

Grafting onto Wool

XXIX. Gamma Rays-Initiated Graft Copolymerization of Ethyl Acrylate and Methyl Acrylate by Mutual Method

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Ethyl acrylate and methyl acrylate have been graft-copolymerized onto wool fibre under nitrogen atmosphere using gamma rays as initiator. Relative mass increase of grafting (w_{rig}) has been determined as a function of total dose and monomer concentration. The effect of solvent composition and of H_2SO_4 as additive has been studied in air, too. It is interesting to note that grafting is higher when an optimum ratio $w(\text{H}_2\text{O}):w(\text{MeOH})$ is used as compared to that obtained in pure H_2O or MeOH as reaction medium. Addition of H_2SO_4 promotes grafting. Grafting is higher in nitrogen atmosphere. A plausible mechanism to explain these results has been suggested.

Grafting is a useful technique to alter some properties of wool fibre. Extensive studies on modification of wool have been reported [1–5]. Radiation grafting is a clean technique which can be used to control degree of grafting. *Stannett et al.* [6, 7] studied the radiation-induced grafting of vinyl monomers onto wool and reported that grafting influences wool-water relationship. *Puig* [8] reported the influence of wetting of wool fibre on grafting. *Misra et al.* [9, 10] reported the effect of solvent composition on graft copolymerization onto wool fibre. Recently, they also reported effect of mineral acids on the graft yields of methyl methacrylate and ethyl methacrylate (EMA) by using gamma rays as initiator [11, 12].

EXPERIMENTAL

Purification of Himachali wool has been described earlier [12]. Ethyl acrylate (EA) and methyl acrylate (MA) were washed with 5 % aqueous NaOH solution and dried over anhydrous Na_2SO_4 . The dried monomers were distilled and middle fraction was used. Nitrogen gas was purified by passing through freshly prepared alkaline pyrogallol solution for removing traces of oxygen.

Graft Copolymerization

Purified Himachali wool (100 mg) was immersed in 20 cm^3 of distilled water in a 50 cm^3 conical flask fitted with two standard joints with hollow stop cocks. A definite amount of monomer (EA/MA) was added to the reaction flask and nitrogen gas was passed through the reaction mixture prior to irradiation for 30 min. Both the stop cocks were closed and nitrogen atmosphere was maintained inside the reaction flask during the reaction. Irradiation of reaction mixture was carried out in a 2100 Co^{60} source at room temperature and graft copolymerization by mutual technique was carried out at different doses at a constant dose rate of $0.34 \times 10^4 \text{ Gy h}^{-1}$. After completion of the reaction time, the reaction mixture was filtered and the homopolymer formed was removed by solvent extractions using acetone as solvent. The extractions were repeated to obtain a constant mass and the fibre was dried in vacuum oven at 50°C . The relative mass increase of grafting was calculated as follows

Relative mass increase of grafting

$$(w_{\text{rig}}) = \frac{m_2 - m_1}{m_1} \times 100$$

where m_1 and m_2 are, respectively, the masses of orig-

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Table 1. Gamma Rays-Initiated Graft Copolymerization of Ethyl Acrylate and Methyl Acrylate onto Wool Fibre (100 mg) in the Millieu of Water—Methanol (20 cm³) and Nitrogen Atmosphere at Dose Rate 0.34 × 10⁴ Gy h⁻¹ and Room Temperature

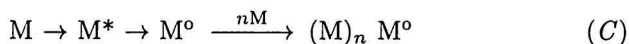
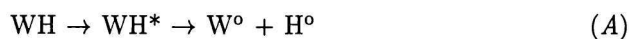
$\rho_2(\text{H}_2\text{O—MeOH})$	[Monomer]	[H ₂ SO ₄]	Total dose	w_{rig}
	10 ⁻² mol dm ⁻³	10 ⁻² mol dm ⁻³	10 ⁴ Gy	%
	Ethyl Acrylate			
1:0	25.0		0.68	8
1:1	25.0		0.68	11
1:2	25.0		0.68	16
1:3	25.0		0.68	18
1:4	9.2	—	0.68	11
1:4	25.0		0.51	15
1:4	25.0		0.68	20
1:4	25.0	8.7	0.68	20
1:4	25.0	17.5	0.68	37
1:4	25.0	17.5	0.68	12 ^a
1:4	25.0	43.7	0.68	25
1:4	25.0		0.85	2
1:4	25.0		1.02	1
1:4	32.0		0.68	10
1:5	25.0		0.68	10
1:6	25.0		0.68	8
1:7	25.0		0.68	7
1:8	25.0		0.68	5
0:1	25.0		0.68	2
	Methyl Acrylate			
1:0	26.7		0.85	5
1:1	5.6		0.68	2
1:1	16.4		0.68	5
1:1	26.7		0.51	2
1:1	26.7		0.68	16
1:1	26.7		0.85	17
1:1	26.7	8.7	0.85	11
1:1	26.7	26.7	0.85	12
1:1	26.7	43.7	0.85	22
1:1	26.7	43.7	0.85	4 ^a
1:1	26.7	60.0	0.85	19
1:1	26.7		1.02	5
1:1	37.0		0.68	14
1:2	26.7		0.68	10
1:3	26.7		0.68	5
0:1	26.7		0.68	1

