

Cellulose Graft Copolymers. III. Effects of Oxygen on Graft Copolymerization of Ethyl Acrylate with γ -Irradiated Cellulose*

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Synopsis

The effects of oxygen on graft copolymerization of ethyl acrylate from methanol-water systems with γ -irradiated fibrous cotton cellulose were investigated by electron spin resonance spectroscopy and by the formation of cellulose-poly(ethyl acrylate) copolymer. The concentrations of free radicals in cellulose irradiated dry in an atmosphere of nitrogen at 25°C decreased during postirradiation storage in nitrogen or oxygen. The concentration of free radicals in the irradiated cellulose, moisture regain of the irradiated cellulose, and formation of cellulose-poly(ethyl acrylate) copolymer decreased with increase in temperature and time of postirradiation storage and to a greater extent when stored in oxygen rather than in nitrogen. From the decrease in moisture regain of irradiated cellulose during postirradiation storage, it was concluded that increased intermolecular bonding occurred in irradiated cellulose during storage in both nitrogen and oxygen atmospheres. When irradiated celluloses which had been stored in either oxygen or nitrogen were copolymerized with ethyl acrylate at 60°C, less formation of copolymer was observed than when the copolymerization reactions were conducted at 25°C. It was concluded that there was no evidence for the formation or decomposition of cellulose peroxides during these reactions and that formation of graft copolymer depended primarily on the concentration of free radicals in the irradiated cellulose at the time of copolymerization.

INTRODUCTION

When cellulose is irradiated by ionizing radiation, oxidative degradative reactions are initiated and trapped free radicals are formed.¹⁻⁴ The macromolecular reactions initiated in irradiated cellulose are predominantly depolymerization⁴ and, to a lesser extent, intermolecular bonding.⁵ The products of the principal chemical reactions in irradiated cellulose are the formation of carbonyl and carboxyl groups and the evolution of hydrogen,

* Presented at the 7th Annual Meeting in Miniature of the Louisiana Section of the American Chemical Society, New Orleans, Louisiana, April 3, 1970.

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carbon monoxide, and carbon dioxide. The reactions initiated in irradiated cellulose in the absence of oxygen are similar to those initiated in the presence of oxygen. However, the extent of oxidative degradation of cellulose is slightly greater when cellulose is irradiated in pure oxygen or air rather than in nitrogen or in vacuo.³⁻⁶ When cellulose is irradiated in pure oxygen or air, oxygen is consumed in the oxidative degradative reactions initiated.⁶ It has been generally assumed that cellulose peroxides are also formed, although direct chemical evidence for the presence of cellulosic peroxides has not been reported.⁶ However, if cellulose peroxides were formed by the reaction of oxygen with trapped free radicals in irradiated cellulose, the concentration of peroxides would be low. Consequently, the presence of peroxides in irradiated cellulose would probably not be detected by the usual analytical methods.

In postirradiation graft copolymerization reactions of cellulose, either irradiated in the presence of oxygen or exposed to oxygen after irradiation, the formation of cellulose peroxides by reaction of oxygen with trapped free radicals could have effects on both the rate and extent of the reactions. For example, by increasing the temperature of the graft copolymerization reactions, the decomposition of the peroxides could lead to an increase in the concentration of free radicals, as has been reported for graft copolymerization reactions of irradiated polyethylene said to contain peroxide groups.⁷⁻¹⁰ This could have an effect of increasing the number of grafting sites on a cellulose molecule at a given radiation dosage. In this report, the reactions of oxygen with irradiated cellulose and the effects of oxygen on graft copolymerization of ethyl acrylate from methanol-water systems with irradiated cellulose at different temperatures, as determined by electron spin resonance spectroscopy, are discussed.

