Grafting onto Wool. XXIV. Graft Copolymerization of Methyl Methacrylate and Ethyl Methacrylate by Use of Ferric Acetylacetonate as Initiator: Comparison of Monomer Reactivities

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ABSTRACT

Ferric acetylacetonate has been utilized as an initiator for effecting grafting of methyl methacrylate (MMA) and ethyl methacrylate (EMA) onto Himachali wool in aqueous medium. The extent of grafting and grafting efficiency have been determined as functions of various reaction variables that influence the grafting reactions. Nitric acid was found to catalyze the graft copolymerization. Rate of grafting (R_p) and induction period (I_p) of MMA and EMA have been determined as a function of total initial monomer concentration. MMA was found to be more reactive than EMA toward graft copolymerization. With MMA, the induction period (I_p) was found to increase with increasing [MMA], while the reverse was true with EMA. A plausible mechanism for graft copolymerization has been suggested to explain the relative reactivities of MMA and EMA toward grafting onto wool.

INTRODUCTION

In recent years considerable attention has been devoted toward modification of a variety of natural polymers by graft copolymerization. A comprehensive research program on modification of Himachali wool has been initiated in our laboratory. Grafting is usually accompanied by the formation of homopolymer which poses a serious problem in the purification of the graft and a considerable amount of monomer is wasted. In order to overcome this difficulty, attempts are being made to select initiating systems [1-3] capable of producing grafting with the formation of very little homopolymer. Metal chelates are known to initiate polymerization of vinyl monomers, and it was therefore thought worthwhile to test them as initiators for graft copolymerization. Misra and co-workers [4-10] have successfully used $Mn(acac)_3$, $Cr(acac)_3$, and $VO(acac)_2$ in effecting grafting of a wide variety of vinyl monomers onto wool and cellulose fiber. Nayak et al. [11] have also reported grafting of vinyl monomer onto silk and wool by using β-diketonates of transition metals. As an extension of our previous study on the utilization of metal chelates as graft initiators, we now report grafting of MMA and EMA onto wool in the presence of $Fe(acac)_3$. A plausible mechanism for grafting is suggested and an attempt is made to compare the reactivities of MMA and EMA toward $Fe(acac)_3$-initiated grafting onto Himachali wool fiber.

EXPERIMENTAL

Preparation of Iron Acetyl Acetonate

The chelate was prepared by the modified method of Arnett et al. [12]. A solution of 5.13 g (0.045 mol) of acetyl acetone in 40 mL of methanol was added to a solution of 1.62 g (0.01 mol) of ferric chloride (anhydrous and sublimed) in 10 mL of distilled water. To the resulting solution, sodium acetate (E. Merck) 8.16 g (0.06 mol) dissolved in 20 mL of distilled water was added slowly with vigorous stirring. The mixture was warmed to 50-70°C for about 15 min and then cooled at 10°C for several hours. The red solid precipitate was collected on a Buchner funnel, washed with water and petroleum ether, and dried at 50°C. After recrystallizing from benzene and petroleum ether, the chelate was dried for 24 hours at 50°C, yield = 50%, mp = 179°C.

Analysis: Calculated for $C_{15}H_{21}O_6Fe$: C, 54.7; H, 6.9; Fe, 14.15%. Found: C, 54.3; H, 6.8; Fe, 14.1%.

Method and Materials

MMA (BDH) and EMA (BDH) were washed with 5% NaOH and dried over anhydrous sodium sulfate. The dried monomers were then distilled and the middle fraction was used. N_2 was purified by passing through alkaline pyrogallol solution. Himachali wool was purified by the method [13] described earlier.

Graft Copolymerization

To 1.0 g of purified Himachali wool dispersed in 200 mL deaerated water in a three-necked flask, a known weight of ferric acetylacetonate $[Fe(acac)_3]$ in nitric acid of known strength was added. Prior to the addition of monomer, purified N_2 was passed through the reaction flask and a continuous flow of N_2 was maintained throughout the reaction. Definite amounts of MMA and EMA were added to the reaction flask. The copolymerizations were carried out with stirring at a temperature between 50 and 75°C for various reaction periods.

