

ESR Studies of Free Radicals in Photo-Initiated Graft Polymerization Reactions with Cotton Cellulose*

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Synopsis

Electron spin resonance (ESR) spectra of free-radical intermediates formed during photo-initiated graft polymerization reactions of acrylamide, methacrylamide, and diacetone acrylamide onto purified cotton cellulose were recorded. Purified cellulose was saturated with aqueous solutions of the vinyl monomers (0.5M) and then photolyzed under nitrogen by near-ultraviolet light (3100–4100 Å, peak near 3500 Å) at -196° and 40°C . Other samples of cellulose were saturated with aqueous solutions of the monomers, dried, and then photolyzed at 40°C . In the absence of cellulose, either poorly resolved or no free-radical spectra were generated on photolysis of the monomers. Photolysis of dried cellulose at 40°C and wet cellulose at -196°C initiated formation of a cellulosic radical that generated a singlet spectrum. Photolysis of wet cellulose at 40°C generated no ESR detectable radical; however, photolysis of wet cellulose that contained monomer at 40°C generated poorly resolved spectra. The ESR spectra of the propagating copolymer radicals recorded were poly(acrylamide), three lines; poly(methacrylamide), five lines; and poly(diacetone acrylamide), two lines (doublet).

INTRODUCTION

When cellulose is exposed to ultraviolet light, oxidative reactions are initiated, and free radicals are formed.^{1,2} Exposure of cellulose to far-ultraviolet light (about 2537 Å) initiates a greater degree of oxidative degradation of cellulose than exposure to near-ultraviolet light (about 3500 Å), both in the presence and absence of oxygen.³ Near-ultraviolet light would have energy that only marginally meets the requirements for energy of oxidative photolysis of cellulose. This characteristic probably accounts for the lower degree of oxidative degradation of cellulose on exposure to near- as compared to far-ultraviolet light. However, the maximum concentration of free radicals was formed in dried, purified cotton cellulose on exposure to near-ultraviolet light.⁴⁻⁶ It was suggested that absorption of near-ultraviolet light by cellulose was not by one specific chromophore

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but by a band absorption with the maximum for near-ultraviolet light near 3600 Å. A semiconductor-type model for the excited cellulose molecule was proposed.⁶

We have reported the photo-initiated graft polymerization of vinyl monomers with cotton cellulose on exposure to near-ultraviolet light (3100–4100 Å, peak near 3500 Å). The cellulose-copolymer products were stable to solvent extraction and to acidic and basic hydrolyses. It was suggested either that cellulose graft copolymer was formed or that the polymer was trapped within the fibrous cellulosic macrostructure.^{7–10} In this report, ESR studies of free radicals formed in purified cotton cellulose on exposure to near-ultraviolet light and of the propagating radicals formed during graft polymerization reactions of vinyl monomers with the activated cellulose are discussed. Monomers were selected so that possibly one, two, or four hydrogens could interact with the propagating radicals formed.

EXPERIMENTAL

Materials

Cotton cellulose of Deltapine variety, spun into 7s/3 yarns, was purified in the usual manner.¹¹ Electrophoresis-grade acrylamide and methacrylamide were obtained from a commercial source and were used without further purification. Diacetone acrylamide, a commercial product with a melting point of 57°C, was used as received. Deoxygenated, distilled water was used to prepare the solutions.

Methods

The near-ultraviolet light source was a Rayonet Photochemical Reactor, manufactured by the Southern New England Ultraviolet Co.³ The reactor was equipped with sixteen RPR-3500 Å lamps mounted vertically around the inside walls of a cylindrical chamber and gave a source of radiant energy with about 90% of the light in the 3500-Å range. The output of the lamps at wavelengths of less than 3100 and greater than 4100 Å was negligible. The intensity at the center of the reactor for 3500-Å radiation was rated at 9200 microwatts/sq cm, with about 1.5 to 5×10^{16} quanta/sec per cu cm.

