

ESR Study of Post-Irradiation Reactions of Cellulose and Acrylonitrile

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Synopsis

An ESR study of the free-radical mechanisms of the post-irradiation reactions of cotton cellulose with acrylonitrile is reported. The effects of atmosphere, moisture content, and solutions of acrylonitrile on the yield and stability of free-radical sites in irradiated cellulose were determined. On interaction of γ -radiation from a ^{60}Co source with cotton cellulose, long-lived free-radical sites were found within the molecular lattice. Short-lived free-radical sites were apparently also formed on chain cleavage, gave strong singlet spectra, and were readily accessible to interaction with water. Other free-radical sites were formed within regions of the cellulosic fiber which were inaccessible to moisture or aqueous solutions even after contact times as long as three days. It was suggested that long-lived free-radical sites in cellulose I (containing regain moisture) resulted from dehydrogenation at C_6 , and in cellulose II (containing regain moisture) resulted from dehydrogenation at C_6 and dehydrogenation of the OH group or dehydroxylation at C_6 . When irradiated cellulose was contacted with a solution of acrylonitrile (15%) in 75% aqueous zinc chloride, the initial rate of decrease in spin concentration was higher than the rate of decrease as the time of contact increased. The ESR spectrum of the reacted cellulose, observed at -100°C ., as compared with the spectrum for the irradiated cellulose, had decreased in signal strength with increase in time of contact and changed from a three-line spectrum to an ill-defined spectrum. The free radical being observed was probably due to unreacted sites in the cellulose. The extent of the graft copolymerization reaction was directly related to the initial spin concentration in the irradiated cellulose.

INTRODUCTION

The use of ionizing radiation to initiate graft copolymerization reactions of fibrous cotton cellulose with vinyl monomers has been investigated at this laboratory for a number of years.¹⁻¹³ The reactions of the cellulose with vinyl monomers are apparently initiated at free-radical sites, formed on the interaction and localization of the energy of the ionizing radiation in the cellulose molecule. One procedure is to irradiate the cellulose while the monomer is present. This technique, usually referred to as the simultaneous procedure, has the apparent advantage of making use of both short-lived and long-lived free-radical sites; however, the formation of homopolymer probably also results. Another procedure is to irradiate

the cellulose in one step to form the free-radical sites, to remove the cellulose from the irradiation field, and then to react the activated cellulose with vinyl monomers. This technique, usually referred to as the post-irradiation procedure, has advantages in that the formation of homopolymer is probably minimized and in that the radiation step and the graft copolymerization step can be separated. Some of the important experimental factors influencing the radiochemical yields and the free-radical mechanisms of these graft copolymerization reactions, by either procedure, have been reported.¹⁻¹³ In the post-irradiation procedure, only the longer-lived free-radical sites would be major factors in initiating graft copolymerization reactions. The experimental conditions under which the radiation activation step occurred and under which the vinyl monomer was contacted with the free-radical site determine the radiochemical yield of a given reaction.

Experimental data are presented in this report, based on an electron spin resonance (ESR) spectroscopy study, on the effects of experimental conditions on the free-radical mechanisms of these reactions. The effects of atmosphere, moisture content, and solutions of acrylonitrile and other reagents on the yield and stability of free-radical sites in cotton cellulose are presented. The relationships between the amount of grafted polyacrylonitrile and the change in concentration of the free-radical sites are discussed.

EXPERIMENTAL

Preparation of Samples

Cotton cellulose of the Deltapine variety in 7/3s yarn form 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 solution 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.¹⁴ After the cellulose was conditioned at 21°C. and 65% R.H., the resulting product had a moisture content of about 7% and a viscosity-average molecular weight of about 700,000.¹⁵ The purified cellulose gave the typical cellulose I x-ray diffractogram.¹⁶ Samples of purified cellulose I were immersed in sodium hydroxide solution (23%) at 25°C. for 10 min. These samples were left in a slack condition, washed free of sodium hydroxide, and conditioned at 21°C. and 65% R.H. These mercerized samples gave the typical cellulose II x-ray diffractogram.¹⁶ To obtain samples of cellulose with varying moisture contents, the cellulose was conditioned from the dry side in a closed system in air or nitrogen atmospheres at 25°C. having different relative humidities (determined by using solutions of sulfuric acid) or was dried in vacuum over P₂O₅ at 25°C.

Methods

The SRRL ^{60}Co radiation source, previously described by Arthur et al.,¹⁷ was used. The dose rate, determined by ferrous–ferric dosimetry,¹⁸ was about 1.1×10^{19} e.v./g.-hr. over the experimental volume irradiated. The samples of cellulose were irradiated, with γ -irradiation from the ^{60}Co source, at ambient temperature in air or in vacuum in quartz tubes (3 mm. diameter) to the desired dosage. The samples irradiated in vacuum were placed in quartz tubes (near one end), then closed under vacuum. After irradiation the end of the tube containing the irradiated cellulose was cooled, and the other end of the tube was heat-annealed to remove any signal induced in the quartz. After cooling the tube to ambient temperature, the sample was moved to the heat-annealed end of the tube; then the end of the tube containing the cellulose was cooled while the remainder of the quartz was heat-annealed to remove any induced signal. The samples, irradiated in quartz tubes in air at ambient temperature, were transferred to other quartz tubes after irradiation.