After completion of the reaction, the reaction mixture was filtered and the residue was extracted with benzene to remove PMMA and PEMA. The percentage and efficiency of grafting were calculated from the following expression:

$$\% \ G = \frac{W_1 - W_0}{W_0} \times 100$$

$$\% \ E = \frac{W_1 - W_0}{W_2} \times 100$$

where W_0 = weight of original wool

W_1 = weight of grafted wool after solvent extraction

W_2 = weight of monomer used

EVIDENCE OF GRAFTING

(1) A physical mixture of PMMA and PEMA and wool was prepared by dispersing wool in a benzene solution of PMMA and PEMA. This

dispersion was stirred for 48 h. After extraction with benzene the residue was hydrolyzed with 6 $\underline{N}$ HCl at 115°C for 24 h. No residue of PMMA and PEMA was obtained, indicating that benzene extraction completely removed the homopolymer from the physical mixture.
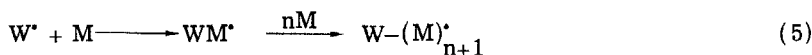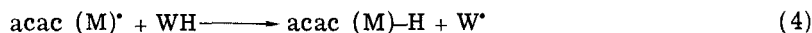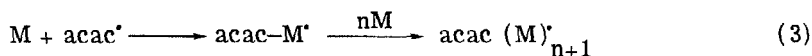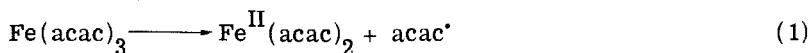
(2) The IR spectra of grafted PMMA and grafted PEMA showed absorption at 1720 and 1730 cm^{-1} attributed to C=O of PMMA and PEMA, respectively. No such band was observed in the IR spectrum of wool.
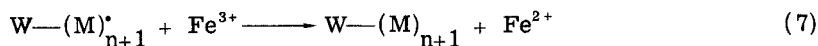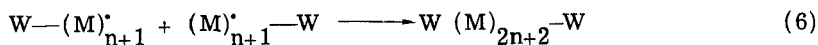
(3) Comparison of scanning electron micrographs [5] of wool and grafted wool indicated considerable deposition of polymer on wool.

(4) Ninhydrin test. The grafted polymer obtained from the acid hydrolysis of grafted wool was thoroughly washed with water and dried. The dried polymer was dissolved in acetone and a few drops of ninhydrin solution in acetone were added. There was no violet coloration but, when a Whatman filter paper soaked in the above solution was dried at 90°C, a violet color developed. This indicates the presence of residual amino acid groups in the polymer isolated from the graft. The detection of amino acid in the polymer isolated from the graft constitutes additional evidence for grafting.

RESULTS AND DISCUSSION

Metal chelates have been reported [14] to decompose on heating into free radical species capable of initiating the polymerization of vinyl monomers. It was pointed out by Kastning et al. [15] that not all metal chelates are equally reactive in polymerizing vinyl monomers. The ease of polymerization is dependent upon the nature of the central metal atom of the chelate as well as the nature of the monomer. Kastning et al. [15] have reported that, among simple acetylacetonates, those of Mn(III) and Co(III) are the most active initiators for vinyl polymerization. In graft copolymerizations also, metal chelates vary in their reactivity. In the presence of Fe(acac)$_3$, grafting of MMA and EMA can be explained by the following mechanism:

$$\text{Fe(acac)}_3 \longrightarrow \text{Fe}^{II}\text{(acac)}_2 + \text{acac}^{\bullet} \tag{1}$$

$$\text{WH} + \text{acac}^{\bullet} \longrightarrow \text{W}^{\bullet} + \text{acac–H} \tag{2}$$

$$\text{M} + \text{acac}^{\bullet} \longrightarrow \text{acac–M}^{\bullet} \xrightarrow{\text{nM}} \text{acac (M)}^{\bullet}_{n+1} \tag{3}$$

$$\text{acac (M)}^{\bullet} + \text{WH} \longrightarrow \text{acac (M)–H} + \text{W}^{\bullet} \tag{4}$$

$$\text{W}^{\bullet} + \text{M} \longrightarrow \text{WM}^{\bullet} \xrightarrow{\text{nM}} \text{W–(M)}^{\bullet}_{n+1} \tag{5}$$

$$W\text{—}(M)^{\bullet}_{n+1} + (M)^{\bullet}_{n+1}\text{—}W \longrightarrow W\,(M)_{2n+2}\text{—}W \qquad (6)$$

$$W\text{—}(M)^{\bullet}_{n+1} + Fe^{3+} \longrightarrow W\text{—}(M)_{n+1} + Fe^{2+} \qquad (7)$$

In accordance with this postulated mechanism, initiation of grafting can occur either by Process (2), by Process (4), or by both. If such a mechanism operates, then the percentage of grafting would be expected to increase with an increase in the concentrations of monomer and chelate. It is apparent from Tables 1 and 2 that the extent of grafting increases with an increase in monomer concentration as well as with the chelate concentration and reaches maximum values (152.2%) at $[MMA] = 25.7 \times 10^{-2}$ mol/L; and (114.0%) at $[EMA] = 15.9 \times 10^{-2}$ mol/L. Beyond these concentrations, the extent of grafting decreases. This is due to the fact that at higher monomer concentrations, homopolymerization becomes the preferred process. Similarly, there is an optimum concentration of $Fe(acac)_3$ at which the percentage of grafting is maximum. This result may indicate that, at higher concentration, $Fe^{III}(acac)_3$ participates in the termination of the growing grafted chain by Process (7). Tables 1 and 2 show that maximum grafting of MMA and EMA occurs at chelate concentrations of 2.8×10^{-3} and 4.9×10^{-3} mol/L, respectively.

