Grafting onto Wool. XXIII. Graft Copolymerization of Methyl Methacrylate by Use of Chromium Acetyl Acetonate–Perchloric Acid System: Effect of Tertiary Butyl Hydroperoxide

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Synopsis

Methyl methacrylate (MMA) has been graft copolymerized onto Himachali wool in an aqueous medium by using chromium acetyl acetonate in the presence of perchloric acid at 45, 55, 65, and 75°C for various reaction periods. Percentage of grafting has been determined as functions of various reaction variables. Tertiary butyl hydroperoxide (TBHP) was found to influence grafting of MMA. Rate of grafting (R_p) and induction period (I_p) of MMA towards graft copolymerization were determined as function of total initial monomer concentrations. In the absence of TBHP, R_p does not change markedly with the increase in monomer concentration. When the graft copolymerization was carried out in the presence of TBHP, an increase in R_p and a decrease in I_p were observed.

INTRODUCTION

The acetylacetonates of transition metals are called as β-diketonates. Bamford et al.[1,2] have extensively studied the use of metal acetylacetonates in vinyl polymerization. However, the uses of metal acetylacetonates as initiators of graft copolymerization of vinyl monomer onto natural as well as synthetic substrates are limited. A variety of initiating systems are known to effect grafting of vinyl monomers onto wool. One of the major problems in wool grafting is the formation of a large amount of homopolymer along with the graft, the separation of which poses a serious problem. In order to overcome this difficulty, attempts have been made to find newer initiating systems that would minimize the formation of homopolymer.

In our laboratory it has been possible to effect grafting of various vinyl monomers onto wool in the presence of (i) ceric ion,[3] (ii) ceric-amine system,[4] (iii) Fenton's reagent,[5] (iv) FAS–KPS system,[6] (v) FAS–TBHP system,[7] and BPO[8] as initiators. Use of metal chelates as graft initiators has not been extensively studied. Recently, we have initiated a comprehensive research program on the utilization of a variety of metal chelates as initiators of graft copolymerization.[9–14]

Tripathy et al.[15] have used Mn(acac)$_3$ in graft copolymerization of MMA onto cellulose. Misra et al.[9,10] have used a number of metal acetylacetonates as initiators of graft copolymerization of vinyl monomers onto cellulose. Recently, Misra et al. have also used VO(acac)$_2$:[11,12] and Mn(acac)$_3$[13,14] for graft copolymerization of different vinyl monomers onto wool fiber. In the present article, we report grafting of MMA onto wool using Cr(acac)$_3$ in the

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presence of perchloric acid as initiator. The effect of TBHP on the rate of grafting of MMA has been studied.

EXPERIMENTAL

Preparation of Chromium Acetylacetonate

The chromium acetylacetonate was prepared by the method reported in inorganic synthesis,[16] mp 212°C (lit. 216°C) and elemental analysis:
ANAL. Calcd: C, 51.57%; H, 6.06%. Found: C, 51.05%; H, 6.40%

Materials and Methods

Purification of Himachali wool has been described by Misra and Chandel.[3] Methyl methacrylate (BDH) was washed with 5% NaOH solution and dried over anhydrous sodium sulphate. The dried monomer was then distilled and the middle fraction was used. Perchloric acid (E. Merck) 70% and TBHP (Koch Light) were used as received. Nitrogen gas was purified by passing through alkaline pyrogallol solution.

Graft Copolymerization

Purified Himachali wool fiber (1.0 g) was dispersed in 200 mL of deaerated water in a three-necked flask. To this dispersion a known quantity of chromium acetylacetonate dissolved in known volume of perchloric acid was added. Prior to the addition of monomer, nitrogen was passed through the reaction flask for 30 min, and then a continuous supply of nitrogen was maintained throughout the reaction period. Vinyl monomer was added dropwise to the reaction flask. The copolymerization reactions were carried out under stirring at different temperatures for various reaction period.

After the reaction was over, the reaction mixture was filtered, and the residue extracted with acetone and benzene for 48 h for the removal of homopolymer. The grafted material was dried until constant weight was obtained. From the increase in weight of original wool fiber, the percentage of grafting was calculated as follows:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 denote, respectively, the weights of wool fiber and grafted wool fiber after solvent extraction.

