

# Grafting onto Wool. XI. Graft Copolymerization of Poly(vinyl Acetate) and Poly(methyl Acrylate) onto Reduced Wool in Presence of Potassium Persulfate–Ferrous Ammonium Sulfate (KPS—FAS) System as Redox Initiator

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## Synopsis

In an attempt to ascertain the role of —SH groups of Himachali wool during graft copolymerization, poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PMA) were graft copolymerized onto reduced wool by using potassium persulfate–ferrous ammonium sulfate (KPS—FAS) redox pair in aqueous medium. Reduction of wool was carried out by sodium bisulfite solution of varying concentrations for different reaction periods. Concentration of reducing agent and the extent of reduction were found to influence grafting of vinyl monomers. Maximum grafting of methyl acrylate (MA) and vinyl acetate (VAc) occurred when wool was reduced by 1% and 0.5% NaHSO<sub>3</sub> solution, respectively, for 24 h. Increase in percent grafting of MA onto reduced wool compared to that of unreduced wool has been ascribed to the production of more —SH groups by reduction of —SS— groups of wool fiber.

## INTRODUCTION

Graft copolymerization of a variety of vinyl monomers onto cellulose,<sup>1,2</sup> starch,<sup>3,4</sup> rubber,<sup>5</sup> and synthetic polymers<sup>6</sup> by various methods has been extensively studied. Comparatively less attention has been paid to modification of wool fibers by the graft copolymerization technique. Among fibrous proteins, collagen and silk have been subjected to graft copolymerization by using different initiators. Nayudamma and co-workers<sup>7</sup> were successful in preparing the graft of collagen and poly(methyl methacrylate) (PMMA) by using ceric ammonium nitrate (CAN) as redox initiator. Styrene and acrylonitrile (AN) were grafted to silk by  $\gamma$ -irradiation, and from the infrared spectra of the grafted samples it was concluded that grafting of polystyrene (PS) and poly(acrylonitrile) (PAN) occurred on silk.<sup>8</sup> Kenyon and Garnett<sup>9</sup> have recently reported that ethyl acrylate (EA) can be successfully grafted to wool in the presence of nitric acid and a good swelling solvent. Various redox systems have been successfully utilized in effecting grafting of vinyl monomers onto wool. Recently, Misra and co-workers have reported grafting of MA,<sup>10</sup> EA,<sup>11</sup> methylmethacrylate (MMA),<sup>12</sup> acrylic acid (AAc),<sup>12</sup> and VAc<sup>13</sup> onto wool fiber by using ceric ion initiators. Other workers also have reported grafting of vinyl monomers to wool fiber by the use of ceric ion initiators. Misra et al.<sup>14</sup> studied grafting of PS onto wool fiber in the presence of benzoyl peroxide (BPO) and observed that BPO alone was ineffective but, in the presence of acetic acid–pyridine mixture, it produced

significant grafting. Metal chelates are finding uses as graft initiators in recent years. Nayak et al.<sup>15</sup> were able to graft copolymerized MMA onto wool by using hexavalent chromium ion as initiator. Misra et al.<sup>16</sup> have reported on grafting of MMA, AAc, and VAc onto Himachali wool in the presence of vanadium oxy-acetyl-acetate [VO(acac)<sub>2</sub>] as initiator.

The role of sulphur compounds in initiating and modifying polymers has been known for a long time. In recent years, attempts have been made to utilize sulphur compounds for effecting grafting of vinyl monomers onto wool. As early as 1949, Lipson<sup>17</sup> studied polymerization of methacrylic acid in the presence of untreated and reduced wool and concluded that —SH of wool provides sites for grafting. Among various redox initiators that have been studied, persulphates and Fenton's reagent were found effective in producing grafts of methacrylic acid, styrene, and VAc onto wool. Negishi and Arai<sup>18</sup> pointed to the definite role played by —SH groups during grafting of MMA onto reduced wool fiber.

