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Peroxosalts initiated graft copolymerization of aniline onto wool fibre—a comparative kinetic study

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Chemical grafting of aniline (ANI) onto wool fibre was carried out in aqueous acidic medium by using peroxosalts such as peroxodisulphate (PDS) and peroxomonosulphate (PMS) as an initiator for various [Monomer], [Initiator] and (fibre weight). It was observed that both R_h and R_g increased with increase in the concentration of each component. The chemical grafting was confirmed using FTIR spectroscopy, cyclic voltammetry (CV) and conductivity measurements. *© 2000 Kluwer Academic Publishers*

1. Introduction

For certain end use applications, the textile fibres are modified through graft copolymerization techniques. Recently Gopalan *et al.* [1, 2] grafted polyacrylonitrile (PAN) onto PET and Nylon6 fibres initiated by a redox system. Kawahara and co-workers [3] grafted methacrylamide onto silk fibre and studied the mechanical properties and structure of the grafted fibre. The mechanical and thermal properties of PET fibre was altered through the graft copolymerization of various vinyl polymers onto PET fibre [4, 5]. Graft copolymerization of PAN and PMMA onto PET fibre by using various redox system was currently reported by Gopalan and co-workers [6]. PMS-TGA redox initiated graft copolymerization of 4-Vinyl pyridine onto wool and nylon6 fibre was communicated [7].

Aniline and its derivatives are polymerized by different techniques [8–10]. Among those, chemical method is a preferable one due to minimum side reactions. Aniline is polymerized by PDS [11], potassium dichromate [12], ceric ion [13] and chromic acid [14]. Although the method of preparation is easy, the processability is found to be very difficult. In order to diversify these difficulties, the electrically conducting polymers are made blend with conventional polymers. Polyaniline (PANI)/cellulose acetate composites were prepared and its conductivity and electrochromic properties were studied by Depaoli *et al.* [15]. Electroactive PPy/polystyrene sulphonate was reported by Prezyna and co-workers [16]. Punkka *et al.* [17] prepared a blend of P(3OCT)/ethylene vinyl acetate and its thermal stability and conductivity values were reported.

Currently we reported the kinetic results on the PDS initiated graft copolymerization of aniline and o-toluidine onto PET fibre [18]. Peroxosalts initiated graft copolymerization of aniline onto nylon6 fibre was reported [19]. Kinetic results onto the chemical grafting of PANI onto nylon66 fibre in different media were communicated by our research team [20]. PDS initiated graft copolymerization of o-toluidine (OT), onto wool and nylon6 fibre was reported [21]. The isolation procedure for the separation of PANI grafted wool fibre from the homopolymer was reported in our earlier communication [22]. Graft copolymerization of aniline and OT onto PET fibre initiated by PMS was reported by Gopalan and co-workers [23]. Gregory and Tzou [24] grafted PANI onto PET fibre and they reported the kinetic results. Bhadani and Kumari [25] prepared a conducting fibres from natural fibres by electrochemical method. Such a conducting polymer grafted textile fibres are used in electromagnetic interference shielding (EMI) and sensors as represented in our earlier communications [18, 22].

The present report deals with the graft copolymerization of aniline onto wool fibre by using peroxo salts as initiators individually.

2. Experimental

Aniline (Fischer AR) was used after distilled under vacuum. PDS (CDH AR), PMS (E. Merck), HCl (Fischer AR), acetone (Ranbaxy AR) and other chemicals were used without further purification. Wool (a gift sample from M/S. J.K. Synthetics, Kota, Rajasthan) fibre was soxhlet extracted with acetone for 24 h and dried at room temperature before used.

2.1. Grafting procedure

A typical graft copolymerization study was carried out as given below.

Wool (W_1 g) was immersed in definite concentration of HCl (to adjust acidity) in a polymer tube and thermostated at 45 °C for 30 min. The solution was

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deaerated by passing pure nitrogen gas for 30 min. Required amount of monomer, aniline was added and deaerated for another 15 min. Graft copolymerization was initiated by the addition of calculated volumes of PDS or PMS (using standard solutions). The time of adding the oxidizing agent, PDS or PMS, was taken as the starting time for the reaction (polymerization conditions were selected in such a way that no polymerization occured in the absence of added oxidant). This was ascertained by a separate experiment. At the end of the reaction time, the reaction was arrested by blowing air into the polymer tube to freeze further reactions.

The grafted wool fibre along with the homopolymer (PANI) were filtered from the reaction mixture using a G4 sintered crucible and washed well with 1 M HCl for several times, dried (at 80 °C for 4 h) and weighed till to get constant weight. This gives the total weight of the grafted polymer along with the homopolymer (W_2 g). The mixture of the grafted wool/nylon6 fibre and the homopolymer, PANI, was soxhlet extracted with NMP for several hours to separate the homopolymer. The extraction process was repeated till the separation of the homopolymer from the grafted sample was completed. This was ascertained by drying the fibre in vacuum till to get constant weight (W_3 g). The difference in ($W_3 - W_1$) gives the weight of the grafted polymer. The difference in ($W_2 - W_3$) gives the weight of the homopolymer, PANI, formed.

