

Grafting onto Wool. XIV. Graft Copolymerization of Vinyl Monomers by Use of $\text{Mn}(\text{AcAc})_3$ as an Initiator

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Synopsis

Ethyl acrylate (EA), butyl acrylate (BA), and vinyl acetate (VAc) have been graft copolymerized onto Himachali wool fiber in an aqueous medium by using $\text{Mn}(\text{AcAc})_3$ as an initiator. Graft copolymerization was studied at 45°, 55°, 65° and 75°C for various reaction periods. Percentage of grafting and percent efficiency were determined as functions of concentration of monomer, concentration of initiator, concentration of nitric acid, time, and temperature. Several grafting experiments were carried out in the presence of various additives which included: (i) pyridine and (ii) Et_3N . EA, BA, and VAc were found to differ in reactivity towards grafting and followed the order: EA > BA > VAc.

INTRODUCTION

Among various methods which are available for effecting modification of polymers, graft copolymerization appears to be highly attractive. During graft copolymerization, a new polymeric chain is anchored to another preformed polymer backbone by covalent bonds. A variety of initiating systems are known to affect grafting of vinyl monomers onto natural and synthetic polymeric backbone. In recent years, considerable attempts have been made to modify wool fiber by graft copolymerization technique. One of the major problems in wool grafting is the formation of homopolymer which is difficult to separate. Besides, formation of homopolymer leads to wastage of expensive monomer. In order to overcome these difficulties, a constant search has been made to find newer initiating systems that would minimize formation of homopolymer. Various initiating systems have been tried with varying degree of success. Ceric ion has been found suitable for effecting grafting of a variety of vinyl monomers onto wool fiber.¹⁻³ Other redox systems⁴⁻⁷ have also been found effective in producing grafts of wool fiber.

Conventional radical initiators such as BPO, AIBN, and TBHP are not suitable for effecting grafting onto wool fiber. Recently Misra and Chandel,⁸ however, were able to successfully graft polystyrene (PS) onto wool fiber by using BPO in the presence of pyridine (Py) and acetic acid mixture which acted as pH modifier. A comprehensive research program on grafting of a variety of vinyl monomers onto wool has been initiated in our laboratory. It has been possible to effect grafting of a variety of vinyl monomers onto wool in presence of (i) ceric ion,¹⁻³ (ii) ceric amine system,⁹⁻¹¹ (iii) Fenton's reagent,⁵ and (iv) radical initiator.⁸

In an attempt to find a newer initiating system, we have studied the suitability of metal chelates as graft initiators. The ability of certain metal chelates to produce free radicals when heated was first pointed out by Arnett and Mendelsohn¹² in the course of investigation on oxidation of these compounds. They observed that, at 110°C, some chelates are able to initiate polymerization of

styrene. Kastning, Naarmann, Reis, and Berding¹³ reported that of the simple acetyl acetonates, those of Mn^{III} and Co^{III} are most active initiators. Indicator and Linder¹⁴ reported that Co^{II}, Co^{III}, Cr^{III}, and Fe^{III} acetyl acetonates in the presence of TBHP can be used as initiators for polymerization of styrene. Recently, Prabha and Nandi¹⁵ have been able to effect polymerization of MMA by using chelates of Fe^{III}.

The use of metal chelates in graft copolymerization has not been extensively investigated. Recently Misra et al.¹⁶ were able to graft MMA, AAc, and VAc onto wool by using VO(AcAc)₂ as initiator. Nayak et al.¹⁷ were able to graft copolymerize MMA onto wool by using hexavalent chromium as initiator. In the present article, we report grafting of EA, BA, and VAc onto wool in the presence of Mn(AcAc)₃ as initiator. The percentage of grafting and percent efficiency were determined in the following manner:

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

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

EXPERIMENTAL

Preparation of Manganese Acetyl Acetonate

The chelate was prepared by the method reported in *Inorganic Synthesis*.¹⁸

To a solution of 5.2 g of manganese(II) chloride-4-hydrate and 13.6 g of sodium acetate-3-hydrate in 200 mL of water were added 20.0 g of acetyl acetone. To

TABLE I
Effect of Concentration of EA, Mn(AcAc)₃, Nitric Acid, Time, and Temperature on Grafting of Ethyl Acrylate onto Wool^a

Expt no.	[EA] ×10 ² mol/L	[Mn(AcAc) ₃] ×10 ³ mol/L	[HNO ₃] ×10 ² mol/L	Time (min)	Temp. (°C)	% Grafting	% Efficiency
1	23.0	14.55	24.0	180	65	6.0	1.30
2		17.40				12.0	2.60
3	23.0	20.24				8.0	1.73
4			20.0			12.0	2.60
5			28.0			14.0	3.04
6			32.0			9.0	1.95
7	32.2					14.0	2.17
8	41.4	17.40				26.0	3.14
9	50.6					41.0	4.05
10	59.8		28.0			27.0	2.25
11				150		28.0	2.76
12				210		18.0	1.77
13	50.6			180	55	16.0	1.58
14				180	75	18.0	1.77

^a Wool = 1 g; water = 200 mL.

