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Ceric Ion-Induced Redox Polymerization of Acrylonitrile on Cellulose*

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Synopsis

The ceric ion–cellulose redox system has been studied for grafting acrylonitrile on cotton fibers. Grafting yields are very high as compared to the persulfate–thiosulfate redox system reported earlier. Traces of copper sulfate in the reaction mixture do not increase grafting yields, unlike the persulfate–thiosulfate system. The high polymerization rate on cotton fibers is shown to be due to the reducing action of cellulose and not to the large surface area of cotton fibers. The Ce^{+4} consumption during grafting is higher than during oxidation of cellulose, indicating formation of homopolymer during the grafting reaction. Studies on the consumption of Ce^{+4} by model compounds such as D-glucose and α-methyl-D-glucoside show that the hemiacetal group in D-glucose is responsible for a faster rate of Ce^{+4} consumption. Formation of a Ce^{+4}–alcohol complex also contributes to the initial fast rate of Ce^{+4} consumption. Studies on the oxidation of cellulose by Ce^{+4} indicate that the initial oxidative attack occurs on carbon atom 2, with the formation of a >C=O group. On further oxidation, cleavage of the C_2–C_3 bond occurs as shown by the presence of glycol aldehyde determined chromatographically. Cellulose–polyacrylonitrile grafts have been isolated by an acetolysis treatment followed by extraction with dimethylformamide. Number-average molecular weights of the isolated fractions are approximately 50,000–55,000. A theoretical method to calculate the number-average molecular weights, based on the PAN and the COOH contents of the grafted cellulose, is described.

INTRODUCTION

The use of ceric ions for initiating graft polymerization of vinyl monomers on cellulosic materials has gained considerable importance recently, due to the high grafting efficiency of this redox system.[1–4] Kaizerman et al.[1] have reported that ceric ammonium nitrate is more efficient for graft polymerization than the corresponding sulfate. It is believed that the initiation of free radicals on the cellulose molecule occurs through a single electron transfer according to a mechanism proposed by Mino et al.[5]

$$RCH_2OH + Ce^{+4} \leftrightharpoons B \rightarrow R\dot{C}HOH + Ce^{+3} + H^+$$

B represents a ceric–cellulose complex which then produces free radicals directly on the cellulose backbone. This mechanism therefore favors grafting much more than homopolymer formation. However, since the ceric ion is a powerful oxidizing agent for alcohols containing a 1,2 glycol

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group,[6,7] both grafting and oxidation of cellulose would proceed simultaneously. The latter reaction is believed to occur mainly at the C_2—C_3 glycol group of the anhydroglucose unit with cleavage of the C—C bond. Thus, the mode of oxidation of cellulose with Ce^{+4} appears similar to that with sodium metaperiodate and has been supported by many workers on the basis of studies on the oxidation of alcohols such as poly(vinyl alcohol)[6] and pinacol[7] and of model compounds such as *trans*-1,2-cyclohexanediol.[4] Recently Arthur et al.[8] have also supported this postulate by ESR studies on Ce^{+4}-oxidized cellulose. However, only scanty information is available on the Ce^{+4}–cellulose system with respect to the efficiency of grafting (i.e., monomer utilization), consumption of Ce^{+4} during grafting and oxidation reactions, and nature of the grafted products (i.e., number-average molecular weights, composition, etc.). The mode of oxidation of cellulose with Ce^{+4} also involves examination of another postulate in addition to that of glycol bond cleavage, viz., the role of the hemiacetal group in the cellulose chains. Terasaki et al.[9] have postulated that the presence of hemiacetal groups in cellulose leads to an initial fast rate of Ce^{+4} consumption. Iwakura et al.[3] have also supported this view based on the finding that D-glucose is very effective for initiation with Ce^{+4}.

Considering these aspects, it was thought that a direct study of the Ce^{+4}–cellulose system would be very useful in elucidating (*a*) some of the important parameters of the grafting reaction and (*b*) the mechanism of oxidation and free radical initiation on cellulose. For this purpose, the ceric ion–cellulose redox system was used together with acrylonitrile monomer (AN) for grafting. This system was selected primarily on account of a slightly higher solubility of AN (approx. 7%) in water than most other vinyl monomers, thus offering a simple reaction system.

MATERIALS AND METHODS

Acrylonitrile monomer, (B.D.H), reagent grade was used after distillation.

Ceric ammonium nitrate, (B.D.H), technical grade, was estimated according to a method reported by Mino et al.[10] All ceric solutions were acidified with fuming nitric acid (1% v/v).

Egyptian cotton slivers were used for the grafting and oxidation studies after scouring and bleaching. Scouring was done with 3% NaOH, 1% Na_2CO_3, 0.5% sodium silicate and 0.05% wetting agent (Lissapol D) on weight of the cotton slivers in a laboratory pressure kier for 8 hr. at a liquor to goods ratio of approximately 10:1 and a temperature and pressure of 120°C. and 18 lb./in.^{2}, respectively. After thorough washing, the scoured material was bleached with sodium hypochlorite (2 g./l. available chlorine; buffered with sodium carbonate to pH 10–11) for 2 hr. at 30°C. It was then washed and given an antichlorine treatment with sodium thiosulfate (0.5%), washed well and dried.

Model compounds such as α-methyl-D-glucoside, D-glucose, and D-mannose were B.D.H. reagent chemicals.

Copper number of the cellulose samples was measured according to a standard method.[11] Carboxyl group determinations were carried out in accordance with the method of Ludtke and Davidson.[12]

The per cent grafted polymer was estimated by weighing the conditioned samples at 65 ± 2% R.H. and 80°F. before and after grafting, the samples being given a light soaping (5% soap solution) in order to remove the loosely adhering polymer. It was observed that the grafted samples did not show any further loss in weight on extraction with cold dimethylformamide (DMF) for 24 hr.; hence extraction of homopolymer in DMF was not considered necessary. It was also reported earlier[13] that the per cent polyacrylonitrile (PAN) grafted to cellulose as estimated by the nitrogen content showed a satisfactory correlation with the increase in weight of the grafted samples. The extent of oxidation of cellulose with chromic acid was determined by measuring the oxygen consumption of the dichromate solution.[14]

Periodate consumption of cellulose samples with sodium metaperiodate was estimated by titration with sodium arsenite.[15] Reduction of the oxidized samples was carried out with sodium borohydride according to a method reported by Nevell.[16]

EXPERIMENTAL PROCEDURES

All polymerization, grafting, and oxidation reactions with ceric ions were carried out at 40 ± 0.05°C. in a thermostat.

Polymerization and Grafting

A 30-ml. portion of acidified ceric solution previously conditioned to 40°C. was taken in 50-ml. glass-stoppered Erlenmeyer flasks. The required quantity of freshly distilled AN was then added to it through a buret, followed immediately with 1 g. of the conditioned cellulose fiber. The flask was immediately stoppered and kept in the thermostat for the required reaction period (2.5–60 min.). During the reaction, the cotton fibers were kept well immersed in the solution. The grafted fibers were then removed, washed well with running water, soaped lightly, washed, and dried. The per cent PAN grafted was calculated by difference in weight between the grafted and the original samples.

It was observed from separate experiments that if the material was kept well immersed in the Ce^{+4} solution, the per cent graft yields obtained in air and in oxygen-free system were comparable with each other.

Oxidation

The cellulose fibers (1 g.) were oxidized with 30 ml. of the acidified ceric ammonium nitrate solution for periods ranging from 2.5 to 60 min., then washed well with distilled water and dried.

The estimation of ceric ion consumption during grafting and oxidation was carried out by pipetting out 5–10 ml. of the ceric solution, neutralizing

it with excess ferrous ammonium sulfate, and back-titrating the excess ferrous salt with ceric sulfate with *o*-phenanthroline as an indicator.

