Grafting onto Wool Fibers: Graft Copolymerization of Methyl Methacrylate onto Wool Fibers Initiated by $KHSO_5/Fe(III)$ Couple

GITISUDHA GIRI and RAJANI K. SAMAL*

Macromolecular Research Laboratory, Department of Chemistry, Ravenshaw College, Cuttack-753003, Orissa, India

SYNOPSIS

Graft copolymerization of methyl methacrylate (MMA) onto wool fibers has been carried out in an aqueous medium under deaerated condition initiated by potassium monopersulphate ($KHSO_5$)/Fe(III) system, at varying concentration of the reactants and temperature. The effect of various salts and organic solvents on the extent of grafting has also been studied. Maximum graft percentage of 210.8% was obtained in 4 h at 40°C with the concentration of MMA (0.46 *M*), $KHSO_5$ (0.0195 *M*), Fe(III) (1.25×10^{-4} *M*) in the presence of 50% formic acid. Various improved properties of the grafts have been studied and compared with the parent fiber.

INTRODUCTION

Modification of wool fibers through functionality changes, graft copolymerization, and chemical treatments to improve their tensile strength, rot resistance, dyeability, durability, prevention of shrinkage and pilling, bacterial resistance, hygroscopicity, thermal stability, etc. has been the subject of interest of researchers since 1945.[1-39] However, no report seems to be available on graft copolymerization onto wool fibers using potassium monopersulfate ($KHSO_5$), an acidic peroxygen initiator of recent origin, except our recent report on graft copolymerization of acrylamide (AM),[40] acrylic acid (AA),[41] and acrylonitrile (AN)[42] onto wool fibers. The present communication includes the results of graft copolymerization of MMA onto wool fibers initiated by $KHSO_5$/Fe(III) couple and various improved properties of the grafts.

EXPERIMENTAL

Materials. Wool fibers were purified as per our previous method.[40] Methyl methacrylate (MMA) monomer (E. Merck) was washed with 5% NaOH followed by distilled water to remove the inhibitors. It was then dried over anhydrous $CaCl_2$ or $MgSO_4$. The dried monomer was distilled under vacuum and the middle fraction was collected for experimental use. Potassium monopersulfate ($KHSO_5$) was a gift sample from DuPont and used without further purification. A stock solution of 13×10^{-2} *M* of the triple salt initiator in deionized water was stored in the refrigerator and used for all experiments. The strength of the stock solution from time to time was checked by iodometry.

Graft copolymerization was carried out as per our previous method.[40] The homopolymers were extracted with hot acetone repeatedly, till the extract gave no precipitate with methanol. From the weight of the graft copolymers and base polymer, the percent grafting was calculated.

RESULTS AND DISCUSSION

Methyl methacrylate was graft copolymerized onto defatted wool fibers initiated by potassium monopersulfate alone and in the presence of metal salts under identical reaction conditions.

The results showed that potassium monopersulfate alone and in the presence of metal salts like $Cr_2(SO_4)_3$, $CdCl_2$, KBr, Na_2SO_4, $ZnSO_4$, and $MnSO_4$ in the reaction mixtures did not initiate

* To whom correspondence should be addressed.

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grafting onto wool fibers, where as the presence of the salts like $FeSO_4$, $FeCl_3$, $CoSO_4$, $Cu(OAc)_2$, and $CuSO_4$ in the reaction mixture favored grafting in the order: $FeCl_3 > FeSO_4 > Cu(OAc)_2 > CoSO_4 > CuSO_4$ (Table I).

From the grafting results in Table I, $FeCl_3$ was selected as the activator for the present studies.

(*i*) *Effect of Monomer/Polymer Ratio:* The effect of monomer/polymer ratio on the graft copolymerization of MMA onto wool fibers has been studied at different concentrations of monomer (0.12–1.87 *M*), initiator (3.25×10^{-3}–26.0×10^{-3} *M*) with a fixed concentration of Fe(III) (1.25×10^{-4} *M*), for a reaction time of 4 h and at 40°C (Fig. 1). The results of such studies showed that the percent grafting increased on increasing the m/p ratio up to 9.4 beyond which it decreased.

