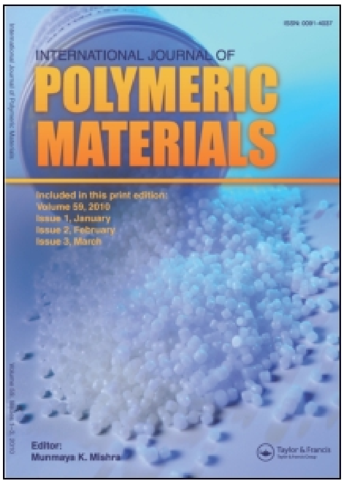

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REDOX INITIATED GRAFT COPOLYMERIZATION OF 4-VINYL PYRIDINE ONTO WOOL FIBER

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The graft copolymerization of 4-Vinyl Pyridine (4VP) onto wool fiber in aqueous medium by peroxomonosulphate (PMS)—thioglycolic acid (TGA) redox pair in an inert atmosphere has been investigated. The effect of concentrations of 4VP, PMS, TGA on R_h, and graft parameters have been studied. In addition, the effect of time, temperature, and amount of wool fiber on R_h and graft parameters were also determined. Chemical grafting of 4VP onto wool fiber was confirmed by FTIR spectroscopy. The tensile strength of the grafts have been analyzed.

Keywords: graft−polymerization, redox reaction, poly(4−vinyl pyridine), wool, redox system, tensile strength

INTRODUCTION

Modification of polymers by grafting is an active area of current interest. Grafting can lend some additional properties to the polymer backbone that may be useful in different applications. Graft copolymerization of methylmethacrylate (MMA) onto wool fiber was carried out in aqueous medium under nitrogen atmosphere initiated by a PMS-Fe^{2+} redox

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couple at varying concentrations of reactants and temperature. Various improved properties of the grafts were studied and compared with those of wool fiber [1]. Redox initiated graft copolymerization of poly-(acrylonitrile)(PAN) onto PET [2], nylon6, and nylon66 [3] fibers were reported. Peroxydiphosphate (PDP) was used as an initiator for the graft copolymerization of MMA onto wool fiber [4–5]. Grafting of 4VP has been carried out in various initiating systems such as ceric ion [6], $Fe^{2+}-H_2O_2$ [7], UV [8] and radiation [9]. Masahiro et al. [10] reported the photo initiated graft copolymerization of 4VP onto polyethylene film. Recently, Anbarasan and colleagues reported the peroxosalts initiated graft copolymerization of aniline onto wool fiber [11–12]. Peroxydisulphate (PDS) [13] and PMS [14] initiated graft copolymerization of poly(o-toluidine) (POT) onto wool fiber was reported by the authors. Itaconic acid was grafted onto LDPE by using different peroxides [15]. Currently the authors' active research team reported the graft copolymerization of 4VP onto nylon6 fiber and the grafted backbone was tested by water retention capacity [16]. The present investigation reports how different reaction parameters such as reaction time, concentrations of 4VP, PMS, TGA, amount of wool fiber, and temperature influence grafting reaction and yield with simultaneous homopolymer formation. The tensile properties of the grafted fiber were tested.

EXPERIMENTAL

Materials Used

4-Vinyl pyridine (Aldrich, AR) was distilled twice over KOH and CaH_2, respectively under nitrogen atmosphere. Potassium peroxomonosulphate (PMS) (E.Merck), and Thioglycolic acid (PMS) (SRL, AR) were used as such. Wool fiber (a gift sample from M/S.J.K. Synthetics, Kota, Rajasthan) was used after soxhlet extracted with acetone to remove any adhering impurities and was dried at room temperature.

Grafting Procedure

Wool (W_1 g), required amount of 4VP, TGA, and water were taken in a polymer tube and thermostated at 45°C for 30 min. The solution was deaerated by passing pure nitrogen gas for 30 min. The polymerization was initiated by the addition of calculated volumes of pre-deaerated PMS (using standard solutions). The time of adding the oxidizing agent, PMS, was taken as the starting time for the reaction (polymerization conditions were selected in such a way that no polymerization occurred in the absence of added oxidant). This was ascertained by separate experiment. At the end of the reaction time the reaction was arrested by immersing the reaction vessel in ice cold water and blowing air into the reaction vessel. Here all the graft copolymerization experiments were carried out at 45°C for 45 min.