Polymerization in Absence of Cellulose Fibers

A 1-ml. portion of AN was added to 30 ml. of the Ce^{+4} solution and placed in the thermostat. At the end of the specified reaction period, the PAN formed was separated by filtration through a No. 3 sintered crucible and the weight of the polymer estimated after drying and conditioning the sample.

RESULTS AND DISCUSSION

The Grafting Reaction

Figure 1 shows the per cent grafting yields on cellulose fibers and the corresponding polymerization yields in solution in absence of cellulose.

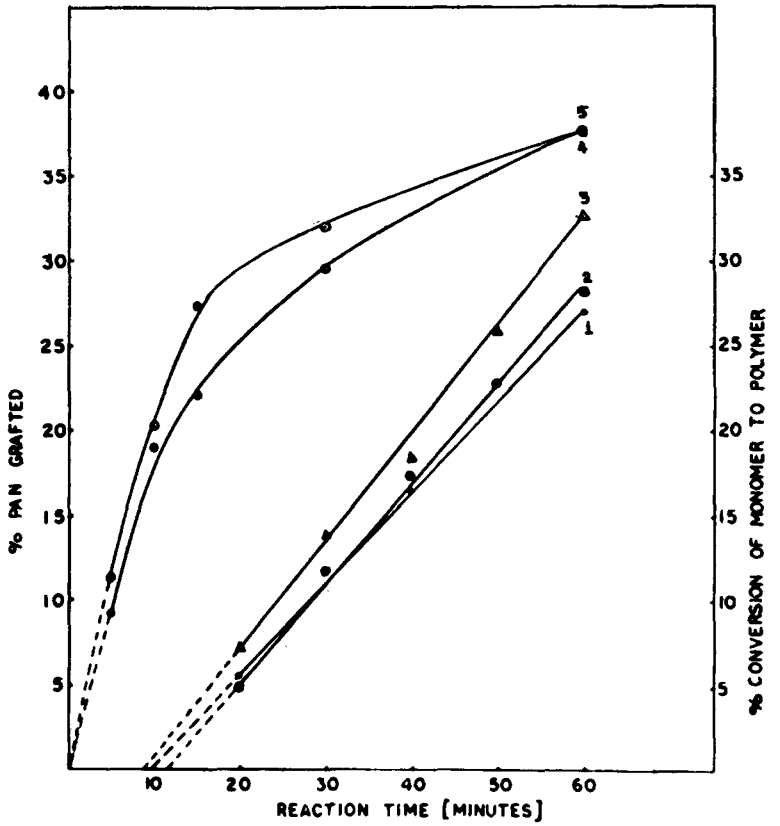


Fig. 1. Effect of surface area and addition of copper sulfate traces, on acrylonitrile polymerization in presence and absence of cellulose: (*1*) polymerization in presence of silica spheres; (*2*) polymerization in absence of cellulose; (*3*) polymerization with traces of copper sulfate (without cellulose); (*4*) grafting in presence of copper sulfate traces; (*5*) grafting without copper sulfate. [Ce^{+4}], 0.006*M*; liquor ratio, 30; acrylonitrile, 1 ml.; cellulose, 1 g.; temperature of reaction, 40°C.

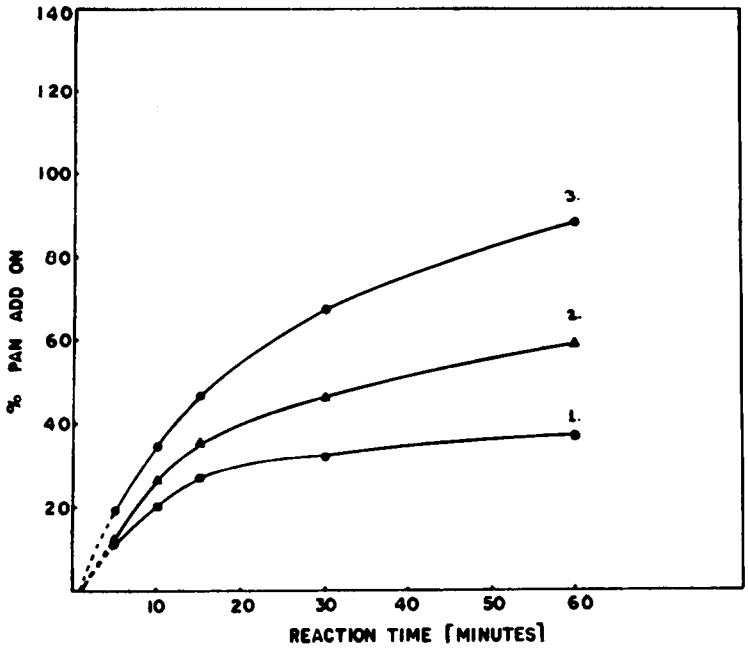


Fig. 2. Effect of monomer concentration on grafting yields at various monomer/cellulose ratios: (*1*) 1 ml./g.; (*2*) 1.5 ml./g.; (*3*) 2.0 ml./g. [Ce^{+4}], 0.006*M*; liquor ratio, 30; temperature of reaction, 40°C.

It is noticed that the grafting reaction proceeds much faster than polymerization without cellulose, showing the high grafting efficiency of the Ce^{+4}–cellulose system. The increased polymerization rates could be due to the large surface area offered by the cellulose fibers. In order to determine the influence of this factor, separate polymerization experiments were conducted on silica spheres (supplied by courtesy of the National Bureau of Standards, U.S.A.) having a surface area of 24 $m.^2/g.$ Assuming a surface area of 112 $m.^2/g.$ for cellulose,[17] 4.6 g. of the silica spheres were used to give the same surface area as 1 g. of cellulose. These data are shown in Figure 1. It is clearly seen that presence of a large surface area, *per se*, for the reaction has not increased the polymerization yields. Hence the high polymerization rates in presence of cellulose fibers must be due to the reducing action of cellulose.

The effect of adding traces of copper sulfate in the grafting and polymerization mixture was also studied. Unlike the persulfate–thiosulfate system[13] in which addition of cupric ions significantly accelerated the grafting reaction by reducing the induction period from 7 min. to 3 min., the rate of grafting remains unaffected in the Ce^{+4}–cellulose system.

The effect of increasing monomer concentration on grafting yields is shown in Figure 2. It is observed that increasing the quantity of monomer from 100% to 200% (on weight of the cellulose fibers) increases the graft yields considerably. In Figure 3, these data are expressed as conversion of

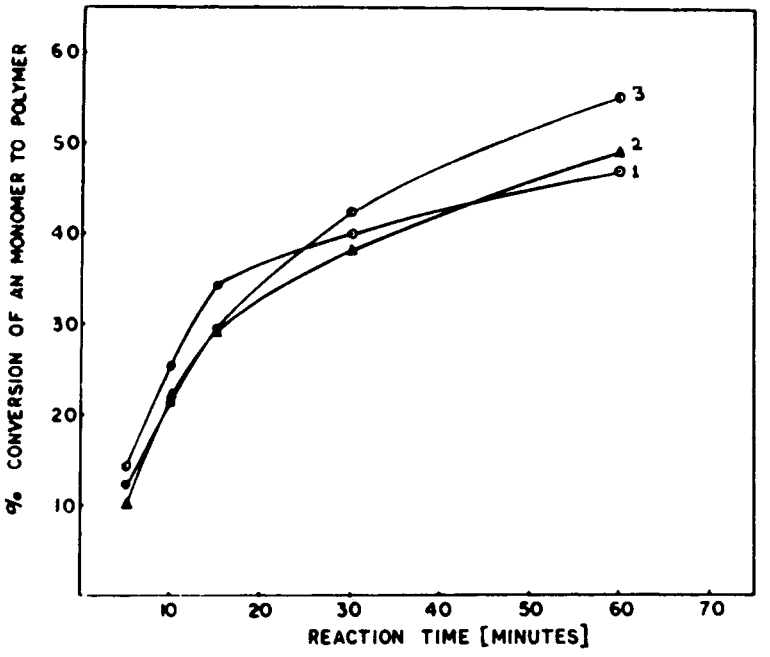


Fig. 3. Conversion of monomer to polymer with increasing acrylonitrile concentration at various monomer/cellulose ratios: (*1*) 1 ml./g.; (*2*) 1.5 ml./g.; (*3*) 2.0 ml./g. [Ce^{+4}], 0.006*M*; liquor ratio, 30; temperature of reaction, 40°C.

