ESR Study of Reactions of Cellulose Initiated by the Ceric Ion Method*

JETT C. ARTHUR, JR., PETER J. BAUGH,† and OSCAR HINOJOSA, *Southern Regional Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, New Orleans, Louisiana 70119*

Synopsis

The ESR spectra of microcrystalline cellulose and purified cotton cellulose reacted with ceric ammonium nitrate in nitric acid were determined. The effects of the concentration of ceric ion, atmosphere, temperature, and graft copolymerization with acrylonitrile on the rates of formation and decay of radicals in the cellulose molecule were determined under both static and dynamic conditions. Under static conditions, after the desired conditions of reaction, the samples were frozen at -100 or $-160°C.$, and then the concentration of free radicals was determined. Under dynamic conditions ceric ion solution was continuously flowed through the celluloses while these determinations were being made at $25°C.$ In the presence of oxygen the rate of decay of free radicals was decreased. On initiation of copolymerization reactions with acrylonitrile, there was an increase in radical concentration, then a decrease. Apparently, during graft copolymerization the radical site initially on the cellulose molecule was retained on the end of the growing polymer chain. Then additional ceric ion coordinated with the hydroxyl groups of the cellulose, leading to the formation of additional radical sites. An Arrhenius interpretation of the effect of temperature on the formation of these additional radical sites gave apparent activation energies for radical formation on cotton cellulose as 34 kcal./mole and on microcrystalline cellulose as 29 kcal./mole.

INTRODUCTION

The formation of graft copolymers of fibrous cellulose is the basis of many possible processes for the useful modifications of its properties. Copolymerization reactions initiated by free radicals formed in the cellulose molecule by thermal bond cleavage, by absorption of photochemical or high energy radiation, and by redox systems, have been extensively investigated.[1,2] The use of the ceric–cerous redox system to initiate graft copolymerization of vinyl monomers with cellulose, including fibrous cotton cellulose, has been reported by a number of investigators.[3–10] The mechanism of the copolymerization reactions has been reported to be a free-radical process in which the transfer of electrons from the hydroxyl

groups of the cellulose to the ceric ion results in the formation of a free radical on the cellulose molecule.[1,2,11]   Then graft copolymerization reactions with vinyl monomers are initiated at these radical sites.

Experimental data are presented in this report, based on the electron spin resonance (ESR) spectroscopy study of the effects of the concentration of ceric ion, atmosphere, temperature, and graft copolymerization with acrylonitrile on the rates of formation and decay of free radicals in microcrystalline cellulose and in purified fibrous cotton cellulose.   The experimental determinations were made under both static and dynamic conditions.   The experimental results demonstrated that free radicals do, indeed, play an important role in the reactions of cellulose initiated by the ceric ion method.

EXPERIMENTAL

Preparation of Samples

Cotton cellulose of the Deltapine variety was purified by extraction with hot ethanol followed by boiling in dilute sodium hydroxide solution, precautions being taken to minimize air oxidation,   The sodium hydroxide was removed by washing the cellulose with distilled water, then followed by souring with dilute acetic acid, neutralizing with dilute ammonium hydroxide, and again washing with distilled water.[12]   The purified cellulose was allowed to condition at 21°C. and 65% R.H., resulting in a product with a moisture content of about 7%.   The viscosity-average molecular weight of the purified cellulose was about 700,000.

The microcrystalline cellulose, obtained from a commercial source, was prepared by the hydrolysis of a purified wood high α-cellulose with 2.5N HCl at 105°C.   The average level-off degree of polymerization was about 220.[13]

Methods

The ESR spectra and free-radical concentrations formed during reactions of cellulose initiated by the ceric ion method were determined in a Varian 4502-15 EPR spectrometer system.   The system was equipped with a variable temperature accessory allowing operation from about −185 to 300°C., a dual sample cavity, and both aqueous-solution and solid-sample cell accessories.   When determinations were made under static conditions, the celluloses were reacted in quartz tubes (3 mm. diameter) or glass tubes (1.6 mm. diameter) under the desired experimental conditions.   Then the reactions were stopped by freezing the samples by immersing them in liquid nitrogen.   The frozen samples were transferred to the resonant cavity of the spectrometer.   After warming, the ESR spectra and free-radical concentrations were determined at −100 or −160°C.   When determinations were made under dynamic conditions, the celluloses were reacted in aqueous-sample cells located within the resonant cavity of the spectrometer.   The reactions were conducted under the desired experimental

conditions while ceric ion or monomer solutions were drawn through the celluloses by using a high-capacity vacuum pump. This enabled the experimental conditions to be rapidly changed. A small porous plug of cotton cellulose was inserted in the sample tube outside of the resonant cavity of the spectrometer to prevent the evacuation of the sample. In most dynamic determinations a series of short time-base sweeps were made, and the changes in the peak values of the spectra were related to the free-radical concentration. However, the rate data, recorded in Figures 5 and 11, were obtained directly by setting the sweep on the major peak of the ESR spectra and using the time-base axis of the X-Y recorder; the figures are tracings of the experimentally recorded rate curves.

The variation in the sensitivity of the resonant cavity of the spectrometer from its center to either its top or its bottom was used to determine the reaction boundary in graft copolymerization reactions, as discussed below.

