

## Cerium-Initiated Grafting of Acrylonitrile onto Cellulosic Materials

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### Synopsis

Grafting of acrylonitrile onto native cotton, swollen cotton, viscose, ramie, and hydro-cellulose was studied with tetravalent cerium as initiator. The effect of temperature on the graft yields is examined. With ceric ammonium nitrate the grafting yields are found to be higher at 20 and 40 than at 60°C. Ceric ammonium sulfate, on the other hand, produces more grafting at 60 than at 20 and 40°C. The consumption of ceric ions is less, whereas the per cent graft yields are higher for the swollen cottons and viscose than for native cotton. Graft yields are shown to be related to substrate accessibility if the grafting reaction is carried out under conditions that suppress homopolymerization. Oxidation of these celluloses with  $\text{Ce}^{\text{IV}}$  has also been studied. It is found that more  $\text{Ce}^{\text{IV}}$  is consumed during grafting than during oxidation of cellulose under identical reaction conditions. Excess  $\text{Ce}^{\text{IV}}$  consumed in the grafting reaction has been shown to be directly related to extent of homopolymerization, which accompanies grafting. Some data on the storage stability of the free-radical activity produced by oxidation of cellulose with  $\text{Ce}^{\text{IV}}$  are also reported. It is observed that the cerium-oxidized samples can initiate graft polymerization even after 4-5 hr. if stored in nitrogen.

### INTRODUCTION

In recent years the use of tetravalent cerium as an initiator of the graft polymerization of vinyl monomers on cellulosic and other textile materials such as nylon has gained considerable importance on account of its high grafting efficiency<sup>1-11</sup> compared with other known redox systems, such as ferrous-hydrogen peroxide and thiosulfate-persulfate.<sup>12-14</sup> However, very few workers have reported detailed results of the effect of cellulose fine structure on rate and extent of graft polymerization with the ceric initiation method.

The available literature on grafting has been extensively reviewed in several papers.<sup>15-19</sup> Literature review is therefore restricted to papers of direct relevance to the present study.

In a study of the grafting of vinyl monomers (acrylic acid, 2- and 4-vinylpyridine, and acrylamide) onto cellulosic materials such as viscose rayon, mercerized cotton, hydrocellulose, and oxycellulose Cumberbirch and Holker<sup>6</sup> devoted attention mainly to the mechanical properties (such as water retention, load at yield, dry and wet tenacity, and extension at break) of the grafted products. In a similar study of grafting on polyamide

fibers Howarth and Holker<sup>5</sup> showed that slow diffusion of the monomer in nylon 66 fibers contributed to nonuniform distribution of the grafted polymer. Conductivity and antistatic properties of the grafted nylon were examined.

The initiation mechanism of  $Ce^{IV}$  with respect to certain alcohols such as pinacol, poly(vinyl alcohol),<sup>21-22</sup> and cellulose<sup>23-25</sup> has been studied. Recently Arthur et al.<sup>26</sup> reported an ESR study of cerium-oxidized cellulose and postulated a cleavage of the  $C_2-C_3$  bond of anhydroglucose units with formation of free radicals at C-2. Kulkarni and Mehta<sup>27</sup> recently made a detailed study of the mechanism of oxidation of cellulose with  $Ce^{IV}$ .

In the present communication we report some studies of the  $Ce^{IV}$  initiation of the grafting of acrylonitrile onto various cellulosic materials, such as cotton treated with sodium hydroxide (NaOH-cotton), ethylenediamine (EDA-cotton), and zinc chloride ( $ZnCl_2$ -cotton), native cotton, viscose rayon, hydrocellulose, and ramie.

## MATERIALS AND METHODS

Egyptian Karnak Cotton Slivers were purified by a mild alkaline scouring (2.0%  $Na_2CO_3$ , 1.0%  $Na_3PO_4$ , and 0.2% wetting agent, on weight of material) for 5 hr. at 110°C. and 10-15 psi in a laboratory kier with a liquor ratio of 10.

The swelling was done by treatment of the purified cotton slivers with aqueous solutions of sodium hydroxide (24% w/w), ethylenediamine (78% w/w), and zinc chloride (70% w/w), respectively at 20°C. for 1 hr., followed by washing and drying in air at room temperature.

Hydrocellulose was obtained by treatment of the purified cotton fibers with 1N HCl at 65°C. for 24 hr. followed by thorough washing, neutralizing, etc.

Viscose staple fibers (1.5 den.) were purified by boiling in 0.5% soap solution for 2 hr., washed well, and air-dried.

Undegummed ramie fibers were purified by scouring with  $Na_2CO_3$  (2%),  $Na_3PO_4$  (1%), and wetting agent (0.2%) for 2 hr., followed by washing and drying. These were given a peroxide bleaching (3 g. of  $H_2O_2$ , 4 g. of sodium silicate, 0.13 g. of  $MgSO_4$ , and 3.2 g. of NaOH per liter) at 70°C. for 4 hr., washed thoroughly, and dried.

Ceric ammonium nitrate (CAN) and ceric ammonium sulfate (CAS), B.D.H. reagent-grade, were used after standardization with ferrous sulfate according to a method described by Mino et al.<sup>28</sup> Acrylonitrile monomer was freshly distilled before use.

The polymerization treatment of all the cellulosic fibers was carried out in 50-ml. stoppered Erlenmeyer flasks. To 30 ml. of acidified ceric salt containing concentrated  $HNO_3$  or  $H_2SO_4$  (1% each for the nitrate and sulfate, respectively) kept at a specified temperature 1 ml. of acrylonitrile was added, followed immediately by 1 g. of cellulose. The flask was well

TABLE I  
Grafting, Homopolymerization, and Total Conversion of Acrylonitrile with Different Cellulose Substrates\*

Substrate	Graft, %, at temp. (°C.)			Homopolymer, %, at temp. (°C.)			Conversion, %, at temp. (°C.)			Homopolymer, % of grafted polymer, at temp. (°C.)		
	20	40	60	20	40	60	20	30	60	20	40	60
Native cotton	39.50 (47.38)	43.00 (51.63)	27.53 (32.90)	15.62	20.12	13.35	63.00	71.75	46.25	32.96	38.96	40.57
NaOH-cotton	52.15 (60.62)	52.84 (61.38)	32.05 (37.25)	4.25	10.87	9.37	64.87	72.25	46.62	7.01	17.70	25.15
EDA-cotton	40.80 (47.87)	48.38 (56.87)	26.60 (31.25)	12.00	14.25	14.37	59.87	71.12	45.62	25.00	25.05	45.98
ZnCl <sub>2</sub> -cotton	44.27 (52.50)	47.37 (56.25)	27.68 (32.87)	10.75	15.25	13.50	63.25	71.50	46.37	20.47	27.11	41.07
Hydrocellulose	38.73 (46.50)	37.48 (45.00)	22.47 (27.00)	16.00	26.87	19.25	62.50	71.87	46.25	34.40	59.71	71.29
Viscose	42.46 (48.87)	43.43 (49.88)	20.19 (23.00)	10.75	21.87	24.37	59.62	71.75	47.37	21.99	43.84	105.95
Ramie	40.58 (47.62)	40.84 (47.38)	14.05 (16.25)	15.25	25.62	30.50	62.87	73.00	46.75	32.02	54.07	187.69
None	—	—	—	—	—	—	4.87	57.26	38.24	—	—	—

\* [CAN] = 0.006M in 1% HNO<sub>3</sub>; cellulose, 1 g; acrylonitrile, 1 ml.; liquor ratio 1:30; reaction time 3 hr. Values in parentheses based on weight of monomer.

stopped and the contents stirred 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, given a light soaping, 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 and washing. The per cent grafting was calculated on dry weights, determined by storing the materials in weighing bottles over P<sub>2</sub>O<sub>5</sub> at room temperature in a vacuum desiccator until a constant weight was obtained.

$$\% \text{ grafting} = \frac{[(\text{dry weight of grafted product}) - (\text{dry weight of original cellulose})]}{(\text{dry weight of cellulose})} \times 100$$

Oxidation of the cellulosic samples with CAN and CAS was carried out under conditions identical with those described above except that the monomer was not added.

