Creation of Reactive Centers on Cotton.   IV. Reaction of Acrylamidomethylated Cotton with Some Sulfur Compounds*

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Synopsis

The addition of mercaptoethanol and hydrogen sulfide to the pendent double bonds of acrylamidomethylated cotton (AMC) has been investigated.   The interaction of acrylonitrile with the modified celluloses so obtained (substrate I and II) and with AMC treated with ammonium hydroxide (substrate III) in the presence of Ce(IV) is studied. Substrate I shows higher initial grafting yields than AMC; the opposite holds true for the maximum graft yields.   The graft yields obtained with substrate II are lower than those of AMC.   All modified cottons studied are less amenable to grafting compared with the unmodified cotton.   The graft yields of AMC and substrate III are comparable due to the fact that both substrates are crosslinked.   Probable reasons for the inferior reactivity of substrates I and II are also given.

INTRODUCTION

In part II of this series,[1] the behavior of acrylamidomethylated cellulose (AMC) toward sodium hydroxide, ammonium hydroxide, and hydrochloric acid solutions was investigated.   In the present paper, a study of the addition of mercaptoethanol and hydrogen sulfide to the pendent double bonds of AMC is attempted.   Furthermore, the grafting of acrylonitrile (AN) on the modified cellulose substrates so obtained and on AMC crosslinked by the action of ammonium hydroxide solutions is also investigated.

EXPERIMENTAL

Materials

Cellulose.   Mill-scoured, bleached, and mercerized cotton fabric (poplin, Kafr El-Dawar, Alexandria) was treated with a solution containing 10 g/l. sodium carbonate and 5 g/l. soap at the boil for 4 hr.   It was then thoroughly washed and air dried at ambient temperature.

* Part III.   M. Kamel, S. A. Amin and Ilham El-Kharadly, *Colouristical Review* (Hungary), accepted for publication (1974).

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Modified Celluloses. Acrylamidomethylated cellulose (AMC) was prepared by reacting the cotton fabric mentioned above with N-methylol-acrylamide in the presence of ammonium chloride as a catalyst. Details of the experimental procedure were described elsewhere.[1]

Cellulose bearing $CH_2 \cdot NHCO \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot OH$ groups was prepared by treating AMC with an aqueous solution of mercaptoethanol (0.5%, 0.75%, and 1%) at 25°C for different intervals of time (5, 15, 30, and 60 min) under constant shaking using a liquor ratio of 1:40. The product so obtained is referred to as substrate I.

Cellulose bearing $(-CH_2 \cdot NHCO \cdot CH_2 \cdot CH_2 \cdot S)_2$ groups was prepared by passing hydrogen sulfide gas in an absolute ethanolic medium containing AMC in the presence of sodium sulfide for 3 hr. The modified cellulose thus obtained is referred to as substrate II.

Substrate III was obtained by treating AMC with concentrated ammonium hydroxide (14.2N) at 25°C using a liquor ratio of 1:40 under continuous shaking for 1 hr.

Monomer. Freshly distilled acrylonitrile monomer (AN) was used.

Initiator. Ceric ammonium sulfate, B.D.H. reagent grade, was used after standardization with ferrous sulfate.[2]

Methods

The graft copolymerization of AN was carried out according to a method described by Hebeish and Mehta.[3] Ceric ammonium sulfate solution (0.05M containing 1% sulfuric acid, 30 ml) in a 50-ml stoppered Erlenmayer flask was kept in a thermostat of 40°C for 10–15 min. Acrylonitrile (1 ml) was then added, followed immediately by the cellulosic material (1 g). The flask was well stoppered, and the contents were shaken occasionally during the course of polymerization. At the end of the desired reaction period, the samples were washed well by extraction with several portions of water, with little soap solution to remove the loosely adhering polymer, washed, and dried. It was observed that on further extraction with dimethylformamide (for 24 hr at 30°C), the grafted samples showed a negligible loss. Hence, all the results are based on the increase in weight of the substrate after grafting followed by thorough soaping, washing, and drying. Calculation of the percent grafting was based on dry weights, determined by storing the material in weighing bottles over P_2O_5 at room temperature in a vacuum desiccator until constant weight was obtained:

$$\text{Per cent grafting} = \frac{\text{dry wt of grafted product-dry wt of cellulose}}{\text{dry wt of cellulose}} \times 100.$$