The ESR spectra and free-radical concentrations during the post-irradiation reactions of the cellulose were determined in a Varian 4502-15 EPR spectrometer system. The system was equipped with a variable temperature accessory, a dual sample cavity, and cell accessories for both solution and solid sample. To minimize the effects of absorption of microwave power by the solvents used, particularly water, the samples were frozen by immersing them in liquid nitrogen. After warming to -100°C ., the ESR spectra and free-radical concentrations were determined. When the determinations were made at 25°C ., the samples were transferred to glass tubes (1.6 mm. diameter) to minimize the loss of microwave power due to the solvent.

The determination of the number of electron spins in a sample was made with the use of diphenyl picryl hydrazyl (DPPH) in benzene as a reference standard.

RESULTS

ESR Spectra of Irradiated Cellulose

The ESR spectra of irradiated cotton cellulose I and cellulose II are shown in Figures 1 and 2, respectively. The spectra of both cellulose I and II, irradiated at low relative humidity or dry in vacuum, were similar, as shown in Figures 1 and 2, curve A. Irradiated cellulose I (Fig. 1B), conditioned at 25°C . and 65% R.H. prior to irradiation gave a three-line spectrum. When water was added to irradiated cellulose II (Fig. 2A), the spectrum changed to give a five-line spectrum, as shown in Figure 2B. A comparison of the properties of these spectra is made in Table I.

TABLE I
Comparison of the ESR Spectra of Irradiated Cellulose

Property	Moisture content ^a	
	High moisture	Low moisture
Spectrum, lines		
Cellulose I	3	1 + 3
Cellulose II	5	1 + 5
Line width, gauss		
Cellulose I		
Major peak ^b	17	14
Minor peak	46	53
New peak	—	(26) ^c
Cellulose II		
Major peak ^b	12	14
Nearest to major peak	40	57
Other peak	57	53
New peak	—	(30) ^c

^a See Figs. 1 and 2.

^b Spectroscopic splitting factor near free electron value.

^c Estimated from one-half of spectra.

Moisture Effects

The effects of the relative humidity of the atmosphere in which cellulose I was conditioned for 20 hr. at 25°C. to an equilibrium moisture content

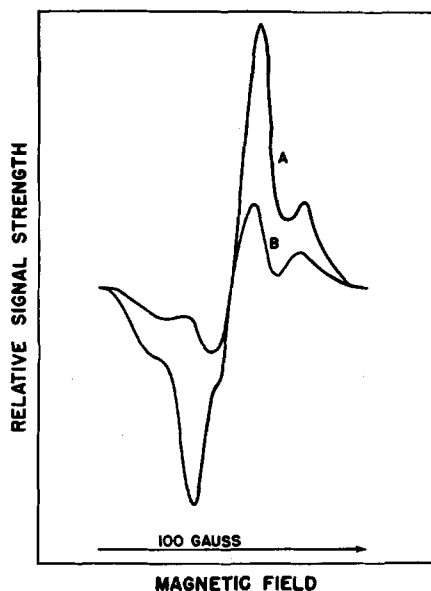


Fig. 1. ESR spectra of irradiated cellulose I (dosage: 2.6×10^{19} e.v./g.): (A) irradiated dry in vacuum or at low relative humidity; (B) conditioned at 25°C. at 65% R.H. then irradiated in air.

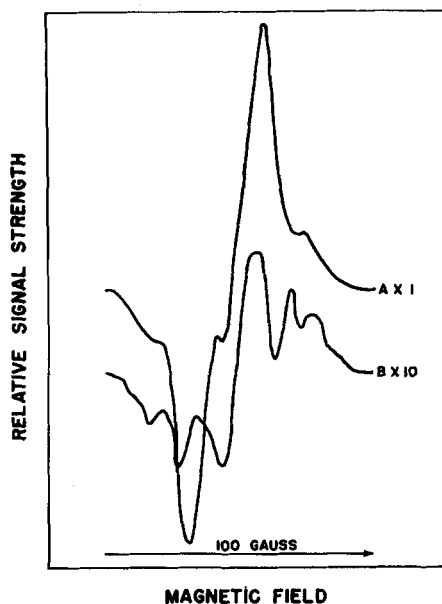


Fig. 2. ESR spectra of irradiated cellulose II (dosage: 2.6×10^{19} e.v./g.): (A) irradiated dry in vacuum or conditioned at 25°C. at 19% R.H. and then irradiated in air; (B) the irradiated sample A wet out with water.