Samples of cotton yarn were saturated with aqueous solutions of the monomers (0.5*M*) or with water. These samples were placed in quartz tubes (3-mm diameter), then evacuated at 25°C to less than 1 torr, filled with nitrogen, and sealed at atmospheric pressure. These samples were photolyzed for 60 min at 40° or –196°C. Other samples similarly treated were dried and then photolyzed for 60 min at 40°C.

The ESR spectra of free radicals formed in the photolyzed celluloses were recorded at the desired temperature with a Varian 4502-15 EPR spectrometer system which was equipped with a variable-temperature accessory. No detectable ESR spectra were recorded when the quartz tubes were photolyzed empty.

RESULTS AND DISCUSSION

ESR Spectra

The ESR spectra of cotton cellulose samples which were saturated with water and aqueous solutions of the monomers and then photolyzed for 60 min at 40°C and recorded at 22°C are shown in Figure 1. The ESR spectra of photolyzed cellulose saturated with water (Fig. 1A) and with 0.5*M* acrylamide (Fig. 1B) showed little evidence of free-radical formation. The spectra of photolyzed cellulose saturated with 0.5*M* diacetone acrylamide (Fig. 1C) and with 0.5*M* methacrylamide (Fig. 1D) showed evidence of free-radical formation. When water or the aqueous solutions of the monomers were photolyzed in the absence of cellulose, no ESR-detectable formation of free radicals occurred.

The ESR spectra of cotton cellulose samples which were saturated with water and aqueous solutions of the monomers and then photolyzed for 60 min at -196°C and recorded at -196°C are shown in Figure 2. At this temperature, ESR-detectable formations of free radicals were recorded in all cases. Photolyzed cellulose that contained water (Fig. 2A) and 0.5*M* diacetone acrylamide (Fig. 2C) generated singlet spectra. Photolyzed cellulose that contained 0.5*M* acrylamide generated a poorly resolved triplet spectrum (Fig. 2B). Photolyzed cellulose that contained 0.5*M* methacrylamide generated a five-line spectrum (Fig. 2D). When water or solutions of monomers were photolyzed for 60 min at -196°C, no ESR-detectable formation of free radicals occurred.

The ESR spectra of cotton cellulose samples that were saturated with aqueous solutions of the monomers, dried, and then photolyzed for 60 min at 40°C and recorded at 22°C are shown in Figure 3. Photolyzed, dried cellulose generated a singlet spectrum (Fig. 3A). Photolyzed, dried cellulose which initially contained acrylamide generated a three-line spectrum (Fig. 3B); that which initially contained diacetone acrylamide, a doublet spectrum (Fig. 3C); and that which initially contained methacrylamide, a five-line spectrum (Fig. 3D). When pure monomers were photolyzed for 60 min at 40°C, poorly resolved or no free-radical spectra were generated.

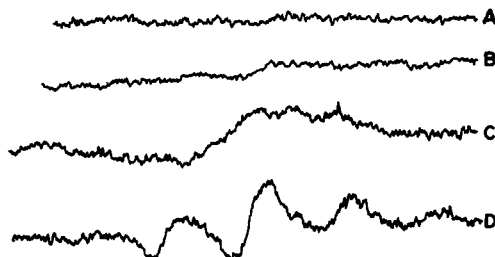


Fig. 1. ESR spectra of cotton cellulose photolyzed for 60 min at 40°C and recorded at 22°C: (A) saturated with water; (B) saturated with 0.5*M* acrylamide; (C) saturated with 0.5*M* diacetone acrylamide; (D) saturated with 0.5*M* methacrylamide. Magnetic field increasing left to right; sweep, 100 gauss.

