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Grafting onto Wool. XXVI. Graft Copolymerization of Vinyl Monomers by Use of $\text{Cr}(\text{acac})_3$ -TBHP as Initiator

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ABSTRACT

Methyl methacrylate (MMA), methyl acrylate (MA), and ethyl acrylate (EA) have been graft copolymerized onto wool fiber in aqueous medium using the chromium acetylacetonate-tertiary-butyl hydroperoxide ($\text{Cr}(\text{acac})_3$ -TBHP) system as initiator. The percentage of grafting has been determined as a function of the concentrations of monomer, chelate, and TBHP, and the time and temperature under optimum conditions. MMA produced a maximum grafting of 119.8%, MA produced a maximum grafting of 56%, while EA afforded maximum grafting to the extent of 41.9%. Different vinyl monomers were found to follow the following reactivity order toward grafting onto wool fiber in the presence of the $\text{Cr}(\text{acac})_3$ -TBHP system: $\text{MMA} > \text{MA} > \text{EA}$.

INTRODUCTION

Synthetic as well as natural polymers can be modified by graft copolymerization. During graft copolymerization, a new polymeric chain is anchored to another preformed polymeric backbone by covalent bonds. Many attempts have been made in recent years to modify wool

fiber by the graft copolymerization technique. One of the major problems in wool grafting is the formation of homopolymer which is difficult to separate. It has been possible to effect grafting of a variety of vinyl monomers onto wool in the presence of 1) ceric ion [1], 2) ceric amine [2, 3], 3) Fenton's reagent [4], and 4) radical initiator [5] in our laboratory.

In order to find newer initiating systems, we have studied the suitability of metal chelates as graft initiators. The ability of metal chelates to produce free radicals when heated was first pointed out by Arnett and Mendelsohn [6]. They observed that, at 100°C, some chelates are able to initiate the polymerization of styrene. Kastning et al. [7] reported that simple acetyl acetonates of Co^{III} and Mn^{III} are most active initiators. Bamford et al. [8] have made extensive studies on vinyl polymerization by using a variety of metal chelates as initiators. Nandi et al. [9] were able to effect the polymerization of MMA in the presence of $\text{Fe}(\text{acac})_3$. Relatively less attention has been paid to the utilization of metal chelates as graft initiators. Recently Misra et al. have used $\text{Mn}(\text{acac})_3$ [10, 11] and $\text{VO}(\text{acac})_2$ [12, 13] in the graft copolymerization of a number of vinyl monomers onto wool fiber. Nayak et al. [14] were able to effect grafting of MMA onto wool fiber in the presence of hexavalent chromium.

Use of TBHP in conjunction with metal acetylacetonates in vinyl polymerization has been reported. Osawa and Shibamiya [15] have reported the polymerization of MMA by $\text{Co}(\text{II})$ or $\text{Co}(\text{III})$ acetylacetonates-tert-butyl hydroperoxide or -dioxane hydroperoxide systems. They observed that the degree of polymerization increases markedly with an increase in hydroperoxide concentration. Indictor and Linder [16] reported that $\text{Co}(\text{II})$, $\text{Co}(\text{III})$, $\text{Cr}(\text{III})$, and $\text{Fe}(\text{III})$ acetyl acetonates in the presence of TBHP can be used as initiators in effecting styrene polymerization.

Shahani and Indictor [17] have recently studied the polymerization of MMA initiated by TBHP and $\text{Cu}(\text{acac})_2$ in DMSO solution. They earlier studied the effect of several metal acetylacetonates present in small amounts ($\approx 10^{-4}$ M) on the TBHP-initiated polymerization of MMA in 1-chlorooctane and benzene media [18]. It was shown that in 1-chlorooctane the $\text{Cu}(\text{acac})_2$ exerted a catalytic effect on the decomposition of TBHP as well as on the polymerization of MMA. In benzene, however, the catalytic effect was less.