EXPERIMENTAL

Materials

Cotton cellulose of Deltapine variety, spun into 7s/3 yarns, was purified in the usual manner.¹¹ Ethyl acrylate, obtained from a commercial source, was purified by passing the monomer through a column of activated alumina to remove inhibitors of polymerization. Certified A.C.S. methanol was dehydrated and distilled at atmospheric pressure prior to use as methanol. Deoxygenated, distilled water was used to prepare the solutions.

Methods

An SRRL ⁶⁰Co radiation source was used.¹² The dose rate, determined by ferrous-ferri dosimetry,¹³ was about 5.4×10^{19} eV/g-hr. Samples of cotton cellulose, which had been dried overnight under vacuum at 50°C, were irradiated to a dosage of 1.3×10^{19} eV/g (0.25 Mrad) at ambient temperature (about 25°C) in a nitrogen atmosphere. Samples of the irradiated cellulose were transferred to quartz tubes (3-mm diameter) at

25°C, by using a dry-box under a nitrogen atmosphere. Several of the samples were then exchanged, so that they were in dry oxygen atmospheres. Then samples of these irradiated celluloses, under nitrogen or oxygen atmospheres, were stored at 25°, 30°, 40°, 50°, or 60°C for various periods of time. The ESR spectra of and free-radical concentrations in the stored irradiated celluloses were determined using a Varian 4502-15 EPR spectrometer system. In order to determine the ESR spectra of the free radicals scavenged by oxygen, temperature annealing, and/or crosslinks formed, the EPR spectrometer was connected to a Varian C-1024 time-averaging computer which was used to subtract the ESR spectra of the stored sample from the ESR spectra of the sample prior to reaction with oxygen and/or storage.

Other samples of cotton cellulose yarns were irradiated to a dosage of 5.2×10^{19} eV/g (1.0 Mrad) at ambient temperature in a nitrogen atmosphere. Samples of these irradiated celluloses were stored in nitrogen or oxygen atmospheres at different temperatures for different periods of time, as outlined above. After storage for selected periods had passed, samples of irradiated cellulose were immersed in methanol-water (50/50 volume ratio) solutions containing ethyl acrylate (9 vol-%) at 25° or 60°C.¹⁴ The solutions were evacuated several times and flushed with nitrogen. The graft copolymerization reaction was allowed to proceed for different periods of time. After the desired time of reaction had elapsed, unreacted monomer was removed by washing the samples with methanol; homopolymer was removed by extracting the cellulose-poly(ethyl acrylate) copolymer with acetone at 55°C for 50 hr. The extracted samples were then washed with distilled water and dried under vacuum at 50°C. The extent of graft copolymerization of ethyl acrylate with cotton cellulose was determined as the increase in weight of the grafted yarn over that of a control yarn.

The development of increased intermolecular bonding in irradiated cellulose, stored under nitrogen or oxygen atmospheres at different temperatures, was estimated by determining the changes in moisture regain of the samples, equilibrated at 21°C and 65% R.H. for seven days. A decrease in moisture regain was interpreted as reflecting an increase in intermolecular bonding.⁵

RESULTS AND DISCUSSION

ESR Spectra

The effects of atmosphere and temperature of postirradiation storage on the ESR spectra of irradiated cellulose are shown in Figures 1 and 2. The ESR spectrum of irradiated cellulose after storage in nitrogen for 48 hr at 25°C (Fig. 1a) was the same as that generated by the irradiated cellulose immediately after removal from the radiation source; it indicated the presence of a free radical which generated a singlet spectrum and of a free radical which generated a triplet spectrum.² The ESR spectrum of irradiated cellulose after storage in nitrogen for 48 hr at 60°C (Fig. 1b) indicated

a change in the concentrations of the free radicals generating the singlet and triplet spectra. The ESR spectrum of the free radicals scavenged by temperature annealing are shown in Figure 2a (obtained by subtracting the spectrum shown in Fig. 1b from the spectrum shown in Fig. 1a). Examination of these spectra indicated that the free radical which generated the triplet spectrum was largely scavenged (note disappearance of the dis-

