

ESR Studies of the Photodegradation of Cellulose Graft Copolymers

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Synopsis

Ultraviolet light induced free radicals in cellulose and cellulose graft copolymers were studied by means of ESR spectroscopy. At least six kinds of free radicals were formed in cellulose when the polymer was irradiated with ultraviolet light. Polystyrene and poly(methyl methacrylate) are more resistant to ultraviolet light than cellulose; however, the cellulose graft copolymers of polystyrene and poly(methyl methacrylate) were degraded by ultraviolet light. ESR studies revealed that photoinduced free radicals in cellulose graft copolymers were formed at the grafting branches of the copolymers rather than the cellulose backbone. The mechanisms of light stabilization and energy transfer reactions of cellulose and cellulose graft copolymers are discussed.

INTRODUCTION

Chemical modification of cellulose and cellulosic materials by grafting with suitable monomers has resulted in the improvement of a wide variety of properties,¹⁻³ including tensile strength; resistance to microbial degradation, abrasion, and acid; dye receptivity; wet strength of paper; and adhesion.

It is known that cellulose is susceptible to degradation by ultraviolet light⁴ and solar irradiation,⁵ yet research in the improvement of light stability of cellulose is still meager, especially in regard to grafting techniques. Only a few papers published by Russian chemists have indicated that light resistance of cellulose can be improved by grafting with polyacrylonitrile (PAN)^{6,7} and with poly(methylvinylpyridine) (PMVP).^{6,7}

In this paper we are reporting our study on the light stability of cellulose grafted with poly(methyl methacrylate) (PMMA) and with polystyrene. Electron spin resonance (ESR) spectra and tensile strengths of grafted and ungrafted cellulose on photoirradiation are compared with discussed. The results demonstrate that in PMMA- and polystyrene-grafted celluloses the intramolecular energy transfer and localization of energy in the grafted branches result in a cellulose backbone that is less degraded by light. Photoprotection of cellulose by grafting techniques is verified.

EXPERIMENTAL

Materials

Commercial bleached sulfate pulp from softwood was used as the cellulose sample (degree of polymerization 870; α -cellulose 92%). The air-dried pulp was beaten in a blender for 60 sec, the portions passing through a 40 mesh screen were discarded, and the remaining parts were used. Methyl methacrylate (MMA)

and styrene were used as vinyl monomers. They were purified by extraction with 5% sodium hydroxide solution and with 20% sodium chloride solution, followed by distillation under reduced pressure.⁸

METHODS

Graft Copolymerization

Cellulose graft copolymers with differing degrees of grafting were prepared by the following method: Graft copolymerization was carried out in a system consisting of 1.5-g oven-dried cellulose sample, 10-ml monomer, and 150-ml water in a quartz flask at 45°C. The mixture was photoirradiated with a high-pressure mercury lamp (Toshiba Denki, H-400P, 400 W) which provided predominant wavelengths of 4538, 3650 (strongest), 3132, and a trace of 2537 Å for a certain period to produce a copolymer with the desired percent of grafting. Polymerization products were washed with distilled water and extracted with acetone and benzene for 48 hr for the MMA and styrene systems, respectively, to remove homopolymers. Percent grafting was calculated as follows:

$$\text{percent grafting (\%)} = \frac{A - B}{B} \times 100$$

where *A* is weight of cellulose after copolymerization and extraction and *B* is weight of original cellulose (oven dry).

Photoirradiation and ESR Measurements

The test samples were packed uniformly into clear fused Suprasil quartz tubes (O.D. 4 mm), which did not produce any signal during the irradiation sequences. The quartz tubes containing the samples were evacuated to constant pressure (10^{-6} Torr) and sealed. The source of ultraviolet irradiation was a high-pressure mercury lamp (Toshiba Denki, H-400P, 400 W), emitting mainly at 3650 Å as described earlier. In all cases of photoirradiation, the samples were kept in Dewar flasks at the temperature of liquid nitrogen.