The grafted wool along with homopolymer {poly(4-vinyl pyridine)(P4VP)} was filtered from the reaction mixture using G4 sintered crucible, washed well with distilled water for several times, dried at 80°C (for 4 h) and weighed to constant weight. This gives the total weight of the grafted polymer with the homopolymer (W_2 g). The mixture of the grafted wool fiber along with homopolymer, P4VP, was soxhlet extracted with acetone or benzene for 24 h to separate the homopolymer. After the separation of the homopolymer, the grafted sample was dried at room temperature and weighed to constant weight (W_3 g). The difference in ($W_3 - W_1$) gives the weight of the grafted P4VP. The difference in ($W_2 - W_3$) gives the weight of the homopolymer, P4VP, formed. This experimental approach makes way to follow the kinetics of both graft copolymerization and simultaneous homopolymerization.

Rate Measurements

Rate of grafting (R_g), rate of homopolymerization (R_h),% grafting, and % grafting efficiency were calculated as follows:

$$\%\,\text{grafting} = \frac{(W_3 - W_1)}{W_1} \times 100$$

$$\%\,\text{grafting efficiency} = \frac{(W_3 - W_1)}{\text{weight of monomer used } (W_4)} \times 100$$

$$R_g = \frac{(W_3 - W_1)}{V.t.M} \times 1000$$

$$R_h = \frac{(W_2 - W_3)}{V.t.M} \times 1000$$

where V = total volume of the reaction mixture, t-reaction time in sec, M = molecular weight of the monomer, $W_3 - W_1$ = weight of the grafted polymer, $W_2 - W_3$ = weight of the homopolymer.

FTIR Spectroscopy

The FTIR spectra of the grafted fiber was taken in KBr pellets by using a Bruker Equinox55 model FTIR spectrophotometer.

Tensile Strength

The tensile strength of pure wool backbone and P4VP grafted backbone were determined by using an Instron tensile tester as follows:

$$\text{Tensile strength (Kgf/cm}^2\text{)} = \frac{\text{Breaking load (Kg)}}{\text{Cross-sectional area (cm}^2\text{)}}$$

RESULTS AND DISCUSSIONS

Effect of Time on R_h and Graft Parameters

R_h and graft parameters were determined at various time intervals while keeping other experimental conditions as given in Table 1. Both R_h and R_g show an initial increase with time and thereafter they fall. To follow the kinetics of graft copolymerization in a smooth fashion, a reaction time of about 45 min was selected for the present study based on trial experiments. The % grafting and % grafting efficiency were observed to increase with increase in time (Table 1).

Effect of [4VP] on R_h and Graft Parameters

The [4VP] was varied in the range from 0.02 to 0.12 mol L^{-1} while keeping other experimental conditions constant. It is interesting to note that both R_h and R_g increase with increase in [4VP]. It was observed that the % grafting increases steadily with increase in [4VP] but the % grafting efficiency remains unaffected by change in [4VP] (Table 2). In order to find out the order dependence of [4VP] on R_h and R_g, the plots of $\log R_h$ Vs log[4VP] (Figure 1 A) and $\log R_g$ Vs log[4VP] (Figure 1B) were drawn and found to be straight lines with unit slopes, indicating a first order dependence of R_h and R_g on [4VP]. Further, the

TABLE 1 Effect of Time on R_h and Graft Parameters

Time (sec)	$R_h \times 10^6$ mol $L^{-1}sec^{-1}$	$R_g \times 10^7$ mol $L^{-1}sec^{-1}$	% grafting	% grafting efficiency
900	23.5	11.6	1.65	10.4
1800	19.1	8.40	2.40	15.2
3600	13.4	5.72	3.25	20.6
5400	9.72	4.28	3.65	23.2
7200	7.22	3.74	4.25	27.0

[4VP] = 0.07 mol L^{-1} , [PMS] = 0.005 mol L^{-1} , [TGA] = 0.005 mol L^{-1} , Weight of wool fiber = 0.20 g, Temperature = 45°C.