The homopolymer formed during grafting was estimated by filtering out the polymer in a sintered crucible (No. 3) and drying at 105–110°C. until a constant weight was obtained. The per cent conversion to homopolymer was calculated as follows:

$$\% \text{ homopolymer} = \frac{(\text{weight of homopolymer})}{(\text{weight of monomer})} \times 100$$

To make the per cent grafting yields comparable to the per cent homopolymer formed, the graft yields were also calculated on the weight of monomer taken at the start of the grafting reaction. These values are given in brackets in Table I.

The consumption of Ce<sup>IV</sup> by cellulose during grafting and oxidation was determined according to a method reported by Mino et al.<sup>28</sup> The copper number was determined according to Braidy's method,<sup>29</sup> and carboxyl groups were estimated according to the Indian standard method.<sup>30</sup>

## RESULTS AND DISCUSSION

### Effect of Temperature on Grafting Yields

Figure 1 shows the per cent grafting yields on the various substrates at 40°C. with CAN as initiator. Figure 2 shows the corresponding homopolymer formed in solution during grafting at this temperature. Similar behavior was observed at 20 and 60°C. The maximum graft yields and the per cent homopolymer formed in solution during grafting in 3 hr. at these three temperatures are shown in Table I. It was observed that the grafting reaction showed no induction period at the three temperatures, whereas polymerization in the absence of cellulose showed induction periods of 2–3, 13–15, and 90–95 min. at 60, 40, and 20°C., respectively (Fig. 3).

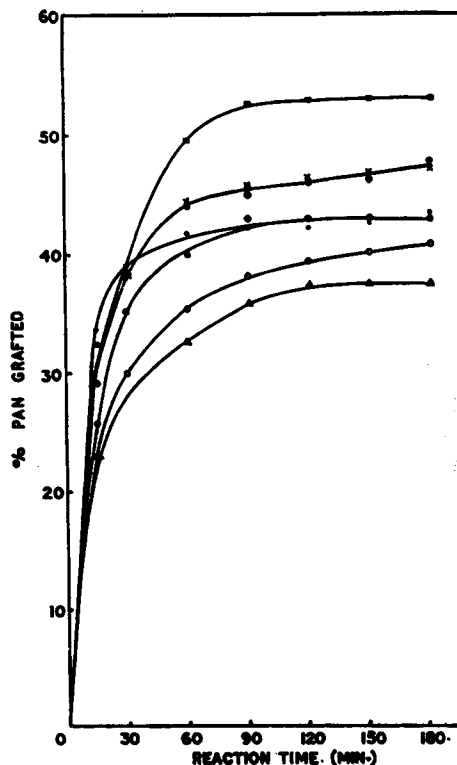


Fig. 1. Grafting of polyacrylonitrile on different cellulose materials with CAN at 40°C.: (○) native cotton; (■) NaOH-cotton; (●) EDA-cotton; (×) ZnCl<sub>2</sub>; (Δ) hydrocellulose; (·) viscose; (○) ramie; [Ce<sup>IV</sup>] = 0.006M in 1% HNO<sub>3</sub>; cellulose, 1 g.; acrylonitrile, 1 ml.; liquor ratio 30.

Like many other cellulose reactions, such as oxidation with periodate, the grafting reaction also shows an initial fast rate followed by a slower one. This could be due to a rapid fall in the concentration of the monomer and the initiator as well as to a decrease in the available sites for grafting on the cellulose molecule. As expected, the swollen cottons showed higher grafting yields than native cotton, ramie, and hydrocellulose. Surprisingly, the grafting yields from the three swollen cottons were higher than from viscose. A similar observation has been reported by Huang and Rapson<sup>31</sup> for the grafting of styrene on cotton, mercerized cotton, and viscose with the irradiation technique.

The grafting yields at 20 and 40°C., are comparable, and those at 60°C. are significantly lower. In a complex system such as this several reactions take place simultaneously, and the ultimate grafting yields depend on the net influence of the following factors taken together: (a) solution of the monomer in water and its diffusion from the solution phase to the fiber phase, (b) adsorption of the monomer on the fiber, (c) initiation and termination of free-radical sites on the cellulose backbone by Ce<sup>IV</sup>, (d)

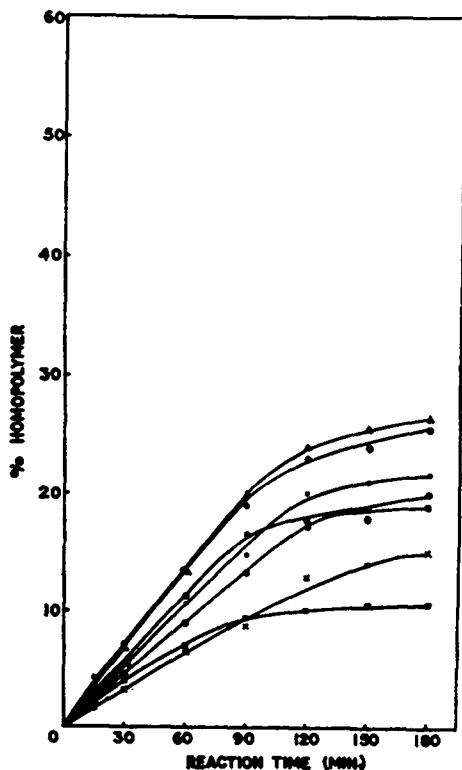


Fig. 2. Homopolymer formed in solution during grafting of polyacrylonitrile on different cellulosic materials with CAN at 40°C.; (○) native cotton; (■) NaOH-cotton; (⊖) EDA-cotton; (×) ZnCl<sub>2</sub>; (Δ) hydrocellulose; (·) viscose; (○) ramie; reaction conditions as in Figure 1.

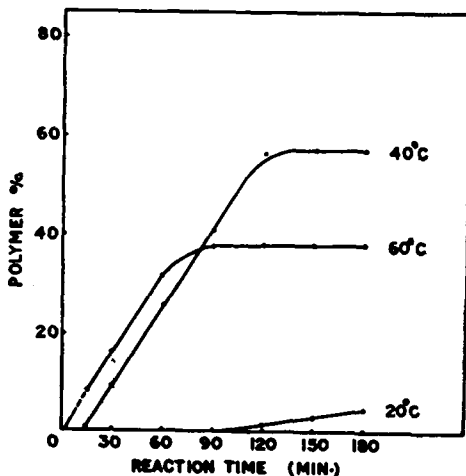


Fig. 3. Polymerization of acrylonitrile (in the absence of cellulose) with CAN:  $[Ce^{IV}] = 0.006M$  in 1% HNO<sub>3</sub>; acrylonitrile, 1 ml.

formation and propagation of graft on fiber, and (e) homopolymerization in solution. Since, as will be seen later, the grafting yields with CAS at 60°C. are higher than at 40°C., factors such as less adsorption of the mono-

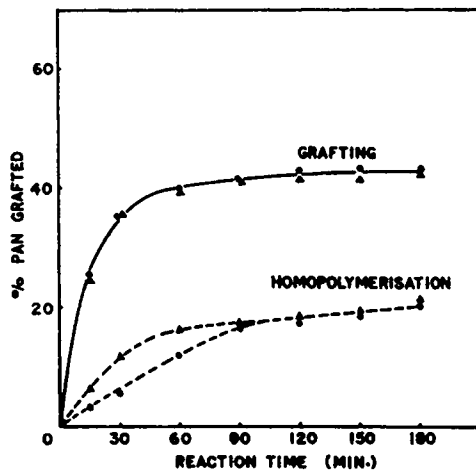


Fig. 4. Grafting of polyacrylonitrile in native cotton with CAN in the presence and in the absence of nitrogen: (—) per cent PAN grafted; (---) per cent homopolymer formed in solution during grafting; ( $\Delta$ ) in nitrogen; ( $\odot$ ) in air. Reaction conditions as in Figure 1.