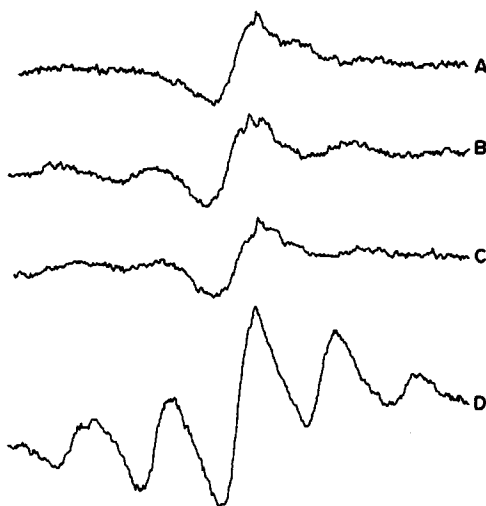
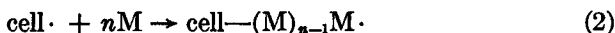


Fig. 2. ESR spectra of cotton cellulose photolyzed for 60 min at -196°C and recorded at -196°C . Legends same as for Fig. 1; samples frozen prior to photolysis.

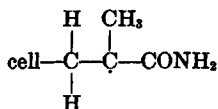
Propagating Radicals

The ESR-detectable propagating vinyl monomer radicals were not formed by direct photolysis but were generated only when monomer was photolyzed in the presence of cellulose. Evidently, the cellulose radical formed on photolysis added to the double bond of the vinyl monomer to yield the vinyl monomer radicals, as follows:



where cell-H represents the cellulose molecule; cell·, the cellulose radical; M, monomer; and M·, monomer radical. The proposed mechanism is similar to the reported formation of secondary radicals through photolysis¹² and to the recently reported addition of cellulose radical, formed by γ -radiation,¹⁸ to methacrylic acid and of methanol and acetone radicals, formed by photolysis,^{14,15} to several vinyl monomers to yield propagating radical species.

The cellulose radical evidently added to the double bond of methacrylamide to yield



In the rigid matrices in which these additions occurred (Figs. 1D, 2D, and 3D), restricted rotation about the $\text{C}_\alpha-\text{C}_\beta$ bond allowed only one of the methylene hydrogens and the methyl group to interact with the unpaired

electron to generate a five-line spectrum (compare Fig. 3D). The restriction of rotation about the $C_\alpha-C_\beta$ bond may be due to the fact that the cellulose backbone has a high molecular weight and is a bulky group. Alternatively, increased hydrogen bonding may also restrict rotation about

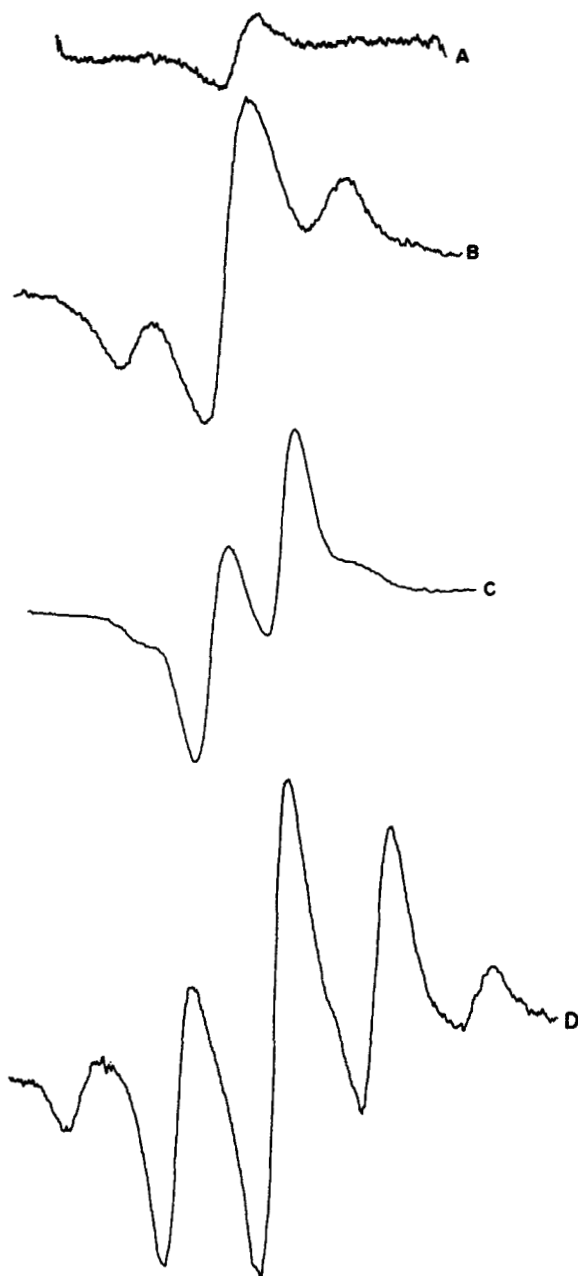
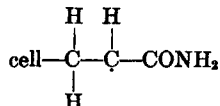