In the present article we report the grafting of MMA, MA, and EA onto wool in the presence of the $\text{Cr}(\text{acac})_3$ -TBHP system as initiator. The percentage of grafting (G) and percent efficiency (E) were calculated by

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

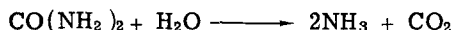
$$\% E = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1 , W_2 , and W_3 denote the weight of wool, weight of grafted wool after extraction with solvent, and the weight of vinyl monomer added, respectively. The percentage of grafting and percent efficiency were expressed as functions of various reaction variables, and the results are presented in Tables 1, 2, and 3.

EXPERIMENTAL

Preparation of Chromium Acetylacetonate

Preparation of the chromium chelate involved the following steps. Synthesis was carried out by the method described in Inorganic Synthesis [19].



To a solution of 2.66 g of chromium(III) chloride-6-hydrate in 100 mL of water, 20 g of urea and 6 g of acetylacetone were added. The reaction mixture was covered with a watch glass and heated overnight on a steam bath. As urea hydrolyzed to release ammonia, deep maroon, plate-like crystals formed. They were removed by suction filtration and dried in air.

The crude, air-dried compound was dissolved in 20 mL of hot benzene, and 75 mL of hot petroleum ether was added slowly. The mixture was cooled to room temperature, chilled in a mixture of ice and salt, and filtered. The crystals were air dried, mp 212°C.

Elemental analysis: Calculated, 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 [1]. Methyl methacrylate (BDH), methyl acrylate (BDH), and ethyl acrylate (BDH) were washed with 5% NaOH solution, then dried over anhydrous sodium sulfate. The dried monomer was then distilled, and the middle fraction was used. Nitric acid (BDH) of known strength was used. TBHP (Koch Light) was used as received.

Nitrogen gas was purified by passing it through an alkaline pyrogallol solution.

TABLE 1. Effect of Concentration of MMA, Cr(acac)₃, TBHP, Temperature, and Time on Percent Grafting of Methyl Methacrylate onto Wool^a

No.	Temperature (°C)	Time (min)	[MMA] × 10 ² mol/L	[Cr(acac) ₃] × 10 ³ mol/L	[TBHP] × 10 ² mol/L	% Grafting	% Efficiency
1	55	180	23.5	7.3	2.5	19.0	4.04
2	"	"	"	"	5.0	8.2	1.74
3	"	"	"	"	10.0	7.0	1.48
4	"	"	"	4.29	2.5	24.2	5.14
5	"	"	"	5.87	"	58.0	12.34
6	"	"	"	8.88	"	18.0	3.82
7	"	"	14.1	5.87	"	26.0	9.21
8	"	"	32.9	"	"	119.0	18.08
9	"	"	42.3	"	"	111.5	13.17
10	"	120	32.9	"	"	91.3	13.87
11	"	150	"	"	"	107.0	16.26
12	"	210	"	"	"	67.7	10.28
13	45	180	"	"	"	75.2	11.42
14	65	"	"	"	"	119.8	18.20
15	75	"	"	"	"	101.5	15.42
16	65	"	"	"	—	25.8	3.93

^aWool = 1 g, water = 200 mL, [HNO₃] = 16.0 × 10⁻² mol/L.

TABLE 2. Effect of Concentration of MA, Cr(acac)₃, TBHP, Temperature, and Time on Percent Grafting of Methyl Acrylate onto Wool^a

No.	Temperature (°C)	Time (min)	[MA] × 10 ² mol/L	[Cr(acac) ₃] × 10 ³ mol/L	[TBHP] × 10 ² mol/L	% Grafting	% Efficiency
1	55	180	27.6	7.44	5.0	6.0	1.26
2	"	"	"	"	10.0	8.5	1.78
3	"	"	"	"	15.0	6.5	1.36
4	"	"	"	4.72	10.0	11.0	2.31
5	"	"	"	6.01	"	18.0	3.78
6	"	"	"	8.88	"	8.0	1.68
7	45	"	"	6.01	"	11.0	2.31
8	65	"	"	"	"	43.0	9.05
9	75	"	"	"	"	31.0	6.52
10	65	120	"	"	"	13.0	2.73
11	"	150	"	"	"	17.0	3.57
12	"	210	"	"	"	21.0	4.42
13	"	180	16.5	"	"	29.0	10.17
14	"	"	38.6	"	"	56.0	8.42
15	"	"	49.7	"	"	25.0	2.92
16	"	"	38.6	"	—	18.0	2.70

^aWool = 1 g, water = 200 mL, [HNO₃] = 24.0 × 10⁻² mol/L.

