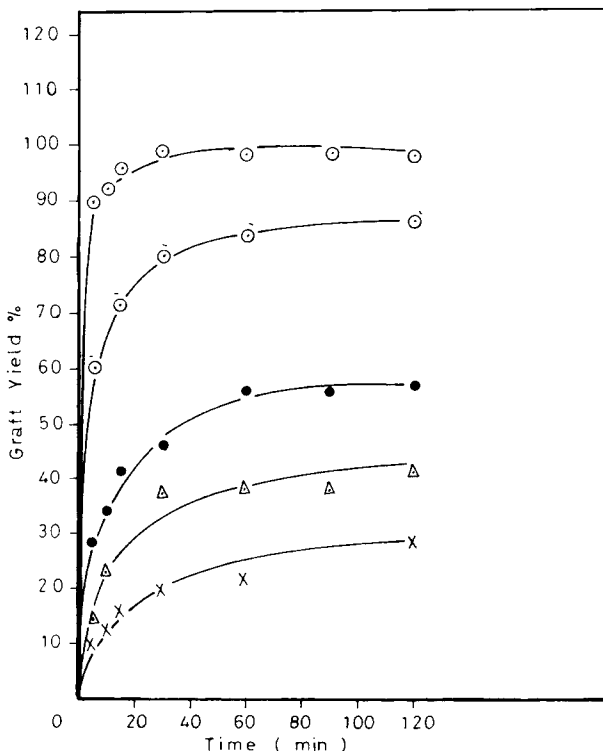

Fig. 4. Rates of grafting of acrylonitrile on cotton cellulose treated with DMEU. Temperature, 70°C; AN concentration, 2%; (⊙) magnesium-chloride-treated cotton; (⊚) untreated cellulose; cotton samples treated with DMEU: (●) 0.4% N (△) 0.966% N; (✕) 1.62% N.
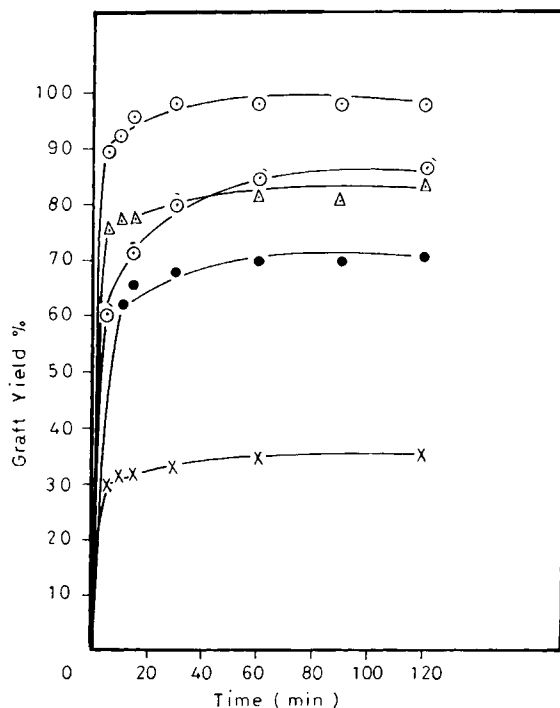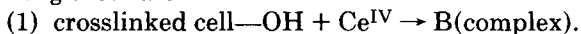
Fig. 5. Rates of grafting of acrylonitrile on cotton cellulose treated with DMDEU. Temperature, 70°C; AN concentration, 2%; (○) magnesium-chloride-treated cotton; (⊙) untreated cellulose; cotton samples treated with DMDEU: (▲) 0.108% N; (●) 0.472% N; (×) 1.32% N.

(d) that treatment of cotton with $MgCl_2 \cdot 6H_2O$ enhances significantly its susceptibility toward grafting.