TABLE II
Effect of Concentration of BA, Mn(AcAc)₃, Nitric Acid, Time, and Temperature on Grafting of Butyl Acrylate onto Wool^a

Expt no.	[BA] ×10 ² mol/L	[Mn(AcAc) ₃] × 10 ³ mol/L	[HNO ₃] ×10 ² mol/L	Time (min)	Temp (°C)	% Grafting	% Efficiency
1	17.5	15.99	24.0	180	65	18.0	4.00
2		18.75	24.0			26.0	5.77
3	17.5	20.88				28.0	6.22
4		23.01				17.0	3.77
5			16.0	180		16.0	3.55
6			32.0		65	18.0	4.00
7	24.6					35.0	5.55
8	31.6	20.88				37.0	4.56
9	38.6					29.0	2.92
10			24.0	150		19.0	2.34
11	31.6			210		7.0	0.86
12				180	55	20.0	2.46
13				180	75	29.0	3.58

^a Wool = 1 g; water = 200 mL.

the resulting mixture, a solution of 1.04 g of potassium permanganate in 50 mL of water was slowly added at room temperature, with stirring. After stirring for a few minutes, a solution of 13.6 g of sodium acetate-3-hydrate in 50 mL of water was added in small amounts, with stirring. The mixture was heated on the hot plate for about 10 min and cooled to room temperature, and the dark solid filtered through Buchner funnel. The product was washed with water and dried in vacuo. The dried chelate is dissolved in 20 mL of warm benzene, filtered, and chelate-precipitated by cooling the solution and adding 75 mL of petroleum ether. The recrystallized material was dried over anhydrous calcium sulphate, decomposed at 152°C. The IR spectrum showed a band at 1600 cm⁻¹ assigned to C=O of the chelate.

TABLE III
Effect of Concentration of VAc, Mn(AcAc)₃, Nitric Acid, Time, and Temperature on Percent Grafting of Vinyl Acetate onto Wool^a

Expt no.	[VAc] ×10 ² mol/L	[Mn(AcAc) ₃] ×10 ³ mol/L	[HNO ₃] ×10 ² mol/L	Time (min)	Temp (min)	% Grafting	% Efficiency
1	27.0	15.76	24.0	180	65	9.0	1.93
2		17.32	24.0			18.0	3.87
3	27.0	19.03				8.0	1.72
4			16.0	180		7.0	1.50
5			32.0		65	6.0	1.29
6	38.8					20.0	3.07
7	48.6	17.32				7.0	0.83
8			24.0	150		5.0	0.76
9	38.8			210		6.0	0.92
10				180	55	5.0	0.76
11				180	75	8.0	1.22

^a Wool = 1 g; water = 200 mL.

Elemental analysis: calculated: C, 51.1%; H, 6.01%; found: C, 51.2%; H, 6.26%.

Materials and Methods

Ethyl acrylate and *n*-butyl acrylate were washed with 5% NaOH and dried over anhydrous sodium sulphate. Dried EA and BA were then distilled and middle fraction was used. Vinyl acetate was freshly distilled before use. Pyridine was distilled over potassium hydroxide, and triethylamine was freshly distilled. Nitric acid (BDH) of known strength was used. Nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution. Himachali wool was purified by the method described earlier.¹

Graft Copolymerization

One gram of purified wool was dispersed in 200 mL of deaerated water in a three-necked flask. The known quantity of metal chelate is added. Prior to the addition of the monomer, nitrogen was passed through reaction flask for about 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 reaction was carried out under stirring at different temperatures for various reaction periods, in the presence of nitric acid.

After the reaction was over, the reaction mixture was filtered and the residue was extracted with benzene for removal of PEA and PBA and with acetone for removal of poly(VAc).

