JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, PP. 887-895 (1975)

Factors Affecting the Photo-Induced Graft Copolymerization of Methyl Methacrylate Onto Fibrous Polymer

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Synopsis

The effects of sample swelling, photosensitizer, and solvent on the photo-induced graft copolymerization of methyl methacrylate onto fibrous polymers such as Vinylon, nylon 6, and polyester were examined. Each separate factor, sample swelling, or solvent, or their combination, increased activity of polymerization. Only some sensitizers were effective. Studying the ESR spectra of photo-irradiated polymers also showed that either the sample swelling, the photosensitizer, or the organic solvent is very effective for the formation of polymer radicals under irradiation.

INTRODUCTION

It has been known that the location of grafting on a photo-irradiated polymer is generally limited to the surface of the material,[1] which makes it very difficult to obtain a high per cent grafting. In the previous paper,[2] the authors examined the photografting of methyl methacrylate (MMA) onto cellulose to show effective copolymerization by means of sample swelling, organic solvent, or photosensitizer. They reported that there is a possibility of effective initiation by the correct combination of the three, as each factor works independently. The purpose of this study is to find improved conditions for the photografting onto fibrous polymers such as polyester, nylon 6, and Vinylon, by employing the same three factors. Measurements of ESR spectra on radicals formed in the irradiated substrates were carried out.

EXPERIMENTAL

Untreated Samples

Commercial poly(vinyl alcohol) fibers (4 to 5 denier) named Vinylon and produced by Kurare Co., Ltd., and nylon 6 and poly(ethylene terephthalate) (PET) fibers (4 to 5 denier) produced by Toyo Spinning Co., Ltd., were used as fibrous polymers. Vinylon was extracted with hot water for 2 hr; nylon 6 and PET fibers were extracted with ethanol for 5 hr at a liquor ratio of 100. These fibers were dried under vacuum.

Swollen Samples

Vinylon and nylon 6 fibers were treated with 5% and 3% aqueous solution of phenol at room temperature for 48 hr; PET fibers were treated with benzyl alcohol at 100°C for 1 hr. Swollen samples were obtained by immersing them in water for 24 hr. The degree of swelling for samples was represented as water retention value (WRV). WRV[3] was determined as follows: After the sample was immersed in water for 24 hr, it was filtered and formed to a mat. The mat was dehydrated with a centrifuge at 3000 *g* for 15 min, and then the moisture in the samples was measured and expressed as a percentage of the oven-dried weight. The swollen samples were used in the wet state for graft copolymerization.

Sensitized Samples

Photosensitizers: Acetylacetone, hydrogen peroxide (H_2O_2), riboflavin, ferric chloride (Fe^{3+}), silver nitrate (Ag^+), and sodium anthraquinone-2,7-disulfonate (AQ), were dissolved in water, azobisisobutyronitrile (AIBN) and benzophenone in acetone, and benzoyl peroxide (BPO) in benzene, respectively. Fibrous polymers were immersed in the photosensitizer solutions at a liquor ratio of 100, 45°C, for 1 hr, and then dried under vacuum.

Graft Copolymerization

Graft copolymerization was carried out in a system consisting of 0.50 g (oven dry) fibrous polymer, 2.5 ml MMA, and 40 ml water or water–organic solvent solution under nitrogen at 45°C with light irradiation for a given time. A Toshiba high-pressure mercury lamp H400-P (400 W) was used as light source, and the irradiation was carried out in a hard-glass tube at about 10 cm from the light source. Polymerization products were washed with water and then extracted with acetone to remove homopolymers. The per cent grafting and the grafting efficiency were taken as the percentage of weight increase of the original fibrous polymer and the weight per cent of grafted polymer relative to total conversion of monomer in a system.

Methanol (MeOH), ethanol (EtOH), acetone, dioxane, dimethyl sulfoxide (DMSO), and tetrahydrofuran (THF) were used as organic solvents, after purification by distillation.

