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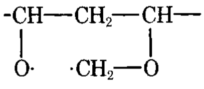
Photo-Induced Graft Copolymerization of Methyl Methacrylate on Oxidized Poly(vinyl Alcohol) Fiber

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

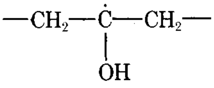
Synopsis

Photo-induced graft copolymerization of methyl methacrylate on oxidized poly(vinyl alcohol) fiber was investigated. Oxidation of the fiber sample with sodium hypochlorite or periodic acid led the radical formation by photo-irradiation to intensify markedly. ESR spectra of the irradiated oxidized sample proved that a considerable amount of triplet component radical was contained in it, whereas the unoxidized sample mostly indicated a singlet. The spectra found in the irradiated unoxidized sample was assigned to two radicals, I and II, and for the oxidized sample, to III and IV. The spectrum for I must be a singlet, and a triplet for II, III, and IV. Among the last three, II was less stable toward heat. As the oxidized sample has a high activity for photoinitiation, the radicals of III and IV are presumed to be the sites of graft copolymerization:



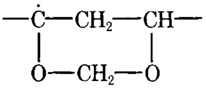
$$-\underset{\underset{\text{O}\cdot}{|}}{\text{CH}}-\text{CH}_2-\underset{\underset{\cdot\text{CH}_2-\text{O}}{|}}{\text{CH}}-$$

I II



$$-\text{CH}_2-\underset{\underset{\text{OH}}{|}}{\dot{\text{C}}}-\text{CH}_2-$$

III



$$\begin{array}{l}-\dot{\text{C}}-\text{CH}_2-\text{CH}-\\ \;\;|\qquad\qquad\;\;|\\ \;\;\text{O}-\text{CH}_2-\text{O}\end{array}$$

IV

INTRODUCTION

A number of reports[1-7] have been published on the graft copolymerization of various vinyl monomers on poly(vinyl alcohol) (PVA) fiber, indicating that the polymerization can be improved by the use of factors such as swelling of fiber with water or preimpregnation of radical initiators in fiber. The authors[8] reported the effective graft copolymerization using PVA fiber samples oxidized by hydrogen peroxide or sodium hypochlorite (NaClO). The purpose of the present study is to verify the contributions of oxidized state of sample to the photo-induced graft copolymerization on PVA fiber.

EXPERIMENTAL

PVA Fiber Sample

Commercial PVA fiber Vinylon (5 to 6 denier) was cut to lengths of 1 cm, extracted with boiling water, and dried under vaccuum. The above unoxidized sample was treated with aqueous solutions of NaClO acidified with hydrochloric acid (pH 3.0) or periodic acid (HIO_4) at 60°C for 120 min. Oxidized samples with different carbonyl content were prepared by changing the concentration of the reagents.

Determination of Carbonyl Content

The carbonyl content was determined by a conventional method[9] using hydroxylamine. PVA fiber sample was immersed at 55°C for 2 hr in aqueous hydroxylamine hydrochloride solution (50 g/l.) whose pH was adjusted to 5.2 with 1*N* sodium hydroxide, and the filtrate was titrated with 0.1*N* hydrochloric acid. The pH for standardization was adjusted to 3.2. The PVA fiber sample treated under the above conditions was named the oximated PVA fiber sample.

Measurements of ESR Spectra

A quartz tube of 5-mm diameter filled with PVA fiber sample and substituted with nitrogen was put in an insertion-type Dewar bottle and exposed at 77°K for 60 min to ultraviolet light. 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.

Graft Copolymerization

After filling the hard glass tube containing 0.50 g (oven dry) PVA fiber and 40 ml water with nitrogen, 2.5 ml methyl methacrylate (MMA) was injected into this system. Graft copolymerization was carried out by irradiating the system with a Toshiba high-pressure mercury lamp H400-P at a distance of 10 cm. The polymerized product was extracted with acetone to exclude homopolymers. Per cent grafting was expressed as the percentage of weight increase.

RESULTS AND DISCUSSION

ESR Spectra of Photo-Irradiated PVA Fiber

As shown in Figure 1, the spectrum of the irradiated unoxidized sample was a three-line shape with a splitting constant of 32 gauss, which changed into a singlet spectrum with a line width of 20 gauss by warming the sample for 2 min to room temperature and bringing it to 77°K again for recording. On the other hand, the three-line spectrum of the oxidized sample was kept fairly stable even after the warming. Therefore, it can be said that a singlet spectrum component is predominant in the unoxidized sample, whereas a three-line spectrum component is markedly intensified in the oxidized sample.