Evidence of Grafting

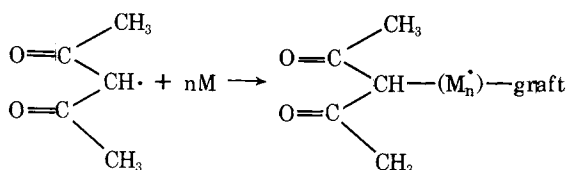
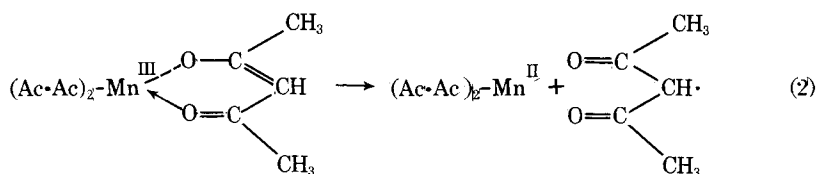
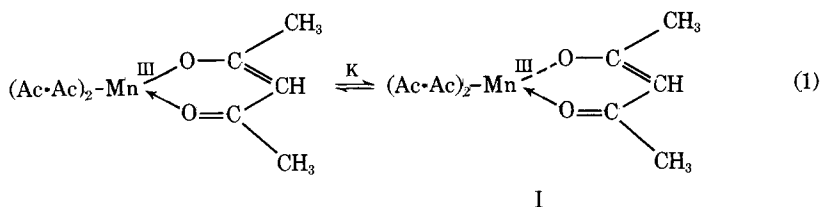
Wool-*g*-P(EA) and wool-*g*-P(BA) were hydrolyzed with 6N HCl at 115°C for 24 h. After all the wool goes into solution, resinous masses were obtained which were characterized by IR spectroscopy as PEA and PBA, respectively.

In the case of wool grafted with PVAc no such mass was obtained because PVAc upon hydrolysis gave poly(vinyl alcohol), which is soluble in water.

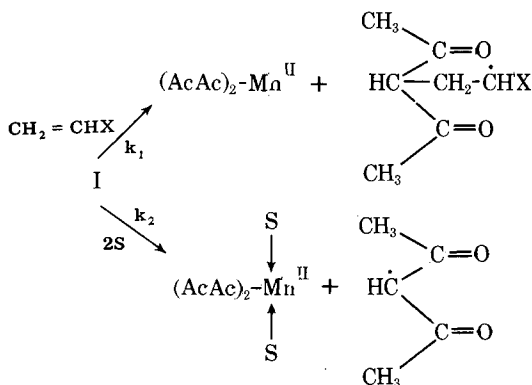
RESULTS AND DISCUSSION

When a metal is capable of existing in more than one valence state, the combination of an organic ligand with the higher valence 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 Mendelsohn¹² that metal chelate upon heating decomposes to generate free radicals. When the decomposition of metal chelate is carried out in presence of a vinyl monomer and a backbone polymer (WH), grafting may occur. The following mechanism [eqs. (1)–(3)] is suggested to explain initiation of grafting

of EA, BA, and VAc onto wool in the presence of $\text{Mn}(\text{AcAc})_3$:



In the above postulated mechanism, it is assumed that metal chelate upon heating first loosens the Mn–O bond followed by transfer of one electron to generate the free radical species which are responsible for grafting. The above processes can occur at the decomposition temperature of chelate (152°C). But it is observed from Tables I, II, and III that maximum grafting occurs at 65°C much below the decomposition temperature of $\text{Mn}(\text{AcAc})_3$. This indicates that the chelate receives some assistance either from the monomer or solvent or both for the facile decomposition at lower temperature. It is presumed that the chelate instead of undergoing spontaneous decomposition by step (2), undergoes monomer-assisted or solvent-assisted decomposition in the following manner:



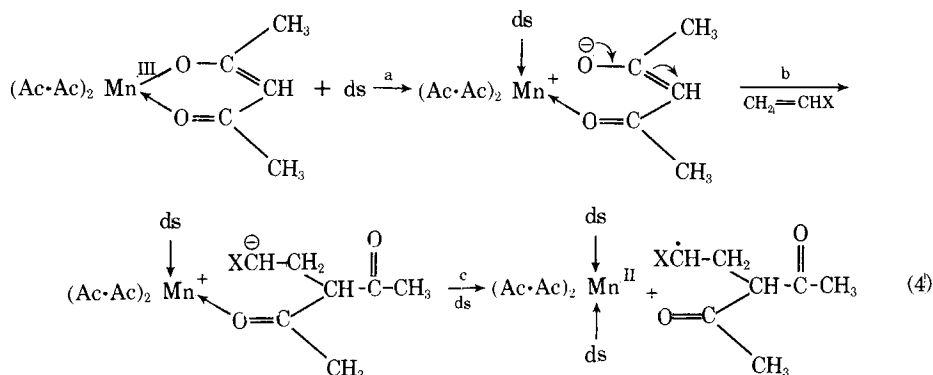
A similar mechanism involving monomer assisted decomposition of metal chelate has been proposed by Misra et al.¹⁹ for explaining grafting of VAc onto cellulose.

