Grafting onto Wool. XXVIII. Effects of Acids on Gamma-Radiation Induced Graft Copolymerization of Ethylmethacrylate onto Wool Fiber

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SYNOPSIS

Graft copolymerization of ethylmethacrylate (EMA) onto Himachali wool fiber has been investigated in aqueous medium by mutual gamma irradiation from a Co^{60} source in air and in nitrogen atmosphere. Percentage of grafting has been evaluated as a function of (i) total dose, (ii) concentration of monomer, and (iii) effect of concentration of different acids such as hydrochloric acid, sulfuric acid, nitric acid, perchloric acid, and acetic acid. Maximum percentage of grafting has been obtained in the presence of sulfuric acid. Following reactivity order of different acids towards grafting has been observed: $H_2SO_4 > HCl > HNO_3 > HClO_4 > CH_3COOH$. A plausible mechanism to explain the effect of acids on percentage of grafting of EMA has been suggested.

INTRODUCTION

In recent years, chemical modification of wool through grafting has received considerable interest.[1-3] Grafting promises to be a potentially powerful method for producing substantial modification of wool properties. Grafting by radiation is a uniform and clean method and the degree of grafting can be easily controlled. Stannett and co-workers[4] studied the radiation grafting of vinyl monomers onto wool. A number of vinyl monomers have been grafted to wool by mutual radiation method. Stannett[5] has reported the effect of grafted polymer on the wool–water relationship. Burke et al.[6] have grafted acrylonitrile onto wool containing trapped radicals. Grafting of styrene, methyl methacrylate, and acrylonitrile onto wool by mutual irradiation method has been carried out by Hario and co-workers.[7] The importance of wetting of the wool fiber to effect adequate grafting has also been pointed out by Puig.[8] Recently Misra and Rawat[9] have studied the effect of mineral and organic acids on radiation-induced graft copolymerization of methyl methacrylate onto wool. In order to study effect of additional methylene group on the ester moiety, we report grafting of EMA onto wool initiated by gamma radiations in the present article.

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EXPERIMENTAL

Materials and Methods

Purification of Himachali wool fiber has been described earlier. EMA was washed with 5% sodium hydroxide and then dried over anhydrous sodium sulfate. The dried monomer was distilled and the middle fraction was used. Nitrogen was flushed through the reaction medium after passing it through alkaline pyrogallol solution.

Graft Copolymerization

Purified Himachali wool (100 mg) was immersed in 30 mL of distilled water in a 50-mL two-necked flask. A definite amount of monomer was added to the reaction flask and nitrogen was flushed through the mixture for 30 min prior to irradiation. The nitrogen inlet was removed and the flask was closed with air tight stopcocks. Irradiation of the reaction mixture was carried out in a 2100 Ci Co^{60} source at room temperature for different time periods at a constant dose of 0.35 MR/h. After the completion of the reaction, the product was filtered. Homopolymer was removed from the graft copolymer by solvent extraction using acetone as solvent. The percentage of grafting was calculated from increase in the weight of original wool in the following manner:

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

where W_1 and W_2 are, respectively, the weights of original wool and grafted wool after solvent extraction.

Evidence of Grafting

1. On comparison of IR spectra of wool and wool-*g*-PEMA, it is observed that a strong peak at 1730 cm^{-1} in the grafted sample assigned to $>C=O$ group of PEMA is absent in the IR spectra of wool, which indicates the formation of the graft.
2. Hydrolysis of wool-*g*-PEMA: Hydrolysis of wool-*g*-PEMA was carried out by 6*N* HCl at 130°C for 24 h when all the wool protein goes into solution as amino acids. A resinous mass was left which was washed and dried and was identified as PEMA by IR spectroscopy.
3. Ninhydrin test: The hydrolytic product of wool was filtered. The residue identified as PEMA and the filtrate contained various amino acids which gave a positive ninhydrin test after neutralization. The PEMA solution in acetone gave negative ninhydrin test; however, it gave a positive test when applied on the Whatman filter paper. This may be explained by the fact that any amino acid residue attached with the polymer when dissolved in acetone can react with the solvent to give Schiff's base and hence cannot complex with ninhydrin to give violet coloration:

$$CO_2H-CHR-NH_2 + O=C(CH_3)_2 \rightarrow CO_2H-CHR-N=C(CH_3)_2$$

   But when the solution is applied to the filter paper, acetone evaporates and the amino acid residue is free to complex with ninhydrin to give positive colour test. The presence of amino acid residue in the isolated grafted polymer indicates that the polymer is covalently attached to the wool fiber.
4. Comparison of scanning electron micrographs of wool and grafted wool indicates that considerable amount of polymer is deposited onto the surface of the wool fiber.

