

# Factors Affecting Vapor Phase Photografting of Vinyl Monomers on Cellulose

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## Synopsis

Effects of water contained in the sample, the type of sensitizer, and the nature of vinyl monomer on vapor phase photografting on cellulose were investigated at 60°C. The grafting was enhanced by the water contained in the cellulose sample, resulting in an increased percent grafting with increasing the quantity of water. The use of sensitizers such as ferric chloride, ferrous sulfate, ceric ammonium nitrate, hydrogen peroxide, benzophenone, and sodium anthraquinone-2,7-disulfonate led to accelerated graftings. However, the maximum grafting was observed at an optimum quantity of sensitizer for each sensitized system, and the formation of grafted polymer was restricted by the use of sensitizer beyond the quantity. Ferric chloride and hydrogen peroxide exhibited higher activities among the sensitizers. With respect to the nature of monomer, methyl methacrylate, acrylic acid, methacrylic acid, and acrylonitrile were observed to be introduced into cellulose substrate by the vapor phase photografting, though no initiation was recorded for styrene and *N*-vinylpyrrolidone. However, the latter monomers were introduced by using monomer mixtures with acrylonitrile, affording a maximum percent grafting at a certain monomer composition.

## INTRODUCTION

In previous papers<sup>1,2</sup> vapor phase photografting was observed to be a useful method to introduce various vinyl monomers into polyethylene and polypropylene films. In such systems the monomers were supplied in their gaseous states to the polyolefin substrates, and benzophenone (BP) and anthraquinone were used as sensitizers, which are coated on the films. This paper deals with various conditions necessary to fit for the vapor phase photografting on cellulose.

Studies<sup>3-5</sup> on photografting on cellulose have been extensively investigated in the system of liquid phase, but very few for the vapor phase. The vapor phase photografting on cellulose has been reported in unsensitized<sup>6</sup> and sensitized<sup>7-9</sup> systems. In the latter, biacetyl, metal oxide, and ferric ion were employed as sensitizers. In the present study the effects of water contained in the cellulose sample, type and concentration of sensitizer, and nature of monomer on vapor phase photografting on cellulose were examined.

## EXPERIMENTAL

### Samples

Dissolving pulp from softwoods was used as cellulose samples. The cellulose sample was treated with aqueous periodic acid solution at 45°C for 60 min (ratio of material to liquid, 1:100) to prepare aldehyde cellulose. After the

treatment, the sample was washed with water, dried under reduced pressure, and used for further experiments.

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Fe}^{3+}$ ),  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ( $\text{Fe}^{2+}$ ),  $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$  ( $\text{Ce}^{4+}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), sodium anthraquinone-2,7-disulfonate (AQ), and BP were used as sensitizers. A given amount of aqueous solution of sensitizer was atomized on the cellulose samples, and then the water contained was excluded by drying under reduced pressure to prepare a sensitized sample with a known amount of water. To obtain a BP-sensitized sample, the cellulose was immersed in acetone solution containing known amounts of BP at room temperature for 60 min, which was dried under reduced pressure. Water content and the amount of sensitizer added were taken as a percentage of the sample weight.

Methyl methacrylate (MMA), acrylonitrile (AN), acrylic acid (AA), *N*-vinylpyrrolidone (VP), methacrylic acid (MAA), and styrene (St) were purified by distillation.

### Photografting

Vapor phase photografting was carried out at 60°C for 60 min using a Pyrex glass tube, which was reported in a previous paper.<sup>10</sup> A cylindrical net of 20 mm diameter filled with a 0.1-g cellulose sample was kept at the center part of the tube, and 2 mL of monomer or monomer mixture was placed at the bottom of the tube. After freeze-thaw cycles, the pressure of the system was adjusted to 1 mm Hg. Irradiation with a high-pressure mercury lamp (400 W) was conducted in a Riko rotary photochemical reactor RH400-10W, around which Pyrex glass tubes were rotated. Polymerized sample was extracted with a suitable solvent to exclude homopolymers. Namely, hot water was used for polyAA, polyMAA, and polyVP. Acetone, benzene, and *N,N*-dimethylformamide were chosen for polyMMA, polySt, and polyAN, respectively. The percent grafting and the grafting efficiency were taken as the percentage of weight increase of the original cellulose and the weight percent of grafted polymer relative to total conversion of monomer in a system, respectively.