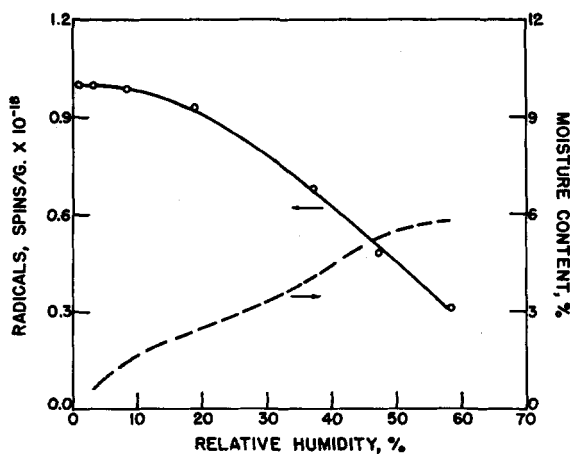


Fig. 3. Effect of relative humidity (and moisture content) on the formation of long-lived radicals in cellulose I (dosage: 2.6×10^{19} e.v./g. in air).

prior to irradiation on the formation of stable free radicals in the cellulose molecule are shown in Figure 3. The presence of moisture in concentrations greater than about 3-4% (equivalent to the regain above about 20% R.H.) significantly decreased the concentration of stable free radicals in cellulose for a given radiation exposure. Similar effects were observed when cellulose II containing different moisture contents was irradiated.

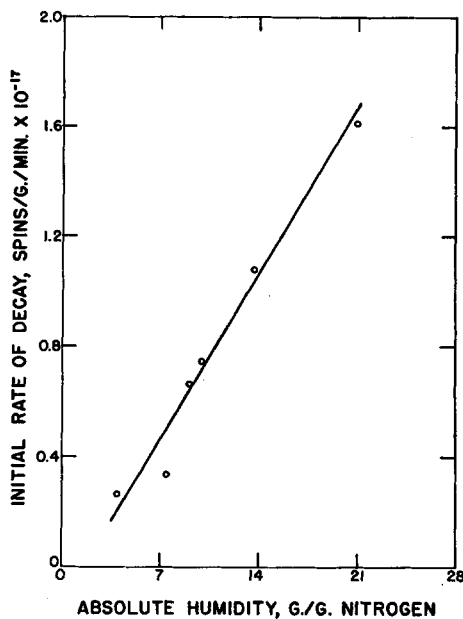


Fig. 4. Effect of absolute humidity on the initial rate of decay of free radicals in cellulose I (dosage: 2.6×10^{19} e.v./g. irradiated dry in vacuum).

Cellulose I was dried to constant weight in vacuum over P_2O_5 at $25^\circ C$. Then the cellulose was irradiated dry in vacuum at ambient temperature to a dosage of 2.6×10^{19} e.v./g. The irradiated samples were placed in open-ended tubes in the resonant cavity of the spectrometer. Nitrogen containing different amounts of moisture was passed through the irradiated sample, and the initial rate of decay in free-radical concentration was determined as a function of the absolute humidity of the nitrogen, as shown in Figure 4. The initial rate of decay of free radicals in the irradiated cellulose was directly related to the absolute humidity of the nitrogen being passed through the sample. An equilibrium concentration of free radicals in the sample was obtained in about 15 min. This concentration was higher than that found when the cellulose containing the equivalent amount of moisture was irradiated. For example, cellulose exposed to nitrogen having 60% R.H. prior to irradiation at a dosage of 2.6×10^{19} e.v./g. had a concentration of free radicals of about 3×10^{17} spins/g. (Fig. 3). When the cellulose was irradiated dry to the same dosage and then exposed to nitrogen having 60% R.H., the concentration of free radicals, was about 5×10^{17} spins/g.

Solution Effects

In post-irradiation reactions of irradiated cellulose with vinyl monomers, the effect of the solvent for the monomer on the stability of the free radicals and the ability of the solvent to interact with the cotton cellulose to make

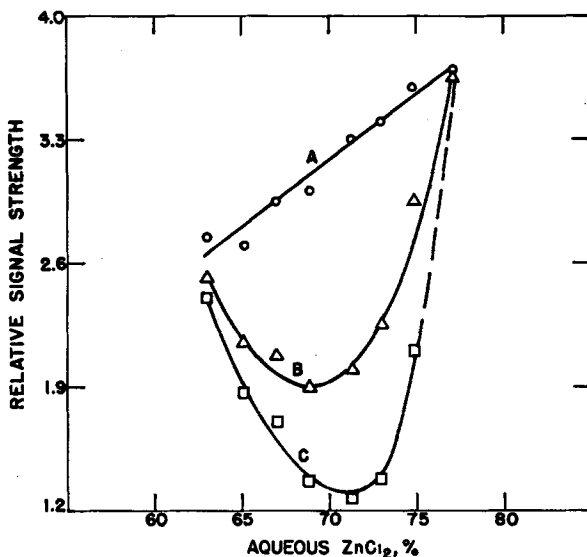


Fig. 5. Effect of the concentration of aqueous $ZnCl_2$ on the stability of free radicals in irradiated cellulose I: (A) after 3 min.; (B) after 15 min.; (C) after 25 min.