TABLE 3. Effect of Concentration of EA, Cr(acac)₃, TBHP, Temperature, and Time on Percent Grafting of Ethyl Acrylate onto Wool^a

No.	Temperature (°C)	Time (min)	[EA] × 10 ² mol/L	[Cr(acac) ₃] × 10 ³ mol/L	[TBHP] × 10 ² mol/L	% Grafting	% Efficiency
1	55	180	23.0	7.87	2.5	6.8	1.47
2	"	"	"	"	5.00	9.2	2.00
3	"	"	"	"	10.00	7.5	1.63
4	"	"	"	6.44	5.00	6.5	1.41
5	"	"	"	9.16	"	5.5	1.19
6	45	"	"	7.87	"	8.0	1.73
7	65	"	"	"	"	38.5	8.36
8	75	"	"	"	"	34.0	7.39
9	65	120	"	"	"	18.0	3.91
10	"	150	"	"	"	31.5	6.84
11	"	210	"	"	"	24.0	5.21
12	"	180	13.8	"	"	19.2	6.95
13	"	"	32.2	"	"	41.9	6.39
14	"	"	41.4	"	"	28.0	3.38
15	"	"	32.2	"	—	14.0	2.17

^aWool = 1 g, water = 200 mL, [HNO₃] = 24.0 × 10⁻² mol/L.

Graft Copolymerization

One gram of purified Himachali wool fiber was dispersed in 200 mL of deaerated water in a three-necked flask. To this dispersion a known quantity of metal chelate dissolved in a known strength of nitric 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 periods. After the reaction was over, the reaction mixture was filtered. The residue was extracted with acetone and benzene separately for 48 h for the removal of homopolymer.

Evidence of Grafting

a) The infrared spectrum of wool-g-poly(MMA), wool-g-poly(MA), and wool-g-poly(EA) showed strong absorption bands at 1730, 1720, and 1725 cm^{-1} , respectively, whereas the IR spectrum of pure wool fiber showed strong absorption at 1650 cm^{-1} .

b) The physical mixture of wool and benzene solutions of PMMA, PMA, and PEA were prepared by stirring 1.0 g of wool in 100 mL of benzene solution of PMMA, PMA, and PEA for 24 h. The wool fiber was separated by filtration, and the residue was subjected to extraction by benzene for 24 h and dried to constant weight. No change in the weight of the wool was observed. This indicates that the homopolymer is quantitatively removed from a physical mixture of wool and homopolymer by extraction with benzene.

c) Grafted wool samples were hydrolyzed in a mixture of benzene-5% potassium hydroxide in a 1:1 ratio for 12 h. The grafted wool formed an opaque emulsion. The emulsion was acidified with concentrated HCl. The benzene layer was taken out, and the polymer was precipitated with petroleum ether. The grafted polymer was characterized by IR spectroscopy as PMMA, PMA, and PEA.

Ninhydrin Test for Residual Amino Acids

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

Examination of scanning electron micrographs of wool-g-poly(MMA) (Fig. 1), wool-g-poly(MA) (Fig. 2), wool-g-poly(EA) (Fig. 3) indicates that, upon grafting, a considerable amount of polymer is deposited on the wool surface.