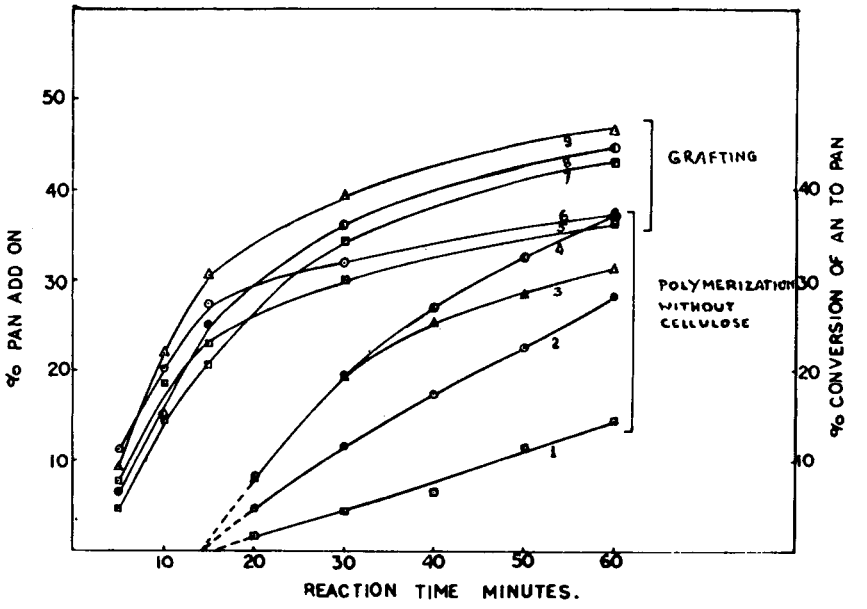


Fig. 4. Effect of initiator concentration on grafting and polymerization yields a various Ce^{+4} concentrations: (*1,5*) 0.005*M*; (*2,6*) 0.01*M*; (*3,9*) 0.05*M*; (*4,8*) 0.10*M*; (*7*) 0.15*M*. Acrylonitrile, 1 ml.; cellulose, 1 g.; liquor ratio, 30; temperature of reaction, 40°C.

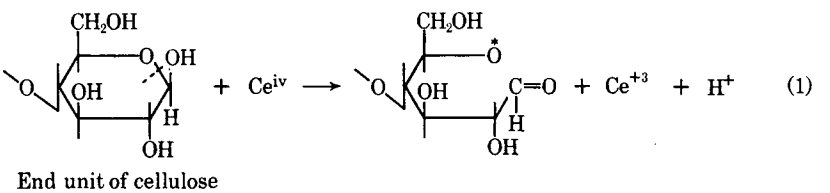
monomer to polymer. Although the per cent conversion increases slightly with the monomer concentration at 60 min., no particular trend is observed at lower reaction periods.

The effect of initiator concentration on the rates of grafting and of polymerization is shown in Figure 4. The rate of polymerization of AN in absence of cellulose increases with increasing Ce^{+4} concentration. There is no slowing down of this rate with time at the two lowest Ce^{+4} concentrations used. The grafting reaction on the other hand, behaves differently. The rate of grafting is very fast initially for all Ce^{+4} concentrations studied, after which it slows down. The difference between the initial and subsequent rates is particularly marked for the two lowest Ce^{+4} concentrations. Possibly this is due to a rapid exhaustion of the initiator from the system. At the higher Ce^{+4} concentrations, rates of grafting as well as grafting yields (after 60 min.) show an inverse relation with the Ce^{+4} concentration. For the ethylene glycol–Ce^{+4}–AN system, Katai et al.[18] also showed that the rate of grafting R_p is inversely related to the Ce^{+4} concentration. They have suggested this system as a model for the Ce^{+4}–cellulose system for grafting.

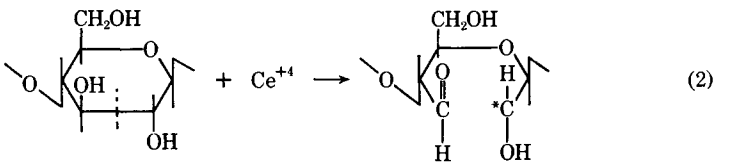
Oxidation of Cellulose by Ceric Ion

As discussed earlier the oxidation of cellulose with Ce^{+4} required examination of two postulates, viz., contribution of the hemiacetal group of the cellulose molecule and cleavage of the C_2—C_3 bond of the anhydroglucose unit.

Contribution of the Hemiacetal Group. When the Ce^{+4} consumption during oxidation of cellulose fibers is plotted as a first-order reaction it does not show a uniform rate (Fig. 5). An initial fast rate is noticed during the first 2.5 min., followed by a slower one. Terasaki et al.[9] have postulated that the hemiacetal groups at the end of cellulose chains receive the initial oxidative attack and hence the initial Ce^{+4} consumption is faster than that during the remaining period. They have distinguished the hemiacetal groups of cellulose as the more reactive groups [eq. (1)] and the C_2—C_3 glycol groups as less reactive [eq. (2)].



End unit of cellulose molecule



In order to examine the contribution of hemiacetal groups, the rates of Ce^{+4} consumption were studied on α-methyl-D-glucoside and D-glucose (Fig. 6). While present data are inadequate for a detailed kinetic treatment, results in Figure 6 indicate the following. Both D-glucose and α-methyl-D-glucoside show a faster initial rate of Ce^{+4} consumption. This rate is significantly higher for the former, which may be due to the greater reactivity of the hemiacetal groups as postulated by Terasaki.

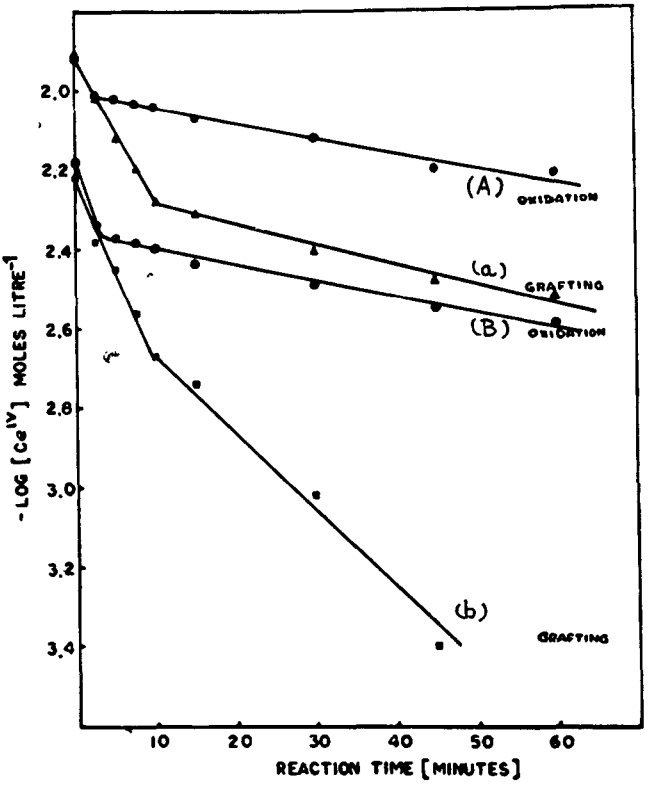


Fig. 5. First-order plot of ceric ion consumption during oxidation and grafting on cellulose: (*A*) oxidation, 0.012*M* Ce^{+4}; (*a*) grafting, 0.012*M* Ce^{+4}; (*B*) oxidation, 0.006*M* Ce^{+4}; (*b*) grafting, 0.006*M* Ce^{+4}. Acrylonitrile, 1 ml.; cellulose, 1 g.; liquor ratio, 30; temperature of reaction, 40°C.