ESR spectra were measured with an X-band ESR spectrometer (Japan Electron Optics Lab Co., Model JES, 3BS-X, 100-kHz magnetic field modulation). To avoid distortion of the spectra by power saturation, the ESR measurements were carried out at microwave power of 1 mW. All spectra were recorded at 77 K by inserting a Dewar flask with a quartz finger into the cavity.

Measurements of Photochemical Degradation

Handsheets of grafts were prepared according to Tappi Standard T200 os-70 after the pulp had been beaten in a blender for 2 min. The handsheets were then subjected to testing. The tensile strength of the handsheets was determined on a table-model Instron tensile tester with a gauge length of 5 cm and a chart speed of 50 cm/min. The strength of the samples was taken as the highest point reached in the load–elongation curve. The results are based on the average of 10 breaks with a test length of 25 cm. The change in intrinsic viscosity of cellulose, poly(methyl methacrylate) (PMMA), and polystyrene during irradiation

was measured respectively in cupriethylenediamine, acetone, and benzene solutions by using capillary viscometers. The measurements were carried out in a thermostat at $(25.00 \pm 0.05)^\circ\text{C}$.

Ultraviolet absorption spectra were recorded by a Hitachi 124 spectrophotometer.

RESULTS AND DISCUSSION

Absorption Spectra of Cellulose, PMMA, and Polystyrene

A polymer must absorb light in order to initiate photochemical reactions.⁹ Hence, the primary step must be the absorption of a quantum of light or photon by certain chromophoric groups in the polymer. Ultraviolet absorption spectra of films of cellulose (cellophane), PMMA, and polystyrene are shown in Figure 1. As seen in the spectra, all of these films begin to absorb strongly below 200 nm, with indications of some weak absorption beyond 300 nm. There are weak peaks at 265 nm for cellulose and PMMA and at 260 nm for polystyrene. As a consequence, it is apparent that all of these polymers are degradable by light of 2537 Å, and the degradation process is generally considered as going by a free-radical route.¹⁰

Photo-Induced Free Radicals in Cellulose, PMMA, and Polystyrene

Before embarking on any discussion of photo-induced free radicals in polymers, it is worthwhile to mention that free radicals were not detected by ESR spectroscopy from cellulose, PMMA, and polystyrene prior to photoirradiation. This infers that these polymers do not contain any intrinsic free radicals. After photoirradiation, ESR signals were detected, verifying that photo-induced free radicals were created in all of the polymers. The typical ESR spectra of these polymers are shown in Figure 2.

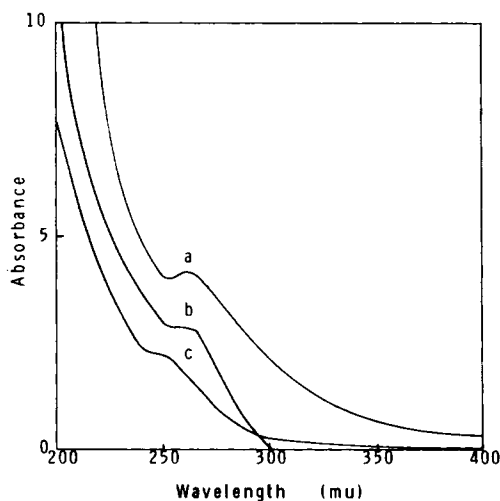


Fig. 1. Ultraviolet absorption spectra of (a) cellulose; (b) poly(methyl methacrylate); (c) polystyrene.

