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Graft Copolymerization of Vinyl Monomers on Modified Cotton. IV. Ceric-Induced Grafting of Vinyl Monomers on Cellulose Bearing Different Substituents

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Synopsis

The influence of introducing various functional groups into the cellulose molecule on its susceptibility toward grafting with vinyl monomers such as acrylonitrile and methyl methacrylate using the Ce(IV)–cellulose redox system was studied. While cellulose bearing either cyanoethyl or carboxymethyl groups showed higher graft yields, cellulose bearing both groups showed lower yields. Presence of acrylamidomethyl groups in the cellulose molecule reduced its reactivity to grafting. The same holds true for cellulose bearing acrylamidomethyl groups along with carboxymethyl groups. On the other hand, introducing carbamoylethyl groups in the cellulose molecule enhances significantly the susceptibility of cellulose toward grafting. This is also observed with cellulose bearing cyanoethyl and carboxyethyl groups. Treating cellulose with N-methylolacrylamide in alkaline medium seems to produce a crosslinked cellulose with lower reactivity to grafting. The results obtained with the different substrates were discussed on the basis of the change in the physical and/or chemical structure of cellulose brought about during its modification as well as on the nature of the substituent groups introduced. The mode of Ce(IV) attack on cellulose was also clarified.

INTRODUCTION

Graft polymerization of vinyl monomers onto cellulose and related substrates has been studied extensively using a variety of methods, e.g., chain transfer, high-energy radiation, low-energy radiation in the presence of a sensitizer, and redox systems, to initiate free-radical formation. The mechanisms involved in the grafting reactions have been reviewed in detail.[1,2] Comparatively recently, ceric ion, Ce (IV) has been disclosed to be a very effective initiator for inducing grafting of vinyl monomers such as acrylamide, acrylonitrile, and esters of acrylic and methacrylic acids,[3–10] in contrast to other redox systems such as Fe^{2+}–H_2O_2 or persulfate–thiosulfate.[11–13]

On account of its ease of application, the Ce(IV)–cellulose redox system has gained considerable importance in grafting reactions. It has been postulated that cleavage of the C_2–C_3 glycol bond occurs during graft-

ing.[5,14–16] Results of the oxidation of cellulose with Ce(IV)[17] as well as kinetic studies of grafting of vinyl monomers on acetylated cotton[18] are in full agreement with this postulation.

The effect of the accessibility of cellulose on the graft yields using the Ce(IV)–cellulose redox system has been studied by Hebeish and Mehta.[9] By suitably modifying the grafting method, they have shown that maximum graft yields are directly related to accessibility of the substrate. We have recently reported results of grafting different vinyl monomers to a number of modified cottons, viz., partially carboxymethylated cotton,[19] acetylated cotton,[18] and cyanoethylated cotton,[20] having different degree of substitution.

The present work was undertaken to clarify the influence of the change in the physical and/or chemical structure of cellulose brought about when cellulose was treated with various etherifying agents on the behavior of cellulose toward grafting. The effect of the nature of the new functional groups introduced into the cellulose molecule on the grafting reaction was another objective of this work.

EXPERIMENTAL

Materials

Cellulose. Egyptian Monofi cotton slivers were purified by a mild alkaline scouring (2% NaOH and 0.2% wetting agent, based on weight of material) for 5 hr at 110°C and 6–10 lb/in.^{2} using a liquor ratio of 10.

Alkali-Treated Cellulose. Sodium hydroxide treated cotton (NaOH–cotton) was prepared by treating the purified cotton slivers with aqueous sodium hydroxide (12*N*) at room temperature for 1 hr, followed by washing and drying in air at room temperature.

Modified Celluloses. Partially carboxymethylated cotton (PCMC) was prepared by the method of Kamel et al.[21] using 12*N* sodium hydroxide and 3*N* sodium chloroacetate.

Acrylamidomethyl cellulose was prepared as follows: The alkali-treated cotton or partially carboxylated cotton was impregnated with a solution containing 20% N-methylolacrylamide (MAM) and 1% ammonium chloride. The sample was padded to obtain 95%–100% wet pickup. The samples were then placed for 5 min in an oven at 150°C. Washing of the samples was done in an aqueous solution of 2% sodium nitrite at 80°C followed by washing in soap solution and finally rinsing with cold water. Acrylamidomethyl cellulose having different D.S. was obtained by using different concentration of MAM.

Cellulose bearing cyanoethyl and carboxymethyl groups (PCMC–CEC) was prepared by cyanoethylation of partially carboxymethylated cotton according to a method described by Reinhardt et al.[22]

Cellulose bearing cyanoethyl and carboxyethyl groups was obtained by partially hydrolyzing cyanoethylated cotton with 40% NaOH. After hy-

drolysis, the samples were neutralized with dilute HCl, washed thoroughly with water, and air dried.

Carbamoylethyl cellulose was prepared according to a method described by Frick et al.[23]

Reaction of cellulose with N-methylolacrylamide in alkaline medium was carried out by impregnating the purified cotton slivers in a solution containing 25% N-methylolacrylamide and 2% KOH. After being squeezed to a wet pickup of ca. 80%, the samples were placed in an oven of temperature 150°C for 5 min. The samples were then neutralized with dilute acetic acid, washed thoroughly with water, and finally air dried.

Ceric ammonium nitrate (CAN) and ceric ammonium sulfate (CAS), B.D.H. reagent grade, were used after standardization with ferrous sulfate.[14]

Freshly distilled acrylonitrile (AN) was used. Methyl methacrylate (MMA) was shaken with 10% NaOH solution, washed with distilled water, and dried over calcium sulfate.

Methods

The graft polymerization of AN and MMA was conducted according to a method described elsewhere.[18–20]

Oxidation of cellulosic samples with CAN and CAS was carried out under conditions identical with those of grafting, except that the monomer was omitted as also described earlier.[18–20]

Ce(IV) consumption during grafting and oxidation was determined according to a method reported by Mino et al.[14]

The carboxymethyl group was determined as —COOH group according to a method described by Lüdtke[24] using potentiometric titration.