The rate of grafting (R_p) at initial stages of reaction and the induction period (I_p) for different total initial concentrations of MMA were determined from the slopes of the plots of percent grafting versus time as shown in Figure 1.

Evidence of Grafting

(a) The infrared spectrum of W-g-poly(MMA) shows a strong band at 1730 cm^{-1} whereas the infrared spectrum of pure wool fiber showed strong absorption at 1650 cm^{-1}.
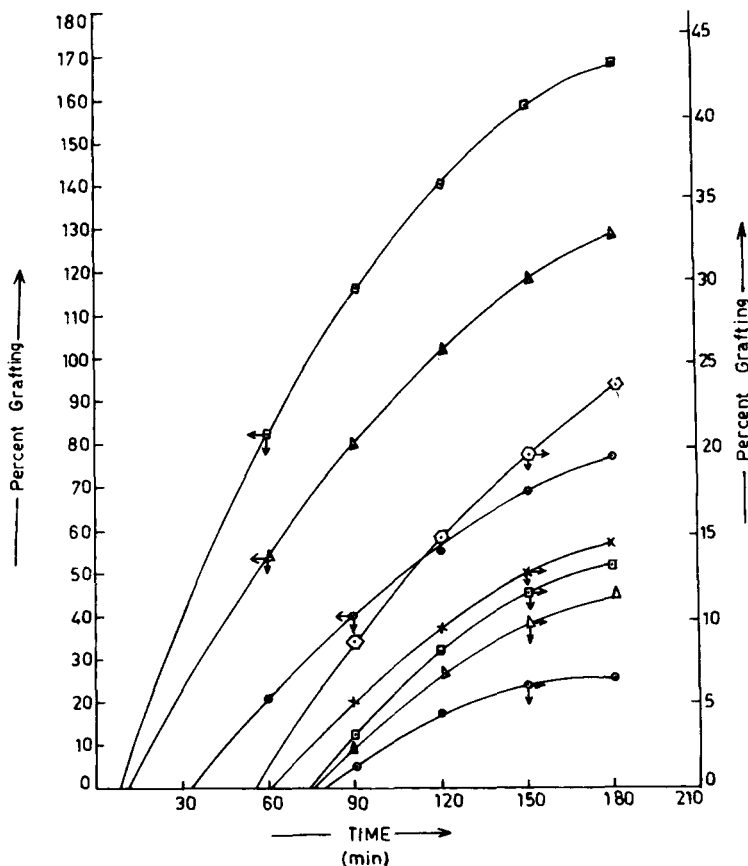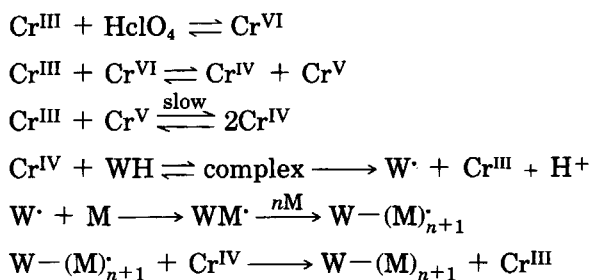
Fig. 1. Effect of [M] on percent grafting in absence of TBHP (ㄴ): temperature = 65°C; [Cr(acac)$_3$] = 7.16 × 10^{-3} mol/L; [HClO$_4$] = 25.2 × 10^{-2} mol/L; in presence of TBHP (ㄱ):[TBHP] = 2.5 × 10^{-2} mol/L; [Cr(acac)$_3$] = 8.88 × 10^{-3} mol/L; temperature = 65°C; [HClO$_4$] = 25.2 × 10^{-2} mol/L. [MMA] (mol/L): (⊚) 51.7 × 10^{-2}; (X) 42.3 × 10^{-2}; (⊡) 32.9 × 10^{-2}; (△) 23.5 × 10^{-2}; (⊙) 14.1 × 10^{-2}.

(b) Grafted wool samples were hydrolysed with a mixture of benzene–5% KOH in 1:1 ratio for 12 h. Grafted wool formed opaque emulsion. The emulsion was acidified with concentrated HCl. Benzene layer was taken out, and polymer was precipitated with petroleum ether. The isolated polymer was characterized by IR spectroscopy as PMMA.