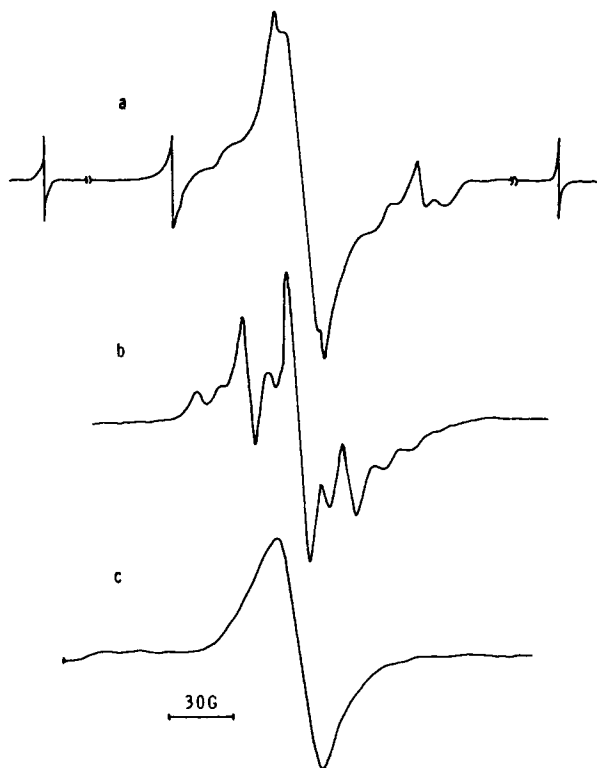
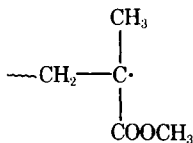


Fig. 2. ESR spectra of (a) cellulose; (b) poly(methyl methacrylate); (c) polystyrene, irradiated with light of $\lambda > 2537 \text{ \AA}$ at 77 K and recorded at 77 K.

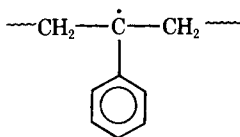
As reported previously,⁴ when cellulose is irradiated in the solid state by ultraviolet light, the energy transfer effects lead to localization of the energy within the molecule, resulting in its degradation. The localization of energy in the molecule results in the production of free radicals, and a number of chemical reactions are initiated. These reactions include depolymerization, dehydrogenation, dehydroxylation, and dehydroxymethylation and production of hydrogen, carbon monoxide, and carbon dioxide. The ESR spectrum of cellulose thus observed, as shown in Figure 2(a), is quite complicated and has been resolved to a superposition of six kinds of signals, namely, doublet (508G splitting), doublet (129G splitting), doublet (43G splitting), triplet (34G splitting), quartet (overall width 88G), doublet (24G splitting), and singlet signals.¹¹ In short, six kinds of radical components are produced in photoirradiated cellulose.

A nine-line (5 + 4) spectrum was observed from photoirradiated PMMA, Figure 2(b), and this signal is derived from free radicals generated in the polymer after cleavage of the carbon-to-carbon main chain, i.e., the propagating radicals,^{10,12}



A broad singlet spectrum ($\Delta H_{msl} = 23\text{G}$) was detected from photoirradiated

polystyrene, Figure 2(c), when it was irradiated under the identical irradiation conditions, and this signal was attributed to the free radicals located at the tertiary carbon atom^{10,12}:



Calculating the overall signal intensities of photoirradiated samples, with exactly the same weight, by using a Varian pitch as a standard it was found that cellulose exhibited the strongest ESR signal intensity, followed by PMMA and polystyrene at any irradiation time. This implied that cellulose interacted with light more strongly than PMMA and polystyrene; more free radicals were generated in cellulose. From this, cellulose appears to be degraded more severely by light than the other two polymers. This proposition is further substantiated by comparing the rates of decrease in viscosity of the polymers during photoirradiation.

Change of Viscosity of Polymers During Photoirradiation

Photodegradation of cellulose, PMMA, and polystyrene is also substantiated by the change in viscosity of the polymers during photoirradiation. Results are depicted in Figure 3. Of these three samples, it is apparent that the decrease in viscosity was significant in cellulose, and that PMMA suffered less and polystyrene least. This is in accordance with the previous supposition on free-radical concentration deduced from the ESR spectra. As mentioned earlier, cellulose absorbs light between 200 and 400 nm; it is susceptible to photodegradation. PMMA does not absorb much light beyond 280 nm; hence, photodegradation is relatively small. And polystyrene, although it absorbs light, degraded less

