Grafting onto Wool. XVI. Graft Copolymerization of Vinyl Monomers by Use of TBHP–FAS as· Redox Initiator*

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Synopsis

Methyl acrylate (MA), methyl methacrylate (MMA), and n-butyl vinyl ether (n-BVE) have been graft-copolymerized onto Himachali wool in an aqueous medium by using tertiary butyl hydroperoxide ferrous ammonium sulfate (TBHP–FAS) redox system at 40°C, 50°C, 60°C, and 70°C for various reaction periods. Percentage of grafting and percent efficiency have been determined as functions of concentration of monomers, molar ratios of [TBHP]/[FAS], time, and temperture. Molar ratios of [TBHP]/[FAS] were found to influence grafting of different monomers studied. Chemical evidence indicates that a covalent bond formation occurs between grafted polymeric chain and backbone polymer. The rate of grafting (R_p) and induction period (I_p) of different monomers towards graft copolymerization were determined as function of total initial monomer concentrations. R_p and I_p of n-BVE are independent of total initial monomer concentrations while R_p and I_p of both MA and MMA were found to depend on the total initial monomer concentrations. MA, MMA, and n-BVE were found to differ in reactivity towards grafting onto wool in the presence of (TBHP–FAS) redox system; the following reactivity order was observed: MMA > MA > n-BVE.

INTRODUCTION

In recent years considerable attempts have been made to modify the properties of wool fiber by the graft copolymerization technique. Various initiation methods that have been tried with varying degree of success include initiation by chemical[1-3] and radiation[4,5] methods. One of the major problems in graft copolymerization is the simultaneous formation of a homopolymer which presents difficulty in the purification of the graft. For this reason, attempts are being made to select proper initiating systems that would selectively cause grafting. Chemical methods for initiation of graft copolymerization are often preferred over radiation-induced grafting because high-energy radiation brings about considerable degradation of the backbone polymer. Among chemical methods, redox-initiated grafting offers advantages since, in the presence of redox systems, grafting can be carried out under milder conditions and side reactions are minimum.

Wool contains numerous functional groups in the side chain which can provide active sites for graft copolymerization. Ceric ion has been found to enter into redox reaction with the functional groups present in wool to form a complex which disproportionates to generate active sites where appropriate vinyl

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monomers can be grafted.   By utilizing ceric ion technique, Kantouch et al.[6] were able to graft MMA onto wool fiber.   Verma and Sarker[7,8] have also been able to effect grafting of acrylates onto wool by using the ceric ion method.   Following

TABLE I
Effect of Temperature, Time, Monomer Concentration, and Molar Ratio of [TBHP]/[FAS] on
Percent Grafting of MA[a]

Sample no.	Temp (°C)	Time (min)	[MA] × 10^2 (mol/L)	Molar ratio of [TBHP]/[FAS]	% grafting	% efficiency
1	60	120	27.61	2.38	37.5	7.89
2	60	120	27.61	1.89	22.5	4.73
3	60	120	27.61	1.61	14.0	2.94
4	60	120	27.61	2.94	30.4	6.40
5	60	120	27.61	3.94	24.0	5.05
6	60	120	27.61	1.58	21.0	4.42
7	60	120	27.61	3.17	30.0	6.31
8	60	120	27.61	3.96	25.4	5.34
9	40	120	27.61	2.38	6.5	1.36
10	50	120	27.61	2.38	16.5	3.47
11	70	120	27.61	2.38	26.0	5.47
12	60	90	27.61	2.38	25.5	5.36
13	60	150	27.61	2.38	48.1	10.12
14	60	180	27.61	2.38	41.0	8.63
15	60	150	16.56	2.38	42.0	14.73
16	60	150	38.66	2.38	67.0	10.07
17	60	150	49.70	2.38	56.0	6.54

[a] Wool = 1 g; water = 200 mL.