TABLE 2 Effect of [4VP], [PMS] on % Grafting and % Grafting Efficiency

[a][4VP] mol L^{-1}	% grafting	% grafting efficiency	[b]$[PMS]^{1/2} \times 10^2$ $mol^{1/2}\ L^{-1/2}$	% grafting	% grafting efficiency
0.02	0.95	18.1	3.16	1.62	10.2
0.05	1.78	17.1	5.48	2.19	14.0
0.07	2.65	16.8	7.07	2.75	17.5
0.10	3.55	16.9	7.75	3.15	20.0
0.12	4.35	16.5	8.94	3.40	21.6

[a][PMS] = 0.005 mol L^{-1}, [TGA] = 0.005 mol L^{-1}, Weight of wool fiber = 0.20 g, Temperature = 45°C.

[b][4VP] = 0.07 mol L^{-1}, [TGA] = 0.005 mol L^{-1}, Weight of wool fiber = 0.20 g, Temperature = 45°C.

first order dependence was confirmed by plotting R_h Vs [4VP] (Figure 1C) and R_g Vs [4VP] (Figure 1D). These plots were found to be linear. The increase in R_h and R_g may be due to increase in monomer radicals.

Effect of [PMS] on R_h and Graft Parameters

The [PMS] was varied between 0.001 and 0.008 mol L^{-1} whereas other experimental conditions were kept constant. Here again, both R_h and R_g increase with increase in [PMS]. The % grafting and % grafting efficiency are also increase with [PMS] and are represented in Table 2. The plot of log R_h Vs log[PMS] (Figure 2A) and log R_g Vs log[PMS] (Figure 2B) were drawn and found to show half order dependence. This was further confirmed by plotting R_h Vs $[PMS]^{1/2}$ (Figure 2C) and R_g Vs $[PMS]^{1/2}$ (Figure 2D). The plots were found to be straight lines and passing through the origin, indicating half order dependence of R_h and R_g on [PMS]. The increase in R_h and R_g may be due to increase in initiator radicals.

Effect of [TGA] on R_h and Graft Parameters

As represented in Table 3, [TGA] was varied between 0.001 to 0.008 mol L^{-1} while keeping other experimental conditions constant. Both R_h and R_g steadily increase with [TGA]. The % grafting and % grafting efficiency were found to have increasing trend with [TGA] (Table 3). To determine the order dependence, the plots of log R_h Vs log[TGA] (Figure 3A) and logR_g Vs log[TGA] (Figure 3B), were drawn and indicated a half order dependence of both R_h and R_g on [TGA]. The half order dependence of R_h and R_g on [TGA] was further confirmed by plotting R_h Vs $[TGA]^{1/2}$ (Figure 3C) and R_g Vs $[TGA]^{1/2}$ (Figure 3D).