Oxidation of the cellulosic samples with ceric ammonium sulfate was carried out under conditions identical to those described above, except that the monomer was omitted. The ceric consumption during grafting and oxidation was determined according to a method reported by Mino et al.[2]

RESULTS AND DISCUSSION

Addition of Sulfur Compounds

Previous investigators[4] have used mercaptoethanol in the presence of $2N$ sodium hydroxide for the quantitative determination of the double bonds in acrylamide and/or in AMC. A study of the reaction of the same reagent with AMC in the absence of alkali has now been attempted. It is believed that here, too, the reaction would proceed by a nucleophilic addition as follows:

$$Cell-OCH_2NH-\overset{O}{\overset{\|}{C}}-CH=CH_2 + HSCH_2CH_2OH$$
$$\longrightarrow Cell-OCH_2NHCOCH_2CH_2SCH_2CH_2OH$$
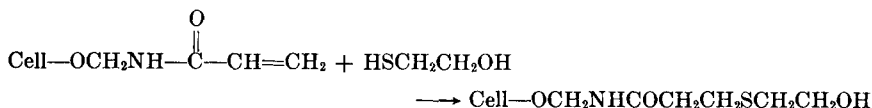
Since the pendent double bonds of AMC are immobile, the extent of the reaction would essentially depend on the concentration of the mercaptoethanol molecules in the proximity of the double bonds; at higher concentrations of the reagent and prolonged time of contact, the reaction increases (Fig. 1).

It is evident from the curves in Figure 1 that full consumption of double bonds occurs in less than 60 min when a concentration of 1% mercapto-
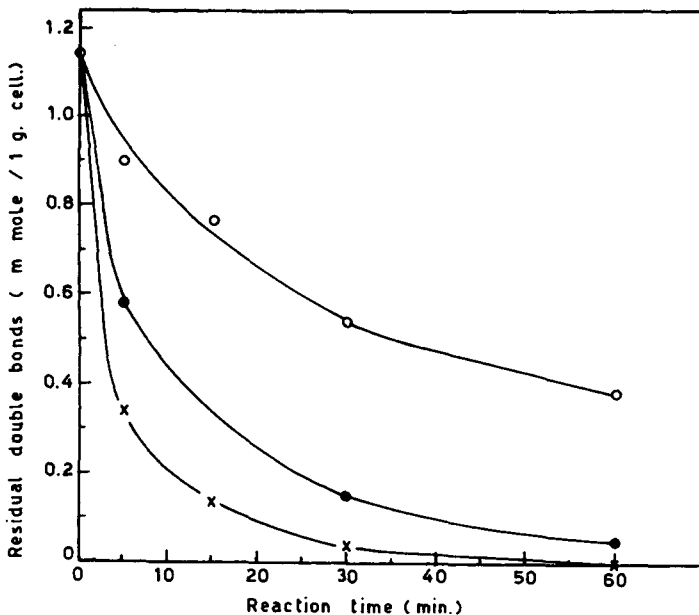

Fig. 1. Residual double bonds as a function of reaction time upon treatment of acrylamidomethylated cellulose with mercaptoethanol: (O) 0.5% mercaptoethanol; (●) 0.75% mercaptoethanol; (×) 1% mercaptoethanol. Temperature, 25°C; M/L ratio, 1:40.
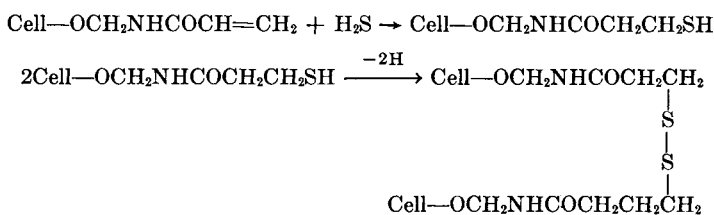
ethanol was used. On the other hand, residual double bonds of ca. 4.5% and 34.5% (based on the original amounts of the double bonds) remained intact when the reaction was carried out even for 60 min using concentrations of 0.75% and 0.5% of the reagent, respectively.