RESULTS

Microcrystalline Cellulose

The ESR spectrum of microcrystalline cellulose, saturated with ceric ammonium nitrate (0.05M) in HNO_3 (0.05M), allowed to react for 15 sec.
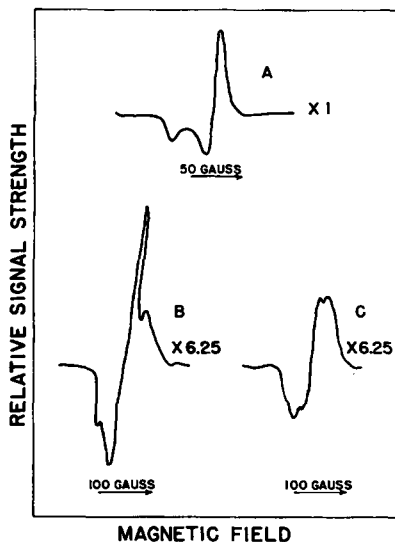

Fig. 1. ESR spectra of microcrystalline cellulose reacted with ceric ion and/or acrylonitrile: (A) saturated with ceric ammonium nitrate (0.05M) in HNO_3 (0.05M) for 15 sec. at 25°C., then frozen at -100°C. before determination; (B) saturated with ceric ion solution and excess solution drawn off for 40 sec., followed by reaction with acrylonitrile for 35 sec. at 25°C., then frozen at -100°C. before determination; (C) saturated as in B and excess solution drawn off for 40 sec., followed by reaction with acrylonitrile for 35 sec. at $\cdot$-10°C., then frozen at -100°C. before determination.
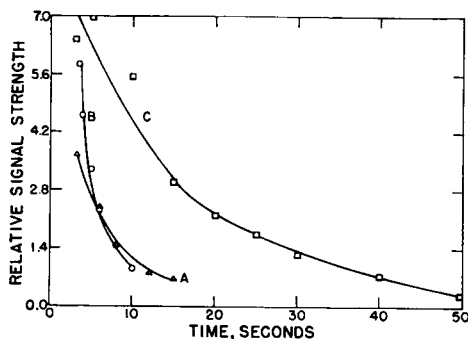
Fig. 2. Decay of free radicals initiated in microcrystalline cellulose by its saturation with ceric ammonium nitrate in HNO_3 at 25°C.: (A) 0.0025M; (B) 0.005M; (C) 0.05M. Time measured from saturation at 25°C. to freezing at −100°C. before determination.

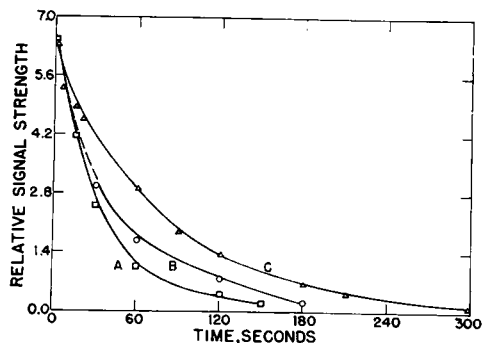Fig. 3. Decay of free radicals initiated in microcrystalline cellulose by its saturation with ceric ammonium nitrate in HNO_3 at 25°C.: (A) 0.005M; (B) 0.01M; (C) 0.05M. After a constant time of treatment for 40 sec., during which time the excess solution was drawn off by vacuum, the time was measured from saturation at 25°C. to freezing at −100°C. before determination.

at 25°C. before freezing in liquid nitrogen, and then determined at −100°C. is shown in Figure 1A. An asymmetric doublet spectrum was obtained, clearly indicating the presence of free radicals in the activated micro-crystalline cellulose. Unreacted cellulose showed no ESR signal. Ceric ammonium nitrate solution in the presence or absence of HNO_3 and cerous nitrate also showed no ESR signal. The ESR spectra of microcrystalline cellulose, saturated with ceric ion and the excess solution drawn off for 40 sec. at 25°C., then followed by reaction with purified acrylonitrile mono-mer, drawn onto the activated cellulose, for 35 sec. at either 25 or −10°C., are shown in Figure 1B and 1C, respectively. The spectra were deter-mined at −100°C. The ESR spectra of the graft copolymers were broader and more symmetrical than the spectrum of the activated cellulose.

The decay of free radicals, initiated in microcrystalline cellulose by its saturation with ceric ion solutions in nitric acid at 25°C., is shown in Fig-
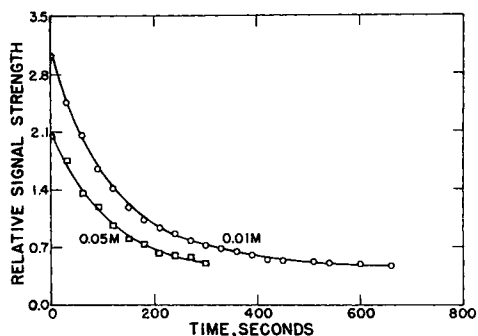
Fig. 4. Decay of free radicals initiated in microcrystalline cellulose while continuously drawing ceric ammonium nitrate in HNO_3 at 25°C. through the cellulose.
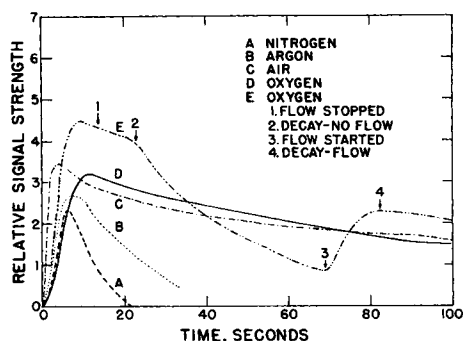

