

Grafting onto Wool. XX. Graft Copolymerization of Vinyl Monomers by Use of Redox Initiators. Comparison of Monomer Reactivities

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Synopsis

Methyl methacrylate (MMA) and ethylacrylate (EA) have been graft copolymerized onto Himachali wool in aqueous medium by using a ferrous ammonium sulfate–hydrogen peroxide (FAS—H₂O₂) system as redox initiator. Percentage of grafting has been determined as functions of concentration of monomer, molar ratio of [FAS]/[H₂O₂], time, and temperature. Percentage of grafting is found to depend upon the molar ratio of [FAS]/[H₂O₂]. An attempt has been made to compare the reactivities of the acceptor monomer (MMA and EA) with that of the donor monomer (VAc) toward grafting onto wool.

INTRODUCTION

Modification of proteins by the graft copolymerization method is an area which has not been extensively investigated. In recent years, considerable activities have been devoted to effect modification of fibrous proteins by this method. Nayudamma and co-workers¹ were successful in preparing graft copolymer of collagen and poly(methyl methacrylate) by using ceric ammonium nitrate as redox initiator. Azimov et al.² polymerized styrene and acrylonitrile with silk by using gamma irradiation. Negeshi and co-workers³ were able to prepare grafts of various acrylate monomers and wool by using a novel initiator system which consisted of K₂S₂O₈—LiBr in an aqueous medium. Earlier Lipson⁴ attempted grafting of vinyl monomers onto wool by use of persulfate and Fenton's reagent as redox initiator. Ceric ion has been successfully used for effecting grafting of vinyl monomers onto wool fiber.⁵ A comprehensive research program on grafting onto wool fiber has been initiated in our laboratory, and it has been possible to effect grafting of a number of vinyl monomers by use of a conventional radical initiator,^{6,7} various redox systems,^{8,9} Ce⁴⁺—amine systems,^{10,11} metal chelates, and γ -irradiation. Among various initiators, redox systems were found particularly suitable for effecting grafting under milder conditions. In a recent paper,¹² we have reported that Fenton's reagent (Fe⁺²—H₂O₂) is capable of effecting grafting of poly(vinyl acetate) onto wool at 45°C and that the graft yield was highly dependent upon the molar ratio [Fe²⁺]/[H₂O₂]. As an extension of this work we have studied grafting of EA and MMA onto wool fiber by using Fenton's reagent as redox initiator. Optimum conditions for affording maximum grafting have been evaluated, and an attempt has been made to determine the relative reactivities of different acceptor and donor monomers towards grafting onto wool fiber in the presence of Fenton's reagent as an initiator.

EXPERIMENTAL

Materials and Method

Purification of wool has been described by Misra and Chandel⁵. Methyl methacrylate and ethylacrylate were washed with 5% NaOH and then dried over anhydrous sodium sulfate. The dried monomers were then distilled, and the middle fraction was used. Ferrous ammonium sulfate was recrystallized from hot water. Reagent grade 30% H₂O₂ (W/V) was used. Nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution for removing traces of oxygen.

Graft Copolymerization

1 g of the purified wool was immersed in 200 mL of deaerated water. Known weight of FAS and H₂O₂ was added to the reaction mixture. Nitrogen was passed through the reaction mixture for 20 min prior to the addition of monomer. The monomer was added dropwise and graft copolymerization was carried out at 30°C, 40°C, 50°C, 60°C, 70°C, and 75°C for various time periods. A continuous supply of nitrogen was maintained during the reaction period. After the reaction was over, the ingredients were 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 from increase in weight of wool after grafting in the following manner:

$$\% \text{ grafting} = \frac{W_2 - W_1}{W_1} \times 100$$
$$\% \text{ efficiency} = \frac{W_2 - W_1}{W_3} \times 100$$

where W_1 , W_2 , and W_3 denote, respectively, the weight of the original wool, weight of the grafted wool after solvent extraction, and the weight of the monomer added.

Evidence of Grafting

The grafted material was refluxed with 6N HCl at 115°C for 24 h. All the wool went into the solution, leaving resinous mass, which was identified as PMMA and PEA. The IR spectrum of the residue showed a band at 1730 cm⁻¹ and 1775 cm⁻¹, which were attributed to grafted PEA and PMMA, respectively. These bands were not present in the IR spectrum of original wool which instead showed an amide band at 1640 cm⁻¹.