the free-radical sites on the cellulose molecule more accessible to initiate graft copolymerization reactions with the monomer are important factors. When aqueous zinc chloride solution is the solvent for the monomer, these two factors are interdependent. The effects of saturating irradiated cotton cellulose with aqueous zinc chloride solution on the stability of the free-radical sites are shown in Figure 5. The maximum free-radical concentration measured gave a relative signal strength of about 3.7. Concentrations of aqueous zinc chloride solution of about 77%, approaching saturation at 25°C., had little effect on decreasing the radical concentration. As the concentration of zinc chloride solution was decreased, the interaction with the irradiated cellulose increased as evidenced by a

TABLE II
Effect of Reagent on the Stability of Free Radicals in Irradiated Cellulose

Reagent in 75% aqueous $ZnCl_2$	Time of treatment at 25°C., hr.	Radicals, spins/g. $\times 10^{-16}$			
		Dosage 0.26 e.v./g. $\times 10^{-19}$	Dosage 0.52 e.v./g. $\times 10^{-19}$	Dosage 2.6 e.v./g. $\times 10^{-19}$	Dosage 5.2 e.v./g. $\times 10^{-19}$
Control	0	3.6	7.2	40	86
Acrylonitrile (15%)	5	3.3	5.6	—	—
	71	2.0	2.7	11	24
Acetone (15%)	5	3.8	6.5	—	—
	71	—	—	5.2	9.8
Ethanol (15%)	5	2.6	4.4	—	—
	71	1.2	1.5	2.6	8.1

decrease in signal strength, that is, free-radical concentration. After 3 min. (Fig. 5A) the effect appeared to vary inversely with the concentration of zinc chloride in the solution. After 15 min. (Fig. 5B) and 25 min. (Fig. 5C) the concentration of zinc chloride in the solution between 69 and 73% gave a maximum interaction with the cellulose, as evidenced by the decrease in signal strength.

The effects of adding different reagents to aqueous zinc chloride solution on the stability of free radicals in irradiated cellulose are summarized in Table II. Cotton cellulose I, containing normal regain moisture of about 7%, was irradiated at ambient temperature in air to different dosages. A three-line ESR spectrum was obtained, and the signal strength of the spectrum, measured within a few minutes after removal from the radiation field, was stable for several days. The irradiated cellulose was saturated with the indicated solution. After 5 and 71 hr. the samples were frozen in liquid nitrogen. Then on warming to -100°C . the ESR spectra and the concentration of free radicals in these samples were determined. Even after contact of the irradiated cellulose with the solutions for 71 hr., a significant number of free-radical sites was found.

Copolymerization Effects

Post-irradiation reaction of irradiated cellulose with acrylonitrile caused a decrease in the number of free radical sites, as shown in Table II and Figure 6. Cotton cellulose I, containing normal regain moisture of about 7%, was irradiated at ambient temperature in air to dosages over the range $0.026\text{--}5.2 \times 10^{19}$ e.v./g. The irradiated cellulose was suspended in a solu-

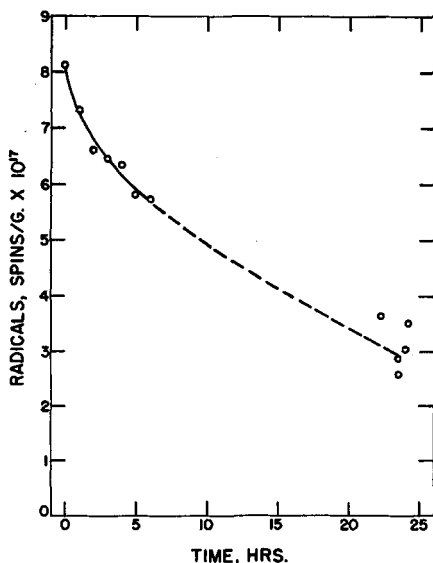


Fig. 6. Effect of acrylonitrile (15%) in aqueous ZnCl_2 (75%) on the rate of decay of free radicals in irradiated cellulose (dosage: 5.2×10^6 e.v./g. in air).