## RESULTS AND DISCUSSION

### Effect of Water in Cellulose Sample

Figure 1 shows the results of vapor phase photografting of MMA on unsensitized and sensitized cellulose samples. The abscissa in the figure represents the water content in the sample. It was proved for each dry sample that the grafting is hard to initiate. However, the initiation was observed for water-containing samples. The percent grafting increased with increasing the water content, which effected especially for  $\text{Fe}^{3+}$ - and  $\text{H}_2\text{O}_2$ -sensitized samples. Figure 2 shows the relationship between grafting efficiency and water content. The grafting efficiency increased with water content, resulting in a higher efficiency for the sensitized samples. Thus, water in the sample was found to be effective for the formation of grafted polymer.

Figure 3 presents the results of photografting on aldehyde cellulose. It is well known that aldehyde groups<sup>11,12</sup> are introduced into cellulose substrate by treatment with periodic acid. The aldehyde groups were reported to be

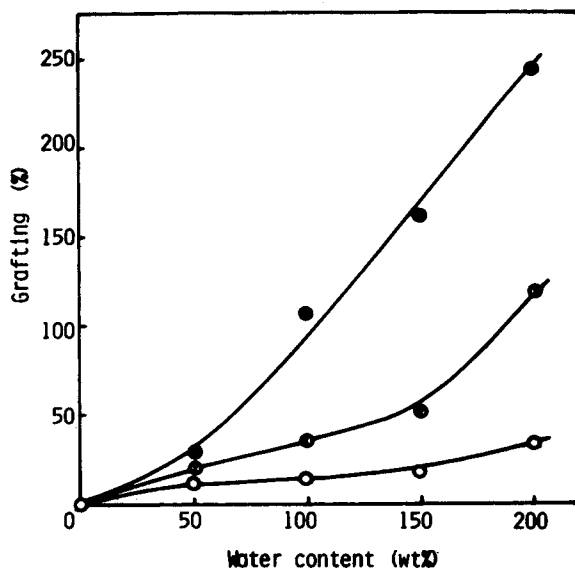


Fig. 1. Effect of water on percent grafting in vapor phase photografting of MMA on unsensitized and sensitized samples: (○) Unsensitized sample; (◐) H<sub>2</sub>O<sub>2</sub>-sensitized sample; (●) Fe<sup>3+</sup>-sensitized sample. Amount of sensitizer was 0.1 wt %. Irradiation was carried out at 60°C for 60 min.

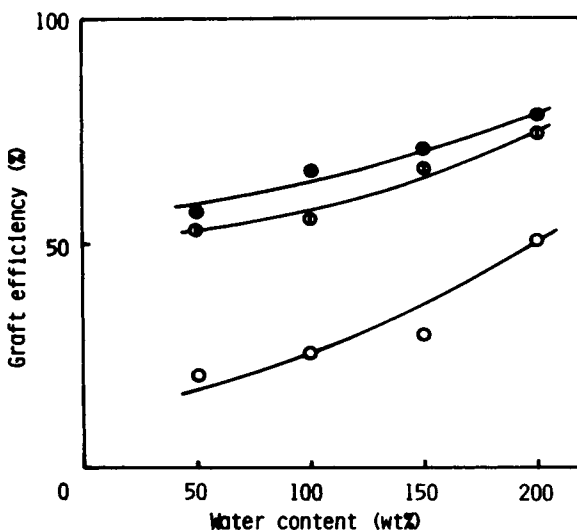


Fig. 2. Relationship between grafting efficiency and water content: (○) Unsensitized sample; (◐) H<sub>2</sub>O<sub>2</sub>-sensitized sample; (●) Fe<sup>3+</sup>-sensitized sample. Polymerization conditions were the same as those in Figure 1.

highly active in liquid phase photografting.<sup>13</sup> The percent grafting of aldehyde cellulose increased with increasing the water content, which was a fairly higher level than that of the untreated sample, and as same as those of the Fe<sup>3+</sup>- and H<sub>2</sub>O<sub>2</sub>-sensitized samples, which are shown in Figure 1. Thus, it was confirmed that aldehyde cellulose has a high ability to initiate photografting smoothly in vapor phase system.