2.2. Rate measurements

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

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

$$\%\,\text{efficiency} = \frac{W_3 - W_1}{W_4} \times 100$$

S

$$R_g = \frac{W_3 - W_1}{VtM} \times 1000$$

where ($W_3 - W_1$) = weight of the grafted polymer, t = reaction time and M = molecular weight of the monomer and W_4 is the weight of monomer used.

$$R_h = \frac{W_2 - W_3}{VtM} \times 1000$$

where V = total volume of the reaction mixture and $W_2 - W_3$ = weight of the homopolymer formed.

2.3. FTIR spectroscopy

The FTIR spectrum was recorded for wool-g-PANI and PANI samples by using Bruker-FTIR Equinox 55 model instrument by KBr pelletization method.

2.4. Cyclic voltammetry

The PANI grafted wool fibre (green coloured) was allowed to stand overnight in 0.5 N aqueous ammonia solution (the fibre turns into blue colour) then the fibre was washed well with acetone for 2–3 times to remove any adhering materials which were absorbed on the surface of the fibre. The dried fibre was immersed in formic acid and made into a paste. The paste was dip coated onto a Pt micro working electrode (surface area 9.50×10^{-2} cm^2). CV were recorded (by using BAS 100 A Electrochemical Analyzer) for wool-g-PANI by cycling the potential in the range of 0.00 to 0.90 V using Ag/AgCl as a reference electrode at various sweep rates. For the sake of comparison the CV of PANI film was recorded at various sweep rates.

2.5. Conductivity measurements

Conductivity of both PANI grafted wool and pure wool fibre were measured by using Keithley 617, programmable electrometer instrument for various % PANI grafted wool fibre. 1 cm length of the fibre was taken and its two end was fixed by the two pole of the instrument and current was passed. The display meter directly showed the conductivity value.

3. Resuls and discussion

3.1. Effect of monomer concentration on R_h and graft parameters

Experimental results obtained by changing the [ANI] in the range from 0.20 to 0.60 mol l^{-1} using PDS or PMS as an initiator is given in Table I while keeping

TABLE I Effect of [ANI] on R_h and graft parameters

	$R_h \times 10^6$		$R_g \times 10^7$					
[ANI]	mol l^{-1}	s^{-1}	mol l^{-1}	s^{-1}	% grafting		% efficiency	
mol l^{-1}	a	b	a	b	c	d	c	d
0.20	2.41	0.84	1.61	9.76	2.37	6.59	0.51	1.41
0.30	3.59	1.28	2.32	15.2	3.13	5.63	0.50	1.39
0.40	4.67	1.69	3.08	20.7	3.94	10.8	0.51	1.39
0.50	5.95	1.93	3.89	23.9	4.83	12.4	0.52	1.33
0.60	7.16	2.54	4.12	30.5	5.59	14.8	0.52	1.36

a, b: HCl = 1 M weight of wool = 0.20 g. Temperature = 45 °C.
a: [PDS] = 0.01 mol l^{-1}.
c, d: HCl = 1 M, Weight of wool = 0.30 g.
c: [PDS] = 0.015 mol l^{-1}, d: [PMS] = 0.03 mol l^{-1}.

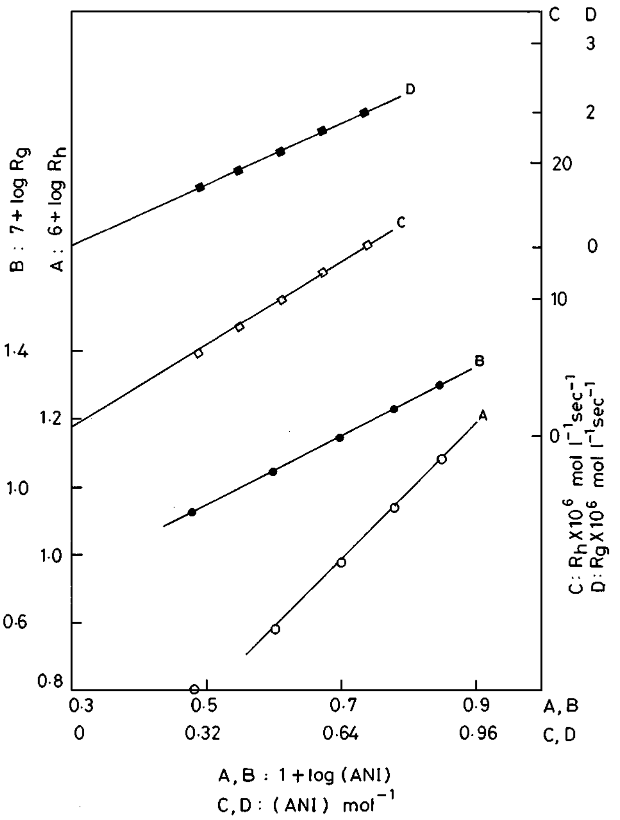

Figure 1 [PDS] = 0.01 mol l^{-1}, [HCl] = 1.00 M, weight of wool = 0.20 g.