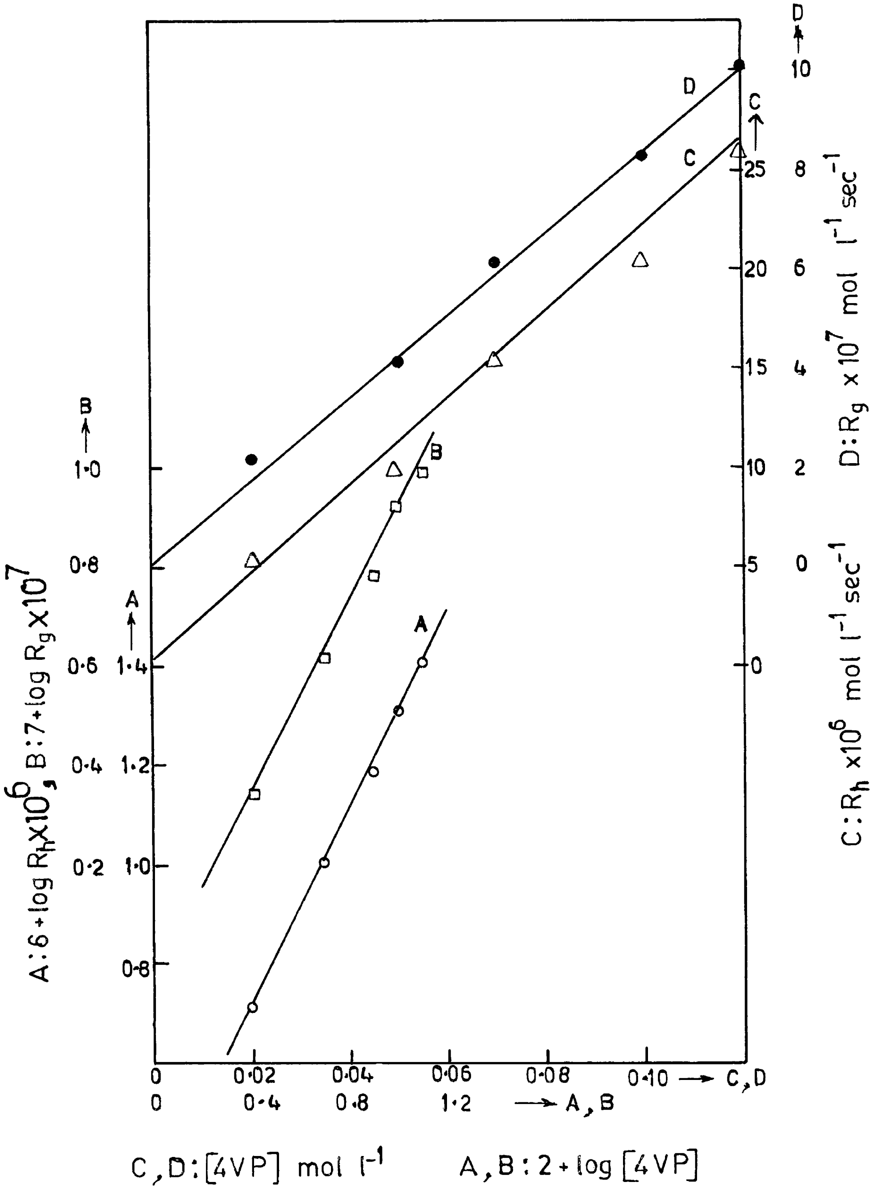

FIGURE 1 Effect of [4VP] on R_h and R_g [PMS] = 0.005 mol L^{-1}, [TGA] = 0.005 mol L^{-1}, Weight of wool = 0.20 g, Temperature = 45°C.

