

Cellulose Graft Copolymers. I. Graft Copolymerization of Ethyl Acrylate with γ -Irradiated Cellulose from Methanol-Water Systems

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Synopsis

Ethyl acrylate was graft-copolymerized with γ -irradiated, purified cotton cellulose from methanol-water systems. The accessibility of the free radicals in the irradiated cellulose to water, methanol, ethyl acrylate, and methanol-water solutions was determined by electron spin resonance spectroscopy. The maximum scavenging of the radicals was recorded when the irradiated cellulose was immersed in methanol-water solution which had a composition of 50/50 vol-%. When ethyl acrylate was added to methanol-water solution (50/50 vol-%), maximum grafting on the irradiated cellulose occurred at a concentration of ethyl acrylate of about 20 vol-%. As the concentration of ethyl acrylate was decreased, maximum grafting occurred in solutions containing less than 50 vol-% methanol. It was also noted that maximum grafting of ethyl acrylate in methanol-water solutions to irradiated cellulose occurred at boundary conditions, that is, conditions where the ternary mixture was still one phase, slightly different from compositions which caused the mixture to separate into two phases. From methanol solution, maximum grafting occurred at a concentration of ethyl acrylate of 80 vol-%. The extent of grafting from methanol was less than that obtained from methanol-water solutions at lower concentrations of ethyl acrylate. The accelerative effects of water was considered to be due to the Trommsdorff effect.

INTRODUCTION

In previous papers we reported that viscose rayon fibers grafted with ethyl acrylate by the ceric ion method gave fibrous products with rubber-like elastomeric behavior at add-ons of poly(ethyl acrylate) greater than about 1000%, especially when grafted onto crosslinked celluloses.^{1,2} It was concluded that elastomeric properties of the fibrous product could be essentially attributable to the uniform distribution of the rigid cellulose in the flexible graft polymer. On the other hand, we found that after grafting with ethyl or *n*-butyl acrylate by the ceric ion method, cotton fabrics cross-linked with formaldehyde or *N*-methylol acrylamide gave increased wrinkle

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recovery angles without much loss of breaking and tear strengths.^{3,4} Moreover, it was also found that after grafting with alkyl methacrylates by means of γ -radiation, the cotton fabrics crosslinked with dimethylol dihydroxyethylene urea showed increased wash-wear ratings, abrasion resistances, tear strengths, and wrinkle recovery angles.^{5,6} On the basis of the above results, we are attempting to prepare modified cottons which have all of these desirable properties simultaneously by the combined effects of swelling, crosslinking, and grafting by γ -radiation. Experimental data are presented in this report on an ESR spectroscopy study of reactions of free radicals formed on irradiated cellulose in methanol-water systems. The irradiated cotton fabrics are grafted in the above mixed system containing ethyl acrylate; the effects of composition of the grafting system on the graft copolymerization reactions are considered in relation to the results obtained by ESR spectroscopy.

EXPERIMENTAL

Materials

Cotton cellulose of Deltapine variety, spun in 7s/3 yarns, was purified in the usual manner by extraction with hot ethanol, followed by boiling in dilute sodium hydroxide solution. The sodium hydroxide solution was removed by washing the cellulose with distilled water, followed by souring with dilute acetic acid, neutralizing with dilute ammonium hydroxide, and again washing with distilled water.⁷ Commercial print cloth, 3.4 oz/yd², 80 × 80, was subjected to enzyme desizing, alkali scouring, and peroxide bleaching on a pilot-plant scale. Then the fabric was further purified in the same manner as in the case of the yarn.

Ethyl acrylate was obtained from a commercial source and was purified by passing the monomer through columns of activated alumina in order to remove inhibitors of polymerization. Purified methanol, as solvent, was obtained by dehydration of certified A.C.S. methanol and then distillation at atmospheric pressure.

Methods

The SRRL ⁶⁰Co radiation source previously described by Arthur et al.⁸ was used. The dose rate, determined by ferrous-ferri dosimetry,⁹ was about 5.9×10^{19} eV/g-hr. Dried cotton cellulose yarn was irradiated to a dosage of 5.2×10^{19} eV/g (1.0 Mrad) at ambient temperature in a nitrogen atmosphere and then transferred to quartz tubes (3 mm diameter) at 25°C by using a dry-box under nitrogen atmosphere. The ESR spectra and free radical concentrations during the postirradiation reactions of the cellulose were determined using a Varian 4502-15 EPR spectrometer system which was equipped with a variable temperature accessory and a dual sample cavity. To minimize the effects of absorption of microwave power by the solvent used, the samples were frozen by immersion in liquid nitro-