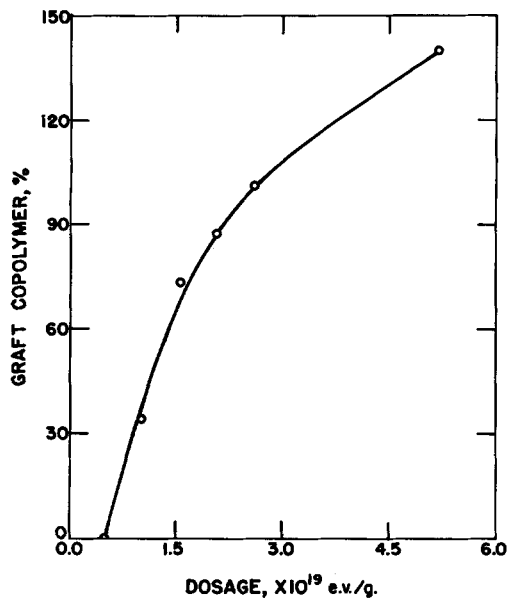


Fig. 7. Effect of radiation dosage on extent of graft copolymerization.

tion of acrylonitrile (15%) in 75% aqueous zinc chloride solution at 25°C. After a predetermined time the cellulose sample was frozen in liquid nitrogen. After warming to -100°C ., the ESR spectrum and free-radical concentration were determined. As shown in Figure 6 for cellulose irradiated to a dosage of 5.2×10^{19} e.v./g., the number of free-radical sites decreased rapidly and then almost linearly with time of contact with the solution. More than 30% of the initial number of free-radical sites were present after 24 hr., indicating that some of the sites were present in the less accessible regions of the molecular lattice.

The extent of graft copolymer formation was related to the irradiation dosage, that is, concentration of free-radical sites in the irradiated cellulose, as shown in Figure 7. The cellulose was irradiated as described above and then reacted with acrylonitrile (15%) in 75% aqueous zinc chloride for 48 hr. at 25°C. The cellulose sample was washed with water to remove the unreacted solution and extracted with *N,N*-dimethylformamide to remove any residual monomer or homopolymer. The increase in dry weight of the cellulose sample was calculated as graft copolymer. At a dosage of 0.5×10^{19} e.v./g. only about one electron spin (that is, free-radical site) for every 12 cellulose molecules was indicated. At this dosage, based on an increase in dry weight of the cellulose, no graft copolymer was indicated. However, there was a decrease in the number of spins in the irradiated cellulose when contacted by the solution (Table II). A small amount of graft copolymer (less than 0.5%) may have been formed. At lower dosages the amount of copolymer formed would have been much less than 0.5%.

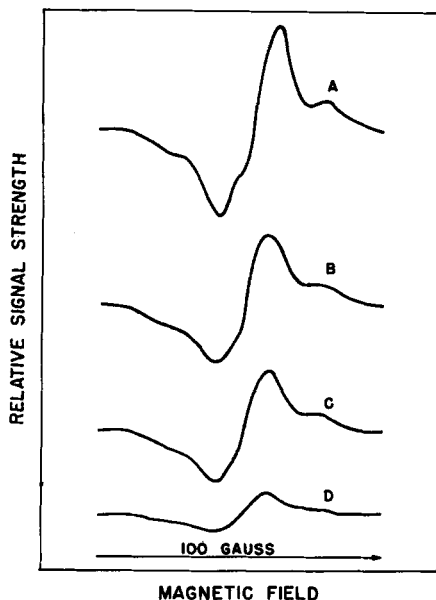


Fig. 8. ESR spectra of irradiated cellulose after treatment with acrylonitrile (15% in aqueous ZnCl_2 (75%)) (dosage: 5.2×10^{19} e.v./g. in vacuum; spectra determined at -100°C .): (A) irradiated cellulose; (B) A contacted with solution and frozen immediately; (C) A contacted with solution for 34 min. at 25°C . then frozen; (D) A contacted with solution for 17 hr. at 25°C . then frozen.

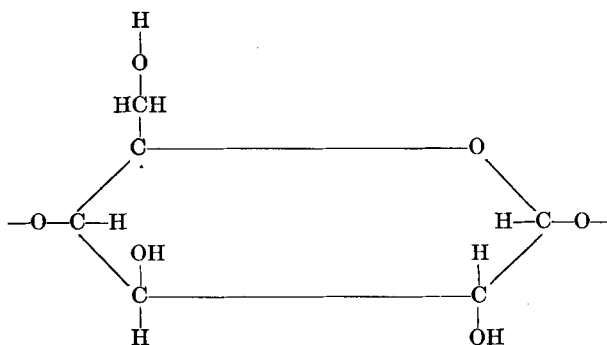
The ESR spectra of irradiated cotton cellulose after treatment with acrylonitrile (15%) in 75% aqueous zinc chloride are shown in Figure 8. Cellulose was irradiated in a vacuum at ambient temperature to a dosage of 5.2×10^{19} e.v./g. The ESR spectrum, as shown in Figure 8A was determined in vacuum at -100°C . A sample of the irradiated cellulose was placed in contact with the solution and frozen immediately in liquid nitrogen and warmed to -100°C . The ESR spectrum obtained is shown in Figure 8B. When the irradiated cellulose was contacted by the solution for 34 min. before freezing, an ESR spectrum, as shown in Figure 8C was obtained. When the contact time was 17 hr. before freezing, the ESR spectrum obtained is shown in Figure 8D. The ESR spectra decreased in signal strength and changed from an apparent combination of single-line and three-line spectra (Fig. 8A) to a single-line, or possibly a three-line, spectrum (Fig. 8D) on interaction with the solution and copolymerization of the irradiated cellulose with acrylonitrile monomer.

