

Poly(vinyl Alcohol) Fiber Radicals Induced by Photo-Irradiation at Room Temperature

YOSHITAKA OGIWARA, TOSHIO YASUNAGA, and HITOSHI KUBOTA, *Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan*

Synopsis

The decay behavior of radicals produced on poly(vinyl alcohol) (PVA) fiber by photo-irradiation at room temperature and the graft copolymerization of methyl methacrylate (MMA) on the irradiated PVA fiber were investigated. Two kinds of stable radicals showing singlet and triplet spectra were indicated for both unsensitized and ferric ion-sensitized samples, especially with the emphasis of triplet component radical. The decay of radicals was promoted by contact with various organic solvent-water solutions, which effects were in the order of dimethyl sulfoxide (DMSO)-water > acetone-water > water > dioxane-water > methanol-water. On the other hand, graft copolymerization of MMA on the preirradiated sample was effectively initiated with the aid of a little water or a mixed solution of organic solvent and water. Methanol and dioxane, which decay radicals milder than acetone and DMSO do, contributed to give a higher per cent grafting. As no initiation took place with the unirradiated sample, it is concluded that the ability of preirradiated samples to initiate graft copolymerization should be caused by the PVA fiber radicals, which are smoothly produced by photo-irradiation at room temperature and show a triplet spectrum.

INTRODUCTION

In the previous papers,^{1,2} we reported that the ESR spectrum of poly(vinyl alcohol) (PVA) fiber irradiated at 77°K was a three-line type, which could be separated into a triplet spectrum with a splitting factor of 32 gauss and a singlet one with a line width of 20 to 22 gauss. We observed further that the formation of radicals was markedly enhanced by the use of photosensitizer¹ such as ferric chloride (Fe^{3+}) as well as of oxidized sample² treated by sodium hypochlorite or periodic acid, indicating the emphasized formation of triplet component radicals. These factors proved effective in the graft copolymerization^{1,2} of methyl methacrylate (MMA) on PVA fiber, too.

The authors examined, at room temperature, the formation of radicals in the photo-irradiated PVA fiber and observed the generated stable radicals at the same conditions. In this paper, the decay of radicals formed at room temperature and the ability to initiate graft copolymerization on the sample were investigated with the purpose of proving the initiating species of PVA fiber.

EXPERIMENTAL

PVA Fiber Sample

Commercial PVA fiber Vinylon (4 to 5 denier) was cut into about 1-cm lengths, boiled for 2 hr in water, and then dried under reduced pressure to obtain unsensitized sample. The unsensitized sample was treated with 10 mmole/l. aqueous solution of Fe^{3+} at 45°C for 60 min to prepare Fe^{3+} -sensitized sample. The amount of Fe^{3+} adsorbed on PVA fiber sample was determined by iodometry,³ showing 4.2 mmole/100g of PVA fiber.

Graft Copolymerization

After irradiating the quartz glass tube containing 0.50 g (oven dry) PVA fiber sample with light at room temperature for 30 min under nitrogen, 15 ml MMA-water or MMA-water-organic solvent of a known concentration was injected into the system. Irradiation was conducted using a Toshiba high-pressure mercury lamp H400-P(400 W) with a reaction tube about 10 cm from the light source. Graft copolymerization was carried out by keeping the system at 50°C for 60 min without further irradiation. The products were washed with water and then extracted with acetone to remove homopolymers. The per cent grafting was taken as the percentage of weight increase of the original PVA fiber.

Methanol, acetone, dioxane, and dimethyl sulfoxide (DMSO) were purified by distillation. MMA was distilled under reduced pressure before use.

