FUTURE LINES OF WORK

It is hoped that the studies reported in this thesis increase our understanding of the general kinetics of the grafting of polyacrylonitrile to cellulose using ceric ion as an initiator. Further research to evaluate other transition metal ions such as \( \text{V}^{5+} \) and \( \text{Co}^{3+} \), as well as oxidants such as sodium meta periodate to initiate grafting with vinyl monomers would be useful and of interest. In particular the mechanism of free radical initiation with these systems would be of value in understanding the mechanism of the grafting reaction.

Another worthwhile direction of study seems to be to explore methods to improve the efficiency of the grafting reaction still further and to increase graft yields. Using the simultaneous initiation - grafting reaction, it has been seen that the grafting yields tend to level off at approximately 50 to 70% for acrylonitrile. Recent work from this laboratory has shown that by separating initiation and grafting it is possible to increase the graft yields to over 150%. Further studies along these lines should be useful.

Evaluation of cotton fabrics grafted with vinyl polymers has not so far indicated any modifications in the fabric properties significant enough to be of utilisation interest. Possibly, one reason for this is that with the methods of grafting followed so far, one gets long polymer chains grafted at very few sites in and on the fibre. The primary interest from the utilisation point of
view would seem to be the possibility of modifying the properties of the fibre or fabric surface so as to impart such properties as water repellency and thermoplasticity. For such an objective, it would be necessary to modify the methods of grafting so that this reaction would occur predominantly at the fibre surface and secondly that it would result in a large number of short grafted polymer chains rather than a small number of very long grafted polymer chains. Research in this direction should also be of great value.
Ceric Ion Induced Red-ox Polymerization of Acrylonitrile in Presence of Cellulose

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Reprinted from the Proceedings of the Sixth Technological Conference, January 1965

THE BOMBAY TEXTILE RESEARCH ASSOCIATION
BOMBAY
CERIC ION INDUCED RED-OX POLYMERIZATION OF ACRYLONITRILE IN PRESENCE OF CELLULOSE

A. Y. KULKARNI & P. C. MEHTA,
ATIRA, Ahmedabad.

Ceric Ammonium Sulphate and nitrate form very effective red-ox systems in presence of alcohols containing a 1,2 glyccl linkage, e.g., Pinacolone. Free radicals are produced on the carbon atoms of the alcohol through a single electron transfer, and in presence of vinyl monomers grafting of the polymer to alcohol occurs.

In the present investigation, polymerization of Acrylonitrile is studied using a cellulose-ceric red-ox system. In presence of cellulose the rate of polymerization is much faster than in its absence. Polymerization data in presence of silica spheres show that the increased rate of polymerization with cellulose is not due to the large surface area of cellulose.

Unlike earlier data with the persulphate-thiosulphate red-ox system, traces of copper in the ceric-cellulose system do not increase the grafting yields.

The rate of consumption of ceric ions during cellulose oxidation, in presence and absence of Acrylonitrile, is also studied. These data are interpreted for useful information about the grafted products, e.g., the number of anhydro-glucose units per branching (including free radical sites), molecular weight of the grafted side chains, etc.

Introduction

Many red-ox systems such as Ferrous-Hydrogen peroxide and Thiosulphate-Persulphate have been investigated for grafting vinyl polymers on to cellulose. Grafting occurs mainly due to a chain transfer mechanism through free radicals formed in the vicinity of a cellulose molecule. Recently however Mino et al have reported that ceric salts (Ammonium cereto nitrate and sulphate) form a very effective red-ox system with organic reducing agents such as alcohols, amines, thiols, etc. Such a red-ox system is ideal for grafting vinyl polymers on the organic reducing agent since free radicals are directly formed on the reducing component through transfer of a single electron. Thus in a system such as ceric-cellulose-vinyl monomer, the initiation, propagation and termination reactions are expected to be as follows:

\[
\begin{align*}
(1) \quad \text{Ce}^{IV} + \text{Cellulose} & \xrightleftharpoons{K} \text{B (complex)} \\
& \downarrow \\
& \text{Cellulose}^* + \text{Ce}^{III} + \text{H}^+ \\
(2) \quad \text{Cellulose}^* + M & \xrightarrow{K_i} \text{Cell.} - M^* \text{ Initiation for grafting.} \\
(3) \quad \text{Ce}^{IV} + M & \xrightarrow{K_i} M^* + \text{Ce}^{III} + \text{H}^+ \text{ Initiation for homopolymerization.} \\
(4) \quad \text{Mn}^* + M & \xrightarrow{K_p} \text{Mn}^* + 1 \text{ Propagation (grafting and homopolymerization).} \\
(5) \quad \text{Mn}^* + \text{Ce}^{IV} & \xrightarrow{K_t} \text{Mn} + \text{Ce}^{III} + \text{H}^+ \text{ termination (grafting and homopolymerization).} \\
(6) \quad \text{Cellulose}^* + \text{Ce}^{IV} & \xrightarrow{K_o} \text{Cellulose oxidation product} + \text{Ce}^{III} + \text{H}^+
\end{align*}
\]