Treatment with H_2S and Sodium Sulfide

It is known that the reaction of acrylamide with H_2S and sodium sulfide affords β,β'-thiodipropionamide[5] according to the following equation:

$$2CH_2{=}CHCONH_2 \xrightarrow[Na_2S]{H_2S} S(CH_2{-}CH_2CONH_2)_2$$
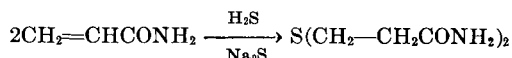
However, it is now found that the same reagents react with AMC to afford disulfide groups which have been detected by reduction with sodium sulfite and treatment with phosphotungtic acid.[6] It is therefore plausible that the reaction proceeds as follows:

$$Cell{-}OCH_2NHCOCH{=}CH_2 + H_2S \rightarrow Cell{-}OCH_2NHCOCH_2CH_2SH$$

$$2Cell{-}OCH_2NHCOCH_2CH_2SH \xrightarrow{-2H} Cell{-}OCH_2NHCOCH_2CH_2$$
$$| \\ S \\ | \\ S \\ |$$
$$Cell{-}OCH_2NHCOCH_2CH_2$$

The consumption of the pendent double bonds of AMC when treated with H_2S and sodium sulfide as described above is shown in Table I. Obviously, increasing the reaction time is accompanied by a significant decrease in the residual double bonds. Complete disappearance of the latter is accomplished after 3 hr.

Grafting Studies

Grafting of Cellulose Bearing $-CH_2NHCOCH_2CH_2SCH_2CH_2OH$
Groups (Substrate I)

Treatment of AMC having 2.72 mmoles double bonds/g cellulose with mercaptoethanol was carried out under conditions which permit complete

TABLE I
Consumption of Double Bonds of AMC Versus Reaction Time Upon Treating
with H_2S and Sodium Sulfide[a]

Reaction time, min	Residual double bonds, mmole/g cellulose
15	0.610
30	0.420
60	0.250
120	0.060
180	0.000

[a] Initial concn. of double bonds = 0.840 mmole/g cellulose.

consumption of the double bonds. The product so obtained was then treated with acrylonitrile (AN) 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 Figure 2 are shown the graft yields obtained with substrate I. Data for the yields obtained under similar grafting conditions with AMC and unmodified cotton are also shown for comparison. It is clear that, with the three substrates, the grafting reaction shows an initial fast rate followed by a slower rate, in conformation with previous results.[3] However, the initial fast rate observed with substrate I and AMC is much lower than that of the unmodified cotton. Moreover, the maximum graft yields obtained with the modified cottons are much less than that of the unmodified cotton.

Comparison between initial grafting yields of AMC and that of substrate I reveals that the latter shows somewhat higher initial yields than the former. The opposite holds true for the maximum graft yields (Fig. 2). The higher initial grafting yields of substrate I may be due to (a) absence of the
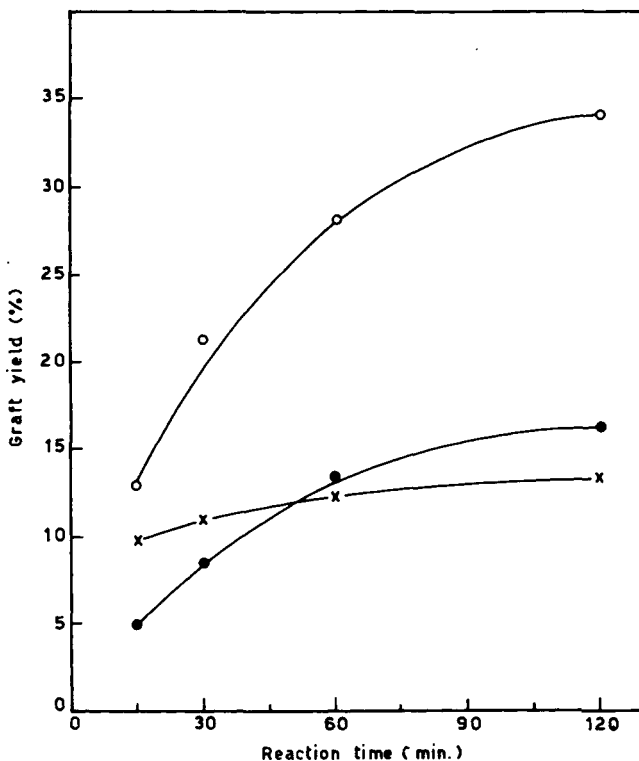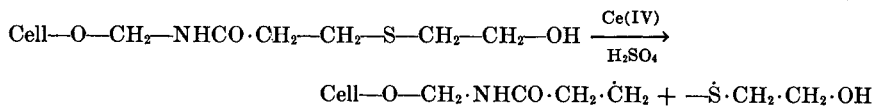