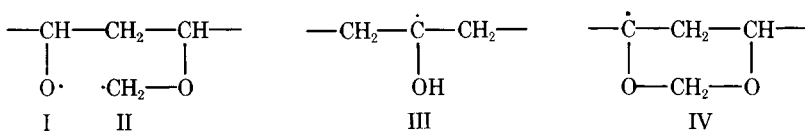
Measurements of ESR Spectra

A quartz glass tube (5 mm diameter) filled with PVA fiber sample and flushed with nitrogen was exposed at room temperature for a given duration. All ESR measurements were made at room temperature with a Japan Electron Optics Laboratory JES-ME-X instrument. Resonance spectra were observed with x-band and 100 kcps field modulation.

RESULTS AND DISCUSSION

ESR Spectra of Photo-Irradiated PVA Fiber

Figure 1 shows ESR spectra of the unsensitized and Fe^{3+} -sensitized samples irradiated at room temperature for 60 min. Both samples exhibited a three-line spectrum with a splitting factor of 32 gauss which kept the intensity positive at a high level even after leaving the samples at room temperature for several hours. ESR spectra of the sample irradiated and recorded at 77°K were also included in the figure. In the 77°K-irradiating system, the three-line spectrum of Fe^{3+} -sensitized sample appeared more distinct than that of unsensitized one. In the previous paper,² the authors examined ESR spectra of photo-induced radicals in oxidized PVA fiber, and observed that radicals I and II were main products in unoxidized samples, while radicals III and IV were dominant in oxidized samples.



Radical I should indicate a singlet, and radicals II, III, and IV, a triplet spectrum. By the way, radical II has already proved unstable toward heat as compared to I, III, and IV. Therefore, it is conceivable that the three-line spectra recorded here have to be constructed of two components, namely, triplet III or IV in addition to singlet I. In the room temperature-irradiating system, a sharp three-line spectrum was obtained even for unsensitized sample, which seems to indicate an emphasized formation of triplet component

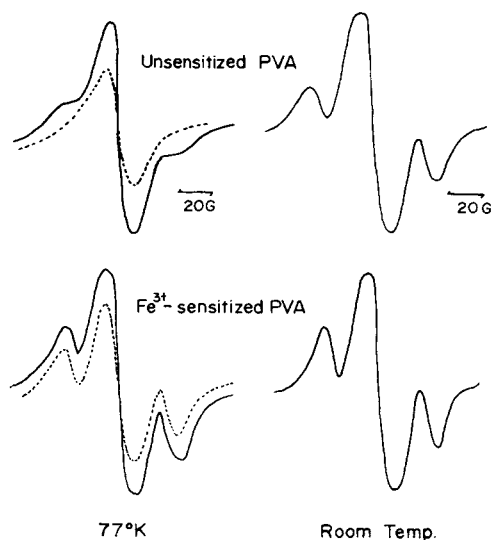


Fig. 1. ESR spectra of PVA fibers irradiated at 77°K and room temperature for 60 min. Dotted lines represent the ESR spectra after warming to room temperature for 2 min.

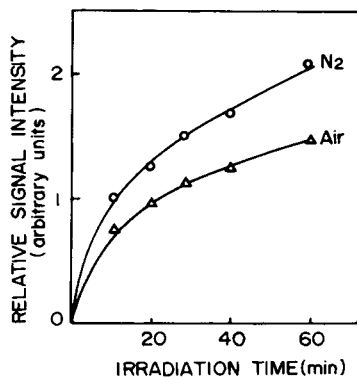


Fig. 2. Effect of atmosphere on radical formation by photo-irradiation. The Fe^{3+} -sensitized sample was irradiated at room temperature.

