

Graft Copolymerization of Vinyl Monomers on Modified Cottons. III. Grafting of Acrylonitrile and Methyl Methacrylate on Cyanoethylated Cotton by the Ceric Ion Method

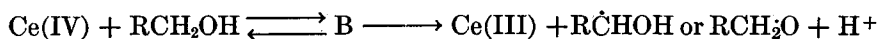
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Synopsis

The interaction of acrylonitrile and methyl methacrylate with cyanoethylated cotton in the presence of ceric ion has been studied under a variety of conditions. Increasing the reaction time, the monomer concentration, and the temperature favorably influences the degree of grafting. The same holds true for initiator concentration up to a certain limit, after which a decrease in the graft yield was obtained. On the other hand, ceric consumption during grafting and oxidation increases by increasing the magnitudes of all these factors. However, the consumption during grafting is always higher than that during oxidation. The graft yields obtained with cyanoethylated cotton are greater than those of the control, being increased by increasing the degree of substitution (D.S.) of the cyanoethylated cotton, suggesting that the cyanoethyl groups afford additional sites of grafting. On the other hand, the ceric consumption during oxidation of cyanoethylated cotton was much lower than that of the control, being increased also by increasing the D.S., indicating perhaps that ceric ion attacks the cyanoethylated cotton exclusively at the cyanoethyl groups. Based on these findings, a scheme for the mechanism of reaction of a vinyl monomer with cyanoethylated cotton was proposed.

INTRODUCTION

Ceric ion-induced graft polymerization of vinyl monomers was first reported by Mino and Kaizerman¹ using organic reducing agents such as alcohols, thiols, glycols, etc., along with ceric ammonium nitrate and sulfate. These authors proposed the following mechanism for initiation of graft polymerization:



where B represents a ceric-alcohol complex, and R $\dot{\text{C}}\text{HOH}$ and RCH $_2\dot{\text{O}}$, free radicals produced on the alcohol. Thus, when cellulose is used as a reducing agent, the formation of homopolymer is greatly suppressed and high graft yields are obtained since the free radicals occur exclusively on the cellulose backbone.

On account of its high grafting efficiency compared to other known redox systems such as persulfate-thiosulfate and ferrous-H $_2\text{O}_2$ systems,²⁻⁴ this

system has gained considerable importance in grafting reactions.⁵⁻¹⁸ Iwakura and co-workers¹¹ have shown that primary alcohols and glycols as graft initiators are more effective than secondary and tertiary alcohols. Mino and co-workers have also shown that in the case of glycols, e.g., pinacol, the 1:2 glycol group is cleaved during the oxidation reaction with Ce(IV). Thus, during grafting of cellulose, too, cleavage of the C₂-C₃ glycol bond is expected in this system of graft initiation. Terasaki and Matsuki,¹⁵ Cumberbirth and Holker,¹³ and Arthur and his associates¹⁶ have also postulated glycol bond cleavage in cellulose during grafting initiated by Ce(IV). Results of the oxidation of cellulose by Ce(IV) reported by Kulkarni and Mehta¹⁷ are in full agreement with this postulation. Hebeish and co-workers¹⁸ also strongly support the same postulation on the basis of kinetic studies of grafting vinyl monomers on acetylated cottons.

The use of Ce(IV) to initiate graft copolymerization of vinyl monomers with various cellulosic materials has been reported.^{10,12,19} Hebeish and Mehta¹⁹ have studied the effect of the fine structure of cellulose on the rate and extent of grafting and have shown that maximum graft yields are directly related to accessibility of the substrate under certain conditions. Recently, we have disclosed that substitution of the cellulose hydroxyls by carboxymethyl²⁰ or acetyl groups¹⁸ greatly affects the graft yields, depending on the degree of substitution (D.S.) of the modified cellulose and the nature of the substituent.

This work presents the results of studies of graft copolymerization of acrylonitrile (AN) and methyl methacrylate (MMA) on cyanoethylated cotton using tetravalent cerium as initiator with a view of investigating the general kinetics of the reaction. The mechanism of the interaction of cyanoethylated cotton with the vinyl monomers was also elucidated.