Fig. 2. Grafting of acrylonitrile on substrate I (acrylamidomethylated cellulose pretreated with mercaptoethanol), acrylamidomethylated cellulose (AMC), and unmodified cellulose using ceric ammonium sulfate as initiator: ceric concn., $0.05M$; acrylonitrile, 1 ml; cellulose, 1 g; temperature, 40°C; M/L ratio, 1:30; (×) substrate I; (●) AMC; (○) unmodified cellulose.

adverse effect of the double bonds owing to the addition of mercapto-ethanol molecules to these groups, (b) the probable formation of additional sites for grafting via homolytic scission of —CH—S— bonds under the catalytic influence of Ce(IV):

$$\text{Cell—O—CH}_2\text{—NHCO·CH}_2\text{—CH}_2\text{—S—CH}_2\text{—CH}_2\text{—OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Ce(IV)}}$$

$$\text{Cell—O—CH}_2\text{·NHCO·CH}_2\text{·}\dot{\text{C}}\text{H}_2 + \text{—}\dot{\text{S}}\text{·CH}_2\text{·CH}_2\text{·OH}$$

The lower values of maximum graft yields of substrate I may be attributed to (a) the termination by coupling of radicals formed by the homolytic scission of the —CH$_2$—S— bonds before the monomer has penetrated; (b) penetration of this monomer in the latter stages of the reaction may be impeded by the already present grafted polymer chains; (c) the —$\dot{\text{S}}$—CH$_2$-—CH$_2$OH formed as described above may speed up the homopolymerization of AN, thus causing a depletion in monomer concentration, or combine to form dihydroxyethyl disulfides which would be further oxidized by Ce(IV), thus causing a decrease in the concentration of this initiator.

It has been assumed above that the side groups of substrate I decompose to yield the active species —$\dot{\text{S}}$—CH$_2$—CH$_2$OH which would participate in initiation of homopolymerization during grafting. To check the validity of this assumption, qualitative analysis of sulfur in the homopolymer formed during grafting of substrate I, in the graft copolymer of substrate I, and in substrate I oxidized with Ce(IV) was carried out. Results of these experiments are shown in Table II. As can be seen, of all the possible products of the grafting reaction, only the homopolymer contains sulfur. This may be taken as a direct evidence for the involvement of the free radicals (—$\dot{\text{S}}$—CH$_2$—CH$_2$OH) formed from the decomposition products of the side groups of substrate I.

The consumption of ceric ion by the cellulosic materials in the absence of monomer, i.e., oxidation, and during grafting reaction using ceric ammonium sulfate as initiator is shown in Figure 3 for unmodified cotton, AMC, and substrate I. It is clear that, during grafting and oxidation, the ceric consumption increases by increasing the reaction time regardless of the nature of the cellulosic substrate used. However, with respect to unmodified cotton and AMC, the Ce(IV) consumption during grafting is somewhat

TABLE II
Detection of Sulfur[a] in the Vinyl Copolymerization Products of Cellulose[b]

Reaction time, min	Cellulose graft copolymer	Homopolymer formed during grafting	Oxidized cellulose
15	sulfur absent	sulfur present	sulfur absent
30	sulfur absent	sulfur present	sulfur absent
120	sulfur absent	sulfur present	sulfur absent

[a] The sodium fusion test was used for detection of sulfur.