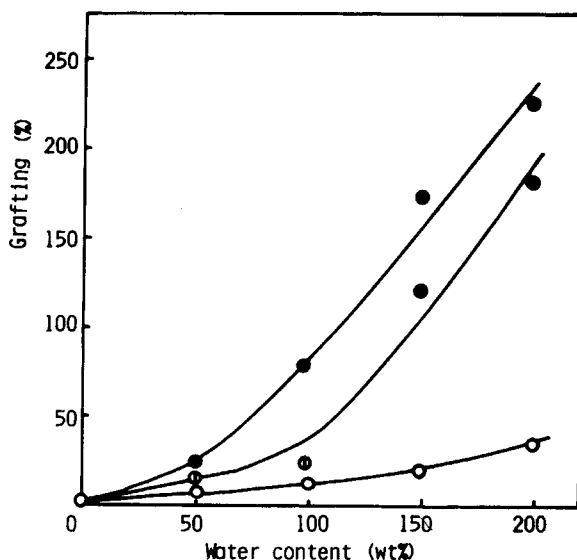


Fig. 3. Effect of water content on percent grafting in vapor phase photografting of MMA on aldehyde cellulose: (○) Untreated sample; (◐, ●) aldehyde celluloses prepared by treating the untreated sample with 10 and 20 mmol/L aqueous solution of periodic acid, respectively. Irradiation was carried out at 60°C for 60 min.

As above, water contained in the sample proved to lead to highly active vapor phase photografting, which was commonly true for each cellulose sample. Accordingly, water in the sample is conceivable as an effective factor performing vapor phase photografting on cellulose.

#### Effect of Sensitizers

It was reported that  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  are an effective sensitizer in liquid phase photografting on cellulose<sup>14-16</sup> with water medium. Figure 4 shows vapor phase photografting of MMA on  $\text{Fe}^{3+}$ -sensitized samples. The abscissa in the figure represents the quantity of  $\text{Fe}^{3+}$  added. Each water-containing sample commonly exhibited a maximum percent grafting at about 0.1 wt %  $\text{Fe}^{3+}$ . The maximum percent grafting of the sample with 200 wt % water content was about five times higher than that of the unsensitized sample, indicating that  $\text{Fe}^{3+}$  has an outstanding sensitizing function also in the vapor phase system. Figure 5 shows a relationship between total conversion of monomer and quantity of  $\text{Fe}^{3+}$  added. The relation between the both was the same as that of Figure 4. That is, an excess quantity of  $\text{Fe}^{3+}$  beyond about 0.1 wt % was found to affect the polymerization negatively. Figure 6 shows the results of  $\text{H}_2\text{O}_2$ -sensitized samples. An optimum quantity of  $\text{H}_2\text{O}_2$  for the grafting was shown in this system, too, and the percent grafting decreased in the range beyond the quantity. Thus, it is necessary to control the quantity of sensitizer properly in order to contrive the effective initiation of grafting. The excess quantity of sensitizer is sure to suppress the grafting reaction.

Table I presents the results of vapor phase photografting of MMA using various sensitizers. The quantity of sensitizer corresponding to a maximum

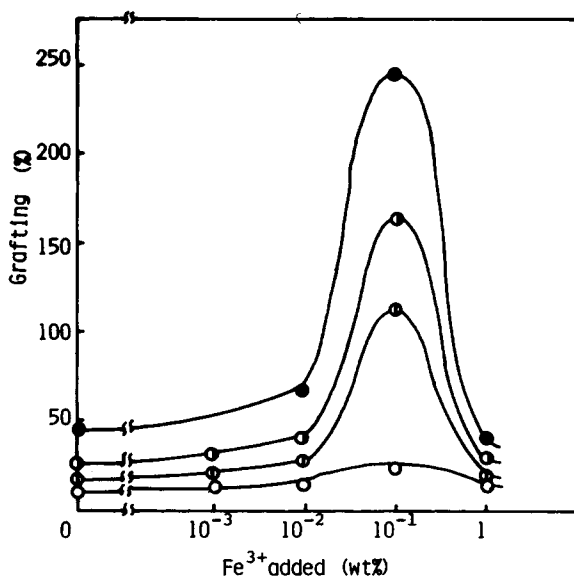


Fig. 4. Effect of amount of  $\text{Fe}^{3+}$  on percent grafting in vapor phase photografting of MMA on  $\text{Fe}^{3+}$ -sensitized sample. Water content (wt %): (○) 50; (◐) 100; (◑) 150; (●) 200. Irradiation was carried out at  $60^\circ\text{C}$  for 60 min.