The enhancement of the grafting brought about by treatment of cotton with $MgCl_2 \cdot 6H_2O$ prior to grafting suggests that this treatment increases the accessibility of cotton cellulose. It is likely that loosening of the cellulose structure occurs under the influence of $MgCl_2 \cdot 6H_2O$ at the high temperature used during the treatment. However, the effect of $MgCl_2 \cdot 6H_2O$ as a weak Lewis acid catalyst on increasing the reducing properties of cotton cellulose cannot be ruled out. Increasing the reducing characteristics of cotton cellulose may favor the effectiveness of the cellulose—Ce^{IV} redox system, thereby enhancing block copolymer formation with the cellulose. Previous reports[11,14] have disclosed that Ce^{IV}-induced polymerization in presence of cellulose results in a mixture of graft and block copolymers.

The decrement in the graft yield by crosslinking of cotton prior to grafting could be associated with decreased accessibility of the crosslinked cotton. In earlier work[15] it has been shown that cotton crosslinked with formaldehyde is less amenable to grafting than noncrosslinked cotton. Nevertheless, this does not seem plausible in accounting for the significant decrement in the graft yield observed with cotton crosslinked with N-methylol finishing agents to different extents.

During grafting of crosslinked cotton, several reactions are expected to occur. Among these are:

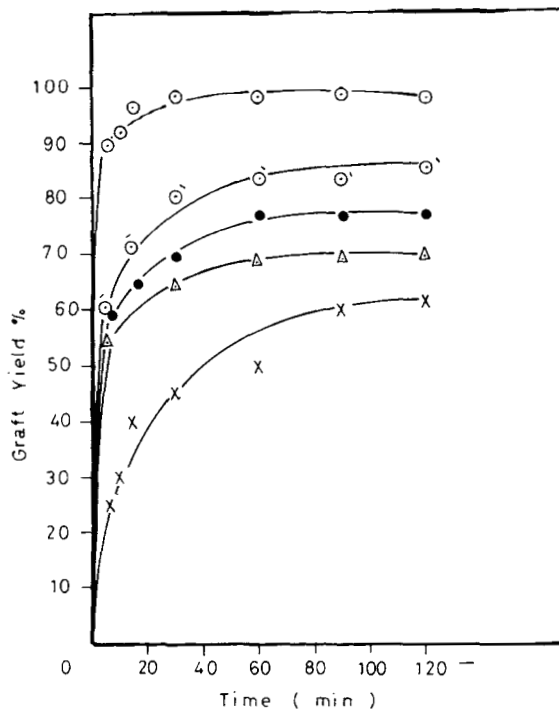(1) crosslinked cell—OH + Ce^{IV} → B(complex).

Fig. 6. Rates of grafting of acrylonitrile on cotton cellulose treated with DMC. Temperature, 70°C; AN concentration, 2%; (⊙) magnesium-chloride-treated cotton; (⊙) untreated cellulose; cotton samples treated with DMC: (●) 0.318% N; (△) 0.502% N; (×) 0.92% N.

$B \rightarrow$ crosslinked cell—O· + Ce^{III} + H^+

crosslinked cell—O· + M $\rightarrow$ crosslinked cell—O—M·

crosslinked cell—O—M· + nM $\rightarrow$ grafted crosslinked cotton,

(2) cell—O—CH_2—N—R—N—CH_2—O—cell

$$\xrightarrow[acid]{Ce^{IV}} \text{cell—OCH}_2\text{—N—R—N—CH}_2\text{—OH} + \text{cell—OH},$$

(3) cell—OCH_2—N—R—NCH_2—OH

$$\xrightarrow[acid]{Ce^{IV}} \text{cell—O—CH}_2\text{—N—R—N—}\overset{.}{C}H\text{—OH} + H^+ + Ce^{III},$$

(4) cell—O—CH_2—N—R—NCH_2—OH

$$\xrightarrow[acid]{Ce^{IV}} \text{cell—O—CH}_2\text{—N—R—NH}_2 + \text{HCHO},$$

(5) cell—O—CH_2—N—R—NH_2

$$\xrightarrow[]{Ce^{IV}} \text{cell—O—CH}_2\text{—N—R—}\overset{.}{N}H + H^+ + Ce^{III},$$