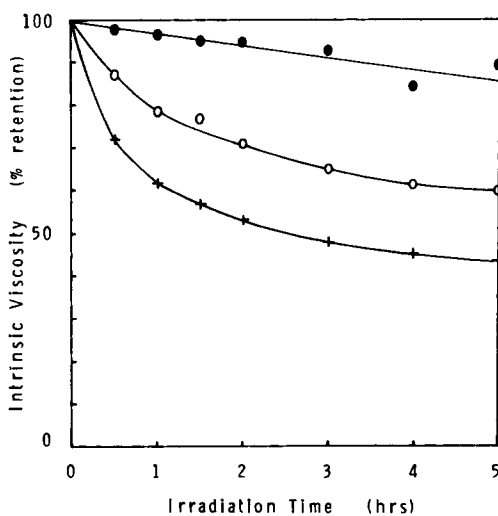


Fig. 3. Decrease of intrinsic viscosity of polymers irradiated with light of $\lambda > 2537 \text{ \AA}$ at 25°C : (●) polystyrene; (○) poly(methyl methacrylate); (+) cellulose.

than other polymers probably due to the radiative energy being dissipated by the aromatic rings before any photochemical reactions take place.

Photostability of Cellulose Graft Copolymers

Although the tensile strength of cellulose was not significantly improved by grafting with PMMA and polystyrene, it was noticed that cellulose graft copolymers have improved light stability compared to untreated cellulose.

Due to the insolubility of cellulose graft copolymers in solvents normally used for cellulose, the change in degree of polymerization or molecular weight cannot be measured. The degradation process is indirectly estimated from the changes in tensile strength. The effects of ultraviolet irradiation on the tensile strength of cellulose and of cellulose graft copolymers are shown in Figure 4.

When cellulose was irradiated with ultraviolet light under vacuum for 3 hr, the decrease in the tensile strength of the cellulose fiber was significant (about 45% reduction of its original value). However, this inexorable photoeffect can be mitigated by grafting the cellulose with PMMA and polystyrene. As shown in Figure 4, with increased degree of grafting the loss of tensile strength of photoirradiated cellulose was greatly diminished; and between the graft copolymers, the polystyrene-grafted cellulose has a better performance than that grafted with PMMA.

ESR Spectra of Cellulose Graft Copolymers

Although PMMA and polystyrene are less degradable than cellulose by ultraviolet light, the behavior of cellulose graft copolymers toward ultraviolet light is of interest. Again, no intrinsic free radicals are detected from cellulose graft copolymers before photoirradiation.

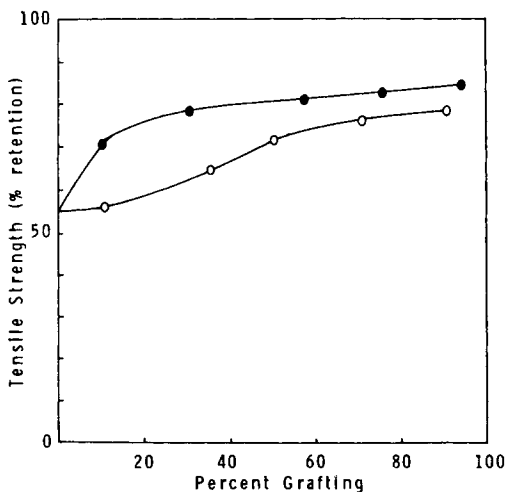


Fig. 4. Effects of ultraviolet irradiation on tensile strength retained by cellulose graft copolymers as a function of percent grafting: (●) cellulose—polystyrene; (○) cellulose—PMMA.

PMMA-Grafted Cellulose

Cellulose samples grafted with different percentages of PMMA were irradiated with ultraviolet light for 60 min under vacuum. ESR signals were detected as shown in Figure 5. The cellulose sample with 10.7% grafting exhibited a poorly resolved multiplet signal resembling that observed from photoirradiated cellulose, Figure 2(a). However, signals derived from hydrogen atoms (508G splitting) were not detected. When the sample with 35.6% grafting was irradiated, some new peaks appeared in the spectrum, Figure 5(b), and these new peaks increased gradually and enlarged with increase in the percent of grafting. It is believed that the multiplet spectra of PMMA-grafted cellulose are due to the superimposition of free radicals from cellulose backbone as well as from PMMA grafted branches; and the formation of radicals in PMMA appears to be of paramount importance as the percent of grafting is increased. The overall signal intensities were increased as compared to that obtained from cellulose only, Figure 6.