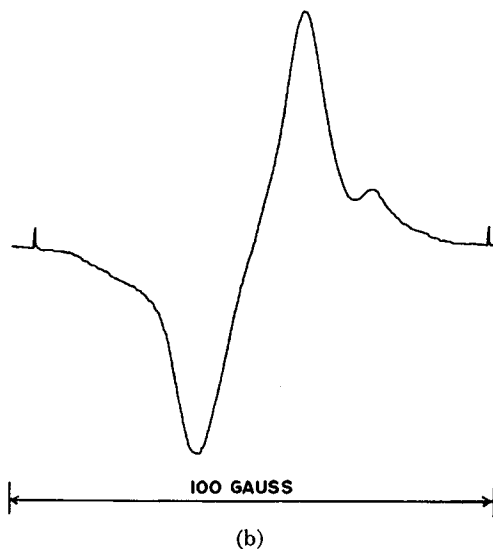
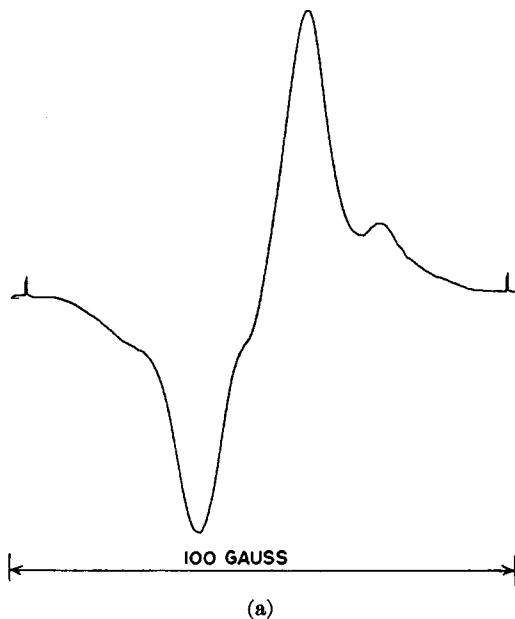


Fig. 1 (continued)

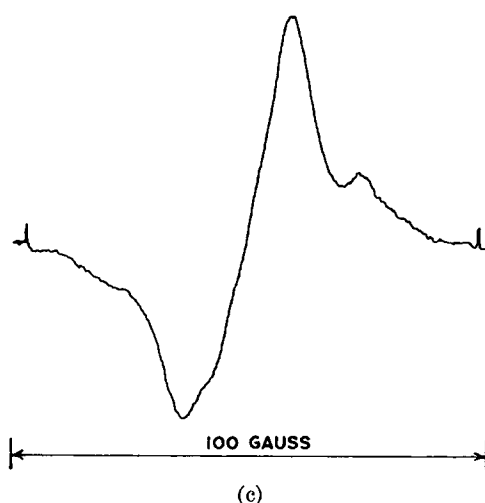


Fig. 1. Effects of oxygen and temperature on the ESR spectrum of irradiated cotton cellulose: (a) irradiated, dried, purified cellulose after 48 hr in nitrogen at 25°C; (b) after 48 hr in nitrogen at 60°C; (c) after 48 hr in oxygen at 60°C.

continuity in the central line of the spectrum—Fig. 1a) and that the free radical which generated the singlet spectrum was scavenged to a lesser degree.