The nitrogen content of treated cellulosic fibers was determined by a standard Kjeldahl procedure. This is done for cellulose treated with acrylonitrile, acrylamide, and N-methylolacrylamide.

RESULTS AND DISCUSSION

In order to investigate the influence of the nature of the side groups in modified cellulose on the behavior of the latter toward grafting, cellulose bearing different substituents was treated with acrylonitrile (AN) and methyl methacrylate (MMA) in the presence of ceric ion, Ce(IV), as initiator. The grafting reaction was studied with respect to the graft yield and ceric consumption. In the following, the results obtained with the various substrates examined are independently discussed.

Grafting of Cellulose Bearing Acrylamidomethyl Groups

Graft Yield

Figure 1 shows the rate of grafting of acrylamidomethyl cellulose and unmodified cellulose (control) using either CAS or CAN as initiator. It is ob-

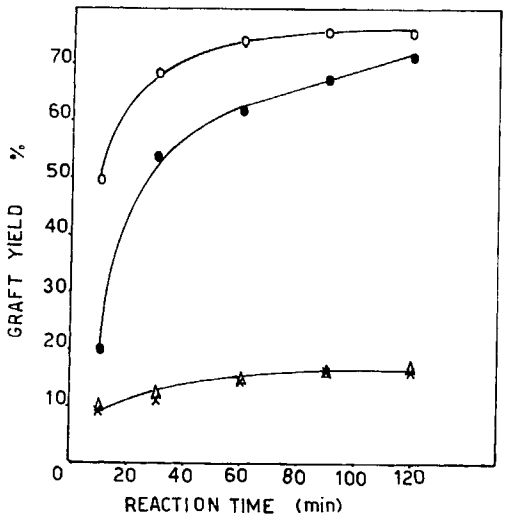


Fig. 1. Grafting of acrylonitrile on acrylamidomethyl cellulose and cellulose treated with sodium hydroxide (control) using CAN and CAS as initiators. Ceric concn., 0.01*M*; AN, 1 g; cellulose, 1 g.; temp., 40°C; M/L ratio, 1:30: (△) acrylamidomethyl cellulose using CAN; (×) acrylamidomethyl cellulose using CAS; (○) control using CAN; (●) control using CAS.

vious that with both substrates the grafting reaction is characterized by an initial fast rate followed by a slower one. However, the initial fast rate observed with modified cellulose is significantly lower than that of the control. Also, the maximum graft yield obtained with the modified cotton is less than that of the control. These observations may be explained as follows:

The presence of bulky side groups such as $CH_2OCONHCH{=}CH_2$ in the cellulose molecule would be expected to perform the following functions: (a) blocking some of the cellulose hydroxyls, (b) opening up the cellulose structure, (c) increasing the reactivity of cellulose owing to the presence of a pendant double bond, (d) decreasing the swellability of cellulose owing to its hydrophobic nature, and (e) crosslinking of cellulose by homopolymerization of the double bond by the action of Ce(IV). Functions (a), (d), and (e) would bring about a decrease in the graft yield, whereas functions (b) and (c) would cause an increase. It is likely that the influence of functions (a), (d), and (e) is more pronounced than that of (b) and (c), thereby giving rise to a lower rate of grafting.

CAS Versus CAN

A comparison between the efficiency of CAS and CAN in inducing may be realized from Figure 1. In the case of acrylamidomethyl cellulose, there is no difference in the graft yields obtained with CAN and CAS. On the other hand, the graft yields of the control obtained with the two initiators differ considerably, and CAN is more efficient than CAS in the range studied. The identical graft yield obtained with both initiators in the case

of the modified cotton could be attributed to crosslinking of cellulose through homopolymerization of the double bond. The effect of this is to make cellulose less susceptible toward grafting in the case of the two initiators.

Effect of Degree of Substitution

The graft yield per cent as a function of the degree of substitution (D.S.) of acrylamidomethyl cellulose is shown in Figure 2. These data make it evident that the graft yield decreases by increasing the D.S. This suggests that the pendant double bond reduces the ability of cellulose to be grafted. The pendant double bonds appear to be homopolymerized with the catalytic action of Ce(IV). This conversion increases with acrylamidomethyl con-

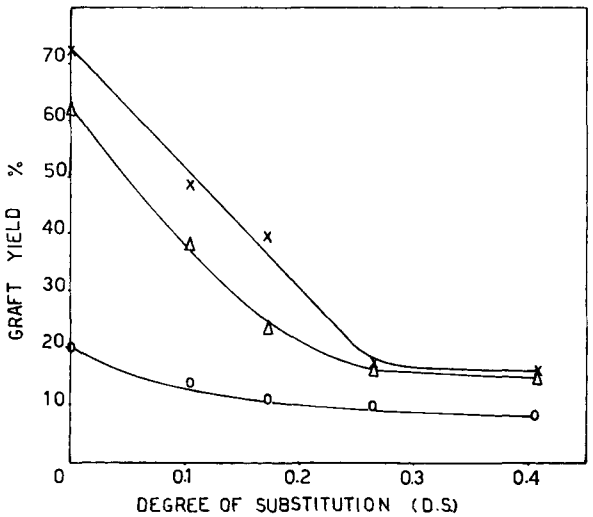


Fig. 2. Graft yield as a function of degree of substitution of acrylamidomethyl cellulose CAS concn., 0.01*M*; AN, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30: (O), (Δ), (×) for reaction of 10, 60, and 120 min, respectively.

tent of the cellulose, because with increasing acrylamidomethyl content the probability that there is a double bond near enough to any given double bond to be able to react with it also increases.

Ceric Consumption

Ce(IV) consumption by cellulose material in the absence of the monomer, that is, oxidation and during grafting reaction using CAS and CAN as initiators, is shown in Figure 3. This consumption is expressed in mmoles Ce(IV)/100 g cellulose.

