

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

HITOSHI KUBOTA and YOSHITAKA OGIWARA,

Department of Chemistry, Faculty of Engineering, Gunma University, Kiryu, Gunma 376, Japan

Synopsis

Photo-induced graft copolymerization of methyl methacrylate on poly(vinyl alcohol) (PVA) was examined in aqueous solutions. In unoxidized samples, only a few percent of PVA used took part in the formation of grafts, and the percent grafting was very low. However, if Fe^{2+} , Fe^{3+} , anthraquinone-2,7-disulfonate, or oxalic acid was used as sensitizer, the percent grafting was somewhat improved. Among them, the effect of Fe^{3+} was most remarkable. Oxidized PVA showed a higher initiating activity and was more susceptible to the sensitizing action of Fe^{3+} than unoxidized PVA. As Fe^{3+} has an ability to accelerate the photo-induced scission reaction of PVA chains for both oxidized and unoxidized PVA, it is thought to be very probable that the copolymer formed in the photo-induced systems has a block polymer-type structure like that in systems initiated by ceric ion or hydrogen peroxide.

INTRODUCTION

It has been clarified that the scission of trunk poly(vinyl alcohol) (PVA) is related to the formation of grafts in the graft copolymerization of methyl methacrylate (MMA) on PVA initiated by ceric ion¹ and ferric ion-hydrogen peroxide.² It has also been reported that the structure of the copolymer formed should be considered as a block polymer type. Sakurada et al.^{3,4} have examined the composition of copolymers obtained by gamma ray-induced graft copolymerization of MMA on PVA film and reported that the molar ratio of trunk PVA to grafts is approximately 1:1. As for photo-induced graft copolymerization, Geacintov et al.⁵ tried graft copolymerization on PVA films using anthraquinone dyes as sensitizer, and Tsunooka et al.^{6,7} tried grafting onto PVA containing carbonyl groups. These sensitizers and sensitizing groups were found to contribute effectively to the initiation.

In the present investigation, photo-induced graft copolymerization of MMA was carried out in aqueous solutions of PVA. The effects of sensitizers and the oxidation of samples were examined to clarify the characteristics of photo-induced copolymerization.

EXPERIMENTAL

Samples

Commercial PVA powder was rinsed with distilled water and acetone, followed by drying to obtain unoxidized sample. The sample was then oxidized with sodium hypochlorite acidified with hydrochloric acid (at pH 3.0) to yield oxidized sample. The carbonyl group content was determined by the hydroxylamine method.⁸ A description of the PVA samples employed in this study is given in Table I. Oxalic acid, anthraquinone-2,7-disulfonate (AQ), ferric chloride (Fe^{3+}), and ferrous sulfate (Fe^{2+}) were used as sensitizers.

TABLE I
Description of PVA Samples

Sample	Amount of sodium hypochlorite for PVA, % ^a	Total carbonyl content, mmole/100 g of PVA	\overline{DP}
Unoxidized sample	0	0.50	1030
Oxidized sample ^b	0.32	8.62	830
Oxidized sample ^b	0.64	30.5	965

^a Values are presented as weight percent of available chlorine for PVA.

^b Oxidation time, 2 hr; temperature, 60°C.

Graft Copolymerization

After the hard-glass tube containing 40 ml of a given concentration of aqueous PVA solution, with or without sensitizer, was filled with nitrogen, 2.5 ml MMA was injected into this system. Graft copolymerization was carried out by keeping the system at 45°C for a given time under irradiation with ultraviolet light (UV). The resulting products were treated with water at 70°C for 1 hr to remove unreacted PVA, followed by the extraction with acetone for 48 hr to obtain graft copolymer. The grafted poly(MMA) was isolated by treating the graft copolymer with 30% nitric acid at 70°C for 5 hr. Weight-average molecular weight of grafts was determined from the viscosity of its acetone solution at 25°C.⁹ The percent grafting and the number of grafts were determined in the manner described previously.^{1,2} The degree of conversion of PVA into graft copolymer and the grafting efficiency were calculated according to the following equations:

$$\text{Conversion of PVA (\%)} = \frac{\text{PVA fraction in copolymer (g)}}{\text{PVA used in reaction (g)}} \times 100$$

$$\text{Grafting efficiency (\%)} = \frac{\text{weight of grafts}}{\text{total weight of grafts plus homopolymer}} \times 100$$

Using a Toshiba high-pressure mercury lamp H400P as light source, the distance between it and the reaction system was kept at about 10 cm.