† This work forms part of a Ph.D. Thesis of one of the authors (A. Y. Kulkarni).
In case of an alcohol containing a 1:2 glycol linkage (such as pinacole or a head to head combination of polyvinyl alcohol chains) oxidation of the alcohol takes place through scission of the 1:2 carbon linkage. The same authors have shown that the termination step in these reactions involves conversion of CeIV ions to CeIII ions with formation of acetone equivalent to the CeIV reduced. Thus:

\[
\begin{align*}
(1) & \quad \text{Ce}^{IV} + (\text{CH}_3)_2\text{C} \xrightarrow{\text{OH}} \xrightarrow{\text{OH}} \text{pinacole} \\
& \quad (\text{CH}_3)_2\text{CO} + (\text{CH}_3)_2\text{COH} + \text{H}^+ + \text{Ce}^{III} \\
(2) & \quad \text{Ce}^{IV} + (\text{CH}_3)_2\text{COH} \xrightarrow{\text{H}^+} (\text{CH}_3)_2\text{CO} + \text{H}^+ + \text{Ce}^{III}
\end{align*}
\]

The oxidation of pinacole and 3-chloro-1-propanol by ceric ammonium nitrate follows a first order reaction with respect to the initial concentration of ceric ions in the system. Katai et al. have derived a relationship for the number average molecular weight of the grafted polymer chains, for the system Acrylonitrile-ethylene glycol in presence of ceric ammonium nitrate.

This is based on the equation:

\[
\bar{M}_n = \frac{[M]}{[\text{Ce}^{IV}]} \times \frac{k_p}{k_t} \times 53.06
\]

where \([M]\) and \([\text{Ce}^{IV}]\) are the concentrations of monomer and ceric ions in moles.

\(k_p\) is the rate constant for propagation.

\(k_t\) is the rate constant for termination.

The present work was undertaken to study the general kinetics of graft formation of Acrylonitrile in presence of cellulose, using ammonium cereto nitrate as the initiator. It is also thought that the ceric-ion cellulose red-ox system would be very useful for determination of the average molecular weight (number average) of the grafts.

**Materials Used:** Ceric Ammonium nitrate and Acrylonitrile used were B.D.H. reagent grade chemicals. Ferrous sulphate, and ceric ammonium sulphate were E. Merk reagent grade chemicals. Egyptian Cotton fibres (slivers) were used after scouring and bleaching for grafting experiments.

Freshly distilled Acrylonitrile was used for all polymerization experiments.

Silica spheres used in some of the polymerization experiments were obtained from the National Bureau of Standards, U.S.A.

**Experimental Work**

(a) **Polymerization Procedure:** 30 ml of ceric ammonium nitrate solution containing 1 ml of concentrated nitric acid per 100 ml of ceric solution was taken in a 150 ml conical flask and kept in a thermostat bath for 5-10 minutes to bring the solution temperature to 40 ± 0.2°C. 1 g. of the cotton sample was then introduced in the flask and immediately the required quantity of acrylonitrile monomer was added in the flask through a micro burette. The flask was well stoppered and the contents stirred occasionally during the course of the polymerization reaction. At the end, the sample was washed well with water, given a light soaping to remove the loosely adhering polymer, washed and dried. The percent grafting yields were determined by weighing the conditioned samples before and after polymerization. It was found that a negligible quantity of homopolymer could be extracted from the grafted samples after a 12 hour cold extraction with dimethyl formamide. Hence it was not necessary to correct the final weight of the grafted samples. These data are shown in Table I.

**Table I**

<table>
<thead>
<tr>
<th>No.</th>
<th>Experimental conditions</th>
<th>% PAN added by wt.</th>
<th>refractive index at 30.2°C.</th>
<th>% PAN extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CeIV = 0.01M (\times) cellulose 1g.</td>
<td>blank DMF</td>
<td>1.4219</td>
<td>—</td>
</tr>
<tr>
<td>2.</td>
<td>Temp. 40°C</td>
<td>6.7</td>
<td>1.4218</td>
<td>less than 0.2</td>
</tr>
<tr>
<td>3.</td>
<td>AN. 1 ml. reaction time max. 1 hr.</td>
<td>15.0</td>
<td>1.4218</td>
<td>&quot;</td>
</tr>
<tr>
<td>4.</td>
<td></td>
<td>25.0</td>
<td>1.4217</td>
<td>&quot;</td>
</tr>
<tr>
<td>5.</td>
<td></td>
<td>36.3</td>
<td>1.4217</td>
<td>&quot;</td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td>44.8</td>
<td>1.4217</td>
<td>&quot;</td>
</tr>
</tbody>
</table>
(b) Polymerization on Silica spheres was carried out as described in (a) using silica spheres of known surface area in place of the cellulose samples. 4.67 g. of silica spheres (surface area 24 m²/g) were used in place of 1 g. of cellulose (surface area 112 m²/g).