EXPERIMENTAL

Egyptian Monofi cotton was purified by a mild alkaline scouring (2% sodium hydroxide and 0.2% wetting agent on weight of material) for 5 hr at 110°C and 6-10 lb/in.² using a liquor ratio of 10.

Cyanoethylated cotton having different degrees of substitution were prepared according to a reported method²¹ as follows: The cotton was impregnated with 2% sodium hydroxide solution for 1 hr followed by padding to a pickup of ca. 100%. At this point, the sample was treated with acrylonitrile at 60°C for varying lengths of time. Finally, the sample was soured with dilute acetic acid, washed thoroughly with water, and air dried.

The degree of substitution (D.S.) of cyanoethylated cotton (CEC) was obtained by estimating the nitrogen content of the cotton sample and calculating as follows:

$$\text{D.S.} = 162 \times (\% \text{ N}) / 1400 - [53 \times (\% \text{ N})]$$

A control was prepared by treatment of the cotton slivers with 2% sodium hydroxide for 1 hr. Washing and drying were performed as described above for the cyanoethylated cotton sample.

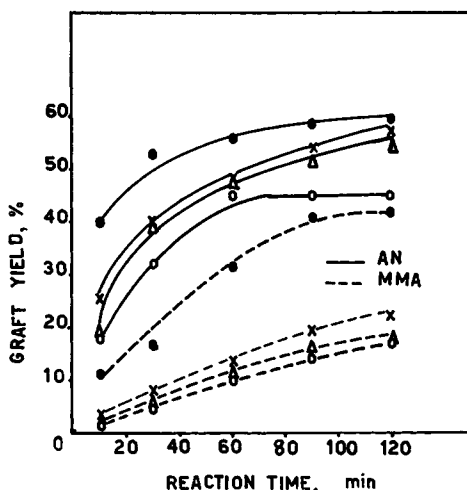


Fig. 1. Effect of D.S. of cyanoethylated cotton (CEC) on rate of grafting: D.S. = (O) 0.0; (Δ) 0.2; (\times) 0.337; (\bullet) 0.515. CAS concn. = 0.01M; temp. = 40°C; M/L ratio = 1:30; AN, MMA, 1g.

Ceric ammonium sulfate (CAS) and ceric ammonium nitrate (CAN), 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% sodium hydroxide solution, washed with distilled water, and air dried over anhydrous calcium sulfate.

The graft copolymerization was carried out according to a method described elsewhere.^{18,20}

A 30-ml portion of ceric salt solution of known concentration containing HNO₃ or H₂SO₄ (1% each for CAN and CAS, respectively) at a specific temperature (30°, 40°, and 60°C) was taken in a 50-ml stoppered Erlenmeyer flask. The required quantity of freshly distilled AN and MMA was then added, followed immediately with 1 g dry cellulosic material. The flasks were immediately stoppered and kept in the thermostat for periods between 10 and 120 min. After the desired reaction time, the samples were washed well by extraction with several portions of water, with a little soap to remove the loosely adhering polymer, washed, and dried. For grafting with AN, it was observed that further extraction of grafted samples with dimethylformamide caused negligible loss in weight. Removal of homopolymer from the fiber was therefore carried out by a thorough soaping and washing; solvent extraction was not considered necessary. In case of MMA, the grafted samples were extracted repeatedly with dry acetone to constant weight. Calculation of the per cent grafting was based on dry weight:

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

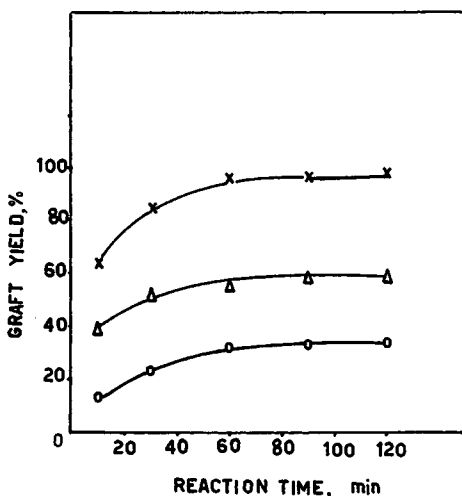


Fig. 2. Influence of acrylonitrile (AN) concentration on the rate of grafting: CEC D.S. = 0.515; CAS concn. = 0.01M; temp. = 40°C; M/L ratio = 1:30. (O) 0.5 g AN; (Δ) 1.0 g AN; (\times) 2.0 g AN.