Average Degree of Polymerization (DP) of PVA Samples

A 42.5-ml portion of an aqueous solution containing 0.50 g of PVA and a given amount of Fe^{3+} was irradiated with UV at 45°C for 2 hr under nitrogen. An aliquot was taken up from the irradiated solution and its viscosity was measured at 30°C¹⁰ to determine the DP of the PVA sample.

RESULTS AND DISCUSSION

Graft Copolymerization on Unoxidized PVA

The results of the graft copolymerization onto unoxidized PVA without sensitizer are shown in Table II. The induction period of polymerization was about 2 hr and the percent grafting was generally low. The percent grafting tended rather to decrease with irradiation of more than 10 hr. Such a phenomenon was also observed in the photo-induced graft copolymerization onto cellulose,¹¹ and it could be attributed to the depolymerization of grafted poly(MMA) by UV because of the extremely low average molecular weight of grafts of samples after 10 hr of irradiation. On the other hand, it is interesting that the number of grafts continues to increase with irradiation time. The carbonyl groups in unoxidized PVA were very few, about 0.50 mmole/100 g of PVA. Tsunooka et al.⁶ reported that in the photo-induced graft copolymerization of acrylonitrile onto PVA, trace amounts of carbonyl groups or residual acetyl groups existing in the samples showed an apparent initiating activity. The grafting efficiency was as low as 10% to 18%, and this is attributed to easier formation of homopolymers in the present systems.

TABLE II
Effect of UV Irradiation on Graft Copolymerization
in the Absence of Sensitizer^a

Time, hr	Percent grafting, %	Grafting efficiency, %	\bar{M}_w of grafts $\times 10^{-4}$	Number of grafts $\times 10^3$, mmole/100 g of PVA
2	0.00	—	—	0.00
3	4.06	10.0	508	0.80
4	7.74	12.4	641	1.21
6	10.3	17.4	483	2.14
10	4.56	18.0	147	3.11

^a Polymerization system consists of 2.5 ml MMA and 40 ml distilled water containing 0.50 g PVA. Polymerization temperature, 45°C.

The effect of the amount of PVA in the systems is shown in Table III. When more than 0.50 g of PVA was used, both the amount of graft forma-

tion and the molar number of grafts decreased, and the graft copolymerization was depressed. This seems to suggest a depression of the formation of grafting sites because of the marked increase in viscosity of the systems to disturb the homogeneity of the copolymerization along with the concentration of PVA. Thus generally, the conversion of PVA to graft copolymer was as low as a few per cent and decreased with increase in PVA.

TABLE III
Effect of Amount of PVA on Graft Copolymerization
in the Absence of Sensitizer*

Amount of PVA, g	Amount of grafts $\times 10^3$, g	\bar{M}_w of grafts $\times 10^{-4}$	Molar number of grafts $\times 10$, mmole	Conversion of PVA, %
0.5	5.15	483	1.07	3.68
1.0	4.60	483	0.95	1.09
1.5	3.27	345	0.94	0.89
2.0	2.94	370	0.79	0.51

* Irradiation time, 6 hr; temperature, 45°C; total volume of system, 42.5 ml.