(*ii*) *Effect of Initiator Concentration:* The effect of initiator concentration on the graft copolymerization of MMA onto wool fibers has been studied at a number of initiator concentrations (3.25×10^{-3}–26 *M*), with a series of m/p ratios (2.35–37.6) and at a fixed concentration of Fe(III) (1.25×10^{-4} *M*) at 40°C for a reaction time of 4 h (Fig. 2). It has been observed that the percent grafting increases on increasing the initiator concentration up to 19.5×10^{-3} *M*, beyond which it decreases.

(*iii*) *Effect of Activator Concentration:* Graft copolymerization onto wool fibers has been studied at a number of $FeCl_3$ concentrations (0.25×10^{-4}–30×10^{-4} *M*) at fixed concentration of monomer (0.23 *M*), initiator (0.013 *M*) for a reaction time of 4 h (Fig. 3). The results of such studies showed that the percent grafting increased on increasing the concentration of $FeCl_3$ up to 1.25×10^{-4} *M*, beyond which it decreased.

Table I Variation of Percent Grafting with Fixed Time: Effect of Various Salts[a]

Salt	% Grafting
No salt	0
$Cr_2(SO_4)_3$	0
$CdCl_2$, $2\frac{1}{2}H_2O$	0
KBr	0
Na_2SO_4	0
$ZnSO_4$, $7H_2O$	0
$MnSO_4$, H_2O	0
$FeSO_4$, $7H_2O$	44
$FeCl_3$	58.6
$CoSO_4$, $7H_2O$	38.6
$Cu(OAc)_2$	39.6
$CuSO_4$, $5H_2O$	25.2

[a] Wool = 0.2 g, [$KHSO_5$] = 0.013*M*, [MMA] = 0.23*M*, [salt] = 2.5×10^{-4}*M*, time = 6 h, temp = 35°C.

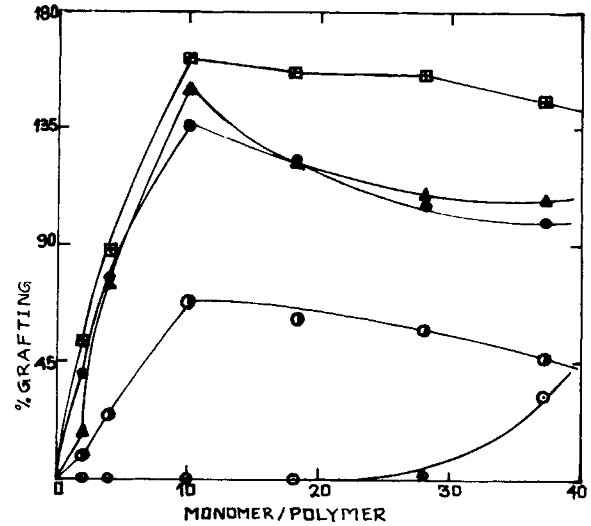

Figure 1 Variation of percentage of grafting at fixed time: Effect of monomer/polymer ratio at various [$KHSO_5$]: (⊙) 3.25×10^{-3} *M;* (◑) 6.5×10^{-3} *M;* (●) 13.0×10^{-3} *M;* (⊞) 19.5×10^{-3} *M;* (▲) 26×10^{-3} *M*. wool = 0.2 g; [Fe(III)] = 1.25×10^{-4} *M*, time = 4 h, temperature = 40°C.