(6) cell—O—CH_2—N—R—NH_2

$$\xrightarrow[acid]{Ce^{IV}} \text{cell—OH} + \text{HO—CH}_2\text{—N—R—NH}_2,$$
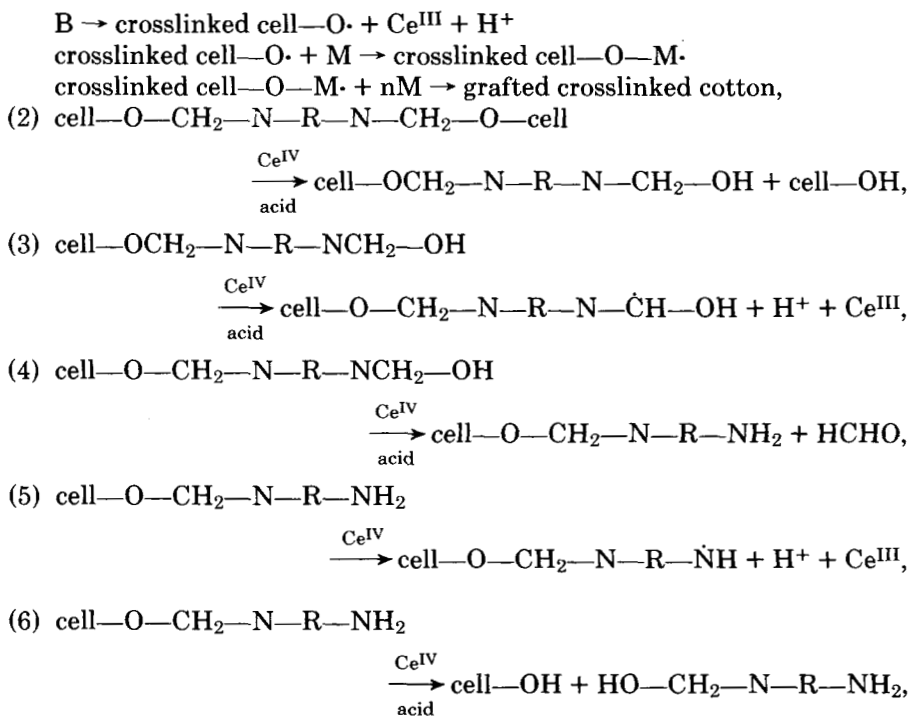
TABLE I

Effect of Ceric Ammonium Nitrate on the Nitrogen and Formaldehyde Content of Cotton
Crosslinked with Different n-Methylol Finishing Agents

Substrate	% N			g formaldehyde/100 g cellulose		
	Original	After Oxidation	After grafting	Original	After Oxidation	After Grafting
DMDEU-crosslinked cotton	0.504	0.0084	0.042	2.4	1.6	1.9
DMC-crosslinked cotton	0.3	0.0756	0.0924	4.3	1.2	3.5
DMEU-crosslinked cotton	0.966	0.0168	0.052	4.8	2.1	3.8

$$(7) \quad HO-CH_2-N-R-NH_2 \xrightarrow[acid]{Ce^{IV}} HN_2-R-NH_2 + HCHO,$$
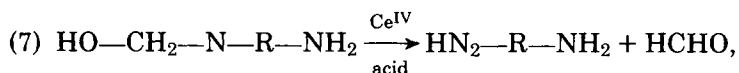
where crosslinked cell—OH represents crosslinked cotton having free hydroxyl group besides the crosslinks; B is the Ce^{IV}—cellulose complex; cell—O· is crosslinked cellulose macroradical, M is the vinyl monomer, and R is the parent substance of the n-methylol crosslinking agent.

