

Some Aspects of Photo-Initiated Grafting to Poly(vinyl Alcohol)

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

Synopsis

Three radicals showing singlet, triplet, and quartet, respectively, were observed in the photo-irradiated poly(vinyl alcohol) (PVA). The signal intensity was increased by the ferric ion (Fe^{3+}) sensitization and the formalization of samples. The triplet component radicals proved to keep fairly stable at room temperature, indicating a high stability of the radical toward warming. Since the Fe^{3+} sensitization and the formalization of samples brought about a very favorable graft copolymerization, the triplet spectrum was assumed to have to do closely with the initiation of graft copolymerization. The spectra of singlet and quartet were assigned to alkoxy and methyl radicals, respectively, originated from the acetyl group remaining in PVA samples and the triplet spectrum to radicals on the α -carbon of the hydroxyl group in the PVA molecule.

INTRODUCTION

In the previous paper,¹ the photo-induced graft copolymerization of methyl methacrylate (MMA) in aqueous poly(vinyl alcohol) (PVA) system was studied, in which notable initiation activities of graft copolymerization were observed in the case of using a photosensitizer or employing oxidized PVA samples, whereas the untreated samples could hardly initiate under the same conditions.

Among the sensitizers oxalic acid, sodium anthraquinone-2,7-disulfonate, and ferrous and ferric ions, the effect of ferric ion was the largest. Geacintov et al.² and Tsunooka et al.^{3,4} reported the advanced initiating reaction of photo-induced graft copolymerization, employing PVA films sensitized with anthraquinone dyes and carbonyl group-introducing samples, respectively.

The purpose of the present study is to elucidate the relationship between the radical formation and the initiating characteristics of graft copolymerization by examining the effects of irradiation time, sensitizer, and formalization on the radical formation in photo-induced PVA.

EXPERIMENTAL

PVA Sample

Two kinds of sample with different degree of saponification (D.S.) and degree of polymerization (D.P.), PVA-1 (D.S., 96%; D.P., 1500) and PVA-2 (D.S.,

99%; D.P., 600), were used. The PVA powder was dissolved in water and next precipitated with acetone, and dried under vacuum for the experiments.

Formalized PVA samples of various degrees of formalization were prepared from 5% aqueous solution of PVA with the addition of hydrochloric acid and formaldehyde at 45°C. The degree of formalization was measured according to the literature.⁵

The sensitized PVA samples were prepared from 3% aqueous solution of PVA with the addition of sensitizer such as sodium anthraquinone-2,7-disulfonate (AQ), benzoyl peroxide (BPO), ferric chloride (Fe^{3+}), and silver nitrate (Ag^+) at 45°C. After 60 min of reaction, it is precipitated with acetone and dried under vacuum.

Graft Copolymerization

Graft copolymerization was carried out at 45°C in a system consisting of 2.5 ml MMA and 40 ml distilled water dissolving a 0.50-g PVA sample under nitrogen in a 200-ml quartz tube with light irradiation for a given duration. A Toshiba high-pressure mercury lamp H400-P was used as the light source, and the light irradiation was carried out in a reaction tube at about 10 cm from the light source.

After the polymerization was stopped by adding a small amount of hydroquinone, polymerization products were treated with hot water at 70°C for 60 min to eliminate unreacted PVA, followed by the extraction with acetone for 48 hr to remove homopolymers. In order to calculate the per cent grafting poly(MMA) was isolated by treating the graft copolymer with 30% nitric acid at 70°C for 5 hr according to Danelyan's method.⁶

The per cent grafting was determined according to the following equation:

$$\text{per cent grafting (\%)} = \frac{\text{grafted poly(MMA) (g)}}{\text{PVA used in reaction (g)}} \times 100.$$

The per cent grafting on the formalized PVA was calculated from the weight increase based on formalized PVA.

Measurements of ESR Spectra

A quartz tube of 5-mm diameter filled with PVA sample and substituted with nitrogen was put in an insertion-type Dewar bottle and exposed at 77°K for 60 min to ultraviolet light. The samples for the photo-irradiation were used in the oven-dried state. ESR measurements were recorded at 77°K with a Japan Electron Optics Laboratory JES-ME-X. Resonance spectra were observed with the x-band and 100 Kc field modulation.