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

The Ce(IV) consumption during grafting and oxidation was determined by a method of Mino et al.¹⁴

RESULTS AND DISCUSSION

Grafting of AN and MMA on cyanoethylated cotton (CEC) was effected by using the Ce(IV) ion method under a variety of conditions. Variables studied include the D.S. of CEC, temperature, type of initiator, reaction time, and concentration of both monomer and initiator. Kinetics of the reaction were studied with respect to the graft yield and Ce(IV) consumption during grafting and oxidation of the modified cotton with Ce(IV).

Graft Yield

The effect of the D.S. of cyanoethylated cotton on the rate of grafting at 40°C is shown in Figure 1. A similar trend was also observed at 30°C and 60°C. It is apparent that increasing the D.S. causes an appreciable increment in the rate of grafting, in particular at higher D.S. in the range studied. However, with all substrates studied, the grafting reaction proceeds very fast, specially in the earlier stages of the reaction. This holds true for both monomers i.e., AN and MMA. However, the rate of grafting of AN is much higher than that of MMA. Lower solubility in the reaction medium as well as the effect of the two methyl groups in MMA, making growing of the polymer chain sterically more difficult compared to AN, would account for this.

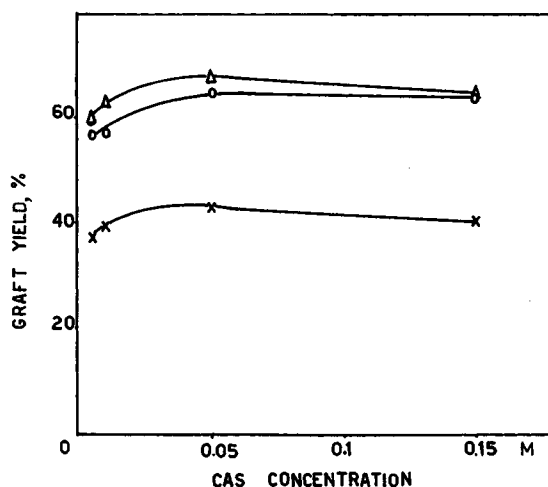


Fig. 3. Graft yield as a function of ceric ammonium sulfate (CAS) concentration: (X) 15 min; (O) 60 min; (Δ) 120 min. CEC D.S. = 0.515; temp. = 40°C; M/L ratio = 1:30; AN, 1 g.

Increasing the D.S. from about 0 to 0.3 is accompanied by an increase in the graft yield. This increase becomes more significant when cyanoethylated cotton of higher D.S., i.e., about 0.5, was grafted. This suggests that the presence of cyanoethyl groups on the cellulose chain offers sites for increased interaction of monomers with the cellulose upon Ce(IV) treatment. A similar observation was reported when AN was grafted on cyanoethylated cotton under high-energy radiation.²²

The effect of monomer concentration on the rate of grafting of cyanoethylated cotton (D.S. = 0.515) with AN may be realized from Figure 2. The rate of grafting is favorably influenced by increasing the concentration of the monomer. With an increase in the monomer concentration from 0.5 g to 2 g, the maximum graft yield obtained increased about threefold.

Figure 3 shows the graft obtained with AN on cyanoethylated cotton (D.S. = 0.515) as a function of the concentration of CAS. It is clear that increasing the CAS concentration up to 0.05M is accompanied by an increase in the graft yield, while further increase brings about lower yields. This is in harmony with previous results^{18,20} where this phenomenon was ascribed to fast termination of the growing polymer chain owing to the presence of excess ceric ion.