Besides, reaction (1), reaction (3), and reaction (5) would lead to increased graft yields by creating additional sites for grafting. Against these are reaction (4) and reaction (7), in which formaldehyde is formed as a by product. The reaction of the formaldehyde with Ce^{IV} would lead to a depletion in Ce^{IV} concentration, thereby decreasing the graft yield. Current work suggests that reactions (4) and (7) prevail and are mainly responsible for the decreased grafting observed with cotton crosslinked with n-methylol finishing agents. Evidences for this are: DMDEU-crosslinked cotton having 0.504% N loses 98.33% and 91.66% of its ni-
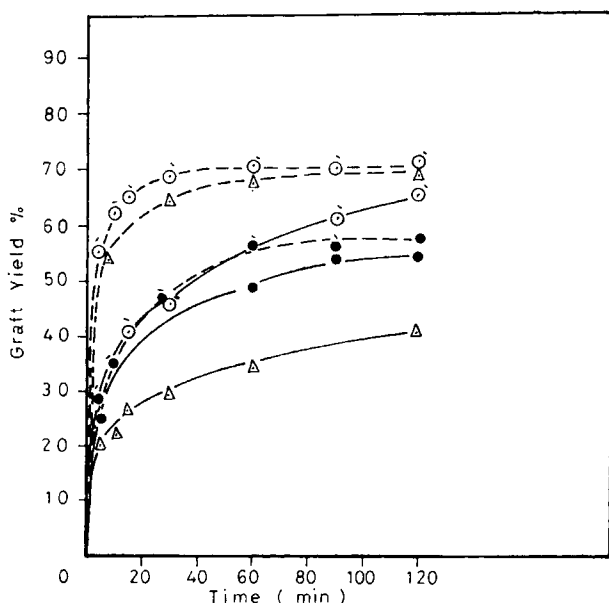

Fig. 7. Rates of grafting of acrylonitrile and methyl methacrylate on cotton cellulose having nearly equal nitrogen content by using different N-methylol finishing agents. Temperature, 70°C; monomer concentration, 2%; (○) DMDEU: 0.472% N; (●) DMEU: 0.422% N; (△) DMC: 0.502% N: (——) MMA; (- - -) AN.
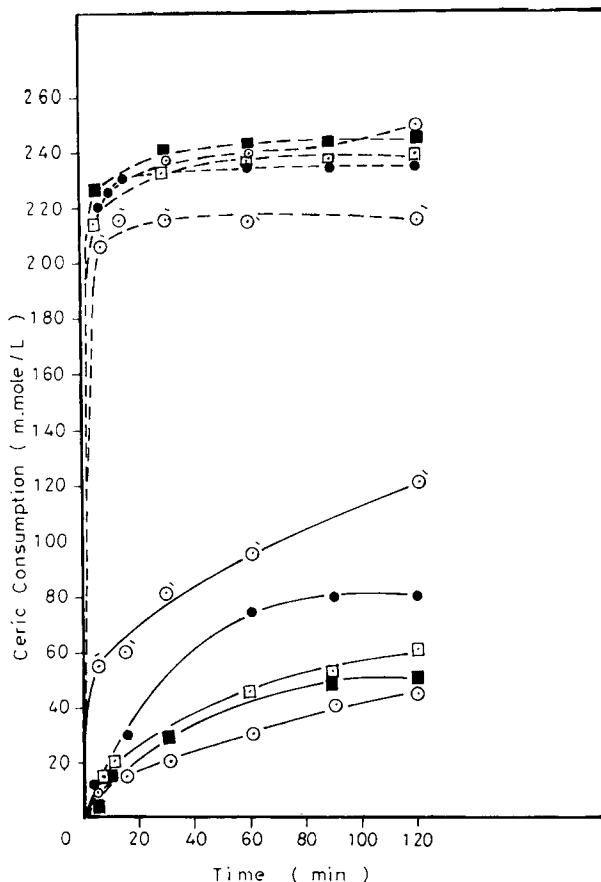
Fig. 8. Ceric consumption during oxidation and grafting of acrylonitrile on cotton cellulose treated with DMDEU. Temperature, 70°C; AN concentration, 2%; (⊖) untreated cellulose; (⊙) magnesium-chloride-treated cotton; cotton samples treated with DMDEU: (●) 1.32% N; (⊡) 0.47% N; (■) 0.108% N; (——) oxidation; (- - -) grafting.

trogen when subjected to Ce^{IV} oxidation and grafting, respectively. Similarly DMC-crosslinked cotton having 0.3% N loses 74.8% and 69.2% of its nitrogen, respectively, during treatment with Ce^{IV} alone (i.e., oxidation) and in presence of monomer (i.e., grafting). The same trend was obtained when the crosslinked samples were analyzed for total formaldehyde before and after Ce^{IV} oxidation and grafting (cf. Table I).

