

Graft Polymerization of Methyl Methacrylate onto Wool Initiated by Ferric Acetylacetonate/ Dichloroacetic Acid System

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Synopsis

The graft polymerization of methyl methacrylate (MMA) initiated by ferric acetyl acetonate/dichloroacetic acid [$\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$] system onto wool has been investigated in a mixture of water and dioxane. No grafting occurred in organic solvent; water was essential to the grafting. Both the total conversion and the percentage of grafting showed maxima when the mole ratio of $\text{Fe}(\text{acac})_3$ and Cl_2CHCOOH was $\frac{1}{3}$. Increasing wool content increased the percentage of grafting, while homopolymer conversion was independent of wool content. The rate of grafting was not proportional to MMA concentration. The grafting mechanism was discussed from these results.

INTRODUCTION

The graft polymerization of vinyl monomers onto natural products has been studied for a long time, and several aspects has been disclosed by a number of researchers.¹⁻⁴ The modification of wool fiber by grafting has been studied because of practical importance and interest.⁵⁻¹¹

In previous articles, we reported the butylborane-initiated graft polymerization of methyl methacrylate (MMA) onto cotton,¹² silk,¹³ and wool.¹⁴ It is well known that metal acetyl acetonate initiates the polymerization of various monomers and that additives, such as pyridine,¹⁵ phenanthroline,¹⁶ and some carbonyl compounds,¹⁷ promoted these polymerizations. We found that the homopolymerization of MMA initiated by ferric acetylacetonate [$\text{Fe}(\text{acac})_3$] was extremely accelerated by the addition of dichloroacetic acid (Cl_2CHCOOH) at ordinary temperature.¹⁸

In the present investigation, we studied the graft polymerization of MMA onto wool by the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system. Effects of reaction media, wool content, mole ratio of $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$, and initiator concentration were studied. Electron microscope observation was also carried out on wool-g-poly(MMA) to obtain more information on the grafting.

EXPERIMENTAL

Materials

Fine Australian Merino wool fibers were purified by Soxhlet extraction with acetone for about 24 hr, washed with methanol, and dried under reduced pressure. Commercial MMA was purified by distillation in a usual manner. Dotite

metal acetyl acetonates (Donin Chemical Lab) were used without further purification. Dichloroacetic acid was carefully distilled twice under reduced pressure in nitrogen stream; boiling point 94.1–94.5°C/17 torr. Commercial keratin, silk, cellulose, and wool were all refluxed in acetone for 24 hr, washed with methanol, and dried *in vacuo* to constant weight.

Typical Graft Copolymerization Procedure

A mixture of 0.3 g of wool fiber, 15 ml of water, and 5 ml of dioxane was placed in a tapered joint glass tube (~60 ml) and allowed to stand at 25°C for 24 hr. In another glass tube, the desired amount of Fe(acac)₃ was dissolved in 10 ml of MMA. To the first glass tube the Fe(acac)₃–MMA solution was immediately added, and finally dichloroacetic acid was added with a microsyringe. Then the glass tube was shaken in a thermostatted shaking apparatus at 50°C for 2 hr. The grafting reaction was stopped by pouring the mixture into 200 ml of methanol. The precipitate was filtered, washed with methanol, and then dried at 50°C *in vacuo* to constant weight. The dried precipitate was extracted with acetone in a Soxhlet extractor for 72 hr. The acetone-soluble extract was reprecipitated with methanol to yield homopolymer. Both the acetone-insoluble residue (graft copolymer) and the homopolymer were dried at 50°C *in vacuo* to constant weight.

