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Graft Copolymerization of Poly(ethyl Acrylate) onto Wool in the Presence of Ceric Ammonium Nitrate as Redox Initiator

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ABSTRACT

Poly(ethyl acrylate) has been grafted onto Himachali wool in an aqueous medium by using ceric ammonium nitrate (CAN) as redox initiator. Copolymerization was studied at five different temperatures: 40, 45, 50, 55, and 60°C. Maximum grafting occurred at 45°C. Nitric acid was found to catalyze the graft copolymerization reactions. Percentage and efficiency of grafting were found to be dependent upon concentrations of CAN (initiator) and of monomer. Percentage of grafting has been determined as function of time, and from the slope of percent grafting versus time plot, the initial rate of graft copolymerization (R_p) has been determined.

INTRODUCTION

Modification of natural polymers such as cellulose and starch by graft copolymerization has been extensively studied in recent years [1-5]. However, relatively few studies have been reported on modification of natural wool fiber by graft copolymerization. Among

fibrous proteins, collagen, and silk have been subjected to graft copolymerization by using different initiating systems. Nayudamma and co-workers [6] were successful in preparing the graft of collagen and poly(methyl methacrylate) by using CAN as redox initiator. Styrene and acrylonitrile were grafted to silk by γ -irradiation and from the infrared spectra of the irradiated samples it was concluded that grafting of PS and PAN occurred on silk [7]. Negishi et al. [8] have used a novel one-electron transfer initiating system comprising $\text{LiBr-S}_2\text{O}_8^{2-}$ and reported that grafting of MMA to wool proceeded without homopolymer formation. Lipson et al. [9] used persulfates and Fenton's reagent as initiators and observed that untreated wool was resistant to grafting. Misra et al. [19] were successful in effecting grafting of poly(vinyl acetate) by using Fenton's reagent as redox initiator. Madaras and Speakman [10] were able to produce significant amount of grafting of methacrylic acid onto wool by using persulfates as initiators in aqueous medium. Kenyon and Garnett [11] have recently reported that ethyl acrylate can be successfully grafted to wool in presence of nitric acid and a good swelling solvent. Very few studies have been reported on mechanism of grafting of vinyl monomers onto wool by ceric ion initiation. However, ceric ion has been extensively used in effecting grafting of a variety of vinyl monomers onto starch and cellulose. With both cellulose and starch, ceric ion is known to form a complex [12-15] which decomposes to generate active site directly on the polymeric backbone where grafting may occur. In presence of ceric ion, grafting occurs exclusively on polymeric backbone without formation of homopolymer, and for this reason ceric ion is often preferred over other redox initiator. Wool is a natural polypeptide and contains various functional groups, such as $-\text{OH}$, $-\text{NH}_2$, $-\text{SH}$, $-\text{CO}_2\text{H}$, and $=\text{NH}$. All these groups are also capable of forming a complex with ceric ion. The complex of wool and ceric ion may decompose to give free radical sites directly on wool where grafting of appropriate vinyl monomer can occur. With this idea in mind, a systematic study on grafting onto wool by ceric ion has been initiated in our laboratory, and it has been observed that poly(methyl acrylate) can be successfully grafted to wool by use of CAN as redox initiator [16]. Ethyl acrylate ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_3$) has a $-\text{CH}_2-$ group between oxygen and CH_3 in ester function. We were interested to see if extra $-\text{CH}_2-$ in the monomer (EA) exerts any effect on percentage of grafting. In this paper, we report on grafting of poly(ethyl acrylate) onto wool as functions of various reaction parameters. From the plot of percentage of grafting versus time the initial rate of grafting has been calculated.

MATERIALS AND METHODS

Characterization of Himachali Wool

Himachali wool was obtained from Himachal Pradesh, India and its physical characterization was done by standard method. Results are reported in Table 1.

Himachali wool was then purified by extraction with acetone and petroleum ether for 48 hr, washed with water, and dried at 50°C for 48 hr.

Ethyl acrylate (reagent grade) was freshly distilled and the middle fraction was used. Ceric ammonium nitrate was of reagent grade and was used as received. Nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution.

Graft Copolymerization

Pure Himachali wool (1.0 g) was dispersed in 200 ml of cold deaerated distilled water in a three-necked flask. A definite amount of CAN in minimum amount of 0.08 M nitric acid was added to the reaction flask under stirring by magnetic stirrer. Prior to the reaction, the mixture was purged with purified nitrogen for 30 min and then a continuous supply of nitrogen was maintained throughout the reaction. Weighed amount of monomer (ethyl acrylate) was added dropwise to the reaction mixture, and copolymerization was carried out at 40, 45, 50, 55, and 60°C for periods of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 3.5 hr. After completion of the reaction grafted material was separated and purified by the method described [16]. Percentage of grafting was determined from increase in weight of wool [16, 19]. The initial rate of grafting R_p was determined from slopes of percentage of grafting versus time plot (Fig. 1).