The dependence of the extent and rate of grafting on the nature of the n-methylol finishing agents may be realized from Figure 7 where cotton crosslinked to nearly the same degree (ca. 0.5% N) with DMDEU, DMEU, and DMC was grafted with MMA. It is apparent that the extent and rate of grafting for DMDEU-crosslinked cotton are much higher than those of DMC-crosslinked cotton, whereas DMEU-crosslinked cotton lies somewhere in between. Stated in other words of the three crosslinked cottons, DMDEU-crosslinked cotton is the most accessible for grafting. As indicated above, cleavage of the crosslinks in DMDEU-treated cotton occurs to greater extents than in DMC-treated cotton. This might be the reason for the higher susceptibility of DMDEU-treated cotton
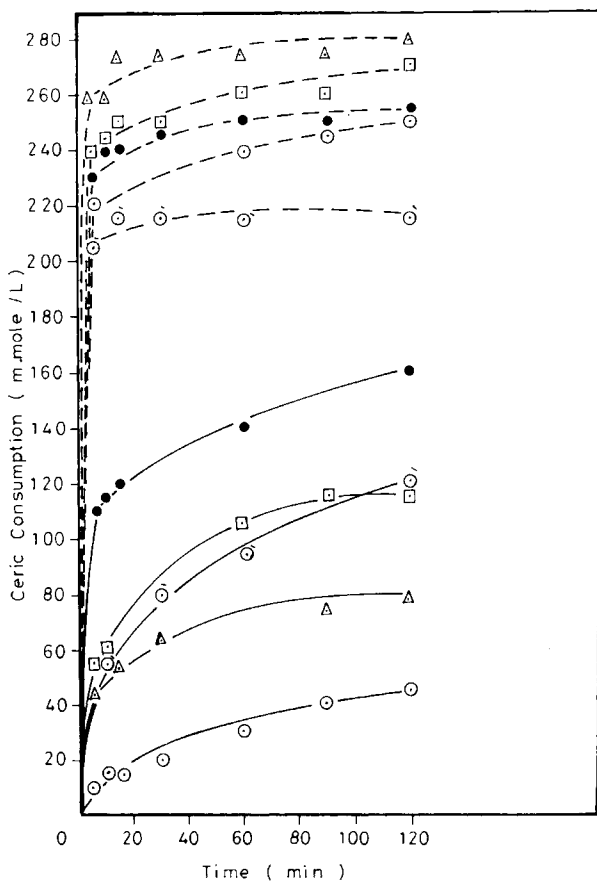
Fig. 9. Ceric consumption during oxidation and grafting of acrylonitrile on cotton cellulose treated with DMEU. Temperature, 70°C; AN concentration, 2%; (⊖) untreated cellulose; (○) magnesium-chloride-treated cotton; cotton samples treated with DMEU: (▲) 0.472% N; (□) 0.966% N; (●) 1.62% N; (——) oxidation; (- - -) grafting.

for grafting as compared with DMC-treated cotton. In accordance with this are the results of the graft yields obtained after acid hydrolysis when samples of DMDEU-, DMEU-, and DMC-treated cotton having graft yields of 68%, 54%, and 40%, respectively, were subjected to acid hydrolysis (1 N HCl at 65°C for 1 h). The graft yields fall to 62%, 46%, and 24%. Since the acid hydrolysis will remove grafts attached to side groups of n-methylol finishing agent on the cellulose chains, this finding would indicate that less residual side groups are present in DMDEU-treated cotton than DMEU- and DMC-treated cotton.

It may be further noted that differences in the magnitude of grafting (Fig. 7) observed with cotton samples pretreated with n-methylol finishing agents in question could be traced back to differences in number, nature, location, and distribution of the crosslinks. Furthermore, the mode of reaction of free formaldehyde present in the finishing bath and/or liberated via decomposition of the finishing agent during curing would differ considerably, depending upon the nature of the N-methylol finishing agent used. Both intracrosslinks and intercrosslinks would adversely affect the magnitude of grafting.[37] Current data

suggest that reaction of free formaldehyde with cotton cellulose is more pronounced with DMC-treated cotton than DMDEU- and DMEU-treated cottons.