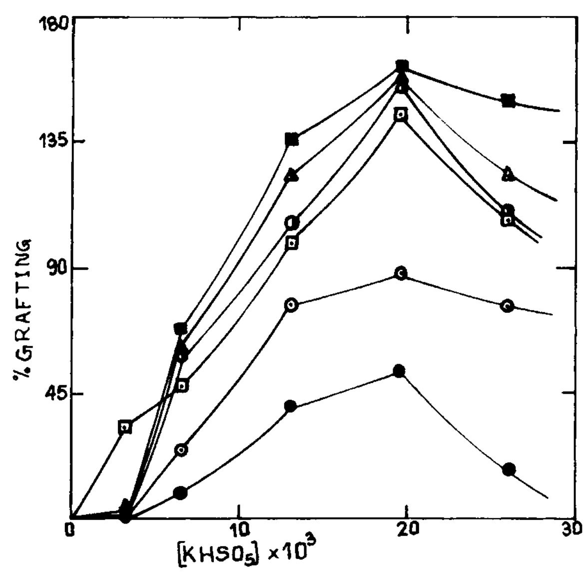

Figure 2 Variation of percentage of grafting at fixed time: Effect of [$KHSO_5$] at various monomer/polymer ratios: (●) 2.3; (⊙) 4.7; (■) 9.4; (△) 18.8; (◑) 28.2; (⊡) 37.6. wool = 0.2 g, [Fe(III)] = 1.25×10^{-4} *M*, time = 4 h, temp = 40°C.

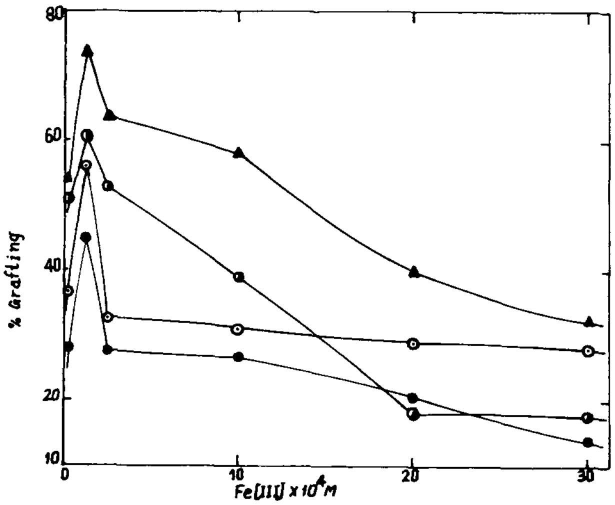

Figure 3 Variation of percentage of grafting at fixed time: Effect of [Fe(III)] at different temperatures (T): (●) 30°C; (⊙) 35°C; (▲) 40°C; (◑) 45°C. Wool = 0.2 g, [MMA] = 0.23 M, [$KHSO_5$] = 0.013 M, time = 4 h.

(*iv*) *Effect of Temperature:* The effect of reaction temperature on percent grafting has been studied at various temperatures (30–45°C) at a series of Fe(III) concentrations (0.25 $\times 10^{-4}$–30 $\times 10^{-4}$ M) and at fixed concentration of monomer (0.23 M) and initiator (0.013 M) for a reaction time of 4 h. It has been shown that the percent grafting increases on increasing the temperature up to 40°C, beyond which it decreases (Fig. 4).

(*v*) *Effect of Organic Solvents:* The effect of various organic solvents like methyl alcohol, acetic acid, acetone, formaldehyde, and formic acid on the graft copolymerization of MMA onto the wool fibers has been studied at fixed concentration of monomer (0.46 M), initiator (0.0195 M), $FeCl_3$ (1.25 $\times 10^{-4}$ M) at various solvent compositions (5 : 95–50 : 50 v/v) for a reaction time of 4 h and at 40°C. The values of such studies are shown in Figure 5. From the results it has been observed that the percent grafting increases in the presence of solvent like formic acid and with rest of the solvents the percent grafting decreases from the control value.

MECHANISM

The mechanism of graft copolymerization of methyl methacrylate onto wool fibers initiated by $KHSO_5$,