TABLE 1. Physical Characterization of Himachali Wool

<u>Parameter</u>	
Moisture content	16.0%
Ash content	1.67%
Acetone soluble fraction	7.05%

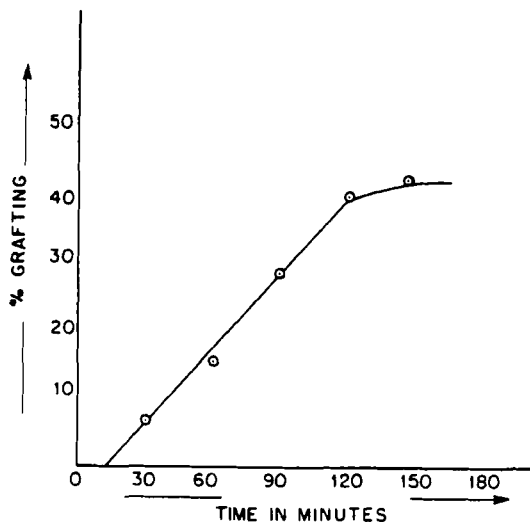


FIG. 1. Percent grafting vs. reaction time. Reaction conditions: wool, 1 g; [EA], 13.93×10^{-2} mole/liter; water, 200 ml; temperature, 45°C ; $[\text{Ce}^{4+}]$, 1.25×10^{-3} mole/liter; $[\text{HNO}_3]$, 8×10^{-2} mole/liter.

Evidence of Grafting

The grafted material was refluxed with 6 *N* HCl at 135°C for 24 hr. All wool went into solution, leaving resinous mass which was identified as poly(ethyl acrylate). The IR spectra of the residue showed a band at 1730 cm^{-1} which was attributed to C=O of poly(ethyl acrylate). A physical mixture of poly(ethyl acrylate) and wool after extraction with benzene was subjected to HCl treatment; no residue was obtained, indicating that homopolymer is completely removed by benzene extraction. Isolation of polymer after treatment with HCl from the grafted material constituted evidence for grafting.

Physical Characterization of Graft Copolymer

Solubility behavior of grafted material in 4 *M* hydrochloric acid, 0.1 *N* sodium hydroxide, peracetic acid solution, and in sodium metabisulfite-urea solution was compared with that of pure wool. Results are reported in Table 2.

TABLE 2. Solubility Behavior of Ungrafted and Grafted Wool

Solvent	Weight loss (%)	
	Ungrafted wool	Grafted wool
0.1 <u>N</u> NaOH	85.5	68.7
4 <u>M</u> HCl	10.7	14.8
Peracetic acid	12.5 (large swelling)	9.7 (less swelling)
Urea-bisulfite	12.9	2.9

Acid Treatment. Grafted and ungrafted wool were exposed to 4 M hydrochloric acid for 1 hr at 65°C and the loss in weight measured.

Alkali Treatment. The sample was immersed in 0.1 N NaOH at 65°C for 1 hr and the loss in weight measured.

Solubility in Oxidizing Solvent. The sample was immersed in solution containing 3 ml of 30 vol % H₂O₂ and 100 ml of glacial acetic acid at room temperature, then treated with 0.3% aqueous NH₃, and the loss in weight was measured.

Urea-Bisulfite Treatment. The sample was immersed in a solution of 3% sodium metabisulfite and 50% urea at 65°C for 1 hr at pH 7.0 and the loss in weight determined.

RESULTS AND DISCUSSION

Ceric ion is known [17] to form complexes with alcohols, aldehydes, amines, and thiols. Wool (WH) contains numerous functional groups which are capable of forming complexes with ceric ion. If such complex formation between wool and ceric ion occurs then the following mechanism involving complex formation between ceric ion and wool holds [Eqs. (1)-(4)].

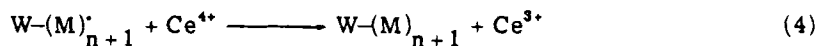
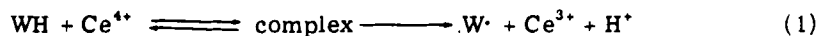


TABLE 3. Effect of Concentration of Ceric Ion upon Percentage Grafting of Poly(ethyl Acrylate)^a

No.	Ce ⁴⁺ × 10 ³ (mole/liter)	Grafting (%)	Efficiency (%)
1	1.0	35.89	12.8
2	1.25	39.01	13.9
3	1.50	72.24	25.8
4	2.00	0.36	.12
5	2.50	0.12	.04

^aWool = 1.0 g, water = 200 ml; [Monomer] = 13.93×10^{-2} mole/liter; [HNO₃] = 8×10^{-2} mole/liter; temperature = 45°C.