TABLE II
Effect of Temperature, Time, Monomer Concentration, and Molar Ratio of [TBHP[/[FAS] on
Percent Grafting of MMA[a]

Sample no.	Temp (°C)	Time (min)	[MMA] × 10^2 (mol/L)	Molar ratio of [TBHP]/[FAS]	% grafting	% efficiency
1	60	120	23.5	2.88	100.5	21.37
2	60	120	23.5	2.27	72.5	15.42
3	60	120	23.5	1.87	70.0	14.89
4	60	120	23.5	1.57	50.0	10.63
5	60	120	23.5	3.94	94.0	20.00
6	60	120	23.5	1.92	67.0	14.25
7	60	120	23.5	3.84	81.1	17.25
8	60	120	23.5	4.80	72.5	15.42
9	40	120	23.5	2.88	37.0	7.87
10	50	120	23.5	2.88	74.6	15.87
11	70	120	23.5	2.88	55.7	11.85
12	60	90	23.5	2.88	80.04	17.10
13	60	150	23.5	2.88	108.0	22.97
14	60	180	23.5	2.88	55.0	11.70
15	60	150	14.1	2.88	84.1	29.82
16	60	150	32.9	2.88	145.6	22.12
17	60	150	42.3	2.88	119.0	14.06

[a] Wool = 1 g; water = 200 mL.

the findings of Lipson and Speakman[9] that Fenton's reagent is capable of effecting grafting of methacrylic acid onto wool, a number of vinyl monomers were successfully grafted onto wool in the presence of Fenton's reagent.[10,11] Arai et al.[12] have used $S_2O_8{}^{2-}$—LiBr for grafting MMA onto wool without homopolymer formation. Hebeish and co-workers[13,14] were able to graft MMA onto wool in the presence of Fe^{3+}—TU and H_2O_2—TU redox systems. A comprehensive research program on modification of Himachali wool fiber by the graft copolymerization technique has been initiated in our laboratory, and it has been possible to effect grafting of a number of vinyl monomers by using Ce^{4+},[1] Ce^{4+}–amines[15] system, BPO,[2] and metal chelates[3,16] as initiators. Recently we have reported on grafting of vinyl monomers onto unreduced and reduced wool in the presence of potassium persulphate–ferrous ammonium sulfate (KPS–FAS)[17,18] and Fenton's reagent[19,20] as redox initiators. The use of tertiary butyl hydroperoxide (TBHP) as a redox component in graft copolymerization has not been investigated. In the present article we have studied the suitability of the TBHP–FAS system as redox initiator for grafting of methyl acrylate (MA), methyl methacrylate (MMA), and normal butyl vinyl ether (n-BVE) onto wool fiber with a view to comparing relative reactivities of these monomers towards graft copolymerization. Percentage of grafting and percent efficiency have been determined as functions of different reaction variables. The induction period (I_p) and rate of grafting (R_p) have been evaluated for each monomer as function of total initial monomer concentrations. Results are presented in Tables I–VII.

EXPERIMENTAL

Methods and Materials

MA and MMA (BDH) were washed with 5% sodium hydroxide and dried over anhydrous sodium sulfate. Dried MA and MMA were then distilled and middle fraction was used. n-BVE (Koch Light) was freshly distilled before use. Ferrous ammonium sulfate (BDH) was recrystallized before use. TBHP (Koch Light) was used as such; nitrogen was purified by passing through freshly prepared alkaline pyrogallol solution.

Characterization of Himachali Wool

Himachali Wool was obtained from Himachal Pradesh, India, and its physical characterization has been reported.[1]

Graft Copolymerization

1 g of purified Himachali wool was dispersed in 200 mL of deaerated water in a three-necked flask. A known quantity of FAS was added followed by the addition of a definite amount of TBHP. Prior to the addition of the monomer, nitrogen was passed through the reaction flask for about 30 min, and then a continuous supply of nitrogen was maintained throughout the reaction period. Monomer was added dropwise to the reaction flask. Copolymerization reaction was carried out under stirring at different temperatures for various reaction periods.