However, the fact that the glucoside also shows a similar behavior suggests that some other factor, besides presence of hemiacetal groups, contributes to a rapid consumption of Ce^{+4} in the initial stages of oxidation. A similar behavior was shown earlier (Fig. 5) also for the oxidation of native cotton cellulose, in which the concentration of hemiacetal groups is so small that it is unlikely to influence significantly the rate of Ce^{+4} consumption. Since the phenomenon is observed for both homogeneous and heterogeneous reactions, accessibility factors cannot explain it.

Formation of a complex with Ce^{+4} may account for the fast initial rate observed in all these cases. Such a complex formation has been shown to occur in the case of transition metals such as Co (III) and V (V) during oxidation of alcohols.[19]

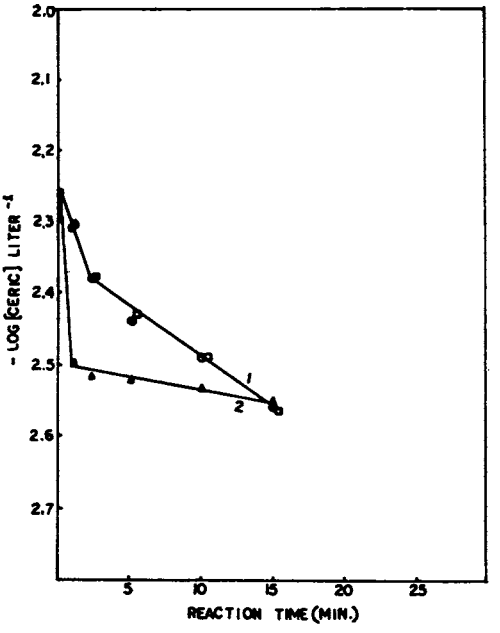


Fig. 6. First-order plot of ceric ion consumption during oxidation of model compounds: (*1*) α-methyl-D-glucoside (□) and α-methyl-D-mannoside (○). (*2*) D-glucose. [Ce^{+4}], 0.006*M*; liquor ratio, 50; temperature of reaction, 40°C.

Thus,

$$R_3C{-}OH + \{Co(H_2O)_6\} \overset{3+}{\rightleftharpoons} \left\{ R_3C{-}\underset{\displaystyle H}{O} \rightarrow Co(H_2O)_5 \right\}^{3+} + H_2O \qquad (3)$$

$$R_2CH(OH) + \{V(OH)_3\} \overset{2+}{\underset{\text{fast}}{\rightleftharpoons}} \text{Complex} \underset{\text{slow}}{\rightarrow} \text{Oxidation Products} \qquad (4)$$

Table I shows data on the (COOH) content of the Ce^{+4} oxidized cellulose fibers, after a further oxidation with chlorous acid to oxidize the aldehyde and carbonyl groups to carboxyls according to a method described by Davidson et al.[20] These data show that the Ce^{+4} consumption is much higher than the (COOH) content of the oxidized cellulose. Assuming that the oxidation proceeds through the steps shown in eqs. (5) and (6),

$$Cell{-}CH_2OH \rightarrow Cell{-}\dot{C}HOH \rightarrow Cell{-}CHO \rightarrow Cell{-}COOH \qquad (5)$$

$$Cell{-}CHOH \rightarrow Cell{-}\dot{C}{-}OH \rightarrow Cell{-}C{=}O \rightarrow Cell{-}COOH \qquad (6)$$

TABLE I
Relationship of Ceric Ion Consumption and Carboxyl Content of the Oxidized Cellulose

$[Ce^{+4}]$/a.g.u.	[COOH]/a.g.u. before chlorous acid oxidation	[COOH]/a.g.u. after chlorous acid oxidation	$[Ce^{+4}]$/[COOH] after oxidation
0.049	0.00045	0.0063	7.85
0.127	0.00089	0.0078	16.28
0.294	0.00089	0.0102	28.82
0.557	0.00112	0.0106	52.54
0.908	0.00112	0.0129	70.38
1.231	0.00134	0.0138	89.20
1.449	0.00224	0.0138	105.00

the theoretical Ce^{+4} consumption would be only three times the (COOH) content when the oxidation reaction reaches completion. Since the actual Ce^{+4} consumption is much higher than the (COOH) content, the formation of a Ce^{+4}–cellulose complex is strongly indicated. The formation of alcohol complexes with cobalt(III) and vanadium(V) are easily noticed due to immediate color change of the oxidizing solutions. In the case of Ce^{+4} also, the solution immediately changed its color from yellow to orange on addition of D-glucose or α-methyl-D-glycoside. The bleached cellulose fiber on oxidation with Ce^{+4} were also colored yellow, and this color persisted even after repeated washing with hot water. These observations support the formation of a complex of Ce^{+4} with the polyhydroxy compound. Such a complex formation would also lead to a rapid consumption of Ce^{+4} in the initial stages of oxidation.

Data in Figure 6 also show that the rate of Ce^{+4} consumption of α-methyl-D-glucoside and α-methyl-D-mannoside is faster than that of D-glucose during the later stages of oxidation. When α-methyl-D-glucoside was treated with dilute nitric acid (1% v/v) at 40°C. for 15 min., the hydrolyzate on neutralization and chromatographic analysis showed some D-glucose and α-methyl-D-glucoside. The hemiacetal groups released

TABLE II
Ceric Ion Consumption during Oxidation and Grafting of Cellulose[a]

Reaction time, min.	Ce^{+4} consumed during grafting, moles	Ce^{+4} consumed during oxidation, moles	Ce^{+4} consumed for homopolymer formation, %
2.5	0.0124	0.0101	18.4
5.0	0.0159	0.0113	29.0
7.5	0.0189	0.0121	36.1
10.0	0.0204	0.0129	36.9
15.0	0.0246	0.0144	41.2
30.0	0.0273	0.0164	39.8

[a] Ceric concentration, 0.006*M*, AN, 1 ml.; liquor ratio, 30; cellulose, 1 g.