It is apparent that the consumption increases with increasing reaction time, being more significant in the initial stages of the reaction (particularly in the case of CAN) than in the later stages perhaps owing to lowering of

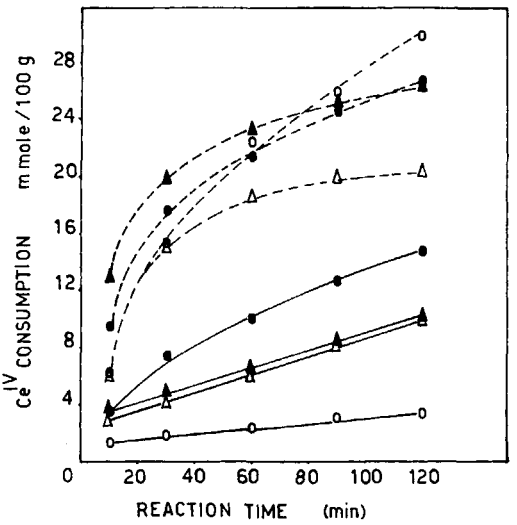


Fig. 3. Ceric consumption during grafting and oxidation of acrylamidomethyl cellulose and cellulose treated with sodium hydroxide (control) using CAN and CAS. Ceric concn. 0.01*M*; AN, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30; (——) CAS; (- - -) CAN; (▲) during grafting of acrylamidomethyl cellulose; (△) during oxidation of acrylamidomethyl cellulose; (●) during grafting of the control; (○) during oxidation of the control.

the ceric concentration as well as shortage of reactive sites on the substrate backbone as the reaction proceeds. This is observed with both substrates, i.e., acrylamidomethyl cellulose and the control. However, the Ce(IV) consumption during oxidation of acrylamidomethyl cellulose is higher than the corresponding consumption in the case of the control when CAS was used. The opposite holds true for CAN.

Besides the direct attack of Ce(IV) on the cellulose hydroxyls, attack on the pendant double bond seems to occur. As a result, homopolymerization of the double bonds occurs, thereby bringing about a crosslinked cellulose. Formation of the latter would be expected to rely mainly on the number and distribution of the double bonds as well as availability of Ce(IV) in the reaction medium. Since the rate of dissociation of CAN is much higher than that of CAS,[25,26] availability of Ce(IV) for oxidation of acrylamidomethyl cellulose would be more with CAN than with CAS. As pointed out above, this would result in a crosslinked cellulose. The lower rate of oxidation of acrylamidomethyl cellulose at the later stages of the reaction in the case of CAN suggests that the crosslinked cellulose is less susceptible to Ce(IV) attack than the control.

On the other hand, formation of crosslinked cellulose seems to occur in a relatively lower rate in the case of CAS owing to its slower rate of dissociation.[25,26] Consequently, the change in the chemical structure of cellulose by crosslinking would not be that striking. This and the fact that Ce(IV) is available in a considerable amount in the reaction medium would account

for the high Ce(IV) consumption of acrylamidomethyl cellulose compared to the control in the case of CAS.

Another point of interest is that the magnitudes of Ce(IV) consumption also differ considerably, being dependant on the nature of the substrate and type of initiator. Regardless of all this, however, the Ce(IV) consumption during grafting is higher than that consumed during oxidation. Hebeish and Mehta[9] observed the same with various cellulosic materials and ascribed this to homopolymer formation.

Grafting of Cellulose Bearing Carboxymethyl and Acrylamidomethyl Groups

Graft Yields

The effect of introducing carboxymethyl and acrylamidomethyl groups in the cellulose molecule on grafting of AN may be realized from Figure 4. A similar trend was observed with MMA. It is obvious that the rate of grafting of cellulose containing carboxymethyl groups is significantly higher than that of cellulose containing both carboxymethyl and acrylamidomethyl groups, being more significant at higher content of the latter. This implies that further modification of partially carboxymethylated cotton by acrylamidomethylation reduces the susceptibility of cellulose toward grafting, a phenomenon which is in full agreement with our observation previously discussed.

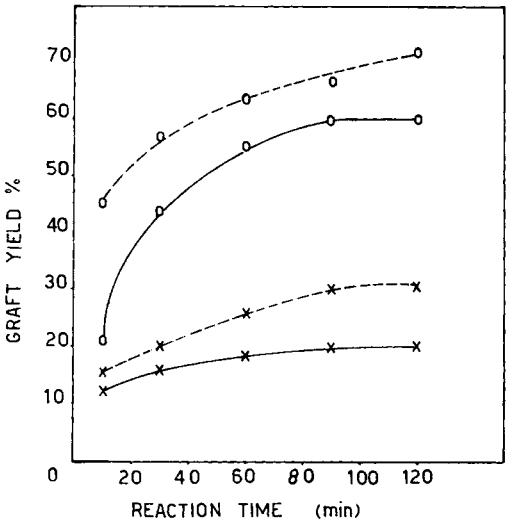


Fig. 4. Graft yields obtained with cellulose bearing acrylamidomethyl groups and carboxymethyl groups and those obtained with partially carboxymethyl cellulose of various reaction times using CAN and CAS as initiators. Ceric concn., 0.01*M*; AN, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30; (——) CAS; (- - -) CAN; (×) cellulose bearing acrylamidomethyl groups (D.S. = 0.22) along with carboxymethyl groups (D.S. = 0.0324); (O) partially carboxymethyl cellulose (D.S. = 0.0324).