RESULTS AND DISCUSSION

In the present investigation, grafting of EMA onto wool fiber has been studied by mutual gamma irradiation method. Wool possesses a number of pendant functional groups such as $-NH_2$, $-COOH$, $-SH$, $-OH$, etc., which can be activated by γ-radiations to generate active sites where appropriate monomer can be grafted. Following plausible mechanism is proposed to explain grafting:

$$WH \rightsquigarrow WH^* \rightarrow W^\bullet + H^\bullet \quad \text{(i)}$$

$$H_2O \rightsquigarrow H_2O^* \rightarrow H^\bullet + \dot{O}H \quad \text{(ii)}$$

$$M \rightsquigarrow M^* \rightarrow M^\bullet \quad \text{(iii)}$$

$$R^\bullet + M \rightarrow RM^\bullet \xrightarrow{nM} R-(M)^\bullet_{n+1} \quad \text{(iv)}$$

$$W^\bullet + M \rightarrow WM^\bullet \xrightarrow{nM} \underset{\text{Graft}}{W-(M)^\bullet_{n+1}} \quad \text{(v)}$$

$$W^\bullet + {}^\bullet(M)_{n+1}-R \rightarrow \underset{\text{Graft}}{W-(M)_{n+1}-R} \quad \text{(vi)}$$

$$W-(M)^\bullet_{n+1} + {}^\bullet(M)_{n+1}-R \rightarrow \underset{\text{Graft}}{W-(M)_{2n+2}-R} \quad \text{(vii)}$$

$${}^\bullet(M)_{n+1}-R + {}^\bullet(M)_{n+1}-R \rightarrow \underset{\text{Homopolymer}}{R-(M)_{2n+2}-R} \quad \text{(viii)}$$

where WH = wool fiber, M = monomer, and $R^\bullet$ = radical species arising from the irradiation of polymeric backbone, monomer, or solvent molecule.

It is apparent from the mechanism proposed that once the radical species are generated, they either can initiate vinyl polymerization (process iv) to form polymeric chains which can terminate to give homopolymer (process viii) or can attach to the active site of the wool to give the graft copolymer (process vi, vii).

Effect of Total Dose

It is observed from Figure 1 that percentage of grafting increases slightly with increase in total dose.

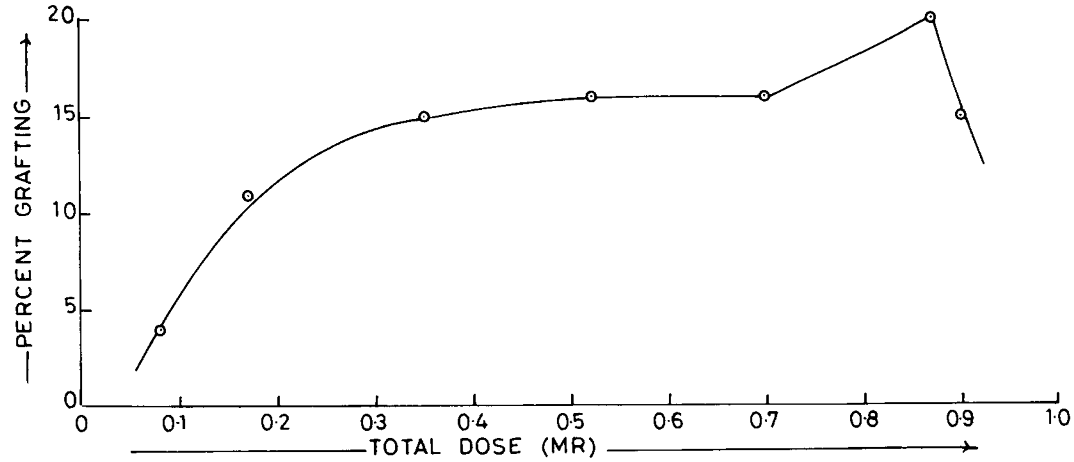
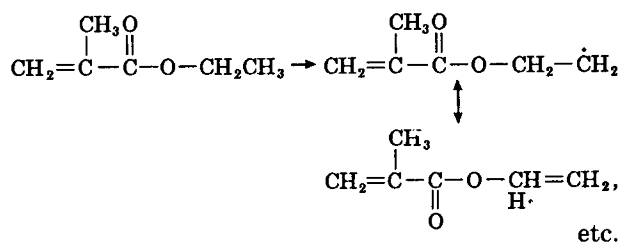


