

## Radiation-Induced Vapor-Phase Grafting of Methyl Methacrylate onto Poly(Vinyl Alcohol)

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Vapor-phase grafting of methyl methacrylate (MMA) was carried out at 60°C onto poly(vinyl alcohol) (PVA) by mutual irradiation technique. Dry or water-swollen films were placed above pure monomer or monomer-swelling agent mixture in sealed glass ampoules and irradiated with gamma-rays to a dose of  $1.1 \times 10^6$  R.

When the grafting was carried out onto dry films, no appreciable weight increase was observed in the case of the absence of swelling agents in the monomer. However, grafting took place, when methanol or water was added to the monomer. On the other hand, in the case of the grafting onto water-swollen films, high values of percent graft were attained, irrespective of the presence of the swelling agent. The molecular weights of homo-PMMA formed in the films were lower by one order than those obtained in liquid-phase graftings.

### INTRODUCTION

Relatively little effort has been devoted to the investigations on radiation-induced grafting with the use of monomers in vapor-phase,<sup>1-5)</sup> compared with those of liquid-phase grafting. However, some advantages have been pointed out for the vapor-phase grafting; for instance, homopolymerization takes place to an insignificant extent, fairly small amounts of monomer are sufficient to get high degrees of grafting, and the rate of grafting is far larger than that in liquid-phase grafting.<sup>2)</sup>

In our laboratory the radiation grafting onto poly(vinyl alcohol) (PVA) has been hitherto made exclusively with liquid-phase monomers.<sup>6-8)</sup> No work has been published concerning the vapor-phase grafting onto PVA. The purpose of the present work is to study the vapor-phase grafting of methyl methacrylate (MMA) onto PVA films by mutual irradiation method and compare the results with those of liquid-phase grafting.

### EXPERIMENTAL

PVA films were prepared by casting method from aqueous solutions of unfractionated PVA with number-average molecular weight of  $8.8 \times 10^4$ , and dried at room temperature under a reduced pressure. MMA monomer and other chemicals were purified with the usual method.

The apparatus used for the grafting was shown schematically in Fig. 1. The monomer solution was placed in a glass ampoule with a neck and the dry or water-swollen films were put on the neck. The ampoules were degassed by

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freezing and thawing cycle, sealed under a reduced pressure of  $10^{-4}$  mmHg, and then put in a thermostat kept at  $60^{\circ}\text{C}$ . The vapor pressure of MMA at  $60^{\circ}\text{C}$  is known to be 189 mmHg. Merely the ampoule part above the neck was allowed to be irradiated with gamma-rays from a Co-60 source by shielding the monomer part with lead blocks. The radiation dose was always  $1.1 \times 10^6$  R, the dose rate being  $4.0 \times 10^4$  R/hr.

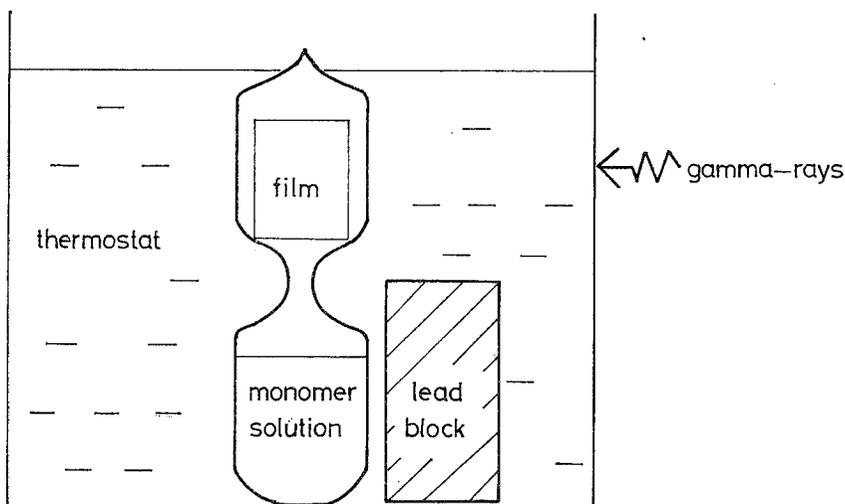


Fig. 1. Method of vapor-phase grafting.

