

# Grafting onto Wool. XXX. Effects of Solvent Composition on the Radiation-Induced Graft Copolymerization of Some Acrylates onto Wool Fiber

GHANSHYAM S. CHAUHAN,<sup>1</sup> LALIT K. GULERIA,<sup>1</sup> B. N. MISRA,<sup>1</sup> B. R. RAWAT<sup>2</sup>

<sup>1</sup> Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla-171005, India

<sup>2</sup> Himachal Pradesh State Forensic Laboratory, Shimla, India

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**ABSTRACT:** Radiation-induced graft copolymerization of ethyl methacrylate (EMA), ethyl acrylate (EA), methyl acrylate (MA), and methyl methacrylate (MMA) onto wool fiber by mutual method has been studied as a function of the composition of water–alcohol medium. Grafting of EMA, EA, and MA has been studied in nitrogen atmosphere, whereas grafting of MMA was carried out in air. Percentage of grafting (Pg) has been determined as a function of different reaction parameters that influence graft copolymerization. For all the monomers studied, it is observed that (1) maximum grafting is obtained at an optimum composition of water–alcohol medium; (2) Pg is considerably less in pure water or alcohol; (3) Pg of MA falls more sharply on addition of larger amount of MeOH to water–methanol medium as compared to EA and EMA; (4) in the case of grafting of MMA, water–isopropanol is a better reaction medium than the water–ethyl alcohol; and (5) Pg decreases considerably in air for all the monomers studied. A suitable explanation is suggested to account for these observed trends. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 191–195, 1997

**Key words:** graft copolymerization; radiation-induced method; Himachali wool; acrylates; solvent composition

## INTRODUCTION

Modification of wool by chemical grafting has received considerable interest.<sup>1–6</sup> However, grafting by the radiation-induced method is a cleaner technique in which Pg can be controlled to a desired extent. A number of vinyl monomers has been graft-copolymerized onto wool fiber by gamma radiation initiated methods. Grafting of styrene, methyl methacrylate, and acrylonitrile onto wool by mutual irradiation method has been reported by Horio et al.<sup>7</sup> Armstrong and Rutherford<sup>8</sup> made extensive study of radiation grafting onto wool fi-

ber using the vapor phase technique. Recently, Misra et al.<sup>9–10</sup> have reported grafting of vinyl monomers onto wool fiber by radiochemical methods in the presence of organic and mineral acids. Stannett<sup>11</sup> reported that grafted wool has a different wool–water relationship than natural wool. They also grafted styrene onto wool fiber in dioxane and reported that water and methanol were necessary for successful grafting.<sup>12</sup> Puig<sup>13</sup> reported on the impact of wetting of wool fiber by solvent on the graft yield. Earlier studies in our laboratory indicate that the solvent composition of water–methanol system significantly affects grafting of MMA onto wool.<sup>14</sup> The present study is an attempt to investigate the role of composition of water–alcohol mixed solvent system on the graft copolymerization of some acrylate monomers.

Correspondence to: G. S. Chauhan.

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**Table I Effects of Water–Methanol Composition on Percent Grafting of Poly(EMA) onto Wool Fiber in the Nitrogen Atmosphere by the Mutual Method**

Sl. No.	H <sub>2</sub> O : MeOH	[EMA] × 10 <sup>2</sup> (mol/L)	Grafting (%)
1	1 : 1	19.9	30.0
2	1 : 2	19.9	33.0
3	1 : 3	19.9	34.0
4	1 : 4	19.9	33.0
5	1 : 5	19.9	31.0
6	1 : 6	19.9	24.0
7	1 : 7	19.9	19.0
8	1 : 8	19.9	10.0
9	1 : 9	19.9	5.0
10	Pure MeOH	19.9	5.0
11	Pure H <sub>2</sub> O	7.9	15.0
12 <sup>a</sup>	1 : 3	7.9	50.0
13 <sup>b</sup>	1 : 3	7.9	85.0

Reaction conditions: wool = 100 mg; dose rate = 0.34 MR/h; total dose = 9.68 MR; reaction time = 2.0 h; H<sub>2</sub>O—MeOH = 20 mL; at room temperature.

<sup>a</sup> Result in air in the presence of 17.5 × 10<sup>-2</sup> mol/L of H<sub>2</sub>SO<sub>4</sub>.

<sup>b</sup> Result in nitrogen in the presence of 17.5 × 10<sup>-2</sup> mol/L H<sub>2</sub>SO<sub>4</sub>.