The ESR spectrum of irradiated cellulose after storage in oxygen for 48 hr at 60°C (Fig. 1c) showed a decrease in concentration of the free radicals. The free radicals in the irradiated cellulose scavenged by temperature annealing and oxygen are indicated by the ESR spectrum shown in Figure 2b (obtained by subtracting the spectrum shown in Fig. 1c from the spectrum shown in Fig. 1a). Scavenging of the free radicals in irradiated cellulose stored in oxygen was greater than that when stored in nitrogen. The free radical which generated the singlet spectrum was scavenged to a greater extent in oxygen than in nitrogen; compare the spectra in Figures 2a and 2b. In the case of temperature annealing, considering the vibrational states of energy involved, it is suggested that scavenging of the free radicals occurs primarily in the more ordered regions of cellulose. In the case of oxygen, scavenging probably occurs primarily in the less ordered regions of cellulose. As previously proposed, the free radicals which generated singlet spectra are probably located in the less ordered regions of cellulose.^{1,2}

Free-Radical Concentration

The effects of time, temperature, and atmosphere of storage on the stability of free radicals in irradiated cellulose are shown in Figure 3. An estimation of the free-radical concentration in irradiated cellulose was made by measuring the peak-to-peak height of the principal line of the ESR spectrum and is reported as relative signal strength. The scavenging of the free radicals increased with increase in time and temperature of

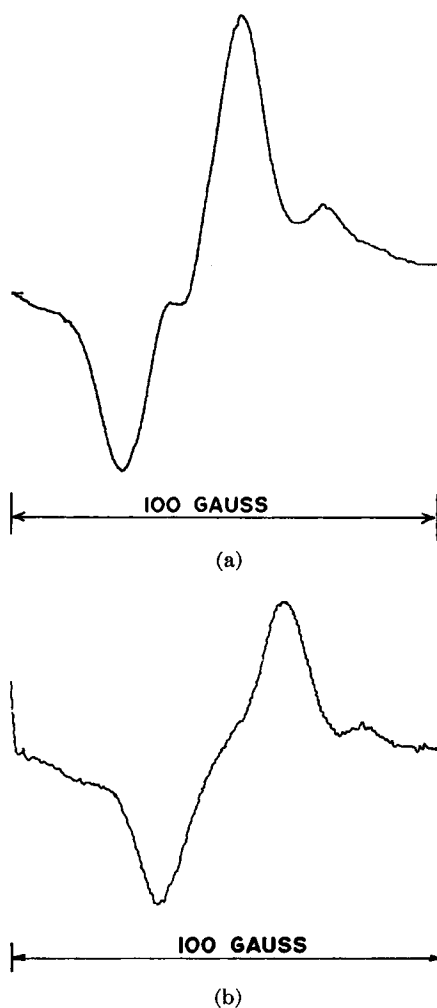


Fig. 2. ESR spectrum of free radical scavenged in irradiated cotton cellulose: (a) by temperature annealing (Fig. 1a, — Fig. 1b); (b) by oxygen (Fig. 1b, — Fig. 1c).

storage and was greater in an atmosphere of oxygen than in an atmosphere of nitrogen. At a given temperature, the scavenging of free radicals in irradiated cellulose increased with time in storage, which indicated that micro-Brownian motion was probably occurring in the heated cellulose molecule. The scavenging of free radicals in irradiated cellulose by oxygen is probably due to the formation of cellulose peroxide.

Graft Copolymerization

The effects of time, temperature, and atmosphere of storage of irradiated cellulose and of copolymerization reaction time and temperature on the extent of grafting of irradiated cellulose with ethyl acrylate from methanol-

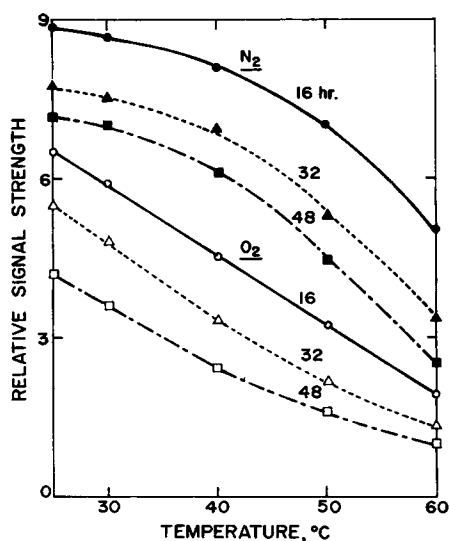


Fig. 3. Effects of time, temperature, and atmosphere on the stability of free radicals in irradiated cotton cellulose, after storage in nitrogen for: (●) 16 hr; (▲) 32 hr; (■) 48 hr; after storage in oxygen for: (○) 16 hr; (△) 32 hr; (□) 48 hr.