[b] Polymerization of AN was conducted at 40°C in the presence of substrate I. Ce(IV) concn. = 0.05M; AN = 1 ml; material/liquor ratio = 1:30.
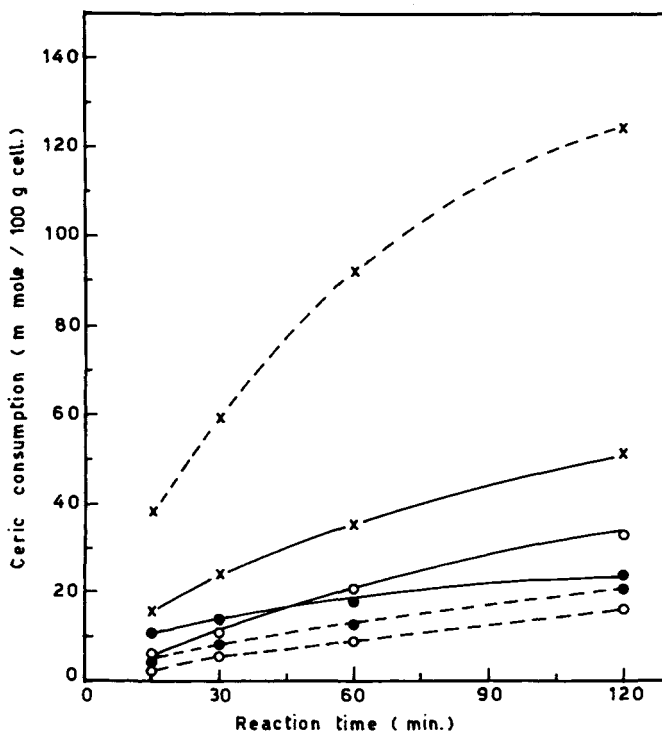
Fig. 3. Ceric consumption during grafting and oxidation of substrate I (acrylamido-methylated cellulose pretreated with mercaptoethanol), acrylamidomethylated cellulose (AMC), and unmodified cellulose using ceric ammonium sulfate: ceric concn., $0.05M$; acrylonitrile, 1 ml; cellulose, 1 g; temperature, 40°C; M/L ratio, 1:30; (———) during grafting; (...) during oxidation; (×) substrate I; (●) AMC; (○) unmodified cellulose.

higher than that during oxidation. The opposite holds true for substrate I. Ceric consumed during grafting in excess of that consumed during oxidation could be attributed to initiation and termination by ceric of homopolymer formed during grafting of the unmodified and AMC.[3,7]

The excess ceric consumption during oxidation over that consumed during grafting in case of substrate I could be interpreted in terms of the decomposition of the side groups to yield —Ṡ—CH_2—CH_2OH radicals. Reaction of such type of radicals among themselves by combination to give the disulfide and/or with hydrogen to give the thioalcohol and further oxidation of these products with Ce(IV) ion would be much easier in the absence of monomer, i.e., during oxidation of substrate I than during grafting. Indeed, this is to be expected since in the presence of monomer (grafting) the —Ṡ—CH_2—CH_2OH radical would participate in initiation and/or termination of the homopolymer formed during grafting.

An additional point of interest is that the values of Ce(IV) consumption for substrate I, in particular during oxidation, are significantly higher than those of unmodified cotton and AMC. This again indicates a reaction

between Ce(IV) ion and the decomposition products of the side groups in substrate I.