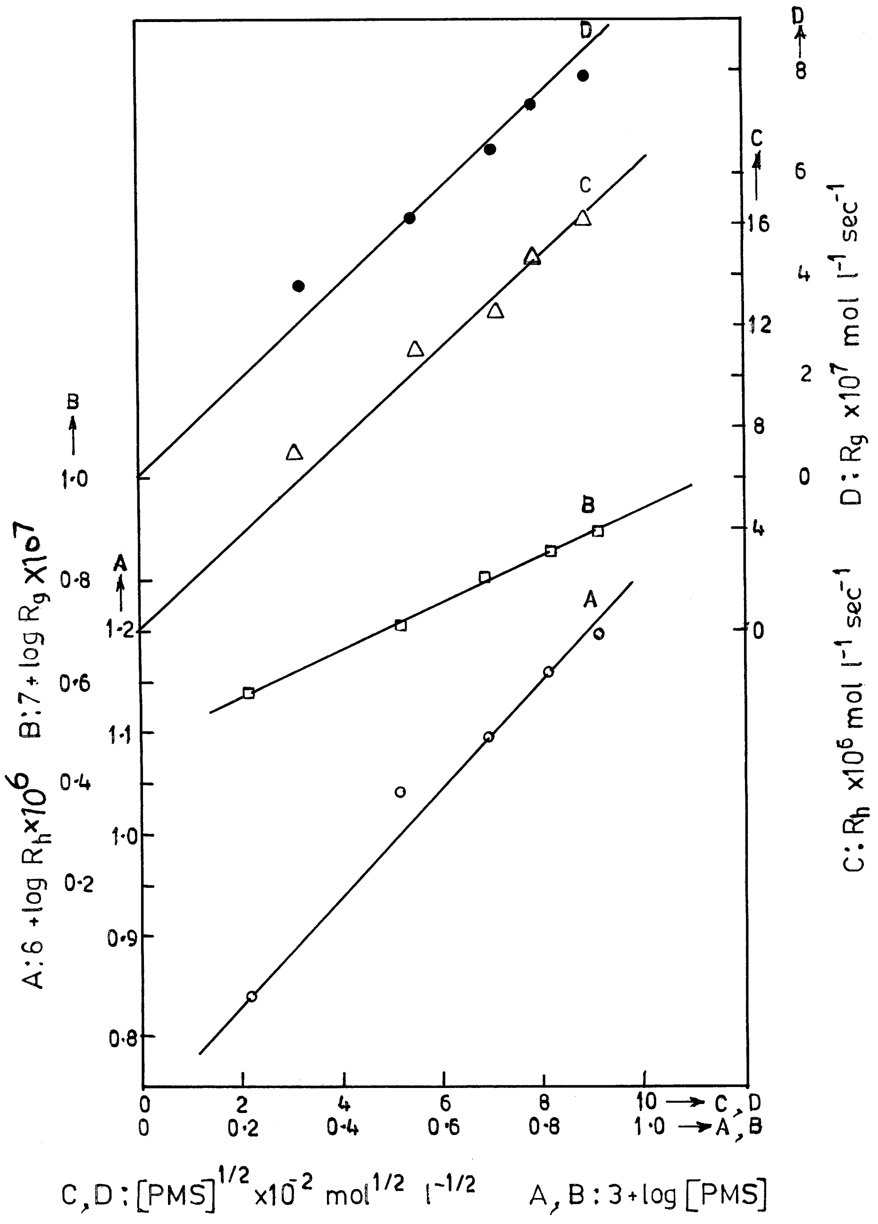

FIGURE 2 Effect of [PMS] on R_h and R_g [4VP] = 0.07 mol L^{-1}, [TGA] = 0.005 mol L^{-1}, Weight of wool = 0.20 g, Temperature = 45°C.

TABLE 3 Effect of [TGA] and (Weight of Wool Fiber) on % Grafting and % Grafting Efficiency

[a]$[TGA]^{1/2} \times 10^2$ $mol^{1/2}\ 1^{1/2}$	% grafting	% grafting efficiency	[b](Wt. of wool fiber)$^{1/2}$(g)$^{1/2}$	% grafting	% grafting efficiency
3.16	1.44	9.21	0.32	3.83	12.1
5.48	2.10	13.3	0.39	3.13	14.9
7.07	2.60	16.5	0.50	2.41	19.1
7.75	3.02	19.1	0.55	2.23	21.3
8.94	3.49	22.2	0.59	2.05	22.9

[a] $[4VP] = 0.07\,mol\,L^{-1}$, $[PMS] = 0.005\,mol\,L^{-1}$, Weight of wool fiber = 0.20 g, Temperature = 45°C

[b] $[4VP] = 0.07\,mol\,L^{-1}$, $[PMS] = 0.005\,mol\,L^{-1}$, $[TGA] = 0.005\,mol\,L^{-1}$, Temperature = 45°C.

The reason for increase in R_h and R_g may be due to increase in initiator radicals.

Effect of (Amount of wool fiber) on R_h and Graft Parameters

The weight of backbone material was varied from 0.10 to 0.35 g while keeping other experimental conditions constant. It was observed that both R_h and R_g values increase steadily with increase in the weight of wool fiber. The % grafting and % grafting efficiency values obtained with the change in backbone weight are given in Table 3. It was observed that the % grafting increase initially and then decreases, on the other hand the % grafting efficiency showed an increasing trend with the weight of backbone material. The plot of $\log R_h$ Vs log(amount of wool fiber) (Figure 4A), $\log R_g$ Vs log (amount of wool fiber) (Figure 4B), R_h Vs (amount of wool fiber)$^{1/2}$ (Figure 4C) and R_g Vs (amount of wool fiber)$^{1/2}$ (Figure 4D) were drawn and found to show 0.5 order dependence of both R_h and R_g on (amount of wool fiber). When the amount of wool fiber is increased, the grafting sites, surface effect, and macro radicals also increase.