Fig. 5. Effect of atmosphere on the decay of free radicals initiated in microcrystalline cellulose by flowing through ceric ammonium nitrate $(0.05M)$ in HNO_3 $(0.05M)$ at 25°C.

ure 2. The time was measured from the time of saturation of the cellulose with ceric ion solution to the time of immersion of the sample in liquid nitrogen. With increased concentration of ceric ion in solution, there was an increased concentration of free radicals in the cellulose and a decreased rate of decay of the free-radical sites. Since inactivation of a radical site could occur by the reaction of ceric ion with the radical, after saturation of the cellulose with solution an attempt was made to draw off the excess ceric ion solution by a high capacity vacuum pump. The decay of free radicals under these experimental conditions, as a function of the concentration of ceric ion, is shown in Figure 3. With increased concentration of ceric ion in the initial solution, there was a decreased rate of decay of the free radical sites. However, at the constant time of contact of the cellulose with the ceric ion solution (40 sec. at 25°C.) after drawing off the excess solution, the concentration of free radicals appeared to be independent of the concentration of ceric ion in the saturating solution.

The decay of free radicals, initiated in microcrystalline cellulose while continuously drawing ceric ion solution through the cellulose at 25°C., is

shown in Figure 4.   Under these dynamic conditions, the rate of decay of radical sites was about the same for each concentration of ceric ion; however, the effective concentration of radical sites was greater in the cellulose reacted with the lower concentration of ceric ion.

The effects of atmosphere on the rate of formation and of decay of free radicals in microcrystalline cellulose, while continuously drawing ceric ion solution through the cellulose at 25°C., are shown in Figure 5.

These experimental curves were obtained directly by setting the sweep on or near the major peak of the ESR spectra and using the time-base axis of the X–Y recorder.   Since there could be a small error in setting the sweep exactly on the peak, the data are not necessarily directly comparable on the basis of relative signal strength.   However, the rates of formation and decay of the free radicals should be very similar whether the setting was exactly on the peak or near the peak of the spectra.   The presence of
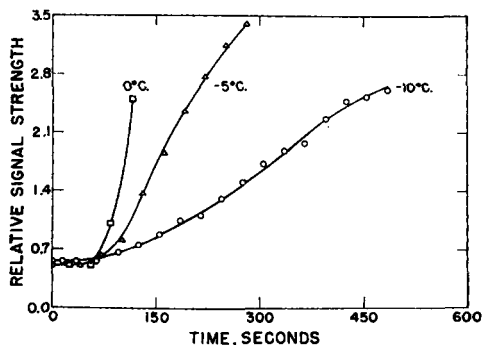

Fig. 6. Effect of temperature on the rate of formation of free radicals during copolymerization of acrylonitrile with microcrystalline cellulose initiated by ceric ion.

oxygen, in either air or pure oxygen, significantly increased the half-life of the free radicals.   The times from the maximum value for relative signal strength to one-half that value for the different atmospheres were approximately as follows: nitrogen, 6 sec.; argon, 13 sec.; air, 88 sec.; and oxygen, 74 sec.   It was interesting to note that under a selected atmosphere, oxygen, the rate of decay of the free-radical sites on the cellulose increased when the flow of ceric ion solution through the cellulose was stopped.   When the flow of ceric ion solution through the cellulose was again started, the free-radical concentration in the cellulose increased to a maximum value, somewhat lower than the initial maximum, and then decreased.

The effects of temperature on the rate of free-radical formation during copolymerization of acrylonitrile with microcrystalline cellulose initiated by ceric ion are shown in Figure 6.   The cellulose in glass tubes was saturated with ceric ammonium nitrate $(0.05M)$ in HNO_3 $(0.05M)$ at 25°C. and the excess solution drawn off for 40 sec.   Then purified acrylonitrile monomer, about a twofold pickup, was drawn onto the cellulose; the sample

was immediately immersed in liquid nitrogen. The frozen sample was placed in the resonant cavity of the spectrometer and allowed to warm to $-20°C$. The spectrometer was tuned at this temperature, and the ESR spectra of the sample indicated that little or no reaction had occurred. Then the sample was allowed to warm to the desired temperature (-10, -5, or $0°C$.), and the rate of formation of additional free radicals during the copolymerization reaction was determined. As shown in Figure 6, there was an induction period of 60–90 sec. while the sample was warming to the desired temperature. Any drift in the leakage readings of the spectrometer was manually corrected. There is obviously a temperature dependence on the rate of formation of additional free radicals during the copolymerization reaction.
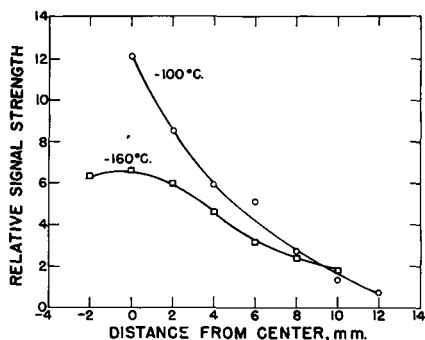

Fig. 7. Determination of reaction boundary between microcrystalline cellulose and graft copolymer. Cellulose saturated with $0.05M$ ceric ammonium nitrate in $0.05M$ HNO_3 and excess solution drawn off for 40 sec., then reacted with acrylonitrile for 35 sec. at $25°C$., followed by freezing at $-100°$ or $-160°C$. before determination.