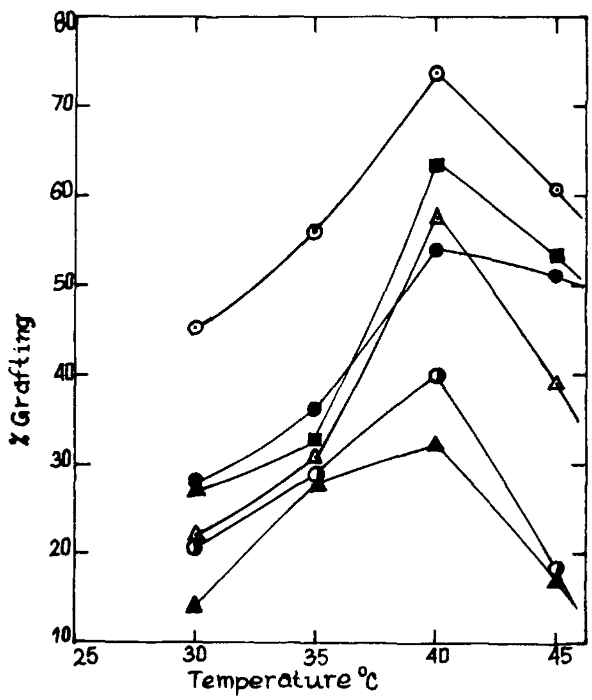

Figure 4 Variation of percentage of grafting at fixed time: effect of various temperatures at various [Fe(III)]: (●) 0.25 $\times 10^{-4}$ M; (■) 2.5 $\times 10^{-4}$ M; (△) 10 $\times 10^{-4}$ M; (◑) 20 $\times 10^{-4}$ M; (▲) 30 $\times 10^{-4}$ M; (⊙) 1.25 $\times 10^{-4}$ M. Wool = 0.2 g, [MMA] = 0.23 M, [$KHSO_5$] = 0.013 M, time = 4 h.

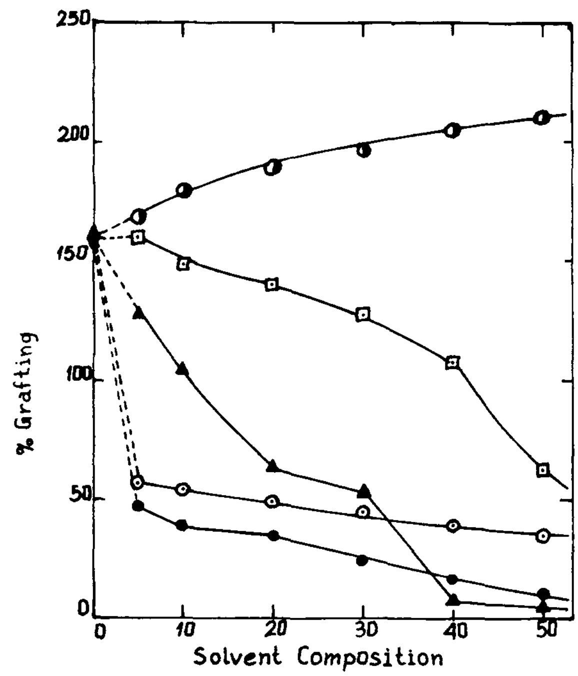

Figure 5 Variation of percentage of grafting at fixed time: effect of solvent composition. Wool = 0.2 g, [MMA] = 0.46 M, [$KHSO_5$] = 0.0195 M, [$FeCl_3$] = 1.25 $\times 10^{-4}$ M, time = 4 h, temperature = 40°C. (♦) Controlled value (▲) methyl alcohol; (□) acetic acid; (●) acetone; (⊙) formaldehyde; (◑) formic acid.

Table II Water Retention Values of PMMA Samples with Various Percent Grafting

Samples	% Grafting	Water Retention (g/g)
Parent fiber	0	3
Wool-*g*-PMMA	16.85	2.8
	75.85	2.0
	127.8	1.4
	188.1	1.0
	288.28	0.6
	515.1	0.2

activated by Fe(III), may be pictured as involving the generation of macrowool radicals formed by the attack of primary radical species, generated from the $KHSO_5$/Fe(III) couple on the fiber backbone. The wool radicals so formed subsequently attack the monomer at the immediate vicinity leading to graft initiation. The termination of graft copolymerization may be due to the interaction with Fe(III); mutual combination of growing grafted chains on different backbones and may also be due to excess of primary radicals.

Properties of the Grafts

Methyl methacrylate grafted wool fibers have the following properties.

(*a*) *Absorption of Water and Water Vapors (Water Retention):* The extent of absorption of water and water vapors of both the virgin and grafted wool fibers was determined through measurement of water retention of the samples following the method of Rannby and co-workers[43] with slight modification.[41] The water retention regularly decreased on increasing the percent grafting (Table II).