The physical mixtures of wool and benzene solution of PMMA and PEA were prepared by stirring 1.0 g of wool fiber in benzene solution of PMMA and PEA for 24 h. The wool fiber was separated by filtration and the residue subjected to extraction by benzene for 24 h and dried. Recovery of 0.99 g of wool fiber indicated that homopolymer (PEA and PMMA) is quantitatively separated by benzene extraction from the mixture. Comparison of scanning electron micrographs of wool-*g*-PEA (Fig. 1) and wool-*g*-PMMA (Fig. 2) indicates that, upon grafting, a considerable amount of polymer is deposited onto the wool surface.

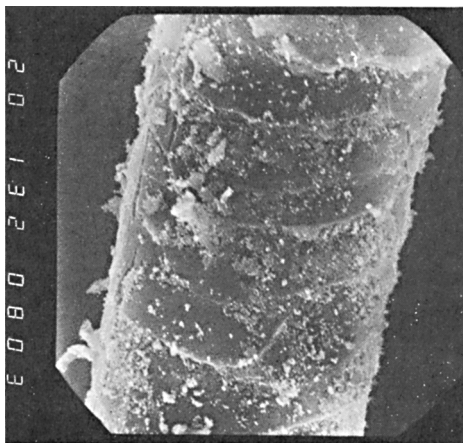


Fig. 1. Scanning electron micrograph of Wool—*g*-PEA (Sample 12 of Table II) (1300 \times).

RESULTS AND DISCUSSION

The ability of Fenton's reagent to effect vinyl polymerization was recognized by Haber and Weiss^{13,14} as early as 1932. It was postulated that FAS interacts with H_2O_2 to produce $\dot{\text{O}}\text{H}$, which is responsible for chain reaction. Following this discovery, attempts have been made to utilize Fenton's reagent as a convenient redox system for synthesizing a number of vinyl polymers and synthetic rubber. However, very few studies have been reported on the use of such a versatile redox system in graft copolymerization. Grafting by chemical means essentially involves generation of active sites on the backbone polymer by radical species, and consequently various side reactions such as chain transfer, branching, and hydrogen abstraction occur along with graft copolymerization and homopolymerization. In order to minimize side reactions, attempts have been made to generate active sites onto polymeric backbone (WH) by use of redox systems. Ceric ion is an excellent redox initiator for effecting grafting of a variety of vinyl monomers onto wool fiber, but the efficiency of ceric ion was found to depend upon rigorous control of H^+ , which seems to affect greatly the graft yield. No such stringent control of H^+ is required when grafting of vinyl monomer onto

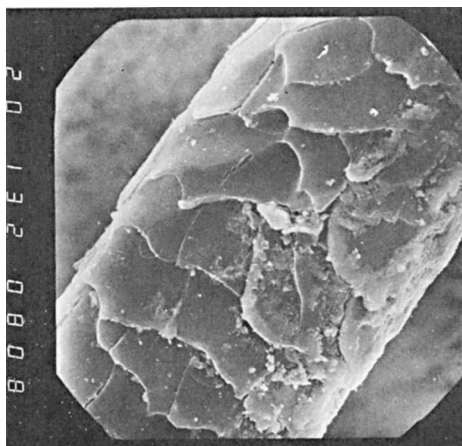


Fig. 2. Scanning electron micrograph of Wool—*g*-PMMA (Sample 14 of Table I) (1300 \times).

TABLE I
Effect of Concentration of Monomer, Molar Ratio of [FAS]/[H₂O₂], Temperature, and Time on Percent Grafting of MMA onto Wool^a

Sample no.	[FAS]/[H ₂ O ₂] molar ratio	[MMA] × 10 ² (mol/L)	Temp (°C)	Time (min)	% Grafting	% Efficiency
1	0.575	23.5	50	180	57.0	12.1
2	0.575	23.5	30	180	7.0	1.5
3	0.575	23.5	40	180	11.0	2.3
4	0.575	23.5	60	180	75.0	16.0
5	0.575	23.5	70	180	70.0	14.9
6	0.674	23.5	60	180	104.0	22.1
7	0.719	23.5	60	180	120.0	22.5
8	0.772	23.5	60	180	80.5	17.1
9	0.810	23.5	60	180	64.0	13.6
10	1.079	23.5	60	180	64.5	13.7
11	0.539	23.5	60	180	61.0	13.0
12	0.431	23.5	60	180	14.0	3.0
13	0.719	14.1	60	180	24.0	5.1
14	0.719	32.9	60	180	165.0	35.1
15	0.719	42.8	60	180	76.0	16.1
16	0.719	32.9	60	120	51.0	10.8
17	0.719	32.9	60	210	94.0	20.0