Graft Copolymerization on Unoxidized PVA Using Sensitizer

Fe^{3+} , Fe^{2+} , AQ, and oxalic acid were examined, for which sensitizing action was noticed in the photo-induced graft copolymerization on cellulose.^{12,13} As seen in Figure 1, the polymerization was initiated after an irradiation of 1 to 2 hr in the systems using various sensitizers, but the initia-

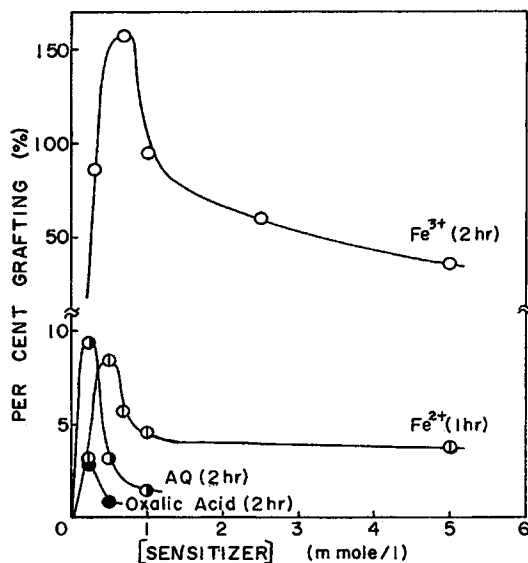


Fig. 1. Graft copolymerization onto unoxidized PVA using various sensitizers under UV irradiation. Each irradiation time is presented in parenthesis. Polymerization temperature, 45°C; amount of PVA, 0.50 g; total volume of system, 42.5 ml.

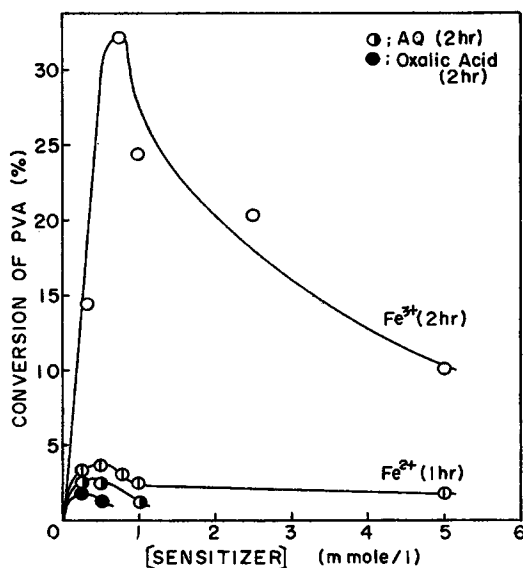


Fig. 2. Relationship between conversion of PVA and concentration of sensitizers. Polymerization conditions were same as those in Fig. 1.

tion almost did not occur by 2 hr of irradiation without sensitizer. Among the sensitizers, Fe^{2+} and Fe^{3+} were remarkably effective compared to AQ and oxalic acid, especially Fe^{3+} . The number of grafts was only 0.31×10^{-2} mmole/100 g of PVA, even after 10 hr of irradiation, without sensitizer, whereas when using 1 mmole/l. of Fe^{3+} , the induction period of polymerization was not observed, and the number of grafts after 1 hr of irradiation became 6.89×10^{-2} mmole/100 g of PVA. However, a maximum percent grafting existed at each concentration used, and the copolymerization was rather depressed at higher concentrations. This is attributed to the accelerated homopolymerization of MMA by sensitizers. The fraction of PVA which participated in the formation of grafts differed with each metallic ion (Fig. 2) and increased upto about 30% with Fe^{3+} .

In the photo-induced grafting onto cellulose¹³ as well as onto PVA, an apparent difference has been observed between the sensitizing actions of Fe^{2+} and Fe^{3+} . This difference was attributed, first, to the difference in the active species produced by the metallic ions absorbing UV in the aqueous solutions. It has been reported that Fe^{2+} and Fe^{3+} can produce protons¹⁴ and hydroxyl radicals^{14,15} respectively, in such conditions, initiating vinyl polymerizations. Secondly the difference in the affinity between the metallic ions and the materials must be considered. Regarding the cellulose samples, the formation of grafts was accelerated by both Fe^{2+} and Fe^{3+} in their adsorbed states. However, in the systems in which aqueous metallic salt solutions were added, Fe^{2+} depressed the formation of grafts and promoted the formation of homopolymers. On the other hand, Fe^{3+} acted effectively on the formation of grafts even in the added state. In the pres-