Figure 1 Effect of Total Dose on Percentage of Grafting.

Maximum percentage of grafting is obtained at a total dose of 0.875 MR beyond which grafting decreases. This indicates that, with increasing dose, EMA participates in hydrogen abstraction reactions which do not contribute towards grafting.

Effect of Monomer Concentration

Figure 2 represents the effect of monomer concentration on percentage of grafting. It is observed from the figure that grafting increases with increasing monomer concentration. Maximum grafting (15%) is obtained at [EMA] = 79.8 × 10^{-2} mol/L. Further increase in monomer concentration decreases percentage of grafting. This may be explained by the fact that at higher monomer concentration, homopolymer formation as well as wastage reactions due to monomer transfer are accelerated (C_M for EMA at 45°C = 0.248 × 10^{-4}):



On comparison, methyl methacrylate (MMA) is found to be more reactive than EMA. Under optimum conditions, MMA affords maximum grafting[9] of 63% whereas EMA produces grafting to the extent of only 28% in the presence of sulpuric acid. This is explained by the fact that the additional methylene ($-CH_2$) group present in the ester moiety of

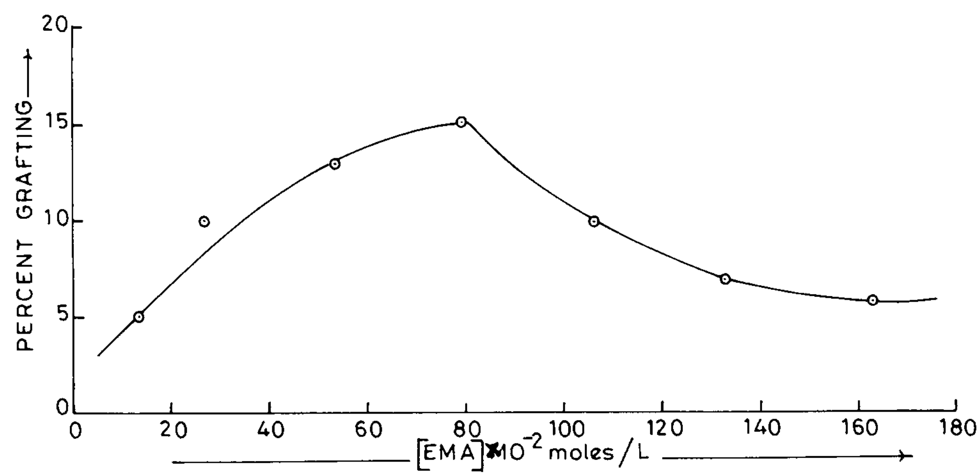


Figure 2 Effect of [EMA] on Percentage of Grafting.