The dotted lines in Figure 4 show the graft yields obtained when CAN was used instead of CAS. It is clear that the graft yields obtained with the former are much higher than those of the latter. This is in harmony with the results given above as well as previous reports.[9,19]

Ceric Consumption

Data for Ce(IV) consumption during grafting and oxidation of partially carboxymethylated cotton before and after its modification by acrylamidomethylation are given in Figure 5. It is clear that the consumption showed a trend which is similar to that obtained with acrylamidomethyl cellulose (see above). The explanation given for the latter would work out here

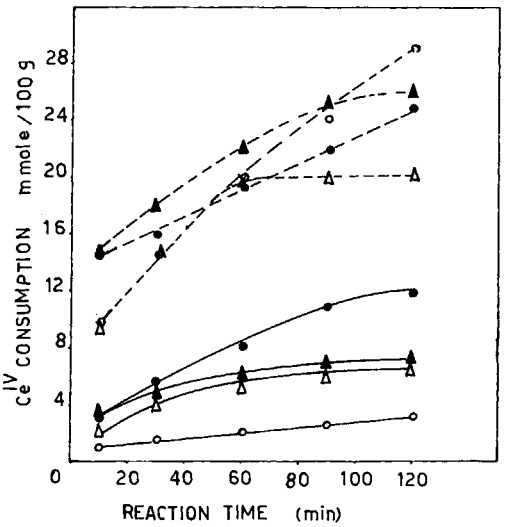


Fig. 5. Ceric consumption by cellulose bearing acrylamidomethyl groups (D.S. = 0.22) and carboxymethyl groups (D.S. = 0.0324) and by partially carboxymethyl cellulose (D.S. = 0.0324) during grafting and oxidation with CAN and CAS. Ceric concn., 0.01*M;* AN, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30; (——) CAS; (- - -) CAN; (▲), (△) during grafting and oxidation, respectively, of cellulose bearing acrylamidomethyl and carboxymethyl groups; (●), (○) during grafting and oxidation, respectively, of partially carboxymethyl cellulose.

also. Here, too, the difference in the Ce(IV) consumption during grafting of the two substrates using CAN and CAS suggests that the magnitude of Ce(IV) consumption during grafting seems to rely on the type of initiator, nature of substrate, and rate of initiation and termination of the homopolymer formed in solution.

Grafting on Cellulose Bearing Cyanoethyl and Carboxymethyl Groups

Graft Yield

In a previous paper, we have reported that changing the chemical structure of cellulose by carboxymethylation up to D.S. 0.124 (PCMC) en-

hances the behavior of cellulose toward grafting.[19] The same holds true when the chemical modification of cellulose is performed with cyanoethylation (CEC), but the graft yield increases by increasing the D.S.[20] It appears, therefore, of interest to study the behavior of cellulose bearing both groups, i.e., cyanoethyl and carboxymethyl (PCMC–CEC) toward grafting. For this purpose, partially carboxymethylated cotton of D.S. 0.0324 was cyanoethylated up to a D.S. 1.425. The latter was then grafted with AN and MMA under similar conditions. The results are given in Figure 6.

It is clear that, for a given reaction time, the graft yield of PCMC is significantly higher than that of cellulose bearing the same amount of carboxymethyl groups together with cyanoethyl groups. This implies that further

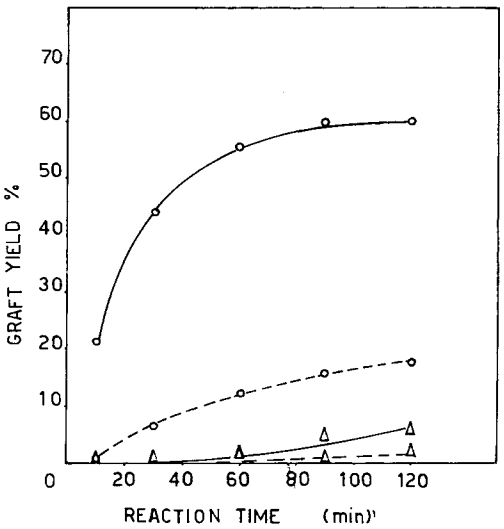
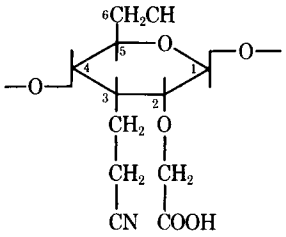


Fig. 6. Grafting of acrylonitrile and methyl methacrylate on cellulose bearing cyanoethyl group (D.S. = 1.425) along with carboxymethyl group (D.S. = 0.0324) using CAS as initiator. CAS concn., 0.01*M;* monomer, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30: (——) AN; (- - - - -) MMA; (Δ) cellulose bearing cyanoethyl and carboxymethyl groups; (O) partially carboxymethyl cellulose.

modification of partially carboxymethylated cotton by cyanoethylation greatly reduces its susceptibility toward grafting. A possible explanation for this observation, may be as follows:

As etherification reaction, carboxymethylation and cyanoethylation would be expected to take place preferably at C_2 and C_3 of the anhydroglucose unit of cellulose,[27] at least in the range studied. This means that carboxymethyl groups would be located in an O-position to the cyanoethyl groups. Thus, increasing the reactivity of cellulose to grafting by increasing the cyanoethyl group[20] is partially inhibited by the moiety of the O-position:



anhydroglucose unit in the cellulose molecule

This and the fact that blocking some of the cellulose hydroxyls by carboxymethyl groups at either C_2 or C_3, which reduces the Ce(IV) attack on cellulose, would account for the lower graft yields obtained with cellulose bearing carboxymethyl and cyanoethyl groups.

Ceric Consumption

The consumption of Ce(IV) during grafting and oxidation of PCMC and PCMC–CEC is shown in Figure 7. It is apparent that introducing cyanoethyl groups along with carboxymethyl groups in the cellulose molecule has practically no effect on the susceptibility of cellulose to oxidation with Ce(IV). This is rather a surprise, since the graft yields obtained with PCMC–CEC are significantly lower than those of PCMC. There seems to be a considerable difference in the mode of Ce(IV) attack on both substrates

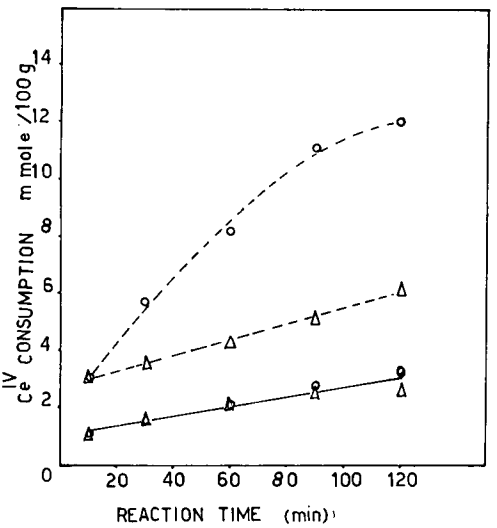


Fig. 7. Ceric consumption during grafting and oxidation of cellulose bearing cyanoethyl group (D.S. = 1.425) along with carboxymethyl group (D.S. = 0.0324) and partially carboxymethyl cellulose (D.S. = 0.0324) using CAS. CAS concn., 0.01*M;* AN, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30: (——) oxidation; (- - -) grafting; (Δ) cellulose bearing cyanoethyl and carboxymethyl groups; (O) partially carboxymethyl cellulose.

as well as in the rate of initiation and termination of the free radicals on the substrate backbone.

