

## ***Radiation-Induced Graft Copolymerization of Methyl Methacrylate Onto Flaky Glass Surface by the Vapor-Phase Method***

Radiation-induced graft copolymerization onto the surface of a flaky aluminosilicate glass by the vapor-phase method was studied using DTA and ESR methods. Percentage of grafting of methyl methacrylate was found to be increased by chemical treatment with solutions of potassium permanganate and chromic acid mixture, while heat treatment of the samples lowered the value. The flaky glasses treated in various ways show the characteristic ESR spectra. It was thought that the structural defects formed on the glass have some correlations with the active sites of grafting.

### **EXPERIMENTAL**

MMA was purified by conventional procedures. Flaky aluminosilicate glass was E glass purchased from Owens Corning Co. The samples, I-VII, examined in the present work were glasses treated in the following seven ways: (I) The glass was washed with hot benzene for defatting, then dried at 80°C. (II) Sample I was heated near 500°C for 5 hr in vacuo. (III) The glass was immersed in a concentrated aqueous solution of ammonium nitrate for a month, then washed with pure water and heated near 500°C for 5 hr in vacuo. (IV) The glass was immersed in aqueous 1M solution of potassium permanganate at 80°C for 4 hr after washing with aqueous 2% solution of hydrofluoric acid, and left at room temperature for a day, then washed with pure water until the effluent became colorless. (V) Sample IV was heated near 500°C for 5 hr in vacuo. (VI) The glass was immersed in a chromic acid mixture at 80°C for 4 hr after washing with aqueous 2% solution of hydrofluoric acid, and left at room temperature for a day, then was washed with pure water until the effluent became colorless. (VII) Sample VI was heated near 500°C for 5 hr in vacuo.

The samples were sealed in glass tubes at  $10^{-5}$  torr after evacuation for 5 hr and irradiated in contact with MMA vapor at a dose rate of about  $6 \times 10^6$  R/hr from a  $^{60}\text{Co}$  source for 48 hr at room temperature.

After the graft copolymerization had ended, unreacted monomer and homopolymer were extracted with benzene using a Soxhlet extractor. The end of the extraction was confirmed by adding methanol as a precipitant to the extract.

ESR spectra were measured on a Japan Electron Optics Laboratory Model JES-3BS.X spectrometer, and DTA was recorded on a Ligaku Denki Thermoflex in the range from room temperature to 450°C.

### **RESULTS AND DISCUSSION**

The amount of grafting was measured as increment in weight of the samples before and after the  $\gamma$ -ray irradiation. The results of the grafting were expressed as the weight increment,  $W - W_0$ , divided by the original weight  $W_0$  of the glass and multiplied by 100. If  $W$  is the weight of the sample before the extraction with benzene, the value is called apparent percentage of grafting; and if it is the weight of the sample after the extraction, it is called true percentage of grafting.

The percentage of grafting of the samples is given in Table I. The apparent grafting was observed for the samples II, IV, V, VI, and VII. It is especially remarkable for the samples treated with solutions of potassium permanganate and chromic acid mixture. Therefore, the MMA vapor is considered to be adsorbed easily on these samples. Most of the MMA on the glass surface was eluted out with benzene, and only samples IV and VI were well-grafted samples. But the value became further lower by heat treatment as indicated by samples V and VII.

The DTA curves of samples IV and VI before the extraction with benzene are given in Figure 1. They show an exothermic pattern near 430°C, which appeared in the DTA curves of the samples after the extraction. But a large endothermic region from

TABLE I  
Percentage of Grafting of the Samples

Sample no.	Percentage of grafting, %	
	Apparent	True
I	0	0
II	18	2
III	0	0
IV	73	10
V	76	1
VI	80	10
VII	106	3

250°C to 400°C accompanied by two or three peaks disappeared after the extraction. So the endothermic reaction is responsible for the part extractable with benzene, and the exothermic reaction is responsible for the part that grafted onto the glass surface.

Figure 2 shows the ESR spectrum of the  $\gamma$ -ray irradiated sample IV. It consists of a broad sextet and a sharp singlet centered at  $g = 2.00$  overlapping on the former. The sextet hyperfine structure results from the coupling with a  $Mn^{2+}$  ion ( $I = 5/2$ ), and is broadened by the dipole-dipole interaction. The hyperfine coupling constant is slightly larger than that of a  $Mn^{2+}$  ion in magnesium oxide used as a ESR marker.

Figure 3 shows the ESR spectrum of the  $\gamma$ -ray irradiated sample VI. The sharp singlet centered at  $g = 2.00$  is the same as the former. The asymmetric spectra centered at  $g = 1.97$  and  $g = 1.96$  appear in the case without  $\gamma$ -ray irradiation. According to Reilley and McIver,<sup>1</sup> these spectra are assigned to the  $\gamma$ -absorption of the  $Cr^{6+}$  ion dispersed in  $Cr^{6+}$  ions. The line shape is similar to the  $\gamma$ -absorption of the  $Cr^{6+}$  ion dispersed in silica-alumina catalysts.<sup>2</sup>

The singlet is common to each sample, but is strong for the samples treated with the solutions of potassium permanganate and chromic acid mixture. This absorption

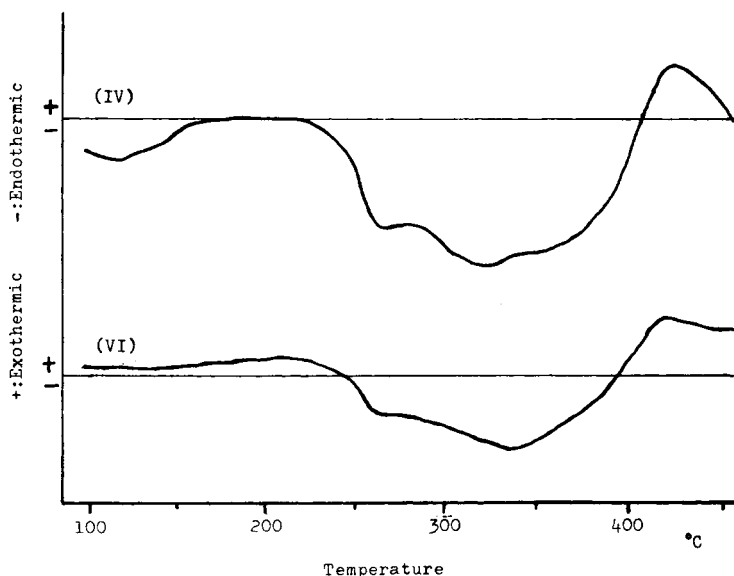


Fig. 1. DTA curves of the MMA grafted samples IV and VI, before extraction with benzene.



Fig. 2. ESR spectrum of  $\gamma$ -ray irradiated sample IV, treated with solution of potassium permanganate.

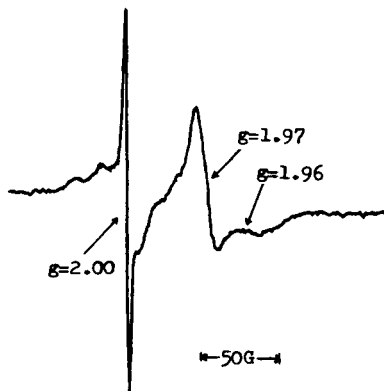


Fig. 3. ESR spectrum of  $\gamma$ -ray irradiated sample VI, treated with chromic acid mixture.

is difficult to assign correctly. However, it is thought that the structural defects caused by these treatments have a correlation with this absorption and are active sites of the grafting. But the coordination of the carbonyl group of a MMA molecule to the chromium ions and the manganese ions on the glass surface is thought to be possible, too.

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