(c) Oxidation of Cellulose with Ce⁴⁺: 1 g. of the conditioned cellulose sample was placed in a 150 ml. conical flask and 30 ml. of ceric ammonium nitrate solution was poured in the flask after it was brought to 40°C. The flask was immediately stoppered and placed in the thermostat bath maintained at 40 ± 0.2°C. During the oxidation reaction, the flask was gently stirred at regular intervals. 10 ml. of the ceric solution was pipetted out in a titration flask at the end of the reaction period and the Ce⁴⁺ concentration was estimated according to a method described by Mino et al.7 using excess of ferrous sulphate to reduce the Ce⁴⁺ ions. The excess ferrous sulphate was back titrated against ceric sulphate using O-phenanthroline as an internal indicator.

Results and Discussion

1. General Considerations:

Fig. 1 shows (a) effect of copper traces in the polymerization bath on grafting yields, (b) effect of a large surface area available for polymerization, and (c) homopolymer formation in absence of cellulose.

Fig. 2 shows the effect of varying the concentration of Ammonium cerenonitrate on grafting yields. The effect of increasing monomer concentration on grafting yields as well as the % conversion of monomer to polymer, is shown in Figs. 3 and 4 respectively. The rate and efficiency of grafting polyacrylonitrile to cellulose is found to be very high as compared to the persulphate-thiosulphate red-ox polymerization studies reported earlier.5,6 Whereas presence of a trace of
copper sulphate accelerates the rate and yields of grafting in the persulphate-thiosulphate system, it has an adverse effect in the ceric-cellulose red-ox system. However, the formation of homopolymer in absence of cellulose is accelerated in presence of traces of copper sulphate. Thus copper may reduce grafting yields in the ceric cellulose system due to increased homopolymer formation outside the cellulose phase. It is also noted that in absence of cellulose the inhibition time is very high (10-12 mts.) and the rate and extent of homopolymer formation is low as compared to graft formation. Also grafting starts almost as soon as the monomer is added to the ceric cellulose system.

As cellulose offers a large surface for the polymerization reaction it was necessary to ascertain if the high rate and yield of grafting on cellulose was due to (a) its surface area being available for the polymerization reaction, or (b) its reducing action in presence of CeIV ions, to generate free radicals, as postulated earlier. The contribution of a large surface area to the polymerization reaction was examined by substituting for cellulose, a non-reducing substance, namely silica spheres of known surface area (Fig. 1). It is observed that the polymer formation on silica spheres is almost equal to the homopolymer formation in absence of any cellulose. This strongly indicates that the increased efficiency of grafting PAN to cellulose is mainly due to the efficiency of cellulose as a reducing component in the ceric-cellulose red-ox system.

2. Effect of Initiator Concentration:

As shown in Fig. 2, grafting yields vary with change in the CeIV ion concentration. At low ceric concentrations (0.005-0.01 M), the grafting rate during first 15 minutes is high and then slows down considerably. At high concentrations of CeIV ions (0.05-0.15 M), the grafting yield increases from 36% (0.005 M ceric) to almost 47% for a 1 hour reaction. In a recent publication Katai et al. have derived a relationship for Rp, the rate of polymerization in an ethylene glycol-AN-CeIV system. According to this relationship, Rp is inversely related to the CeIV concentration, thus leading to an interesting situation where the rate of polymerization at low ceric ion concentration is actually greater than at high ceric concentration. They have also indicated the possibility of using this system as typical of what may be used if it is desired to graft a water insoluble polymer on to cellulose. However, studies on the CeIV consumed during oxidation of cellulose have shown that at low ceric concentrations, most of the ceric is consumed by cellulose during the first 10-15 minutes (Fig. 6). Hence although the initial rate of polymerization is higher at low ceric concentrations, the subsequent rate may slow down due to exhaustion of ceric ions in the reaction bath.

3. Conversion of Monomer to Polymer:

It is observed that increasing the monomer concentration from 100% to 200% (on weight of cellulose) increases the grafting yields from 38% to 88% in a 1 hour reaction. The % conversion of monomer to polymer also increases from 47% to 55% as shown in Figs. 3 and 4.

4. Oxidation of Cellulose with Ceric Ammonium Nitrate:

Fig. 5 shows the consumption of CeIV ions by cellulose (a) in absence of monomer and (b) during the grafting reaction. This is plotted as moles of ceric [CeIV] consumed per mole of anhydroglucose unit [cellulose] as a function of time. In Fig. 6 the logarithm of [CeIV] consumed during oxidation and grafting is plotted against time. Table II shows in a typical case the consumption of [CeIV] ions for estimating the ratio

No. of anhydroglucose units/Free radical site.