Measurements of ESR Spectra

A quartz tube (5 mm diameter) filled with the fibrous polymers and substituted with nitrogen was put in an insertion-type Dewar bottle and exposed at 77°K for 1 hr to light. The polymers were irradiated in the oven-dried state or water- and organic solvent-containing states. ESR measurements were made at 77°K with a Japan Electron Optics Laboratory JES-ME-X. Resonance spectra were recorded with the x-band and 100 Kc field modulation.

RESULTS AND DISCUSSION

Factors Affecting Photo-Induced Graft Copolymerization

H_2O_2,[4,5] Fe^{3+},[4,6] and riboflavin[7] have been reported to have remarkable sensitizing activities in the photografting onto cellulose. Effects of sensitizers on

TABLE I
Effect of Sensitizers on Photografting of MMA[a]

Sensitizer	PET (5 hr)		Nylon 6 (3 hr)		Vinylon (3 hr)	
	G, %	*G.E.*, %	*G*, %	*G.E.*, %	*G*, %	*G.E.*, %
No	0.5	...	16.1	...	16.0	76.7
H_2O_2	0.4	2.6	...	...	...	...
Fe^{3+}	5.4	4.1	23.9	63.8	107.6	86.5
Riboflavin	5.3	15.8	9.7	33.5	...	...
AIBN	1.2	3.2	...	...	...	...
Benzophenone	16.7	14.6	25.2	...	58.9	73.3
BPO	5.1	5.4	0	...	19.9	1.0

[a] *G*, per cent grafting; *G.E.*, grafting efficiency. Samples were pretreated with solution of sensitizer at 45°C for 60 min.

TABLE II
Effect of Sample Swelling on Photografting[a] of MMA

Sample	Swelling agent	WRV, %	Per cent grafting, %	Grafting efficiency, %
PET	none	4.5	0.5	...
PET	benzyl alcohol	7.1	105.7	80.3
Nylon 6	none	15.2	16.1	...
Nylon 6	phenol	18.0	18.3	83.7
Nylon 6	phenol	21.8	36.5	86.4
Vinylon	none	21.7	16.0	76.7
Vinylon	phenol	25.2	156.3	92.5

[a] Irradiation time: PET, 5 hr; Vinylon and nylon 6, 3 hr.

PET, nylon 6, and Vinylon are shown in Table I. Amounts of graftings on PET were generally low, and benzophenone was the only effective sensitizer. The grafting efficiency was very low in the PET samples, indicating that the formation of homopolymers was activated by sensitizers to depress the grafting reaction. Only benzophenone and Fe^{3+} were effective sensitizers for both nylon 6 and Vinylon. Especially, the effect of Fe^{3+} on Vinylon was outstanding, just as in the case of cellulose. It is conceivable that the sensitizing action of Fe^{3+} can be very effective in both cases, because of the large affinity[8] of Fe^{3+} to such substrates.

The copolymerizations on swollen samples are shown in Table II. A marked improvement in the per cent grafting was observed in the swollen sample, in spite of a slight increase in its WRV. Sample swelling seems to be an important factor contributing to graft copolymerization. The effect of organic solvent, which might also play an important role in the interaction between substrate and monomer in the copolymerization system, was examined and is summarized in Table III. A water–organic solvent ratio of 3:1 in volume was employed, the same as in the study[2] on cellulose.

Organic solvents had almost no effect on the untreated sample of PET. Sample of PET swollen with water–organic solvent showed a marked increase in

TABLE III
Effect of Organic Solvent on Photografting of MMA

Sample	Solvent[a]	Per cent grafting, %	Grafting efficiency, %
PET[b]	water	0.5	5.0
	acetone	0	...
	MeOH	1.6	21.3
Swollen PET[b]	water	105.7	80.3
	MeOH	133.2	92.2
	acetone	208.1	77.6
	EtOH	182.9	90.1
	dioxane	136.4	79.6
Nylon 6[c]	water	16.1	..
	MeOH	59.7	64.3
	acetone[d]	236.1	68.2
Swollen nylon 6[c]	water	18.3	83.7
	MeOH	107.9	83.2
Vinylon[c]	water	16.0	76.7
	MeOH	198.4	91.9
	EtOH	198.4	96.5
	acetone[d]	218.4	66.8
Swollen Vinylon[c]	water	156.3	92.5
	MeOH	237.1	93.9