## EXPERIMENTAL

### Purification of Wool, Monomers, and Nitrogen

Purification and characterization of Himachali wool fiber has been described elsewhere.<sup>15</sup> Purifi-

cation of monomers and nitrogen was carried out by a procedure reported earlier.<sup>10</sup>

### Graft Copolymerization

Purified wool (100 mg) was dispersed in 20 mL of the water–alcohol medium in a 50 mL conical flask specially fabricated and equipped with two standard joints with hollow stop cocks. Monomers were added to the reaction flask, and a continuous flow of nitrogen gas was maintained throughout the reaction period. The reaction mixture was irradiated in gamma chamber-900. After completion of the reaction, the reaction mixture was filtered out, and the homopolymer was removed from the graft by solvent extraction using acetone as a solvent. The graft copolymer was dried in a vacuum oven at 50°C until a constant weight was obtained. The percentage of grafting (Pg) was determined from the increase in the weight of wool fiber after complete removal of the homopolymer, as follows:

$$\text{Percent Grafting (Pg)} = W_2 - W_1/W_1 \times 100$$

where  $W_1$  and  $W_2$  denote the weight of wool and grafted wool, respectively. The results are presented in Tables I–V and in Figure 1.

### Evidence of Grafting

On comparison of the infrared (IR) spectra of wool and wool-g-poly (EMA), wool-g-poly (EA), wool-

**Table II Effect of Water–Methanol Composition on Percent Grafting of Poly(EA) onto Wool Fiber in the Nitrogen Atmosphere by the Mutual Method**

Sl. No.	H <sub>2</sub> O : MeOH	[EA] × 10 <sup>2</sup> (mol/L)	Grafting (%)
1	1 : 1	25.0	11.0
2	1 : 2	25.0	16.0
3	1 : 3	25.0	18.0
4	1 : 4	25.0	20.0
5	1 : 5	25.0	10.0
6	1 : 6	25.0	8.0
7	1 : 7	25.0	7.0
8	1 : 8	25.0	5.0
9	Pure MeOH	25.0	2.0
10	Pure H <sub>2</sub> O	25.0	8.0
11 <sup>a</sup>	1 : 4	25.0	12.0
12 <sup>b</sup>	1 : 4	25.0	37.0

Reaction conditions: wool = 100 mg; dose rate = 0.34 MR/h; total dose = 0.68 MR; reaction time = 2.0 h; H<sub>2</sub>O—MeOH = 20 mL; at room temperature.

<sup>a</sup> Result in air in the presence of H<sub>2</sub>SO<sub>4</sub> = 17.5 × 10<sup>-2</sup> mol/L.

<sup>b</sup> Result in the presence of nitrogen in presence of 17.5 × 10<sup>-2</sup> mol/L of H<sub>2</sub>SO<sub>4</sub>.

**Table III Effect of Water–Methanol Composition on Percent Grafting of Poly(MA) onto Wool Fiber in the Nitrogen Atmosphere by the Mutual Method**

Sl. No.	H <sub>2</sub> O : MeOH	[MA] × 10 <sup>2</sup> (mol/L)	Total Dose in MR	Reaction Time (h)	Grafting (%)
1	1 : 1	26.7	0.68	2.0	16.0
2	1 : 2	26.7	0.68	2.0	10.0
3	1 : 3	26.7	0.68	2.0	5.0
4	Pure MeOH	26.7	0.68	2.0	1.0
5	Pure H <sub>2</sub> O	26.7	0.85	2.5	5.0
6 <sup>a</sup>	1 : 1	26.7	0.85	2.5	4.0
7 <sup>b</sup>	1 : 1	26.7	0.85	2.5	22.0

Reaction conditions: wool = 100 mg; dose rate = 0.34 MR/h; H<sub>2</sub>O—MeOH = 20 mL; at room temperature.

<sup>a</sup> Result for reaction in air in the presence of  $43.7 \times 10^{-2}$  mol/L of H<sub>2</sub>SO<sub>4</sub>.

<sup>b</sup> Result in presence of nitrogen in presence of  $43.7 \times 10^{-2}$  mol/L of H<sub>2</sub>SO<sub>4</sub>.

g-poly (MMA), and wool-g-poly (MA), it is observed that a strong peak assigned to  $\begin{array}{c} \backslash \\ \text{C}=\text{O} \\ / \end{array}$  appeared in the grafted samples at 1730, 1720, 1740, and 1725 cm<sup>-1</sup>, respectively, for poly(EMA), poly(EA), poly(MMA), and poly(MA); whereas pure wool fiber showed strong absorption at 1650 cm<sup>-1</sup>.