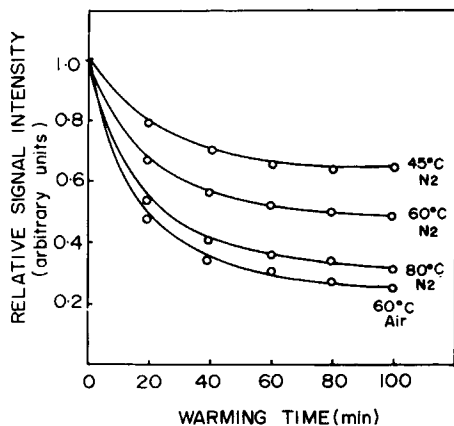


Fig. 3. Effect of temperature on decay of radicals produced by photo-irradiation. The Fe^{3+} -sensitized sample was irradiated at room temperature for 60 min.

radicals, III and IV, being stable toward heat. The formation of stable radicals under nitrogen proved more easier than under air (Fig. 2).

Decay of Photo-Induced PVA Fiber Radicals

The samples irradiated at room temperature for 60 min were kept at 45°, 60°, and 80°C in order to examine the decay behavior of PVA fiber radicals. The radical decay proceeded somewhat faster in air and at high temperature (Fig. 3). The effect of organic solvent-water solutions on the decay phenomenon was examined by injecting a known amount of solution into the system containing 60-min irradiated sample, followed by keeping it at 50°C for a given duration. The changes of relative signal intensity are shown in Figure 4. The magnitude of the solution effect on the radical decay was in the order of DMSO-water > acetone-water > water > dioxane-water > methanol-water. Compared to methanol and dioxane, which affected radical decay

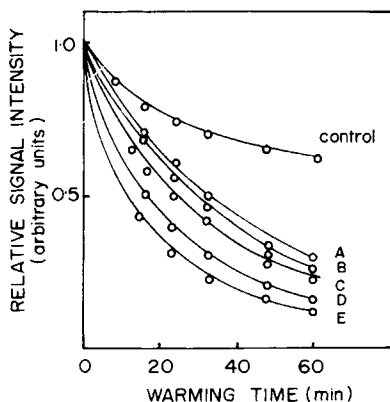


Fig. 4. Effect of various organic solvent-water solutions on decay of radicals produced by photo-irradiation. The Fe^{3+} -sensitized sample was irradiated at room temperature for 60 min: (A) methanol-water; (B) dioxane-water; (C) water; (D) acetone-water; (E) DMSO-water.

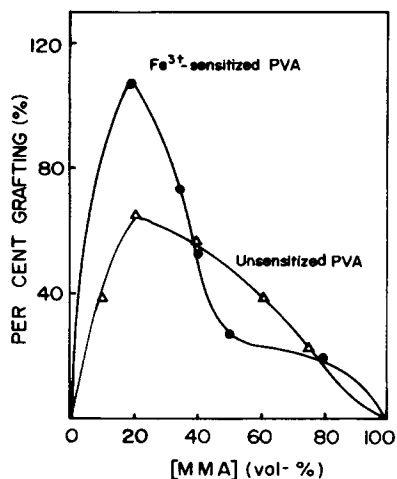


Fig. 5. Graft copolymerization of MMA on PVA fiber preirradiated at room temperature for 30 min. Graft copolymerization was carried out at 50°C for 60 min in aqueous solution.

weakly, DMSO and acetone, the strong decay-producing solvents, were found to contribute much more to the triplet component radical declination as compared to the singlet.

The authors⁴ previously reported that the effect of organic solvents on the decay of photo-induced cellulose radicals decreases in the order of water \approx methanol \gg acetone $>$ dioxane. Reine et al.⁵ and Mares et al.⁶ reported that the effect of solvents on the cellulose radicals induced by γ -irradiation reduces in the order of methanol $>$ water $>$ acetone $>$ DMSO, depending upon the ability of the solvent to diffuse into the fiber tissue. The action of solvents toward PVA radicals in our study does not always quite agree with the results of cellulose radicals. This seems to come from the differences in the fiber tissue between cellulose and PVA fibers and/or in the affinity to each organic solvent.

