

Cellulose Graft Copolymers. II. Graft Copolymerization of Ethyl Acrylate with γ -Irradiated Cellulose from Acetone-Water Systems

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Synopsis

Ethyl acrylate was graft-copolymerized from acetone-water systems with γ -irradiated, purified cotton cellulose. The scavenging of the free radicals in the irradiated cellulose by water, acetone, and water-acetone systems was determined by electron spin resonance spectroscopy. The ESR spectra of free radicals, scavenged by water and acetone, were recorded by the use of a time-averaging computer attached to the ESR spectrometer, in which the ESR spectrum of the irradiated cellulose, which had been immersed in water and/or acetone, was electronically subtracted from the ESR spectrum of the irradiated cellulose control. For both water and acetone, the ESR spectra of the scavenged free radicals were singlets. This indicated that free radical sites formed on carbon C₁ or C₄ on radiation-initiated depolymerization, which would generate singlet ESR spectra, were readily accessible to these solvents. The maximum scavenging of the radicals was observed when irradiated cellulose was immersed in acetone-water solution which had a composition of 25/75 vol-%. The scavenging of the free radicals in irradiated cellulose when immersed in acetone-water solutions was less than when immersed in methanol-water solutions. Also, the extent of graft copolymerization of ethyl acrylate from acetone solutions with irradiated cellulose was less than that of ethyl acrylate from methanol solutions. These differences were probably due to differences in the diffusion rates of acetone and methanol into the cellulosic structure. The Trommsdorff-type effect in the acetone solutions would be less than in the methanol solutions, since acetone is a better solvent for poly(ethyl acrylate) than methanol.

INTRODUCTION

It was reported that graft copolymerization of ethyl acrylate from methanol-water systems with irradiated cotton cellulose was primarily dependent on the accelerative effects of water and methanol due to the Trommsdorff-type effect.¹⁻³ Apparently, a major fraction of the free radicals in the irradiated cellulose, as determined by electron spin resonance spectroscopy, was scavenged by methanol-water solutions without initiat-

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ing graft copolymerization reactions between ethyl acrylate and irradiated cellulose. In this report, the graft copolymerization reactions of ethyl acrylate with irradiated cellulose from acetone-water systems are reported. Since acetone is a better solvent for poly(ethyl acrylate) than methanol, the Trommsdorff-type effects of the two solvents are compared. Also, the nature and extent of scavenging of the free radicals in the irradiated cellulose by the solutions are reported.

EXPERIMENTAL

Materials

Cotton cellulose of Deltapine variety, spun into 7s/3 yarns, and commercial cotton print cloth, 3.4 oz/sq yd, 80 × 80, were purified in the usual manner.^{1,4} Ethyl acrylate, obtained from a commercial source, was purified by passing the monomer through columns of activated alumina in order to remove inhibitors of polymerization. Certified A.C.S. acetone and methanol were dehydrated and distilled at atmospheric pressure prior to use. Deoxygenated, distilled water was used to prepare the solutions.

Methods

The SRRL ⁶⁰Co radiation source⁵ was used. The dose rate, determined by ferrous-ferri dosimetry,⁶ was about 5.9×10^{19} eV/g-hr. Samples of cotton cellulose (either yarn or fabric), which had been dried overnight under vacuum at 50°C, were irradiated to a dosage of 5.2×10^{19} eV/g (1.0 Mrad) at ambient temperature in a nitrogen atmosphere. Samples of irradiated cotton yarn were then transferred to quartz tubes (3-mm diameter) at 25°C, by using a dry-box under a nitrogen atmosphere, for examination in the EPR spectrometer. About 24 hr after irradiation, samples of cotton fabric were immersed in acetone-water solutions at 25°C containing ethyl acrylate. The solutions were evacuated several times and flushed with nitrogen.^{4,7,8} The graft copolymerization reaction which was initiated was allowed to proceed at 25°C for 60 min. Then the grafted fabric was washed several times with methanol to remove unreacted monomer. Homopolymer was removed by extracting the grafted fabric at 55°C for 50 hr with acetone. The sample was then washed in distilled water and dried overnight in 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 fabric over that of a control fabric similarly treated except for the omission of ethyl acrylate.