After saturation of microcrystalline cellulose with ceric ion solution in a quartz tube and then initiation of the graft copolymerization reaction with acrylonitrile by drawing the monomer onto the cellulose, there was a noticeable color change from yellow to white as the reaction proceeded through the cellulose. To determine if this was a reaction boundary between the activated microcrystalline cellulose and the monomer, advantage was taken of the increase in free-radical concentration on copolymerization and of the variation in sensitivity of the areas within the resonant cavity of the spectrometer. A reaction was allowed to proceed for a desired time, then frozen in liquid nitrogen and observed in the spectrometer at -100 or $-160°C$. The colored boundary was placed at the center or above or below the center of the cavity. The apparent free-radical concentration decreased as the colored boundary was moved away from the center of the cavity, as shown in Figure 7. The boundary, except in one case at $-160°C$., was moved, so that the yellow or unreacted part of the cellulose was moved into the center of the cavity.

Fibrous Cotton Cellulose

The ESR spectrum of fibrous cotton cellulose, saturated with ceric ammonium nitrate (0.05M) in HNO$_3$ (0.05M), allowed to react for 20 sec. at 25°C. before freezing in liquid nitrogen, and then determined at −100°C., is shown in Figure 8A. A fairly symmetrical spectrum was obtained, clearly indicating the presence of free radicals in the activated cotton cellulose. Unreacted cotton cellulose showed no ESR signal. The ESR spectrum of cotton cellulose reacted with the ceric ion solution for 20 sec. at 25°C., then followed by reaction with purified acrylonitrile monomer, about a twofold pickup, drawn onto the activated cellulose, for 6 min. at 25°C., is shown in Figure 8B. The spectrum was determined at −100°C. The ESR spectrum of the graft copolymers was broader than the spectrum of the activated cellulose. Also, the formation of a second type of free radical was indicated.

The decay of free radicals, initiated in fibrous cotton cellulose by its saturation with ceric ion solution in nitric acid, at 25°C. is shown in Figure 9. The time was measured from the time of saturation of the cellulose with ceric ion solution to the time of immersion of the sample in liquid nitrogen. The concentration of free radicals, as indicated by the relative signal strength, was determined at −100°C.

The effects of temperature on the rate of free-radical formation during copolymerization of acrylonitrile with cotton cellulose initiated by ceric
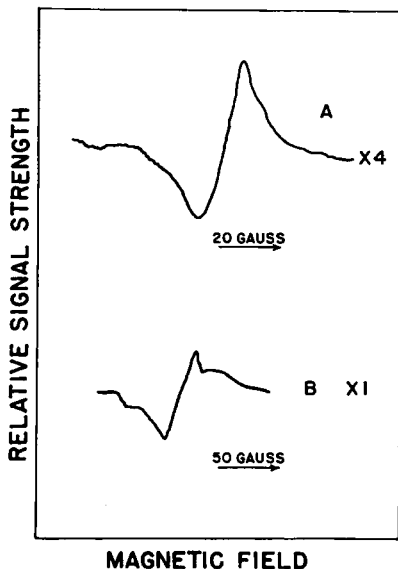

Fig. 8. ESR spectra of cotton cellulose reacted with ceric ion and/or acrylonitrile: (A) saturated with ceric ammonium nitrate (0.05M) in HNO$_3$ (0.05M) for 20 sec. at 25°C., then frozen at −100°C. before determination; (B) saturated as in A for 20 sec., followed by reaction with acrylonitrile for 6 min. at 25°C., then frozen at −100°C. before determination.
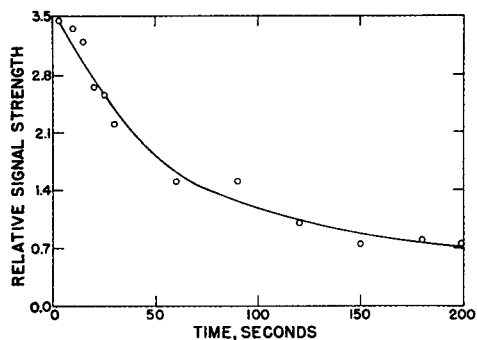
Fig. 9. Decay of free radicals initiated in cotton cellulose by its saturation with ceric ammonium nitrate $(0.05M)$ in HNO_3 $(0.05M)$ at 25°C. Time measured from saturation at 25°C. to freezing at -100°C. before determination.
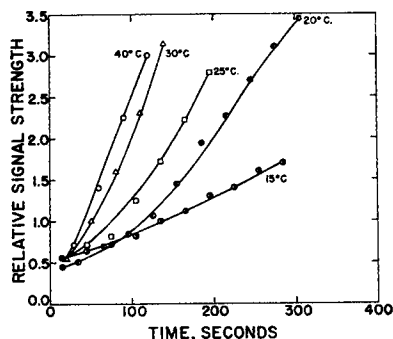

Fig. 10. Effect of temperature on the rate of formation of free radicals during copolymerization of acrylonitrile with cotton cellulose initiated by ceric ion.

ion are shown in Figure 10. The cellulose in glass tubes was saturated with ceric ammonium nitrate $(0.05M)$ in HNO_3 $(0.05M)$ at 25°C. for 5 sec. and the excess solution drawn off for 5 sec. Purified acrylonitrile monomer was drawn onto the cellulose; then the sample was cooled and placed in the resonant cavity of the spectrometer at 5°C. The spectrometer was tuned at this temperature, and the ESR spectra of the sample indicated that very little reaction had occurred. Then the sample was allowed to warm to the desired temperature (15, 20, 25, 30, or 40°C.), and the rate of formation of additional free radicals during the copolymerization reaction was determined. Any drift in the leakage readings of the spectrometer was manually corrected. There is obviously a temperature dependence on the rate of formation of additional free radicals during the copolymerization reaction with fibrous cotton cellulose, as was observed with microcrystalline cellulose.