Calculation

Total conversion (%)

$$= \frac{\text{weight of poly(MMA) grafted and homopolymer}}{\text{weight of MMA charged}} \times 100$$

Percentage of grafting (%) = $\frac{\text{weight of poly(MMA) grafted}}{\text{weight of MMA charged}} \times 100$

Efficiency of grafting (%)

$$= \frac{\text{weight of poly(MMA) grafted}}{\text{weight of poly(MMA) grafted and homopolymer}} \times 100$$

Weight increase (%) = $\frac{\text{weight of poly(MMA) grafted}}{\text{weight of wool charged}} \times 100$

Homopolymer conversion (%) = $\frac{\text{weight of homopolymer}}{\text{weight of MMA charged}} \times 100$

Viscosity Measurement

Intrinsic viscosities of the homopolymer were determined at 30°C in a Ubbelohde-type viscometer on benzene solution, and average molecular weights were estimated according to the following equation¹⁹:

$$[\eta] = 5.2 \times 10^{-5} \times \bar{M}^{0.76} \quad (\text{dl/g, } 30^\circ\text{C})$$

RESULTS AND DISCUSSION

Backbone Polymer

Graft polymerization of MMA by $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system was carried out in the presence of various backbone polymers in mixed medium of dioxane and water at 60°C for 2 hr. These results are shown in Table I. The $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system was effective particularly for the graft polymerization onto keratin. The grafting onto cellulose was not initiated by $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$.

Medium

In our previous article,¹⁸ it was found that MMA was polymerized most effectively by $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system in dioxane. Though the polymerization of MMA was carried out in dioxane by this system in the presence of wool, no graft polymer was obtained. And it was found that water was essential to the graft polymerization of MMA onto wool initiated by the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system. Similar results were also observed in other cases of graft polymerization.¹⁴ Even the homopolymerization had not occurred in water. These results show that both dioxane and water are essential to the graft polymerization of MMA onto wool by the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system.

Homopolymerization of MMA was found to be initiated by the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system only in solvents having $70\text{--}110\text{ cm}^{-1}$ of electrodonating power ($\Delta\nu$),²⁰ such as dioxane, dimethylformamide (DMF), and tetrahydrofuran (THF) (77 , 107 , and 90 cm^{-1} , respectively).¹⁸ As shown in Table II, graft polymerization was also initiated in dioxane, DMF, and THF, while no graft polymer was obtained in benzene ($\Delta\nu = 0$).

Volume Ratio of Dioxane and Water

Figure 1 shows the result of the graft polymerizations that varied the volume ratio of dioxane and water and kept all the volume of media constant (20 ml). The larger the volume of dioxane, the higher both the total conversion and the percentage of grafting. However, the efficiency of grafting was not influenced by dioxane volume above 2 ml. These results indicate that dioxane play an important role not only in homopolymerization but also in grafting. We believe that the percentage of grafting has a maximum point at the large volume of di-

TABLE I
Graft Polymerization onto Various Backbone Polymers^a

Backbone polymer	Total conversion (%)	Percentage of grafting (%)	Efficiency of grafting (%)	Weight increase (%)
Cellulose	0	—	—	—
Silk	1.4	0.5	37.6	24.7
Keratin	13.4	4.0	29.7	74.4

^a Reaction condition: $\text{Fe}(\text{acac})_3$, 2×10^{-2} mole/liter; Cl_2CHCOOH , 8×10^{-2} mole/liter; MMA, 10 ml; water, 18 ml; dioxane, 2 ml; backbone polymer, 0.5 g; temperature, 60°C ; time, 2 hr.

TABLE II
 Graft Polymerization onto Wool in Various Media^a

Reaction medium	Total conversion (%)	Percentage of grafting (%)	Efficiency of grafting (%)	Weight increase (%)
Benzene	3.0	0	0	0
DMF	8.2	3.7	44.5	114.0
THF	42.0	6.1	14.6	191.6
Dioxane	19.7	7.5	38.2	234.6

^a Reaction condition: $\text{Fe}(\text{acac})_3$, 2×10^{-2} mole/liter; Cl_2CHCOOH , 8×10^{-2} mole/liter; MMA, 10 ml; water, 18 ml; reaction medium, 2 ml; wool, 0.3 g; temperature, 60°C; time, 2.5 hr.

oxane, as shown in Figure 1, because no grafting was observed both in the absence of dioxane and in the absence of water. It seems that only small portions of water should be needed for the grafting, though water is essential to the grafting.