Effect of Temperature on R_h and Graft Parameters

The obtained values of R_h and R_g by changing the temperature from 32°C to 60°C are given in Table 4. Both R_h and R_g increase initially up to 50°C and then they fall (Table 4). The % grafting and % grafting efficiency also follow the same trend. The depletion and evaporation of monomer at higher temperature is responsible for decrease in R_h and graft parameters. The Arrhenius plots of $\log R_h$ Vs 1/T (Figure not included) and $\log R_g$ Vs 1/T (Figure not included) were drawn and the

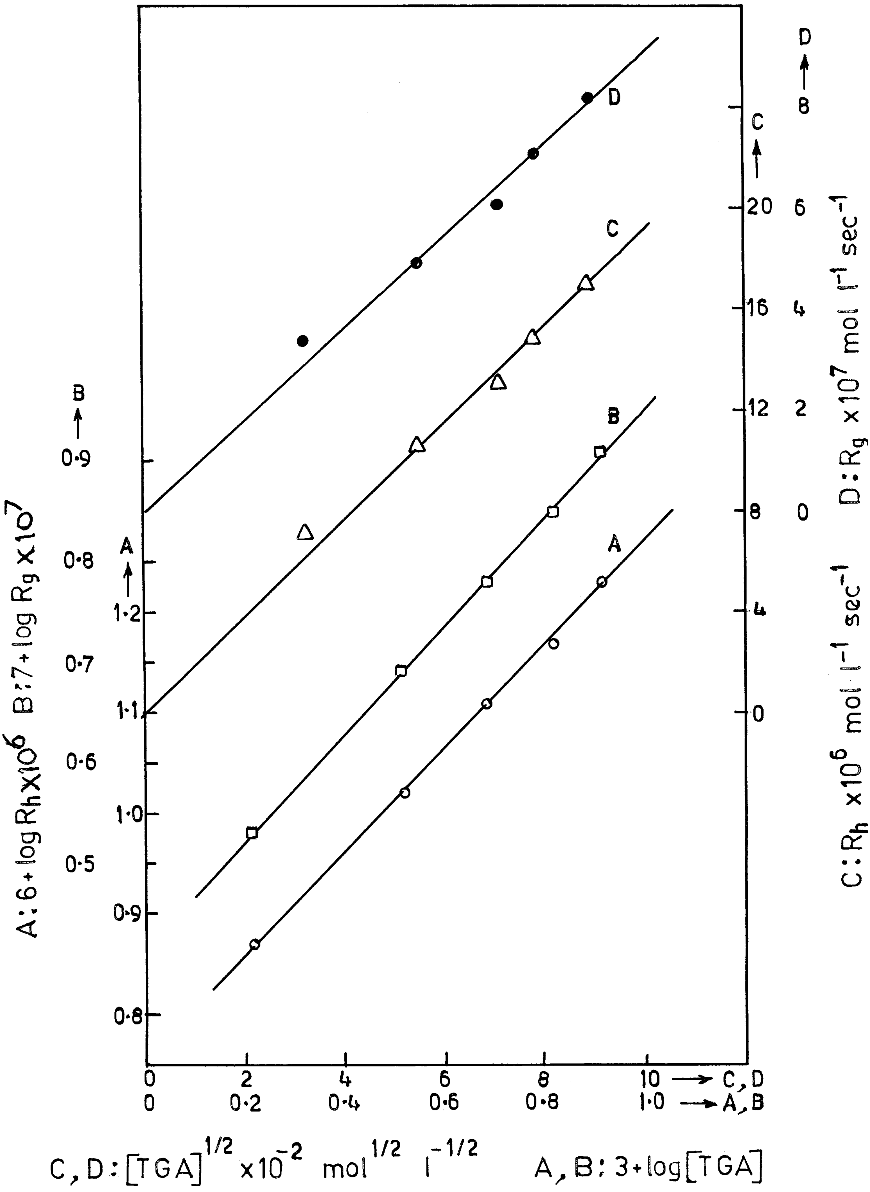

FIGURE 3 Effect of [TGA] on R_h and R_g [4VP] = 0.07 mol L^{-1}, [PMS] = 0.005 mol L^{-1}, Weight of wool = 0.20 g, Temperature = 45°C.