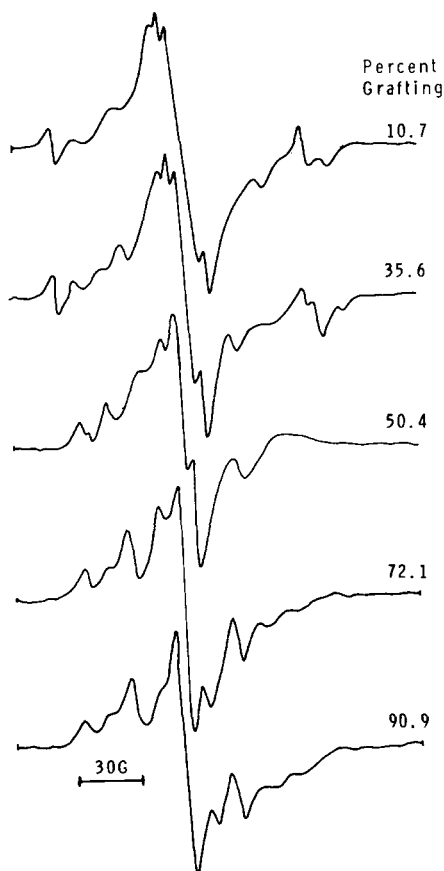


Fig. 5. ESR spectra of PMMA-grafted cellulose irradiated with light of $\lambda > 2537 \text{ \AA}$ at 77 K and recorded at 77 K.

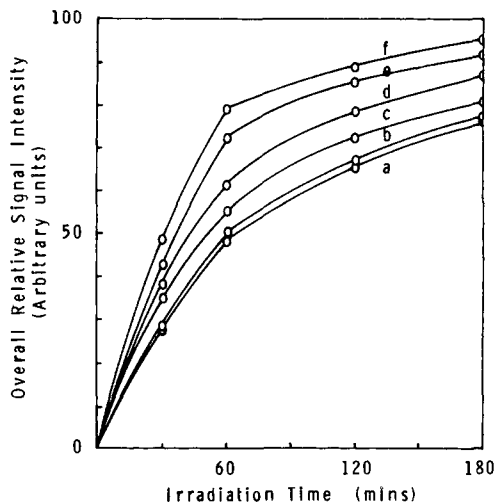


Fig. 6. Rate of formation of free radicals in PMMA-grafted cellulose when irradiated with light of $\lambda > 2537 \text{ \AA}$ at 77 K. Percent grafting: (a) 0 (control); (b) 10.7; (c) 35.6; (d) 50.4; (e) 72.1; (f) 90.9.

Styrene-Grafted Cellulose

Interestingly, polystyrene-grafted cellulose exhibited different ESR features when irradiated under identical conditions. ESR spectra are shown in Figure 7. The cellulose sample with 10.3% grafting indicated little decrement of ESR intensity of cellulose; and the intricate multiplet signal was consequently converted to a broad singlet signal with a linewidth of 23 G. The overall intensity also dwindled as compared to that obtained from cellulose only, Figure 8. Since this singlet signal is very similar to those derived from photoirradiated polystyrene, it is conceivable that the singlet signal was predominantly generated from the polystyrene component; and this signal was probably superimposed with the weaker signals from cellulose.

Based on these findings, photoinduced free radicals in cellulose graft copolymers are apparently prevalingly located at the grafting branches rather than the cellulose backbone. Overall free-radical concentration appears to be increased in the photoirradiated PMMA-grafted cellulose and to be decreased in the photoirradiated polystyrene-grafted cellulose. Comparing the improvement of tensile strength of these graft copolymers, it appears that both of these graft copolymers have increased the light stability of the cellulose backbone.

Light Stabilization and Energy Transfer Reactions

When cellulose is photoirradiated in the solid state, the absorption of light by cellulose is evidently on the acetal chromophoric groups of the polymer.^{4,13} The transfer and localization of absorbed energy within the cellulose molecule initiate photochemical reactions, i.e., depolymerization, dehydrogenation, dehydroxylation, and dehydroxymethylation, with the production of free radicals.⁴ However, when PMMA and polystyrene were grafted to the cellulose, the mechanisms of transfer and localization of energy appear to be influenced.