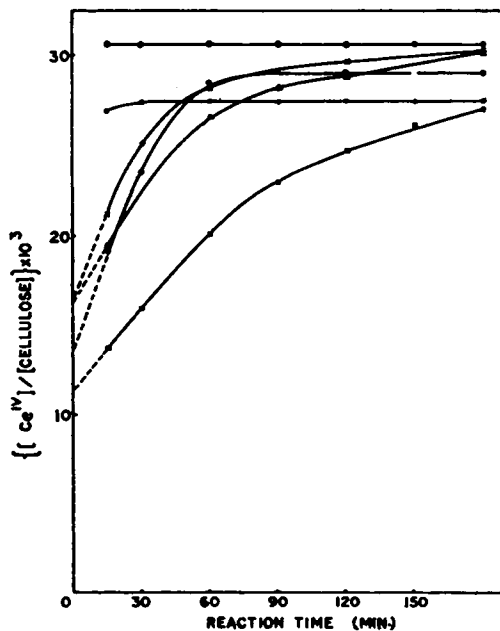


Fig. 5. Consumption of cerium during grafting and oxidation of native cotton at different temperatures. Grafting at (°C.): ( $\odot$ ) 20; ( $\times$ ) 40; ( $\odot$ ) 60; oxidation at (°C.): ( $\blacksquare$ ) 20; ( $\Delta$ ) 40; ( $\odot$ ) 60; reaction conditions as in Figure 1.

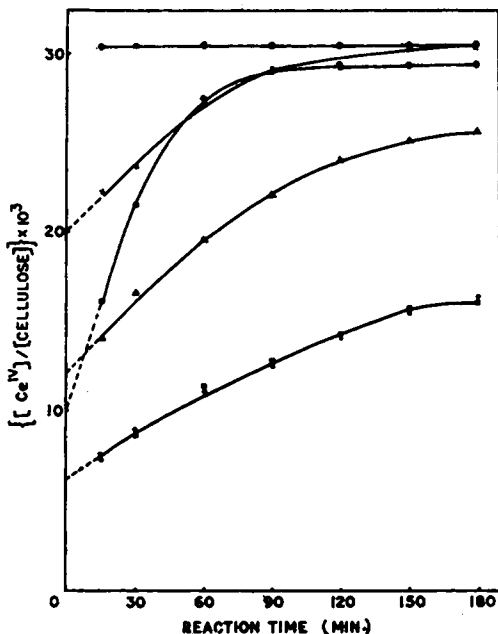


Fig. 6. Consumption of cerium during grafting and oxidation of NaOH-cotton at different temperatures. Grafting at ( $^{\circ}\text{C}.$ ): ( $\odot$ ) 20; ( $\times$ ) 40; ( $\ominus$ ) 60; Oxidation at ( $^{\circ}\text{C}.$ ): ( $\blacksquare$ ) 20; ( $\triangle$ ) 40; ( $\bullet$ ) 60; reaction conditions as in Figure 1.

mer or its evaporation at the higher temperature (i.e.,  $60^{\circ}\text{C}.$ ) cannot be responsible for the lower grafting yields at this temperature with CAN.

A possible explanation of this behavior could be the increased rate of termination of growing polymer chains at  $60^{\circ}\text{C}.$  in the case of CAN. If the rates of initiation and termination of free radicals are different for the two initiators, and if termination is faster in the case of CAN at  $60^{\circ}\text{C}.$ , the observed behavior can be accounted for. To check this possibility, the polymerization of acrylonitrile with these two initiators was studied at the three temperatures. These data are shown in Figures 3 and 16. It is apparent that with CAN as initiator the overall conversion of acrylonitrile monomer to polymer is much less at  $60^{\circ}\text{C}.$  than at  $40^{\circ}\text{C}.$  With CAS as initiator, however, the percent conversion of acrylonitrile increases between  $40^{\circ}\text{C}.$  and  $60^{\circ}\text{C}.$ , whereas at  $20^{\circ}\text{C}.$  no polymerization takes place at all in 3 hr.

The percent total conversion of monomer to polymer in the presence of different cellulosic materials as well as in the absence of any cellulose at 20, 40, and  $60^{\circ}\text{C}.$  in 3 hr. with CAN initiator is shown in Table I. The maximum conversions at a particular temperature are nearly the same for all the substrates but are considerably higher than the corresponding conversion percent in the absence of any cellulose. They also follow the order  $40 > 20 > 60^{\circ}\text{C}.$  The nature of the substrate appears to influence the relative magnitudes of grafting and homopolymer formation without affecting the overall extent of conversion of monomer to polymer.



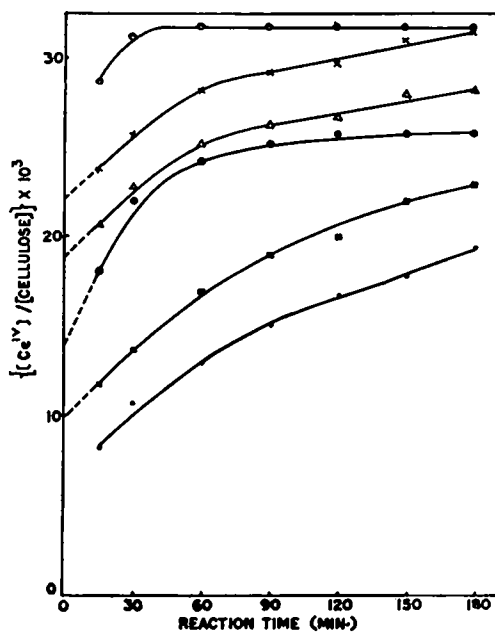


Fig. 7. Consumption of cerium during grafting and oxidation of viscose at different temperatures. Grafting at ( $^{\circ}\text{C}.$ ): ( $\odot$ ) 20; ( $\times$ ) 40; ( $\ominus$ ) 60; oxidation at ( $^{\circ}\text{C}.$ ): ( $\blacksquare$ ) 20; ( $\Delta$ ) 40; ( $\bullet$ ) 60; reaction conditions as in Figure 1.