After the reaction was over, the reaction mixture was filtered, and the residue

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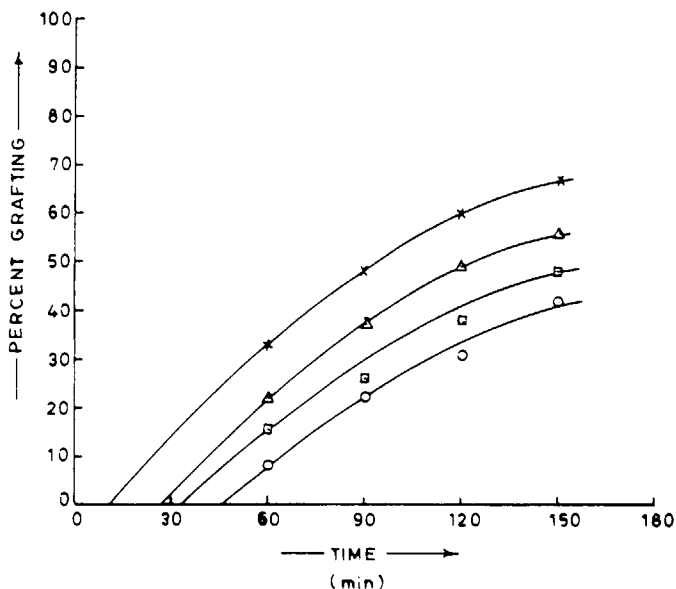
Fig. 1. Plot of percent grafting vs time. Reaction conditions: wool = 1.0 g; H_2O = 200 mL; [TBHP]/
[FAS] = 2.38; temp = 60°C; [MA]: (X) ≈ 38.66 × 10^{-2} mol/L, (△) ≈ 49.70 × 10^{-2} mol/L, (□) ≈ 27.61
× 10^{-2} mol/L, (O) ≈ 16.56 × 10^{-2} mol/L.

TABLE III
Effect of Temperature, Time, Monomer Concentration, and Molar Ratio of [TBHP]/[FAS] on
Percent Grafting of n-BVE[a]

Sample no.	Temp (°C)	Time (min)	[n-BVE] × 10^2 (mol/L)	Molar ratio of [TBHP]/[FAS]	% grafting	% efficiency
1	60	120	19.5	2.27	17.8	4.56
2	60	120	19.5	1.87	5.0	1.28
3	60	120	19.5	1.59	4.5	1.15
4	60	120	19.5	1.38	4.5	1.15
5	60	120	19.5	2.94	3.5	0.89
6	60	120	19.5	1.51	4.0	1.02
7	60	120	19.5	3.03	13.6	3.48
8	60	120	19.5	3.78	8.2	2.10
9	40	120	19.5	2.27	3.0	0.76
10	50	120	19.5	2.27	15.4	3.94
11	70	120	19.5	2.27	7.2	1.84
12	60	90	19.5	2.27	11.0	2.82
13	60	150	19.5	2.27	10.0	2.56
14	60	180	19.5	2.27	9.0	2.30
15	60	120	11.7	2.27	14.8	6.32
16	60	120	27.3	2.27	16.1	2.94
17	60	120	35.1	2.27	11.5	1.63

[a] Wool = 1 g; water = 200 mL.