It is established[17] that Ce(IV) consumption during oxidation of cellulose is due to (a) formation of a Ce(IV)–cellulose complex perhaps through a chelate compound between Ce(IV) and cellulose hydroxyls, (b) formation of free radicals at the hemiacetal group of the end anhydroglucose unit of the cellulosic chain, and (c) termination of free radicals resulting from dissociation of Ce(IV)–cellulose complex and those formed at the hemiacetal group. Assuming that (b) and (c) are equal for PCMC and PCMC–CEC, the extent of Ce(IV)–cellulose complex formation would be much greater in the case of PCMC than that of PCMC–CEC, presumably owing to the greater availability of cellulose hydroxyls in the former. Thus, the fact that the Ce(IV) consumption during oxidation of PCMC and PCMC–CEC is very close suggests that excess Ce(IV) consumption for complex formation during oxidation of PCMC is outweighed by the direct attack of Ce(IV) on cyanoethyl groups[20] of PCMC–CEC.

On the other hand, the following two possibilities may explain the lower graft yields obtained with PCMC–CEC as compared with PCMC: (a) Dissociation of the Ce(IV)–cellulose complex to produce free radical capable of initiating grafting[17] may be easier in the case of PCMC than that of PCM–CEC. (b) Termination of free radicals formed on cyanoethyl groups may be much faster than those brought about by dissociation of the Ce(IV)–cellulose complex.

Grafting on Cellulose Bearing Cyanoethyl and Carboxyethyl Groups

Graft Yield

It has been shown above that the presence of cyanoethyl along with carboxymethyl groups in the cellulose molecule reduces greatly the susceptibility of cellulose toward grafting, perhaps owing to moiety effect. To obviate the latter, creation of carboxyethyl groups along the cellulose molecule was effected by partial hydrolysis of cyanoethyl cellulose having a D.S. of 0.515. In this range, the cyanoethyl groups are perhaps located at C_2 of the anhydroglucose unit in the cellulose molecule.[20,27] After being hydrolyzed with 40% sodium hydroxide, the cellulose was found to contain cyanoethyl groups (D.S. 0.06) and carboxyethyl groups (D.S. 0.0376). The sum of both groups expressed as D.S. amounts to 0.0976, a value which is much lower than that of the original cyanoethyl cellulose, i.e., D.S. 0.515. This suggests that ether bond cleavage occurs during alkaline hydrolysis.

Figure 8 shows the effect of the creation of carboxyethyl groups in cyanoethyl cellulose on the reactivity of the latter toward grafting with AN and CAS. Using the same system, the graft yields achieved by cellulose treated with 2% sodium hydroxide (control of cyanoethyl cellulose) are also given in Figure 8.

It is apparent that the graft yields obtained with cellulose bearing cyanoethyl along with carboxyethyl groups are considerably higher than those of

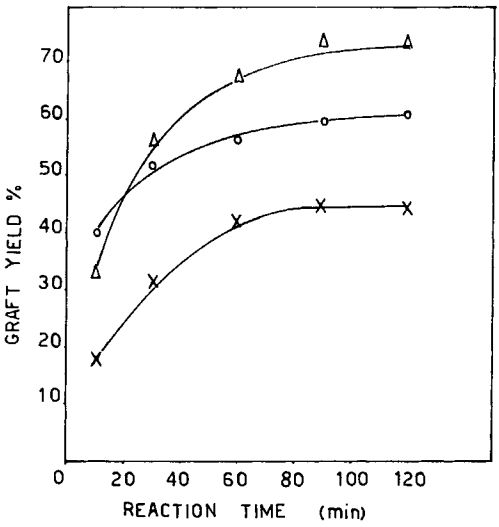


Fig. 8. Graft yield vs. reaction time. CAS concn., 0.01*M;* AN, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30: (Δ) cellulose bearing cyanoethyl groups (D.S. = 0.06) along with carboxyethyl groups (D.S. = 0.0376); (O) cyanoethyl cellulose (D.S. = 0.515); (×) cellulose treated with 2% sodium hydroxide (control of cyanoethyl cellulose).

the cyanoethyl cellulose and control. This could be attributed to the combined influence of the following factors: (a) cyanoethyl groups function as additional sites for grafting, (b) carboxyethyl groups increase the swellability of cellulose, thereby facilitating diffusion of monomer and initiator, and (c) the physical and/or chemical change in the cellulose structure brought about by the effect of concentrated alkali used in hydrolyzing the cyanoethyl groups may cause, in particular, a crystal transformation from cellulose I to cellulose II, thus increasing the reactivity of cellulose.

Ceric Consumption

The consumption of Ce(IV) during grafting and oxidation of cellulose bearing cyanoethyl along with carboxyethyl groups, cyanoethyl cellulose, and the control are illustrated in Figure 9. It is clear that with the three substrates, though it differs considerably during grafting, Ce(IV) consumption is higher than during their oxidation. This is already discussed.