[a] Organic solvent:water = 1:3 (vol).
[b] Irradiation time, 5 hr.
[c] Irradiation time, 3 hr.
[d] Irradiation time, 4 hr.

per cent grafting. This combined effect of the two factors was also observed in nylon 6 and Vinylon. It is concluded that the sample swelling and the organic solvent each contribute to the grafting reaction. An increased solubility of MMA with organic solvent and a faster diffusion of MMA into the fiber because of swelling are believed to be the chief causes in the reaction.

The effect of sensitizer added to the factors of sample swelling and organic solvent are shown in Table IV. With PET and Vinylon, the graft copolymerizations were obviously much lower when sensitizer was added; with nylon 6, the amount of grafting was much higher. It is conceivable that there should be some complex interactions between the substrate and the factors, so that effective grafting depends upon specific conditions.

Results of reactions in quartz glass tubes using wavelengths less than 300 nm are summarized in Table V. Homopolymerization of MMA was favored in this case as in the case of cellulose,[9] resulting in a lower grafting efficiency. Although no high per cent grafting was obtained, a shortening in the induction period for polymerization was noticed. The effects of sample swelling and organic solvent were much the same as with the longer wavelengths.

We conclude that factors such as sample swelling and organic solvent are similar in effect on photografting, but the sensitizer is not always effective depending upon the substrate.

Factors Affecting the Formation of Polymer Radicals

ESR spectra of samples irradiated at 77°K were examined to study the radical formation in the polymer substrate by UV. ESR spectra of irradiated Vinylon

TABLE IV
Effect of Combination of Sample Swelling, Organic Solvent, and Sensitizer on Photografting of MMA

Sample	Solvent[a]	Sensitizer	Per cent grafting, %	Grafting efficiency, %
Swollen PET[b]	water	none	105.7	80.3
	acetone	none	208.1	77.6
	water	benzophenone	29.9	70.7
	water	Fe^{3+}	1.3	9.5
	acetone	benzophenone	44.9	33.3
	acetone	Fe^{3+}	41.3	45.5
Swollen nylon 6[c]	water	none	18.3	83.7
	water	benzophenone	54.9	79.4
	MeOH	benzophenone	203.4	86.9
Swollen Vinylon[c]	water	none	156.3	92.5
	water	benzophenone	12.1	77.9
	MeOH	benzophenone	84.7	87.3

[a] Organic solvent:water = 1:3 (vol).
[b] Irradiation time, 5 hr.
[c] Irradiation time, 3 hr.

TABLE V
Photografting of MMA in Quartz Glass Tube System

Sample	Solvent[a]	Per cent grafting, %		
		PET	Nylon 6	Vinylon
Nonswollen	water	0	5.7	18.6
Nonswollen	MeOH	0	2.0	48.3
Swollen	water	7.0	26.4	20.0
Swollen	MeOH	12.9	60.8	83.0

[a] Organic solvent:water = 1:3 (vol). Irradiation time, 60 min.

are shown in Figure 1. An increased absorption intensity was observed in the photosensitized Vinylon as compared to that the untreated sample with broad three-line absorption, indicating enhanced radical formation with sensitizers. The most distinct three-line spectrum was given by Fe^{3+} among all sensitizers examined. The three-line absorption remained fairly long even at elevated temperature. The decay of relative signal intensity of the spectrum with time at room temperature is shown in Figure 2.

The shape of the spectrum showed a distinct three-line pattern even after a long warming, indicating great stability of the radicals. Taking notice of peaks A and B in the spectra, the thermal behavior of radicals was carefully examined. The decay of peak B proved to be faster than of A, indicating that the three-line spectrum is made up of a mixture of different radicals. Therefore, it is presumed that there is a formation of at least two radicals in the irradiated Vinylon.