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

wool was attempted in the presence of Fenton's reagent. The following equations describe the mechanism of grafting of PEA and PMMA onto wool fiber in the presence of Fenton's reagent:

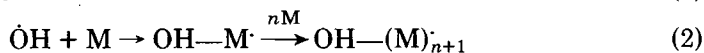
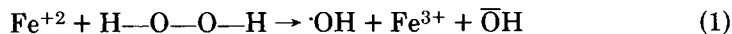


TABLE II
Effect of Concentration of Monomer, Molar Ratio of [FAS]/[H₂O₂], Temperature, and Time on Percent Grafting of EA onto Wool^a

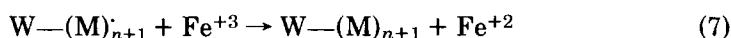
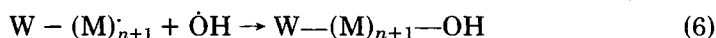
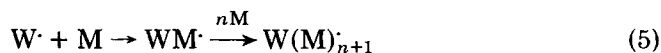
Sample no.	Molar ratio [FAS]/[H ₂ O ₂]	[EA] × 10 ² (mol/L)	Temp (°C)	Time (min)	% Grafting	% Efficiency
1	0.674	23.0	40	180	11.0	2.3
2	0.674	23.0	50	180	16.0	3.4
3	0.674	23.0	60	180	48.0	10.4
4	0.674	23.0	70	180	275.0	59.7
5	0.674	23.0	75	180	11.0	2.3
6	0.575	23.0	70	180	113.0	24.5
7	0.719	23.0	70	180	234.0	50.8
8	0.505	23.0	70	180	220.0	47.8
9	0.404	23.0	70	180	103.0	22.3
10	0.011	23.0	70	180	194.0	42.1
11	0.674	23.0	70	120	219.0	47.6
12	0.674	23.0	70	150	334.0	72.6
13	0.674	23.0	70	210	305.0	66.3
14	0.674	13.8	70	150	58.0	20.9
15	0.674	32.2	70	150	233.0	36.0
16	0.674	41.4	70	150	20.0	2.3

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

TABLE III
Maximum Grafting of Vinyl Monomers onto Wool Initiated by Fenton's Reagent under Optimum Conditions

Sample no.	Monomer	% Grafting
1	MMA	165.0
2	EA	334.0
3	VAc ^a	65.0

^a Taken from Ref. 12.



where WH and M denote respectively the wool fiber and monomer. It is apparent from the above mechanism that initiation of grafting can occur by processes (3) and (4). Since the concentration of Fenton's reagent is very small, generation of active sites by process (3) involving abstraction of hydrogen atom from WH is unlikely. $\dot{\text{O}}\text{H}$ will instead preferentially interact with vinyl monomer to give the growing polymeric chains, which then are expected to create active centers on WH by hydrogen abstraction by process (4). Generation of active sites on WH by the secondary radical species (polymeric chain) by process (4) has been reported¹² during Fenton's reagent-initiated grafting of poly(vinyl acetate). If the growing polymeric chain is responsible for initiation of grafting, the percentage of grafting would be expected to increase with increase in monomer concentration as shown in Tables I and II. However, it is observed from Tables I and II that there exists an optimum monomer concentration at which graft yield is maximum, beyond which homopolymer formation becomes the preferred process that leads to decrease in percent grafting. It is also apparent from Table III that not all vinyl monomers are equally reactive towards graft copolymerization. The following reactivity order was observed:



The molar ratio of $[\text{FAS}]/[\text{H}_2\text{O}_2]$ was found to play an important role in graft copolymerization. Tables I and II show that maximum grafting with EA and MMA occurs at molar ratio of $[\text{FAS}]/[\text{H}_2\text{O}_2] = 0.674 \text{ mol/L}$ and 0.719 mol/L , respectively. Dependence of graft yield upon molar ratio of $[\text{FAS}]/[\text{H}_2\text{O}_2]$ indicates that Fe^{3+} , which is formed by the interaction of FAS and H_2O_2 participates in termination of growing grafted chain by process (7). A similar observation was also reported during grafting of PVAc¹² onto wool fiber in the presence of Fenton's reagent.

Percentage of grafting was found to increase with increase in temperature, and this observation supports the assumption that initiation of grafting primarily occurs by hydrogen abstraction process which has higher activation energy. Tables I and II show that the maximum grafting of MMA and EA occurs within 180 min and 150 min, respectively.

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