was extracted successively with benzene and acetone for removal of PMA,
PMMA, and P(n-BVE) from the graft. The percentage of grafting and percent
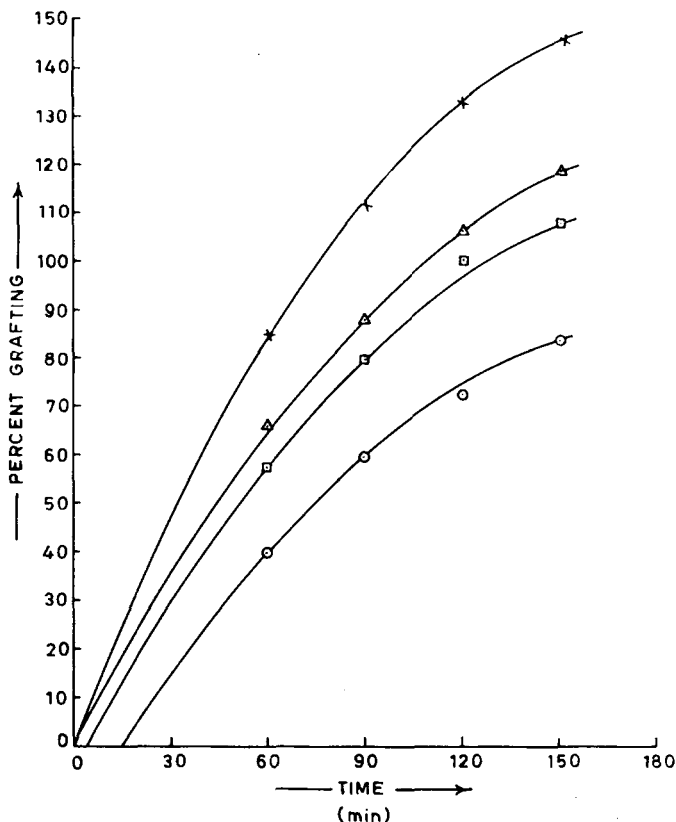efficiency were calculated from the increase in weight of wool after grafting in

Fig. 2. Plot of percent grafting vs time.   Reaction conditions: Wool = 1.0 g; H_2O = 200 mL; [TBHP]/[FAS] = 2.88; Temp = 60°C; [MMA]:   (X) $\approx 32.9 \times 10^{-2}$ mol/L, ($\triangle$) $\approx 42.3 \times 10^{-2}$ mol/L, ($\square$) $\approx 23.5 \times 10^{-2}$ mol/L, (O) $\approx 14.1 \times 10^{-2}$ mol/L.

the following manner:

$$\% \text{ grafting} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\% \text{ efficiency} = \frac{W_1 - W_0}{W_2} \times 100$$

where W_0, W_1, and W_2 denote, respectively, the weight of wool, grafted wool after solvent extraction and vinyl monomer added.

Evidence of Grafting

Wool-g-P(MA), wool-g-P(MMA), and wool-g-P(n-BVE) were hydrolyzed with 6 N HCl at 135°C for 24 h.   After all the wool goes into solution, resinous masses were obtained which were characterized by IR spectroscopy as PMA, PMMA, and P(n-BVE) respectively.   The physical mixtures of wool and benzene solution· of PMA, PMMA, and P(n-BVE) were prepared by stirring 1.0 g of wool fiber in benzene solution of PMA, PMMA, and P(n-BVE) for 24 h.   The wool fiber was separated by filtration and then subjected to extraction by benzene for 24 h and
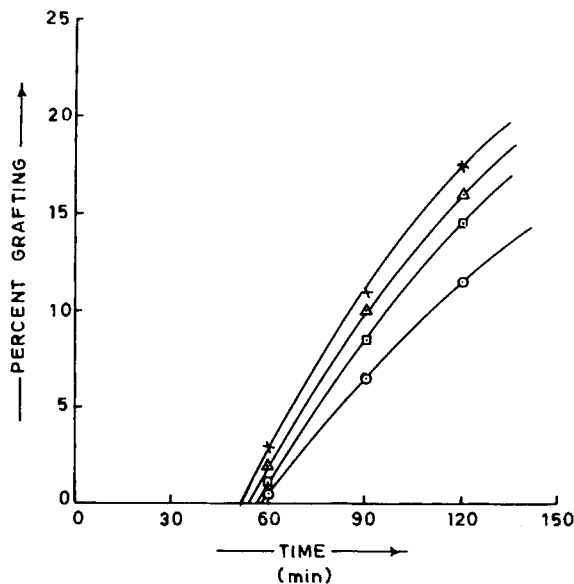
Fig. 3. Plot of percent grafting vs time.   Reaction conditions: Wool = 1.0 g; H_2O = 200 mL; [TBHP]/[FAS] = 2.27; Temp = 60°C; [n-BVE]:   (X) $\approx 19.5 \times 10^{-2}$ mol/L, ($\triangle$) $\approx 27.3 \times 10^{-2}$ mol/L, ($\square$) $\approx 11.7 \times 10^{-2}$ mol/L, (O) $\approx 35.1 \times 10^{-2}$ mol/L.

dried.   Recovery of 0.99 g of wool fiber indicated that homopolymer is quantitatively separated by benzene extraction from the physical mixtures.   Isolation of PMA, PMMA, and P(n-BVE) from the grafted material after treatment with 6 N HCl constituted evidence for grafting.