The ESR spectra of and free radical concentrations in the irradiated celluloses were determined using a Varian 4502-15 EPR spectrometer system which was equipped with a variable temperature accessory and a dual sample cavity. In order to determine the ESR spectra of the free radicals scavenged by the solvents, the EPR spectrometer was connected to a Varian C-1024 time-averaging computer. The ESR spectrum of a sample of

irradiated cellulose was recorded and stored in the computer. Then, without changing the settings on the spectrometer, the ESR spectrum of an identical sample of irradiated cellulose which had been reacted with the solvents was recorded and stored in the computer. When the computer was actuated to record the spectra on the external chart recorder, the ESR spectrum obtained was the ESR spectrum of the irradiated cellulose less the ESR spectrum of the irradiated cellulose which had been reacted with the solvents. In order to minimize the effects of the absorption of microwave power by the solvents used, the samples of irradiated cellulose were frozen by immersing them in liquid nitrogen. After warming to -180°C , the ESR spectra were recorded. The free radical concentrations were indicated by the relative signal strengths of the ESR spectra which were determined by measuring the distance between the peak-to-peak values of the spectra.

RESULTS AND DISCUSSIONS

Effects of Solvents on ESR Spectra

The effects of water on the ESR spectra generated by irradiated cotton cellulose I are shown in Figure 1. The spectrum generated by irradiated, dried cellulose is shown in Figure 1A. Previously, it had been suggested that the spectrum was a summation of a singlet spectrum (generated by free radicals formed on carbon C_1 or C_4 on radiation-initiated depolymerization of cellulose) and a triplet spectrum (generated by free radicals formed on carbon C_5 following dehydrogenation and resonance stabilization).^{1,9,10} The interaction of water with irradiated, dried cellulose I scavenged some of the free radicals, probably those generating singlet spectra, to give a triplet spectrum as shown in Figure 1B. An experimentally determined spectrum has now been recorded, supporting the suggestion that free rad-

TABLE I
Effects of Immersion of Irradiated Cotton Cellulose in Acetone-Water
Solutions on the Stability of the Free Radicals^a

Composition of solutions, vol-%		Free radical concentration, arbitrary units		
(Me) ₂ CO	Water	30 sec	3 min	1 hr
Control ^b		21	21	21
Ethyl acrylate		—	19	—
100	0	21	20	8.0
75	25	9.0	6.4	—
50	50	6.2	5.9	—
25	75	4.8	4.8	—
0	100	6.5	6.6	2.8

^a Immersion at 25°C for indicated time periods.