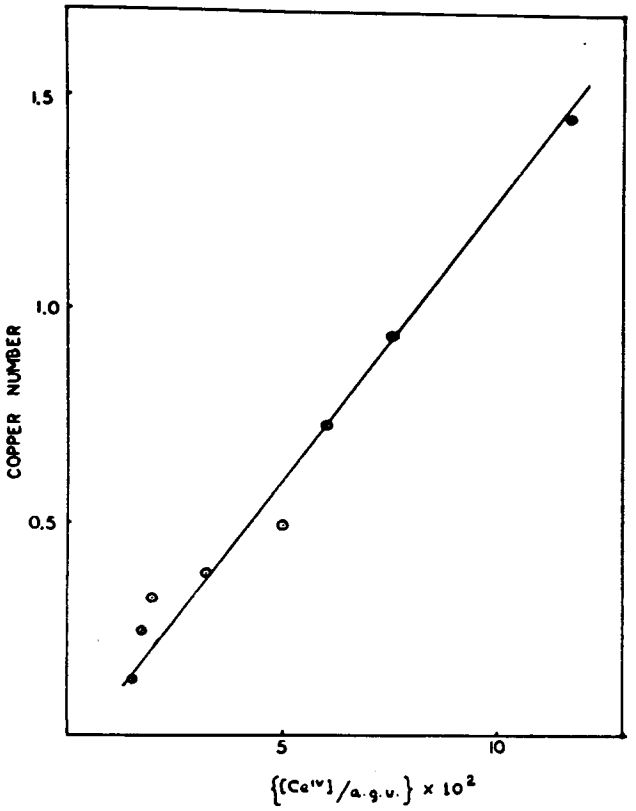


Fig. 7. Relationship between ceric ion consumption and copper number of bleached cotton. Liquor ratio, 30; temperature, 40°C.

by this slow hydrolysis during the course of oxidation are probably responsible for the higher rate of Ce^{+4} consumption by the glucoside in the later stages of oxidation.

Further, it can also be seen from Figure 6, that both α-methyl-D-glucoside and α-methyl-D-mannoside show practically identical Ce^{+4} consumption. This indicates that structural differences in the positions of the C_2—C_3 hydroxyls (e.g., axial and equatorial) do not influence the rate of Ce^{+4} consumption.

Data in Figure 5 show that under similar conditions of reaction, the Ce^{+4} consumption during grafting is higher than that during oxidation. This is probably due to the initiation and termination of polymer chains outside the cellulose phase, i.e., homopolymerization. In Table II, this excess Ce^{+4} consumption during grafting is represented as a measure of the extent of homopolymer formation during grafting. Recent work from this laboratory, to be published shortly, establishes a direct relation between the amounts of homopolymer formed and the difference in Ce^{+4} consumption during oxidation and during grafting.[21]

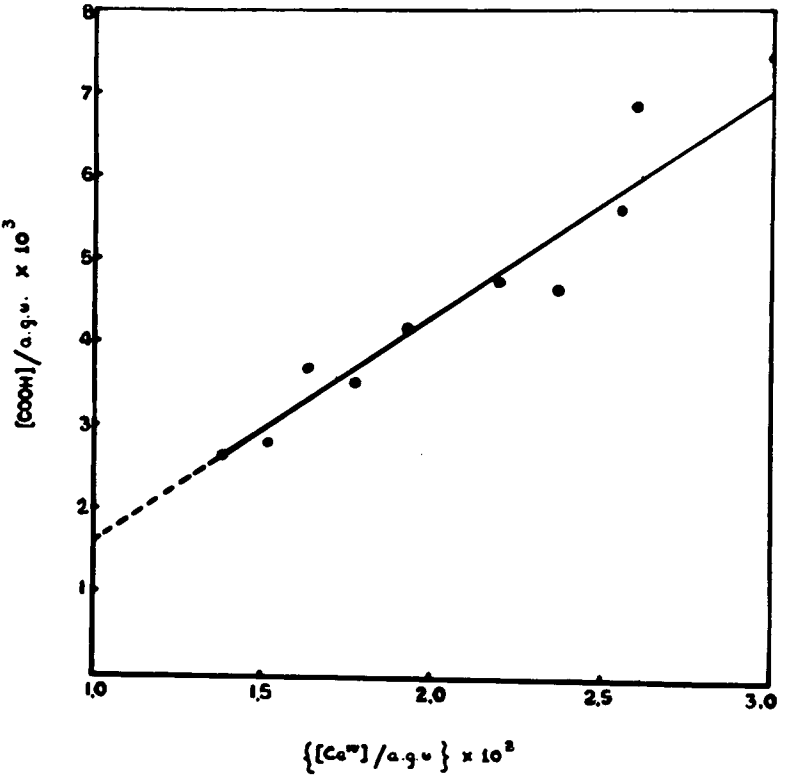


Fig. 8. Relationship between ceric ion consumption and carboxyl content of bleached cotton (after oxidation of the aldehyde/carbonyl groups with chlorous acid). Liquor ratio, 30 (oxidation); temperature, 40°C.

The rise in copper number (Fig. 7) and carboxyl content (Fig. 8) of cellulose is linearly related to the consumption of Ce^{+4} during oxidation.

In order to examine the reactivity of the secondary hydroxyl groups of the anhydroglucose unit to Ce^{+4} oxidation, cellulose was preferentially oxidized at the C_2—C_3 position by sodium metaperiodate and subjected to a second oxidation with Ce^{+4}. Cellulose oxidized with chromic acid (a nonspecific oxidant) was also treated with Ce^{+4} for comparison. These data are shown in Figure 9. Both the oxidized celluloses show a higher Ce^{+4} consumption than the original cellulose, that of the periodate-oxidized cellulose being much higher than of the chromic acid-oxidized one. The effect of increasing the primary hydroxyl groups of cellulose on its Ce^{+4} consumption was also studied, by reducing the periodate oxidized cellulose with borohydride and then subjecting it to a Ce^{+4} oxidation treatment. Since the consumption of periodate was approximately 0.5 mole per anhydroglucose unit in this case, the primary hydroxyl content would have risen approximately twice. However, the Ce^{+4} consumption of the sample was almost seven times that of the original cellulose. The periodate-oxidized (but unreduced) cellulose also showed a Ce^{+4} consumption of nearly the same order.