Dichloroacetic Acid Concentration

The dependence of the grafting on the concentration of dichloroacetic acid is given in Figure 2. There was an optimum concentration of 8×10^{-2} mole/liter of dichloroacetic acid for the total conversion, and for the percentage of grafting. At this optimum concentration, the mole ratio of $\text{Fe}(\text{acac})_3$ and dichloroacetic acid was $\frac{1}{4}$, which was the same as the optimum mole ratio in the homopolymerization by this system. This seems to indicate that the initiation process of grafting includes the reduction of Fe(III) to Fe(II) by Cl_2CHCOOH , as shown in the initiation process of the homopolymerization by the $\text{Fe}(\text{acac})_3$ - Cl_2CHCOOH system in dioxane.

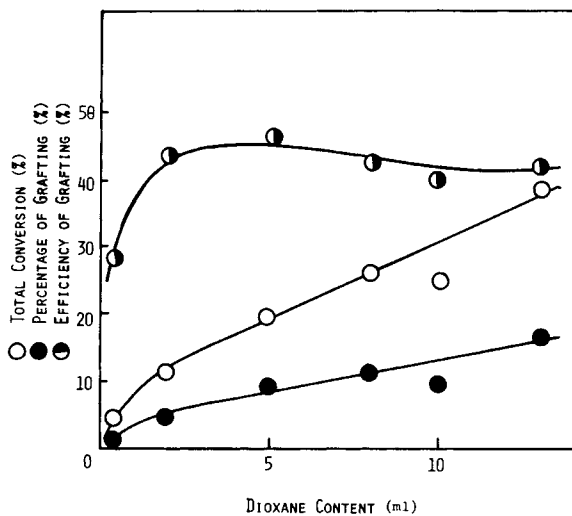


Fig. 1. Effect of dioxane content on the grafting condition: $\text{Fe}(\text{acac})_3$, 0.02 mole/liter; Cl_2CHCOOH , 0.08 mole/liter; dioxane + water, 20 ml; MMA, 3.12 mole/liter; wool, 0.3 g; polymerization temperature, 60°C; time, 2 hr. (○) Total conversion (%); (●) percentage of grafting (%); (●) efficiency of grafting (%).

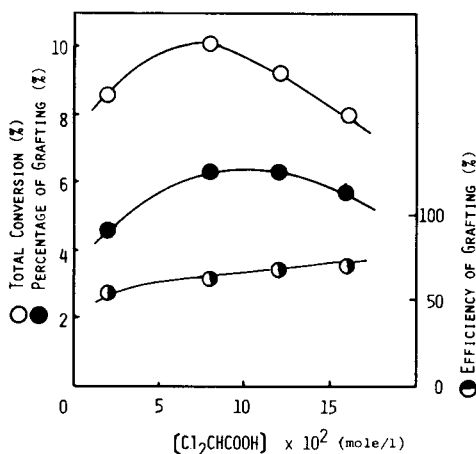


Fig. 2. Effect of dichloroacetic acid concentration condition: $\text{Fe}(\text{acac})_3$, 0.02 mole/liter; wool, 0.3 g; MMA, 3.12 mole/liter; dioxane, 5 ml; water, 15 ml; polymerization temperature, 50°C; time, 2 hr (symbols as in Fig. 1).

Initiator Concentration

The grafting of MMA onto wool was carried out with various initiator concentration, keeping the mole ratio of $\text{Fe}(\text{acac})_3$ and Cl_2CHCOOH constant to $\frac{1}{4}$. This result is shown in Figure 3. Both the percentage and the efficiency of grafting had their maxima at 5×10^{-3} mole/liter of the initiator concentration. It seems that radicals formed on wool are wasted by recombination and by other termination processes beyond 5×10^{-3} mole/liter of the initiator concentration.