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

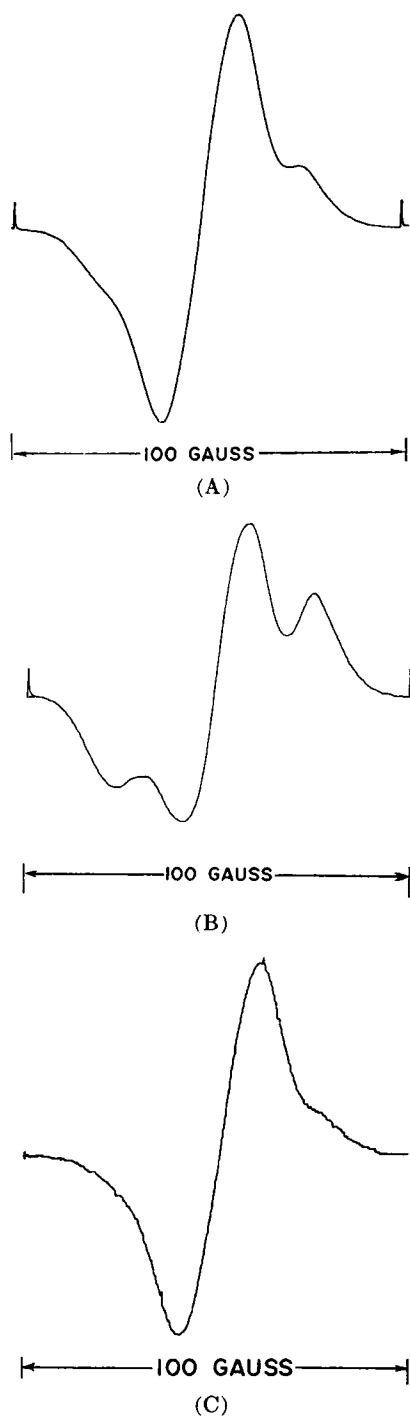
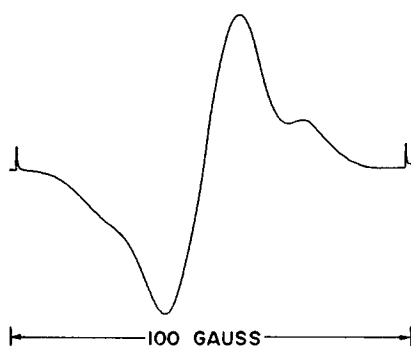
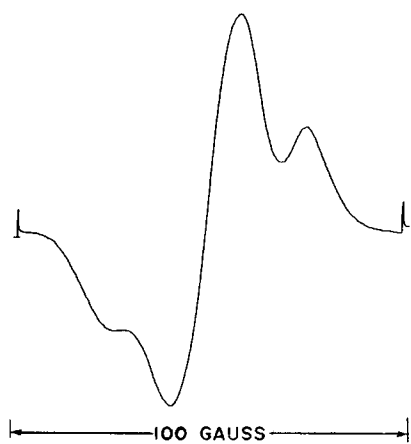


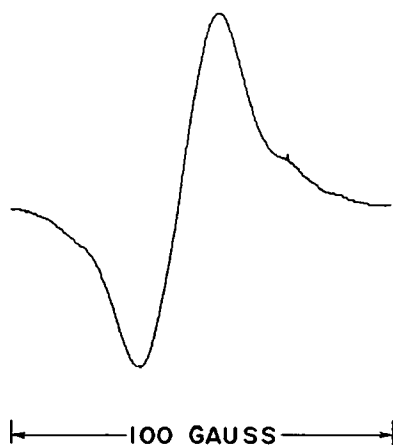
Fig. 1. Effects of immersion of irradiated cotton cellulose at 25°C in water on their ESR spectra recorded at -180°C: (A) irradiated, dried, purified cellulose; (B) immersed in water for 1 hr; (C) free radical scavenged (A - B).



(A)



(B)



(C)

Fig. 2. Effects of immersion of irradiated cotton cellulose at 25°C in acetone on their ESR spectra recorded at -180°C: (A) immersed in acetone for 4 hr; (B) immersed in acetone for 23 hr; (C) free radical scavenged (Fig. 1A - Fig. 2B).

icals which generate singlet spectra are apparently more accessible to and are scavenged by water, as shown in Figure 1C (spectra Fig. 1A minus spectra Fig. 1B). The overall concentration of free radicals was decreased on the interaction of the irradiated, dried cellulose with water as shown in Table I. The singlet spectrum of the scavenged radical had a line width of about 24 gauss and a g -value near the free electron value.

The effects of acetone on the ESR spectra generated by irradiated cotton cellulose I are shown in Figure 2. The extent of scavenging of free radicals by acetone in the irradiated cellulosic structure was apparently less than in the case of water, as shown in Table I. This was probably due to the slower rate of diffusion of acetone into the cellulosic structure as compared with that of water. However, after a long period of immersion of the irradiated cellulose in acetone, a triplet spectrum as shown in Figure 2B was recorded that was similar to that recorded after immersion of the irradiated cellulose in water, as shown in Figure 1B. The ESR spectrum of the free radical scavenged by acetone in the irradiated cellulose is shown in Figure 2C. The singlet spectrum of the acetone-scavenged free radical was similar to that of the water-scavenged free radical. The singlet spectrum of the acetone-scavenged free radical had a line width of about 19 gauss and a g -value near the free electron value.