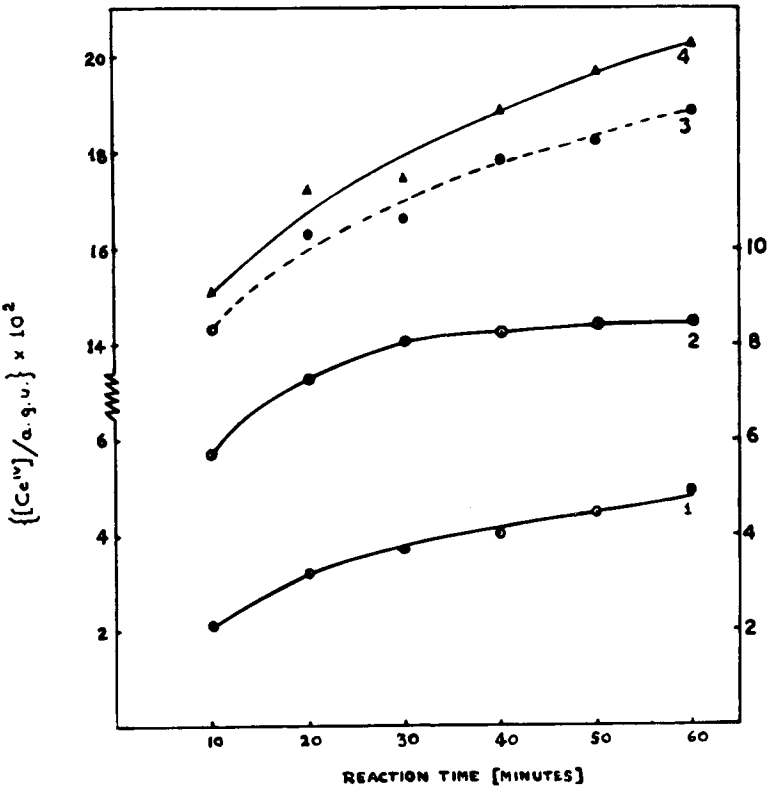


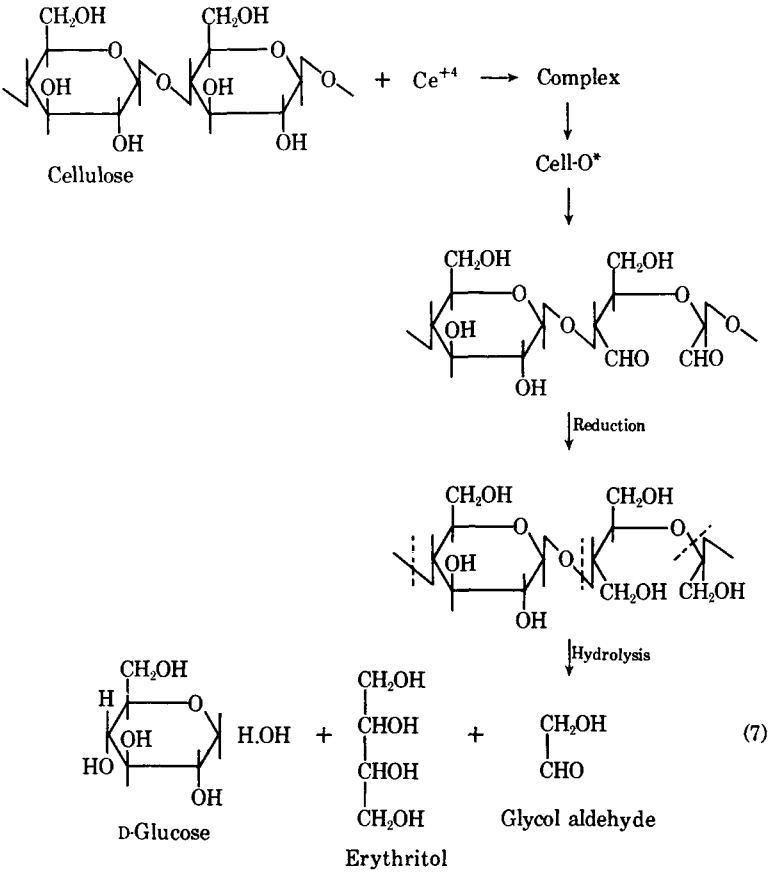
Fig. 9. Consumption of ceric ions by previously oxidized cellulose: (*1*) bleached cotton; (*2*) chromic acid-oxidized cotton (oxygen consumption 3); (*3*) periodate-oxidized cotton (periodate consumption 0.5*M* $NaIO_4$/a.g.u.); (*4*) periodate-oxidized and borohydride-reduced cotton. [Ce^{+4}], 0.05*M*; liquor ratio, 30; temperature of Ce^{+4} oxidation, 40°C.

These data indicate that the Ce^{+4} consumption is not directly proportional to the number of hydroxyl or other functional groups of cellulose. Since the oxidation and reduction treatment produce significant changes in the accessibility of the cellulose fibers, it is likely that the Ce^{+4} consumption would increase due to the net effect of the following factors: (*a*) increase in the accessibility of the modified cellulose, which would increase the rate of Ce^{+4}–cellulose complex formation; (*b*) increase in the terminal end-groups due to a hydrolytic degradation during the chromic acid oxidation, which would increase the hemiacetal groups in the oxidized cellulose.

Oxidation of the C_2—C_3 Glycol Groups of Cellulose

Cumberbirch and Holker,[4] Terasaki et al.,[9] and Arthur et al.[8] have postulated that the C_2—C_3 glycol group of cellulose is cleaved during oxidation of cellulose by Ce^{+4}. Cumberbirch and Holker[4] have supported this postulate on the finding that adipaldehyde is obtained as a product of

oxidation of cyclohexane-1,2-diol by Ce^{+4}, while Arthur et al.[8] have supported this postulate through ESR studies on Ce^{+4}-oxidized cellulose. In the present study, this postulate was examined in detail by following a reaction sequence similar to the oxidation of cellulose by sodium metaperiodate and reduction with sodium borohydride. Assuming that the glycol link at C_2—C_3 is cleaved by Ce^{+4} oxidation, the oxidized cellulose on reduction with borohydride would be converted to a product containing three primary hydroxyl groups in the oxidized anhydroglucose unit. Acid hydrolysis of this product would then yield D-glucose, erythritol, and glycol aldehyde, according to the reactions (7).



The Ce^{+4}-oxidized cellulose was thus reduced with sodium borohydride and hydrolyzed with 72% sulfuric acid in the cold for 16 hr. followed by refluxing with 1*N* H_2SO_4 for 6 hr. The hydrolyzate was neutralized with barium carbonate, filtered, and concentrated. Figures 10 and 11 show these chromatograms. It is evident (Fig. 10) that no erythritol is present in this sample, but along with D-glucose, another sugar is also detected. This has been identified as mannose (Fig. 11). The formation of mannose

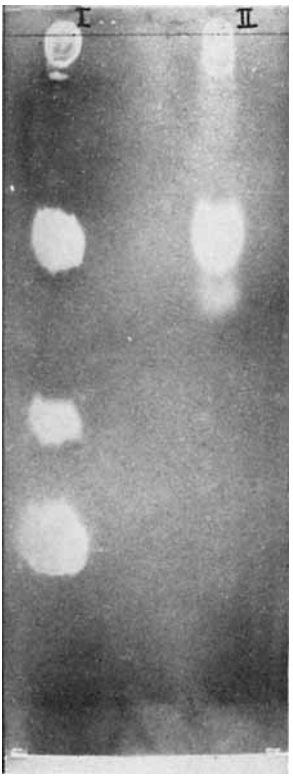
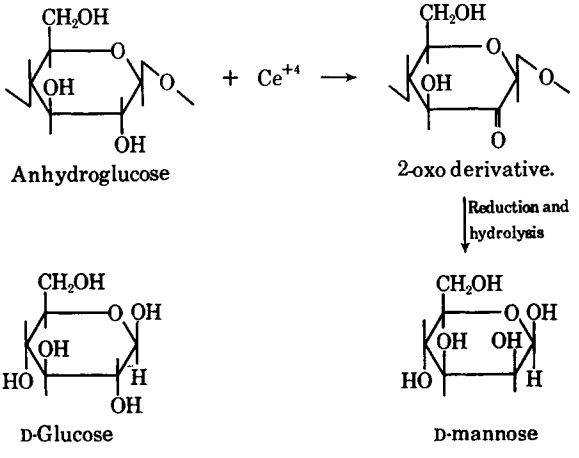


Fig. 10. Chromatographic analysis of Ce^{+4}-oxidized and borohydride-reduced cellulose after acid hydrolysis: (*I*) Galactouronic acid, glucose, erythritol, and glycerol in descending order; (*II*) cellulose oxidized with 0.01*M* Ce^{+4}, 15 min. at 40°C. Chromatography in butanol:pyridine:water (10:3:3).

can be explained by the possibility that the hydroxyl at C_2 is oxidized to a carbonyl group without a C_2—C_3 bond cleavage. Reduction of this 2-oxo anhydroglucose unit with borohydride followed by acid hydrolysis will then yield both glucose and mannose [eq. (8)].



(8)

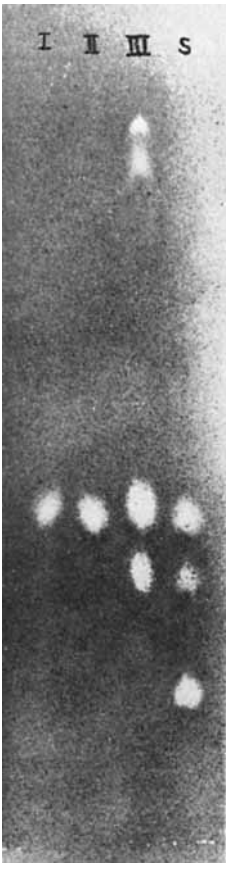


Fig. 11. Chromatographic analysis of ceric-oxidized and borohydride-reduced cellulose after acid hydrolysis: (*I*) original cellulose; (*II*) cellulose treated with 1% HNO_3; (*III*) cellulose oxidized with ceric. (S) Standards (glucose, mannose, and erythritol in descending order). Chromatography in butanol:pyridine:water (6:4:3).