The consumption of ceric ions in presence of cellulose and monomer (i.e. during grafting) is con-
TEMP 4°C, CEU. ULO. 5S IT, H/L R AT IO 130.

CONSUMPTION OF CERC IONS DURING OXIDATION OF CELLULOSE AND GRAFTING RESPECTIVELY

REACTION TIME (MINUTES)

Fig. 5

CONSUMPTION OF CERC IONS DURING OXIDATION OF CELLULOSE AND GRAFTING RESPECTIVELY

1st ORDER PLOT OF CERC CONSUMPTION DURING OXIDATION AND GRAFTING.

Fig. 6

TABLE II

Concentration of CeIV by Cellulose during Oxidation

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction Time (Min.)</th>
<th>Moles CeIV per mole of cellulose</th>
<th>CeIV consumed for initiation alone</th>
<th>No. of anhydroglucose units/free radical site</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>0.01014</td>
<td>0.00597</td>
<td>197</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.0122E</td>
<td>0.00864</td>
<td>177</td>
</tr>
<tr>
<td>4</td>
<td>7½</td>
<td>0.0160E</td>
<td>0.00604</td>
<td>163</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>0.0128C</td>
<td>0.00645</td>
<td>155</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>0.0144C</td>
<td>0.00722</td>
<td>138</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>0.0164E</td>
<td>0.00821</td>
<td>121</td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>0.0184E</td>
<td>0.00925</td>
<td>108</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>0.0195E</td>
<td>0.00978</td>
<td>102</td>
</tr>
</tbody>
</table>

Experimental details:

CeIV Conc. (solution) 0.00658 M.
Temp. of reaction 40°C.

Cellulose 1 gm.
M/L Ratio = 1:30
siderably higher than during cellulose oxidation alone. According to Mino et al. the termination of free radicals during oxidation of cellulose and of growing polymer chains during grafting occur through conversion of CeIV ions to CeIII ions. The total consumption of ceric should be more or less equal for oxidation and grafting reactions respectively, if all the polymer is effectively grafted on to cellulose. The increased rate of CeIV consumption during grafting may therefore be due to initiation (and termination) of monomer to form homopolymer. The difficulty in extracting the homopolymer from the grafted samples with cold DMF may be due to insufficient swelling of the cellulose fibres.

Table III shows the amount of CeIV consumed towards formation of homopolymer during the grafting reaction. This is calculated as

\[
\text{CeIV consumed} - \text{CeIV consumed (grafting)}
\]

This quantity of CeIV expressed as a percentage is consumed for initiation and termination of homopolymer chains.

As shown in Fig. 6, the oxidation of cellulose with CeIV is characterised by a very high initial rate of oxidation during the first 2.5 minutes followed by a slower one. Terasaki et al. have reported that the oxidation of cellulose by CeIV starts in the more reactive part (corresponding to Cx linkage in the end unit of a cellulose molecule) and then proceeds to the less reactive part (corresponding to the C2 and C, linkage in the cellulose molecule).

### Table III

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction Time (Min.)</th>
<th>CeIV consumed during grafting (moles)</th>
<th>CeIV consumed during oxidation (moles)</th>
<th>% CeIV consumed for homopolymer formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5</td>
<td>0.01345</td>
<td>0.01014</td>
<td>18.4</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
<td>0.01586</td>
<td>0.01128</td>
<td>29.2</td>
</tr>
<tr>
<td>3</td>
<td>7.5</td>
<td>0.01884</td>
<td>0.01289</td>
<td>36.1</td>
</tr>
<tr>
<td>4</td>
<td>10.0</td>
<td>0.02044</td>
<td>0.01290</td>
<td>36.9</td>
</tr>
<tr>
<td>5</td>
<td>15.0</td>
<td>0.02457</td>
<td>0.01444</td>
<td>41.2</td>
</tr>
<tr>
<td>6</td>
<td>30.0</td>
<td>0.02726</td>
<td>0.01642</td>
<td>39.8</td>
</tr>
</tbody>
</table>

Experimental Conditions:

- Reaction Temp. = 40°C
- Cellulose = 1 gm.
- CeIV Conc. in Solution = 0.0066 M
- M/L ratio = 1:50

Thus:

(a) more reactive part

\[
\begin{align*}
\text{CH}_2\text{OH} \quad \text{H} + \text{CeIV} \\
\text{end unit of cellulose molecule}
\end{align*}
\]

(b) less reactive part

\[
\begin{align*}
\text{CH}_2\text{OH} \quad \text{H} + \text{CeIV} + \text{H}^+
\end{align*}
\]

These authors have attributed the initial high rates of oxidation to the more reactive parts in cellulose.