The effect of raising the temperature is to bring about a considerable increase in the graft yield. This is quite obvious from the data shown in Figure 4. The rate of grafting of AN and MMA on cyanoethylated cotton (D.S. = 0.515) follows the order 60° > 40° > 30°C. Increasing the temperature seems to cause (a) higher rate of dissociation of CAS, (b) increased solubility of the monomer, (c) increased diffusion of the monomer from the aqueous phase to the cellulosic phase, and (d) enhancement of the rate of initiation and propagation of the grafted chain. All these factors would be

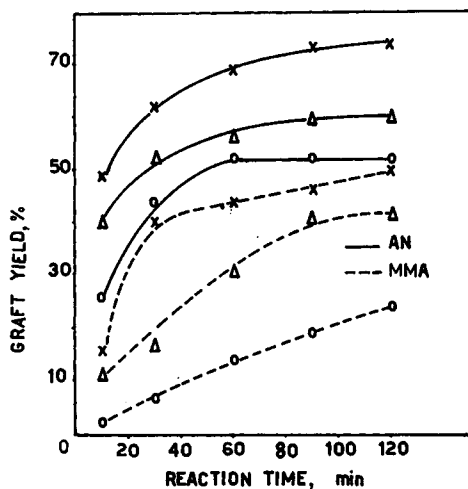


Fig. 4. Grafting of acrylonitrile (AN) and methyl methacrylate (MMA) at different temperatures: (O) 30°C; (Δ) 40°C; (\times) 60°C. CEC D.S. = 0.515; CAS concn. = 0.01M.

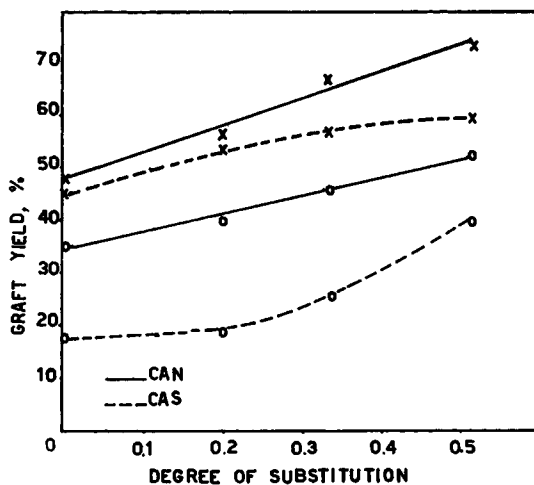


Fig. 5. Graft yield vs. degree of substitution (D.S.) of cyanoethylated cotton when ceric ammonium sulfate (CAS) and ceric ammonium nitrate (CAN) were used: (O) 10 min; (\times) 120 min. CAS, CAN concn. = 0.01M; M/L ratio = 1:30; AN, 1 g; temp. = 40°C.

expected to improve the graft yield. Here, too, at any given temperature the rate of grafting of AN is much greater than that of MMA, a phenomenon which is tallied with the statement given above.

A comparison of the extent of grafting of AN on cyanoethylated cotton having different degrees of substitution when using CAS with that obtained when using CAN may be seen in Figure 5. A similar trend was observed when MMA was used. It is clear that with both initiators the

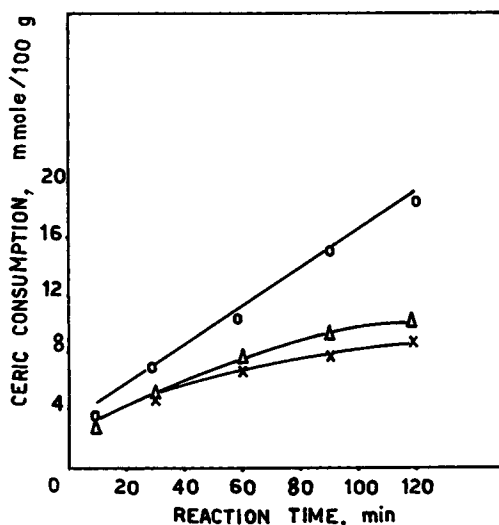


Fig. 6. Ceric consumption during grafting of different concentrations of acrylonitrile (AN) on cyanoethylated cotton (CEC): (O) 0.5 g AN; (Δ) 1.0 g AN; (\times) 2.0 g AN. CEC D. S. = 0.515; CAS concn. = 0.01M; M/L ratio = 1:30; temp. = 40°C.

extent of grafting increases with increasing the D.S. of cyanoethylated cotton. This is in full agreement with the observation pointed out previously. However, the graft yields obtained with CAN are much higher than those obtained with CAS, particularly at short grafting times.