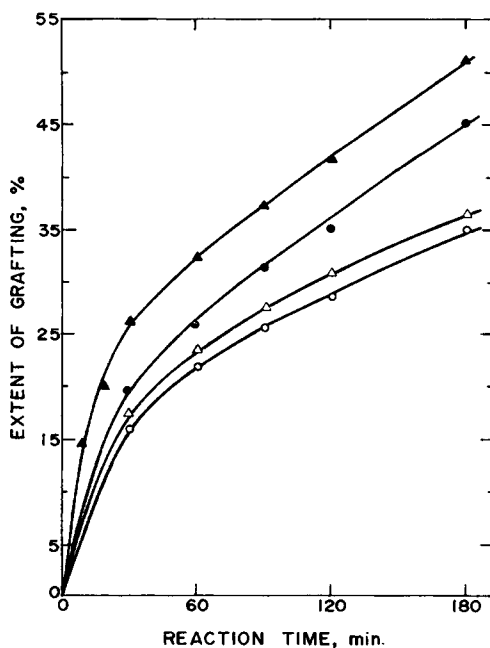


Fig. 4. Effects of postirradiation storage conditions and of copolymerization reaction time and temperature on the extent of grafting of irradiated cellulose with ethyl acrylate from methanol-water solution: (▲) after 16 hr in nitrogen at 25°C, copolymerized at 25°C; (△) after 16 hr in nitrogen at 25°C, copolymerized at 60°C; (●) after 16 hr in oxygen at 25°C, copolymerized at 25°C; (○) after 16 hr in oxygen at 25°C, copolymerized at 60°C.

water solutions are shown in Figures 4, 5, and 6. The extent of grafting increased as the copolymerization reaction time increased (Figs. 4 and 6) and decreased as the copolymerization reaction temperature increased (Figs. 4, 5, and 6). As the postirradiation storage time of the irradiated cellulose, prior to copolymerization, increased, the extent of grafting decreased (Fig. 5). When the irradiated cellulose was stored in oxygen prior to copoly-

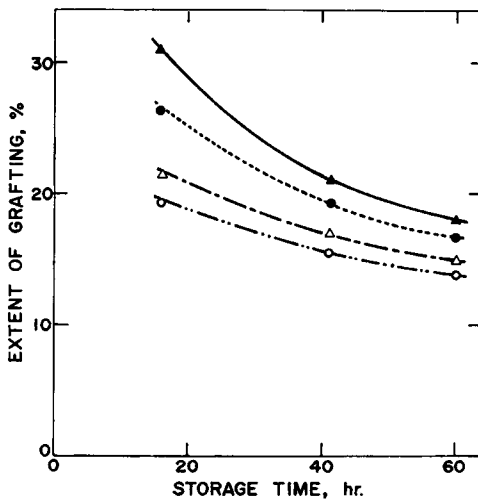


Fig. 5. Effects of postirradiation storage time and copolymerization reaction temperature on the extent of grafting of irradiated cellulose with ethyl acrylate from methanol-water solution (storage temperature, 40°C; copolymerization reaction time, 2 hr): (▲) stored in nitrogen, copolymerized at 25°C; (△) stored in nitrogen, copolymerized at 60°C; (●) stored in oxygen, copolymerized at 25°C; (○) stored in oxygen, copolymerized at 60°C.