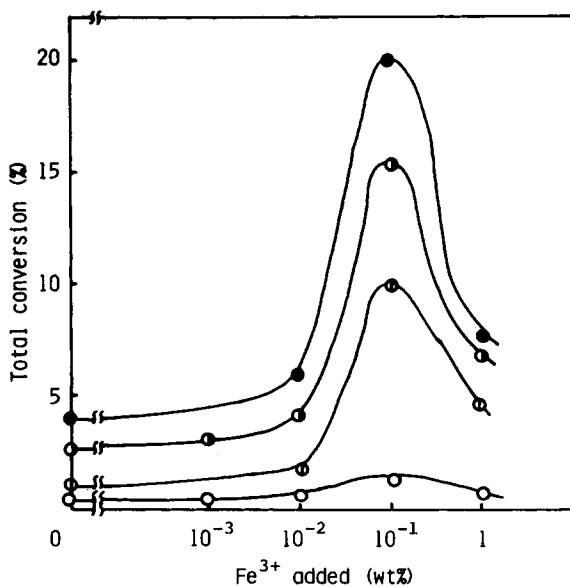


Fig. 5. Relationship between total conversion of monomer and amount of  $\text{Fe}^{3+}$ . Water content (wt %): (○) 50; (◐) 100; (◑) 150; (●) 200. Irradiation conditions were the same as those of Figure 4.

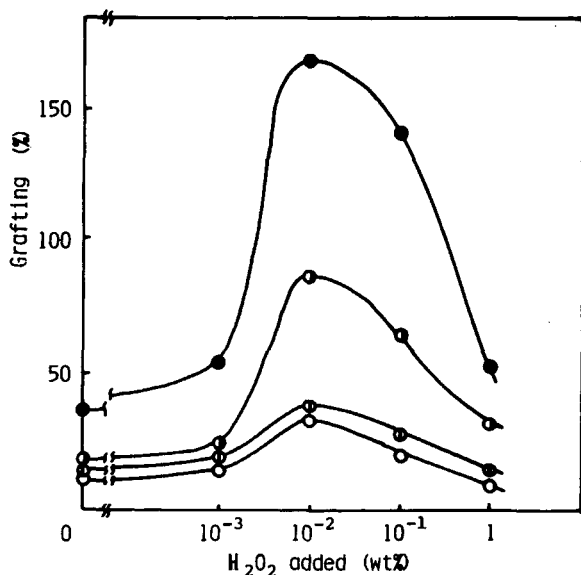


Fig. 6. Effect of amount of H<sub>2</sub>O<sub>2</sub> on percent grafting in vapor phase photografting of MMA on an H<sub>2</sub>O<sub>2</sub>-sensitized sample. Water content (wt %): (○) 50; (◐) 100; (◑) 150; (●) 200. Irradiation was carried out at 60°C for 60 min.

TABLE I  
Effect of Sensitizer on Photografting<sup>a</sup> of MMA on Cellulose Sample<sup>b</sup>

Sensitizer	Amount of sensitizer at maximum percent grafting (wt %)	Maximum percent grafting (%)
None	—	17.2
Fe <sup>3+</sup>	0.1	161.0
H <sub>2</sub> O <sub>2</sub>	0.01	86.6
Ce <sup>4+</sup>	1.0	55.9
Fe <sup>2+</sup>	1.0	37.4
AQ	0.001	47.9
BP	0.1	33.4

<sup>a</sup>Irradiation was carried out at 60°C for 60 min.

<sup>b</sup>Water content in the sample was 150 wt %.

percent grafting was somewhat different among the sensitizers. Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> sensitizers exhibited a remarkable effect for the maximum percent grafting, while the effect of BP, which is a good sensitizer for polyolefins<sup>1</sup> in both vapor- and liquid-phase photograftings, was significantly lower as compared with Fe<sup>3+</sup> and H<sub>2</sub>O<sub>2</sub> sensitizers. It is interesting that the effect of sensitizer on photografting is particular to the kind of polymer substrates.

#### Effect of Vinyl Monomers

Figure 7 shows photografting of various monomers on the unsensitized sample. The percent graftings of AA and AN as well as MMA increased with increasing the water content. With respect to the nature of monomer, the percent grafting decreased in the order AA > MMA > AN. It was observed in

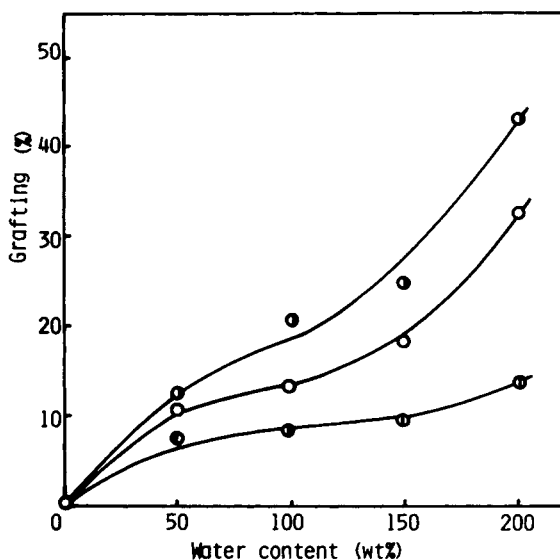


Fig. 7. Vapor phase photografting of various monomers on an unsensitized sample: (○) MMA; (◐) AN; (●) AA. Irradiation was carried out at 60°C for 60 min.