It is observed from Tables I, II, and III that with increase in concentration of monomer percent grafting increases and reaches maximum values at monomer concentration of 50.6×10^{-2} mol/L for EA, 31.6×10^{-2} mol/L for BA, and 38.8×10^{-2} mol/L for VAc. Further increase in monomer concentration reduces percent grafting. This indicates that at higher concentrations vinyl monomers preferentially undergo polymerization to give homopolymer at the expense of graft copolymer. Similar behavior was observed by Garnett²¹ during radiation induced grafting of St onto polyethylene (PE).

Tables I, II, and III show that with increase in concentration of chelate percent grafting increases and reaches maximum values at 17.4×10^{-3} mol/L for EA, 20.88×10^{-3} mol/L for BA, and 17.32×10^{-3} mol/L for VAc. Beyond these concentrations, graft yield decreases. This indicates that $Mn(AcAc)_3$ at higher concentration participates in termination of growing polymeric chain as well as growing grafted polymeric chain. $Mn(AcAc)_3$ is known to act as a retarder of vinyl polymerization at higher concentration.

Maximum percent grafting of EA, BA, and VAc under optimum conditions occurs within 180 min, Tables I, II, and III. Beyond these reaction periods, grafting essentially remains constant. It is also observed that percent grafting increases with increase in temperature and reaches maximum value at $65^\circ C$ for all the monomers studied. At a higher temperature, percent grafting decreases. This would be expected since generation of active sites onto polymeric backbone (WH) by hydrogen abstraction will be facilitated at higher temperature. Beyond $65^\circ C$, it appears that termination reactions are accelerated leading to decrease in percent add on.

In order to study the possibilities of initiations of grafting by ligand displacement, several grafting experiments were conducted in presence of Py and Et_3N . Effect of additives on percent grafting of EA, BA, and VAc was studied under optimum conditions. It is observed from Table IV that both Py and Et_3N promote grafting of EA and BA while in the presence of these additives grafting of vinyl acetate is considerably reduced. This indicates that in presence of electron-donating additives, $Mn(AcAc)_3$ -initiated grafting onto wool shows monomer selectivity. This observation prompts us to suggest the following initiation mechanism of grafting in the presence of electron donors as additives:



Selectivity will be imparted in step 4(b) which occurs most readily with monomers carrying electron attracting groups. Partial ligand displacement (4a) is followed

TABLE IV
Effect of Pyridine and Triethylamine on Percent Grafting of Ethyl Acrylate, Butyl Acrylate and Vinyl Acetate onto Wool Using $Mn(AcAc)_3$ as Initiator

Expt no.	Additives $\times 10^2$ mol/L	% Grafting			% Efficiency		
		EA ^a	BA ^b	VAc ^c	EA	BA	VAc
1	Pyridine						
	6.2	83.0	160.0	10.0	8.20	19.75	1.53
	12.4	16.0	90.0	7.0	1.58	11.11	1.07
2	Triethylamine						
	3.82	11.0	9.0	6.0	1.08	1.11	0.92
	7.65	16.0	33.0	9.0	1.58	4.07	1.38
	11.48	33.0	39.0	12.0	3.26	4.81	1.84

^a Reaction conditions of expt no. 9 from Table I.

^b Reaction conditions of expt no. 8 from Table II.

^c Reaction conditions of expt no. 6 from Table III.

by insertion of monomer (4b) and electron transfer (4c) to produce Mn^{II} and initiating radical. In the light of the above mechanism, it is not surprising that VAc, being an electron-donating monomer produces less grafting. Thus the above mechanism satisfactorily explains the reactivity of different vinyl monomers in presence of electron donor additives.

In the absence of additives, it is observed that the reactivity of different vinyl monomers follows the order $EA > BA > VAc$. The least reactivity shown by VAc is expected, since according to Mayo and Walling,²⁰ VAc is least reactive towards free radical polymerization compared to acrylates.

The higher reactivity shown by EA as compared to BA is explained by consideration of the steric requirements of these two monomers. BA, having higher steric requirement than EA, shows the least reactivity towards both polymerization and grafting by free radical process.

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