The effects of atmosphere and temperature on the rate of formation of free radicals in cotton cellulose during copolymerization with acrylonitrile initiated by ceric ion are shown in Figure 11. The cellulose in glass tubes
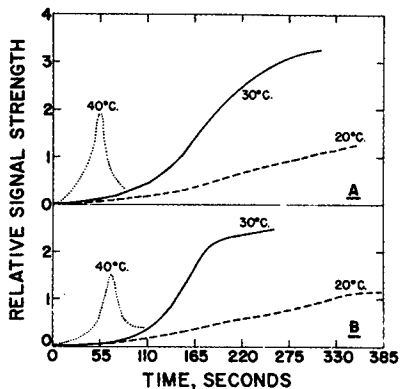
Fig. 11. Effect of atmosphere and temperature on rate of formation and of decay of free radicals during copolymerization of acrylonitrile with cotton cellulose initiated by ceric ion: (A) nitrogen; (B) air.
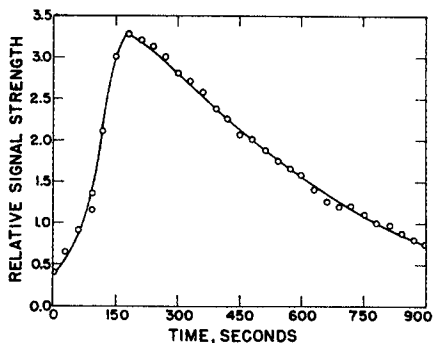

Fig. 12. Rate of formation and of decay of free radicals during copolymerization of acrylonitrile with cotton cellulose initiated by ceric ion at 25°C.

was saturated with ceric ammonium nitrate (0.05M) in HNO$_3$ (0.05M) at 25°C. for 5 sec. and the excess solution drawn off for 5 sec. Purified acrylonitrile monomer was drawn onto the cellulose; then the sample was cooled and placed in the resonant cavity of the spectrometer at 5°C. The initial radical concentration in the cotton cellulose was very low. The sample was allowed to warm to the desired temperature (20, 30, or 40°C.), and the experimental curves were obtained directly, as described for those shown in Figure 5. Under both nitrogen and air the rates of formation of free radicals in cotton cellulose during the copolymerization reaction were similarly temperature dependent. The relative signal strengths of the spectra obtained under nitrogen were slightly greater than those obtained under air, indicating a higher free-radical concentration in celluloses during copolymerization with acrylonitrile under nitrogen than under air.

The increase and then decrease in free-radical concentration during copolymerization of acrylonitrile with cotton cellulose at 25°C., initiated

by ceric ion, are shown in Figure 12. The cotton cellulose in glass tubes was saturated with ceric ammonium nitrate (0.05M) in HNO$_3$ (0.05M) at 25°C. for 5 sec. and the excess solution drawn off for 5 sec. Purified acrylonitrile monomer was drawn onto the activated cellulose, and the sample was placed in the resonant cavity of the spectrometer at 25°C. The rate of increase in free-radical concentration was several times as great as the rate of decrease in radical concentration. In the latter stages of the copolymerization reaction, the relative signal strength was decreasing and approaching its initial value.

A copolymerization reaction of acrylonitrile with cotton cellulose was allowed to proceed until the color changed from yellow to white, indicating reduction of the ceric ion. After the copolymer was extracted with water and N,N-dimethylformamide, usually about 70–75% increase in weight of the cellulose due to grafted polyacrylonitrile was found. The grafted polymer was about one-third of the available monomer.

DISCUSSION

The presence of activated intermediates formed on the interaction of ceric ion with both microcrystalline cellulose and fibrous cotton cellulose was demonstrated. In both cases, the activated celluloses had paramagnetic properties as shown by their ESR spectra. The ESR spectra for the activated cotton cellulose were more symmetrical than those for the microcrystalline cellulose. The molecular weight of the cotton cellulose was about twentyfold greater than the molecular weight of the microcrystalline cellulose and consequently had a lower number of endgroups per unit weight of cellulose than the microcrystalline cellulose. Probably more important was the content of amorphous cellulose in the cotton. The more symmetrical ESR spectra for the activated cotton than for the activated microcrystalline cellulose could be related to greater uniformity of chelation of the ceric ion in the amorphous regions of the cotton cellulose and to a lesser uniformity of chelation of the ceric ion with the microcrystalline cellulose. Also, the chelation of ceric ion with the C$_2$ and C$_3$ atoms of the anhydroglucose units in the amorphous areas of the cotton would result in the formation of a different radical on the cotton cellulose than if the chelation occurred more with endgroups of the cellulose, as could be the case with microcrystalline cellulose.

The short half-life of the radical sites was expected; however, the fact that the presence of oxygen significantly increased the half-life of the radical sites in microcrystalline cellulose was unexpected. There was no significant change in the ESR spectra, indicating that the initial radical formed under nitrogen was similar to the radical formed under oxygen. The longer-lived radical site formed under oxygen could be due to the formation of a peroxy type product.