Hydrolysis of wool graft copolymers was carried out with 6N HCl at 135°C for 24 h. All the wool went into solution as amino acids, and the residue obtained as a resinous mass was identified as poly(EMA), poly(EA), poly(MMA), and poly(MA) by IR spectroscopy.

The filtrate from the hydrolysis experiment gave, on neutralization, a positive ninhydrin test. The solution of the separated polymers poly(EMA), poly(EA), poly(MMA), and poly(MA) in acetone did not respond to the ninhydrin test. It was established, however, by the ninhydrin test

that the residual amino acids attached to the poly(EMA), poly(EA), poly(MMA), and poly(MA) are covalently bonded to the fiber.<sup>10</sup>

Scanning electron micrographs (SEM) of the wool and grafted wool were taken. On comparison, it was found that grafted polymer was deposited on the surface of wool fiber.

## RESULTS AND DISCUSSION

It is evident from Tables I–V that, starting from the 1 : 1 water–alcohol composition, the Pg of all the monomers increases to a maximum value and then decreases progressively as the alcohol content in the water–alcohol system is increased. However, the only exception is found during grafting of MA (Table III), which shows a steady fall in Pg when the composition of H<sub>2</sub>O—MeOH is changed by adding a higher amount of alcohol. However, addition of some alcohols [MeOH,

**Table IV Effect of Water–Ethanol Composition on Percent Grafting of Poly(MMA) onto Wool Fiber in Air by the Mutual Method**

Sl. No.	H <sub>2</sub> O : EtOH	[MMA] × 10 <sup>2</sup> (mol/L)	[H <sub>2</sub> SO <sub>4</sub> ] × 10 <sup>2</sup> (mol/L)	Total Dose in MR	Reaction Time (h)	Grafting (%)
1	1 : 1	23.5	43.7	0.64	2.0	36.0
2	1 : 2	23.5	43.7	0.64	2.0	40.0
3	1 : 3	23.5	43.7	0.64	2.0	50.0
4	1 : 4	23.5	43.7	0.64	2.0	49.0
5	Pure EtOH	23.5	43.7	0.64	2.0	19.0
6	Pure H <sub>2</sub> O	23.5	8.7	0.96	3.0	40.0
7 <sup>a</sup>	1 : 3	23.5	8.7	0.96	3.0	86.0

Reaction conditions: wool = 100 mg; dose rate = 0.32 MR/h; H<sub>2</sub>O—EtOH = 20 mL; at room temperature.

<sup>a</sup> Results in nitrogen atmosphere.

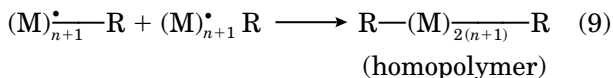
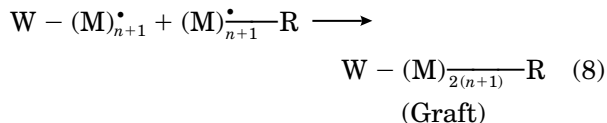
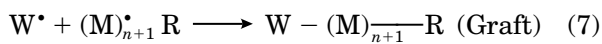
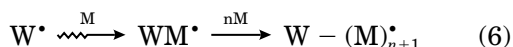
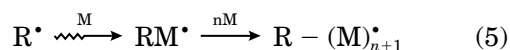
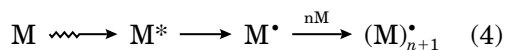
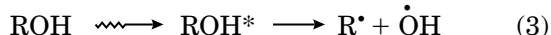
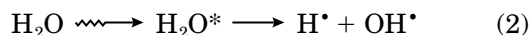
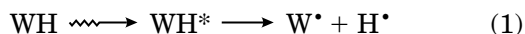
**Table V Effect of Water–Isopropanol Composition on Percent Grafting of Poly(MMA) onto wool Fiber in Air by the Mutual Method**

Sl. No.	H <sub>2</sub> O : Isopropanol	[MMA] × 10 <sup>2</sup> (mol/L)	[H <sub>2</sub> SO <sub>4</sub> ] × 10 <sup>2</sup> (mol/L)	Total Dose in MR	Reaction Time (h)	Grafting (%)
1	1 : 1	23.5	43.7	0.64	2.0	40.0
2	1 : 2	23.5	43.7	0.64	2.0	62.0
3	1 : 3	23.5	43.7	0.64	2.0	60.0
4	1 : 4	23.5	43.7	0.64	2.0	32.0
5	Pure Isopropanol	23.5	43.7	0.64	2.0	18.0
6	Pure H <sub>2</sub> O	23.5	43.7	0.64	2.0	35.0
7 <sup>a</sup>	1 : 2	23.5	43.7	0.64	2.0	81.0

Reaction conditions: wool = 100 mg; dose rate = 0.32 MR/h; H<sub>2</sub>O—Isopropanol = 20 mL; at room temperature.