A close examination of the data in Figure 7 reveals that the extent and rate of grafting obtained with AN on crosslinked cotton samples are higher than their mates for MMA. This could be associated with difference between the two monomers in molecular size, solubility, affinity to the crosslinked cottons, and ability to react with the initiator and/or cellulose macroradicals.

Ceric Consumption

Figures 8, 9, and 10 show the Ce^{IV} consumption during grafting with AN and oxidation of cotton cellulose before and after crosslinking with DMDEU, DMEU, and DMC, respectively. Also included in these figures are data for Ce^{IV} consumption during grafting with AN and oxidation of $MgCl_2 \cdot 6H_2O$-treated cotton for comparison, whereas in Figures 11, 12, and 13 are shown the Ce^{IV} consumption during grafting with MMA and oxidation of these substrates.
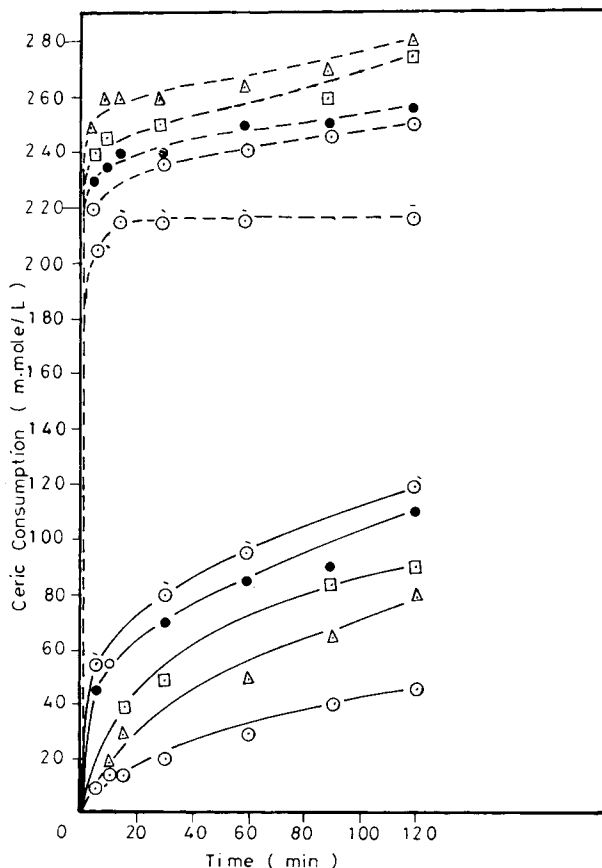

Fig. 10. Ceric consumption during oxidation and grafting of acrylonitrile on cotton cellulose treated with DMC. Temperature, 70°C; AN concentration, 2%,; (⊙) untreated cellulose; (○) magnesium-chloride-treated cotton; cotton samples treated with DMC: (●) 0.92% N; (□) 0.502% N; (▲) 0.318% N; (——) oxidation; (- - -) grafting.
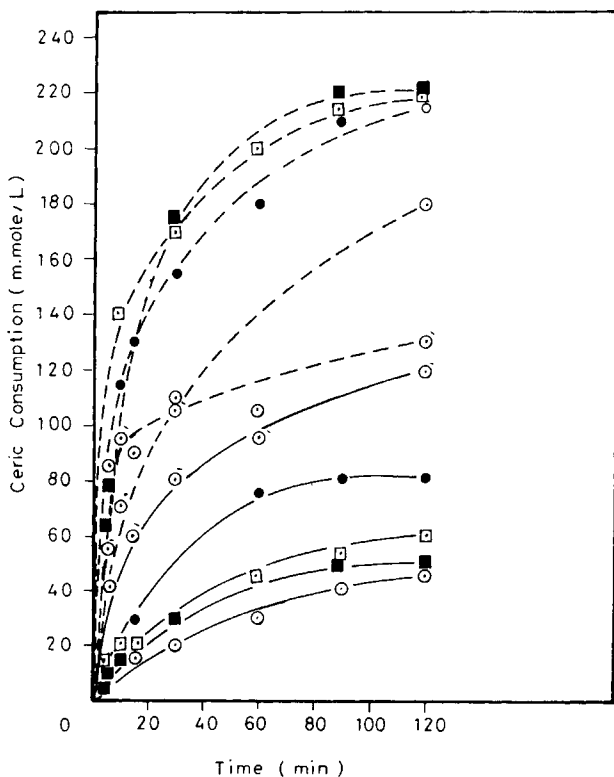
Fig. 11. Ceric consumption during oxidation and grafting of methyl methacrylate on cotton cellulose treated with DMDEU. Temperature, 70°C; MMA concentration, 2%; (⊖) untreated cellulose; (⊙) magnesium-chloride-treated cotton; cotton samples treated with DMDEU: (●) 1.3% N; (▫) 0.472% N; (■) 0.108% N; (——) oxidation; (- - -) grafting.