The rates of decay of radical sites, formed in both cotton cellulose and microcrystalline cellulose, were not altogether dependent on the concen-

tration of ceric ion in solution.   Under static conditions of measurement with microcrystalline cellulose, the lower the concentration of ceric ion in solution, the greater the rate of decay of the radical sites.   Under dynamic conditions of measurement, the rate of decay of the radical sites was apparently independent of ceric ion concentration.   Under static conditions of measurement when the excess ceric ion solution was drawn off the microcrystalline cellulose before freezing, the initial concentration of radical sites appeared to be independent of concentration of ceric ion, and the rate of decay of the radical sites appeared to be dependent on the ceric ion concentration.
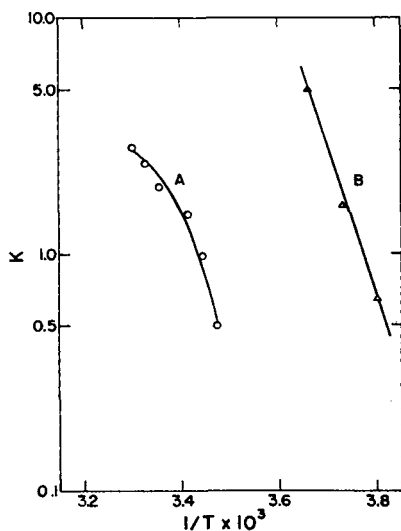

Fig. 13. Arrhenius plot of rate of formation of free radicals in cellulose initiated by ceric ion and during graft copolymerization of acrylonitrile vs. temperature: (A) cotton cellulose; (B) microcrystalline cellulose.
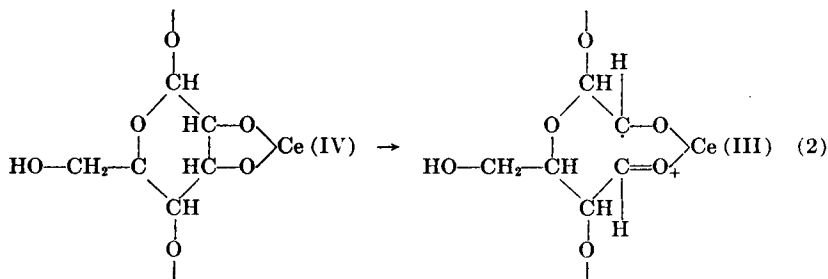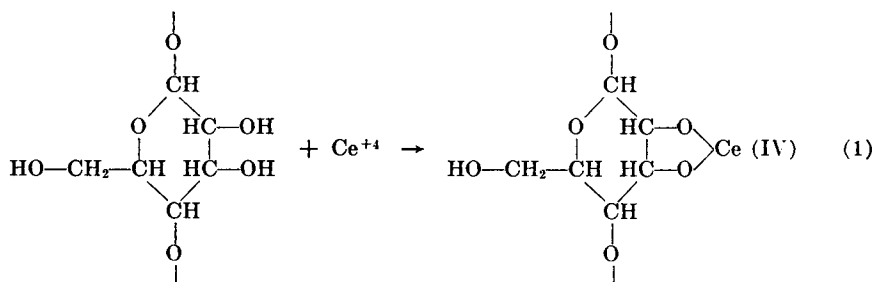
On initiation of graft copolymerization of the activated celluloses with acrylonitrile monomer, there are significant changes in the ESR spectra. The spectra of graft copolymers of microcrystalline cellulose are more symmetrical than those for the activated cellulose.   The spectra also indicate that a different radical site is formed during the reaction.   This would be expected if the initial radical sites on the cellulose were eliminated on grafting and new radical sites were formed on the end of the growing copolymer chain.   The ESR spectra of graft copolymers of cotton cellulose also differ from those of the activated cotton.   From the differences in the spectra, the formation of new radical sites on the growing polymer chain is also indicated.
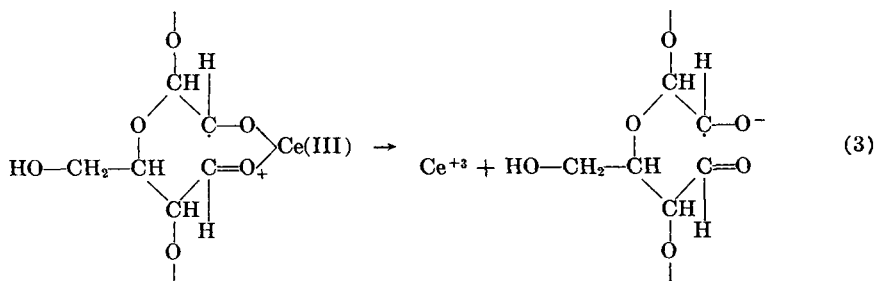
The increases in the relative signal strengths of the ESR spectra of the celluloses during the initial stages of the graft copolymerization reactions were temperature-dependent phenomena.   As discussed earlier, the acti-

vated cellulose and acrylonitrile monomer were maintained at a temperature where little or no reaction occurred, then increased to the desired temperature. When the temperature was being increased, there was an induction period; then the maximum rate of increase in the signal strength, that is, rate of formation of radical sites, was determined. An Arrhenius interpretation of these data is shown in Figure 13. The apparent activation energy for the formation of these additional radical sites on microcrystalline cellulose was about 29 kcal./mole, and on cotton celluloses at 30°C. or lower, about 34 kcal./mole. A similar phenomenon for the rate of formation of radicals in cotton as a function of temperature is shown in Figure 11. Previously,[14] it was reported that the apparent activation energy for the thermal initiation of free radicals in cotton cellulose was about 33 kcal./mole. From these data the increase in free-radical sites on the cellulose during the graft copolymerization reactions could be explained by: (1) the transfer of the initially formed radical sites on the cellulose to the end of the growing copolymer chain and (2) with this decrease in radical sites on the cellulose more ceric ion could chelate with the cellulose forming new radical sites. Within a given sample this could increase the relative signal strength of the ESR spectra of the sample.