On the other hand, the consumption during oxidation of the three substrates is rather interesting. Whereas introducing cyanoethyl groups in the cellulose molecules reduces significantly its susceptibility to Ce(IV) attack by decreasing swellability and partial inhibition of Ce(IV)–cellulose complex formation,[20] further reduction in the susceptibility was brought about by creation of carboxyethyl groups through partial hydrolysis of cyanoethyl groups. Disappearance of some of the cyanoethyl groups (sites for Ce(IV) attack) through either hydrolysis to carboxyethyl and/or cleavage of the ether bond may account for this. In addition, alkali treatment

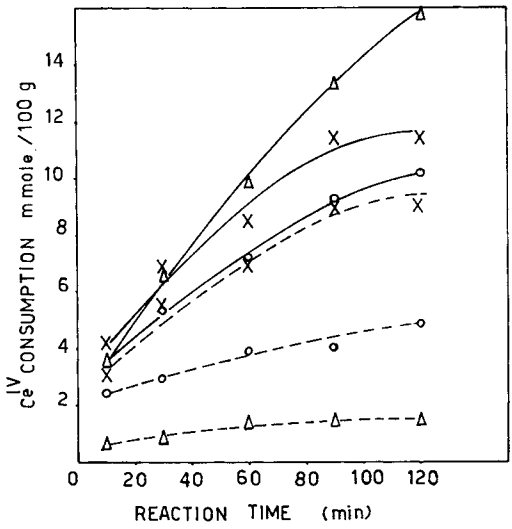


Fig. 9. Ceric consumption as a function of reaction time. CAS concn., 0.01*M*; AN, 1 g; cellulose, 1 g; temp., 40°C; M/L ratio, 1:30: (——) consumption during grafting; (- - -) consumption during oxidation; (△) cellulose bearing cyanoethyl groups (D.S. = 0.06) and carboxyethyl groups (D.S. = 0.0376); (○) cyanoethyl cellulose (D.S. = 0.515); (×) cellulose treated with 2% sodium hydroxide (control of cyanoethyl cellulose).

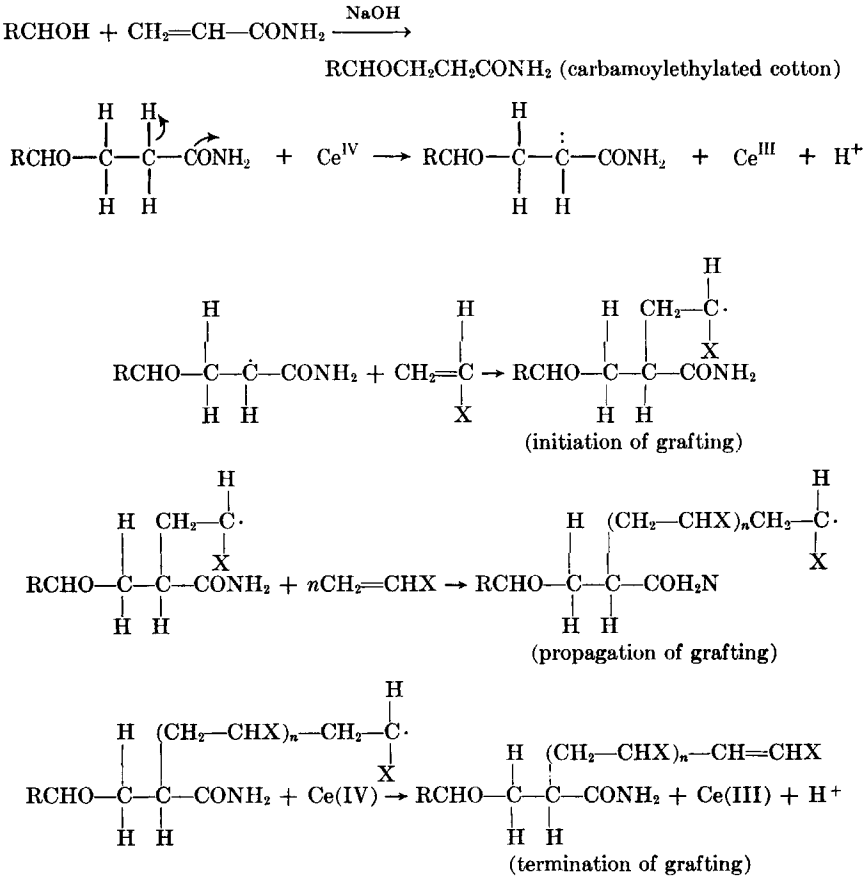
(used for hydrolysis) produces a substrate which acquires higher grafting efficiency (cf. Fig. 8) but with lower efficiency to Ce(IV) attack. A similar observation was reported when cotton treated with concentrated sodium hydroxide showed a higher graft yield and lower Ce(IV) consumption than similar but untreated cotton.[9]

Grafting on Cellulose Bearing Carbamoylethyl Groups

Graft Yields

Figure 10 shows the results of graft polymerization of AN on carbamoylethyl cellulose and those obtained with cellulose treated with 3.8% NaOH (control) using CAS as initiator. A similar trend was obtained when MMA was used as monomer. It is clear that for a given reaction time and at a particular temperature, the graft yield obtained with carbamoylethyl cotton is substantially higher than that of the control. Besides opening up the cellulose structure, the carbamoylethyl groups seem to afford additional sites for grafting. Presence of $-CONH_2$ grouping with negative inductive effect would facilitate the hydrogen transfer during Ce(IV) attack. Thus, beside the free-radical formation at the cellulose hydroxyls, free radicals at the α-carbon atom of the carbamoylethyl groups are very likely to occur.

The following reaction scheme is suggested for initiation, propagation, and termination of the vinyl graft polymerization on the carbamoylethylated cotton that take place at the carbamoylethyl group:



where RCHOH is cellulose and CH_2=CHX is a vinyl monomer.

Ceric Consumption

Data for Ce(IV) consumption during grafting and oxidation of carbamoylethylated cotton and the control are shown in Figure 11. The data indicate that despite the change in the chemical structure of cellulose by carbamoylethylation, its susceptibility towards Ce(IV) oxidation remains practically unaltered. It appears that the adverse effect of blocking some of the cellulose hydroxyls on the susceptibility of cellulose toward Ce(IV) attack in case of carbamoylethylated cotton is counterbalanced by a favorable Ce(IV) attack at the carbamoylethyl groups.