The data (Figs. 8–13) reveal the following common features:

1. Ce^{IV} consumption during grafting is invariably higher than that consumed during oxidation, in accordance with earlier work,[4] which ascribed this to initiation and termination of homopolymer formed during grafting.

2. Ce^{IV} consumption during oxidation increases by increasing the degree of crosslinking (expressed as % N) irrespective of the N-methylol finishing agents used, indicating that reactions (4) and (7) shown above occur to a greater extent with cotton of higher than that of lower degree of crosslinking.

3. Treatment of cotton cellulose with $MgCl_2 \cdot 6H_2O$ in absence of the N-methylol finishing agent reduces considerably the susceptibility of cotton towards Ce^{IV} oxidation, in contrast with the results of graft yields. Although it seems reasonable that the higher graft yields may be due to greater accessibility of $MgCl_2 \cdot 6H_2O$-treated cotton, it is difficult to explain the lower Ce^{IV} consumption of these fibers during oxidation.

4. Except with DMEU-crosslinked cotton having relatively higher percentages of nitrogen, the susceptibilty of all crosslinked cottons in question to Ce^{IV} oxidation is lower than that of untreated cotton, reflecting the influence of residual crosslinks.

One should note as well that the Ce^{IV} consumption during grafting is dependent
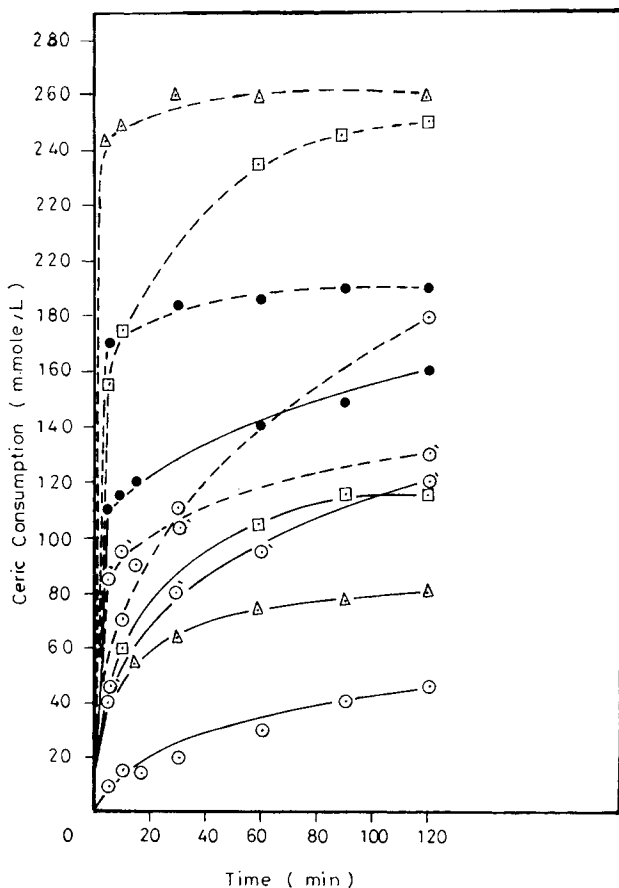
Fig. 12. Ceric consumption during oxidation and grafting of methyl methacrylate on cotton cellulose treated with DMEU. Temperature, 70°C, MMA concentration, 2%; (ō) untreated cellulose; (⊙) magnesium-chloride-treated cotton; cotton samples treated with DMEU: (●) 1.62% N; (□) 0.966% N; (△) 0.422% N; (——) oxidation; (---) grafting.

