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Grafting onto Wool

12. Graft Copolymerization of Ethyl Acrylate onto Reduced Wool by Use of Ceric Sulfate as Redox Initiator

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SUMMARY

In order to ascertain the role of -SH groups in graft copolymerization of vinyl monomers onto Himachali wool fiber, an attempt has been made to graft copolymerize ethylacrylate (EA) onto reduced wool, in the presence of ceric sulfate (CS) as redox initiator in aqueous medium. Reduction of wool was carried out with thioglycolic acid (TGA) in aqueous solution. Percentage of grafting and percent efficiency were determined as functions of (a) Concentration of initiator (CS), (b) Concentration of monomer (EA), (c) Concentration of Sulfuric acid, (d) Time and (e) Temperature. Reduction of wool does not promote grafting of EA. The unreduced wool during ceric ion-initiated grafting of EA was reported earlier from this laboratory to produce more grafting. In ceric ion-initiated grafting of vinyl monomer onto wool, -SH groups do not play significant role. A plausible mechanism of grafting of EA onto reduced wool in the presence of ceric ion initiator has been suggested.

INTRODUCTION

Ceric ion has been widely used as redox initiator for effecting grafting of variety of vinyl monomers onto cellulose (MISRA et al. 1976, 1978), starch (FANTA et al. 1971, SRIVASTAVA et al. 1976) and poly-(vinyl alcohol) (ODIAN, 1968). Ceric ion is known to form complexes with the hydroxyl group of polyhydric alcohols and these complexes then decompose to generate active sites on the polymeric backbone by a one electron transfer process

$$R_{cell}\,OH + Ce^{4+} \rightleftharpoons B \longrightarrow R_{cell}\,O\cdot + Ce^{3+} + H^{+}$$

When the oxidation of polyhydric alcohol is

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carried out in the presence of vinyl monomers, grafting of vinyl monomer occurs without homopolymer formation. For this reason ceric ion is often preferred over other redox initiators for effecting grafting onto natural and synthetic polymeric backbones. Grafting onto proteins in general and wool in particular has not been extensively investigated. In recent years, attempts are being made to modify wool fiber by graft copolymerization technique. A number of workers have reported on wool grafting using different initiating systems.

Wool is a natural polypeptide that contains numerous functional groups such as -OH, $-NH_2$, Imino, $-CO_2H$, -SH and -SS- linkage. All these functional groups are capable of entering into redox reaction with ceric ion. These complexes upon decomposition may generate active sites where grafting of appropriate vinyl monomer can occur. By using this technique, MISRA et al. (1977, 1978, 1979, 1980) have been able to successfully graft MA, MMA, VAc, AAc and EA onto wool fiber. They have evaluated relative reactivities of different vinyl monomers towards ceric ion-initiated grafting onto Himachali wool. However, it has not been possible to identify the functional groups which are responsible for grafting of vinyl monomers onto wool fiber in the presence of ceric ion-initiator. It appears that -OH, $-NH_2$ and -SH may play a major role in providing active sites where grafting occurs. KANTOUCH et al. (1971) have indicated that both -OH and $-NH_2$ of wool are involved in ceric ion-initiated grafting of MMA. Thiols are capable of forming complexes with ceric ion and it is natural that attempts are being made to investigate the role of cystine of wool in ceric ion-initiated grafting. The role of sulfur compounds in initiating, modifying and promoting vinyl polymerizations has been recognized for many years. LIPSON (1949) reported that graft copolymerization in wool occurs through -SH groups formed by the reduction of cystine in wool. The probable role of cysteine in the polymerization occuring in the presence of sulphur containing proteins was illustrated further in the research of LIPSON & HOPE (1950) who showed that methacrylic acid polymerizes in the presence of cysteine and ammonium persulphate. Recently NEGESHI et al. (1967) investigated grafting of MMA onto wool in the presence of $LiBr-S_2O_8=$ initiating system and concluded that -SH of wool provides active sites for grafting. In earlier work we have reported grafting of EA (MISRA et al. 1978) onto wool by using CAN as redox initiator. In the present article, we describe the studies on graft copolymerization of EA onto reduced wool. Percentage of grafting has been expressed as function of various reaction parameters.

EXPERIMENTAL

Purification and physical characterization of Himachali wool have been described (MISRA et al.1977, 1978). Ethyl acrylate was treated with 5% NaOH solution, washed with water and dried over anhydrous sodium sulfate. The dried EA was distilled and the middle fraction was collected. Ceric sulfate (BDH) of analytical grade was used. Sulfuric acid of known strength was used in all experiments. Thioglycolic acid (BDH) was used as received.

Reduction:

One gram of pure Himachali wool was immersed in 0.5% solution of thioglycolic acid for 48 hours. The reduced wool was washed with water and methanol several times and dried.

Graft Copolymerization:

Reduced wool (1.0g) was dispersed in 200 ml of deaerated distilled water. A known weight of ceric sulphate (CS) dissolved in definite amount of H_2SO_4 of known strength was added to the reaction flask which was flushed with purified nitrogen for 30 minutes prior to the addition of monomer. A continuous supply of nitrogen flow was maintained throughout the reaction period. Measured amount of vinyl monomer (EA) was added dropwise to the reaction mixture. Graft copolymerization was carried out at 30°, 45° and 60° for various reaction periods. After the completion of the reaction, the reaction mixture was filtered and the residue was extracted with benzene for 48 hours for the removal of homopolymer (PEA). After extraction, the residue was dried at 50° and weighed to a constant weight. From the increase in weight of reduced wool, percentage 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 reduced wool, the weight of grafted wool sample and the weight of EA added.