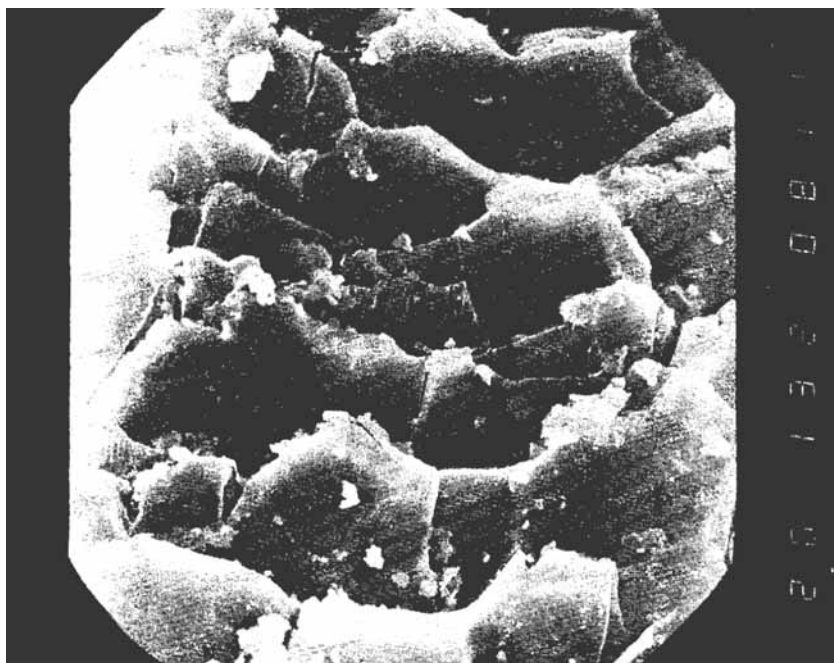


FIG. 1. Scanning electron micrograph of wool-g-poly(MMA) (1300 \times).

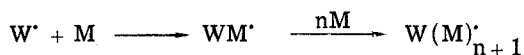
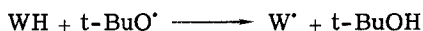
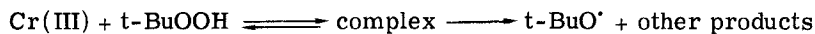
RESULTS AND DISCUSSION

Stannett and Mesrobian [20] have studied the decomposition of hydroperoxides in different solvents. They observed that the rate of decomposition of cumene hydroperoxide in xylene is quite slow even at 110°C. When styrene monomer was added to the solution, however, the decomposition is greatly accelerated. Richardson [21] observed that in the presence of Co(III) ions, decomposition of TBHP is greatly enhanced. This was explained by a mechanism based on Co(III)-TBHP complex formation. He further observed that this complex decomposes to generate t-BuOO \cdot and t-BuO \cdot radicals. 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 [22].

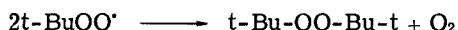
It is proposed that Cr(III) first enters into complex formation with TBHP, and that the complex subsequently decomposes to generate free-radical species which are responsible for grafting:



FIG. 2. Scanning electron micrograph of wool-g-poly(MA) (1800 \times).



The above postulated mechanism finds support in the fact that grafting of MMA, MA, and EA is tremendously enhanced in the presence of TBHP (Tables 1, 2, and 3). It is observed that there exists a critical concentration of TBHP at which the grafting is maximum. A further increase in the concentration of TBHP reduces the percentage of grafting. This is presumably due to the depletion of chelate. At a higher concentration, TBHP also acts as a hydrogen donor to reduce the concentration of the free-radical species:



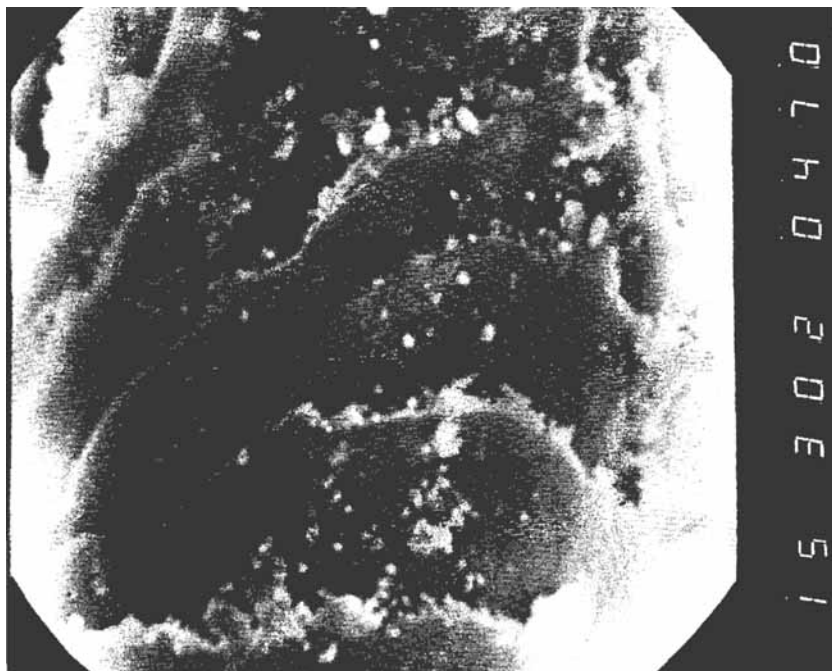


FIG. 3. Scanning electron micrograph of wool-g-poly(EA) (3000 \times).

Effect of Chelate Concentration

Tables 1, 2, and 3 show that maximum grafting occurs at chelate concentrations of 5.87×10^{-3} mol/L with MMA, 6.01×10^{-3} mol/L with MA, and 7.87×10^{-3} mol/L with EA. At higher concentrations, chelate participates in the termination of the growing polymeric chain, with a consequent decrease in percent grafting.

Effect of Time and Temperature

Maximum grafting of vinyl monomers occurs within 180 min (Tables 1, 2, and 3). Beyond this reaction period, grafting remains essentially constant. It is also observed from Tables 1, 2, and 3 that the percent grafting increases with an increase in temperature and reaches a maximum value at 65°C. At higher temperatures percent grafting decreases because various termination reactions are accelerated.

TABLE 4. Solubility Behavior of Ungrafted and Grafted Wool

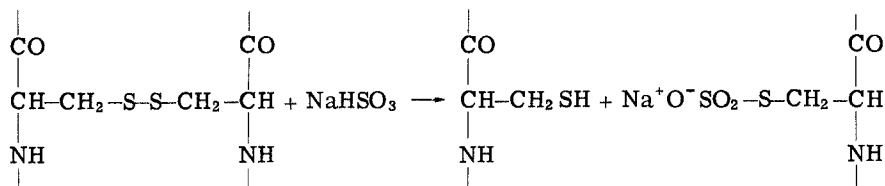
No.	Sample	% Solubility			
		0.1 N NaOH	4 M HCl	Oxidizing solvent	Urea-bisulfite
1	Wool	20.6	10.7	12.5	12.9
2	W-g-PMMA ^a	13.0	6.0	8.0	6.5
3	W-g-PMA ^b	18.0	7.5	7.0	8.0
4	W-g-PEA ^c	10.0	8.0	9.5	7.5

^aRefers to Sample 14 of Table 1.

^bRefers to Sample 14 of Table 2.

^cRefers to Sample 13 of Table 3.

Finally, the solubility of grafted samples in standard solvent systems [23] was compared with that of ungrafted wool. Table 4 shows that grafted samples are superior to ungrafted wool in respect to solubility in 4 M HCl, oxidizing solvent, and urea-bisulfite solution. The reduced solubility of grafted samples in oxidizing as well as in urea-bisulfite solution may indicate that the cystine content of wool has decreased upon grafting. The -SS- linkages of cystine are very sensitive toward reducing agents and undergo cleavage in the presence of sodium bisulfite solution:



From the foregoing discussion it is apparent that vinyl monomers vary in their reactivity toward graft copolymerization onto wool in the presence of the Cr(acac)₃-TBHP system. The following reactivity order was observed (Table 5): MMA > MA > EA.

TABLE 5. Maximum Percentage of Grafting of Different Vinyl Monomers under Optimum Conditions

No.	Vinyl monomer	% Grafting
1	MMA	119.8
2	MA	56.0
3	EA	41.9

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