Effect of Nitric Acid on Percent Grafting

In all our previous studies [7-9] it was observed that a small amount of nitric acid catalyzes the graft copolymerization of vinyl monomers onto wool. In the present study nitric acid is also found to influence grafting. Tables 1 and 2 show that maximum grafting of MMA and EMA occurs at $[HNO_3] = 16.0 \times 10^{-2}$ and 24.0×10^{-2} mol/L, respectively. A further increase in the concentration of the acid leads to a decrease in grafting. It appears that at lower concentrations nitric acid swells the wool fiber and increases the accessibility of functional groups toward grafting. At higher concentrations nitric acid may oxidize the $Fe^{II}(acac)_2$ formed in Process (1) to produce Fe^{3+} which terminates the growing grafted chains.

$Fe(acac)_3$ is known to decompose at 179°C. However, it is observed that maximum grafting of MMA and EMA occurs at 65°C, much below the decomposition temperature of the chelate. This indicates that monomers enter into complex formation with $Fe(acac)_3$ and the decomposition of Complex (I) is facilitated at lower temperatures to generate free radical species. Such complex formation between $Fe(acac)_3$ and vinyl

TABLE 1. Effect of Concentration of $Fe(acac)_3$, MMA, and Nitric Acid, Temperature, and Time on Grafting of Methyl Methacrylate onto Wool[a]

No.	$[Fe(acac)] \times 10^3$ mol/L	$[HNO_3] \times 10^2$ mol/L	$[MMA] \times 10^2$ mol/L	Temperature (°C)	Time (min)	% G	% E
1	1.4	24.0	23.5	65	180	107.0	21.4
2	2.8	"	"	"	"	139.2	27.8
3	4.2	"	"	"	"	87.0	17.4
4	7.0	"	"	"	"	83.0	16.6
5	2.8	8.0	"	"	"	87.0	17.4
6	"	16.0	"	"	"	140.0	28.0
7	"	28.0	"	"	"	132.7	26.5
8	"	40.0	"	"	"	122.0	24.4
9	"	16.0	14.1	"	"	71.0	23.7

10	″	″	18.8	″	″	92.0	23.0
11	″	″	25.7	″	″	152.2	27.6
12	″	″	28.2	″	″	86.2	14.2
13	″	″	25.7	60	″	62.0	12.4
14	″	″	″	70	″	130.2	26.0
15	″	″	″	75	″	100.2	20.4
16	″	″	″	65	60	74.0	13.4
17	″	″	″	″	90	100.2	18.5
18	″	″	″	″	120	120.2	21.8
19	″	″	″	″	150	137.2	24.9

[a]Wool = 1 g, water = 200 mL.

TABLE 2. Effect of Concentration of $Fe(acac)_3$, EMA, and Nitric Acid, Temperature, and Time on Grafting of Ethyl Methacrylate onto Wool[a]

No.	$[Fe(acac)_3] \times 10^3$ mol/L	$[HNO_3] \times 10^2$ mol/L	$[EMA] \times 10^2$ mol/L	Temperature (°C)	Time (min)	% G	% E
1	2.8	24.0	13.6	65	180	49.0	16.3
2	4.2	''	''	''	''	77.0	25.6
3	4.9	''	''	''	''	99.0	33.0
4	7.0	''	''	''	''	61.0	20.3
5	4.9	16.0	''	''	''	76.2	25.4
6	''	20.0	''	''	''	85.2	28.4
7	''	28.0	''	''	''	93.2	31.0
8	''	32.0	''	''	''	61.2	20.5
9	''	24.0	9.1	''	''	85.0	42.5