Effects of Solvents on Free Radical Concentration

The effects of the composition of acetone-water solutions on the extent of scavenging of free radicals in irradiated cellulose are shown in Table I

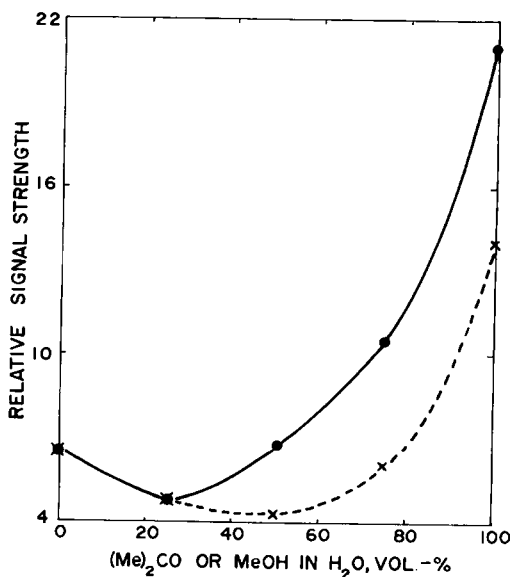


Fig. 3. Comparison of the effects of composition of acetone-water and methanol-water solutions on the scavenging of free radicals in irradiated cellulose, immersed in the solutions at 25°C: (●) acetone-water; (×) methanol-water.

and Figure 3. The maximum extent of scavenging of the free radicals occurred when irradiated cellulose was immersed in acetone–water solution that had a composition of 25/75 vol-%. As the concentration of acetone was increased, the scavenging of the free radicals in the irradiated cellulose decreased sharply. At lower concentrations of acetone, the scavenging of free radicals decreased slightly. As is also shown, the maximum scavenging of free radicals in irradiated cellulose immersed in methanol–water solutions occurred when the solution had a composition of 50/50 vol-%.¹ These compositions of both the acetone–water and methanol–water solutions probably indicate solutions which have the maximum rate of diffusion of solvent into the cellulosic structure. Apparently, methanol–water solutions have a greater penetration into the cellulosic structure than either water, acetone, acetone–water, or methanol solutions, as shown by the extent of scavenging of the free radicals in the irradiated cellulose.

Graft Copolymerization

Acetone–Ethyl Acrylate System. The effects of the addition of acetone to ethyl acrylate on the extent of graft copolymerization of poly(ethyl acrylate) with γ -irradiated cellulose are shown in Figure 4. As the concentration of acetone was increased, the maximum extent of graft copolymer-

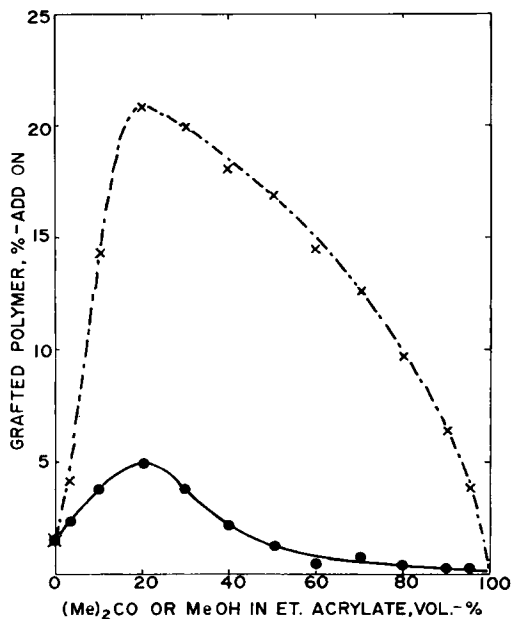


Fig. 4. Comparison of the effects of composition of ethyl acrylate–acetone solution and of ethyl acrylate–methanol solution on extent of graft copolymerization with irradiated cellulose at 25°C and 60 min. Dosage 5.2×10^{19} eV/g; cellulose solution ratio 1/14: (●) ethyl acrylate–acetone; (X) ethyl acrylate–methanol.