In addition to numerous functional groups, wool contains disulfide linkages. Lipson and Speakman were first to show that the polymerization of vinyl monomers is initiated on the wool in the presence of a ferrous ion hydrogen peroxide redox system as a result of the formation of RS-radical-derived from initial attack at the disulfide bond.<sup>19</sup> Kantouch et al.<sup>20</sup> have studied grafting of PMMA onto reduced wool by the ceric ion method and reported that, in the presence of Ce<sup>+4</sup>, reduced wool produces less grafting than untreated wool. The decrease in percent grafting was explained by assuming that ceric ion interacts with —SH groups to give various oxidized products.

In order to elucidate the role of —SS— and —SH groups in wool grafting, attempts have been made to study graft copolymerization of VAc and MA onto reduced wool in the presence of ferrous ion-persulfate redox system. Percentage of grafting has been determined as functions of (i) concentration of monomer, (ii) molar ratio of [FAS]/[KPS], (iii) extent of reduction of wool by sodium bisulphite, (iv) time, and (v) temperature.

## EXPERIMENTAL

Purification of Himachali wool and the monomers (MA and VAc) was carried out as described.<sup>10,13</sup> Potassium persulfate (KPS) of reagent grade was used as received. Ferrous ammonium sulfate (FAS) was purified by recrystallization from hot water. Sodium bisulfite (BDH) was used as received.

Nitrogen was purified by passing through freshly prepared pyrogallol solution for removing any traces of oxygen.

### Reduction

One gram of wool was immersed in a solution of sodium bisulfite of various concentrations for different time periods. The reduced wool was then washed several times with water and methanol. The dried reduced wool was used in grafting experiments.

### Graft Copolymerization

One gram of reduced wool was immersed in 300 mL of cold deaerated distilled water. Definite amounts of KPS and FAS were added to the reaction flask. The flask was purged with nitrogen for 30 min prior to the addition of monomer, and then a continuous supply was maintained throughout the reaction period. A known amount of monomer was added dropwise to the reaction mixture. The reaction was carried out at different temperatures for different time periods.

After completion of the reaction the reaction mixture was filtered and the residue extracted with benzene for 48 h. After complete removal of homopolymer, the grafted wool was dried to a constant weight. Percentage grafting and percent efficiency were calculated in the following manner:

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

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

where  $W_0$ ,  $W_1$ , and  $W_2$  denote respectively the weights of wool, grafted wool after benzene extraction, and the weight of the monomer used.

### Evidence of Grafting

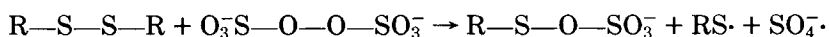
(i) A physical mixture of PVAc or PMA and wool were prepared by dispersing wool in benzene solution of PVAc or PMA. The dispersion was stirred for 24 h and filtered. The residue was extracted with benzene for 48 h. After extraction, the residue was hydrolyzed with 6N HCl at 115°C for 24 h. No residue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

(ii) Wool-*g*-PMA was hydrolyzed with 6N HCl at 115°C for 24 h. A resinous mass was obtained which was identified as PMA by IR spectroscopy. PVAc could not be isolated since during hydrolysis PVAc is converted into poly(vinyl alcohol), which is soluble in water. Isolation of PMA after acid hydrolysis indicated that PMA was covalently attached to wool fiber.

(iii) Comparison of scanning electron micrographs of wool and grafted wool indicated that considerable polymer was deposited onto the wool fiber.