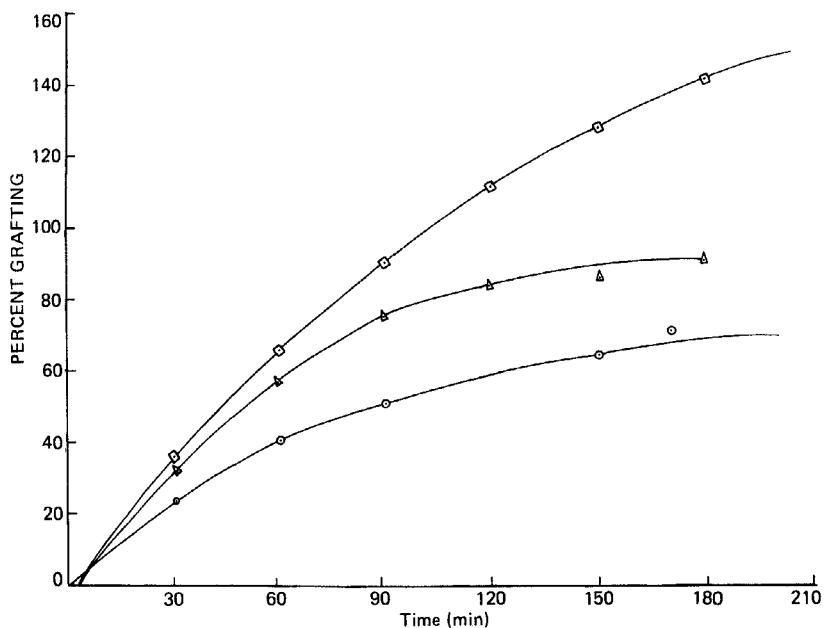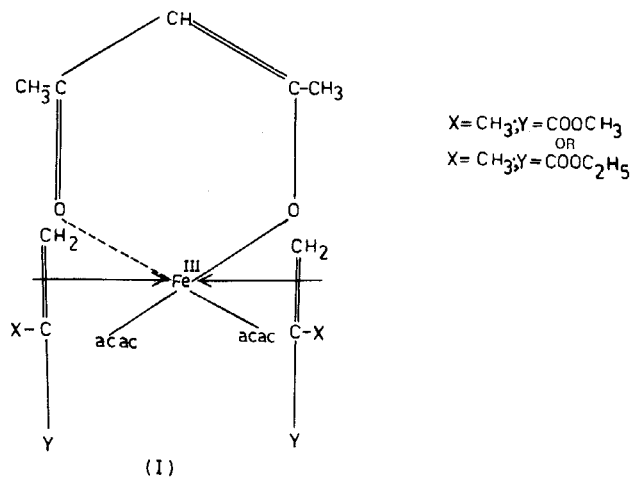|							
10	"	"	15.9	"	"	114.0	32.5
11	"	"	18.2	"	"	94.0	23.5
12	"	"	15.9	50	"	14.2	4.7
13	"	"	"	55	"	53.0	17.6
14	"	"	"	60	"	62.0	20.6
15	"	"	"	70	"	95.0	31.6
16	"	"	"	65	60	53.0	15.1
17	"	"	"	"	90	75.0	21.4
18	"	"	"	"	120	87.2	24.9
19	"	"	"	"	150	100.2	29.1

^{a}Wool = 1 g, water = 200 mL.

$$X = CH_3; Y = COOCH_3$$
OR
$$X = CH_3; Y = COOC_2H_5$$

(I)

FIG. 1. Plot of percent grafting vs time. Reaction conditions: wool = 1 g, water = 200 mL, $[HNO_3]$ = 16.2 × 10^{-2} mol/L, $[Fe(acac)_3]$ = 28 × 10^{-3} mol/L, 65°C, [MMA] = 23.5 × 10^{-2} mol/L, (□), 18.8 × 10^{-2} mol/L (△), 14.1 × 10^{-2} mol/L (⊙).

monomers during grafting onto cellulose was established from spec-troscopic studies by Misra et al. [16].

If complex formation occurs between the metal chelate and mono-mer, then from the consideration of electronic and steric requirement of MMA and EMA, complex formation with MMA is expected to occur more readily than with EMA. This may explain why MMA shows greater reactivity than EMA toward graft copolymerization.