It has been reported that the rate of dissociation of CAN is much faster than that of CAS.^{23,24} Thus, the difference in the graft yield obtained with both initiators could be ascribed to the greater efficiency of CAN in producing active sites on the substrate backbone compared to CAS. This is significant at a short grafting time (10 min) since the rate of initiation is much greater with CAN than with CAS. Allowing the grafting reaction to proceed for a long time (120 min), the difference in the graft yields obtained with both initiators is not that striking. It seems that the slower rate of initiation of CAS encountered at short grafting times is outweighed by a greater creation of new additional grafting sites on the cellulose as the grafting time increases, since more Ce(IV) in the reaction medium would be available compared to CAN. This and the fact that more grafted polymer is obtained with CAN in the early stages of the reaction which impedes diffusion of both monomer and initiator²⁰ would account for the reduction in the difference of the graft yields achieved with the two initiators at long grafting times.

Ceric Consumption

Ce(IV) consumption by cotton and cyanoethylated cottons having different D.S. in the absence of monomer, i.e., oxidation, and consumption during grafting using CAS and CAN as initiators are given in Table I. Consumption is expressed in mmoles/100 g cellulose. It is clear that with all sub-

TABLE I
Ceric Consumption During Oxidation and Grafting of Cyanoethylated Cotton Having Different D.S.^a

Reaction time, min	Oxidation				Grafting (AN)				Grafting (MMA)			
	D.S. = 0.0	0.2	0.337	0.515	D.S. = 0.0	0.2	0.337	0.515	D.S. = 0.0	0.2	0.337	0.515
	Ce(IV) Consumption, 30°C											
10	2.4	0.9	1.34	1.5	3.3	2.7	3.3	3.8	2.7	2.4	2.4	2.4
30	4.2	1.8	2.7	3.0	4.8	5.5	5.7	4.8	4.2	3.3	3.3	3.5
60	5.4	2.7	2.7	3.3	6.2	5.7	6.0	6.0	6.0	4.5	4.2	4.8
90	6.3	3.0	3.0	3.6	7.5	6.3	8.7	7.8	6.6	5.3	5.4	5.4
120	6.3	3.0	3.3	3.8	8.1	7.8	8.7	7.8	7.8	6.3	6.2	6.6
	Ce(IV) Consumption, 40°C											
10	3.0	1.8	2.4	2.4	4.2	3.6	4.2	3.6	2.7	2.7	3.3	3.0
30	5.7	2.4	2.7	3.0	6.9	5.4	5.4	5.4	6.0	4.2	4.9	4.2
60	6.9	3.0	3.6	3.9	8.4	7.8	6.9	6.9	7.8	6.0	7.5	7.2
90	9.0	3.6	3.6	4.0	11.4	9.9	10.2	9.3	9.6	8.7	8.4	9.3
120	9.0	3.6	3.6	4.8	11.3	10.8	11.0	10.2	11.3	10.2	10.1	10.7
	Ce(IV) Consumption, 60°C											
10	6.6	3.6	3.6	4.5	8.7	6.9	7.8	7.8	7.2	5.1	5.4	5.4
30	9.0	3.9	3.9	6.0	19.2	12.3	15.0	14.0	14.4	12.3	12.3	13.8
60	14.7	6.0	6.6	8.4	21.9	14.9	21.3	19.2	24.0	19.8	20.4	19.2
90	18.0	9.0	9.0	9.0	28.8	24.6	25.2	25.8	28.8	25.2	25.2	25.2
120	24.0	10.1	10.5	10.0	30.0	28.8	29.4	29.4	30.0	30.0	30.0	30.0

^a CAS concentration, 0.01M; monomer, 1 g; M/L ratio, 1:30. Ce(IV) consumption expressed in mmoles/100 g cellulose.