Grafting on Cellulose Treated with N-Methylolacrylamide in Alkaline Medium

Graft Yield

Like other etherification reactions of cellulose such as cyanoethylation, reaction of cellulose with N-methylolacrylamide (MAM) in alkaline me-

dium will proceed via addition of the cellulose hydroxyls to the double bond of MAM as follows:

$$\text{Cell—OH} + \text{CH}_2{=}\text{CHCONHCH}_2\text{OH} \rightarrow \text{Cell—O—CH}_2\text{—CH}_2\text{—CONHCH}_2\text{HO}.$$

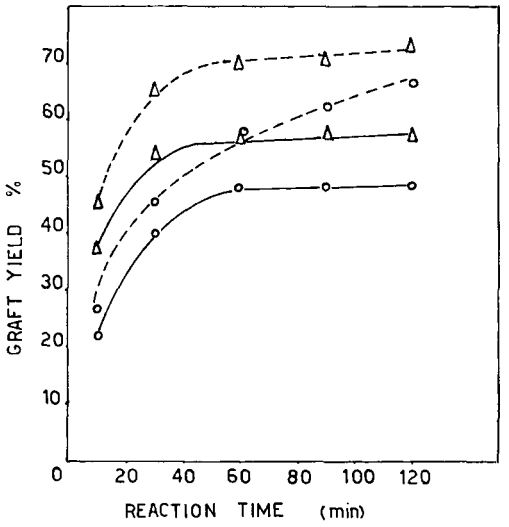


Fig. 10. Graft yields obtained with carbamoylethyl cellulose (D.S. = 0.122) and with cellulose treated with 3.8% sodium hydroxide (control) when acrylonitrile was used as monomer and CAS as initiator. CAS concn., 0.01*M;* AN, 1 g; cellulose, 1 g; M/L ratio, 1:30: (- - -) carbamoylethyl cellulose; (——) control; (O) 40°C; (Δ) 60°C.

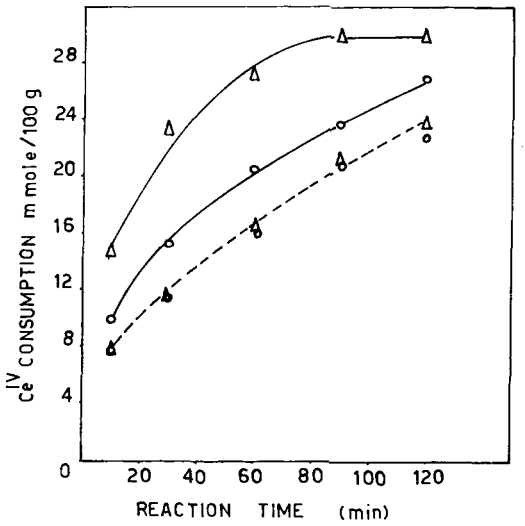


Fig. 11. Ceric consumption during grafting and oxidation of carbamoylethyl cellulose (D.S. = 0.122) and cellulose treated with 3.8% sodium hydroxide (control) using CAS. CAS conc n., 0.01*M;* AN, 1 g; cellulose, 1 g; temp., 60°C; M/L ratio, 1:30: (——) grafting; - - -) oxidation; (Δ) carbamoylethyl cellulose; (O) control.

Introducing such a bulky group, i.e., —$CH_2CH_2CONHCH_2OH$, into the cellulose chains would be expected to improve the reactivity of cellulose toward grafting with Ce(IV), perhaps by opening up the cellulose structure and/or presence of methylol group with its higher known reactivity. However, since the graft yields obtained with cellulose treated with MAM are substantially lower than those of the control, the above expectation is not valid (cf. Table I). This would suggest that MAM reacts with cellulose in alkaline medium as a bifunctional compound to yield a crosslinked cellulose as follows:

$$2\,\text{Cell—OH} + CH_2{=}CHCONHCH_2OH \rightarrow \text{Cell—O—}CH_2\text{—}CH_2\text{—CONHCH}_2\text{—O—Cell.}$$

It is noteworthy to point out that treating cotton fabric with MAM in alkaline medium improves significantly its easy care properties, suggesting a crosslinking reaction.[30] Thus, besides its lower swellability, the crosslinked cellulose acquires less available hydroxyl groups. The effect of this is to adversely affect diffusion of the monomer and initiator as well as reduce the number of grafting sites on the cellulose backbone, thereby lowering the graft yield.

TABLE I
Graft Yields of Cotton Treated with N-Methylolacrylamide in Alkaline Medium (Modified Cotton) D.S. = 0.1, and of Cotton Treated with 2% KOH (Control)[a]

Reaction time, min	Control, graft %		Modified cotton, graft %	
	40°C	60°C	40°C	60°C
10	20	35.3	21	30.8
30	37.4	48.8	34	43.2
60	43.6	54.3	37.6	49.4
90	45.6	58.6	42.5	49.4
120	48.0	58.6	42.8	49.4

[a] CAS concn, 0.01*M*; AN, 1 g; cellulose, 1 g; M/L ratio, 1:30.