Evidence of Grafting:

An intimate physical mixture of reduced wool and PEA was prepared by stirring (1.0g) reduced wool samples in benzene solution of PEA for 24 hours. The mixture was filtered and the residue was extracted with benzene for 48 hours. 0.99g of wool sample was recovered. This indicated that the homopolymer (PEA) is completely removed from a physical mixture by benzene extraction.

The grafted sample was hydrolyzed with 6N HCl at 115°C for 24 hours, when all the wool sample went into solution leaving a resinous mass which was identified as poly(ethylacrylate) by IR spectroscopy. Isolation of PEA from the grafted sample after hydrolysis by 6N HCl indicated that PEA is covalently bonded to wool backbone. The IR spectrum of W-g-PEA showed a band at 1730 cm^{-1} attributed to C=O of grafted PEA.

RESULTS AND DISCUSSION

It is a well established fact that the treatment of wool with thioglycolic acid (TGA) increases the thiol content of wool. The cystine disulfide residue is reduced to -SH group of cystine. Sulfhydryl groups are quite reactive and capable of formation of complex with Ce^{+4}. Reduction of wool was therefore expected to afford enhanced grafting. In a previous paper (MISRA et al. 1978) we investigated grafting of EA onto untreated wool by using CAN as redox initiator and it was observed that under optimum conditions, PEA to the extent of 77.87% could be grafted to untreated wool fiber. In the present study, EA was grafted to TGA-treated wool in the presence of CS as initiator and under optimum conditions EA could be grafted only to the extent of 32.22% (Table I). This indicates that -SH of wool does not promote grafting when Ce^{+4} is used as initiator. CAN is known to form complex with wool which easily decomposes. On the other hand, the complex of CS and wool decomposes less readily. Thus the nature of ligand attached to Ce^{+4} may influence grafting. However, a considerable decrease in percent grafting of PEA onto reduced wool in the presence of CS cannot be satisfactorily explained on the basis of difference in stability of complexes formed between wool and CAN and between wool and CS. It seems that additional -SH groups arising from reduction of cystine instead of promoting adversely affect grafting. Perhaps -SH groups are oxidized by Ce^{+4} to give a variety of oxidized products.

Effect of Concentration of Ce^{+4}:

It is apparent from Table I that with increase in concentration of Ce^{+4}, percent grafting increases and reaches a maximum value of 32.22% at $Ce^{+4} = 2.0 \times 10^{-2}$ mole/l. Beyond this concentration of Ce^{+4}, percent grafting was found to decrease. Under optimum conditions, untreated wool in the presence of CAN afforded maximum grafting (MISRA et al. 1978) to the extent of 77.87%. The decrease in graft yield in the case of reduced wool is explained by assuming the following mechanism:

$$2R - SH + 2Ce^{+4} \longrightarrow R - S - S - R + 2Ce^{+3} + 2H^{+} \quad (1)$$

$$R - S - S - R + Ce^{+4} \longrightarrow \text{Wool oxidation products} \quad (2)$$

$$R - SH + Ce^{+4} \longrightarrow [RS - Ce]^{+3} + H^{+} \quad (3)$$

$$[2R\text{-}S\text{-}Ce]^{+3} + 2R - SH \longrightarrow [2R\text{-}S\text{-}Ce]^{+2} + R\text{-}S\text{-}S\text{-}R + 2H^{+} \quad (4)$$

$$2R - SH + Ce^{+4} \longrightarrow [R - S - Ce - S - R]^{+2} + 2H^{+} \quad (5)$$

$$2[R\text{-}S\text{-}Ce\text{-}SR]^{+2} + 2RSH \longrightarrow 2[R\text{-}S\text{-}Ce\text{-}SR]^{+} + RS\text{-}SR + 2H^{+} \quad (6)$$

It is clear from the above mechanism that reaction (1) leads to rebuilding of disulfide linkages thereby giving rise to original wool. If this reaction predominates it would be expected that the reduced wool would yield the same amount of graft as the unreduced wool. However, the present study indicates that reduced wool produces less grafting and this would be expected since -SH of wool reacts with Ce^{+4} in the manner described above to give a variety of oxidized products of wool. $HgCl_2$ (LEACH 1960) and $AgNO_3$ (KEIGHLEY 1968) are known to react with wool to give a variety of oxidized products.

Effects of concentration of sulphuric acid, monomer, time and temperature on graft copolymerization onto reduced wool were similar as observed during grafting of EA onto unreduced wool (MISRA et al.1978) in the presence of CAN and HNO_3.

From the foregoing discussion it is concluded that -SH groups of wool do not promote grafting of EA in the presence of ceric ion initiator.

Table I: Effect of concentration of CS, EA, H_2SO_4, time and temperature on percent grafting of EA onto reduced wool[a].

S.No.	[CS] x 10^2 mole/l	[H_2SO_4] x 10^2 mole/l	[EA] x 10^2 mole/l	Time (min)	Temp. (°C)	% Grafting	% Efficiency
1.	1.00	3.75	23.25	180	45	19.19	4.17
2.	1.00	4.50	23.25	180	45	22.77	4.95
3.	1.00	5.62	23.25	180	45	20.41	4.43
4.	1.00	7.50	23.25	180	45	3.84	0.83
5.	1.00	4.50	23.25	180	30	10.78	2.34
6.	1.00	4.50	23.25	180	60	4.73	1.03
7.	1.00	4.50	13.93	180	45	9.82	3.52
8.	1.00	4.50	32.55	180	45	15.74	2.41
9.	1.00	4.50	23.25	90	45	4.13	1.03
10.	1.00	4.50	23.25	150	45	12.33	2.68
11.	0.75	4.50	23.25	180	45	9.18	2.00
12.	1.50	4.50	23.25	180	45	23.87	5.18
13.	2.00	4.50	23.25	180	45	32.22	7.00

[a] Reduced wool = 1 gm; H_2O = 200 ml.

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