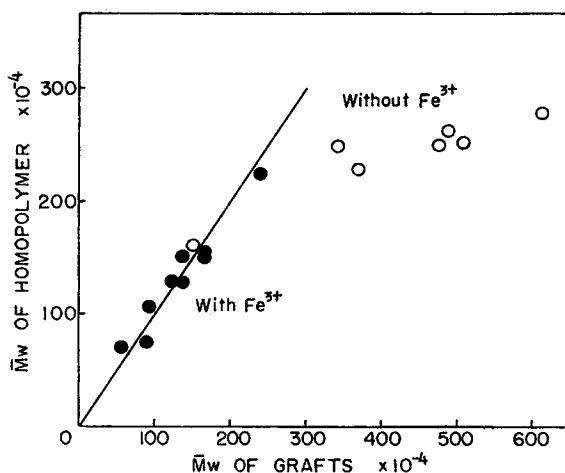


Fig. 3. Comparison of average molecular weight of grafts with that of homopolymers.

ent study, metallic ions acted on the copolymerization systems in the added states. It might be concluded that the depressed conversion of PVA in Fe^{2+} -added systems as compared to that in Fe^{3+} -added systems originates in a weaker affinity of Fe^{2+} than of Fe^{3+} for PVA as well as for cellulose.¹⁶

Figure 3 shows the relationship between the average molecular weight of the grafts and that of homopolymers. In the systems containing Fe^{3+} , these values are the same as indicated by a straight line in the figure. The average molecular weight of grafts obtained in the systems without Fe^{3+} was 1.5 to 2.0 times larger than that of homopolymers. These results seem to suggest a difference of termination reactions between these systems.

Graft Copolymerization on Oxidized PVA

Using Fe^{3+} with a high sensitizing effect, the copolymerization on oxidized samples was examined. Figure 4 shows the relationship between the percent grafting and the Fe^{3+} concentration. The copolymerization on the samples was activated by oxidation and further accelerated considerably in the presence of Fe^{3+} . The concentration dependence of the sensitizing effect of Fe^{3+} on the oxidized samples was found to be larger than that on the unoxidized samples. The relationship between the conversion of PVA and the Fe^{3+} concentration is shown in Figure 5. The conversion of PVA in the oxidized samples increased remarkably, but the rate of increase decreased with increasing degree of oxidation. Takayama¹⁷ reported that photo-oxidized PVA is more easily oxidized with hydrogen peroxide than unoxidized PVA. The authors^{1,2} observed also that by oxidation PVA becomes more reactive to ceric ion and hydrogen peroxide. In the present systems, it was observed that oxidized samples with high reactivity are affected not only by the action of light, but also by the sensitizing effect of Fe^{3+} .

In Figure 6, the average molecular weight of the grafts and that of the homopolymers are shown. In the unoxidized samples, it was observed that both of the average molecular weights decreased with increase in Fe^{3+} concentration, and that Fe^{3+} participated in the termination of polymer

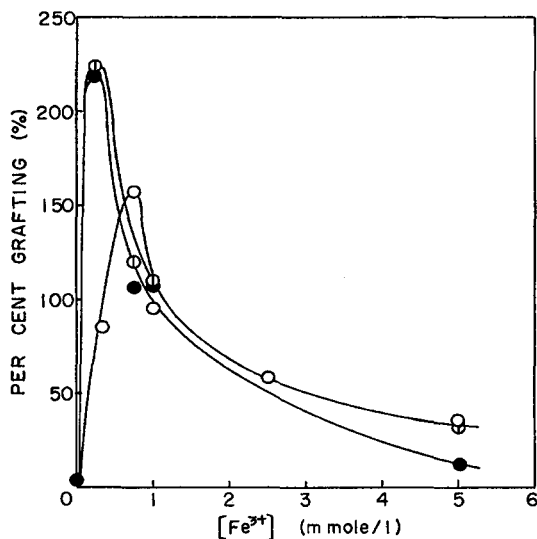


Fig. 4. Graft copolymerization on oxidized PVA using ferric chloride. Polymerization time, 2 hr; temperature, 45°C; amount of PVA, 0.50 g; total volume of system, 42.5 ml. Total carbonyl content (mmole/100 g of PVA): (O) 0.50; (◐) 8.62; (●) 30.5.