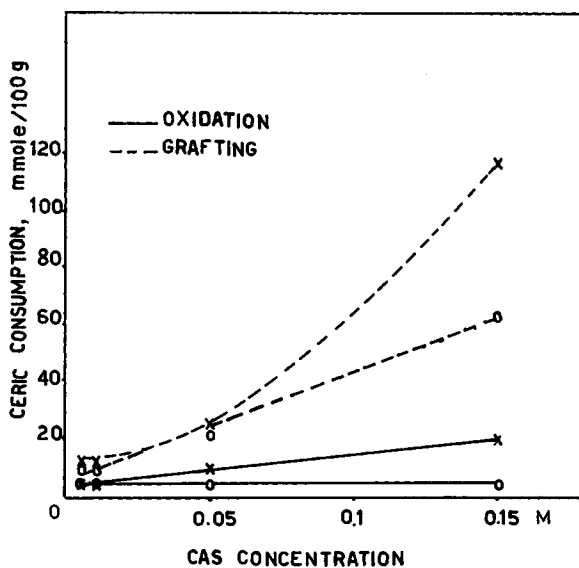


Fig. 7. Effect of ceric ammonium sulfate (CAS) concentration on ceric consumption during grafting and oxidation of cyanoethylated cotton (CEC): (O) 15 min; (X) 60 min. CEC D.S. = 0.515; M/L ratio = 1:30; temp. = 40°C; AN, 1 g.

strates studied, the Ce(IV) consumption increases with increasing reaction time. However, the consumption during grafting is much greater than that during oxidation. Hebeish and Mehta¹⁹ noticed the same with various cellulosic substrates and ascribed this phenomenon to homopolymer formation.

The Ce(IV) consumption during grafting and oxidation depends on the reaction conditions and type of initiators. Raising the temperature causes an appreciable increase in the Ce(IV) consumption (Table I). This is unequivocally due to the greater rate of dissociation of the ceric salt as the temperature increases.

Increasing the monomer concentration is also accompanied by a considerable increment in the consumption (cf. Fig. 6). At higher concentrations, more monomer would be available for grafting as well as for Ce(IV) attack. The effect of the latter on the monomer is to bring about a considerable amount of homopolymer formation. As a result, more Ce(IV) is consumed.

The trend observed with increasing monomer concentration holds true for initiator concentration where the consumption increases with increasing initiator concentration, particularly during grafting (cf. Fig. 7). It is interesting to note that the graft yields are lowered after a certain level of initiator concentration has been reached (cf. Fig. 3). This would suggest that the higher consumption of Ce(IV) is due to a fast termination rate of the growing polymer chain as well as to homopolymerization in solution.

The consumption observed when CAN was used as initiator is much

higher than that of CAS (Table I). It has been reported that ceric sulfate complex is more stable than the ceric nitrate complex.^{23,24} Thus, the fast dissociation rate of CAN may account for its higher consumption. This is substantiated by the graft yield data (Fig. 5) where CAN is more efficient than CAS in effecting grafting.

Table I contains data for Ce(IV) consumed by the control and by cyanoethylated cotton having different D.S., during grafting and oxidation. It is clear that the consumption during oxidation of the control is much higher than that of cyanoethylated cotton regardless of their D.S. However, the difference in the ceric consumption is marginally decreased at higher D.S. The lower consumption observed with cyanoethylated cotton as compared with the control may be explained as follows:

The presence of cyanoethyl groups along the cellulose chain would be expected to bring about (a) opening up the cellulose structure, (b) blocking some of the cellulose hydroxyls, (c) adding new functional centers on the cellulose molecule, and (d) eventual location of the Ce(IV) attack. The effect of (a) and (c) is to promote oxidation by Ce(IV), whereas (b) and (d) would have the reverse effect. Previous reports^{17,18} showed that the total consumption of Ce(IV) during oxidation of cellulose is due to the formation of a Ce(IV)-cellulose complex and termination of the free radicals produced as a result of the partial dissociation of this complex, as well as initiation and termination of free radicals formed on the hemiacetal groups at the end unit of the cellulose molecule. Thus, the excess in the consumption of Ce(IV) by the control could be ascribed to the easier formation of the Ce(IV)-cellulose complex compared to cyanoethylated cotton, where this may be impeded owing to the absence of some of the cellulose hydroxyls. In other words, the effect of functions (a) and (c) prevails over that of functions (b) and (d).