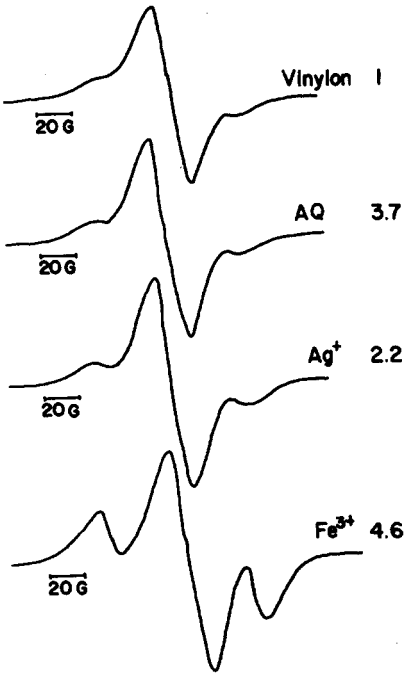

Fig. 1. ESR spectra of Vinylon sensitized with Fe^{3+}, Ag^{+}, and AQ and irradiated at 77°K for 60 min with high-pressure mercury lamp. Number represents the relative signal intensity of the spectrum.

The effect of water on the formation of radicals in the irradiated Vinylon is shown in Figure 3. The higher the water content in the sample, the higher was the intensity of the spectrum, with more conspicuous absorption at satellite peaks. Since it has been believed that the formation of radicals by light is confined to the amorphous part of the substrate, the increased freedom of chain motion of the substrate by swelling, which takes place in the amorphous area, can be said to cause the activated formation of radicals.

Although the spectrum of nylon 6 was singlet with a line width of 17 gauss, as shown in Figure 4, it changed into a three-line spectrum in the sample employing Fe^{3+} or Ag^{+} sensitizer, which changed again into singlet by warming. The same shape of spectrum with a higher relative signal intensity was observed in the swollen nylon 6. As made clear in the figure, a still more increased intensity was given for a swollen sample employing Fe^{3+} sensitizer. Thus, it is found that factors such as sample swelling and sensitizer contribute independently to the formation of radicals in the irradiated nylon 6.

Results of nylon 6 containing various organic solvents are shown in Table VI. With the content of solvent in the range of 22% to 25%, all spectra were three-line, whose relative signal intensities were in the order of MeOH > THF > DMSO > acetone > dioxane with respect to the solvents. A marked lowering in the supply of photoenergy to the substrate seems to be present in the solvents such as acetone, DMSO, and dioxane, which absorb long-wavelength light as seen from the UV-absorbing spectrum in Figure 5. On the other hand, with MeOH as solvent, the absorption is so small that nylon 6 can make the formation of radicals most easily with sample swelling.

Photo-irradiated PET gave a singlet spectrum with a line width of 12 gauss. The spectrum was kept singlet with a little enhanced intensity when the sample was treated with swelling and sensitizer. Thus, radical formation by photo-irradiation is considerably difficult in PET as compared to Vinylon and nylon 6.

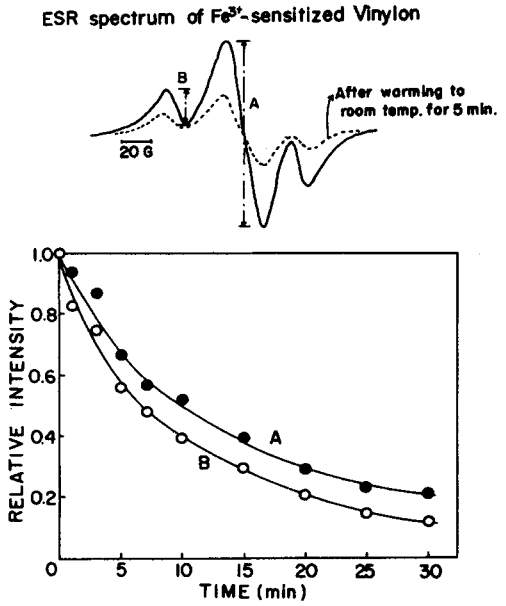

Fig. 2. Stability of Vinylon radicals formed by photo-irradiation. Vinylon sample irradiated at 77°K for 60 min with high-pressure mercury lamp was kept at room temperature for each duration.