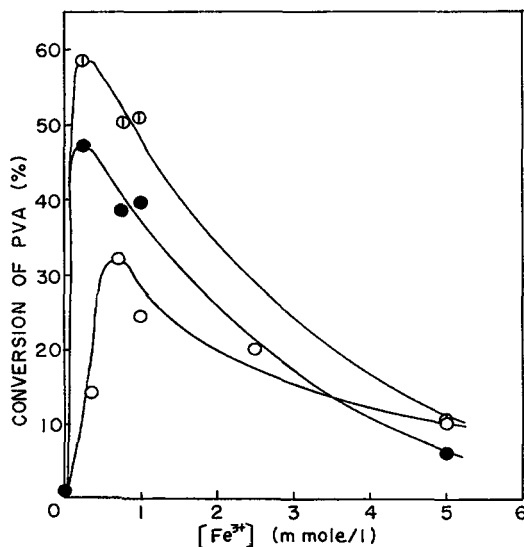


Fig. 5. Relationship between conversion of PVA and concentration of ferric chloride. Polymerization conditions were the same as those in Fig. 4. Total carbonyl content (mmole/100 g of PVA): (O) 0.50; (◐) 8.62; (●) 30.5.

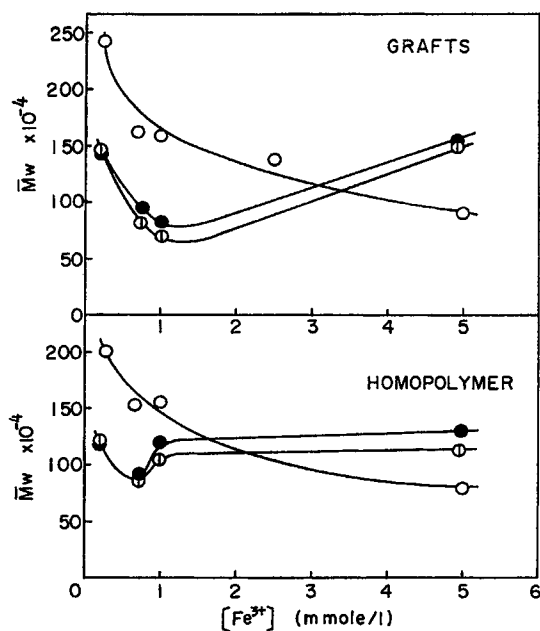


Fig. 6. Relationship between average molecular weight of grafts or homopolymer and concentration of ferric chloride. Total carbonyl content (mmole/100 g of PVA) (○) 0.50; (◐) 8.62; (●) 30.5.

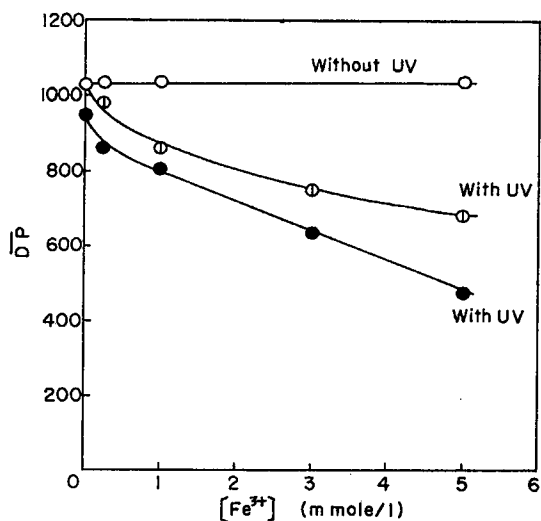


Fig. 7. Effect of UV irradiation on average degree of polymerization of PVA. Irradiation time, 2 hr; temperature, 45°C; amount of PVA, 0.50 g; total volume of system, 42.5 ml; nitrogen atmosphere. Total carbonyl content (mmole/100 g of PVA): (○) and (◐) 0.50; (●) 30.5.

radicals. The action of Fe^{3+} terminating polymer radicals has been examined in the photosensitized polymerization of acrylonitrile using Fe^{3+} in dimethylformamide,^{18,19} and a tendency to increase the effect with higher Fe^{3+} concentration was reported.²⁰ However, in the oxidized samples, the molecular weight increased with increase in Fe^{3+} concentration at concentrations of more than about 1 mmole/l. Taking into consideration that the termination reaction of polymer radicals is depressed in the higher ranges of Fe^{3+} concentration, this phenomenon can be attributed to some extent to the limitation of the mobility of free Fe^{3+} in a solution by the oxidized groups in the oxidized samples.