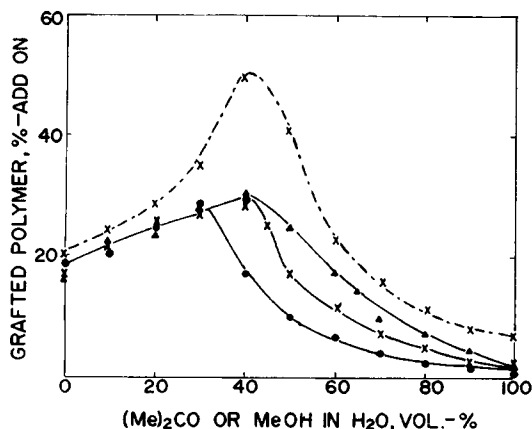


Fig. 5. Comparison of the effects of composition of acetone-water and methanol-water solutions and concentration of ethyl acrylate on extent of graft copolymerization with irradiated cellulose at 25°C and 60 min. Dosage 5.2×10^{19} eV/g; cellulose solution ratio 1/14: (—) acetone-water; (---) methanol-water; (●) 5 vol% ethyl acrylate; (×) 9 vol% ethyl acrylate; (▲) 19 vol% ethyl acrylate.

ization occurred at about 20 vol-% acetone, 80 vol-% ethyl acrylate. The addition of acetone to ethyl acrylate probably increased the rate of diffusion of ethyl acrylate to the free radical sites. However, at higher concentrations of acetone, that is, lower concentrations of ethyl acrylate, a decreased extent of graft copolymerization probably resulted from a dependence on the concentration of monomer. Also shown for comparison, addition of methanol to ethyl acrylate increased the extent of graft copolymerization of ethyl acrylate with γ -irradiated cellulose. The lesser extent of graft copolymerization in acetone-ethyl acrylate, as compared with that in methanol-ethyl acrylate, is probably due to the Trommsdorff-type accelerative effect in methanol-ethyl acrylate. Acetone is a better solvent for poly(ethyl acrylate) than methanol.

Acetone-Water-Ethyl Acrylate System. The effects of the volume ratio of acetone to water on the graft copolymerization of ethyl acrylate with γ -irradiated cellulose, at concentrations of monomer of about 5, 9, and 19 vol-%, are shown in Figure 5. The maximum extent of graft copolymerization of ethyl acrylate with irradiated cellulose with 5 vol-% monomer occurred at about 30 vol-% acetone; at 9 and 19 vol-% monomer, the maximum occurred at about 40 vol-% acetone. For monomer concentrations of 5, 9, and 19 vol-%, the solutions separated into two phases when the concentrations of acetone were less than 30, 47, and 65 vol-%, respectively.

The extent of grafting from water was about the same for each concentration of monomer whenever the systems tended to separate into two phases. As acetone was added to the water-ethyl acrylate system, the extent of grafting increased to a maximum and then decreased. This was

probably due to the Trommsdorff-type accelerative effect of the water. For 5 vol-% monomer the maximum occurred at about 30 vol-% acetone where the system was one uniform phase; this maximum was about the same as the extent of grafting from solutions of 9 and 19 vol-% monomer in this system. As more acetone was added, the extent of grafting from solutions of 9 and 19 vol-% monomer increased to a maximum at about 40 vol-% acetone and then decreased. These solutions were separated into two phases at this concentration of acetone. From these solutions it was considered likely that the Trommsdorff-type effect of water reached a maximum at about 40 vol-% and that the grafting was from the separated phase in which the concentration of monomer was a maximum in each case.

Comparison of grafting from methanol systems with those from acetone systems, as shown in Figure 5, indicates a greater Trommsdorff-type effect of methanol than of acetone on the grafting reactions. To formulate a system of solvent-water-ethyl acrylate to obtain a maximum extent of grafting of ethyl acrylate with γ -irradiated cellulose, it is obvious that a number of interacting factors, particularly Trommsdorff-type effects, must be evaluated.

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

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