## RESULTS AND DISCUSSION

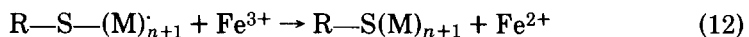
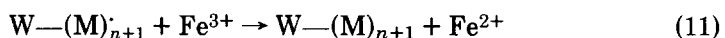
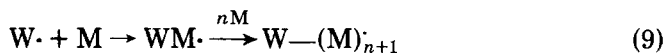
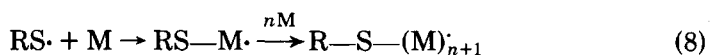
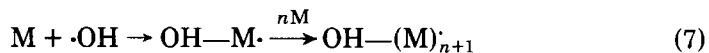
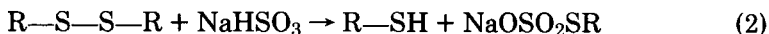
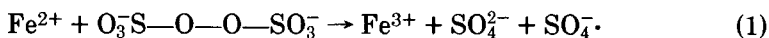
Both —SS— and —SH groups of wool may participate in grafting reactions in the presence of KPS—FAS redox system. Madaras and Speakman<sup>21</sup> observed that persulfate alone was capable of initiating deposition of polymer on wool. This indicated that disulfide linkages of wool could form a redox system with persulfate in the following manner:



Both  $\text{RS}\cdot$  and  $\text{SO}_4^-$  would directly or indirectly initiate graft copolymerization. Schoberl and Wagner<sup>22</sup> pointed to the role of —SH group in graft copolymerization. They observed that alkylation of —SH of wool fiber prevented grafting. In the present article, the role of —SH groups in graft copolymerization in the

presence of KPS—FAS redox initiator has been investigated in detail. Reduction of wool can be conveniently carried out by a number of reducing agents. In the present work, wool fiber was steeped in sodium bisulfite solution of varying concentrations for different time periods. A plausible mechanism [eqs. (1)–(12)] for grafting of VAc and MA onto sodium-bisulfite-treated wool in the presence of KPS—FAS redox initiator is suggested.

Potassium persulfate (KPS) is known to enter into redox reaction with  $\text{Fe}^{+2}$ . The following mechanism can be written:



where W denotes wool fiber and R—S—S—R denotes the cystine of wool fiber.

In the above postulated mechanism, it is observed that thiyl anion ( $\text{RS}^-$ ) resulting from thiol, which in turn was formed upon reduction of cystine (R—S—S—R) of wool can interact with persulfates to generate  $\text{RS}\cdot$  as well as  $\text{SO}_4^-$ . In aqueous medium  $\text{SO}_4^-$  can further interact with water to give  $\cdot\text{OH}$ , which is responsible for vinyl polymerization, as well as for the generation of an active site onto wool fiber by process (6). Generation of active sites onto wool fiber by  $\text{SO}_4^-$  is negligible since the concentration of persulfate is usually small and in aqueous medium  $\text{SO}_4^-$  will immediately react with water to produce  $\cdot\text{OH}$  by process (5). Further, with reduced wool, some more active sites are generated directly on wool backbone by process (4). Thus, it appears that the extent of reduction of disulfide linkages should influence grafting.

### Grafting as Function of Extent of Reduction

Tables I and II show that maximum grafting of MA and VAc occurred to the extent of 78.5% and 22.3% when grafting was carried out in 1%  $\text{NaHSO}_3$  solution and 0.5%  $\text{NaHSO}_3$  solution, respectively, for 24 h. Under the same conditions,

TABLE I  
Effect of Extent of Reduction on Graft Copolymerization on MA onto Reduced Wool<sup>a</sup>

S. No.	Time of reduction (h)	NaHSO <sub>3</sub> (%)	Grafting (%)	Efficiency (%)
1	24	0.5	60.6	12.7
2	24	1.0	78.5	16.5
3	24	1.5	66.3	13.9
4	48	0.5	37.3	7.6
5	48	1.0	53.7	11.3
6	48	1.5	66.6	14.0
7	72	0.5	48.5	10.2
8	72	1.0	59.6	12.5
9	72	1.5	65.4	13.7

<sup>a</sup> Reduced wool = 1 g; water = 300 mL; temperature = 60°C; [MA] = 0.184 mol/L; time = 150 min; [FAS]/[KPS] = 0.713:1.

the untreated wool<sup>23</sup> afforded maximum grafting of MA and VAc to the extent of 72.6% and 12.7%, respectively. The increase in graft yield with MA in the case of treated wool is due to additional —SH groups formed upon reduction of wool fiber [eq. (2)]. It is also observed from Tables I and II that the extent of reduction influences grafting. When the reduction time is increased from 24 h to 48 h, percent grafting decreases and then remains constant. Also, when wool is reduced with more concentrated NaHSO<sub>3</sub> solution, some of the reducing agent is trapped in the fiber matrix which then participates in forming a three-component (Fe<sup>+2</sup>—KPS—NaHSO<sub>3</sub>) redox system. This redox system is more effective in promoting homopolymerization of the vinyl monomers with consequent decrease in percent grafting. During grafting of wool treated with much higher concentrations of NaHSO<sub>3</sub> solution for prolonged periods, a large amount of homopolymer was observed.