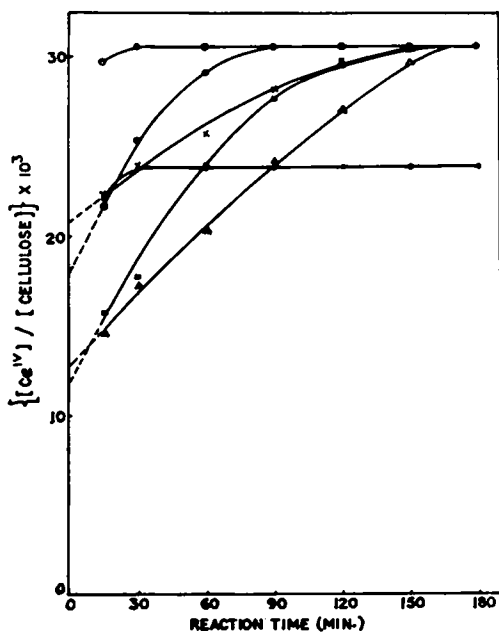
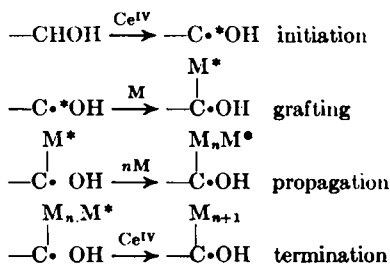


Fig. 8. Consumption of cerium during grafting and oxidation of ramie at different temperatures. Grafting at ( $^{\circ}\text{C}.$ ): ( $\odot$ ) 20; ( $\times$ ) 40; ( $\ominus$ ) 60; Oxidation at ( $^{\circ}\text{C}.$ ): ( $\blacksquare$ ) 20; ( $\Delta$ ) 40; ( $\bullet$ ) 60; reaction conditions as in Figure 1.

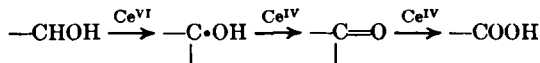
For a study of the effect of occluded air in the substrate and reagents used during grafting a separate experiment was conducted, in which nitrogen was first bubbled through the initiator solution. The monomer and substrates were then added, and circulation of nitrogen continued for another 15 min. The system was then closed and the grafting conducted as usual. These results are shown in Figure 4, from which it is apparent that any traces of air that may be occluded in the system does not inhibit grafting.

The consumption of  $\text{Ce}^{\text{IV}}$  during grafting is higher than that during oxidation of the substrates (Figs. 5-8). The theoretical reaction schemes for grafting and oxidation are shown below.

Grafting:



Oxidation:



Thus in the grafting reaction 2 moles of  $\text{Ce}^{\text{IV}}$  will be consumed for every mole of anhydroglucose unit (AGU) grafted. During oxidation  $\text{Ce}^{\text{IV}}$  consumption will be between 2 and 3 moles per AGU oxidized, depending

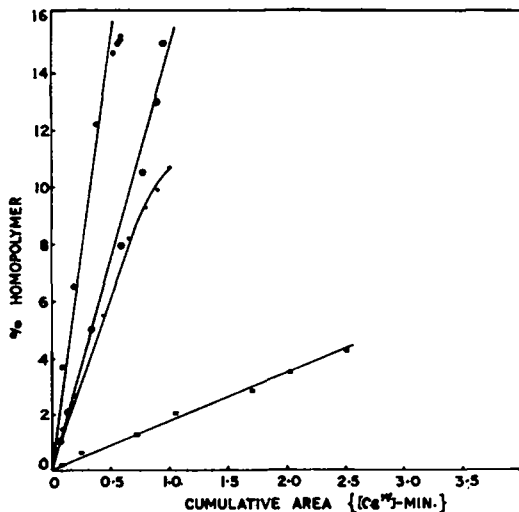


Fig. 9. Relationship between cerium consumed in grafting in excess of that consumed in oxidation and per cent homopolymer formed at 20°C.; (○) native cotton; (■) NaOH-cotton; (●) viscose; (○) ramie; reaction conditions as in Figure 1.

TABLE II  
Homopolymer Formed in Solution during Grafting of Polyacrylonitrile on Different Cellulosic Materials with CAN<sup>a</sup>

Reac. time, min.	Homopolymer, %							
	At 20°C. <sup>b</sup>			At 40°C. <sup>b</sup>				
	N.C.	N.C.	Vis.	Ram.	N.C.	N.C.	Vis.	Ram.
15	1.00	0.25	1.50	3.75	3.12	2.25	3.12	4.25
30	2.25	0.62	2.75	6.50	5.50	4.00	5.50	9.62
60	5.00	1.25	5.50	12.25	12.00	7.00	10.62	14.75
90	7.87	2.05	8.25	14.75	16.62	9.37	14.75	19.00
120	10.50	2.87	9.37	15.00	17.37	10.10	20.00	23.00
150	13.00	3.50	9.79	15.37	18.62	10.70	21.00	24.12
180	15.62	4.25	10.75	15.25	20.12	10.87	21.87	25.62

<sup>a</sup> [CAN] = 0.006M in 1% HNO<sub>3</sub>; cellulose, 1 g.; acrylonitrile, 1 ml.; liquor ratio 1:30.

<sup>b</sup> N.C., native cotton; Na. C., NaOH-Cotton; Vis., viscose; Ram., ramie.

on the extent to which the oxidation proceeds to formation of carboxyl groups. The presence of both aldehyde-keto groups and carboxyl groups in cellulose oxidized with  $\text{Ce}^{\text{IV}}$  has been established, as will be shown. During grafting not all the free-radical sites produced in the initiation step lead to grafting. These would be expected to follow the course of the oxidation reaction. Thus, the consumption of  $\text{Ce}^{\text{IV}}$  during grafting would be expected to be less than or equal to that during oxidation. An excess of  $\text{Ce}^{\text{IV}}$  consumed during grafting would therefore be due to the initiation of free-radical sites on the monomer, that is, to homopolymerization. Kulkarni and Mehta<sup>4</sup> have assumed this in their study of the grafting of acrylonitrile to bleached cotton fibers.

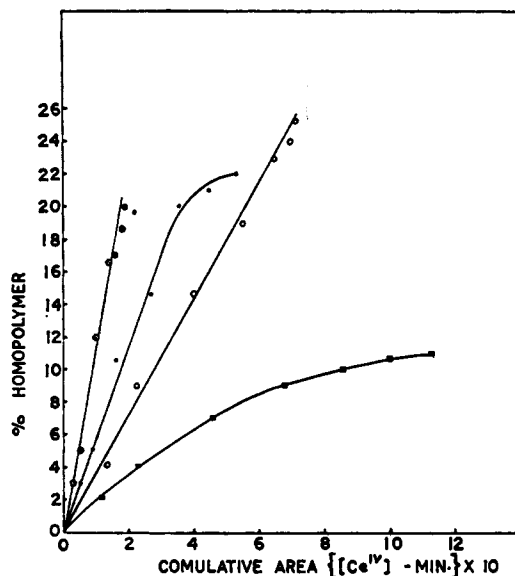


Fig. 10. Relationship between cerium consumed in grafting in excess of that consumed in oxidation and per cent homopolymer formed at 40°C.: (○) native cotton; (■) NaOH-cotton; (●) viscose; (○) ramie; reaction conditions as in Figure 1.