DISCUSSION

On interaction of γ -radiation from ^{60}Co with the cotton cellulose molecule, it can be concluded that long-lived free-radical sites are formed within the molecular lattice. Further, some of the free-radical sites are formed within regions of the cellulose molecule that are inaccessible to moisture

and aqueous solutions of acrylonitrile and other reagents, even after long periods of time. As indicated in previous reports, the initiation of post-irradiation copolymerization reactions of acrylonitrile with irradiated cellulose is diffusion-controlled.^{10,11} The selection of a solvent for the monomer, which would also interact with the cellulose, increased the radiochemical yields of the reaction.¹⁹

From the ESR spectra of irradiated cellulose I and II, containing regain moisture or after being contacted by an aqueous solution, long-lived free-radical sites were apparently formed at carbons C₅ and C₆ of the anhydroglucose unit. For cellulose I (Figure 1B) a fairly symmetrical three-line spectrum was obtained. The equivalent hydrogens on C₆ could couple with an unpaired electron, if the electron was localized on C₅ or C₆ to give a three-line spectrum. A free-radical site could be formed on C₅ by dehydrogenation or on C₆ by dehydroxylation or less probably by dehydrogenation of the OH group. Due to the delocalizing energy available from the oxygen attached to C₅, it is likely that the long-lived radical site in cellulose I containing moisture is as shown by structure I.

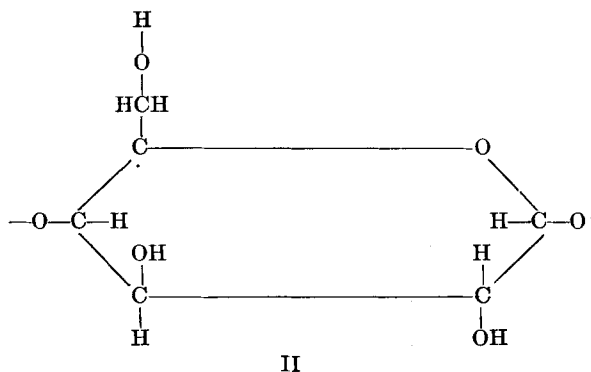


I

For cellulose II (Fig. 2B) a five-line spectrum was obtained. Considering the chemical composition of cellulose II, there is no obvious position for a free electron which could split with four equivalent protons to give five lines. It was concluded that the five-line spectrum could result from the summation of two or more spectra, probably two three-line spectra having their principal lines at about the same resonant magnetic field. For both cellulose I and cellulose II the unit cell is monoclinic and belongs to space group $P2_1$; however, there are some differences in cell dimensions, particularly a lower β angle in cellulose II than in cellulose I. Consequently, in cellulose II the anhydroglucose units are closer together and in a more parallel alignment than those in cellulose I.²⁰ In cellulose II the hydrogen bonds originally present in cellulose I could have been rearranged on mercerization²¹⁻²⁴ to increase the delocalizing energy, at C₆. This would increase the possibility of a long-lived free-radical site being formed at C₆, by one of the processes indicated above, to give a three-line spectrum. The summation of the two three-line spectra from free-radical

sites at C₅ and C₆ in different anhydroglucose units, would give a five-line spectrum (the coupling constants, a_{C_5-H} and a_{C_6-H} , being unequal).

When cellulose I and II with low moisture contents were irradiated similar ESR spectra were obtained (Figs. 1 and 2A). On addition of water to the irradiated celluloses their ESR spectra changed to give the three-line spectrum for irradiated cellulose I (Fig. 1B) and the five-line spectrum for irradiated cellulose II (Fig. 2B). Apparently, in the irradiated celluloses with low moisture contents, a long-lived free-radical site was formed which gave a strong singlet spectrum and which was readily accessible to water. The strong singlet spectrum added to the three-line or five-line spectra to give the observed spectra. From the investigation of the radiation chemistry of cotton cellulose it is known that depolymerization is one of the principal radiation-induced reactions.²⁵⁻²⁷ A strong singlet spectrum could result on the formation of a free-radical site on the oxygen in the cellulose chain attached either to C₁ or C₄. For example, in irradiated cellulose I with a low moisture content, the long-lived free-radical sites could be as shown in structure II.



