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Grafting onto Wool. XXI. Graft Copolymerization of Methyl Methacrylate onto Reduced Wool by Use of Manganese Acetylacetonate as Initiator

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ABSTRACT

In an attempt to ascertain the role of –SH groups of wool fiber in graft copolymerization, methyl methacrylate (MMA) was graft copolymerized onto reduced wool by using manganese acetylacetonate ($Mn(acac)_3$) as the initiator in an aqueous medium. The reduction of wool was carried out with thioglycollic acid (TGA) in an aqueous solution. The percentage of grafting was determined as a function of the concentration of $Mn(acac)_3$, MMA, and nitric acid; the extent of reduction of wool by TGA; and the time and temperature. Under optimum conditions methyl methacrylate was grafted to the reduced wool to the extent of 57.0%. Unreduced wool under optimum conditions was reported earlier to afford a maximum grafting of MMA to the extent of 82.5%. The reduction of wool does not promote grafting of MMA onto wool in the presence of $Mn(acac)_3$.

INTRODUCTION

Modification of natural polymers such as starch [1], cellulose [2], and polyvinyl alcohol [3] by graft copolymerization has been extensively studied. A variety of initiating systems [4-8] have been tried. We have

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initiated a comprehensive research program to modify wool fiber by a graft copolymerization technique in an attempt to improve its fiber properties. Graft copolymerization is usually accompanied by the formation of a large amount of homopolymer. Separation of the homopolymer from the graft entails great difficulty in the purification of the graft. In order to minimize the formation of homopolymer, newer initiating systems have been tried. Arai et al. [9] have reported grafting of PMMA onto wool in the presence of the $K_2S_2O_8$-LiBr system as the redox initiator with minimum homopolymer formation.

The role of sulfur compounds in initiating and modifying polymers has been known for a long time. In recent years, attempts have been made to utilize sulfur compounds for effecting grafting of vinyl monomers onto wool. Lipson [10] in 1949 studied the polymerization of methacrylic acid in the presence of untreated and reduced wool, and he concluded that –SH groups of wool provide sites for grafting. Arai and co-workers [11] pointed to the definite role played by –SH groups during the grafting of MMA onto reduced wool.

Lipson and co-workers [12] were the first to show that the polymerization of vinyl monomers is initiated onto wool in the presence of the ferrous ion-hydrogen peroxide redox system as a result of formation of $RS^{\bullet}$ derived from the initial attack at the disulfide bond. Kantouch et al. [13] have studied grafting of PMMA onto reduced wool by the ceric ion method, and they reported that reduced wool produces less grafting than untreated wool in the presence of Ce^{4+}. The decrease in percent grafting was explained by assuming that ceric ion interacts with –SH groups to give various oxidized products.

Misra et al. [7, 14] have reported studies on grafting of MMA, AAc (acrylic acid), and VAc (vinyl acetate) onto wool fiber in the presence of $VO(acac)_2$ as the initiator, and EA (ethyl acrylate), BA (butyl acrylate), and VAc in the presence of $Mn(acac)_3$ as initiator. Wool contains numerous functional groups such as $-NH_2$, –OH, –COOH, imino, –SS–, and –SH. In the presence of ceric ion, it has been established that both $-NH_2$ and –OH provide active sites for grafting. It has not been possible to locate the active sites during metal chelate initiated grafting of vinyl monomers onto wool. Metal chelates are known to decompose upon heating into free radical species, and these species can abstract hydrogen atoms easily from the sulfhydryl group (–SH) to generate active sites for grafting.

In order to elucidate the role of –SS– and –SH groups in wool grafting, we have studied the grafting of MMA onto freshly reduced wool which contains large numbers of –SH groups arising from reduction of cystine residue. In the present article, grafting of MMA onto TGA-treated wool has been studied in the presence of $Mn(acac)_3$ as initiator.