Grafting onto Substrate II

The graft yields obtained with substrate II, i.e., cellulose bearing $(—CH_2 \cdot NHCO \cdot CH_2 \cdot CH_2 \cdot S—)_2$ groups, are shown in Figure 4. For ease of comparison, the graft yields obtained under identical grafting conditions with AMC and unmodified cotton are also shown in the same figure. Here, too, with the three substrates in question, the grafting reaction is character-ized by an initial rapid rate followed by a slower rate. Nevertheless, the rates achieved with unmodified cotton are much higher than those of modi-fied cottons and follow the order unmodified > AMC > substrate II. The lower grafting rates of AMC as compared with those of unmodified cotton have already been discussed.

The observation that presence of $(—CH_2 \cdot NHCO \cdot CH_2 \cdot CH_2 \cdot S—)_2$ groups in the cellulose molecule makes it less amenable to grafting is expected, since a crosslinked cellulose with lower susceptibility toward grafting is formed.
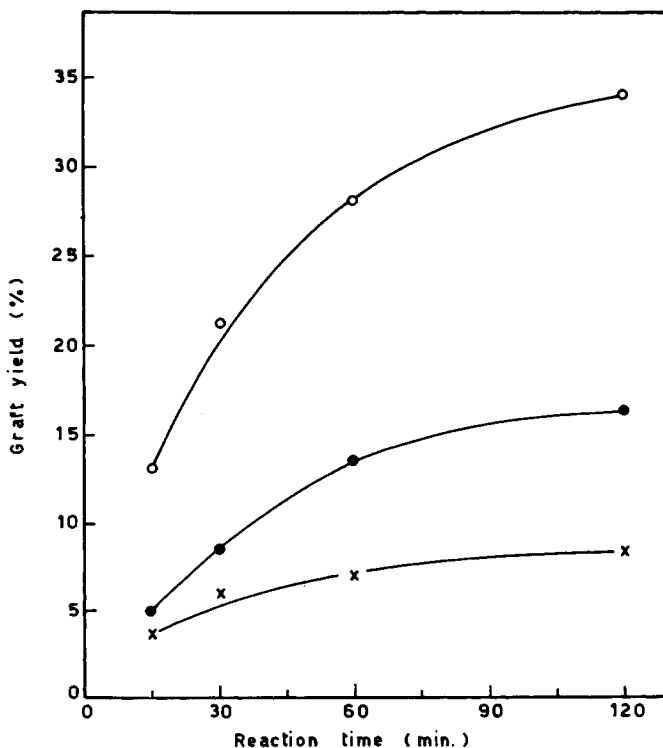

Fig. 4. Graft yields obtained with substrate II (acrylamidomethylated cellulose, AMC, pretreated with H_2S) and those obtained with AMC and unmodified cellulose at various reaction times using ceric ammonium sulfate as initiator: ceric concn., 0.05M; acrylonitrile, 1 ml; cellulose, 1 g; temperature, 40°C; M/L ratio, 1:30; (×) substrate II; (●) AMC; (○) unmodified cellulose.

Consumption of Ce(IV) during grafting and oxidation of substrate II is shown in Figure 5. Similar to substrate I, the consumption of ceric during oxidation of substrate II is much grater than that consumed during its grafting. The values of ceric consumption during oxidation of substrate II are also much higher than those of AMC and unmodified cotton. On the other hand, the values of ceric consumption during grafting of substrate II are comparable to the corresponding values for AMC and unmodified cotton.

The higher values of ceric consumption during oxidation of substrate II compared with those consumed during oxidation of AMC and unmodified cotton could be ascribed to the difference between the redox efficiencies of these substrates with Ce(IV). The presence of disulfide linkages in substrate II renders it more susceptible to oxidation with Ce(IV). The comparable Ce(IV) consumption during grafting of substrate II, AMC, and unmodified cotton would imply that the disulfide bond is hindered in the presence of the monomer during grafting.