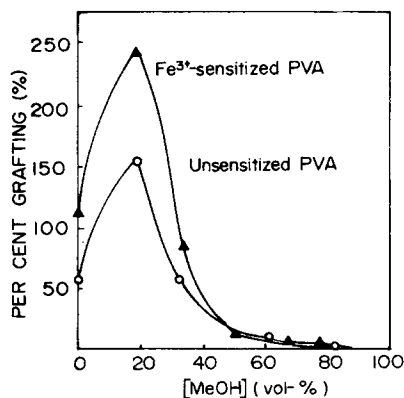


Fig. 6. Graft copolymerization of MMA on PVA fiber preirradiated at room temperature for 30 min. Graft copolymerization was carried out at 50°C for 60 min in methanol-water solution. Concentration of MMA, 20 vol-%.

Graft Copolymerization on Preirradiated PVA Fiber

Graft copolymerization of MMA on the unsensitized and Fe^{3+} -sensitized samples preirradiated at room temperature for 30 min was carried out at 50°C for 60 min, and the results are shown in Figure 5. No copolymerization was initiated at all with the unirradiated sample under the above conditions. On the other hand, the preirradiated samples could initiate the copolymerization easily, attaining maximum per cent grafting with the use of MMA of concentration about 20 vol-% in water. As compared to unsensitized sample, Fe^{3+} -sensitized sample indicated a somewhat higher value in the per cent grafting. However, there was no initiation with the use of MMA of 100% concentration. As one of the reasons of this phenomenon, very poor penetration of 100% MMA into PVA fiber tissue might be cited. The existence of some water might cause sample swelling and easy penetration of MMA into fiber tissue, leading to better conditions for graft copolymerization.

TABLE I
Ability of Preirradiated PVA Fibers to Initiate Graft Copolymerization^a

Solvent	Grafting at various preirradiation times, %		
	0 min	30 min	60 min
Water	0	107	250
Methanol	0	240	400
Dioxane	0	110	270
Acetone	0	50	90
DMSO	0	10	60

^aGraft copolymerization of MMA onto Fe^{3+} -sensitized sample was carried out at 50°C for 60 min in the system with 20 vol-% organic solvent concentration. Concentration of MMA, 20 vol-%.

The results of graft copolymerization of MMA on the preirradiated samples using methanol-water solution are shown in Figure 6. Maximum per cent grafting was attained at a methanol concentration of about 20 vol-%. In this system, the contribution of methanol seems to be very large. The results in various organic solvent-water solutions are shown in Table I. Of course, the unirradiated sample was quite inactive in the graft copolymerization with the use of any solvent. Methanol-water and dioxane-water solutions served to attain higher per cent grafting for preirradiated sample as compared to the case using 100% water, while acetone-water and DMSO-water solutions depressed the graft copolymerization. The effect of organic solvent on the initiation corresponded well with the decay behavior of PVA fiber radicals by means of organic solvent-water solution previously shown in Figure 4. That is, acetone and DMSO decay the PVA radicals faster than methanol and dioxane do.

From the above examinations, it is concluded that the ability of preirradiated samples to initiate graft copolymerization is caused by PVA fiber radicals showing a triplet spectrum which are formed by photo-irradiation at room temperature, and the structures supposedly are III and IV.

References

1. Y. Ogiwara, H. Kubota, and T. Yasunaga, *J. Appl. Polym. Sci.*, **19**, 887 (1975).
2. Y. Ogiwara, T. Yasunaga, and H. Kubota, *J. Appl. Polym. Sci.*, **20**, 1413 (1976).
3. Y. Ogiwara and H. Kubota, *J. Polym. Sci. A-1*, **7**, 2087 (1969).
4. H. Kubota, Y. Ogiwara, and K. Matsuzaki, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 2809 (1974).
5. A. H. Reine, O. Hinojosa, and J. C. Arthur, Jr., *J. Polym. Sci. B*, **9**, 503 (1971).
6. T. Mares, O. Hinojosa, Y. Nakamura, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **15**, 2349 (1971).

Received August 12, 1975

Revised October 2, 1975