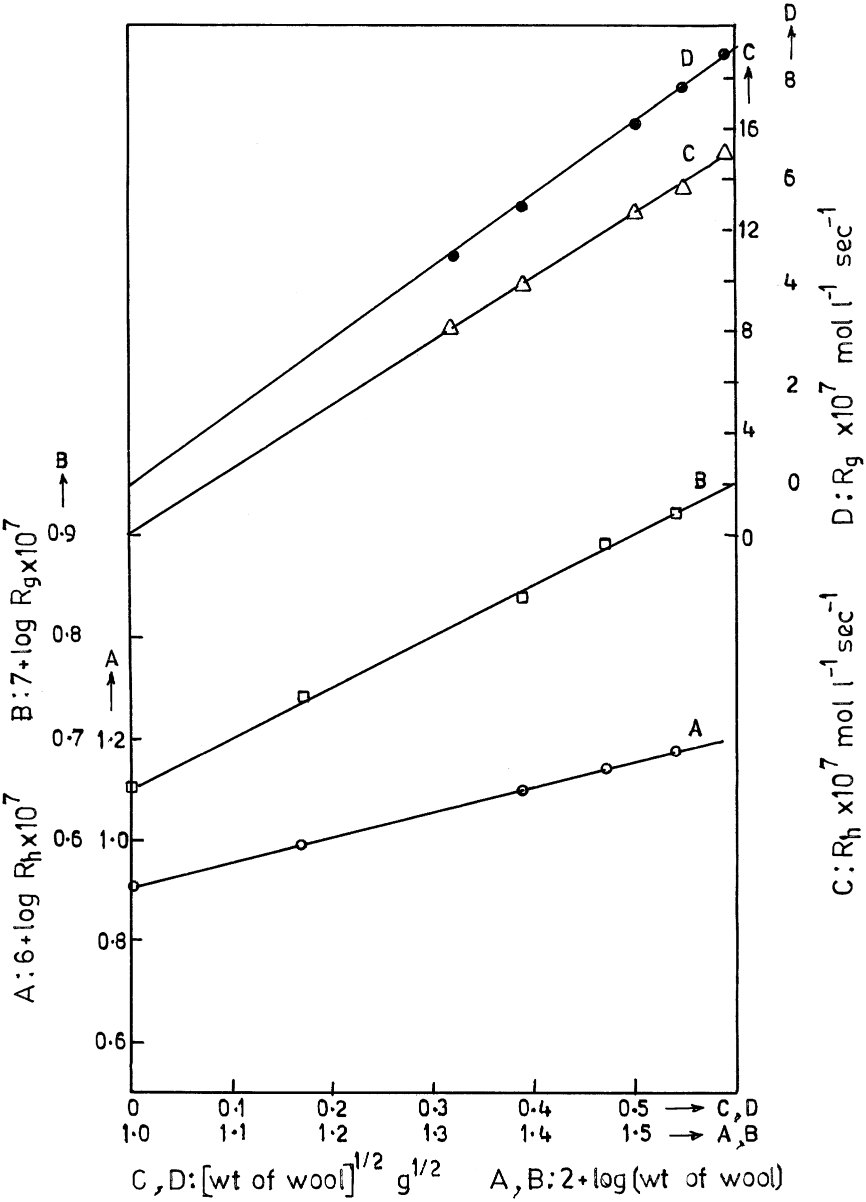

FIGURE 4 Effect of (weight of wool fiber) on R_h and R_g. [4VP] = 0.07 mol L^{-1}, [PMS] = 0.005 mol L^{-1}, [TGA] = 0.005 mol L^{-1}, Temperature = 45°C.