Ceric Consumption

Table II contains data for the Ce(IV) consumption during grafting and oxidation of cellulose treated with MAM and the control. Obviously, while the Ce(IV) consumption during oxidation of cellulose treated with MAM is marginally lower than that of the control at 40°C, it is much greater with the former than with the latter at 60°C, particularly at the later stages of the reaction. This suggests that at higher temperature, i.e., 60°C, and on prolonging the reaction time in acidic medium, breaking of the crosslinks seems to occur:

$$\text{Cell—O—}CH_2CH_2\text{CONHCH}_2\text{—O—Cell} \xrightarrow[\text{Ce(IV)}]{H_2SO_4} \text{Cell—O—}CH_2CH_2\text{CONHCH}_2OH + \text{Cell—OH.}$$

TABLE II
Ceric Consumption During Grafting and Oxidation of Cotton Treated with N-Methylolacrylamide in Alkaline Medium (Modified Cotton), D.S. = 0.1, and of Cotton Treated with 2% KOH (Control)[a]

Reaction time, min	Ce(IV) consumption, mmole/100 g cellulose							
	Control				Modified cotton			
	Oxidation		Grafting		Oxidation		Grafting	
	40°C	60°C	40°C	60°C	40°C	60°C	40°C	60°C
10	4.5	5.7	5.4	7.8	3.6	12.9	5.1	9.3
30	6.8	8.4	6.3	13.2	6.3	14.7	6.9	15.6
60	8.7	11.4	9.3	20.4	6.9	17.4	7.5	20.1
90	9.9	16.5	10.5	22.2	8.4	27.0	9.6	23.4
120	9.9	18.0	10.5	28.0	8.7	28.8	9.9	26.4

[a] CAS concn, 0.01*M*; AN, 1 g; cellulose, 1 g; M/L ratio, 1:30.

It follows from this that during oxidation with Ce(IV) at 60°C, there is a significant change in the physical as well as chemical structure of cellulose treated with MAM. In addition to the molecular rearrangement of the cellulose molecules, CH_2—CH_2—$CONHCH_2OH$ groups are created as side groups along the cellulose molecules. As a result susceptibility of cellulose toward Ce(IV) attack increases. Since the graft yields obtained with cellulose treated with MAM are lower than the control, even at 60°C, the excess Ce(IV) consumed during oxidation of the former is presumably due to fast initiation and termination rates of free radicals formed at the side group of cellulose treated with MAM.

CONCLUSIONS

The effect of the change in the physical and/or chemical structure of cellulose brought about by different etherification reactions on the behavior of cellulose toward grafting was investigated. The following etherification reactions were chosen for this study to represent a wide range of functional groups having different natures: (1) acrylamidomethylation, (2) carboxymethylation followed by acrylamidomethylation, (3) carboxymethylation followed by cyanoethylation, (4) cyanoethylation followed by carboxyethylation, (5) carbamoylethylation, and (6) reaction of cellulose with N-methylolacrylamide in alkaline medium. The grafting reaction was studied with respect to the graft yield and Ce(IV) consumption. Conclusions obtained from these studies are presented below.

Graft Yield

1. With all substrates studied, the grafting reaction shows an initial fast rate followed by a slower rate. This is attributed to a rapid fall in the concentration of monomer and initiator as well as to a decrease in the available sites for grafting on the cellulose molecule.

2. Under the conditions studied, CAN is more efficient than CAS perhaps due to the difference in stability of the nitrate–Ce(IV) and sulfate–Ce(IV) complexes in solutions.

3. Cellulose bearing acrylamidomethyl groups either alone or together with carboxymethyl groups showed lower graft yields than the controls. Increasing the amount of acrylamidomethyl groups causes further reduction in the susceptibility of cellulose toward grafting. This is ascribed to the effect of the acrylamidomethyl group which causes (i) blocking of some of the cellulose hydroxyls, (ii) decrease in the swellability of cellulose, and (iii) production of crosslinked cellulose via homopolymerization of the pendant double bond by the action of Ce(IV), thereby lowering the graft yields.

4. While cellulose bearing either cyanoethyl and carboxymethyl groups showed higher graft yields, cellulose bearing both groups showed lower graft yields. Besides blocking some of the cellulose hydroxyls by carboxymethyl groups, it seems that the latter is located in an O-position to the cyanoethyl group in the anhydroglucose unit of cellulose, thereby inhibiting the function of cyanoethyl groups as additional sites for grafting.

5. Cellulose bearing cyanoethyl and carboxyethyl groups showed higher yields of grafting than cyanoethylated cotton and control, perhaps owing to higher swellability of the former.

6. Introducing carbamoylethyl groups into the cellulose molecules enhances significantly its affinity toward grafting, suggesting free-radical formation at the α-carbon atom of carbamoylethyl groups besides those formed at the cellulose hydroxyls.

7. Treating cellulose with N-methylolacrylamide in alkaline medium seems to produce a crosslinked cellulose with lower susceptibility to grafting.

Ceric Consumption

1. Regardless of the substrate employed or the conditions used, the consumption of Ce(IV) during grafting is higher than that consumed during oxidation, probably due to homopolymer formation.

2. The Ce(IV) consumption during oxidation of acrylamidomethyl cellulose is higher than the corresponding consumption of the control when CAS was used. The situation is reversed on using CAN. The difference in the rate of formation of crosslinked cellulose, which seems to rely on the rates of dissociation of CAN and CAS, would account for this.

3. The above phenomenon was also observed in the case of cellulose bearing acrylamidomethyl and carboxymethyl groups.

4. The Ce(IV) consumption during oxidation of partially carboxymethyl cellulose is very close to that of cellulose bearing carboxymethyl and cyanoethyl groups. This suggests that the Ce(IV) consumption for complex formation, being higher in the case of the former due to more availability of cellulose hydroxyls, is compensated by the direct attack of Ce(IV) on cyanoethyl groups.

5. Cellulose bearing cyanoethyl and carboxyethyl showed lower Ce(IV) consumption during oxidation than the cyanoethylated cotton. Disappearance of some of the cyanoethyl groups (sites for Ce(IV) attack) through

either hydrolysis and/or cleavage of the ether bond, during the introduction of carboxyethyl groups, may account for this.

6. Introducing carbamoylethyl groups into the cellulose chains leaves susceptibility of cellulose toward Ce(IV) oxidation practically unaltered. The adverse effect of blocking some of the cellulose hydroxyls with carbamoylethyl groups seems to be outweighed by a favorable Ce(IV) attack at the carbomoylethyl groups.

7. Treatment of cellulose with N-methyloacrylamide in alkaline medium results in a crosslinked cellulose with higher susceptibility to Ce(IV) oxidation than the control at 60°C. This suggests that breaking of the crosslinks occurs during oxidation with Ce(IV) at this temperature.

This work forms part of a Ph.D. thesis of M. H. El-Rafie.

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