RESULTS AND DISCUSSION

Photo-Induced PVA Radicals

ESR spectra of untreated samples with various durations of irradiation are shown in Figure 1. The spectrum of PVA-1 with 15-min irradiation exhibited a clear quartet with an intensity ratio of 1:3:3:1 and a splitting constant of 23 gauss. The spectrum of the sample after 60 min of irradiation indicated also the same line shape with some increase in signal intensity. By keeping the irradiated

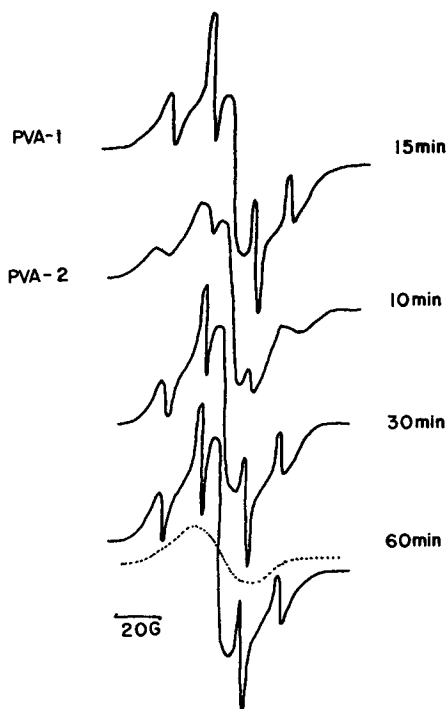


Fig. 1. ESR spectra of untreated PVA samples irradiated at 77°K with various irradiation times. Degrees of saponification of PVA-1 and PVA-2 were 96% and 99%, respectively.

sample at room temperature for 2 min, the ESR spectrum changed to a singlet with a line width of 20 gauss, which is shown with a dotted line. PVA-2 also gave a ESR spectrum with a broad four-line spectrum after 10 min of irradiation, which changed to a distinct quartet with a longer irradiation time, which proved to be changed to a singlet by warming at room temperature. Thus, it is believed that at least two kinds of radicals corresponding to the singlet and the quartet spectra, respectively, were formed in the photo-irradiated PVA.

As the splitting constant of the quartet spectrum, which decayed quickly by warming, agreed nearly with the value given for methyl radical,⁷ the photo-induced radicals were presumed to be methyl and alkoxy radicals originated from the acetyl group remaining in PVA samples in a small amount. It is natural to consider that the acetyl group remaining in PVA is very active toward light. By examining the ESR spectrum of photo-irradiated PVA, Kudrna⁸ supposed the radicals giving singlet and quartet spectra to be acyl or alkoxy radical and methyl radical, respectively.

The effect of sensitizers on the formation of PVA radicals are shown in Figure 2. With the use of sensitizers, the relative signal intensity of the spectrum was generally increased with an appearance of new peaks at both sides of the spectrum, suggesting the formation of a radical other than those giving singlet and quartet spectra. The intensity of the new absorption was affected markedly by the kind of sensitizer, indicating some differences among sensitizing behavior. The effect of Fe^{3+} was observed to be superior to those of Ag^+ and AQ, which was examined successively in more detail.

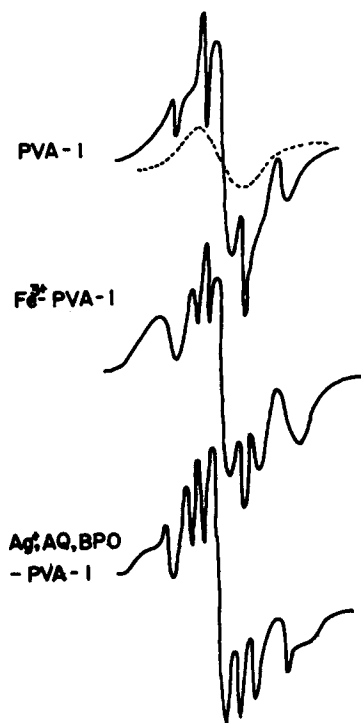


Fig. 2. ESR spectra of various sensitized PVA samples irradiated at 77°K for 60 min.