TABLE 4 Effect of Temperature on R_h and Graft Parameters

$1/T \times 10^3$ (K^{-1})	$R_h \times 10^6$ mol $L^{-1}sec^{-1}$	$R_g \times 10^7$ mol $L^{-1}sec^{-1}$	% grafting	% grafting efficiency
3.28	4.23	3.40	1.45	9.21
3.19	9.57	5.40	2.30	14.6
3.09	18.0	6.81	2.90	18.4
3.05	13.2	5.98	2.55	16.2
3.00	7.61	5.51	2.35	14.9

[4VP] = 0.07 mol L^{-1}, [PMS] = 0.005 mol L^{-1}, [TGA] = 0.005 mol L^{-1}, Weight of wool fiber = 0.20 g.

energy of activation for R_h and R_g were determined as 14.2 K.cal/mol and 6.34 K.cal/mol, respectively.

FTIR Spectroscopy

The FTIR spectrum of wool-g-4VP (Figure 5A) shows some additional peak at 1602 and 1551 cm^{-1} due to the presence of aromatic C-H

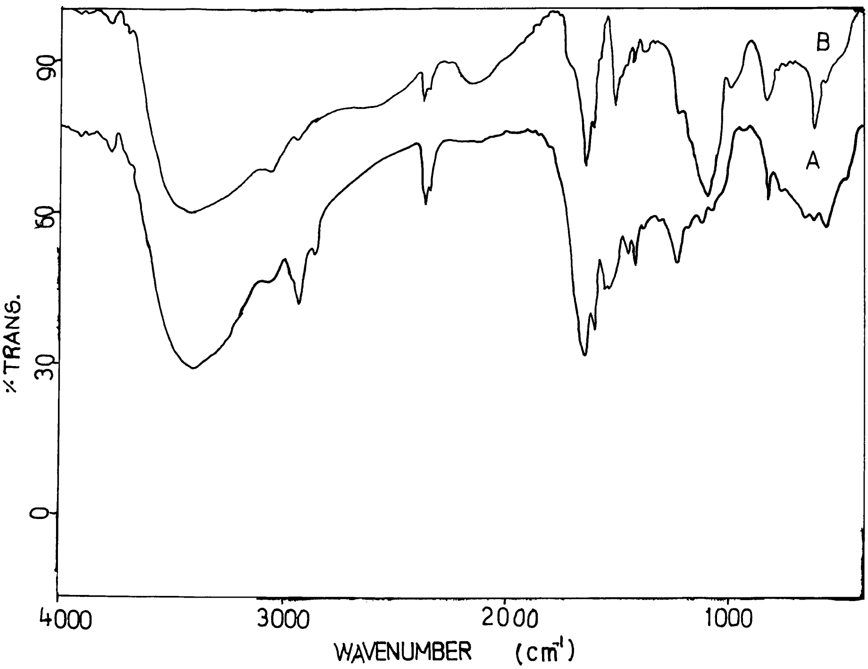

FIGURE 5A A: FTIR spectrum of wool-g-4VP. B: FTIR spectrum of poly(4VP).

TABLE 5 Tensile Strength of Wool Fiber Before and After Grafting

Polymer	% grafting	Tensile strength (GPa)
Wool	–	0.049
Wool-g-P(4VP)	1.78	0.057
	2.65	0.071
	4.35	0.098

stretching vibration. These were not found in pure wool fiber. The appearance of these peaks indicate the chemical grafting of poly(4VP) onto wool fiber. For the sake of comparison the FTIR spectrum of poly(4VP) is given in Figure 5B.

Tensile Strength

The tensile strength of the grafted and virgin wool fibers are shown in Table 5. It was observed that the tensile strength increased with increase in % grafting. This may be due to the bonding of the fibers in fixed positions in the matrix, making their movement restricted. These results are in accordance with earlier publications [17,18].

CONCLUSION

The following conclusions were made from this article's kinetic work:

- Graft copolymerization takes place with simultaneous homopolymerization.
- The chemical grafting was confirmed by FTIR spectroscopy and tensile strength.
- The tensile strength increased with % grafting.
- R_h and R_g was found to increase with increase of [monomer], [initiator], [activator], and (amount of fiber).

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