upon the nature of both monomer and substrate (Figs. 8–13). This is rather expected since the magntiudes of grafting and homopolymerization would rely on: (a) the reactivity of the monomer and its ability to react with cellulose macroradicals brought about by Ce^{IV} attack on the cellulose molecules; (b) the capability of the monomer to form momomer—Ce^{IV} complex with further dissociation to produce activated monomer capable of adding to it other monomer molecules, thereby propagation homopolymer formation; (c) type of termination whether the latter occurs exclusively by Ce^{IV} or by any other means such as chain transfer, combination or disproportionation; and (d) mode of interaction of Ce^{IV} with the cellulosic substrate and of monomer with cellulosic substrates before and after Ce^{IV} attack.

Based on the above, higher Ce^{IV} consumption during grafting of AN than during grafting of MMA would suggest that AN is not only more reactive to Ce^{IV} but also that termination of its growing chain occurs exclusively by Ce^{IV}. Furthermore, the higher Ce^{IV} consumption generally observed with crosslinked cottons during grafting as compared with untreated cotton implies that cleavage
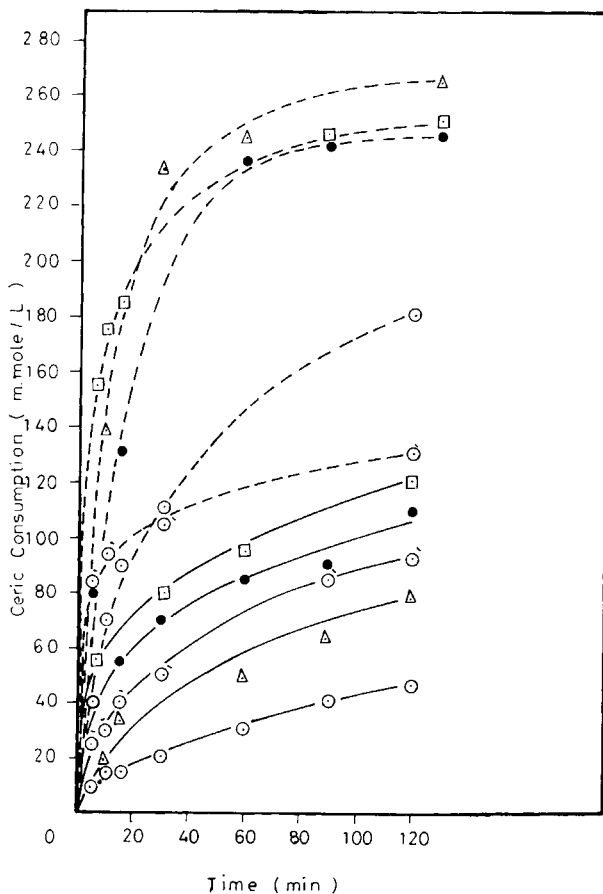
Fig. 13. Ceric consumption during oxidation and grafting of methyl methacrylate on cotton cellulose treated with DMC. Temperature, 70°C; MMA concentration, 2%; (⊖) untreated cellulose; (⊙) magnesium-chloride-treated cotton; cotton samples treated with DMC: (●) 0.92% N; (□) 0.504% N; (△) 0.318% N; (——) oxidation; (- - -) grafting.

of crosslinks takes place with subsequent formation of byproducts such as formaldehyde and/or creation of new groups on the cellulose molecules which are more susceptible to Ce^{IV} attack than cellulose hydroxyls [reactions (2)–(7)].

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