However, the effect of other factors such as accessibility cannot be overruled. Table IV shows some values of the reaction constant (K0) during the initial and later stages of cellulose oxidation, at two initial CeIV concentrations. These data indicate that the rate of oxidation after the first 2.5 minutes is nearly same for both concentrations of CeIV. Moreover, at both CeIV concentrations, log [CeIV] plotted against time of reaction follows a straight line within the
TABLE IV
Rate Constants for Oxidation of Cellulose

<table>
<thead>
<tr>
<th>No.</th>
<th>CeIV concentration (Moles)</th>
<th>K = initial (2.5 minutes)</th>
<th>K = later (2.5 — 60 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$3.6 \times 10^{-2}$</td>
<td>$4.36 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>$3.6 \times 10^{-4}$</td>
<td>$6.8 \times 10^{-2}$</td>
<td>$5.45 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Thus from data given in Fig. 5 and using the value C = 30, the number average molecular weights of the polymer segments in the graft may be calculated. For these calculations the following assumptions are made:

(a) The total quantity of CeIV consumed during polymerization (grafting) consists of:
   (i) CeIV consumed for grafting,
   (ii) CeIV consumed for oxidation of cellulose,
   (iii) CeIV consumed by monomer molecules for homopolymer formation.

(b) The average molecular weight of the grafted polymer chains and homopolymer chains is approximately equal.

Thus the CeIV consumption for formation of polymer (i.e. true graft and homopolymer) will be actually less than the total consumption of CeIV due to reaction (ii). Hence the true molecular weights of the polymer chains would actually be slightly higher than the calculated molecular weights (Mn being inversely proportional to [CeIV]). This data is shown in Table V. The values of Mn obtained range

TABLE V
Data on Molecular Weight Determinations

<table>
<thead>
<tr>
<th>No.</th>
<th>Time of reaction (Min.)</th>
<th>[CeIV]</th>
<th>[M]</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.0001799</td>
<td>0.01024</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>2.5</td>
<td>0.0001559</td>
<td>0.00937</td>
<td>1,40,000</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>0.0001034</td>
<td>0.00878</td>
<td>1,95,000</td>
</tr>
<tr>
<td>4</td>
<td>7.5</td>
<td>0.0000818</td>
<td>0.00819</td>
<td>2,34,000</td>
</tr>
<tr>
<td>5</td>
<td>10.0</td>
<td>0.0000630</td>
<td>0.00765</td>
<td>2,84,000</td>
</tr>
<tr>
<td>6</td>
<td>15.0</td>
<td>0.0000538</td>
<td>0.00673</td>
<td>2,92,000</td>
</tr>
</tbody>
</table>

Experimental Conditions:
CeIV Conc. (Soln.) = 0.006 M.
Cellulose = 1 g.
Temp. of reaction = 40°C.

Acrylonitrile = 1 ml.
M/L ratio = 1: 30
from $1.4 \times 10^5$ to $2.9 \times 10^5$ during the first 15 minutes of the grafting reaction. Since formation of homopolymer in the ceric solution outside cellulose phase, showed an induction period of 15 minutes, polymerization predominantly occurred within cellulose phase during this induction period. It was thought that the values of CeIV consumed after 15 minutes of reaction would be vitiated due to homopolymer formation in the CeIV bath. These values were therefore not used for calculation of Mn.

Attempts are now being made to isolate the PAN component of the grafts by suitable methods for dissolving out the cellulose part. It would then be possible to measure the viscosity average molecular weights of the isolated polymer segments and establish some relationship between experimental and theoretical values of Mn.

Acknowledgements

The authors thank the Director and Council of Administration of ATIRA for permission to present this work at the Sixth Joint Technological Conference.

REFERENCES


DISCUSSION

Q: H. R. Chipalkatti (ATIRA): What was the quantity of ceric-ion left after the initial polymerization?
A: After ten minutes hardly any ceric-ion was left for polymerization, but at higher concentrations enough of ceric ion was left.

Q: R. M. Desai (SRI): What was the type of cellulose used and its purity?
A: Purified Egyptian cotton slivers scoured and bleached with fluidity between 4 to 5 were used.

Q: W. B. Achiwal (UDCT): What would be the condition for preferential grafting over homopolymerization? How do the grafting rates with ceric salts compare with Y-ray irradiation method?
A: Ceric-ion/cellulose redox system gives preferential grafting over other methods, which give rise to homopolymerization, because of free radicals produced outside the cellulose backbone. In high and low energy irradiation methods there is some degradation. With simultaneous method of irradiation there would be lot of homopolymerization, because of excitation of monomers also. The grafting would depend upon the chain transfer efficiency of these free radicals going on to the cellulose phase.

Q: S. N. Pande (TCCC): Why was temperature 40°C selected for studying the reaction? Did you try other temperatures?
A: This is the initial stage of our experimentation. We have not studied all the details. Working at lower temperatures was cumbersome. It was easy to manipulate at temperatures slightly higher than room temperature.