(c) Ninhydrin test for residual amino acid: The grafted polymer obtained by alkaline hydrolysis was thoroughly washed with water and dried. The dried polymer was dissolved in acetone, and to it a drop of ninhydrin in acetone solution was added. There was no violet coloration as such. However, violet color was developed on a filter paper soaked in the above solution and dried at 90°C. The positive ninhydrine test indicates the presence of residual amino acid groups in the polymer isolated from the graft. This constitutes additional evidence for the formation of graft copolymer.

RESULTS AND DISCUSSION

Previous studies have indicated that not all the metal chelates are equally effective in effecting graft copolymerization. Both $Fe(acac)_3$ and $Mn(acac)_3$ were found to produce significant grafting of vinyl monomers onto cellulose[9,10] and wool.[13,14] Chromium acetylacetonate, however, behave quite differently towards grafting onto wool fiber. The present study reveals that $Cr^{III}(acac)_3$ did not produce either homopolymerization or grafting of MMA. However, when perchloric acid was added in small amounts, grafting occurred. This may indicate that $Cr(acac)_3$ is not capable of generating free radicals to afford grafting. Cr^{IV}, on the other hand, is known to undergo series of electron transfer reactions to produce free radical species capable of effecting graft copolymerization.[17,18] The following mechanism is suggested to explain grafting of MMA onto wool in the presence of $Cr(acac)_3$–$HClO_4$ system:

$$Cr^{III} + HclO_4 \rightleftharpoons Cr^{VI}$$

$$Cr^{III} + Cr^{VI} \rightleftharpoons Cr^{IV} + Cr^{V}$$

$$Cr^{III} + Cr^{V} \xrightleftharpoons{slow} 2Cr^{IV}$$

$$Cr^{IV} + WH \rightleftharpoons complex \longrightarrow W^{\cdot} + Cr^{III} + H^{+}$$

$$W^{\cdot} + M \longrightarrow WM^{\cdot} \xrightarrow{nM} W-(M)^{\cdot}_{n+1}$$

$$W-(M)^{\cdot}_{n+1} + Cr^{IV} \longrightarrow W-(M)_{n+1} + Cr^{III}$$

Role of Perchloric Acid and TBHP

The above mechanism explains the role of perchloric acid in graft copolymerization. $HClO_4$ being a highly oxidizing acid readily converts $Cr^{III}(acac)_3$ into Cr^{VI} species which interacts with $Cr^{III}(acac)_3$ to produce Cr^{IV} species, which forms a complex with the functional groups of wool fiber. The complex then undergoes one electron transfer to produce wool macroradical ($W^{\cdot}$), where grafting of MMA occurs. This is further supported by the fact that, in the presence of stronger oxidizing agent such as TBHP, grafting is tremendously enhanced.

A perusal of Table I shows that, in the presence of TBHP, percentage of grafting increases tremendously. Maximum percentage grafting was obtained at $[TBHP] = 2.5 \times 10^{-2}$ mol/L. Tremendous increase in percent grafting in the presence of TBHP may indicate that TBHP enters into complex formation with $Cr^{III}(acac)_3$ and the complex decomposes to produce additional radical species in the following manner:

$$Cr(acac)_3 + TBHP \rightleftharpoons complex \longrightarrow t\text{-}BuOO^{\cdot} + t\text{-}BuO^{\cdot} + \text{other products}$$
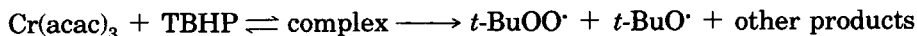
The additional free radicals formed via complex formation may be responsible for the tremendous enhancement of grafting in the presence of TBHP. It is well known that decomposition of tertiary butyl hydroperoxide is catalyzed by various transition metal ions.[19] Richardson[20] observed that the

TABLE I
Effect of Concentration of Monomer, Metal Chelate, t-Butyl Hydroperoxide, Temperature, and Time on Grafting of Methyl Methacrylate[a]