Grafting onto Substrate III

In part II of this series, it has been postulated that treatment of AMC with concentrated ammonium hydroxide (substrate III) resulted in addi-
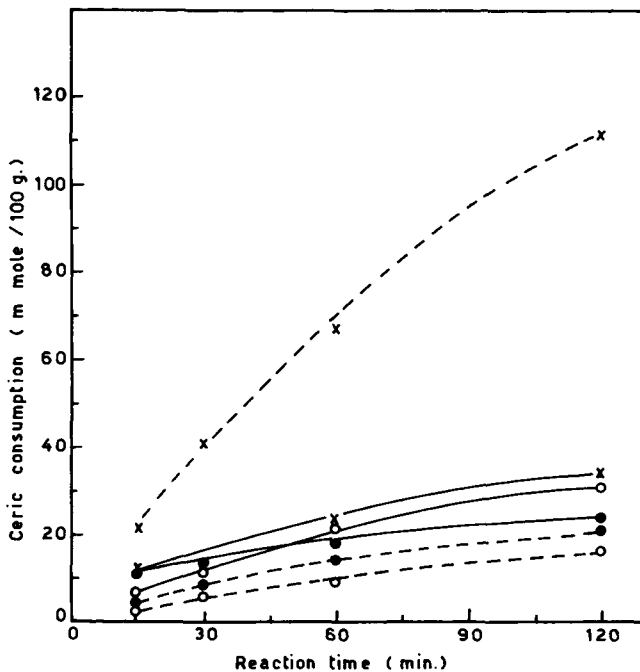

Fig. 5. Ceric consumption by substrate II (acrylamidomethylated cellulose, AMC, pretreated with H_2S), AMC, and unmodified cellulose during grafting and oxidation using ceric ammonium sulfate: Ceric concn., $0.05M$; acrylonitrile, 1 ml; cellulose, 1 g; temperature, 40°C; M/L ratio, 1:30; (———) during grafting; (. . .) during oxidation; (×) substrate II; (●) AMC; (○) unmodified cellulose.
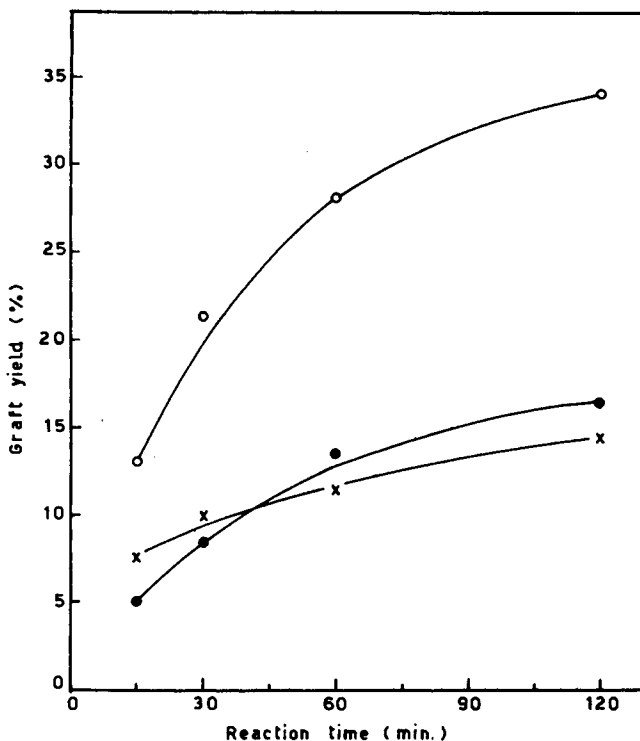
Fig. 6. Grafting of acrylonitrile on substrate III (acrylamidomethylated cellulose, AMC, pretreated with concentrated ammonium hydroxide), AMC, and unmodified cellulose using ceric ammonium sulfate as initiator: ceric concn., $0.05M$; acrylonitrile, 1 ml; cellulose, 1 g; temperature, 40°C; M/L ratio, 1:30; (×) substrate III; (●) AMC; (○) unmodified cellulose.

tion of adjacent cellulose hydroxyls to the pendent double bonds of AMC, i.e., crosslinking. In Figure 6 are shown the graft yields obtained with substrate III together with those of AMC and unmodified cotton.

It is obvious (Fig. 6) that the graft yields obtained with substrate III and AMC are comparable; meanwhile, they are significantly lower than those of unmodified cotton. This would support the postulation that AMC is converted to a crosslinked cellulose either under the catalytic influence of the alkaline medium during ammonium hydroxide treatment or by the action of Ce(IV) during grafting. Thus, besides its lower swellability, the crosslinked cellulose possesses fewer available hydroxyl groups. The effect of this is is to impede diffusion of both monomer and initiator as well as reduce the number of grafting sites.