The change in the average DP of PVA by UV irradiation is shown in Figure 7. The decrease in DP by UV irradiation was small for both the oxidized and unoxidized samples in the absence of Fe^{3+} . However, when Fe^{3+} was used, the scission of PVA chains became larger with increase in Fe^{3+} concentration. Dulog et al.²¹ carried out the photoinduced oxidation of PVA in aqueous solutions using benzophenone-3,3'-disulfonic acid as sensitizer, and observed that the PVA chains were cleaved by oxidation. The number of scissions was calculated from the decrease in average DP according to the method reported previously,^{1,2} and the value was larger for the oxidized samples than for the unoxidized ones.

It was assumed that the scission of PVA chains occurs also in polymerization conditions, but a quantitative relation was not found between the formation of grafts and the scission of trunk PVA. However, as scission of PVA chains to some extent always accompanies photo-induced graft copolymerization onto PVA, it is very probable that the copolymer produced there has a block polymer-type structure.

The authors wish to acknowledge the contributions of Mr. Tetsuji Takami to the experimental work.

References

1. Y. Ogiwara and M. Uchiyama, *J. Polym. Sci. A-1*, **7**, 1479 (1969).
2. Y. Ogiwara and M. Uchiyama, *J. Polym. Sci. A-1*, **8**, 641 (1970).
3. I. Sakurada, Y. Ikada, and F. Horii, *Makromol. Chem.*, **139**, 171 (1970).
4. I. Sakurada, Y. Ikada, H. Uehara, Y. Nishizaki, and F. Horii, *Makromol. Chem.*, **139**, 183 (1970).
5. N. Geacintov, V. Stannett, E. W. Abrahamson, and J. J. Hermans, *J. Appl. Polym. Sci.*, **7**, 54 (1960).
6. M. Tsunooka, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **72**, 1208 (1969).
7. M. Tsunooka, M. Ishikawa, M. Tanaka, and N. Murata, *Kogyo Kagaku Zasshi*, **72**, 1413 (1969).
8. M. Tsunooka, N. Nakajo, M. Tanaka, and N. Murata, *Kobunshi Kagaku*, **23**, 451 (1966).
9. S. Chinai, J. Matlack, and A. Resink, *J. Polym. Sci.*, **17**, 391 (1955).
10. A. Nakajima and K. Furudate, *Kobunshi Kagaku*, **6**, 460 (1949).
11. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **15**, 2717 (1971).
12. Y. Ogiwara and H. Kubota, *J. Polym. Sci. A-1*, **9**, 2549 (1971).
13. H. Kubota and Y. Ogiwara, *J. Appl. Polym. Sci.*, **16**, 337 (1972).

14. Y. Nishijima and M. Yamamoto, *Kogyo Kagaku Zasshi*, **72**, 31 (1969).
15. F. S. Dainton and W. D. Sisley, *Trans. Faraday Soc.*, **59**, 1377 (1963).
16. Y. Ogiwara and H. Kubota, *J. Polym. Sci. A-1*, **7**, 2087 (1969).
17. G. Takayama, *Kobunshi Kagaku*, **17**, 698 (1960).
18. F. S. Dainton and R. G. Jones, *Trans. Faraday Soc.*, **63**, 1512 (1967).
19. R. G. Jones, *Polymer*, **10**, 89 (1969).
20. W. I. Bengough and I. C. Ross, *Trans. Faraday Soc.*, **62**, 2251 (1966).
21. Von L. Dulog, R. Kern, and W. Kern, *Makromol. Chem.*, **120**, 123 (1968).

Received August 20, 1971

Revised November 10, 1971