Q: V. G. Agnihotri (BTRA): What was the pH of the reactant solution?
A: The pH was between 3 and 4 which was rather acidic.

Q: M. G. Modak (Swatantra Bharat Mills): Instead of using non-cellulosic substance, could you have used cellulose of different surface areas?
A: That could be done, but non-cellulosic material was used to avoid polar effects, and the factor of accessibility which is associated with cellulose.
Ceric Ion Induced Redox Polymerization of Acrylonitrile in Presence of Cellulose*

Use of cemic salts (ceric ammonium nitrate and sulfate) for grafting vinyl monomers on to primary alcohols, amines, thiols, etc. has been reported by Mino et al.1-3 In the present investigation cemic ammonium nitrate is used to study grafting of acrylonitrile (AN) on to cellulose (cotton fibers).

Grafting was effected by a solution polymerization technique in stoppered 150-ml. Pyrex flasks using 1 g. cotton fibers. The reaction was carried out at 40 ± 0.2°C. over periods ranging from 5 to 60 min. The grafted samples were washed well and then extracted overnight with cold dimethyl formamide (DMF) for removing the superfluous polyacrylonitrile (PAN).

In general the rate and yields of grafting are very high as compared to those obtained with a persulfate-thiosulfate redox system reported earlier.4

The grafting reaction starts instantaneously, since no induction period could be observed.

Separate studies or silica spheres substituted for the cotton fibers indicate that the high rate of grafting is not merely due to the large surface area of cellulose available for reaction, but is mainly due to the reducing action of cellulose.

The effect of monomer and initiator concentrations respectively on the yield of grafting has also been studied.

Mino et al.2 have shown that during oxidation of alcohols, such as pinacol with cemic salts, the cemic ions are responsible for generation as well as termination of free radical sites.

It may thus be assumed that during the grafting of PAN to cellulose, too, the ceric ions would be consumed in a similar manner, i.e., for initiation and termination of free radical sites. It is observed that the [CeIV] consumption during the grafting reaction is more than that during oxidation of cellulose alone. It is, therefore, postulated that this difference is due to the formation of some ungrafted PAN within the cellulose fibers.

Number average molecular weights (Mn) of the grafted PAN chains, obtained by using the equation of Marchessault et al.5 range between 140,000-290,000.

Osmometric data on the values of Mn are awaited for substantiating the theoretical values mentioned above.

These together with other data on the oxidation of cellulose with cemic ions will be published shortly.

The authors thank the Director and members of the Council of Administration of ATIRA for permission to publish this work.

References

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Received April 12, 1965

* This work forms part of the Ph.D. thesis of A. Y. Kulkarni.
Permanently Amorphous Cellulose

Amorphous cellulose may be produced by severe grinding of native cellulose in a ball mill. The x-ray diffraction of the resulting powder indicates that it is in the amorphous state. Milling must be done dry. On wetting with water, the amorphous cellulose regains some of its lost order and gives an x-ray diffraction diagram corresponding to cellulose II.

Amorphous cellulose can also be produced by anhydrous deacetylation of cellulose acetate. Crystallinity is regained on wetting as with ball-milled cellulose.

In a recent investigation, the accessibility of amorphous cellulose, as measured by hydrogen exchange methods, was found to be 89%. The accessibility measurement required that the cellulose be exposed to water vapor at 50% relative humidity. This is known to produce partial recrystallization of the amorphous cellulose. Therefore, there was some doubt as to whether the accessibility of 89% was for truly amorphous material or for partially recrystallized cellulose.

Some method of "fixing" the amorphous character of the cellulose was then sought. It was considered possible that the introduction of chemical crosslinks into the amorphous cellulose under anhydrous conditions would eliminate molecular reordering processes on subsequent addition of water. After much trial and error, such a method was found and is described in the present note.

Amorphous cellulose was prepared by the saponification of oil-free secondary cellulose acetate fiber (kindly supplied by Chemcell of Canada). The fiber was first Wiley-milled to 40-mesh. Deacetylation was carried out in a non-aqueous medium by use of 1% sodium methylate dissolved in anhydrous methanol. The saponified material was treated with glacial acetic acid to neutralize the alkali. The cellulose was washed with anhydrous methanol and dried in a vacuum oven at 70°C overnight.

The amorphous cellulose was crosslinked with formaldehyde by a modification of the Wagner and Paccou technique. Ten parts of amorphous cellulose were sealed in a Pyrex tube with one part of solid paraformaldehyde and one part of finely powdered boric acid. The tube was shaken to mix the contents, placed in a metal shield, and baked at 125°C for 24 hours. The contents of the tube were then removed and washed with boiling distilled water until free from formaldehyde and boric acid. The crosslinked amorphous cellulose was then dried in a vacuum oven at 70°C. Batches of up to 20 g. were made by the above procedure.