(*b*) *Alkali and Acid Solubility:* The behavior of the grafts and the virgin wool fibers towards alkali was tested by determining the percentage of alkali solubility with time. For this the samples were immersed separately in aqueous solution of 0.1 *M* NaOH solution for various time intervals of 1 h at 65°C using a wool–liquor ratio of 1 : 100. The method adopted was similar to that of Leaveau and co-workers.[44] The treatment showed that the grafted samples are least soluble in alkali and less than about 30% solubility was noticed with the grafted sample of percent grafting 75.85, which still decreases with the increase of percent grafting up to 515.1. The virgin fiber, on the other hand, was soluble up to nearly 80% under identical conditions. Further, the alkali-treated grafted fibers did not lose tensile strength to any appreciable extent.

A similar procedure was adopted with 0.1 *M* HCl using a wool : liquor ratio of 1 : 100. The results of acid treatment showed that the grafted fibers have greater resistance towards acid than the virgin fiber.

(*c*) *Tensile Modulus:* The tensile modulus of the percent and grafted wool fibers was determined through determination of tenacity and elongation at break following the methods of Haque et al.[45] The tenacity was expressed in g/den. After conditioning the samples, they were combed, fiber aggregates of uniform length were taken and weighed, and length was determined. The tenacity of the samples was determined using a "Dutrons" tensile tester. The tensile modulus at break was determined from the values of tenacity and elongation at break using the relationship:

Table III Effect of Percent Graft on Tensile Module of Methyl Methacrylate-Grafted Wool Fibers

Samples	% Grafting	Elongation at Break (B L) (%)	Tenacity at Break (g/den)	Tensile Modulus (g/den)
Parent fiber	0	1.48	2.75	185.8
Wool-*g*-PMMA	16.85	1.50	2.8	186.7
	75.85	1.54	2.9	188.3
	127.8	1.6	3.1	193.7
	188.1	1.64	3.4	207.3
	288.28	1.7	3.7	217.6
	515.1	1.76	3.9	221.6

tensile modulus at break

$$= \frac{\text{tenacity at break}}{\text{elongation at break}} \times 100$$

The results of such studies are presented in Table III. The results in Table III indicate that grafting of MMA onto the wool fibers increases its elongation at break, tenacity, and so also the tensile modulus which increase with increase of graft percent. The enhancement in tensile modulus of the grafts may be attributed to the internal crosslinking of the fiber backbones through bimolecular combination of growing grafted chains and this probably imparts elastic nature to the fibers, which increases with increase of graft percent.