It has not been possible to elucidate the structure of the complex. However, it has been observed that with acetylated wool, the percent grafting is reduced considerably. This indicates that -NH₂ and -OH groups are involved in complex formation. A detailed study on the nature of complex formed between wool and ceric ion is in progress, and the results will be reported in a future communication.

In accordance with this postulated mechanism, the percentage of grafting would be expected to increase at first with increasing ceric ion concentration. Table 3 shows that as the concentration of ceric ion increases, the percentage of grafting also increases and reaches a maximum value at [Ce⁴⁺] = 1.5×10^{-3} mole/liter. Beyond this concentration, the percentage of grafting decreases. This is expected since at higher concentration ceric ion participates more effectively in terminating the growing grafted chains. Termination of a growing chain by ceric ion in acrylonitrile polymerization has been reported [18]. Mishra and Chandel have reported [16] that ceric ion at higher concentration terminates the growing chain of poly(methyl acrylate) grafted to wool.

Nitric acid was found to catalyze grafting as was observed in the case of methyl acrylate [16]. Kenyon et al. [11] also found that mineral acids acted as catalyst in grafting poly(ethyl acrylate) onto wool in presence of good swelling solvents. In the present study, nitric acid of 8.0×10^{-2} mole/liter concentration was used.

Table 4 shows the variation of percentage of grafting with the monomer concentration. The results agree with our findings on poly(methyl acrylate). However, the effect of monomer concentration upon percentage of grafting is much more pronounced in the case of

TABLE 4. Effect of Concentration of Monomer upon Percentage Grafting^a

No.	Concentration of monomer $\times 10^2$ (mole/liter)	Grafting (%)	Efficiency (%)
1	13.95	72.24	25.8
2	23.25	73.35	15.7
3	32.55	77.87	11.9

^aWool = 1.0 g; water = 200 ml; [CAN] = 1.5×10^{-3} mole/liter; [HNO₃] = 8×10^{-2} mole/liter; time = 120 min; temperature = 45°C.

methyl acrylate than with ethyl acrylate. This tends to indicate that steric effects come into play when monomers of varying steric requirements are grafted to wool. Maximum grafting in the case of ethyl acrylate was found to be 77.87% under optimum conditions, while methyl acrylate under optimum conditions afforded 270% grafting [16]. Although ethyl acrylate is larger than methyl acrylate, this small difference does not seem to explain satisfactorily the much pronounced difference in grafting. Misra and Chandel [16], however, used 0.19 M nitric acid for grafting poly(methyl acrylate). In the present case, 0.08 M nitric acid was used. Nitric acid is known to catalyze grafting. Since nitric acid of lower concentration was used in the present study, it is not surprising that grafting with ethyl acrylate is less. However, the large difference in the percentage of grafting observed with ethyl acrylate compared to methyl acrylate indicates that ethyl acrylate is a less reactive monomer than methyl acrylate towards grafting. Ethyl acrylate being larger than methyl acrylate, preferably undergoes homopolymerization which is sterically less hindered process compared to grafting.

Figure 1 shows the variation of percentage of grafting with varying reaction time. It is observed that the induction period is only 10.5 min and that maximum grafting is obtained within 2 hr. From the linear part of the curve in the plot of percentage of grafting versus time, the initial rate of grafting R_p was determined and was found to be 0.353%/min.

In order to find out optimum temperature for maximum grafting several grafting reactions were carried out at five different temperatures, viz. 40, 45, 50, 55, and 60°C. The maximum grafting occurred at 45°C (Table 5). This was also the optimum temperature for grafting of poly(methyl acrylate) onto wool [16].

TABLE 5. Effect of Temperature upon Percent Add-on^a

No.	Temperature (°C)	Grafting (%)	Efficiency (%)
1	40	59.5	9.1
2	45	77.87	11.9
3	50	73.70	11.3
4	55	43.08	6.6
5	60	6.49	0.99

^aWool = 1.0 g; water = 200 ml; [CAN] = 1.5×10^{-3} mole/liter; [HNO₃] = 8×10^{-2} mole/liter; time = 120 min; [M] = 32.55 mole/liter.

An attempt was made to make a comparative study of the solubility behavior of grafted and ungrafted wool in standard solvent systems to provide some idea regarding the changes in the wool due to grafting. Table 2 shows that the grafted wool was superior to ungrafted wool in resistance towards 0.1 N NaOH. Table 2 further shows that solubility of grafted wool in the reducing solvent system is much less than that of ungrafted wool. In the oxidizing solvent, the grafted wool is somewhat less soluble than ungrafted wool, and swelling is greatly decreased by grafting. This would indicate that grafting has resulted in greater stiffness in wool. In 4 M HCl, grafted wool was found to be degraded more than the ungrafted wool. This may indicate that crosslinking due to the -SS- bond is affected during grafting in the presence of nitric acid.

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