The presence of mannose was detected only in the case of cellulose oxidized with low Ce^{+4} concentrations (0.01*M*) for short periods. Oxidation at higher Ce^{+4} concentrations (0.05–0.1*M*) for 1–2 hr., followed by reduction with borohydride, hydrolysis, and chromatography, did not show mannose (Fig. 12).

The absence of mannose in these samples may be due to the rapid conversion, under more drastic oxidation conditions, of the >C=0 group at C_2 to a —COOH group involving a C—C bond cleavage either at C_1—C_2 or at C_2—C_3 carbon atoms of the anhydroglucose molecule. It is also likely that the CH_2OH group at C_6 is oxidized to a —COOH group in this case.

When a severely oxidized cellulose sample (0.05*M* Ce^{+4}; 16 hr. oxidation at 40°C.) was examined chromatographically after reduction and hydrolysis, the hydrolyzate showed the presence of glycolic aldehyde along with D-glucose. Since no erythritol was detected in this sample either, it appears likely

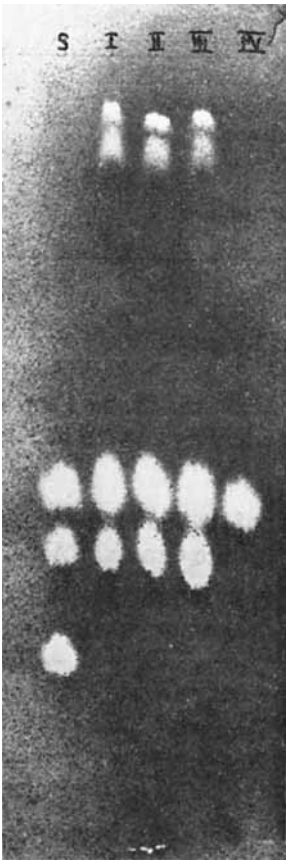


Fig. 12. Chromatographic analysis of ceric-oxidized and borohydride-reduced cellulose after acid hydrolysis under different oxidation conditions: (*I*) 0.01*M* Ce^{+4}, 5 min.; (*II*) 0.01*M* Ce^{+4}, 15 min.; (*III*) 0.01*M* Ce^{+4}, 1 hr.; (*IV*) 0.05*M* Ce^{+4}, 1 hr. (*S*) Standards (glucose, mannose, and erythritol in descending order). Chromatography in butanol:pyridine:water (6:4:3).

that the primary hydroxyl group is also attacked during the oxidation reaction. The occurrence of glycolic aldehyde in this sample is direct evidence of the C_2—C_3 bond cleavage in cellulose during oxidation with Ce^{+4}.

Attempts to isolate and identify D-mannose from the Ce^{+4}-oxidized and borohydride-reduced samples were not successful, due to difficulties in crystallization and fractionation of the products. However, the postulate that the initial oxidative attack occurs at the C_2 position was further substantiated by studies on the oxidation of α-methyl-D-glucoside with ceric ammonium nitrate. A sample of α-methyl-D-glucoside was oxidized with 0.02*M* ceric ammonium nitrate at 20°C. for 15 min. at a liquor ratio of 30. The solution was then neutralized, concentrated, and chromatographed. This sample showed presence of a 2-oxo-α-methyl-D-glucoside along with some D-glucose and unreacted α-methyl-D-glucoside. The

TABLE III
R_f Values of Oxoglucosides (Paper Chromatography)[a]

Glucoside	R_f value
2-Oxo α-methyl glucoside	1.42
3-Oxo α-methyl glucoside	2.05
4-Oxo α-methyl glucoside	1.61
α-Methyl glucoside	1.64
α-Methyl glucoside oxidized with Ce^{+4}	1.41

[a] Solvent: BuOH/EtOH/H_2O = 10:3:5

2-oxo sugar was identified by measuring the R_f value with respect to D-glucose according to a method described by Theander.[22] It was found that the R_f glucose value of the oxidized product corresponded with that of the 2-oxo-α-methyl-D-glucoside having a value of 1.42. These data are given in Table III.

Determination of the Number-Average Molecular Weight of the Grafted PAN Chains.

Theoretical Calculation. Assuming that all the free radicals are ultimately converted to carboxyl groups on a further oxidation treatment with chlorous acid (RĊHOH → R—CHO → R—COOH) and also assuming that during grafting, all the free radicals are captured by monomer molecules, it is possible to obtain some information on the probable range of molecular weights of the grafted chains. In the above case the number-average molecular weight is obtained by the equation:

$$M_{\bar{n}} = \frac{\text{Moles PAN grafted/anhydroglucose unit}}{\text{(COOH)/anhydroglucose unit}} \times 53.06$$

These data are given in Table IV. The COOH content of the ceric oxidized cellulose (measured after a second oxidation with chlorous acid) represents a measure of the number of free-radical sites produced per anhydroglucose unit, while the PAN content, calculated as moles AN/anhydroglucose unit of the grafted cellulose, represents the total acrylonitrile content in the graft.

The values of $M_{\bar{n}}$ given in Table IV, however represent the minimum values, since it is assumed that all free-radical sites initiate graft chains.

Experimental Determination. The cellulose–PAN grafts were isolated by dissolving off the ungrafted cellulose by standard acetolysis treatment.[23] It was observed that cellulose completely dissolved in the acetolysis mixture when kept at 40°C. for 4 hr. A sample of PAN when subjected to acetolysis under the same conditions did not show any change in viscosity when measured in dimethylformamide (DMF). The cellulose–PAN grafts were thus acetolyzed for 4 hr. at 40°C. to remove the ungrafted cellulose, and the insoluble graft was filtered and washed well with glacial acetic acid, 50% acetic acid in water, and finally with water. This residue was

TABLE IV
Molecular Weights M_n, from PAN and COOH Contents of Cellulose

	No.	Reaction time, min.	Ce^{+4} per a.g.u.	COOH per a.g.u.	Grafting, %	PAN per a.g.u.	DP of PAN[a]	M_n = DP × 53.06
Set I	1	2.5	0.01014	0.00160	6.5	0.198	123.7	6'563
0.01*M*	2	5.0	0.01128	0.00190	11.2	0.341	179.4	9'519
Ce^{+4}	3	7.5	0.01209	0.00215	15.5	0.473	200.0	10'612
	4	10.0	0.01290	0.00242	20.5	0.625	258.3	13'705
	5	15.0	0.01440	0.00280	27.5	0.839	299.6	15'897
Set II	1	2.5	0.01134	0.00195	8.4	0.256	131.3	6'966
0.02*M*	2	5.0	0.01147	0.00200	14.0	0.427	213.5	11'328
Ce^{+4}	3	7.5	0.01410	0.00270	20.2	0.616	228.1	12'103
	4	10.0	0.01489	0.00292	21.6	0.658	225.7	11'975
	5	15.0	0.01762	0.00365	26.4	0.806	220.8	11'715
Set III	1	2.5	0.01477	0.00290	2.5	0.076	51.7	2'743
0.05*M*	2	5.0	0.02044	0.00440	9.5	0.290	65.9	3'496
Ce^{+4}	3	7.5	0.02383	0.00530	16.5	0.503	94.9	5'035
	4	10.0	0.02613	0.00590	22.0	0.671	113.7	6'033
	5	15.0	0.03066	0.00700	30.5	0.931	133.0	7'057

[a] DP = PAN per a.g.u./COOH per a.g.u.