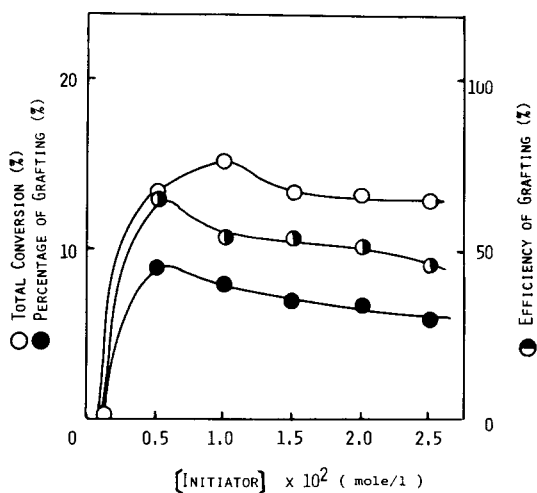


Fig. 3. Effect of initiator concentration on the grafting condition: $[\text{Fe}(\text{acac})_3]:[\text{Cl}_2\text{CHCOOH}] = 1:4$; wool, 0.3 g; MMA, 3.12 mole/liter; dioxane, 5 ml; water, 15 ml; polymerization temperature, 50°C; time, 2 hr (symbols as in Fig. 1).

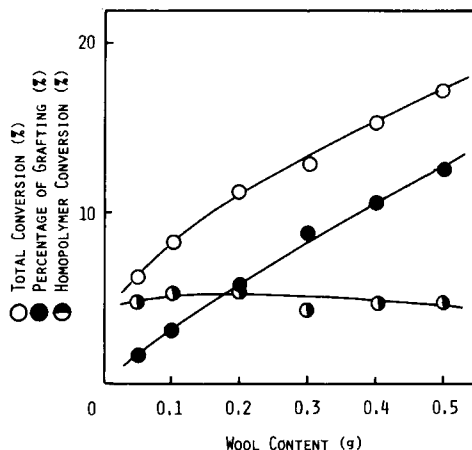


Fig. 4. Effect of wool content on the grafting condition: $\text{Fe}(\text{acac})_3$, 0.02 mole/liter; Cl_2CHCOOH , 0.08 mole/liter; MMA, 3.12 mole/liter; dioxane, 5 ml; water, 15 ml; polymerization temperature, 50°C; time, 2 hr. (○ ●) As in Fig. 1; (●) homopolymer conversion (%).

Wool Content

The effect of wool content on the grafting is shown in Figure 4. Increasing wool content increased the percentage of grafting; homopolymer conversion was independent to the increase of wool content. This result could be explained by assuming that the grafting onto wool is initiated not only by the attack of the primary radicals to wool, which are induced by the reaction of $\text{Fe}(\text{acac})_3$ and Cl_2CHCOOH , but also by the interaction of wool, $\text{Fe}(\text{acac})_3$, dichloroacetic acid, and water.

In Table III, it is shown that average molecular weights of homopolymers obtained in this series were the same as those of the homopolymers obtained in the absence of wool, and independent of wool content charged. This result suggests that graft sites on wool are not produced by the chain transfer of poly(MMA) radicals to wool.

TABLE III
Effect of Wool Content on the Grafting^a

Wool (g)	Total Conversion (%)	Percentage of grafting (%)	Efficiency of grafting (%)	Weight increase (%)	\bar{M} of homopolymer ($\times 10^{-4}$)
0	4.4	—	—	—	86
0.05	6.2	1.6	25.8	299.6	—
0.1	8.2	3.0	36.0	276.4	96
0.2	11.2	5.6	50.1	262.6	91
0.3	12.8	8.8	68.7	279.8	86
0.4	15.2	10.7	70.7	251.5	80
0.5	17.0	12.5	73.8	234.8	87

^a Condition: $\text{Fe}(\text{acac})_3$, 2×10^{-2} mole/liter; Cl_2CHCOOH , 8×10^{-2} mole/liter; MMA, 10 ml; water, 15 ml; dioxane, 5 ml; temperature, 50°C; time, 2 hr.