It is noteworthy that despite the fact that the Ce(IV) consumption during oxidation of the control is higher than that of the cyanoethylated cotton, the graft yields obtained with the latter are much higher than those of the former. The graft yields also increase by increasing the D.S. of cyanoethylated cotton. This suggests that the free radicals formed at the cyanoethyl groups are more easily captured by the monomer during the grafting reaction than those brought about via the dissociation of the Ce(IV)-cellulose complex. It seems that in case of the control, vitiation of some of these free radicals occurred by Ce(IV) even in the presence of the monomer. This implies that the oxidation of the control which may be caused by Ce(IV) during grafting is much higher than that of cyanoethylated cotton. The fact that the Ce(IV) consumptions during grafting of the control and cyanoethylated cotton are comparable would support this supposition.

It is also interesting to point out that the cyanoethyl groups, obtained through nitrogen estimation and expressed as D.S., remain practically unimpaired during oxidation of cyanoethylated cotton with Ce(IV) under various reaction conditions. This may be taken as indication that Ce(IV) oxidation has no effect on the cyanoethyl group in bulk.

Mechanism of the Interaction of Vinyl Monomer with Cyanoethylated Cotton in the Presence of Ceric Ions

When cellulose is oxidized by ceric salts such as ceric ammonium sulfate, free radicals capable of initiating vinyl polymerization are formed on the cellulose. The mechanism proposed for free-radical formation entails a Ce(IV)-cellulose complex of the chelate type, possibly through the C₂ and C₃ hydroxyls. Dissociation of this complex occurs through a transfer of electrons from the cellulose molecule to Ce(IV), thereby causing its reduction to Ce(III), breaking the glycol bond and forming radical sites.¹⁶ Studies on the oxidation of cellulose by Ce(IV) reveal that the reaction proceeds very fast in the initial stage of the reaction owing to the formation of Ce(IV)-cellulose complex and oxidation of the hemiacetal groups of cellulose. At lower ceric concentration, oxidation occurs at C₂ of the anhydroglucose unit of the cellulose molecule without the C₂-C₃ bond cleavage. On the other hand, bond cleavage takes place at high Ce(IV) concentration and prolonged oxidation of cellulose.¹⁷ Recently, this mechanism has been strongly supported by kinetic studies of the grafting reaction of acetylated cotton.¹⁸

Taking this postulation into consideration, one would expect that a substituent group along the cellulose molecules would certainly affect its susceptibility toward grafting, this susceptibility being dependent on the number of groups introduced and the nature of the substituent, as well as its location along the cellulose molecule. Etherification studies have shown that the C₂ group is etherified twice as fast as the C₃ groups.²⁵ Preferential reactivity of C₂ of the anhydroglucose unit of cellulose has also been re-