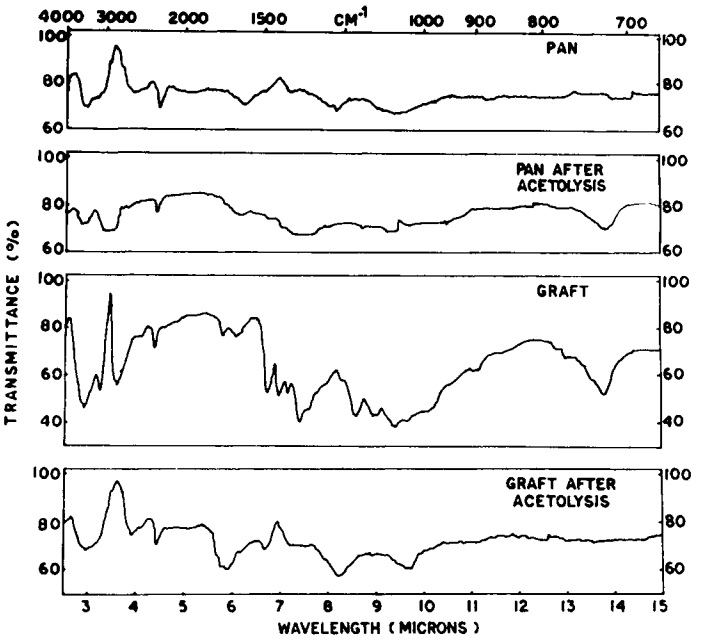


Fig. 13. Infrared spectra of cellulose–PAN grafts before and after acetolysis.

then extracted with DMF to remove those components of the graft which had a high cellulose content and thus were insoluble in DMF. The final product was obtained by precipitating the DMF-soluble fraction in large quantities of ice cold water. The precipitate was filtered and dried in vacuum at 60–70°C.

Data on the isolation of these grafts are given in Table V. These grafts contained mostly PAN chains, since their nitrogen content corresponded

TABLE V
Data on the Acetolysis and Fractionation of Cellulose–PAN Grafts

No.	Reaction period (grafting), min.	Weight of graft, g.	Insoluble fraction after acetolysis, g.	Soluble fraction in DMF, g.	Nitrogen content, % of insoluble fraction	$M_{\bar{n}}$
1	0	1 (cellulose)	Completely soluble	—	—	—
2	2.5	1.065	0.084	0.073	25.8	—
3	5.0	1.112	0.230	0.150	25.5	—
4	7.5	1.155	0.287	0.210	25.1	—
5	10.0	1.205	0.309	0.251	26.0	50'000
6	15.0	1.275	0.352	0.302	25.5	55'000
7	—	PAN blank	—	—	25.9	—

with that of a PAN blank, after 4 hr. acetolysis. It was observed that by this method, isolation of DMF-soluble cellulose–PAN grafts could be achieved only when the Ce^{+4} concentration during grafting was low ($0.01M$), or the reaction period was at least 10–15 min. With higher Ce^{+4} concentrations, isolation was not possible even with 10–15 min. grafting times. Similarly, with very low reaction periods (2.5–10 min.) using $0.01M$ Ce^{+4} concentration, isolation of the grafts was not possible. This indicated that isolation of the graft by the above method could be obtained only when the grafted chains reached a high DP. In Figure 13 the infrared spectra of the cellulose–PAN grafts as well as those of PAN alone are shown before and after the acetolysis treatment. It is seen that the nitrile peak at 4.4 μ remains unaffected after acetolysis of the grafted cellulose. The intensity of the OH and the C—O—C peak, at 2.9 μ and 8.5–9.5 μ, respectively, is considerably diminished in the acetolyzed graft, indicating removal of the cellulose components during acetolysis. The acetolyzed grafts show an additional peak at 5.9 μ characteristic of the —OCO— ester grouping.

These infrared spectra indicate that the isolated cellulose grafts contain some fragments of cellulose chains. These must be of very low DP as compared to the DP of the grafted PAN, since these grafts are completely soluble in DMF.

Using the relationship

$$[\eta] = 4.72 \times 10^{-4}\overline{M}_n^{\,0.733}$$

as given by Bamford et al.[24] for PAN, we obtained the number-average molecular weights by conversion of the intrinsic viscosities of the PAN grafts in DMF. These data are given in Table V. It is observed that this value is almost five times the theoretically calculated value of $\overline{M}_n$, indicating that probably the capture of free radicals by monomer molecules is approximately 20% of the available sites.

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References

1. S. Kaizerman, G. Mino, and L. F. Meinhold, *Textile Res. J.*, **32**, 136 (1962).
2. F. K. Guthrie, *Tappi*, **46**, 656 (1963).
3. Y. Iwakura, T. Kurosaki, and Y. Imai, *J. Polymer Sci. A*, **3**, 1185 (1965).
4. R. J. E. Cumberbirch and J. R. Holker, *J. Soc. Dyers Colourists*, **82**, 59 (1966).
5. G. Mino and S. Kaizerman, *J. Polymer Sci.*, **31**, 242 (1958).
6. G. Mino and S. Kaizerman, *J. Polymer Sci.*, **39**, 523 (1959).
7. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).
8. J. C. Arthur, Jr., P. J. Baugh, and O. Hinojosa, *J. Appl. Polymer Sci.*, **10**, 1591 (1966).
9. I. Terasaki and M. Matsuki, *J. Soc. Textile Cellulose Ind. Japan*, **18**, 147 (1962).
10. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polymer Sci.*, **38**, 393 (1959).

11. *Methods of Test for Textiles*, B. S. Handbook No. 11, London, 1963, p. 511, Heyes, *J. Soc. Chem. Ind.*, **47**, 907 (1928).

12. R. L. Whistler, Ed., *Methods in Carbohydrate Chemistry*, Academic Press, New York, 1963, Part III, p. 32.

13. A. Y. Kulkarni, A. G. Chitale, B. K. Vaidya, and P. C. Mehta, *J. Appl. Polymer Sci.*, **7**, 1581 (1963).

14. R. L. Whistler, Ed., *Methods in Carbohydrate Chemistry*, Academic Press, New York, 1963, Part III, p. 172.

15. R. L. Whistler, Ed., *Methods in Carbohydrate Chemistry*, Academic Press, New York, 1963, Part III, p. 165.

16. R. L. Whistler, Ed., *Methods in Carbohydrate Chemistry*, Academic Press, New York, 1963, Part III, p. 183.

17. S. R. S. Iyer, private communication.

18. A. A. Katai, V. K. Kulshreshtha, and R. H. Marchessault, in *Fourth Cellulose Conference* (*J. Polymer Sci. C*, **2**), R. H. Marchessault, Ed., Interscience, New York, 1963, p. 403.

19. W. A. Waters, *Mechanisms of Oxidation of Organic Compounds*, Methuen, London, 1964, pp. 54–56.

20. G. F. Devidson and T. P. Nevell, *J. Textile Inst.*, **46**, 407T (1955).

21. A. Hebeish and P. C. Mehta, unpublished work.

22. O. Theander, *Acta. Chem. Scand.*, **11**, 1557 (1957).

23. M. L. Wolfram and A. Thompson, in *Methods in Carbohydrate Chemistry*, R. L. Whistler, Ed., Academic Press, New York, 1963, Part III, p. 143.

24. C. H. Bamford, A. D. Jenkins, R. Johnston, and E. F. T. White, *Trans. Faraday Soc.*, **55**, 168 (1959).

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