TABLE IV

Effect of Total Initial Monomer Concentration of MA on Rate of Grafting (R_p) and Induction Period (I_p)[a]

Initial monomer concn (mol/L)	Initial grafting rate (R_P) (%/min)	Induction period (I_p) (min)
16.56×10^{-2}	0.40	46.5
27.61×10^{-2}	0.46	33.0
38.66×10^{-2}	0.55	10.5
49.70×10^{-2}	0.53	27.0

[a] Wool = 1 g; temp = 60°C; [TBHP]/[FAS] = 2.38; water = 200 mL.

TABLE V

Effect of Total Initial Monomer Concentration of MMA on Rate of Grafting (R_p) and Induction Period (I_p)[a]

Initial monomer concn (mol/L)	Initial grafting rate (R_p) (%/min)	Induction period (I_p) (min)
14.1×10^{-2}	0.84	15.0
23.5×10^{-2}	0.99	4.5
32.9×10^{-2}	1.30	1.5
42.3×10^{-2}	1.00	0.0

[a] Wool = 1 g; temp = 60°C; [TBHP]/[FAS] = 2.88; water = 200 mL.

TABLE VI
Effect of Total Initial Monomer Concentration of n-BVE on Rate of Grafting (R_p)
Induction Period (I_p)[a]

| Initial monomer concn (mol/L)	Initial grafting rate (R_p) (% min)	Induction period (I_p) (min)
11.7×10^{-2}	0.23	57.0
19.5×10^{-2}	0.22	51.0
27.3×10^{-2}	0.20	54.0
35.1×10^{-2}	0.18	58.5

[a] Wool = 1 g; temp = 60°C; [TBHP]/[FAS] = 2.27; water = 200 mL.

RESULTS AND DISCUSSION

Hydroperoxides (ROOH) are known to enter into redox reaction with Fe^{2+}. By analogy with Fenton's reagent, their activities towards vinyl polymerization could be attributed to $\cdot OR$ radical arising from the one electron transfer reaction between hydroperoxide and Fe^{2+}:

$$ROOH + Fe^{2+} \rightarrow RO\cdot + OH^- + Fe^{+3}$$

Both hydrogen peroxide and alkyl hydroperoxides have been known to produce free radical species upon thermal decomposition. The radical species are capable of initiating vinyl polymerization. It is known that a redox initiator is superior to conventional radical initiator, since side reactions due to cage recombination[21] are absent. Fe^{+2} is known to enter into redox reaction with a variety of oxidizing agents which include persulphates, peroxides, and hydrogen peroxide. TBHP is known to form an excellent redox system with Fe^{2+}. By analogy with Fenton's reagent (H_2O_2—Fe^{+2}), the activity of the TBHP—Fe^{+2} system may be attributed to t-butoxy radical arising from one electron transfer reaction between TBHP and Fe^{+2}:

$$t\text{-Bu—OO—H} + Fe^{+2} \rightarrow t\text{-BuO}\cdot + \overline{O}H + Fe^{+3}$$
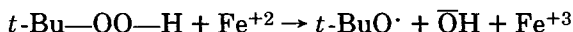
The resulting t-BuO$\cdot$ may participate in homopolymerization as well as in grafting. The latter occurs via hydrogen abstraction from wool by t-BuO$\cdot$ to generate a wool radical (W$\cdot$) capable of initiating grafting. A similar wool radical may also be formed by $\cdot OH$, resulting from the reaction between H_2O and t-BuO$\cdot$ as well as by chain transfer. The growing homopolymer chain may terminate by hydrogen abstraction from wool leading to the wool radical.