TABLE II  
Effect of Extent of Reduction on Graft Copolymerization of VAc onto Reduced Wool<sup>a</sup>

S. No.	Time of reduction (h)	NaHSO <sub>3</sub> (%)	Grafting (%)	Efficiency (%)
1	24	0.3	9.0	2.0
2	24	0.5	22.3	4.8
3	24	1.0	9.4	2.0
4	24	1.5	4.2	0.9
5	48	0.5	2.0	0.4
6	48	1.0	1.7	0.3
7	48	1.5	4.7	1.0
8	72	0.5	1.7	0.3
9	72	1.0	1.0	0.2
10	72	1.5	4.7	1.0

<sup>a</sup> Reduced wool = 1 g; water = 300 mL; temperature = 60°C; [VAc] = 0.18 mol/L; time = 120 min; [FAS]/[KPS] = 0.713:1.

TABLE III  
Effect of Concentration of VAc, Molar Ratio of [FAS]/[KPS], Time and Temperature on Grafting of PVAc onto Reduced Wool<sup>a</sup>

Sample	[FAS]/[KPS]	[VAc] (mol/L)	Temp. (°C)	Time (min)	Grafting (%)	Efficiency (%)
1	0.713:1	0.18	30	120	0	0
2	0.713:1	0.18	45	120	7.6	1.6
3	0.713:1	0.18	60	120	22.3	4.8
4	0.713:1	0.18	60	45	7.3	1.1
5	0.713:1	0.18	60	90	11.9	2.5
6	0.713:1	0.18	60	150	19.5	4.2
7	0.713:1	0.106	60	120	0	0
8	0.713:1	0.253	60	120	4.7	0.7
9	0.336:1	0.36	60	120	1.8	0.2
10	0.336:1	0.18	60	120	1.5	0.3
11	1.049:1	0.18	60	120	2.8	0.6

<sup>a</sup> Reducing agent = 0.5% NaHSO<sub>3</sub> solution; time of reduction = 24 h; water = 300 mL; reduced wool = 1 g.

### Effect of Nature and Concentration of Monomer

It is observed from Tables III and IV that with increase in concentration of VAc, percent grafting increases and reaches a maximum value (22.3%) at a monomer concentration of 0.18 mol/L. Beyond this concentration, percent grafting decreases. This behavior of VAc is consistent with its poor reactivity-

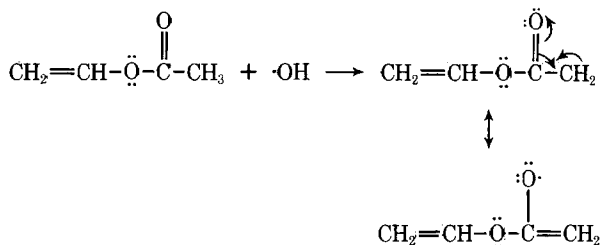


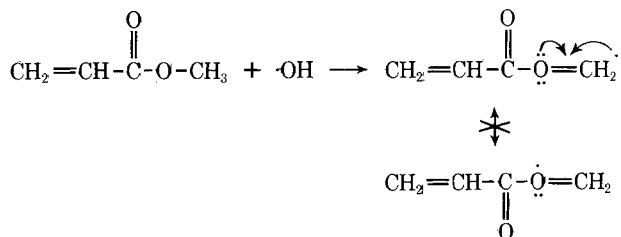
TABLE IV  
Effect of Concentration of MA, Molar Ratio of [FAS]/[KPS], Time and Temperature on % Grafting of MA onto Reduced Wool<sup>a</sup>