Decay curves of the three-line spectrum of the irradiated oxidized sample are shown in Figure 2. The middle peak (A) and the satellite peaks (B) of the spectrum still remained after 30 min of warming, proving that they are fairly stable toward heat. Judging from the fact that the curves for A and B were not identical, it is considered that at least two kinds of radicals are in-

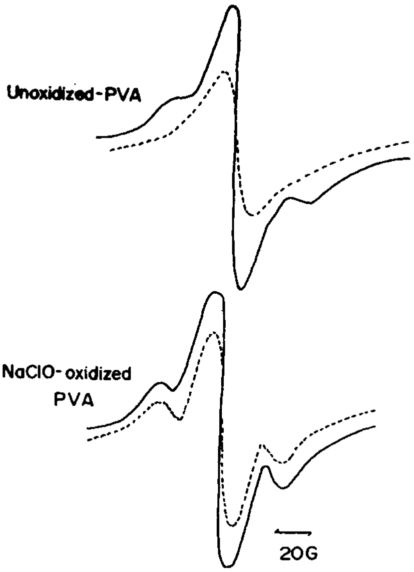


Fig. 1. ESR spectra of unoxidized and NaClO-oxidized PVA samples irradiated at 77°K for 60 min. Dotted lines represent the ESR spectra after warming to room temperature for 2 min.

cluded in the irradiated sample; one is a singlet spectrum component and the other is a triplet. In the previous paper,[10] we reported the same components in three-line spectra observed with ferric ion-sensitized PVA powder irradiated with a high-pressure mercury lamp. Ohnishi et al.[11,12] reported the formation of radicals in γ-ray-irradiated PVA, which indicate a singlet spectrum with a line width of 24 gauss and a triplet with a splitting constant of 36 gauss. As above, it is important to note that one triplet component radical found in the irradiated unoxidized sample is rather unstable, while the other triplet formed in the oxidized sample is rather stable toward heat. Accordingly, these different triplet component radicals must be distinguished from each other. By photolyzing the unoxidized PVA fiber sample, the next type of cleavage is inferred to occur at the formalized position of the PVA mole-

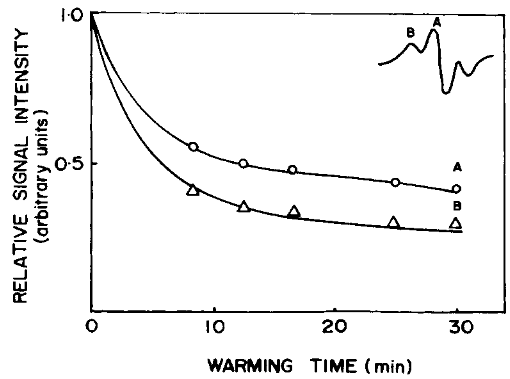


Fig. 2. Decay curves of radicals in NaClO-oxidized PVA sample irradiated at 77°K for 60 min. Warmings were carried out at room temperature.

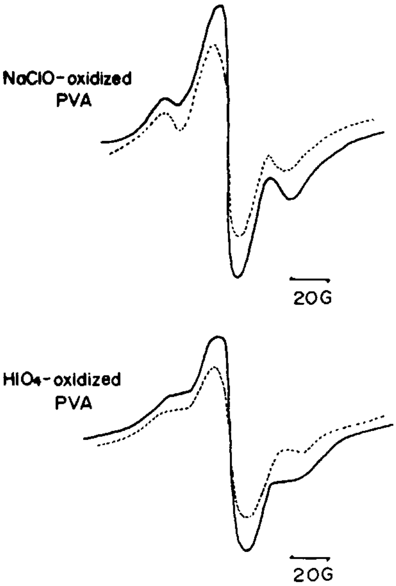
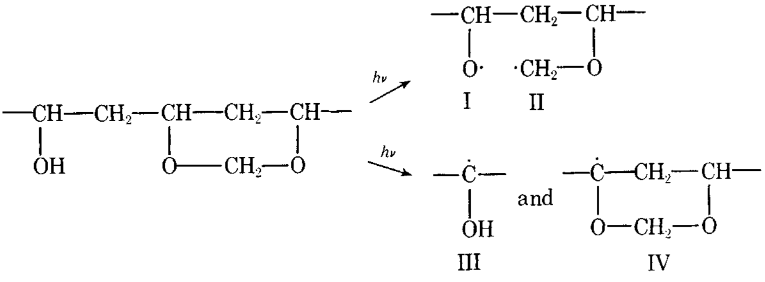


Fig. 3. ESR spectra of oxidized PVA samples irradiated at 77°K for 60 min. Dotted lines represent the ESR spectra after warming to room temperature for 2 min.

cule. The resulting radicals I and II might correspond to the spectra of singlet and triplet,



respectively. The triplet radicals recognized in the oxidized sample presumably are III and IV, which are rather stable toward heat because of the position fixed on a long chain.