To test the validity of this assumption, the per cent homopolymer formed under a given set of reaction conditions (Table II) was plotted, Figures 9 and 10, against the corresponding difference in  $\text{Ce}^{\text{IV}}$  consumed during grafting and during oxidation. The latter was obtained by measuring the cumulative difference in area under the two appropriate curves in Figures 5-8 up to the particular reaction time. Figures 9 and 10 show that there is a direct relation (linear in almost all cases) between the extent of homopolymerization and the excess  $\text{Ce}^{\text{IV}}$  consumed in grafting. It can also be seen that each substrate shows a uniqueness in this relation, and for a given value of excess  $\text{Ce}^{\text{IV}}$  consumed in grafting the amount of homopolymer formed varies widely with different substrates. This is probably a result of the different efficiencies of these substrates with respect to grafting,

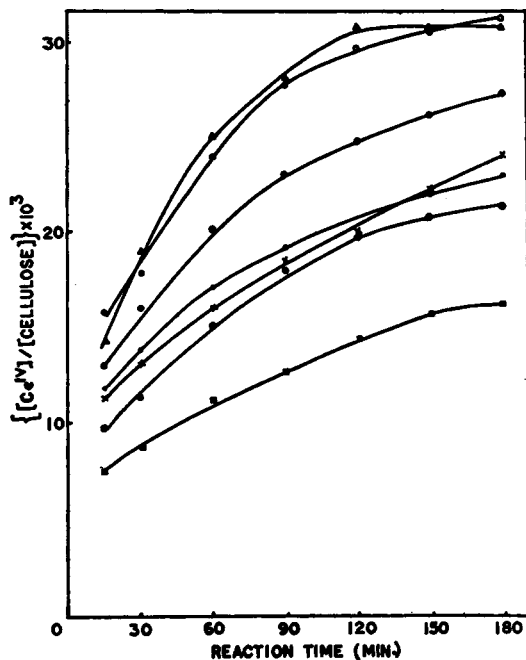


Fig. 11. Consumption of cerium during oxidation of different celluloses: (○) native cotton; (■) NaOH-cotton; (●) EDA-cotton; (×) ZnCl<sub>2</sub>-cotton; (Δ) hydrocellulose; (●) viscose; (○) ramie; [Ce<sup>IV</sup>] = 0.006*M* in 1% HNO<sub>3</sub>; cellulose, 1 g.; liquor ratio 30; temperature 20°C.

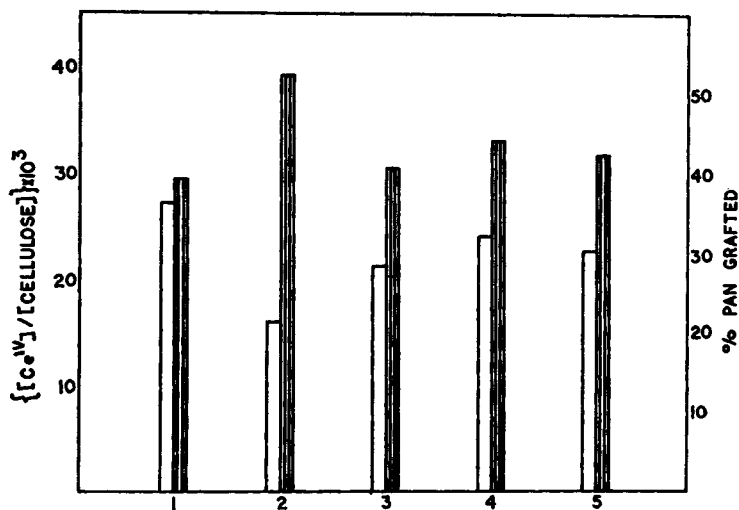


Fig. 12. Comparison of (white bars) consumption of cerium during oxidation and (shaded bars) per cent graft, obtained for different substrates: (1) native cotton; (2) NaOH-cotton; (3) EDA-cotton; (4) ZnCl<sub>2</sub>-cotton; (5) viscose, [Ce<sup>IV</sup>] = 0.006*M* in 1% HNO<sub>3</sub>; cellulose, 1 g.; acrylonitrile, 1 ml.; liquor ratio 30; temperature 20°C.; reaction time 3 hr.

leading to different amounts of monomer available in solution for homopolymerization.

In the case of swollen cotton fibers and viscose the consumption of cerium during oxidation is significantly less than in the case of native cotton at the three temperatures studied. Figure 11 shows these data at 20°C.; the same behavior was seen at 40 and 60°C. On the other hand, the per cent grafting yields are higher for these substrates than for native cotton (Fig. 1 and Table I). For ease of comparison the data on ceric consumption during oxidation and on per cent grafting are shown together in Figure 12 for native cotton, viscose, and the three swollen cottons. Although it seems reasonable that in the case of swollen cottons and viscose the higher graft yields may be due to greater accessibility of the materials, it is difficult to explain the lower  $Ce^{IV}$  consumption of these fibers during oxidation.

### Relation between Accessibility and Maximum Grafting Yields

The maximum graft yields at 3 hr. obtained with various substrates show no consistent relation with the accessibility of the substrate. This unexpected result under the experimental conditions followed could be due to insufficient monomer concentration in the reaction system and to competition between graft formation and homopolymerization. Figure 13 shows clearly that, when grafting yields are low, homopolymer formation is high, and vice versa.

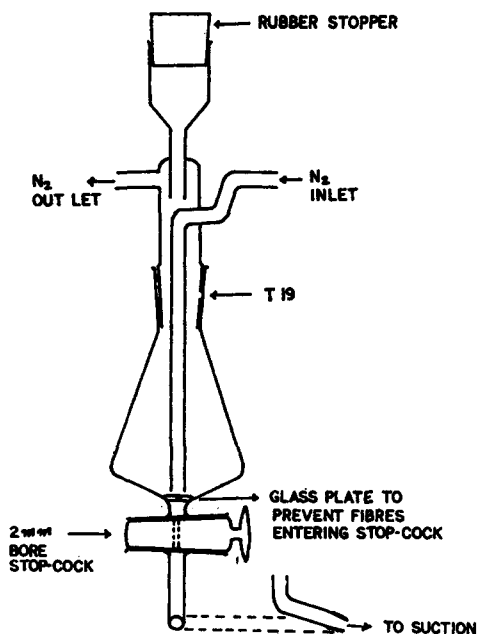


Fig. 13. Apparatus used for study of grafting after initiation with CAN.

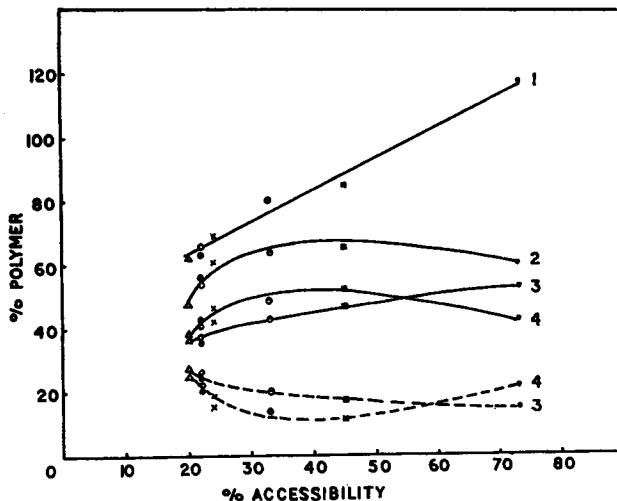


Fig. 14. Relationship between maximum graft yields and accessibility of different substrates: (—) per cent PAN grafted; (---) per cent homopolymer formed in solution; (○) native cotton; (■) NaOH-cotton; (●) EDA-cotton; (×) ZnCl<sub>2</sub>-cotton; (Δ) hydrocellulose; (●) viscose; ramie (○). Curves: (1-4) percent graft yields obtained by methods I-IV, respectively; [Ce<sup>IV</sup>] = 0.006M in 1% HNO<sub>3</sub>; cellulose, 1 g.; temperature 40°C.; reaction time 3 hr. Acrylonitrile: (1, 2) 15 ml.; (3, 4) 1 ml.

In order to study unambiguously the effect of substrate accessibility on grafting the following modified methods were chosen for graft polymerization: carrying out the initiation and grafting separately, to suppress homopolymer formation (methods I and II) and allowing the monomer to be adsorbed on the substrate first, to increase availability of the monomer for grafting (method III). The detailed experimental conditions are described below.