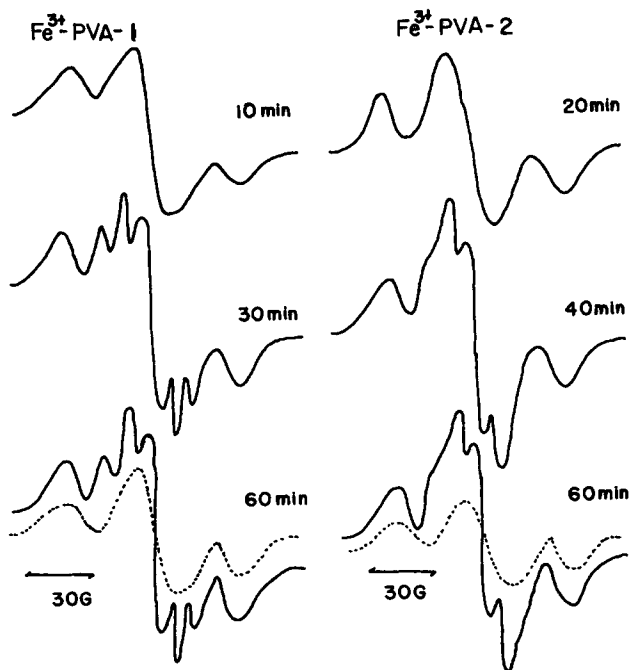


Fig. 3. ESR spectra of Fe³⁺-sensitized PVA irradiated at 77°K. Dotted line represents the spectrum after warming at room temperature for 2 min.

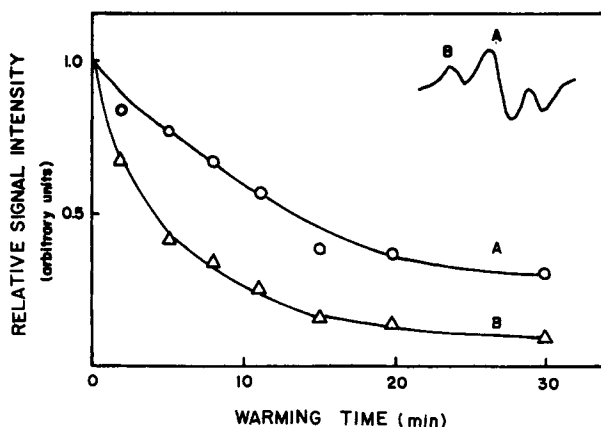


Fig. 4. Decay curves of radicals in Fe^{3+} -sensitized PVA irradiated at 77°K for 60 min. Warming was carried out at room temperature.

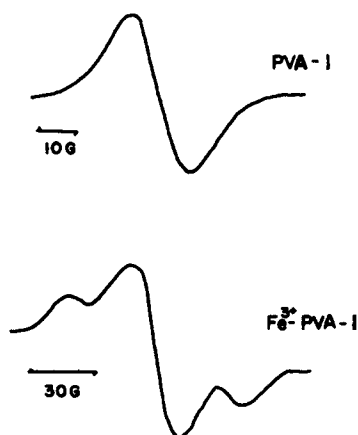


Fig. 5. ESR spectra of PVA samples irradiated at 45°C for 60 min and recorded at 77°K .

Figure 3 shows the change of ESR spectra of Fe^{3+} -sensitized PVA with irradiation time. The spectrum of 20 min-irradiated PVA-2 showed a three-line spectrum with a splitting constant of 32 gauss, which was transferred to a four-line spectrum with a longer irradiation time. When warming at room temperature was carried out, the four-line spectrum of 60 min-irradiated sample was observed to change back to a three-line spectrum. Almost the same change was shown for PVA-1 with some complexity caused by the methyl radical in the sample. Thus, Fe^{3+} was found to be effective for the formation of a radical showing a three-line spectrum.

The decay curves of the three-line spectrum of the irradiated Fe^{3+} -sensitized PVA-1 are shown in Figure 4. The central peak A and the side peak B in the spectrum were fairly stable at room temperature, and each peak still remained even after 30 min of warming. It was observed that two curves are given for peaks A and B, indicating a larger rate of decay for the peak B. It is therefore presumed that at least two kinds of radicals participate in the three-line spectrum, in which a large possibility of the existence of a triplet can be considered.

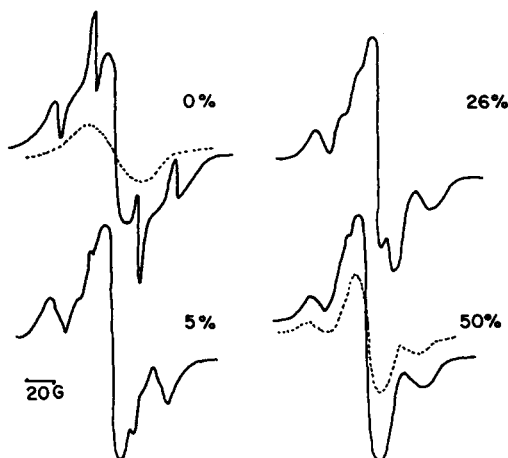


Fig. 6. ESR spectra of formalized PVA irradiated at 77°K for 60 min. Numbers and dotted lines represent the degree of formalization of the samples and the ESR spectra after warming at room temperature for 1 min, respectively.