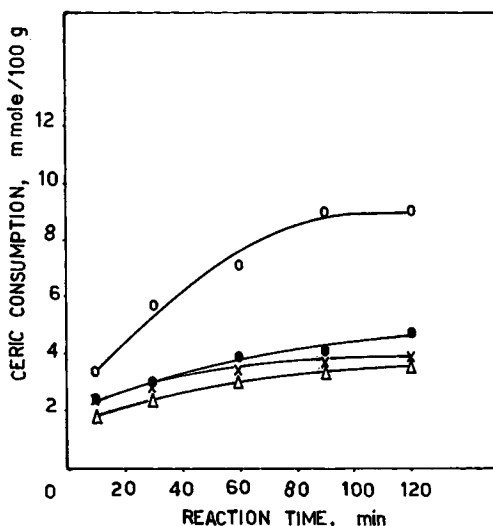
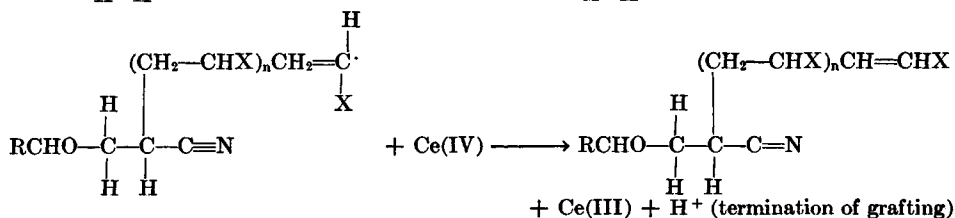
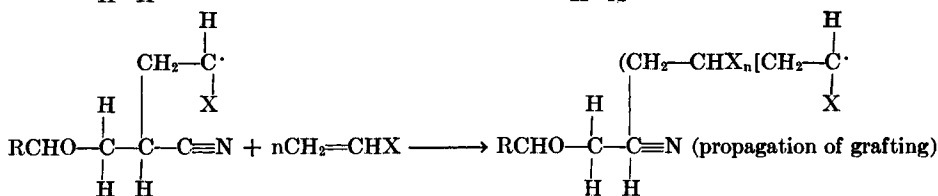
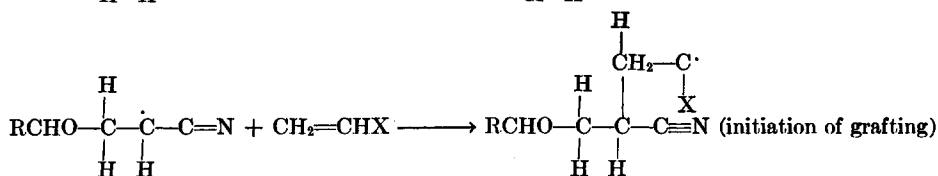
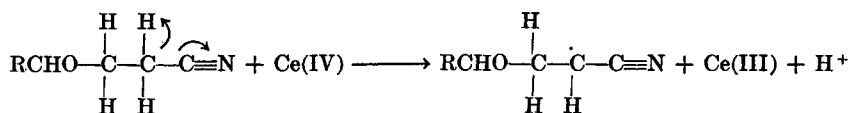


Fig. 8. Rate of oxidation (expressed as ceric consumption) of cyanoethylated cotton having different D.S. values: CEC D.S. (O) 0.0; (Δ) 0.2; (\times) 0.337; (\bullet) 0.515. CAS concn. = 0.01M; M/L ratio = 1:30; temp. = 40°C.

ported.²⁶ Thus, for cyanoethylated cotton and in the range studied, it is possible to assume that most of the cyanoethyl groups are located at C₂. Presence of such groups at this position would definitely inhibit the formation of the Ce(IV)-cellulose complex which involves the glycol groups. As a result, the rate of oxidation of the control is expected to be much greater than that of the cyanoethylated cotton. Indeed, the data given in Figure 8 (cf. Table I) support this expectation.

Figure 1 shows that the graft yields obtained with cyanoethylated cotton are higher than those of the control and that the graft yields increase by increasing the D.S. of cyanoethylated cotton. This suggests, as previously pointed out, that the cyanoethyl groups afford an additional site for Ce(IV) attack. However, since the consumption of Ce(IV) by all samples of the cyanoethylated cotton in the range studied (cf. Table I and Fig. 8) was much lower than that of the control, particularly at the lowest D.S., and since the consumption increases by increasing the D.S., it is possible to state that Ce(IV) attacks the cyanoethylated cotton exclusively at the cyanoethyl group. This is expected, since presence of $-\text{C}\equiv\text{N}$ grouping with $-$ inductive effect would facilitate the hydrogen transfer. Consequently the free radicals very likely form at the α -carbon atom of the cyanoethyl group. The following reaction scheme seems to be plausible for the interaction of a vinyl monomer with cyanoethylated cotton in the presence of Ce(IV):



where RCHOH is cellulose with the hydroxyl group at C₂ of the anhydro-glucose unit and CH₂ = CHX is a vinyl monomer.

It is interesting to note that infrared absorption studies revealed that the hydroxyl band intensities of cyanoethylated cotton grafted with acrylonitrile using γ -radiation were considerably less than the hydroxyl intensity of pure cotton, but that the hydroxyl intensities of cyanoethylated cotton and the cyanoethylated-acrylonitrile graft copolymer were almost the same. It was therefore concluded that grafting had probably occurred at the cyanoethyl group.^{27,28} Our postulation is in full agreement with this conclusion.

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

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