**Method I.** The substrate (1 g.) reacted with CAN (0.006M) for 3 hr. at a liquor ratio of 30. The excess ceric solution was then removed by suction. Acrylonitrile monomer (15 ml.) was then introduced, and grafting was carried out for another 3 hr. The entire sequence of operations was carried out under nitrogen.

**Method II.** The procedure was identical with method I, except that the reactions were carried out in air instead of nitrogen. The apparatus used for methods I and II is shown in Figure 14.

**Method III.** The cellulose sample (1 g.) was immersed for 3 hr. in 30 ml. of acidified, distilled water, to which 1 ml. of acrylonitrile was added in a stoppered Erlenmeyer flask. Then 1 ml. of 0.18M CAN was added, making an initiator concentration of 0.006M in the reaction mixture. The flask was gently shaken, and the grafting reaction was allowed to proceed for another 3 hr.

**Method IV.** The graft polymerization was conducted as described under "Materials and Methods."

The reaction temperature in all cases was 40°C. The accessibility of the substrates was obtained from formylation studies (90% HCOOH) at 40°C. reported by Nair.<sup>32</sup>

The data obtained are given in Figure 13. These studies indicate that graft yields are linearly and directly related to accessibility only when the grafting reaction is conducted under conditions that suppress homopolymerization. In method I it is clear that a linear relationship could be obtained when there was no chance for the homopolymer to be formed. Method II conducted under conditions identical with those of method I but in the presence of air did not show the same relation. The grafting yields obtained by method I are also considerably higher than those obtained by method II. This is probably due to the presence of oxygen in the system, which would accelerate the decay of free radicals. The decay effect seems to be more pronounced in the case of more accessible substrates. Data that will be presented later support this.

In methods III and IV, as expected, the homopolymer formed in solution during the grafting reaction decreased with increasing graft yields, and vice versa (Fig. 13). This clearly indicates that for a given substrate grafting and homopolymerization in solution are inversely related, both being dependent on the efficiency of the grafting reaction. In method III the grafting yield increased with increasing accessibility of the substrate. This is probably due to the greater availability of physically adsorbed monomer on the more accessible substrates. Methods I and II showed higher grafting yields than methods III and IV, presumably because of the significantly larger quantity of monomer used and the absence of homopolymerization.

### Ceric Ammonium Nitrate versus Ceric Ammonium Sulfate

The data presented in Figure 15 show the percent grafting yields at 20, 40, and 60°C with 0.006*N* CAS for two typical substrates, native cotton and EDA-cotton. Hardwick and Robertson<sup>33</sup> and Ardon<sup>34</sup> have shown that the Ce<sup>IV</sup>-sulfate complex is more stable at lower temperatures than the Ce<sup>IV</sup>-nitrate complex. This would explain the lower grafting efficiency of CAS at the lower temperatures, since less Ce<sup>IV</sup> would be available for initiation. Thus for the two initiators studied the rates of initiation and termination of the free radicals appear to differ significantly and change the grafting behavior with temperature, whereas diffusion and adsorption of the monomer and rate of propagation and chemical reaction for graft polymerization are common to both the systems under study. Schwab et al.<sup>35</sup> have also reported maximum graft yields at 40°C. with the CAN-acrylonitrile method of grafting of paper. Further, they have observed that CAS is less efficient in graft polymerization at lower temperatures, whereas at 60°C. it is better than the nitrate.

Figure 16 shows the percent total conversion of monomer to polymer (i.e., graft plus homopolymer in solution) in the presence and in the absence



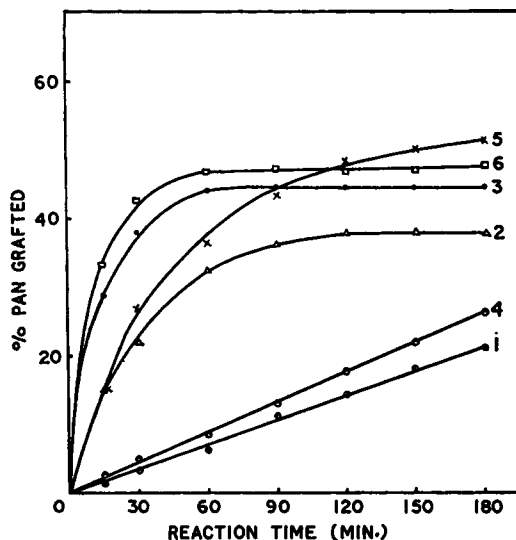


Fig. 15. Grafting of acrylonitrile on native cotton and EDA-cotton with CAS at different temperatures;  $[Ce^{IV}] = 0.006N$  in 1%  $H_2SO_4$ ; cellulose, 1 g.; acrylonitrile, 1 ml.; liquor ratio 30. Native cotton at ( $^{\circ}C$ .): (1) 20; (2) 40; (3) 60. EDA-cotton at ( $^{\circ}C$ .): (4) 20; (5) 40; (6) 60.

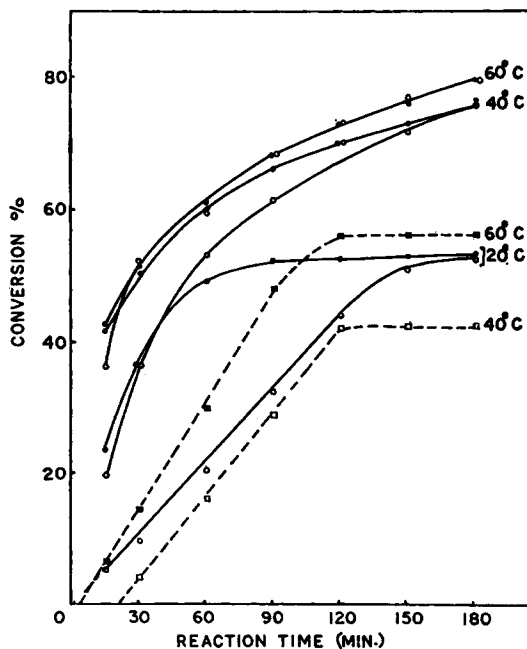


Fig. 16. Per cent conversion of acrylonitrile to polymer in the presence (—) and in the absence (---) of different cellulose substrates with CAS at different temperatures: (O) ramie; (●) viscose;  $[Ce^{IV}] = 0.006N$  in 1%  $H_2SO_4$ ; cellulose, 1 g.; acrylonitrile, 1 ml.; liquor ratio 30.

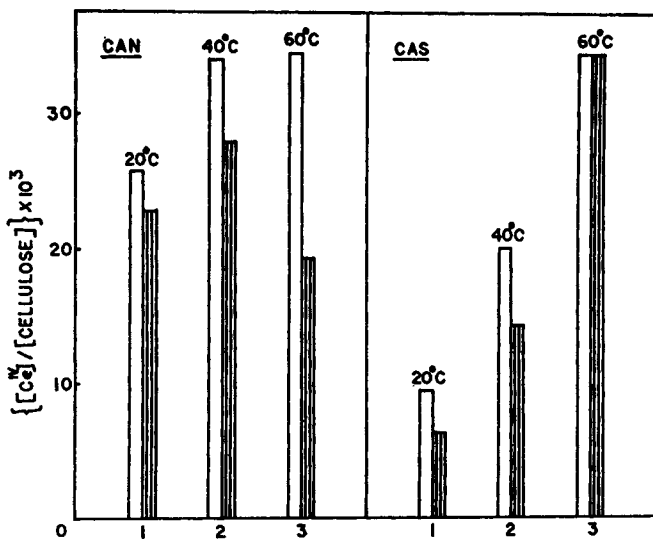


Fig. 17. Consumption of ceric ions by viscose in CAN and CAS during (white bars) grafting and (shaded bars) oxidation, at different temperatures:  $[Ce^{IV}] = 0.006N$  in 1%  $HNO_3$  and 1%  $H_2SO_4$  for CAN and CAS, respectively; cellulose = 1 g.; acrylonitrile, 1 ml.; liquor ratio 30; reaction time 3 hr.