Experimental data reported would support the free-radical mechanisms generally proposed for the oxidation of glycols[15,16] and for initiation of graft copolymerization reactions of cellulose by ceric ion.[2,8,9,17] In summary, we suggest that the ceric ion would form a chelate with the cellulose molecule, possibly through the C_2 and C_3 hydroxyls, as shown in reaction (1). There would follow a transfer of electrons from the cellulose
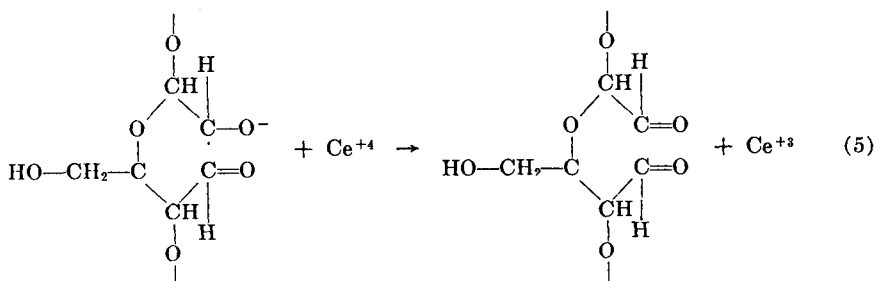
Radical Formation:

$$
\begin{array}{c}
\text{(structure: cellulose-Ce(III) chelate)} \quad \xrightarrow{}\quad Ce^{+3} + \text{HO—CH}_2\text{—CH}\ \ \text{(ring structure)} \quad (3)
\end{array}
$$

Graft Polymerization:

$$
\text{(cellulose radical structure)} \ +\ n\text{H}_2\text{C}=\overset{\text{H}}{\underset{}{\text{C}}}\text{—CN} \ \xrightarrow{}
$$

$$
\text{HO—CH}_2\text{—CH}\quad \text{C}\text{—}\left(\overset{\text{H}\quad \text{CN}}{\underset{\text{H}\quad \text{H}}{\text{C—C—}}}\right)_{n-1}\overset{\text{H}\quad \text{CN}}{\underset{\text{H}\quad \text{H}}{\text{—C—C}\cdot}}\quad (4)
$$

Radical Termination:

$$
\text{HO—CH}_2\text{—C}\ \text{(radical structure)}\ +\ Ce^{+4}\ \xrightarrow{}\ \text{HO—CH}_2\text{—C}\ \text{(C=O structure)}\ +\ Ce^{+3}\quad (5)
$$
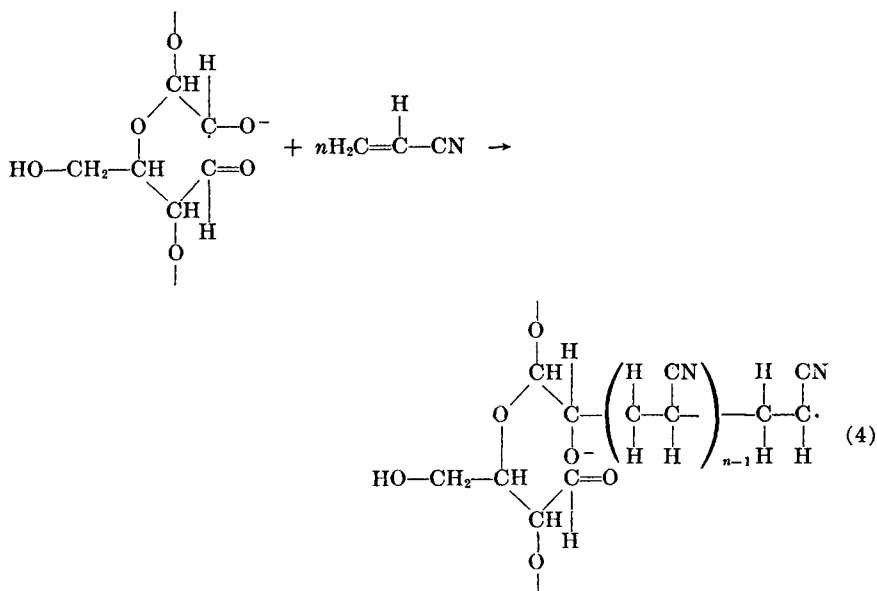
molecule to Ce(IV) which would result in its reduction to Ce(III), breakage of the C_2—C_3 bond, and formation of a radical site, as shown in reactions (2) and (3). On initiation of graft copolymerization at this site, as shown in reaction (4), additional ceric ion could chelate with the cellulose forming additional radical sites in the manner described. This proposed reaction

should be temperature-dependent, since the chelation equilibrium constant should vary with temperature.   This was found to be the case.   The decay of radical sites could result, as has been suggested by others,[1,2,11] on the subsequent reaction of ceric ion with the radical, as shown in reaction (5). However, the rate of decay of radical sites was not found to be directly dependent on an increase in the concentration of ceric ion.

Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers.