Ohnishi et al.⁹ reported the change of PVA spectrum from a three-line with an intensity ratio of 1:3:1 to a singlet after leaving samples for two months in their ESR study of γ -irradiated PVA, presuming the existence of a triplet of 1:2:1 in the spectrum. Abraham et al.¹⁰ also observed the same phenomenon. PVA-2 sensitized with Fe^{3+} gave almost the same results as PVA-1.

ESR spectra of 60 min of irradiation at 45°C are shown in Figure 5. Singlet and triplet spectra were given for untreated and Fe^{3+} -sensitized samples, respectively, which agreed well with those obtained by warming the irradiated samples at 77°K.

The ESR spectra in Figure 6 are those of formalized PVA samples after irradiation for 60 min at 77°K. The spectrum of the sample with 50% degree of formalization shows the feature of a three-line spectrum which held the three-line shape as it was warmed, while the quartet spectrum of the sample without formalization changed to a singlet by warming. Thus, the formalized sample as well as the Fe^{3+} -sensitized one proved to accelerate the formation of radicals giving a three-line spectrum.

Graft Copolymerization of MMA

In Table I, results of graft copolymerization of MMA on PVA are shown with the purpose of verifying the initiation characteristics. Regarding untreated PVA-1 samples, the polymerization was hardly initiated, even in the systems involving a high signal intensity of the spectrum with a long period of irradiation. However, Fe^{3+} -sensitized samples as well as PVA-2 having high activities toward light increased the signal intensity of spectrum easily, which proved to have to do with the initiation of graft copolymerization. From above, it is believed that the radicals, which include a radical on α -carbon of hydroxy group as the most promising one and can give a triplet spectrum, among others, have to do closely with the initiation.

Similar examinations on the formalized PVA samples were carried out, as shown in Table II. It is clear that the higher the degree of formalization of the

TABLE I
Photo-Induced Graft Copolymerization of MMA on PVA Sample^a

Sample	Fe ³⁺	Irradiation time, min	Relative signal intensity, arbitrary units	Per cent grafting, %
PVA-1	Without	10	0.2	—
	Without	30	0.6	0
	Without	60	1.0	0
	With	10	1.4	—
	With	20	1.5	4.3
	With	60	1.7	11.2
PVA-2	Without	20	0.8	—
	Without	40	1.0	0
	Without	60	1.2	0
	With	10	1.3	—
	With	25	1.3	3.8
	With	60	1.5	10.3

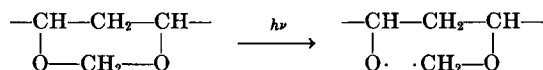
^a Degree of saponification: PVA-1, 96%; PVA-2, 99%; reaction temperature, 45°C.

TABLE II
Photo-Induced Graft Copolymerization of MMA on Formalized PVA Sample^a

Degree of formalization, %	Relative signal intensity, arbitrary units	Per cent grafting, %
0	1.0	0
5	1.2	0
19	1.3	0
26	1.8	20.3
36	3.8	56.5
55	5.3	72.2

^a Irradiation time, 60 min; reaction temperature, 45°C.

sample, the larger was the signal intensity, resulting in an easier initiation. Imoto et al.¹¹ also reported the high grafting activity of the formalized PVA. As shown in Figure 6, the signal intensity of the three-line spectrum is emphasized in a formalized PVA, which is believed to lead to easier initiation. The three-line spectrum can be considered as the superposition of a singlet and a triplet, which are perhaps originated by the radicals formed by the following equation:



References

1. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **16**, 965 (1972).
2. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **7**, 54 (1960).
3. M. Tsunooka, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **72**, 1208 (1969).
4. M. Tsunooka, M. Ishikawa, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **72**, 1413 (1969).
5. I. Sakurada, S. Lee, E. Nagai, and T. Takeshiro, *Gosei Seni Kenkyu*, **1-1**, 252 (1942).
6. G. G. Danelyan and R. M. Livshits, *Vysokomol. Soedin.*, **8**, 1501 (1966).

7. J. R. Morton and W. E. Falconer, *Nature*, **197**, 1103 (1963).
8. S. K. Kudrna, *Vysokomol. Soedin.*, **8**, 1828 (1966).
9. S. Ohnishi, Y. Ikeda, M. Kashiwagi, and I. Nitta, *Polymer*, **2**, 119 (1961).
10. R. J. Abraham and D. H. Whiffen, *Trans. Faraday Soc.*, **54**, 1291 (1958).
11. M. Imoto, K. Takemoto, A. Okura, and M. Izubagashi, *Makromol. Chem.*, **113**, 111 (1968).

Received July 25, 1974

Revised October 8, 1974