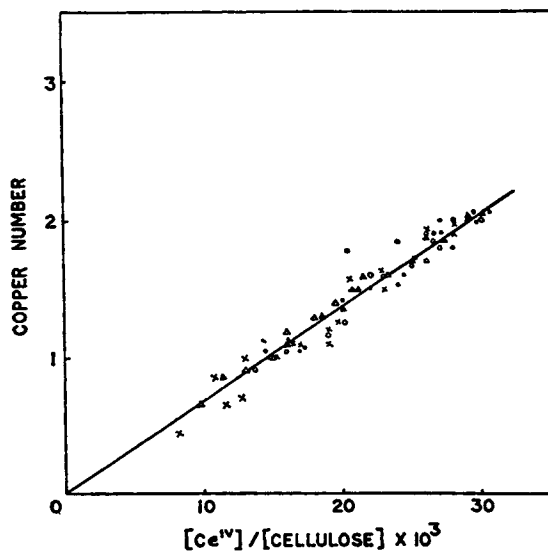


Fig. 18. Copper number versus consumption of cerium during oxidation of different cellulosic materials with CAN at 20, 40, and 60°C.: (O) native cotton; ( $\Delta$ ) EDA-cotton; ( $\times$ ) viscose; ( $\bullet$ ) ramie;  $[Ce^{IV}] = 0.006N$  in 1%  $HNO_3$ ; cellulose, 1 g.; liquor ratio 30; reaction time 15–180 min.

of cellulose, with 0.006*N* CAS at 20, 40, and 60°C. As in the results obtained with CAN, the percent conversion in the presence of cellulose is much higher than in its absence. Moreover, for all the substrates studied the maximum conversions are nearly the same at a given temperature. Unlike the results obtained with CAN, the conversion of monomer to

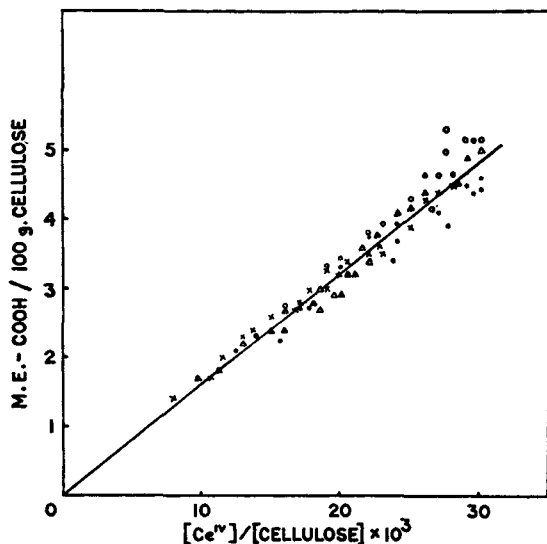


Fig. 19. Carboxyl content versus ceric consumption during oxidation of different cellulosic substrates with CAN at 20, 40, and 60°C.; (O) native cotton; ( $\Delta$ ) EDA-cotton; ( $\bullet$ ) ramie; ( $\times$ ) viscose; reaction conditions as in Figure 18.

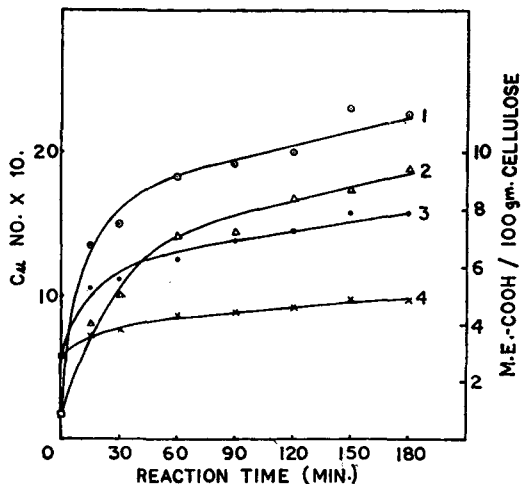


Fig. 20. Copper number and carboxyl content versus reaction time (EDA-cotton samples oxidized with ceric salts) with (1, 3) CAN; (2, 4) CAS;  $[Ce^{IV}] = 0.006N$  in 1%  $HNO_3$  and 1%  $H_2SO_4$  for CAN and CAS, respectively; cellulose, 1 g.; liquor ratio 30; temperature 40°C.

polymer in the presence and in the absence of cellulose shows maximum values at 60°C. and follows the order 60 > 40 > 20°C. Here, too, polymerization in the presence of cellulose proceeded without any induction period, whereas in its absence it showed induction periods of 2-3 and 16-19 min., at 60 and 40°C., respectively. It is interesting to note that at 20°C. no polymerization occurred in the absence of cellulose up to 3 hr., confirming the reported high stability of the  $Ce^{IV}$ -sulfate complex at low temperatures.

The consumption of  $Ce^{IV}$  by different cellulosic materials during their oxidation, besides the grafting with CAS, is much less than in case of oxidation with the corresponding nitrate at 20 and 40°C. This is expected, since at these temperatures the sulfate is not so efficient as the nitrate as a free-radical initiator. These data are shown in Figure 17.

The copper number and carboxyl content of the CAN-oxidized samples showed a single linear relationship with the consumption of  $Ce^{IV}$  during oxidation, irrespective of the nature of the substrate or the temperature of reaction (Figs. 18 and 19). Since the cerium-oxidized samples showed considerable carboxyl content, the oxidation reaction appears to proceed to the formation of carboxyl groups after the formation of carbonyl-aldehyde groups. Similar results have been obtained with CAS, except that the carboxyl content of the oxidized samples was much less. Figure 20 contains typical data on the oxidation of EDA-cotton with CAN and CAS.

#### Effect of Storage on Free-Radical Activity of $Ce^{IV}$ -Oxidized Cellulose

If a cellulose sample in which free radicals have been initiated by oxidation with  $Ce^{IV}$  is stored, one of two things may happen: the free radical may be terminated, owing to exposure to the atmosphere, and there may be a charge transfer, resulting in a termination of the free radical with simultaneous creation of another active site (in other words, the free-radical activity would remain unchanged). Thus, the decay of free-radical activity of the  $Ce^{IV}$ -oxidized cellulose during storage would be a result of these two processes. The following experimental procedure was adopted to study this phenomenon:

The cellulosic material was oxidized with CAN at 20, 40, and 60°C. until maximum  $Ce^{IV}$  consumption was obtained. The reaction time needed for this was available from data on  $Ce^{IV}$  consumption during oxidation at various times of reaction. The excess ceric solution was removed by suction filtration, and the sample (containing approximately 100% its weight of ceric solution) was stored for various intervals of time ranging from 2 to 300 min., before acrylonitrile monomer was added. Figure 14 shows the apparatus used for these studies. The entire sequence of operations, including storage, was carried out in a nitrogen atmosphere.