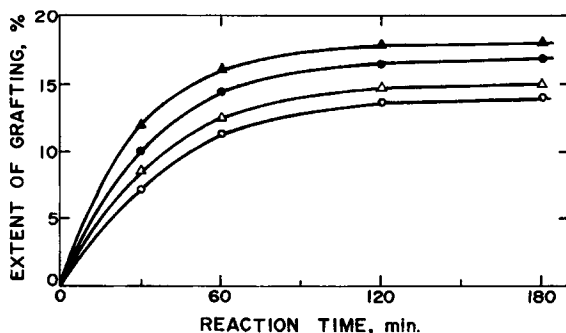


Fig. 6. Effects of postirradiation storage atmosphere and of copolymerization reaction time and temperature on the extent of grafting of irradiated cellulose with ethyl acrylate from methanol-water solution (storage temperature, 40°C; storage time, 60 hr): (▲) stored in nitrogen, copolymerized at 25°C; (△) stored in nitrogen, copolymerized at 60°C; (●) stored in oxygen, copolymerized at 25°C; (○) stored in oxygen, copolymerized at 60°C.

merization, the extent of grafting was less than when the irradiated cellulose had been stored in nitrogen under the same conditions prior to copolymerization (Figs. 4, 5, and 6). These data generally correlate with the effects of postirradiation storage conditions of irradiated cellulose on the stability of the free radicals formed in the cellulose. Apparently, increasing the copolymerization reaction temperature increased the rate of scavenging of the free radicals by the methanol-water solution; this was reflected in a decrease in extent of grafting at the higher copolymerization reaction temperature. Also, the termination reactions of the copolymerization reactions would be favored at the higher temperature.

When irradiated cellulose was stored in nitrogen at 40°C for 60 hr and then graft copolymerized with ethyl acrylate from ethanol-water solution at 60°C for 3 hr, the amount of homopolymer formed was less than 1%. When irradiated cellulose was stored in oxygen and then graft copolymerized under similar conditions, the amount of homopolymer formed was about 5%. This indicated that some cellulose hydroperoxide was probably formed during storage of irradiated cellulose in oxygen and was decomposed on heating to yield hydroxyl radicals. These radicals could then initiate homopolymerization of ethyl acrylate.

Intermolecular Bonding

It has been reported that irradiation of cellulose increases intermolecular bonding, as shown by decreases in moisture regain and liquid water retention of irradiated cellulose as compared with unirradiated cellulose.² To determine if additional intermolecular bonding occurred during postirradiation storage, moisture regains of stored irradiated celluloses were determined, as shown in Table I. When dried, purified cellulose was irradiated under nitrogen at 25°C to 5.2×10^{19} eV/g, the moisture regain of the cellulose was reduced from 7.5% to 6.7%. If the irradiated cellulose was stored in nitrogen at 25°C, there was little further reduction in moisture regain. If the temperature of storage was increased to 40°C, the moisture

TABLE I
Effects of Postirradiation Storage Conditions
on the Moisture Regain of Irradiated Cellulose^a

Storage conditions ^b		Moisture regain, ^c %
Temperature, °C	Atmosphere	
25	nitrogen	6.7
25	oxygen	5.4
40	nitrogen	6.0
40	oxygen	4.8

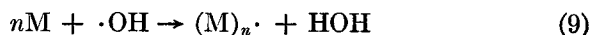
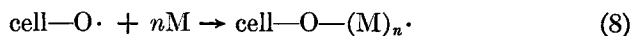
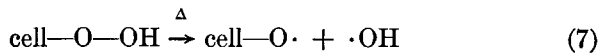
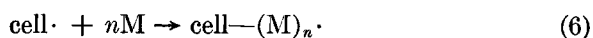
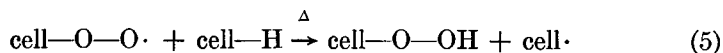
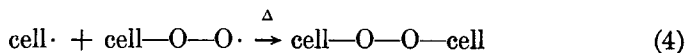
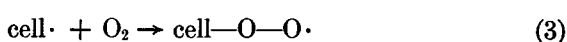
^a Dried, purified cellulose irradiated by ⁶⁰Co γ -radiation at 25°C under nitrogen at atmosphere to 5.2×10^{19} eV/g.