Graft films were extracted with boiling benzene till no more extractable polymer was present, and the conventional percent graft was calculated. To isolate the pure graft copolymer from the reaction products, alternate extraction was further carried out for the homo-PMMA with benzene and the unreacted PVA with water-*n*-propanol (75 : 25) mixture. The true percent graft and the fraction of reacted PVA were calculated by the following equations :

$$\text{apparent percent graft} = \frac{\left( \begin{array}{c} \text{weight increase after} \\ \text{conventional extraction} \end{array} \right)}{\left( \text{weight of starting PVA} \right)} \times 100$$

$$\text{true percent graft} = \frac{\left( \text{weight of graft branch} \right)}{\left( \text{weight of starting PVA} \right)} \times 100$$

$$\text{fraction of reacted PVA} = \frac{\left( \begin{array}{c} \text{weight of PVA participated} \\ \text{in grafting} \end{array} \right)}{\left( \text{weight of starting PVA} \right)}$$

The molecular weights of the homo-PMMA were derived using the equation:<sup>9)</sup>

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_v^{0.76} \quad (\text{in benzene at } 30^{\circ}\text{C}).$$

The chemical composition of the graft copolymer was determined by hydrolysis of acetate groups, after the PVA part in the graft copolymer was completely acetylated.<sup>10)</sup>

## RESULTS AND DISCUSSION

The vapor-phase grafting was carried out in the present study onto dry and

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water-swollen films. Tables 1 and 2 give the data relating to the grafting onto dry films.

In some cases methanol or methanol and water which were known to be very effective to promote the liquid-phase grafting was added to the monomer.<sup>6)</sup> Copper resinate, a nonvolatile inhibitor, was added in the grafting of Exp. No. 1 to 3 with a purpose to prevent the thermal polymerization of the monomer.

Table 1. Vapor-phase grafting onto dry films (reaction conditions).

Exp. No.	Thickness of films (mm)	Composition of monomer solution (by vol.)			Inhibitor
		MMA	methanol	Water	
1	0.03	100	0	0	present
2	0.03	50	50	0	present
3	0.03	30	50	30	present
4	0.03	30	50	30	absent

As can be seen from Table 2, the weight increase of films was quite low and the grafting did not take place practically, when the pure monomer was used. On the contrary, the grafting proceeded to a significant extent in the presence of methanol in the monomer. The results are quite similar to those found in the liquid-phase grafting,<sup>6,11)</sup> except that the radiation dose necessary to get the same order of percent graft is lower by about one order for the liquid-phase grafting than for the vapor-phase grafting. The inhibitor did not influence the extent of grafting as shown in Table 1, but prevented greatly the thermal homopolymerization. When the inhibitor was absent, a large amount of thermally polymerized PMMA was produced in the lower part of the glass ampoules.

Table 2. Vapor-phase grafting onto dry films (reaction results).

Exp. No.	weight <sup>a)</sup> increase (%)	Percent graft (%)		Fraction of reacted PVA	Mole fraction of MMA in graft copolymer	$\bar{M}_n$ of homo-PMMA	Number of branch <sup>b)</sup>
		apparent	true				
1	1.3	0	0	0	—	—	—
2	70.4	28.4	15.5	0.0416	0.622	$2.6 \times 10^5$	1.27
3	61.2	28.1	14.6	0.0538	0.606	—	—
4	36.8	18.5	12.8	0.0534	0.514	$2.5 \times 10^5$	0.85

<sup>a)</sup> weight increase of films after extraction with boiling benzene for an hour.

<sup>b)</sup> per parent PVA molecule.

As mentioned above, the percent graft and the fraction of reacted PVA are not so different from those in the conventional liquid-phase grafting, but the molecular weights of homo-PMMA formed in the interior of films are distinctly lower than those observed in the liquid-phase grafting without chain transfer agent which range usually from  $1 \times 10^6$  to  $5 \times 10^6$ .<sup>11)</sup> The lower molecular weight may be ascribed mainly to degradation of PMMA by irradiation, since a high radiation dose of  $1.1 \times 10^6$  R is more or less effective simultaneously to PMMA formed, whose  $G_d$ -value for degradation has been reported to be 3.2.<sup>12)</sup>

In the present work the graft branches were not separated from the graft

copolymer, and only the viscosity-average molecular weights of homo-PMMA formed in the interior of films were measured. Therefore, it is not possible to estimate the precise number of branches in one molecule of graft copolymer. The number of branches given in the last column of Table 1 was calculated under the assumption that the molecular weight of branch is equal to the viscosity-average molecular weight of homo-PMMA formed in the films.<sup>8,10,13)</sup> The backbone was assumed to consist of one starting PVA molecule. The estimation method for the number is nearly the same as described in the next paper.<sup>13)</sup> It is seen that the branch number is approximately unity as found in the case of liquid-phase grafting.