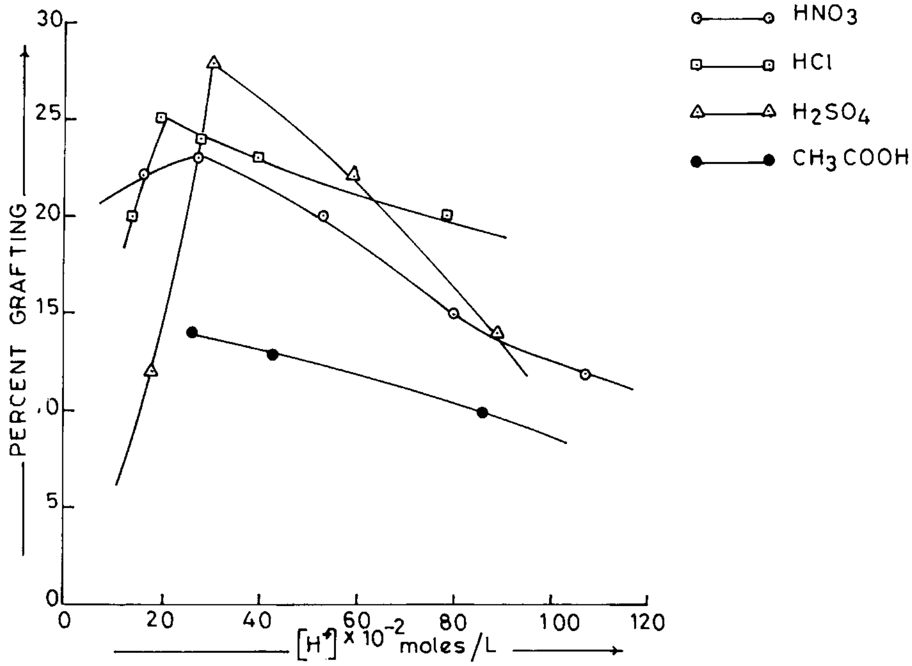
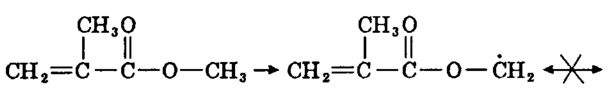


Figure 3 Effect of Acid Concentration on Percentage of Grafting.

EMA offers some steric hindrance to graft polymerization, thereby reducing percentage of grafting. Further, chain transfer constant value of MMA ($C_M = 0.117 \times 10^{-4}$)[10] is less than that of EMA ($C_M = 0.248 \times 10^{-4}$)[10] and as such the wastage of the monomer is minimum during MMA grafting. The free radical species arising from hydrogen abstraction of EMA is resonance-stabilized whereas similar species from MMA are not stabilized and therefore MMA is more reactive towards grafting:



Effect of Acids

Effect of acids on percentage of grafting of EMA has been studied and the results are presented in Figure 3. It is observed from the figure that the addition of acid has an enhancing effect on the percentage of grafting. Maximum increase in percentage of grafting is observed when sulfuric acid is used as an additive. A similar effect has also been reported by Garnett et al.,[11,12] who observed that addition of sulfuric acid accelerated graft copolymerization of many systems. Recently Gupta and Chapiro[13] also reported the enhancing effect of H_2SO_4 during grafting of AAc onto PE. In the presence of H_2SO_4, the swelling of wool occurs, which facilitates diffusion of monomer to the active sites. Such swelling can also arise in the presence of other acids, but, in the presence of strongly oxidizing acids such as $HClO_4$ and HNO_3, side reactions involving oxidations of backbone polymer can occur that may decrease percentage of grafting. Irradiation of HCl probably produces $Cl^{\bullet}$ which does not contribute towards grafting. In the presence of acetic acid, various chain transfer reactions are accelerated, leading to a decrease in the percentage of grafting.

Effect of Air

Effect of air during grafting of EMA in the presence of acid was studied and the results are presented in

Table I Effect of Air on Gamma-Irradiation-Induced Grafting of PEMA onto Wool Fiber by Mutual Method at Room Temperature[a]

Sample No.	Acids	$[H^+]$ (mol/L)	Total Dose (MR)	% G
1	HNO_3	26.6×10^{-2}	0.875	10.0
2	HCl	19.8×10^{-2}	0.875	15.0
3	H_2SO_4	29.6×10^{-2}	0.875	22.0
4	CH_3COOH	43.3×10^{-2}	0.875	9.0

[a] Reaction conditions: wool = 100 mg, water = 30 mL, [EMA] = 79.8×10^{-2} mol/L. Dose rate = 0.35 MR/h.

Table I. It is observed that, in the presence of air, the percentage of grafting is less than that in the presence of nitrogen. This is due to the fact that the oxygen of air destroys some active sites onto wool and causes a decrease in percent grafting.

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