Sample	[FAS]/[KPS]	[MA] (mol/L)	Temp. (°C)	Time (min)	Grafting (%)	Efficiency (%)
1	0.713:1	0.184	60	45	43.8	9.2
2	0.713:1	0.184	60	90	45.3	9.5
3	0.713:1	0.184	60	120	44.6	9.3
4	0.713:1	0.184	60	150	78.5	16.5
5	0.713:1	0.184	60	180	72.5	15.3
6	0.713:1	0.184	30	150	0	0
7	0.713:1	0.184	45	150	5.0	1.05
8	0.713:1	0.11	60	150	27.0	9.5
9	0.713:1	0.257	60	150	82.6	12.4
10	0.713:1	0.368	60	150	105.6	11.1
11	0.336:1	0.368	60	150	25.1	2.6
12	1.049:1	0.368	60	150	24.5	2.57

<sup>a</sup> Reducing agent = 1.0% NaHSO<sub>3</sub> solution; time of reduction = 24 h; water = 300 mL; reduced wool = 1 g.

toward free radical species. With increase in VAc concentration, side reaction of the following type is accelerated resulting in a decrease in percent grafting.

It may be mentioned that VAc afforded higher graft yields<sup>23</sup> with unreduced wool fiber than with reduced wool under optimum conditions. This may indicate that additional —SH groups arising from the reduction of wool fiber act as chain transfer agents toward the donor monomer (VAc) resulting in a decrease in percent grafting. With MA, the situation is different; with an increase in concentration of MA the percent grafting increases and reaches a maximum value (105.6%) at a monomer concentration of 0.368 mol/L. This indicates that the acceptor monomer (MA) being highly reactive toward free radicals is not wasted in side reactions. This is expected since MA upon hydrogen abstraction by OH· affords a radical species which is not stabilized by resonance.



Because of the higher reactivity of MA, chain transfer reactions of additional —SH groups formed after reduction of disulfide linkages of wool do not assume importance.

### Effect of Time and Temperature

In order to determine optimum temperatures for maximum grafting of VAc and MA onto reduced wool, graft copolymerization was carried out at 30°C, 45°C, and 60°C. Tables III and IV show that with increase in temperature percent grafting increases and reaches maximum values at 60°C, beyond which percent grafting was found to decrease due to acceleration of various chain transfer processes that lead to preferential formation of homopolymer as well as wastage of monomer in side reactions. It is observed from Tables III and IV that with an increase in the reaction period percent grafting of VAc and MA increases. Maximum grafting of MA and VAc occurred within 150 and 120 min, respectively. Beyond these reaction periods, percent grafting levelled off.

### Effect of Molar Ratio of [FAS]/[KPS]

It is observed from eqs. (11) and (12) that  $\text{Fe}^{+3}$  which is formed by interaction of ferrous ammonium sulfate with potassium persulfate by eq. (1) is capable of terminating the growing grafted chains. This indicates that there exists a critical molar ratio for  $[\text{Fe}^{+2}]/[\text{KPS}]$  that would afford maximum grafting. This is actually observed. Tables III and IV show that maximum percentage of grafting of VAc and MA onto reduced wool occurred when molar ratio of  $[\text{FAS}]/[\text{KPS}] = 0.713:1$ . Similar behavior was observed during grafting of VAc onto wool fiber in the presence of Fenton's reagent.<sup>24</sup> Maximum grafting of VAc occurred at a molar ratio of  $[\text{FAS}]/[\text{H}_2\text{O}_2] = 1:1.43$ .

The authors (R.D. and K.D.G.) are grateful to CSIR, Govt. of India, for the award of junior research fellowship and pool officership respectively. I.K.M. is grateful to D.A.E., Govt. of India for the award of senior research fellowship. Financial assistance from DAE, Govt. of India, for this work is gratefully acknowledged.

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Received May 27, 1980

Accepted April 6, 1981