The formaldehyde content of the crosslinked material was measured by the method of Hoffpavir, Buckaloo, and Guthrie. It was about 2% which is equivalent to one crosslink for every 9 glucose residues.

X-ray patterns for the amorphous cellulose and the crosslinked amorphous cellulose are shown in Figure 1. Included in the pattern for regenerated cellulose obtained by boiling the amorphous cellulose in distilled water for five minutes and drying in a vacuum over at 70°C. It is quite clear that boiling in water caused the amorphous cellulose to revert to cellulose II. In contrast, the crosslinked amorphous cellulose retained its amorphous pattern even after the prolonged aqueous treatment required to remove the formaldehyde and the boric acid.

Similar preparations were made by crosslinking amorphous cellulose produced by ball-milling cotton linters in a Spex Mixer Mill. However, milled samples were rather impure due to the accretion of metallic residues generated in the milling process.

Accessibilities were measured by the tritium exchange method of Scrail and Mason. Measurements were made at 100% relative humidity. The regenerated cellulose gave an accessibility of 79% in good agreement with previous results for other regenerated celluloses.

The accessibility of the crosslinked amorphous cellulose was 83% of the original —OH content of the cellulose. If formaldehyde crosslinks by formation of a methylene ether, then each Cell—O—CH₂—O—Cell bridge eliminates two hydroxyl groups which would be potential exchangers in uncrosslinked cellulose. The formaldehyde content of 2%
OXIDATION OF CELLULOSE BY CERIC ION

The use of ceric ion for initiating graft polymerization of vinyl monomers onto cellulose has been reported by many workers (1–9). It is believed that the initiation of free radicals on the cellulose molecule involves abstraction of a hydrogen atom from the carbon atom carrying the hydroxyl groups (1). However, since ceric salts also oxidize alcohols containing 1:2 glycol linkages, e.g., pinacol (2), with a C–C bond cleavage, it appears likely that during oxidation of cellulose with ceric

Fig. 1. First-order plots of ceric ion consumption during oxidation and polymerization reaction with cellulose: (A) oxidation with 0.012M ceric, (a) grafting with 0.012M ceric; (B) oxidation with 0.006M ceric (b) grafting with 0.006M ceric; (C) oxidation with 0.003M ceric. Liquor ratio = 30; temperature of reaction = 40°C.
Fig. 2. First-order plots of ceric ion consumption during oxidation of model compounds: (2) $\alpha$-methyl-D-glucoside (o) and $\alpha$-methyl-D-mannoside (□); (1) D-glucose. Oxidation with 0.01M ceric solution. Liquor ratio = 50; temperature of reaction = 40°C.

ion, such a bond cleavage could occur at C₂ and C₃. This view has been supported recently by Cumberbirch and Holker (5) who studied the oxidation of cyclohexane 1:2 diol with ceric ammonium nitrate and obtained adipaldehyde as a major product of oxidation. Terasaki et al. (6), while supporting this view, have also postulated that the initial oxidative attack occurs at the cellulose chain ends containing hemiacetal linkages.

In the following communication, we report some studies on the oxidation of cellulose (scoured and bleached Egyptian cotton slivers) with acidified ceric ammonium nitrate solutions.
Fig. 3. Ceric ion consumption of modified and unmodified cellulose: (1) original cellulose; (2) periodate oxidized cellulose; (3) periodate oxidized and borohydride reduced cellulose. Oxidation with 0.05M ceric solution. Liquor ratio = 30; temperature of reaction = 40°C.

In Figure 1 are shown the first-order plots of the consumption of ceric ion (a) during oxidation of cellulose and (b) during the grafting reaction with acrylonitrile monomer. The ceric ion consumption during grafting is higher than that during oxidation of cellulose. This could be due to initiation and termination of free radicals of the growing polymer chains outside the cellulose phase, i.e., due to homopolymer formation. Further, the rate of ceric ion consumption is faster in the initial period of oxidation (i.e., during the first 2.5 min.) than during the rest of the reaction period. Terasaki et al. have postulated that presence of a hemiacetal group in the end units of cellulose chains leads to this initial fast rate of ceric ion consumption. Verification of this postulate is obtained by an examination of the rates of oxidation of α-methyl-D-glucoside and D-glucose (Fig. 2), when D-glucose shows a faster initial
Fig. 4. Acid hydrolysis of ceric oxidized and borohydride reduced cellulose. Chromatography in butanol–pyridine–water: (5:4:3): (1) original cellulose; (2) cellulose treated with HNO₃ 1%; (3) cellulose oxidized with ceric ammonium nitrate acidified with 1% nitric acid. Standards: glucose, mannose, and erythritol in descending order.

rate of ceric ion consumption than α-methyl-D-glucoside. However, all substrates studied, namely cellulose, D-glucose, α-methyl-D-glucoside, and α-methyl-D-mannoside (Figs. 1 and 2) show this initial fast rate to a greater or lesser extent. It is obvious that besides presence of hemiacetal groups, there must be other causes contributing to this fast initial rate of ceric ion consumption. Accessibility of substrate cannot be responsible for this phenomenon, since it is observed even when the oxidation is in a completely homogeneous system. Mino et al. (1) have suggested that the oxidation of alcohols with ceric ion proceeds via formation of a ceric–alcohol complex in the first stage of the reaction.