a) In air atmosphere.

inal wool and grafted wool after solvent extraction. Evidence of grafting was provided by IR spectroscopy and scanning electron microscopy of the grafted polymers isolated from the grafted wool fibre by the method reported for wool-g-poly(EMA) [11]. Further evidence of grafting was provided by hydrolysis of wool-g-poly(EA) and wool-g-poly(MA) which was carried out with 6 M-HCl at 135°C for 24 h when all the wool goes into solution as amino acids. Resinous masses were left which were washed and dried and were identified as poly(EA) and poly(MA) by IR spectroscopy ($\bar{\nu} = 1730 \text{ cm}^{-1}$ and 1725 cm^{-1} , respectively for C=O) recorded on Beckmann IR spectrometer in KBr pellets.

RESULTS AND DISCUSSION

Wool possesses a number of functional groups such as —NH₂, —COOH, —SH, —OH, *etc.*, which may provide active sites for grafting. In the present work attempts have been made to determine the optimum solvent composition for affording maximum grafting. Following plausible mechanism is proposed to explain grafting [11]



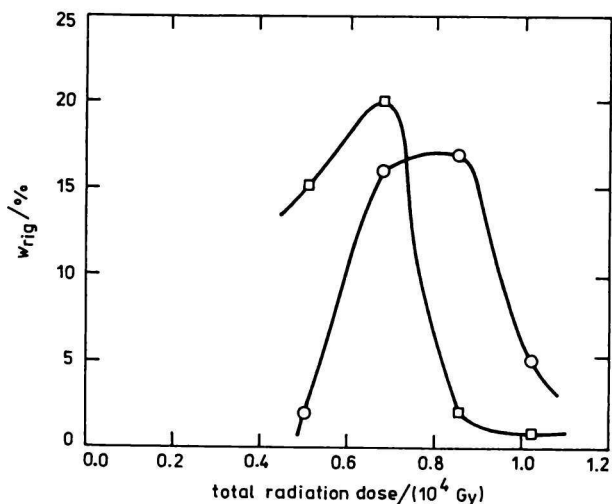


Fig. 1. Effect of total radiation dose on the graft copolymerization of poly(EA) (□) and poly(MA) (○) onto wool fibre under nitrogen atmosphere by mutual method.

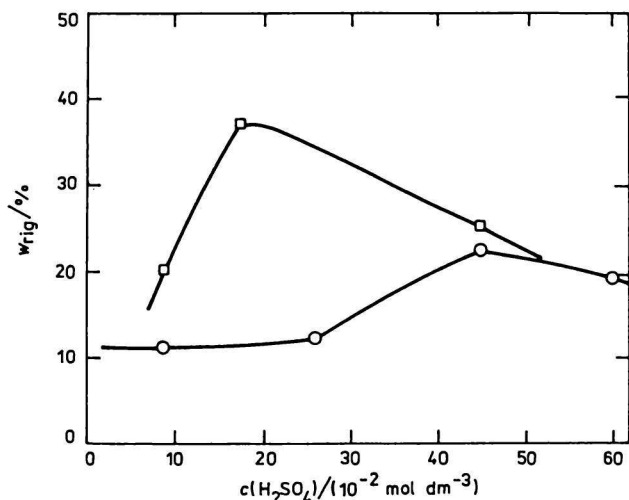
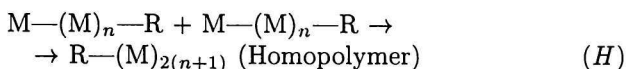
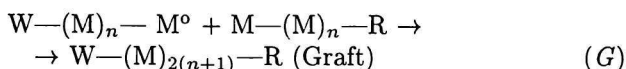
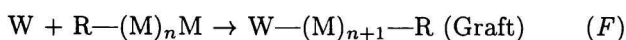
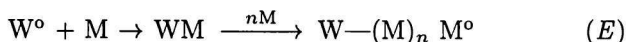