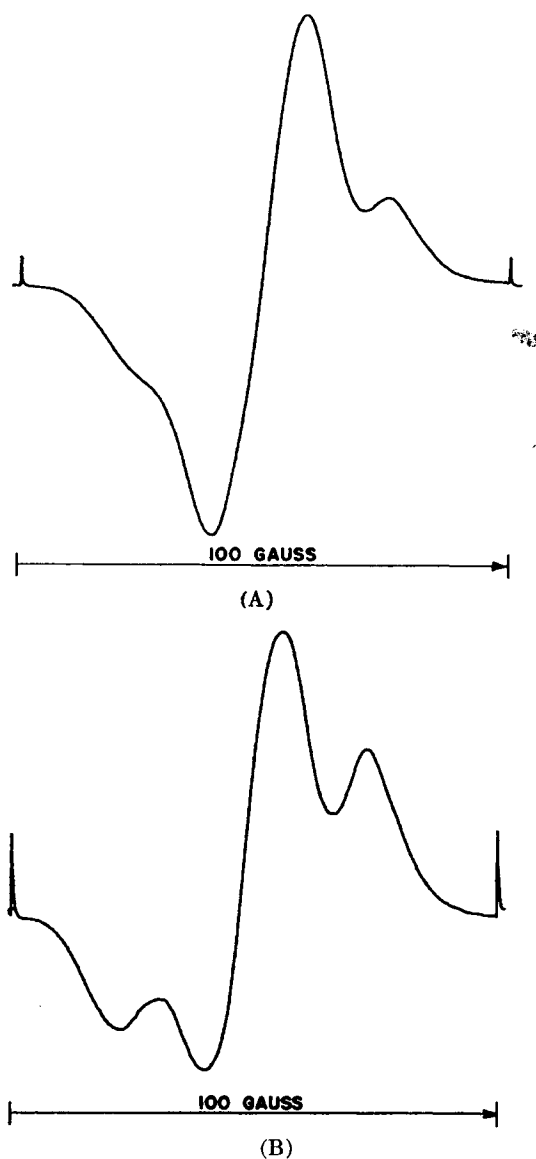
gen. After warming to -180°C , the ESR spectra and free radical concentrations were determined. The free radical concentrations were shown by the relative signal strength which was determined by measuring the distance between the peak-to-peak values in the ESR spectra.

On the other hand, cotton fabrics dried at 50°C under vacuum were sealed in glass tubes under nitrogen atmosphere. The samples were irradiated to 1.0-Mrad dosage at ambient temperature. After a time lapse of 24 hr at 25°C , the irradiated cotton fabrics were graft copolymerized by immersion of the fabrics in solutions containing ethyl acrylate, methanol, and water. The system was evacuated and flushed with nitrogen several times.^{5,6} The irradiated cellulose was allowed to react at 25°C for 60 min. After grafting, unreacted monomer was removed by washing the grafted samples with methanol; homopolymer was removed by extracting the grafted cotton fabrics at 55°C for 50 hr with acetone. The samples were then washed with distilled water and dried under vacuum. The extent of grafting was determined by increase in weight of the reacted fabrics.

RESULTS AND DISCUSSION

Effects of Solvents on ESR Spectra

In previous investigations¹⁰⁻¹² it was found that the trapped free radicals in cotton cellulose I formed by γ -irradiation existed mainly on the C_5 carbon in the more ordered regions of the cellulosic structure and, under certain experimental conditions, both on the C_5 carbon and on the oxygen atom in the cellulose chain attached to either carbon C_1 or C_4 in the amorphous region. The latter site resulted from molecular chain cleavage. We are reporting here graft copolymerization, by the γ -radiation method, onto cotton cellulose in a methanol-water system containing ethyl acrylate. The effects of these solvents on free radicals formed in the cellulose by γ -radiation were investigated by ESR spectroscopy. After irradiation, the ESR spectrum of cotton cellulose, immersed in water at 25°C for 30 sec, was remarkably different from the spectrum of the control sample, being a fairly symmetrical three-line spectrum as in the cases of previous results^{10,12} (Fig. 1). But, in the case of immersion in methanol for the same time, the spectrum was similar to that of the control specimen except that there was a decrease in relative signal strength. However, after 3 min of immersion in methanol, the spectrum resembled markedly the case for 30 sec of immersion in water. The free radicals in the amorphous region of the cellulose are rapidly scavenged by the fast diffusion of water, which has a strong swelling effect. In the case of methanol, the scavenging of the free radicals depended on the slower diffusion of methanol, which has a weak swelling effect, into the amorphous region. The similarity of their spectra, after 3 min of immersion, must be mainly attributable to the contribution of the trapped free radicals formed in the more ordered regions of the cellulosic structure, as reported earlier.^{10,12} Effects of methanol-water