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REFERENCES

1. P. Alexander and R. F. Hudson, *Wool, Its Chemistry and Physics,* Reinhold, New York, 1954, p. 334.
2. N. H. Keening, U.S. Pat. 2, 993, 748 (1961).
3. N. H. Koenig, *Text. Res. J.,* **32,** 117 (1962).
4. H. Fraenkel-Conrat, M. Cooper, and H. S. Olcott, *J. Am. Chem. Soc.,* **67,** 314 (1945).
5. N. H. Koenig, Paper presented at the Technical Wool Conference, San Francisco, California, May 1964 [*Text. Res. J.,* **35,** 708 (1965)].
6. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *J. Appl. Polym. Sci.,* **8,** 1607 (1964).
7. W. Fong, R. E. Whitfield, L. A. Miller, and A. H. Brown, *Am. Dyestuff Rep.,* **51,** 325 (1962).
8. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *Text. Res. J.,* **31,** 704 (1961).
9. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *Text. Res. J.,* **32,** 473 (1962).
10. R. E. Whitfield, L. A. Miller, and W. L. Wasley, *Text. Res. J.,* **33,** 440 (1963).
11. L. Valentine, *J. Text. Inst.,* **46,** 270 (1965).
12. H. Ishibashi and M. Oku, *Proc. Int. Wool. Text. Res. Conf. Paris,* 1965, Sec. III.
13. M. Negishi, K. Arai, and S. Okada, *J. Appl. Polym. Sci.,* **11,** 115 (1967).
14. J. L. Willams and V. Stannett, *Text. Res. J.,* **38,** 1056 (1968).
15. H. L. Needles and W. L. Wasley, *Text. Res. J.,* **39,** 97 (1969).
16. I. C. Watt, *J. Macromol. Sci. Rev. Makromol. Chem.,* **C5,** 176 (1970).
17. H. L. Needles, L. J. Sarfield, and D. M. Dawhaniuk, *Text. Res. J.,* **42,** 558 (1972).
18. K. Arai, M. Negishi, S. Komine, and K. Takada, *Appl. Polym. Symp.,* **18,** 545 (1971).
19. H. L. Needles and L. J. Sarfield, *Appl. Polym. Symp.,* 18 (1971).
20. A. J. Makimon, *J. Appl. Polym. Sci.,* **14,** 3033 (1970).
21. D. S. Varma and R. K. Sarkar, *Text. Res. J.,* **41,** 610 (1971).
22. A. Hebeish and A. Bendak, *Teintex,* **10,** 719 (1971).
23. A. Kantouch, A. Hebeish, and A. Bendak, *Eur. Polym. J.,* **7,** 153 (1971).
24. W. S. Simpson, *Appl. Polym. Symp.,* **18,** 967 (1971).
25. A. Kantouch, S. Abdel-Fattah, and A. Hebeish, *Polym. J.,* **3,** 375 (1972).
26. S. Abdel-Fattah, A. Kantouch, and A. Hebeish, *Angew. Makromol. Chem.,* **43,** 11 (1975).
27. A. Hebeish, A. Bendak, and S. Abdel-Fattah, *Angew. Makromol. Chem.,* **37,** 11 (1974).
28. A. Hebeish, S. H. Abdel-Fattah, and M. H. El-Rafie, *J. Appl. Polym. Sci.,* **20,** 3449 (1976).
29. N. C. Pati, S. Lenka, and P. L. Nayak, *Angew. Makromol. Chem.,* **71,** 189–199 (1978).
30. B. N. Mishra, I. Kaur, and R. K. Sharma, *Polym. Bull. (Berlin),* **4**(11), 635 (1981).
31. P. L. Nayak, G. Sahu, and S. Samal, *J. Macromol. Sci. Chem.,* **A16**(7), 1309 (1981).
32. B. O. Bateup, H. D. Feldtman, and B. E. Fleischfresser, *J. Text. Inst.,* **72**(1), 34 (1981).
33. A. Kantouch, A. Bendak, and M. Sedek, *Text. Res. J.,* **48**(11), 619 (1978).
34. W. J. Thorsen, *Ozone Sci. Eng.,* **1**(3), 219 (1979).
35. J. Dominguez, Garcia, P. Erra, A. Maza Dela, M. R. Julia, A. Barella, and T. Shaw, *J. Text. Inst.,* **71**(3), 165 (1980).
36. H. Nathan Koenig, and Mendel Friedman, U.S. Pat. Appl., 57, 858 (1980); Appl. 57,858 (1980); Appl., 16,14 (1979).
37. R. John Cook and E. Donald Rivett, *Text. Res. J.,* **51**(9), 596 (1981).
38. R. L. Greaves, P. H. Roche, and M. A. White, *Text. Res. J.,* **51**(10), 681 (1981).
39. E. E. Ney, R. Peake, and N. Regos, *Colourage,* **28**(16), 31 (1981).
40. R. K. Samal, C. N. Nanda, and G. Giri, *J. Appl. Polym. Sci.,* **39,** (1990).
41. R. K. Samal, C. N. Nanda, and G. Giri, *Polym. J. Jpn.,* **21**(11), 883–893 (1989).
42. R. K. Samal, C. N. Nanda, and G. Giri, *J. Polym. Mater.,* **7,** 209–214 (1990).
43. B. Rannby and L. Gadda, *Am. Chem. Soc. Symp. Ser.,* **187,** 33–43 (1982).
44. M. Leaveau, M. Caillet, and N. Demronat, *Bull. Inst. Fr.,* **90,** 7 (1960).
45. M. M. Haque and Md. Habibuddowla, *Bangladesh J. Sci. Ind. Res.,* **15**(1–4), 64 (1980).

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