^b Postirradiation storage time 60 hr prior to determination of moisture regain.

^c Unirradiated cellulose, 7.5%.

regain of the irradiated cellulose after 60 hr decreased to 6.0%. When oxygen was substituted for nitrogen, the moisture regains of irradiated celluloses stored at 25° and 40°C for 60 hr decreased to 5.4% and 4.8%, respectively. This would indicate that intermolecular bonding was increasing during the storage of the irradiated cellulose and was dependent on temperature and atmosphere of storage.

The mechanism of this intermolecular bonding and the effects of this bonding on the stability of the free radicals in irradiated cellulose and the graft copolymerization reaction of ethyl acrylate with irradiated cellulose are suggested by the following reactions:



where cell-H represents the cellulose molecule; cell·, the cellulose radical; M, monomer; and M·, monomer radical. The formation of the trapped radical in cellulose on irradiation probably results from a dehydrogenation reaction^{1,2} as shown in eq. (1). When irradiated cellulose is heated in nitrogen, the mobility of the free-radical site on the cellulose molecule, particularly in the more ordered regions, is increased, so that increased intermolecular bonding occurs as in eq. (2) with a reduction in free-radical sites. When irradiated cellulose is heated in oxygen, reactions as shown in eqs. (2)–(5) could occur, particularly in the less ordered regions. These reactions could also lead to increased intermolecular bonding and reduction in free-radical sites. Graft copolymerization could proceed as shown in eqs. (6)–(8). If cellulose hydroperoxide is formed, copolymerization at higher temperatures could lead to formation of ·OH radicals and increased homopolymerization, as shown in eq. (9). The experimental data reported could be explained by these reactions. From these data, it is reasonable to conclude that the formation of cellulose peroxides or hydroperoxides did not play a significant role in the graft copolymerization reaction of irradiated cellulose with ethyl acrylate from methanol-water solutions. The extent

of grafting appeared to depend primarily on the concentration of free radicals in the irradiated cellulose at the time of the copolymerization reaction.

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., Radiation Effects on Cellulose, in *Energetics and Mechanisms in Radiation Biology*, G. O. Phillips, Ed., Academic Press, London, 1968, p. 153.
2. J. C. Arthur, Jr., T. Mares, and O. Hinojosa, *Text. Res. J.*, **36**, 630 (1966).
3. J. C. Arthur, Jr., F. A. Blouin, and R. J. Demint, *Amer. Dyestuff Repr.*, **49**, 383 (1960).
4. F. A. Blouin and J. C. Arthur, Jr., *Text. Res. J.*, **28**, 198 (1958).
5. T. Mares and J. C. Arthur, Jr., *J. Polym. Sci. B*, **7**, 419 (1969).
6. F. A. Blouin and J. C. Arthur, Jr., *J. Chem. Eng. Data*, **5**, 470 (1960).
7. D. S. Ballantine, A. Glines, G. Adler, and D. J. Metz, *J. Polym. Sci.*, **34**, 419 (1959).
8. A. Chapiro, *J. Polym. Sci.*, **23**, 377 (1957).
9. A. Chapiro, *J. Polym. Sci.*, **29**, 321 (1958).
10. A. Chapiro, *J. Polym. Sci.*, **34**, 439 (1959).
11. J. H. Kettering and C. M. Conrad, *Ind. Eng. Chem., Anal. Ed.*, **14**, 432 (1942).
12. J. C. Arthur, Jr., F. A. Blouin, and R. J. Demint, U. S. Dept. Agr., Agr. Res. Serv., *ARS 72-21*, August 1960.
13. R. H. Schuler and A. O. Allen, *J. Chem. Phys.*, **24**, 56 (1956).
14. Y. Nakamura, O. Hinojosa, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **13**, 2633 (1969).

Received October 16, 1970