Thus $R \cdot \text{CH}_2\text{OH} + \text{Ce}^IV \rightarrow \text{B} \xrightarrow{\text{(Complex)}} R \cdot \text{CHOH} + \text{Ce}^II + \text{H}^+$
TABLE I

Relationship Between CeIV Consumed and (COOH) Content of Oxidized Cellulose

<table>
<thead>
<tr>
<th>(CeIV)/a.g.u. before chlorous acid oxidation</th>
<th>(COOH)/a.g.u. after chlorous acid oxidation</th>
<th>(CeIV)/a.g.u. after chlorous acid oxidation</th>
<th>(CeIV)/(COOH) = a/b</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.049</td>
<td>0.00045</td>
<td>0.30629</td>
<td>7.79</td>
</tr>
<tr>
<td>0.127</td>
<td>0.00089</td>
<td>0.30786</td>
<td>16.15</td>
</tr>
<tr>
<td>0.294</td>
<td>0.00089</td>
<td>0.31022</td>
<td>28.76</td>
</tr>
<tr>
<td>0.556</td>
<td>0.00112</td>
<td>0.31062</td>
<td>52.35</td>
</tr>
<tr>
<td>0.908</td>
<td>0.00112</td>
<td>0.31298</td>
<td>69.95</td>
</tr>
<tr>
<td>1.231</td>
<td>0.00134</td>
<td>0.31376</td>
<td>89.46</td>
</tr>
</tbody>
</table>

It is therefore possible that the initial fast rate of ceric ion consumption is mainly due to formation of a ceric–alcohol complex. In case of other transition metal ions such as V^3+ and Co^3+, formation of such a complex with alcohols has been reported (13). The cellulose fibers, after oxidation, are colored deep yellow and this color persists even after repeated washing with hot water. Similarly, a marked color change from yellow to orange is observed in the ceric solutions on addition of alcohols such as D-glucose.

In Table I are shown data on the ceric ion consumption by cellulose fibers and their corresponding carboxyl contents measured after conversion of the aldehyde/carbonyl groups to carboxyl groups with chlorous acid oxidation according to a method reported by Nevell (11). It is evident that the ceric ion consumption is far in excess of the carboxyl content of the cellulose. This finding also substantiates the postulate of a complex formation between ceric and cellulose.

In Figure 3 the rates of ceric ion consumption by cellulose oxidized with sodium periodate (curve 2) and subsequently reduced with sodium borohydride (curve 1) are compared with that of native cellulose (curve 3). Both modified cellulosics show a very high ceric ion consumption (almost 7 times) as compared to native cotton. Since the periodate consumption in this case was only 0.5M/a.g.u., the primary hydroxyl content would have risen by a maximum factor of 2. This, therefore, does not account for the total increase in ceric ion consumption. However, since such a modification is known to bring about significant changes in the accessibility of the cellulose fibers, the rate of formation of
Ceric cellulose complex would also change accordingly, and would account for such an increase in the total ceric ion consumption.

In order to ascertain if the C<sub>2</sub>—C<sub>3</sub> bond is cleaved during oxidation with ceric ammonium nitrate, the ceric-oxidized cellulose was further reduced with sodium borohydride, hydrolyzed completely and the hydrolysate analyzed by paper chromatography (Fig. 4). This chromatogram does not show the presence of erythritol, but shows the presence of mannose in substantial quantity. That mannose is not present in the original cellulose, nor is it formed during oxidation by nitric acid present in ceric ammonium nitrate solutions, is confirmed by the respective blanks 1 and 2 in the chromatogram. The postulate that the C<sub>2</sub>—C<sub>3</sub> bond is cleaved during oxidation is not supported by this finding. Presence of mannose in significant quantity can be understood if the initial attack of the oxidant (Ce<sup>V</sup>) was at C<sub>2</sub>, oxidizing >CHOH to >C=O.

Subsequent reduction of this product would give both glucose and mannose, as shown.

Details of this work and of the confirmation of D-mannose in the hydrolysate will be published shortly.

This work forms a portion of the Ph.D. Thesis of A. Y. Kulkami. The authors thank the Council of Administration of the Ahmedabad Textile Industry’s Research Association for permission to publish this work. They also thank Dr. Prem Pal Singh of the Carbohydrate Section,