At a dosage of 5.2×10^{19} e.v./g. long-lived free-radical sites (8.6×10^{17} spins/g.) were formed in cellulose I. The degree of polymerization of the unirradiated cellulose was about 4400; therefore, at this dosage and spin concentration about one long-lived free-radical site was present for each molecule of cellulose. The effect of the reaction of acrylonitrile (15%) in aqueous zinc chloride (75%) was to decrease the spin concentration (Fig. 6). The high initial rate of decrease in spin concentration probably indicated the interaction of acrylonitrile and the solvent, particularly the water in the solvent, with the more accessible free-radical sites. The rate of decrease in spin concentration became less as the time of reaction increased, indicating that some of the free-radical sites were present in less accessible areas of the cellulosic fiber.

During the graft copolymerization reaction, the ESR spectrum of the irradiated cellulose I (Fig. 8) changed from a three-line spectrum to an ill-defined spectrum. This spectrum indicated that the initial free-radical

site on C₅ had reacted with water and/or acrylonitrile and that the radical being observed after 17 hr. might be on the end of the polyacrylonitrile chain or more probably due to unreacted sites in the cellulose. The extent of graft copolymerization, as measured by the percentage of graft copolymer formed, was dependent on the radiation dosage, that is, free-radical concentration (Fig. 7).

Experimental data reported would support the free-radical mechanisms generally proposed for the post-irradiation reaction of cellulose with acrylonitrile. The initiation of the reactions would depend on the accessibility of the long-lived free-radical sites in the irradiated cellulose. In aqueous systems, as well as probably for other solvent systems, there would be competition between water and monomer for the free radical sites. Consequently, at irradiation dosages where the fibrous textile properties of cotton are retained, it is unlikely that graft copolymers will be formed in a ratio as low as one cellulose molecule to one polymer molecule.²³

Peter J. Baugh is a resident postdoctoral research associate.

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. C. Arthur, Jr. and F. A. Blouin, *Am. Dyestuff Repr.*, **51**, 1024 (1962).
2. J. C. Arthur, Jr. and F. A. Blouin, U. S. At. Energy Com. Document, TID-7643, 319 (1962).
3. J. C. Arthur, Jr. and R. J. Demint, *Textile Res. J.*, **30**, 505 (1960).
4. J. C. Arthur, Jr. and R. J. Demint, *Textile Res. J.*, **31**, 988 (1961).
5. J. C. Arthur, Jr. and R. J. Demint, U. S. Pat. 3,109,798 (November 5, 1963).
6. J. C. Arthur, Jr. and R. J. Demint, U. S. Pat. 3,157,460 (November 17, 1964).
7. J. C. Arthur, Jr., R. J. Demint, W. F. McSherry, and J. F. Jurgens, *Textile Res. J.*, **29**, 759 (1959).
8. J. C. Arthur, Jr. and J. N. Grant, *Textile Res. J.*, **36**, 934 (1966).
9. J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, *Textile Res. J.*, **33**, 896 (1963).
10. F. A. Blouin and J. C. Arthur, Jr., *Textile Res. J.*, **33**, 727 (1963).
11. F. A. Blouin, N. J. Morris, and J. C. Arthur, Jr., *Textile Res. J.*, **36**, 309 (1966).
12. R. J. Demint, J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, *Textile Res. J.*, **32**, 918 (1962).
13. R. J. Demint, J. C. Arthur, Jr., and W. F. McSherry, *Textile Res. J.*, **31**, 821 (1961).
14. J. H. Kettering and C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **14**, 432 (1942).
15. C. M. Conrad, V. W. Tripp, and T. Mares, *J. Phys. Colloid Chem.*, **55**, 1474 (1951).
16. J. C. Arthur, Jr., T. Mares, and O. Hinojosa, *Textile Res. J.*, **36**, 630 (1966).
17. J. C. Arthur, Jr., F. A. Blouin, and R. J. Demint, U. S. Dept. Agr., Agr. Res. Serv., ARS 72-21, August 1960.
18. R. H. Schuler and A. O. Allen, *J. Chem. Phys.*, **24**, 56 (1956).
19. J. C. Arthur, Jr. and F. A. Blouin, *J. Appl. Polymer Sci.*, **8**, 2813 (1964).
20. E. G. U. Percival, *Structural Carbohydrate Chemistry*, J. Garnet Miller Ltd., London, 1962, p. 221.
21. C. Y. Liang and R. H. Marchessault, *J. Polymer Sci.*, **37**, 385 (1959).
22. R. H. Marchessault and C. Y. Liang, *J. Polymer Sci.*, **43**, 71 (1960).