Fig. 1. (*continued*)

systems on the stability of free radicals in irradiated cotton cellulose I are shown in Table I. The free radical concentrations in the control sample and the sample immersed in ethyl acrylate were hardly changed. However, the concentrations of free radicals were remarkably decreased by immersion of the irradiated sample in the methanol-water systems. The maximum scavenging of the free radicals was observed when the irradiated samples were immersed in methanol-water (50/50 volume ratio) for short periods of time. However, after 68 hr of immersion in the methanol-water

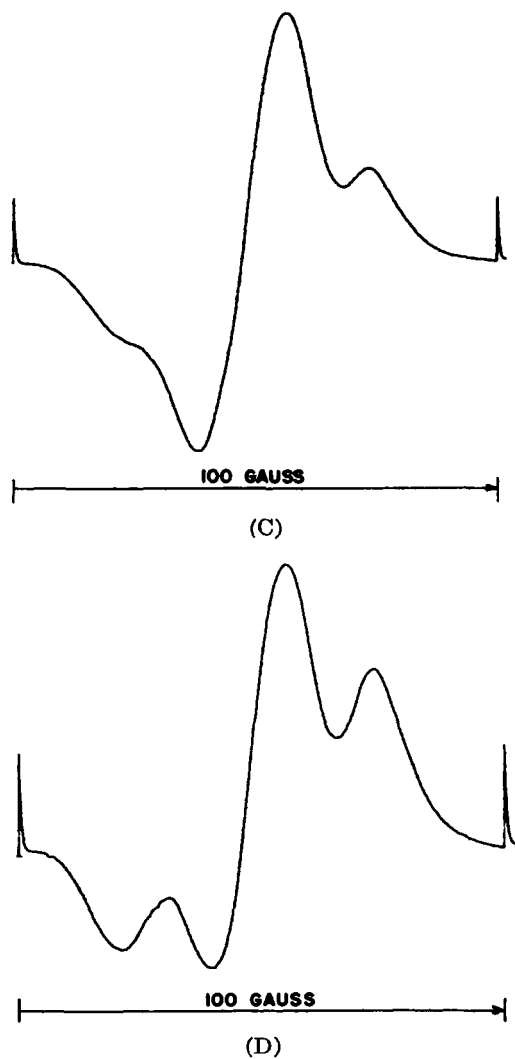


Fig. 1. Effects of immersion of irradiated cotton cellulose at 25°C in methanol, water, and ethyl acrylate on ESR spectra recorded at -180°C : (A) immersed in ethyl acrylate for 30 sec; (B) immersed in water for 30 sec; (C) immersed in methanol for 30 sec; (D) immersed in methanol for 3 min.

systems, the free radical concentrations in the irradiated samples were about the same.

Graft Copolymerization

Methanol-Ethyl Acrylate System. The effect of methanol on graft copolymerization of γ -irradiated cellulose I with ethyl acrylate is shown in

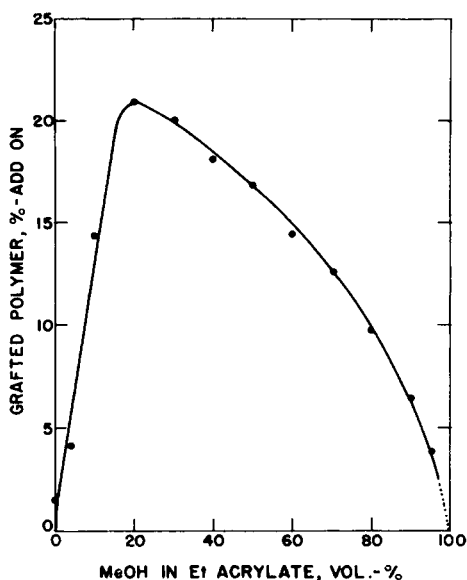


Fig. 2. Effect of composition of ethyl acrylate-methanol solution on extent of graft copolymerization with irradiated cotton cellulose at 25°C and 60 min. Dosage 5.2×10^{19} eV/g; cellulose:solution ratio 1:14.

Figure 2. The extent of grafting increased with increasing concentration of methanol to a maximum value at about 20 vol-% methanol; then the degree of grafting decreased with increased concentration of methanol. The accelerative effect of methanol was previously reported in grafting of styrene onto poly(vinyl alcohol),¹³ cellulose,^{14,15} nylon 6,¹⁶ and polyethylene,¹⁷ being considered to be due to the Trommsdorff type of effect.¹⁸ In the case of grafting γ -irradiated cellulose I with ethyl acrylate containing

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

Composition of solutions		Free radical concentration, arbitrary units ^b		
MeOH, vol-%	Water, vol-%	30 sec	3 min	68 hr
Control ^a		21	21	21
Ethyl acrylate		—	19	—
100	0	14	4.8	3.4
75	25	6.0	5.5	—
50	50	4.2	4.4	3.5
25	75	4.8	4.5	—
0	100	6.5	6.6	2.8