EXPERIMENTAL

Materials and Method

Purification and characterization of Himachali wool has been described earlier [4]. MMA (BDH) was washed with 5% NaOH solution and then dried with anhydrous sodium sulfate. The dried monomer was then distilled and the middle fraction was used. Manganese chelate was prepared by the method reported earlier [10]. Nitric acid of known strength was used. Nitrogen was purified by passing it through freshly prepared alkaline pyrogallol solution to remove traces of oxygen.

Reduction of Wool

Wool samples were placed in an aqueous solution of thioglycollic acid of varying concentration for different time periods at room temperature. The mixture was filtered, and then the reduced wool was washed with water and methanol and dried.

Graft Copolymerization

One gram of reduced wool was dispersed in 200 mL of deaerated distilled water. To it were added a weighed amount of metal chelate and nitric acid of known strength. Purified nitrogen was passed through the reaction mixture for 30 min prior to addition of the monomer. The monomer was added dropwise. The graft copolymerization was carried out at 45, 55, 65, and 75°C for various time periods. A continuous supply of nitrogen was maintained during graft copolymerization. After the reaction was over, the reaction mixture was filtered and the residue was extracted for 48 h with benzene. All the homopolymer was removed from the graft by solvent extraction. The percentage of grafting and percentage efficiency were calculated as follows:

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

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

where W_0, W_1, and W_2 denote the weight of the reduced wool, the weight of the grafted wool after solvent extraction, and the weight of the monomer used, respectively.

Evidence of Grafting

1) A physical mixture of PMMA and wool was prepared by dispersing wool in a benzene solution of PMMA. This mixture was stirred for 24 h and filtered. The residue was extracted with benzene for 48 h. After extraction, the residue was hydrolyzed with 6 N HCl at 115°C for 24 h. No residue of PMMA was obtained, indicating that benzene completely removes homopolymer from the physical mixture.

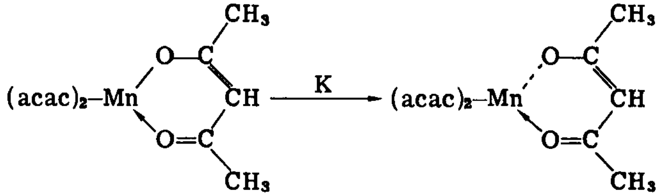
2) Wool-g-PMMA was hydrolyzed with 6 N HCl at 115°C for 24 h. A resinous mass was obtained which was identified as PMMA by IR spectroscopy. Isolation of PMMA after acid hydrolysis indicated that PMMA was covalently attached to the wool fiber.

RESULTS AND DISCUSSION

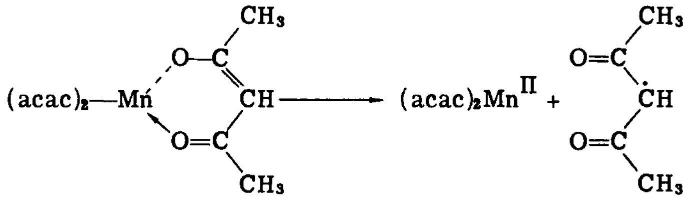
When a metal is capable of existing in more than one valance state, the combination of an organic ligand with a higher valance state of the metal may result in a single electron transfer to the metal. As a consequence of this electron transfer, initiation of vinyl polymerization may occur. It was observed by Arnett and Mendelsohn [15] that metal chelate decomposes upon heating to generate free radicals. If the decomposition of metal chelate is carried out in the presence of vinyl monomer and a backbone polymer (WH), grafting may occur. In a previous paper [16] it was shown that Mn(acac)$_3$ is capable of producing grafts of MMA and MA. However, it was not possible to identify the functional groups of wool responsible for grafting. Upon reduction of the wool fiber by TGA of varying concentrations, –SS– linkages of cystine are reduced to –SH groups:

$$\mathrm{R{-}SS{-}R + 2HSCH_2COOH \rightleftharpoons 2RSH + ({-}SCH_2COOH)_2}$$

A plausible mechanism involving the generation of radical species by one electron transfer in the metal chelate is suggested (Eqs. 1-7) for graft copolymerization of MMA onto reduced wool:



(1)



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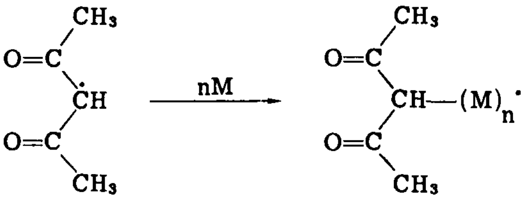

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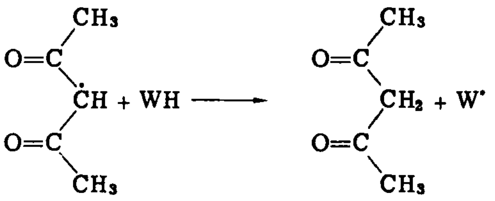

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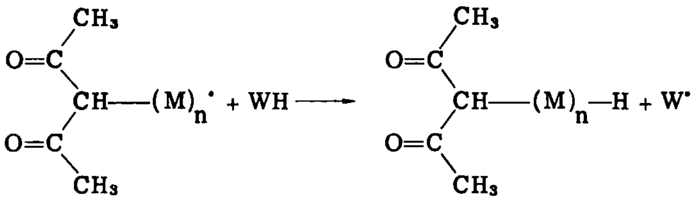
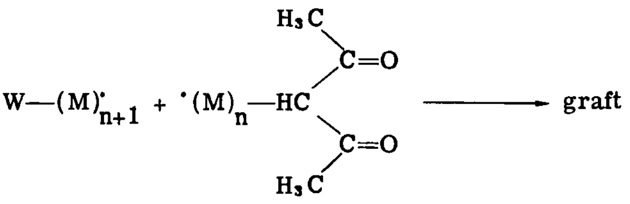


(5)

$$W^{\bullet} + M\text{—}WM^{\bullet}\xrightarrow{nM}W\text{—}(M)^{\bullet}_{n+1} \qquad (6)$$



(7)

where WH denotes reduced wool.

TABLE 1. Effect of [MMA], [HNO_3], [$Mn(acac)_3$], Temperature, Time, and Concentration of Reducing Agent upon Grafting of MMA onto Wool[a]

Sample	Temperature (°C)	Time (min)	[MMA] × 10^2 mol/L	[HNO_3] × 10^2 mol/L	[$Mn(acac)_3$] × 10^3 mol/L	TGA (%)	Reduction time (h)	% Grafting	% Efficiency
1	65	180	23.5	8.0	7.04	0.5	48	15.2	3.2
2	65	180	23.5	8.0	7.04	0.5	72	18.0	3.8
3	65	180	23.5	8.0	7.04	0.5	96	31.0	6.5
4	65	180	23.5	8.0	7.04	0.5	120	55.8	11.8
5	65	180	23.5	8.0	7.04	0.5	144	17.0	3.6
6	65	180	23.5	8.0	7.04	0.3	120	16.0	3.4
7	65	180	23.5	8.0	7.04	1.0	120	9.0	1.9
8	65	180	23.5	8.0	5.68	0.5	120	23.5	5.0
9	65	180	23.5	8.0	8.52	0.5	120	57.0	12.1
10	65	180	23.5	8.0	9.94	0.5	120	52.5	11.1
11	65	180	23.5	4.0	8.52	0.5	120	24.0	5.1
12	65	180	23.5	12.0	8.52	0.5	120	16.2	3.4
13	65	180	14.1	8.0	8.52	0.5	120	20.3	7.1
14	65	180	32.9	8.0	8.52	0.5	120	50.5	7.6
15	65	180	42.3	8.0	8.52	0.5	120	40.5	4.7
16	65	120	23.5	8.0	8.52	0.5	120	15.2	3.2
17	65	150	23.5	8.0	8.52	0.5	120	20.5	4.3
18	65	210	23.5	8.0	8.52	0.5	120	17.5	3.7
19	45	180	23.5	8.0	8.52	0.5	120	20.5	4.3
20	55	180	23.5	8.0	8.52	0.5	120	25.0	5.3
21	75	180	23.5	8.0	8.52	0.5	120	18.3	3.8

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

Effect of Concentration of Reducing Agent and Extent of Reduction on Grafting

It was earlier reported [16] that MMA could be grafted to the unreduced wool to the extent of 82% in the presence of Mn(acac)$_3$.