TABLE IV
 Effect of Monomer Concentration^a

MMA (ml)	Rate of Graftpolymerization (mole/liter sec) ($\times 10^{-4}$)	Rate of homopolymerization (mole/liter sec) ($\times 10^{-5}$)	Efficiency of grafting (%)	Weight increase (%)
3	—	—	—	—
5	1.7	5	75.9	304.1
7	1.2	4	75.6	217.1
10	1.1	7	61.8	200.4
13	1.1	7	62.5	207.9
15	1.0	8	56.1	186.5

^a Reaction condition: $\text{Fe}(\text{acac})_3$, 2×10^{-2} mole/liter; Cl_2CHCOOH , 8×10^{-2} mole/liter; wool, 0.3 g; reaction media, total volume 30 ml (dioxane, 5 ml); temperature, 60°C ; time, 2 hr.

Monomer Concentration

Table IV shows the influence of MMA concentration on the rate of grafting and the rate of homopolymerization initiated by $\text{Fe}(\text{acac})_3/\text{Cl}_2\text{CHCOOH}$ system. MMA concentration was varied, while the total volume of MMA, water, and dioxane (5 ml) was kept constant to 30 ml. The rate of grafting decreased with increasing MMA concentration, while the rate of homopolymerization was proportional to the 1.8 order of MMA concentration. This result indicates that MMA does not participate in the initiation process of the grafting.

Polymerization Time and Temperature

The dependence of the grafting on the polymerization time and temperature was examined at 50, 60, and 70°C . Figure 5 shows the result obtained in the graft polymerization at 60°C . It was found that the induction period was observed

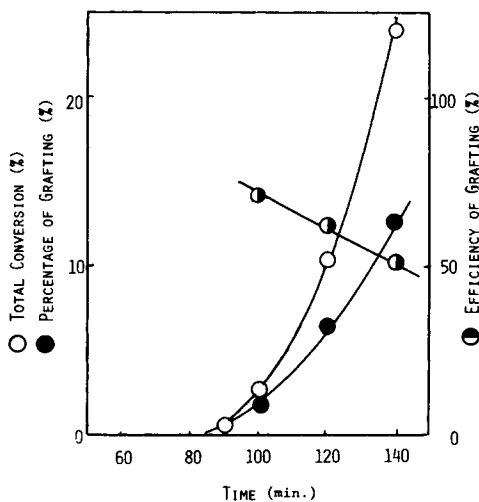


Fig. 5. Effect of polymerization time on the grafting condition: $\text{Fe}(\text{acac})_3$, 0.02 mole/liter; Cl_2CHCOOH , 0.08 mole/liter; wool, 0.3 g; MMA, 3.12 mole/liter; dioxane, 5 ml; water, 15 ml; polymerization temperature, 60°C (symbols as in Fig. 1).

both in the grafting and in the homopolymerization, and that the higher the polymerization temperature was, the longer the induction period became. The activation energies were estimated from the initial rate of polymerization at each temperature and found to be about 10 and about 14 kcal/mole for the grafting and the homopolymerization, respectively.