The results of vapor-phase grafting onto water-swollen films were tabulated in Tables 3 and 4. The swollen films were obtained by soaking the dry films in pure water at 30°C. Water was not added to the monomer in this case.

Table 3. Vapor-phase grafting onto water-swollen films (reaction condition).

Exp. No.	Thickness of films (mm)	Degree of swelling <sup>a)</sup>	Composition of monomer solution (by vol.)		Inhibitor
			MMA	methanol	
5	0.03	2.28	100	0	present
6	0.03	3.43	50	50	present
7	0.1	2.28	100	0	present
8	0.1	2.45	100	0	absent

<sup>a)</sup> (weight of swollen films)/(weight of dry films) - 1

As can be seen clearly from Table 4, the grafting occurred, even when methanol was absent in the monomer. This should be, of course, ascribed to the fact that the films were previously swollen with water which is a promoting agent for grafting. The effect of inhibitor was similar to that in the grafting onto dry films. Comparison of Table 2 with Table 4 leads to the conclusion that there is practically no significant difference between the grafting onto dry and water-swollen films. The somewhat large fraction of reacted PVA observed in the grafting onto water-swollen films may be due to the higher diffusibility of monomer into the water-swollen films than dry ones.

Table 4. Vapor-phase grafting onto water-swollen films (reaction results).

Exp. No.	Weight increase (%)	Percent graft (%)		Fraction of reacted PVA	Mole fraction of MMA in graft copolymer	$\bar{M}_n$ of homo-PMMA	Number of branch <sup>a)</sup>
		apparent	true				
5	263	150	30.7	0.0961	0.584	$2.7 \times 10^5$	1.04
6	296	172	28.4	0.0759	0.622	$4.1 \times 10^5$	0.80
7	150	77.7	19.9	0.0679	0.563	$2.9 \times 10^5$	0.89
8	162	74.0	26.1	0.0731	0.612	$5.0 \times 10^5$	0.63

<sup>a)</sup> per parent PVA molecule.

It should be noted that the difference between the apparent and true percent graft is considerably large in both cases. As mentioned above, it is very likely that the branch PMMA as well as homo-PMMA degrades by simultaneous irra-

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diation, resulting in formation of non-grafted PMMA. Accordingly it seems difficult to confirm to what extent the homopolymerization occurred. More detailed study will be necessary to discuss this point more deeply.

### REFERENCES

- (1) A. A. Armstrong, Jr., and H. A. Rutherford, *Tex. Res. J.*, **33**, 264 (1963).
- (2) T. Takamatsu and K. Shinohara, *J. Polymer Sci.*, **A-1**, **4**, 197 (1966).
- (3) K. Hayakawa and K. Kawase, *J. Polymer Sci.*, **A-1**, **5**, 439 (1967).
- (4) K. Hayakawa, K. Kawase and H. Yamakita, *J. Polymer Sci.*, **6B**, 33 (1968).
- (5) A. A. Kachan, L. L. Chervyatsova, K. A. Kornyeu, E. F. Mertvichenko and N. P. Gnyp, *J. Polymer Sci.*, **C** (No. 16), 3033 (1967).
- (6) I. Sakurada, T. Okada and E. Kugo, *Isotopes and Radiation*, [Japan], **2**, 296, 306, 316, 581 (1959); **3**, 316, 329, 379, 406 (1960); **4**, 240 (1961).
- (7) I. Sakurada, Y. Ikada and T. Yamaoka, *Bull. Inst. Chem. Res., Kyoto Univ.*, **45**, 1 (1967).
- (8) I. Sakurada, Y. Ikada, T. Yamaoka and F. Horii, *Bull. Inst. Chem. Res., Kyoto Univ.*, **46**, 13 (1968).
- (9) T. G. Fox, J. B. Kinsinger, H. F. Mason and E. M. Schuele, *Polymer*, **3**, 71 (1962).
- (10) I. Sakurada, Y. Ikada, H. Uehara, Y. Nishizaki and F. Horii, *Makromol. Chem.*, **139**, 183 (1970).
- (11) I. Sakurada, Y. Ikada and F. Horii, *Makromol. Chem.*, **139**, 171 (1970).
- (12) S. Okamura, Y. Oishi and S. Ijichi, *Isotopes and Radiation* [Japan], **2**, 392 (1959).
- (13) I. Sakurada, Y. Ikada and F. Horii, *Bull. Inst. Chem. Res., Kyoto Univ.*, **49**, 6 (1971).