Fig. 3. ESR spectra of dried cotton cellulose photolyzed for 60 min at 40°C and recorded at 22°C. Legends same as for Fig. 1; samples dried prior to photolysis.

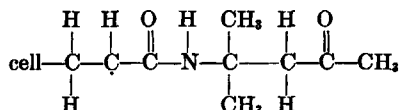
this bond.^{14,15} In the dried cellulose–monomer matrices, the concentration of free radicals trapped on photolysis was higher than those in the other matrices. The addition of methanol or acetone radicals to methacrylamide in rigid glasses also formed a radical that generated a five-line spectrum.^{14,15}

The cellulose radical evidently added to the double bond of acrylamide to yield



Similar to the methacrylamide radical, restricted rotation about the C_α – C_β bond allowed only one of the methylene hydrogens and the other hydrogen to interact with the unpaired electron to generate a three-line spectrum (Fig. 3B). If both methylene hydrogens had interacted with the unpaired electron, a three-line spectrum would have been generated; however, the alpha hydrogen should have also interacted to split this spectrum. Three-line spectra have also been reported for poly(acrylic acid)¹² and poly(acrylamide)¹⁶ formed by γ -radiation. A similar explanation would apply.

The cellulose radical added to the double bond of diacetone acrylamide to yield



Both of the methylene hydrogens were rotated out of the plane of interaction with the unpaired electron, so that the remaining alpha hydrogen interacted with the unpaired electron to generate a doublet spectrum (Fig. 3C). Both the high-polymeric cellulose backbone and the bulky side chain of the monomer probably restricted rotation about the C_α – C_β bond.

Graft Polymerization Reactions

The ESR-detectable concentration of trapped free radicals formed by photolysis at 40°C (Fig. 1) of cellulose–monomer matrices containing water was much lower than the concentrations of ESR-detectable radicals formed by photolysis at –196°C of cellulose–monomer matrices containing water (Fig. 2) or by photolysis at 40°C of dried cellulose–monomer matrices (Fig. 3). However, the presence of water during photolysis increased the extent of photo-initiated graft polymerization of monomer with cellulose.^{8,9} For example, when cellulose that contained about a 1.5-fold amount of a 10% aqueous solution of diacetone acrylamide was photolyzed for about 7 min, the cellulose product contained about 11% graft copolymer—more than 70% conversion of monomer to polymer. When a similarly treated sample of cellulose was dried for 15 min at 60°C before photolysis, the product contained about 4% graft copolymer—less than 30% conversion of monomer to polymer.

Apparently, reactive cellulose and propagating monomer radicals were formed on photolysis of the different cellulose-monomer matrices. The extent of photo-initiated graft polymerization of monomer with cellulose was more dependent on these highly transient cellulose radicals than on the trapped radicals that were ESR detectable. Also, the presence of water probably caused the cellulosic structure to swell, thereby increasing the surface area in contact with the aqueous solutions of monomers. This swelling should minimize diffusion-limiting effects on the initiating step of contacting monomer with cellulose radicals and also on the propagating graft polymerization 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.

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