liquid phase photografting on cellulose<sup>17</sup> that it is difficult for AA to initiate the grafting because of a preferable formation of homopolymers in the system. Therefore, the vapor phase photografting seems to be favorable to the introduction of AA into cellulose substrate. Figure 8 shows the results of the H<sub>2</sub>O<sub>2</sub>-sensitized sample. The quantity of H<sub>2</sub>O<sub>2</sub> corresponding to a maximum percent grafting was recorded for AA, MAA, and AN in common with MMA.

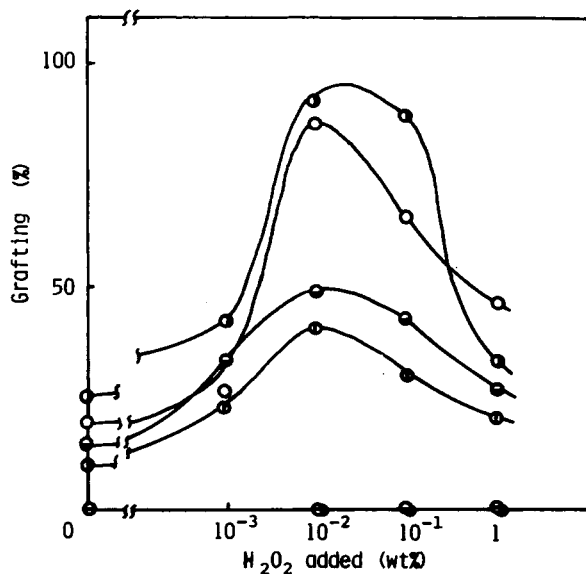


Fig. 8. Vapor phase photografting of various monomers on an H<sub>2</sub>O<sub>2</sub>-sensitized sample: (○) MMA; (◐) AN; (●) AA; (◑) MAA; (◒) St; (◓) VP. Water content in the sample was 150 wt %. Irradiation was carried out at 60°C for 60 min.

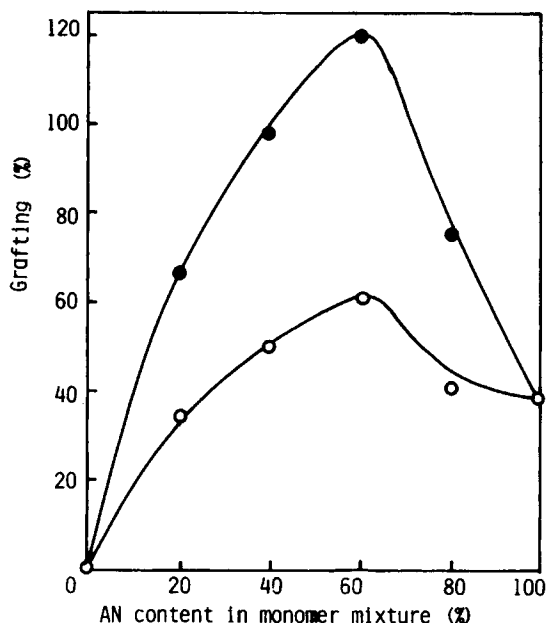


Fig. 9. Vapor phase photografting of monomer mixtures of AN with St and VP on  $H_2O_2$ -sensitized sample: (○) VP/AN; (●) St/AN. Water content and amount of  $H_2O_2$  in the sample were 150 and 0.01 wt %, respectively. Irradiation was carried out at  $60^\circ C$  for 60 min. Total volume of monomer was 2 mL.

Thus, the sensitizing effect of  $H_2O_2$  was observed for all monomer systems with the exception of St and VP.

Attempts<sup>18-21</sup> on the introduction of monomers into polymer substrates by using the combination of monomers, either of which is difficult to initiate polymerization by itself, have been extensively investigated. The method was applied to St and VP, and the results are shown in Figure 9. AN was used as a comonomer. As can be seen from the figure, the combination of St and AN resulted in a smooth initiation of grafting, affording a maximum percent grafting at a certain composition of the monomers. The same phenomenon was recorded for the combination of VP and AN.

Based on the above investigations, it is concluded that an effective initiation of vapor phase photografting on cellulose is attainable by the aid of water in the sample and the proper control of sensitizer concentration. Moreover, the use of monomer mixture can be a useful method introducing a wide range of monomers into the cellulose substrate.

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