Production of cellulosic free radicals decreased, and the loss of tensile strength

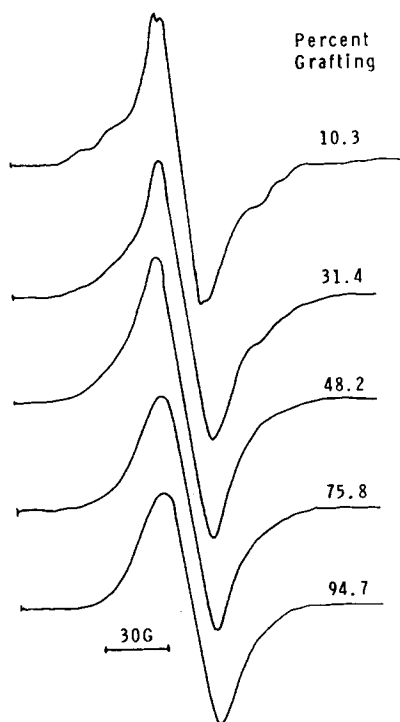


Fig. 7. ESR spectra of polystyrene-grafted celluloses irradiated with light of $\lambda > 2537 \text{ \AA}$ at 77 K and recorded at 77 K.

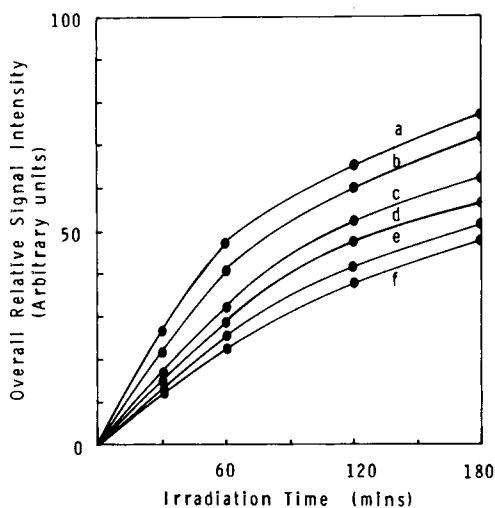


Fig. 8. Rate of formation of free radicals in polystyrene-grafted celluloses when irradiated with light of $\lambda > 2537 \text{ \AA}$ at 77 K. Percent grafting: (a) 0 (control); (b) 10.3; (c) 31.4; (d) 48.2; (e) 75.8; (f) 94.7.

of cellulose also diminished in cellulose graft copolymers upon photoirradiation. Meanwhile, creation of photo-induced free radicals is prevailing at the grafting branches of the copolymers. The presence of grafting branches on the cellulose

molecule apparently decreased localization of energy within cellulose molecules in such a way as to minimize decomposition leading to free-radical formation. The potential energy absorbed may be transferred effectively to the grafted branches from acetal chromophoric groups to generate free radicals; the energy may also be more effectively absorbed by the grafting branches than the acetal groups in cellulose.

As a consequence, the potential energy involved in the degradation of cellulose is lessened. Photoprotection of cellulose by grafting with PMMA and polystyrene is recognized.

CONCLUSIONS

It can be concluded that cellulose light stabilization or photoprotection can be considerably achieved by grafting the polymer with PMMA and polystyrene. This was verified by the high retention of tensile strength of the cellulose with increasing degree of grafting. Grafting of polystyrene also reduced free-radical formation, whereas grafting with PMMA enhances free-radical formation, but this increase is due to the localization of damage at the grafting branches rather than at the cellulose backbone.

It is plausible that the energy of the photon, after absorption by the acetal chromophores in cellulose, is transferred to and localized at the reactive centers of the grafting branches. It is also conceivable that chromophoric groups in PMMA and polystyrene components which are grafted onto the cellulose preferentially absorbed ultraviolet light. Hence, less ultraviolet light is available for degradation of the cellulose backbone. These two mechanisms appear to be the most probable explanation for the stabilization of cellulose molecules.

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