It is observed from Table 1 that reduction of wool does not promote grafting of MMA. When wool was reduced with a 0.5% (v/v) aqueous solution of TGA for 120 h, a maximum grafting of 57% was obtained. When the reduction time was increased from 120 to 144 h, a considerable decrease in the percentage of grafting was observed. This indicates that upon prolonged treatment with TGA solution, some TGA is retained in the wool fiber and acts as a chain transfer agent. When the reduction of wool is carried out with a 0.3% (v/v) or a 1% (v/v) aqueous solution of TGA, percentage grafting decreases. This indicates that there exists a critical concentration of TGA at which percent grafting is maximum. Upon treatment with TGA, wool undergoes swelling and thus the accessibility for radical attack on wool is facilitated. This is why maximum grafting occurs at a much lower concentration of Mn(acac)$_3$.

Effect of Concentration of Initiator

It is observed from Table 1 that maximum grafting of MMA onto reduced wool occurs at [Mn(acac)$_3$] = 8.52×10^{-3} mol/L, whereas unreduced wool produces maximum grafting of 82.5% [16] of MMA at an initiator concentration of 17.4×10^{-3} mol/L. Grafting onto reduced wool at a lower chelate concentration occurs because of greater accessibility of wool fiber due to swelling by TGA solution.

Effect of Monomer Concentration

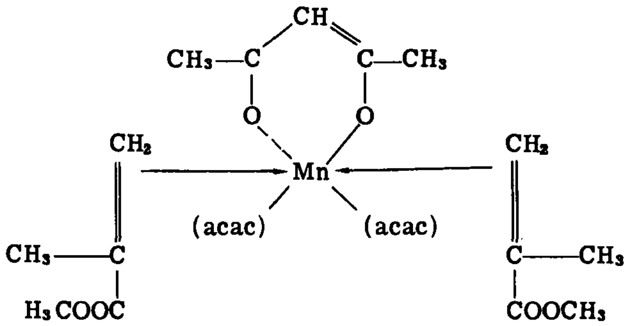
Table 1 shows that percent grafting increases with an increase in monomer concentration and reaches a maximum value at [MMA] = 23.5×10^{-2} mol/L. A further increase in monomer concentration decreases the percent grafting, indicating that homopolymerization is favored at higher monomer concentrations.

Effect of Nitric Acid

In all wool grafting it has been observed that a small amount of mineral acid promotes grafting. In the present study nitric acid was also found to catalyze graft copolymerization. Maximum grafting was obtained at [HNO$_3$] = 8.0×10^{-2} mol/L. The exact role played by nitric acid in metal chelate-initiated grafting of vinyl monomers, however, remains to be elucidated.

Effect of Time and Temperature

It is observed from Table 1 that maximum grafting of MMA onto reduced wool occurs at 65°C which is much below the decomposition temperature of $Mn(acac)_3$. This suggests that the chelate receives some assistance from vinyl monomer in the following manner:



(A)

Formation of monomer-metal chelate Complex (A) was established during grafting of VAc [17] onto cellulose in the presence of $Fe(acac)_3$ and of MMA, Vac, and AAc onto wool in the presence of $VO(acac)_2$ [7] from spectroscopic evidence. Since grafting of MMA occurs at a temperature much below the decomposition temperature of $Mn(acac)_3$, it is presumed that decomposition of $Mn(acac)_3$ is also in the present case facilitated through Complex (A). Maximum grafting under optimum conditions occurred within 180 min. Beyond this period, grafting essentially remains constant. It appears that all the active sites on reduced wool fiber are used up within 180 min. Beyond this time period, only homopolymer formation occurs.

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