It was observed that no polymerization occurred if an aqueous solution of the monomer was used. However, considerable grafting occurred when pure acrylonitrile monomer was used. The percent graft yields shown in Figure 21 were obtained for a 3 hr. reaction period after addition of mono-

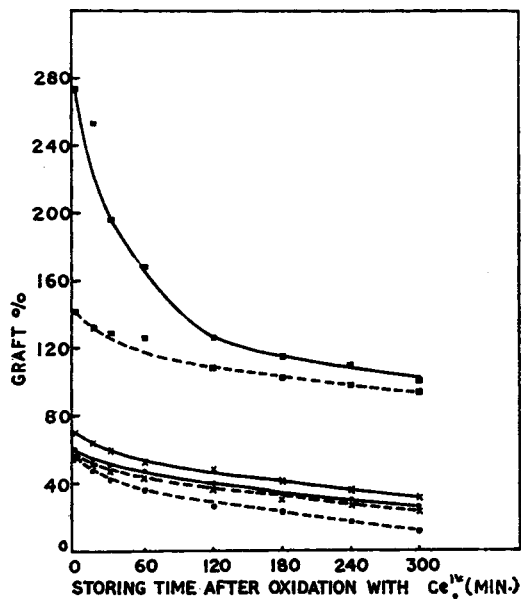


Fig. 21. Rate of decay of free-radical activity of  $Ce^{IV}$ -oxidized cellulose. Per cent graft: (—) in nitrogen; (---) in air. Grafting at ( $^{\circ}C.$ ): (●) 20; (×) 40; (■) 60. Storing time after oxidation with  $Ce^{IV}$ , 2-300 min;  $[Ce^{IV}] = 0.006M$  in 1%  $HNO_3$ ; cellulose, 1 g.; acrylonitrile, 15 ml.

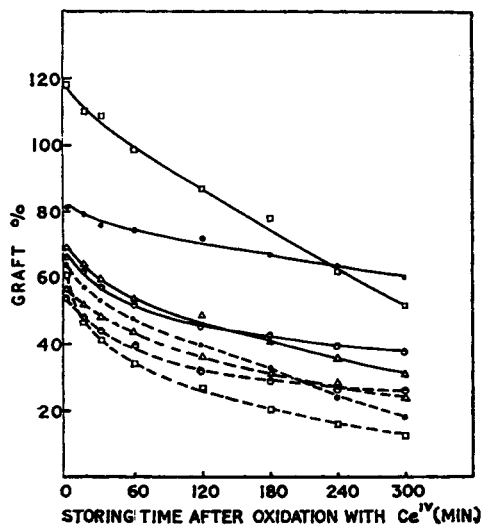


Fig. 22. Effect of accessibility on free-radical activity of  $Ce^{IV}$ -oxidized cellulose at  $40^{\circ}C.$  in (—) nitrogen and (---) air; ( $\Delta$ ) native cotton; (●) EDA-cotton; ( $\square$ ) viscose; ( $\odot$ ) ramie; reaction conditions as in Figure 21.

mer. These data indicate that the rate of decay of free-radical activity increases rapidly with increasing temperature. The presence of air in the atmosphere also accelerates this decay, since the percent grafting yields are much lower in air than in nitrogen. Moreover, it is noticed that with increasing accessibility of the substrate (e.g., viscose and EDA-cotton) the free-radical decay is greater. The difference in the percent grafting yields in nitrogen and in air atmosphere is also greater in these cases than in those of native cotton (Fig. 22).

In these experiments the grafting yields were considerably higher at all temperatures than those obtained by the earlier method, because homopolymer formation was absent and a much higher amount of monomer was used in the reaction system.

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## References

1. G. Mino and S. Kaizerman, *J. Polymer Sci.*, **31**, 242 (1958).
2. S. Kaizerman, G. Mino, and F. Meinhold, *Textile Res. J.*, **32**, 136 (1962).
3. G. N. Richard, *J. Appl. Polymer Sci.*, **5**, 539 (1961).
4. A. Y. Kulkarni and P. C. Mehta, *J. Appl. Polymer Sci.*, **9**, 2633 (1965).
5. S. Howarth and J. R. Holker, *J. Soc. Dyers Colourists*, **82**, 257 (1966).
6. R. J. E. Cumberbirch and J. R. Holker, *J. Soc. Dyers Colourists*, **82**, 59 (1966).
7. Y. Iwakura, T. Kurosaki, K. Uno, and Y. Imai, in *Macromolecular Chemistry, Paris 1963 (J. Polymer Sci. C, 4)*, M. Magat, Ed., Interscience, New York, 1964, p. 673.
8. T'ung Sun, Han-Hsin Chou, Man-Likuo, and Shu-Haun Chang, *Ko Fen Tzu T'ung Hsung*, **6**, 130 (1964); *Chem. Abstr.*, **63**, 18441f (1965).
9. N. M. Berghein, O. Ellegson, K. Kring Sted, and P. Kroken, *Norsk Skogined*, **17**, 347 (1963); *Chem. Abstr.*, **60**, 4332a (1964).
10. H. Narita, N. Uchino, and S. Machida, *Sen-i Gakkaishi*, **19**, 225 (1963); *Chem. Abstr.*, **62**, 13293g (1965).
11. H. Kamogawa and T. Sekiya, *Textile Res. J.*, **31**, 585 (1961).
12. G. Landells and C. S. Whewell, *J. Soc. Dyers Colourists*, **67**, 338 (1951).
13. A. Y. Kulkarni, A. G. Chitale, B. K. Vaidya, and P. C. Mehta, *J. Appl. Polymer Sci.*, **7**, 1581 (1963).
14. A. Y. Kulkarni and P. C. Mehta, *J. Polymer Sci. B*, **1**, 509 (1963).
15. E. H. Immergut and H. F. Mark, *Makromol. Chem.*, **18/19**, 322 (1956).
16. E. Schwab, V. Stannett, and J. J. Hermans, *Tappi*, **44**, 251 (1961).
17. S. K. Majumdar and W. H. Rapson, *Textile Res. J.*, **34**, 1007, 1015 (1964).
18. E. H. Immergut, in *Encyclopedia of Polymer Science and Technology*, Vol. 3, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Interscience, New York, 1965, p. 242.
19. D. B. Mutton, *Pulp Paper Mag. Can.*, **65**, T41 (1964).
20. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).
21. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polymer Sci.*, **39**, 523 (1959).

22. A. A. Katai, V. K. Kulshrestha, and R. H. Marchessault, in *Fourth Cellulose Conference*, (*J. Polymer Sci. C*, **2**), R. H. Marchessault, Ed., Interscience, New York, 1963, p. 403.
23. I. Terasaki and M. Matsuki, *J. Soc. Textile Cell Ind. Japan*, **18**, 147 (1962).
24. Y. Iwakura, T. Kurosaki, and Y. Imai, *J. Polymer Sci. A*, **3**, 1185 (1965).
25. A. Y. Kulkarni and P. C. Mehta, *J. Polymer Sci. B*, **5**, 209 (1967).
26. J. C. Arthur, Jr., P. J. Baugh, and O. Hinojosa, *J. Appl. Polymer Sci.*, **10**, 1591 (1966).
27. A. Y. Kulkarni and P. C. Mehta, *J. Appl. Polymer Sci.*, in press.
28. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polymer Sci.*, **38**, 393 (1959).
29. *Methods in Carbohydrate Chemistry*, Vol. 3, Academic Press, New York-London, 1963, p. 44.
30. *Indian Standard*, **1962**, 1560.
31. R. Y. M. Huang and W. H. Rapson, in *Fourth Cellulose Conference (J. Polymer Sci. C*, **2**), R. H. Marchessault, Ed., Interscience, New York, 1963, p. 169.
32. G. P. Nair, Ph.D. Thesis, Gujarat University, India, 1965.
33. T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).
34. M. Ardon, *J. Chem. Soc.* **1957**, 1811.
35. E. Schwab, V. Stannett, D. H. Rakowitz, and J. K. Magrane, *Tappi*, **45**, 390 (1962).

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