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

^b At indicated time of immersion at 25°C.

methanol, the appearance of a maximum extent of grafting with a given methanol concentration is also probably dependent on the Trommsdorff type of effect. That is to say, the accelerative effect can be ascribed to the fact that the growing poly(ethyl acrylate) chains have become sufficiently immobilized or curled to inhibit their rate of collision and change of termination, because methanol is a poor solvent for poly(ethyl acrylate). Also the accelerative effect of methanol may be due to the fact that the cellulosic structure is somewhat swollen by immersion in methanol-ethyl acrylate as compared with immersion in ethyl acrylate. Ethyl acrylate mixed with methanol is probably more easily diffused into the amorphous regions of the cellulosic structure than ethyl acrylate. The decrease in grafting as the concentration of methanol was increased above 20 vol-% can be attributed to the fact that the Trommsdorff type of acceleration would not be expected to keep pace with the depression in rate due to the decreased monomer concentration. This follows from the fact that further increments in methanol concentration beyond that range in which the growing ethyl acrylate chains are forced to curl up and encage themselves should prove relatively ineffective. Also, the decrease in grafting may be due, in part, to the fact that the free radicals on the γ -irradiated cellulose are scavenged on increasing the concentration of methanol, as indicated by the ESR spectra.

Methanol-Water-Ethyl Acrylate System. Effects of the volume ratio of methanol to water on graft copolymerization of γ -irradiated cellulose with ethyl acrylate were investigated at concentrations of monomer of about 5, 9, and 19 vol-%, as shown in Figure 3. The maximum extent of grafting increased with increase in the concentrations of monomer and methanol in the system. At concentrations of methanol less than the amount at which maximum grafting occurred, the systems tended to separate into two layers. At concentrations of methanol greater than the amount at which maximum grafting occurred, the systems were completely miscible or homogeneous. That is, the maximum extent of grafting was obtained at the boundary conditions between homogeneous and separated systems for each concentration of monomer. In the separated systems which contained water greater than 70 vol-%, the extent of grafting was about the same for each concentration of monomer. In the homogeneous systems, the extent of grafting increased with increase in concentration of ethyl acrylate. This accelerative effect is considered to be due to the possibility that the chance of termination by collision of propagative poly(ethyl acrylate) chains is inhibited by their coiling and immobilizing because of water, which is a poorer solvent for poly(ethyl acrylate) than methanol. Another accelerative effect is ascribed to the fact that, since the cellulose is markedly swollen with water as compared with methanol,¹⁹ ethyl acrylate with methanol-water is easily diffused into the amorphous region of the cellulosic structure containing free radicals. Thus, in the boundary composition, the maximum extent of grafting would be obtained by the combination of these accelerative effects.

The decrease of the extent of grafting with increase in water, that is, decrease in methanol, may mainly be due to the decreased concentration of

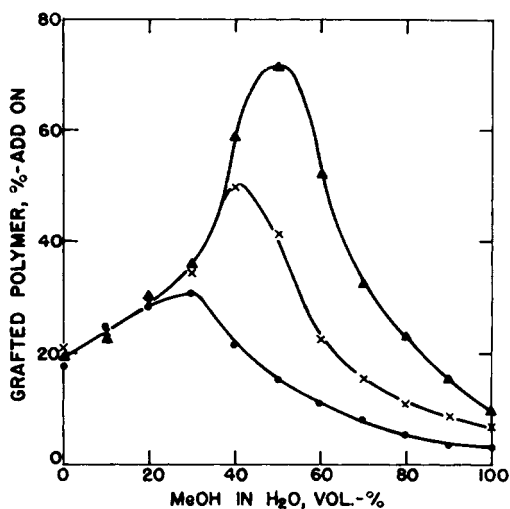


Fig. 3. Effect of composition of methanol-water solution and concentration of ethyl acrylate on extent of graft copolymerization with irradiated cellulose at 25°C and 60 min: (●) 5 vol-% ethyl acrylate; (×) 9 vol-%; (▲) 19 vol-%; dosage 5.2×10^{19} eV/g; cellulose:solution ratio 1:14.

ethyl acrylate in the separated lower layer in which graft copolymerization is proceeding. The extent of grafting, which was independent of the total amount of monomer in the system, was attributed to the fact that, although the composition in the separated lower layer was changed, when the total amount of monomer in the system was changed, this variation was not large enough to influence the extent of grafting. However, the dependence of the extent of grafting in the homogeneous grafting systems on the concentration of monomer is attributed to the increase of concentration of monomer in the homogeneous solution. The reason for the shift of maximum grafting with increase of the total amount of monomer is considered to be due to the increase in methanol necessary to prepare the solution having the boundary composition to give the greatest extent of grafting.

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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