<sup>a</sup> Result in the nitrogen atmosphere.

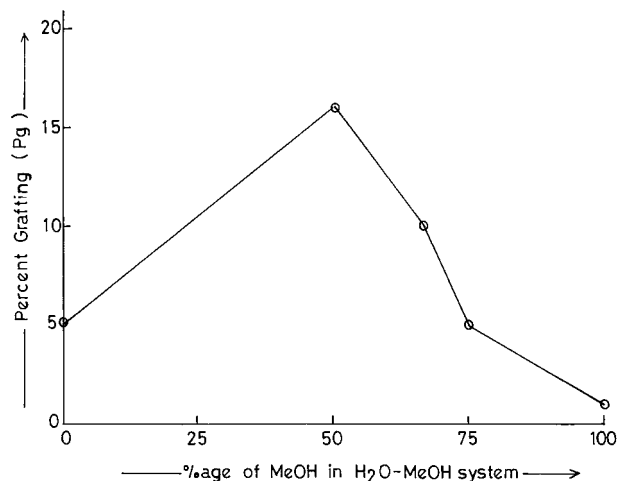
EtOH, and (Me)<sub>2</sub>CHOH] invariably promotes grafting initially. Pg of all the monomers obtained in pure H<sub>2</sub>O and in pure alcohol is considerably less as compared to the Pg obtained in H<sub>2</sub>O : alcohol system. Pg is also less in air when grafting was carried out using optimum conditions worked out in the nitrogen atmosphere for EMA, EA, and MA. For grafting of MMA, optimum conditions were worked out in air; by employing these conditions, graft copolymerization was carried out in a nitrogen atmosphere. Grafting is considerably higher in nitrogen as compared to that obtained in air (Tables I–V). The following mechanism is proposed to explain these results.



where WH and R<sup>•</sup> represents wool fiber and various radical species arising from the solvent and monomer molecules.

The role of water in promoting grafting is well

established in the case of wool fiber. This is attributed to the swelling of wool fiber by water, thus making the functional groups of wool more accessible to the monomer. However, the addition of alcohol to water affords better graft yields, and this synergistic effect is explained by greater swelling of the trunk polymer as MeOH may reach those areas of wool fiber that are not efficiently affected by water alone. The presence of alcohol increases the miscibility of the monomers in the reaction medium. Thus, greater swelling of the trunk polymer and higher miscibility of monomers lead to more diffusion and penetration of monomers to the active sites on the wool fiber. Further, radiolysis of both water and alcohol generates more radical species, which facilitate creation of active sites on wool. However, an increase



**Figure 1** Effect of variation of methanol content (%) in water–methanol system on percent grafting of poly(MA) onto wool fiber. Reaction conditions are the same as in Table III.

in the amount of alcohol facilitates chain transfer reactions and graft yields fall considerably. In pure MeOH, only 5, 2, and 1% grafting was obtained for EMA, EA, and MA, respectively (Tables I–III). The effect of the MeOH content in the reaction medium on the grafting of MA is also depicted graphically in Figure 1A. Huang and Rapson<sup>16</sup> reported zero grafting in the presence of methanol. Sharma and Misra<sup>14</sup> reported that the 1 : 3 water–methanol system afforded highest grafting of MMA onto wool fiber in the nitrogen atmosphere. During graft copolymerization of MMA onto wool fiber, maximum grafting (50%) was observed in 1 : 3 water–ethanol system; a further increase in the amount of ethanol in water–ethanol system shows a steady decrease in grafting (Table IV). In the case of the water–isopropanol system (Table V), optimum grafting (62%) was obtained by using a 1 : 2 water–isopropanol composition; subsequently, it shows decrease. It may be mentioned that pure water affords better grafting than pure ethanol or pure isopropanol. Grafting of MMA in ethanol, isopropanol, and their mixture with water was carried out in air using the same reaction parameters. In pure ethanol and pure propanol, grafting of MMA onto the wool fiber afforded almost identical results. The graft yields of MMA were higher in the case of the water–isopropanol system than water–ethanol system despite the fact that isopropanol has a higher chain transfer constant than ethanol. This indicates that greater miscibility of MMA with the medium plays a more important role in the promotion of grafting. It can be argued further that in

the water–ethanol system, active sites of wool are less accessible to the monomer, resulting in a decrease of grafting.

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