Sample no.	Temp. (°C)	Time (min)	[MMA] × 10² (mol/L)	[Cr(acac)₃] × 10³ (mol/L)	[TBHP] × 10² (mol/L)	% grafting
1	55	180	23.5	7.16	—	11.2
2	55	180	23.5	5.73	—	9.0
3	55	180	23.5	8.59	—	8.5
4	55	180	23.5	7.59	2.5	40.5
5	55	180	23.5	7.59	5.0	23.8
6	55	180	23.5	6.30	2.5	12.0
7	55	180	23.5	8.88	2.5	49.5
8	55	180	23.5	10.17	2.5	44.1
9	45	180	23.5	8.88	2.5	34.0
10	65	180	23.5	8.88	2.5	129.0
11	75	180	23.5	8.88	2.5	109.0
12	65	120	23.5	8.88	2.5	102.0
13	65	150	23.5	8.88	2.5	118.0
14	65	210	23.5	8.88	2.5	75.5
15	65	180	14.1	8.88	2.5	77.0
16	65	180	32.9	8.88	2.5	169.0
17	65	180	42.3	8.88	2.5	111.5

[a] Wool = 1 g; water = 200 mL; [HClO₄] = 25.2 × 10⁻² mol/L.

decomposition of TBHP is enhanced in the presence of Co^{III} ions. This was explained by a mechanism based on Co^{III}–TBHP complex formation. A free radical mechanism involving prior complex formation between Cu^{II} and TBHP for metal-ion-catalyzed decomposition of hydroperoxide has also been proposed by Richardson.[21]

Effect of Monomer Concentration upon R_p and I_p

Figure 1 describes the effect of concentration of monomer upon percent grafting of MMA in the presence of Cr(acac)₃–HClO₄ and Cr(acac)₃–HClO₄–TBHP systems, respectively. It is apparent from Figure 1 that the percentage of grafting increases with monomer concentration. A maximum of 23.5% and 169% grafting was obtained at [MMA] = 51.7 × 10⁻² mol/L and 32.9 × 10⁻² mol/L in the absence and presence of TBHP, respectively.

It is further observed from Table II that, in the absence of TBHP, R_p does not change significantly with increase in monomer concentration, while I_p decreases with increasing monomer concentration, indicating that at higher monomer concentration grafting occurs preferentially. At higher monomer concentrations both grafting and homopolymerization are enhanced, but it seems that homopolymerization prevails over grafting. In the presence of TBHP (Table II), there is a significant increase in R_p with increase in monomer concentration with a consequent decrease in I_p. This may indicate that, in the presence of TBHP, complex formation between TBHP and monomer is enhanced. The resulting complex decomposes to produce additional free radical species which promotes grafting.

TABLE II

Effect of Total Initial Monomer Concentration of MMA on Rate of Grafting (R_p) and Induction Period (I_p)

Initial monomer concn (mol/L)	[TBHP] × 10² (mol/L)	Initial grafting rate (R_p)%/min		Induction period (I_p) (min)	
		In absence of TBHP[a]	In presence of TBHP[b]	In absence of TBHP[a]	In presence of TBHP[b]
14.1 × 10⁻²	2.5	0.11	0.60	78.0	33.0
23.5 × 10⁻²	2.5	0.12	0.87	75.0	13.5
32.9 × 10⁻²	2.5	0.14	1.05	73.5	10.5
42.3 × 10⁻²	—	0.15	—	60.0	—
51.7 × 10⁻²	—	0.19	—	55.5	—

[a] Temperature = 65°C; [Cr(acac)$_3$] = 7.16 × 10⁻³ mol/L; [HClO$_4$] = 25.2 × 10⁻² mol/L.
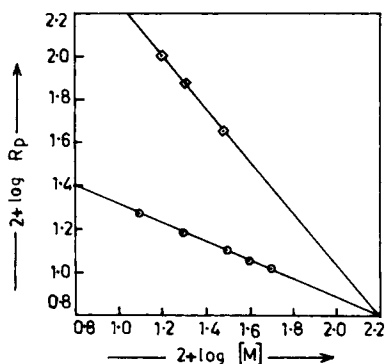[b] Temperature = 65°C; [Cr(acac)$_3$] = 8.88 × 10⁻³ mol/L; [HClO$_4$] = 25.2 × 10⁻² mol/L.

Fig. 2. Plot of log R_p vs. log [M] in the absence [⊙] and in the presence of TBHP [▣].

Figure 2 shows plots of log R_p vs. log [M] in the absence and presence of TBHP. From these plots monomer exponents were determined, and it is observed that, in the absence and presence of TBHP, the monomer exponents are 1.0 and 0.5, respectively. The low value (0.5) for the monomer exponent in the presence of TBHP indicates that monomer is involved in complex formation with TBHP. Walling et al.[22] found good evidence of complex formation between styrene and TBHP.

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