Fig. 2. Effect of acid concentration on the graft copolymerization of poly(EA) (□) and poly(MA) (○) onto wool fibre in nitrogen atmosphere by mutual method.



where WH is wool fibre, M monomer, and R° radical species arising from the irradiation of monomer and solvent molecules. It is apparent that once free radical species are generated, these can either initiate vinyl polymerization to give homopolymer (process (H)) or the growing polymeric chains leading to grafting (processes (F) and (G)).

It is observed from Table 1 and Fig. 1 that w_{rig} of EA and MA increases with an increase in the concentration of monomer and total dose of irradiation. Maximum grafting of 20 % and 17 % is obtained using optimum monomer concentrations of $[EA] = 25 \times 10^{-2} \text{ mol dm}^{-3}$ and $[MA] = 26.7 \times 10^{-2} \text{ mol dm}^{-3}$ at a total dose of $68 \times 10^4 \text{ Gy}$ and $85 \times 10^4 \text{ Gy}$, respectively. Further increase in monomer concentration and total dose decreases graft yields. This indicates that beyond optimum monomer concentration and total dose, homopolymerization becomes the preferred process.

In mutual grafting solvent plays an important role and the composition of solvent system affects graft yields. This is attributed to the wetting and swelling of backbone, diffusion of growing polymeric chains to the active sites, and to higher miscibility of the monomer

with the solvent. In the present study under the optimum conditions of monomer concentration and total dose, maximum w_{rig} of 20 % and 16 % is obtained using 1:4 and 1:1 ratio of $H_2O:MeOH$ for EA and MA, respectively. In pure water and in pure MeOH, w_{rig} of both EA and MA is much less (that is 8.0 % and 2.0 % for EA and 5.0 % and 1.0 % for MA). Any further increase in the amount of MeOH in $H_2O-MeOH$ system leads to acceleration of various chain transfer reactions which terminate the growing polymeric chains. Huang and Rapson [12] have also reported that no grafting occurred in pure MeOH onto cellulose. However, they observed significant grafting in $H_2O-MeOH$ system. Misra *et al.* [9, 10] have observed significant grafting in the presence of $H_2O-MeOH$ system for grafting of MMA and EMA onto wool fibre. Enhancement of grafting in $H_2O-MeOH$ system is ascribed to the increased wetting and swelling of wool fibre surface in the medium of optimum solvent composition and also increased solubility of the monomer in the solvent system.

Effect of H_2SO_4 on w_{rig} of EA and MA has been studied and results are presented in Table 1 and Fig. 2. Maximum grafting of 37 % and 22 %, respectively, was obtained, when an optimum concentration of $17.5 \times 10^{-2} \text{ mol dm}^{-3}$ and $43.7 \times 10^{-2} \text{ mol dm}^{-3}$ of the acid was used, for EA and MA under optimum conditions. Enhancement of w_{rig} in the presence of H_2SO_4 is explained by the fact that various functional groups of wool are protonated, which promotes swelling of fibre and thus the active sites of the fibre are exposed. Consequently upon which accessibility of monomer to the active sites is also enhanced. Similar conclusions have been drawn by Garnett *et al.* [13, 14] during graft copolymerization of several systems. Gupta and Chapiro [15] also reported the role of H_2SO_4 in pro-

moting grafting of acrylic acid onto polyethylene film.

In order to determine the effect of air on w_{rig} experiments using optimum conditions of total dose, monomer concentration, solvent composition, and acid concentration under nitrogen atmosphere were carried out in the presence of air. It was found that in air w_{rig} of both EA and MA decreases considerably. It appears that oxygen destroys a considerable number of active sites in the backbone by forming peroxy radicals which are much less reactive towards grafting. Hence there is considerable decrease in grafting efficiency (Table 1, reaction marked a).

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