The consumption of Ce(IV) during grafting and oxidation of substrate III is shown in Figure 7. Obviously, the values of ceric consumption during grafting of substrate III are comparable with those of AMC, a phenomenon which parallels the graft yields obtained with both substrates. But the
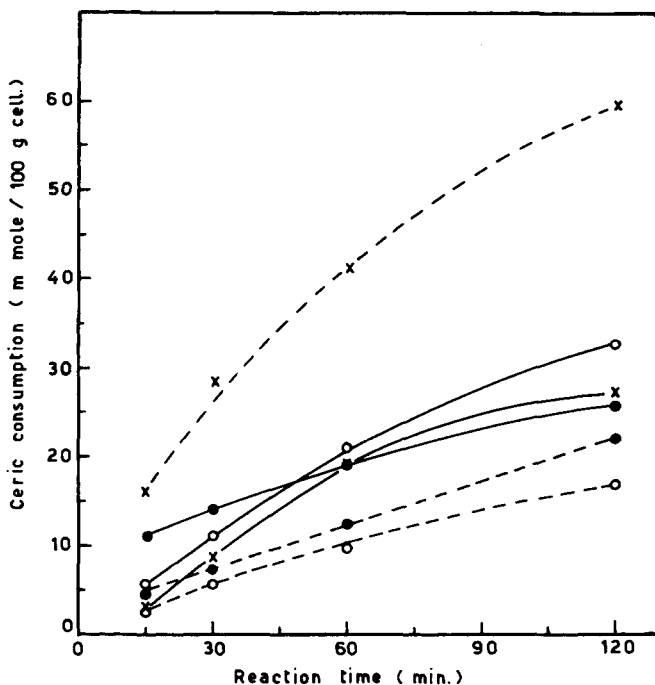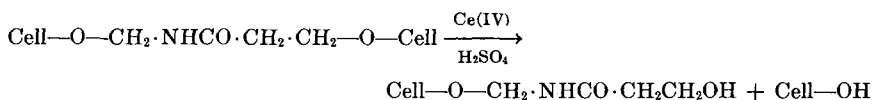
Fig. 7. Ceric consumption during grafting and oxidation of substrate III (acryl-amidomethylated cellulose, AMC, pretreated with concentrated ammonium hydroxide), AMC, and unmodified cellulose using ceric ammonium sulfate as initiator: ceric concn., $0.05M$; acrylonitrile, 1 ml; cellulose, 1 g; temperature, $40°C$; M/L ratio, 1:30; (——) during grafting; (...) during oxidation (×) substrate III; (●) AMC; (○) unmodified cellulose.

consumption of substrate III during grafting is much lower than that during its oxidation, a trend which is opposite to that observed with AMC.

It appears that during oxidation of substrate III with Ce(IV), breaking of the crosslinks occurs:

$$Cell—O—CH_2 \cdot NHCO \cdot CH_2 \cdot CH_2—O—Cell \xrightarrow[H_2SO_4]{Ce(IV)}$$

$$Cell—O—CH_2 \cdot NHCO \cdot CH_2CH_2OH + Cell—OH$$

Hence, there will be significant changes in the physical as well as chemical structure of substrate III during oxidation with Ce(IV). In addition to the molecular rearrangement of the cellulose molecules, $—CH_2 \cdot NHCO \cdot CH_2 \cdot —CH_2OH$ groups are created as side groups in the cellulose molecules. As a result, the susceptibility of cellulose toward Ce(IV) attack, and therefore the ceric consumption, increase. This would not be the case with AMC, since the crosslinks are produced by the action of Ce(IV) in acid medium during oxidation. It is also of interest to point out that breaking of cross-links in substrate III seems to be hindered by the presence of monomer,

since the values of consumption of Ce(IV) during grafting of substrate III are comparable to those of AMC.

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