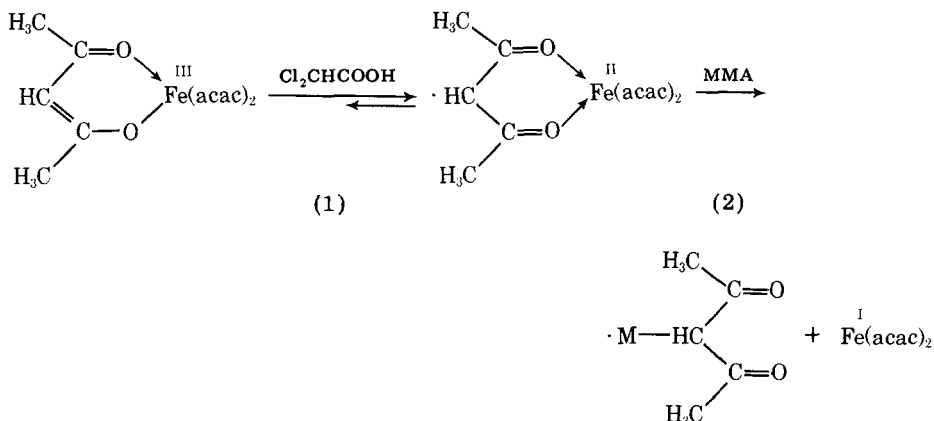
Scanning Electron Microscopy

Figure 6 shows the view of untreated wool fiber and grafted wool fiber by a scanning electron microscope. It was observed that the larger percentage of grafting the fiber had, the wider it grew. And obviously the surface structure of fiber was also altered by grafting, although it is known that the structure is altered to some degree by chemical treatment.

Grafting Mechanism

It is well known that metal acetyl acetonate initiates the polymerization of vinyl monomers via radical mechanism, and that the rate of polymerization is proportional to more than a one order of monomer concentration. The high order with monomer has been explained by the formation of chelate-monomer complex in initiation step.

We have previously reported the homopolymerization of MMA initiated by the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system and shown the following initiation mechanism:



However, in the present graft polymerization of MMA by the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system onto wool, it was found that the rate of grafting was not proportional to monomer concentration, contrary to the homopolymerization occurring simultaneously in this system. Therefore, it was supposed that grafting sites on wool were generated by the coordination reaction of $\text{Fe}(\text{II})$ chelate radical with wool prior to the reaction of it with MMA in step (2) of the above scheme.

As mentioned above, the rate of grafting was the highest at $\frac{1}{4}$ mole ratio of $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$. This result seems to support that step (1), where the addition of Cl_2CHCOOH displaces the equilibrium, occurs both in the grafting and in the homopolymerization.

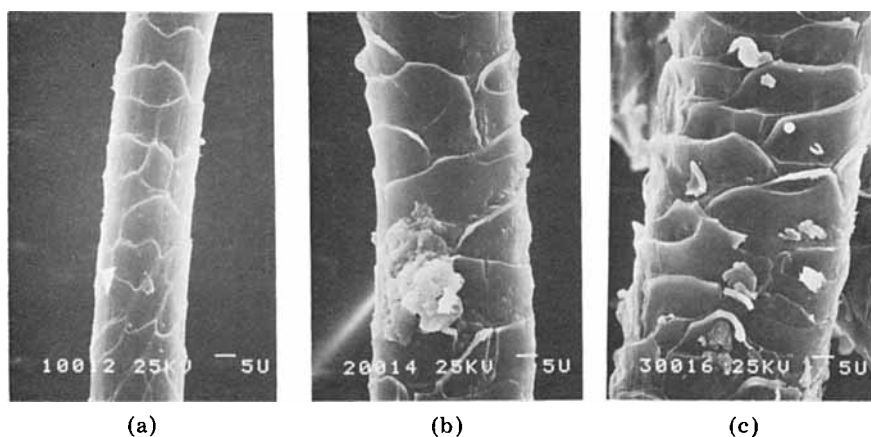


Fig. 6. Scanning electron microscopic photographs of an untreated wool and grafted wools ($\times 1000$). (a) Untreated wool fiber; (b) and (c), grafted wools; weight increase, (b) < (c).

Another possible initiation mechanism is that an acetyl acetate radical attacks simultaneously wool and MMA. However, this mechanism should not be accepted in the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system, because the homopolymer conversion was found to be independent of the wool content.

CONCLUSIONS

MMA was grafted effectively onto wool by the $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$ system in a mixed medium of dioxane and water at ordinary temperature. The grafting of MMA onto wool was influenced by the nature of the medium. Water was essential to the grafting; no grafting was obtained in usual organic solvent. The percentage of grafting was the highest at $\frac{1}{4}$ mole ratio of $\text{Fe}(\text{acac})_3\text{-Cl}_2\text{CHCOOH}$. The rate of grafting was not proportional to monomer concentration. The percentage of grafting increased with increasing wool content, but homopolymer conversion was independent of wool content.

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