23. M. L. Nelson and R. T. O'Connor, *J. Appl. Polymer Sci.*, **8**, 1311 (1964).
24. R. T. O'Connor, E. F. Dupre, and D. Mitcham, *Textile Res. J.*, **28**, 382 (1958).
25. J. C. Arthur, Jr., F. A. Blouin, and R. J. Demint, *Am. Dyestuff Reprtr.*, **49**, 383 (1960).
26. F. A. Blouin and J. C. Arthur, Jr., *J. Chem. Eng. Data*, **5**, 470 (1960).
27. F. A. Blouin and J. C. Arthur, Jr., *Textile Res. J.*, **28**, 198 (1958).
28. J. C. Arthur, Jr. and D. J. Daigle, *Textile Res. J.*, **34**, 653 (1964).

Résumé

L'étude ESR des mécanismes par radicaux libres des réactions de post-irradiation de la cellulose de coton avec l'acrylonitrile a été rapportée. Les effets de l'atmosphère, de la teneur en humidité et de solutions d'acrylonitrile sur le rendement et la stabilité des sites radicalaires dans la cellulose irradiée ont été déterminés. Par interaction de la radiation- γ du Co^{60} avec la cellulose de coton, des sites de radicaux libres de longue durée de vie ont été trouvés au sein du réseau moléculaire. Des sites radicalaires de courte durée de vie étaient apparemment également formés par scission de la chaîne, donnaient un spectre singulet fort et étaient facilement accessibles à une interaction avec l'eau. D'autres sites radicalaires étaient formés à l'intérieur des régions de la fibre cellulosique qui étaient inaccessibles ni à l'humidité ni aux solutions aqueuses même après des durées de contact aussi longues que trois jours. On a suggéré que les sites radicalaires de longue durée de vie dans la cellulose I (contenant une certaine humidité) consistaient dans la déhydrogénation au carbone-5 et dans la cellulose II (contenant également de l'humidité) consistaient dans la déhydrogénation au carbone-5 et déhydrogénation du groupe OH ou déshydroxylation en C_6 . Lorsque la cellulose irradiée était mise en contact avec une solution d'acrylonitrile à 15% dans une solution aqueuse de chlorure de zinc à 75%, les vitesses initiales de diminution de concentration de spin étaient plus élevées que la vitesse de décroissance lorsque la durée de contact est accrue. Les spectres ESR de la cellulose qui a réagit, observés à -100°C , comparés avec les spectres de la cellulose irradiée, diminuaient de force de signal avec un accroissement de la durée de contact et changeaient d'un spectre à trois lignes à un spectre mal défini. Le radical libre observé était probablement dû à des sites qui n'ont pas réagi au sein de la cellulose. Le degré d'avancement de la réaction de copolymérisation greffée était directement lié à la concentration initiale en spin dans la cellulose irradiée.

Zusammenfassung

Es wird über eine ESR-Untersuchung des radikalischen Mechanismus der Bestrahlungsnachreaktionen von Baumwollcellulose mit Acrylnitril berichtet. Der Einfluss der Gasatmosphäre, des Feuchtigkeitsgehaltes und der Acrylnitrillösungen auf die Anzahl und Stabilität radikalischer Stellen in bestrahlter Cellulose wurde bestimmt. Bei Einwirkung von ^{60}Co - γ -Strahlung auf Baumwollcellulose wurden im Molekülgitter langlebige freie Radikale aufgefunden. Bei der Kettenspaltung wurden offenbar auch kurzlebige freie Radikale gebildet, welche starke Singulettenspektren lieferten und leicht mit Wasser reagierten. Andersartige freie Radikale entstanden in den für Feuchtigkeit oder wässrige Lösungen auch nach Kontaktdauern bis zu drei Tagen unzugänglichen Bereichen der Cellulosefaser. Es wird angenommen, dass langlebige freie Radikale in Cellulose I (mit aufgenommener Feuchtigkeit) von einer Dehydrierung an C_5 und in Cellulose II (mit aufgenommener Feuchtigkeit) von einer Dehydrierung an C_6 und einer Dehydrierung der OH-Gruppe oder Dehydroxylierung an C_6 herkommen. Bei Einwirkung einer Lösung von Acrylnitril (15%) in 75%igem wässrigen Zinkchlorid auf bestrahlte Cellulose, war die Anfangsgeschwindigkeit der Abnahme der Spinkonzentration höher als die Abnahmegeschwindigkeit bei fortgeschrittener Einwirkungsdauer. Das ESR-Spektrum der Cellulose nach der Reaktion wurde bei -100°C gemessen und hatte

im Vergleich zur bestrahlten Cellulose an Signalintensität mit zunehmender Einwirkungsdauer abgenommen und sich von einem Drei-Linien-Spektrum in ein schlecht definiertes Spektrum umgewandelt. Das beobachtete freie Radikal war wahrscheinlich auf die nicht-reagierten Cellulosestellen zurückzuführen. Das Ausmass der Propf-copolymerisation stand in direkter Beziehung zur Anfangskonzentration in der bestrahlten Cellulose.

Received November 1, 1966

Prod. No. 1520