References

1. J. H. Baxendale, in *Polymer Processes (High Polymers*, Vol. X), C. E. Schildknecht, Ed., Interscience, New York, 1956, p. 1.
2. 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.
3. J. C. Arthur, Jr. and R. J. Demint, *Textile Res. J.*, **31**, 988 (1961).
4. Y. Iwakura, T. Kurosaki, and Y. Imai, *J. Polymer Sci. A*, **3**, 1185 (1965).
5. S. Kaizerman, G. Mino, and F. Meinhold, *Textile Res. J.*, **32**, 136 (1962).
6. G. Mino and S. Kaizerman, *J. Polymer Sci.*, **31**, 242 (1958).
7. G. Mino and S. Kaizerman, U. S. Pat. 2,922,768 (January 26, 1960).
8. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Am. Chem. Soc.*, **81**, 1494 (1959).
9. G. Mino, S. Kaizerman, and E. Rasmussen, *J. Polymer Sci.*, **38**, 393 (1959).
10. G. N. Richard, *J. Appl. Polymer Sci.*, **5**, 539 (1961).
11. A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds*, Prentice-Hall, Englewood Cliffs, N. J., 1952, p. 380.
12. J. H. Kettering and C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **14**, 432 (1942).
13. O. A. Battista and P. A. Smith, *Ind. Eng. Chem.*, **54**, 20 (1962).
14. J. C. Arthur, Jr. and O. Hinojosa, *Textile Res. J.*, **36**, 385 (1966).
15. F. R. Duke and A. A. Forist, *J. Am. Chem. Soc.*, **71**, 2790 (1949).
16. F. R. Duke and R. F. Bremer, *J. Am. Chem. Soc.*, **73**, 5179 (1951).
17. A. A. Katai, U. Kulshrestha, and R. H. Marchessault, in *Fourth Cellulose Conference (J. Polymer Sci. C, 2)*, R. H. Marchessault, Ed., Interscience, New York, 1963, p. 403.

Résumé

On a déterminé les spectres ESR de la cellulose microcristalline et de la cellulose de coton purifiée après réaction avec le nitrate cérique ammonique dans l'acide nitrique. Les effets de la concentration en ion cérique, de l'atmosphère, de la température et de la copolymérisation greffée de l'acrylonitrile sur les vitessses de formation et de disparition des radicaux au sein de la molécule de cellulose ont été déterminés à la fois dans des conditions statiques et dynamiques.   Dans des conditions statiques après les conditions de réaction souhaitées, les échantillons sont refroidis à −100 ou −160°C et ensuite la concentration en radicaux libres a été déterminée.   Dans des conditions dynamiques, la solution d'ion cérique est continuellement passée à travers les celluloses alors que ces déterminations sont faites à 25°C.   En présence d'oxygène, la vitesse de disparition des radicaux libres est fortement diminuée.   Lorsque l'on initie des réactions de copolymérisation d'acrylonitrile, il y a accroissement en concentration de radicaux, ultérieurement une diminution.   Apparemment, au cours de la copolymérisation greffée, le site radicalaire initialement présent dans la molécule cellulosique est retenu à la fin de la chaîne polymérique en croissance.   Ensuite, l'ion cérique coordiné avec les groupes hydroxy de la cellulose amène à la formation de sites radicalaires additionnels.   Une interprétation de l'effet de la température sur la formation de ces sites radicalaires additionnels suivant l'équation d'Arrhénius permet d'obtenir des énergies d'activation apparentes pour la

formation de radicaux sur la cellulose de coton elle est égale à 34 Kcal/mole et pour la cellulose microcristalline 29 Kcal/mole.

Zusammenfassung

Die ESR-Spektren von mikrokristalliner Cellulose und gereinigter Baumwollcellulose wurden nach Reaktion mit Cerammonnitrat in Salpetersäure bestimmt. Der Einfluss der Cerionenkonzentration, der Gasatmosphäre, der Temperatur und einer Pfropf-copolymerisation mit Acrylnitril auf Bildungs- und Abklinggeschwindigkeit der Radikale im Cellulosemolekül wurde unter statischen und dynamischen Bedingungen bestimmt. Unter statischen Bedingungen wurden nach Einstellung der gewünschten Reaktions-bedingungen die Proben bei −100° oder −160°C eingefroren und dann die Konzentra-tion an freien Radikalen bestimmt. Unter dynamischen Bedingungen wurde während der Durchführunt der Bestimmung bei 25°C ein kontinuierlicher Fluss der Cerionen-lösung durch die Cellulose sufrechterhalten. In Gegenwart von Sauerstoff nahme die Abklinggeschwindigkeit der freien Radikale ab. Beim Start der Copolymerisation mit Acrylnitril nahm die Radikalkonzentration zuerst zu und dann ab. Offenbar wurde während der Pfropfcopolymerisation das ursprünglich am Cellulosemolekül befindliche Radikalzentrum an das Ende der wachsenden Polymerkette verlagert. Dann trat eine Koordination eines zusätzlichen Cerions mit der Hydroxylgruppe der Cellulose unter Bildung weiterer Radikalzentren ein. Die Interpretation des Temperatureinflusses auf die Bildung dieser zusätzlichen Radikalzentren nach einer Arrheniusbeziehung lieferte für die Radikalbildung an Baumwollcellulose eine scheinbare Aktivierungsenergie von 34 kcal/Mol und für diejenige an mikrokristalliner Cellulose eine solche von 29 kcal/Mol.