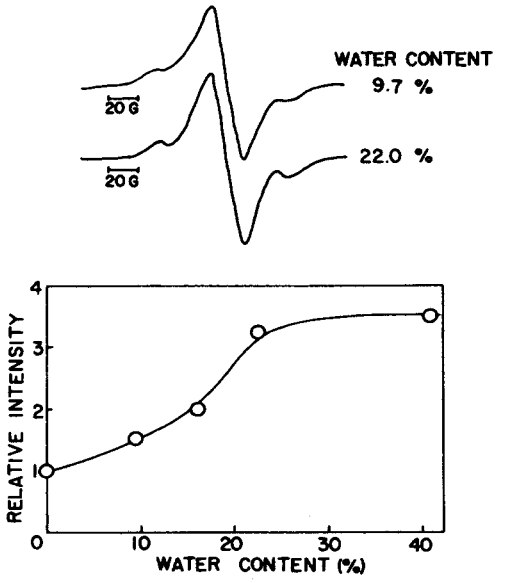

Fig. 3. Effect of water on radical formation of Vinylon irradiated at 77°K for 60 min with high-pressure mercury lamp.

TABLE VI
Effect of Organic Solvent on Radical Formation of Nylon 6[a]

Solvent	Absorption number	Relative signal intensity, arbitrary units
None	1	1.0
Acetone	3	3.3
MeOH	3	14.3
DMSO	3	4.3
THF	3	10.9
Dioxane	3	3.0

[a] Amount of organic solvent, 22% to 25%. Irradiation time, 60 min.

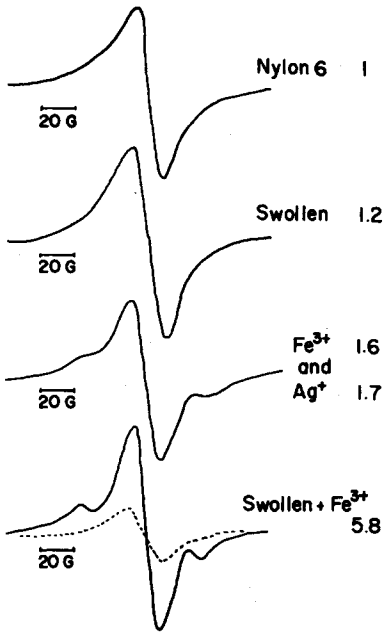

Fig. 4. ESR of nylon 6 irradiated at 77°K for 60 min with high-pressure mercury lamp. Dotted line represents spectrum after warming at room temperature for 2 min.

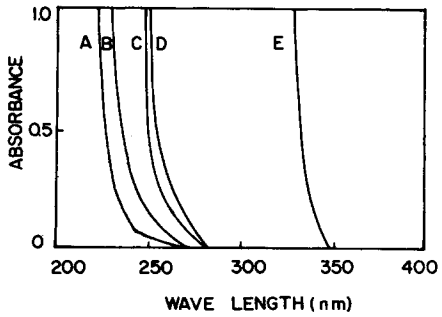

Fig. 5. Absorption spectra of solvents: (A) methanol; (B) tetrahydrofuran; (C) dimethyl sulfoxide; (D) dioxane; (E) acetone.

Photo-irradiation on Vinylon, nylon 6, and PET fibers applying sample swelling, sensitizer, and organic solvent is very favorable for the formation of radicals. With Vinylon and nylon 6, these three factors caused the formation of other radical species, and this is believed to contribute very much to the initiation of photo-initiated graft copolymerization.

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Received June 26, 1974
Revised September 13, 1974