TABLE VII
Solubility Behavior of Ungrafted and Grafted Wool

Sample no.	Sample	% solubility			
		0.1 N NaOH	4M HCl	Oxidizing solvent	Urea–bisulfite
1	Wool	20.6	10.7	12.5	12.9
2	W-g-PMA[a]	11.0	10.5	4.5	10.0
3	W-g-PMMA[b]	9.5	7.5	6.5	8.0
4	W-g-poly(n-BVE)[c]	7.5	9.0	3.0	6.0

[a] Refers to the sample corresponding to sample no. 16 of Table I.
[b] Refers to sample corresponding to sample no. 16 of Table II.
[c] Refers to sample corresponding to sample no. 1 of Table III.

Effect of Molar Ratio of [TBHP]/[FAS]

Since Fe^{3+}, resulting from the reaction of TBHP and Fe^{2+}, may terminate the growing grafted chain, the molar ratio of [TBHP]/[FAS] should influence grafting. Tables I–III show that the maximum graft yield of MA, MMA, and n-BVE occurs at molar ratios of [TBHP]/[FAS] = 2.38:1, 2.88:1, and 2.27:1, respectively. When the molar ratio of [TBHP]/[FAS] exceeds these values, the percentage of grafting decreases with all the monomers studied. At a higher molar ratio of [TBHP]/[FAS], the redox system is disturbed and Fe^{+3} formed participates in termination of growing grafted chains resulting in a net decrease in percent grafting. A similar behavior was observed during Fenton's reagent $(Fe^{+2}—H_2O_2)$-initiated grafting of PVAc onto wool.[20] The maximum grafting of PVAc occurred at a molar ratio of $[H_2O_2]/[Fe^{2+}]$ = 1.43. It is apparent from Tables I, II, and III that the critical molar ratio of [TBHP]/[FAS] is almost the same for the grafting of acceptor and donor monomers. This indicates a lack of selectivity of monomers towards grafting. This would be expected, since the rate of grafting will depend upon the rate of formation of the alkoxy radical which is responsible for homopolymerization as well as grafting.

Effect of Monomer Concentration upon Rate of Grafting (R_p) and Induction Period (I_p)

It is apparent from Tables I–III that percent grafting increases with increase in monomer concentration and reaches maximum value at 38.66×10^{-2} mol/L for MA, 32.9×10^{-2} mol/L for MMA, and 19.5×10^{-2} mol/L for n-BVE. A further increase in monomer concentration leads to a decrease in percent grafting, which indicates that, at higher monomer concentration, homopolymerization becomes the preferred process.

Figures 1, 2, and 3 show that percent grafting increases steadily with time. Maximum grafting of MA and MMA occurred within 150 min and that of n-BVE occurred within 120 minutes. Percent grafting of each monomer was plotted against time as a function of total initial monomer concentrations. By extrapolating the curves to the time axis, induction periods (I_p) as a function of total initial monomer concentrations were determined. From the slopes at initial stages of reactions, R_p values were evaluated. Tables IV–VI show the effect of monomer concentrations upon R_p and I_p. With reactive monomers, e.g., MMA and MA, it is observed that R_p increases rapidly with increasing monomer concentration while, with n-BVE, R_p essentially remains constant. It is also apparent from Tables IV and V that I_p of MA and MMA decreases with increase in monomer concentration. This would be expected since n-BVE being a very less reactive monomer towards free radical shows reluctance to form a growing polymeric chain and, consequently, grafting also remains unaffected.

Finally, solubility behavior of grafted samples in standard solvent systems[22] was compared with that of ungrafted wool. Table VII shows that grafted samples are superior to ungrafted wool in respect of solubility in 0.1 N NaOH, oxidizing solvent, and in urea–bisulfite solution, while the solubility of wool as well as grafted samples is essentially the same in $4M$ HCl. It is also observed from the Table VII that n-BVE, which is less readily grafted, produces significant improvement in fiber properties and that the grafted sample shows greater resistance towards solubility in 0.1 N NaOH, oxidizing solvent and in urea–bisulfite solution.

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