Effect of Monomer Concentration upon Rate of Grafting (R_p)

Figures 1 and 2 show that percent grafting of MMA and EMA in-creases steadily with time. Maximum grafting was obtained within 180 min. Percent grafting of each monomer was plotted against time as a function of total initial monomer concentration. By extrapolating
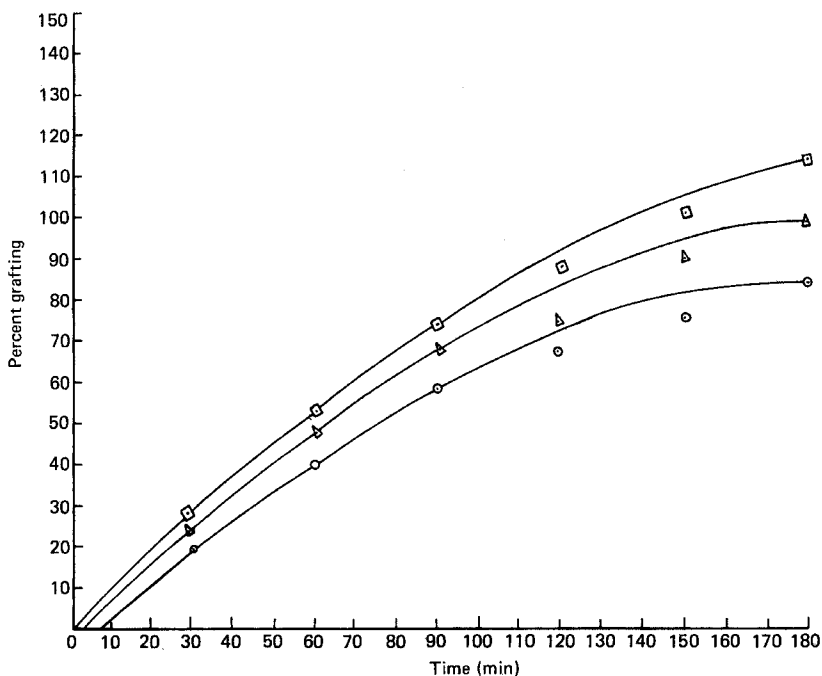

FIG. 2. Plot of percent grafting vs time. Reaction conditions: wool = 1 g, water = 200 mL, $[HNO_3]$ = 240 × 10^{-2} mol/L, $[Fe(acac)_3]$ = 4.9 × 10^{-3} mol/L, 65°C, [EMA] = 15.9 × 10^{-2} mol/L (▣), 13.6 × 10^{-2} mol/L (▵), 9.1 × 10^{-2} mol/L (☉).

TABLE 3. Rate of Grafting (R_p) and Induction Period (I_p) of MMA[a]

No.	Initial concentration of MMA (mol/L)	Initial rate of grafting grafting (R_p) (% min)	Induction period (I_p) (min)
1	14.1×10^{-2}	0.32	0
2	18.8×10^{-2}	0.60	2
3	23.5×10^{-2}	0.87	3

[a]Wool = 1 g, water = 200 mL, 65°C, $[HNO_3]$ = 16.0×10^{-2} mol/L, $[Fe(acac)_3]$ = 2.8×10^{-3} mol/L.

TABLE 4. Rate of Grafting (R_p) and Induction Period (I_p) of EMA[a]

No.	Initial concentration of EMA (mol/L)	Initial rate of grafting grafting (R_p) (% min)	Induction period (I_p) (min)
1	9.1×10^{-2}	0.55	7
2	13.6×10^{-2}	0.71	2
3	15.9×10^{-2}	0.80	0

[a]Wool = 1 g, water = 200 mL, 65°C, $[HNO_3]$ = 24.0×10^{-2} mol/L, $[Fe(acac)_3]$ = 4.9×10^{-3} mol/L.

the curves to the time axis, induction periods (I_p) as a function of total monomer concentration were determined. From the slopes in the initial stages of reaction, R_p values were evaluated. Tables 3 and 4 show the effect of monomer concentration upon R_p and I_p. It is apparent from the tables that R_p of MMA attains a maximum value of 0.87%/min at [MMA] = 23.5×10^{-2} mol/L. With EMA the maximum rate of grafting (R_p = 0.80%/min) is obtained at [EMA] = 15.9×10^{-2} mol/L.

The higher rate of grafting shown by MMA than by EMA under optimum conditions may be explained by considering the "polymerizability" of these two monomers. The polymerizability ($k_p/k_t^{1/2}$) of MMA [17] and EMA [18] as obtained from the literature are 0.056 and 0.046, respectively. The higher $k_p/k_t^{1/2}$ value of MMA over EMA indicates that the given amount of chelate in a given time will produce more MMA polymer than EMA. In other words, MMA will produce more grafted

polymeric chains which will generate additional active sites by Process (4) on wool than EMA. As a consequence, a higher percentage of grafting will be obtained with MMA. Besides, MMA, being more efficient than EMA in the formation of Complex (I), is more reactive than EMA toward graft copolymerization. Thus, it is concluded that $Fe^{III}(acac)_3$ is capable of producing grafts of PMMA and PEMA on wool and that MMA is more reactive than EMA toward graft copolymerization.

ACKNOWLEDGMENTS

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