The shape of the spectrum differs somewhat depending upon the oxidizing reagent. As seen in Figure 3, the NaClO-oxidized sample showed more clear-cut absorption than the HIO_4-oxidized sample. However, the same tendency was true in the comparison between samples after warming.

Effect of Oxidation Level on Radical Formation

The oxidation level was expressed as the carbonyl content of the sample. In Figure 4, which shows changes of signal intensity with irradiation time, the value of NaClO-oxidized sample was relatively higher than that of the HIO_4-oxidized one. Common to both samples, the maximum signal intensity was

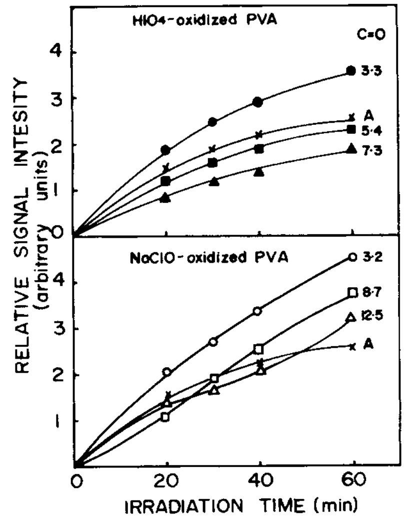


Fig. 4. Photo-induced formation of radicals in unoxidized (A) and oxidized PVA samples. Numbers represent the carbonyl content (mmole/100 g PVA) of oxidized sample.

shown at a range of low oxidation level inspite of the marked contribution of carbonyl group to the radical formation. The phenomenon of depressed signal intensity at a higher oxidation level suggests the formation of a certain structure which is unsuitable to the radical formation by photolysis, in the oxidizing process of PVA sample.

The carbonyl group in the oxidized samples can be changed to an oxime group by treatment with hydroxylamine. As shown in Figure 5, the oximated sample gave a lower signal intensity in comparison with the unoxidized sample similarly to the NaClO- and HIO_4-oxidized samples. Therefore, it must be said that carbonyl group plays an important role in the photochemical reaction of PVA sample.

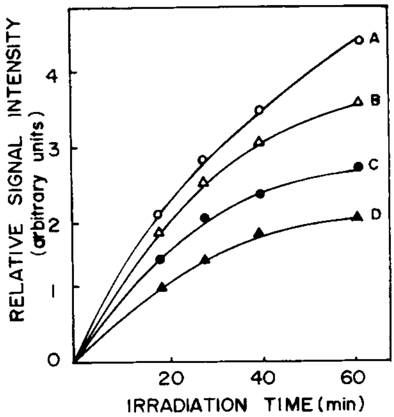


Fig. 5. Photo-induced formation of radicals in oximated PVA samples: (A) NaClO-oxidized sample; (B) HIO_4-oxidized sample; (C) A oximated with hydroxylamine; (D) B oximated with hydroxylamine.

Photo-Induced Graft Copolymerization

Results of graft copolymerization of MMA on oxidized PVA fiber samples are summarized in Table I. Higher per cent grafting was obtained for oxidized samples as compared with unoxidized sample. The induction period of polymerization was also found to be very short for oxidized samples, and these effects were more conspicuous for NaClO-oxidized samples than for HIO_4-oxidized ones. Values in parentheses in the table show the per cent grafting on oximated samples, indicating a marked lowering effect caused by the oximation of oxidized samples. As for the oxidation level, lightly oxidized samples were best for the photografting like the tendency shown for radical formation.

TABLE I
Photo-Induced Graft Copolymerization of MMA on Oxidized PVA Fiber[a]

PVA sample	Carbonyl content, mmole/100 g PVA	Irradiation time min	Per cent grafting, %
Unoxidized	0	60	0
		120	60
		180	98 (23)
NaClO-Oxidized	6.1	60	159
		120	226 (184)
		180	269 (176)
	8.7	60	64
		120	191 (69)
		180	219 (127)
	12.5	60	38
		120	76
		180	187
HIO_4-Oxidized	3.3	60	34
		120	121 (7)
		180	186 (20)
	5.4	60	53
		120	88 (8)
		180	176 (14)
	7.3	60	4
		120	108 (1)
		180	118 (7)

[a] Graft copolymerization was carried out at 45°C in the hard glass system. Values in parentheses are per cent grafting of oximated samples.

Accordingly, it may be concluded that the carbonyl group introduced in the oxidized PVA fiber samples works actively to produce a triplet component radical, which takes place on the main chain of the PVA polymer, is fairly stable toward heat, and contributes directly to the initiation of graft copolymerization.

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