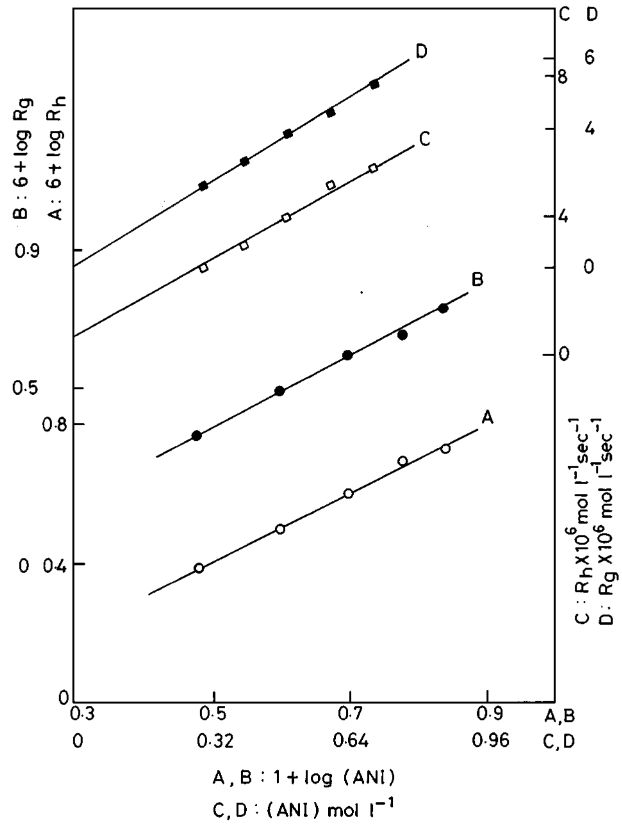

Figure 2 [PMS] = 0.02 mol l^{-1}, [HCl] = 1.00 M, weight of wool = 0.20 g.

other experimental conditions as constant. The R_h and R_g value increased with increase in [ANI]. The R_h value for PDS case is higher than that of PMS initiated system whereas the R_g value is higher with PMS system.

In an attempt to have further confirmation about the dependence of R_h and R_g on [ANI] a different set of experimental conditions were made as represented in Figs 1 and 2. The plots of log R_h vs. log [ANI] (Fig. 1A), log R_g vs. log [ANI] (Fig. 1B), R_h vs. [ANI] (Fig. 1C) and R_g vs. [ANI] (Fig. 1D) were drawn. The log-log plot indicates the first order dependence of R_h and R_g on [ANI]. The intercept of the plots R_h vs. [ANI] (Fig. 1C) and R_g vs. [ANI] (Fig. 1D) were noted. The % grafting and % efficiency are also shown in Table I.

Similar attempts were made for PMS initiated graft copolymerization of ANI onto wool system (Fig. 2). Here also the same rate order dependence was noticed. The intercept of the plots R_h vs. [ANI] (Fig. 2C) and R_g vs. [ANI] (Fig. 2D) were noted.

3.2. Effect of initiator concentration on R_h and graft parameters

The effect of varying the [PDS] or [PMS] on R_h and graft parameters are represented in Table II. The [PDS] was varied from 0.005 to 0.025 mol l^{-1} while keeping other experimental conditions as constant. Here again the R_h and R_g value showed increasing trend with [PDS] or [PMS]. The R_h value case is higher for PDS case whereas the R_g value is higher for PMS case.

In a separate set of experimental conditions different from the above mentioned conditions, the effect of [PDS] or [PMS] on R_h and graft parameters were studied (Figs 3 and 4). The plots of log R_h vs. log [PDS] (Fig. 3A), log R_g vs. log [PDS] (Fig. 3B), R_h vs. [PDS]

TABLE II Effect of [PDS] and [PMS] on R_h and graft parameters

[PDS]/[PMS] mol l^{-1}	$R_h \times 10^6$ mol l^{-1} a	$R_h \times 10^6$ s^{-1} b	$R_g \times 10^6$ mol l^{-1} a	$R_g \times 10^6$ s^{-1} b	% grafting c	% grafting d	% efficiency c	% efficiency d
0.005/0.01	2.02	0.96	0.13	1.13	2.93	3.69	0.38	0.48
0.010/0.02	3.64	1.85	0.26	2.20	5.84	7.30	0.75	0.94
0.015/0.03	5.77	2.91	0.38	3.35	8.88	11.0	0.87	1.41
0.020/0.04	8.17	4.03	0.54	4.21	11.7	14.2	1.51	1.83
0.025/0.05	10.1	5.15	0.69	5.53	14.6	18.1	1.88	2.33

a: PDS system, b: PMS system.
a, b: [ANI] = 0.30 mol l^{-1}, HCl = 1 M, weight of wool = 0.20 g.
c, d: [ANI] = 0.50 mol l^{-1}, HCl = 1 M, weight of wool = 0.30 g.
c: PDS system, d: PMS system.

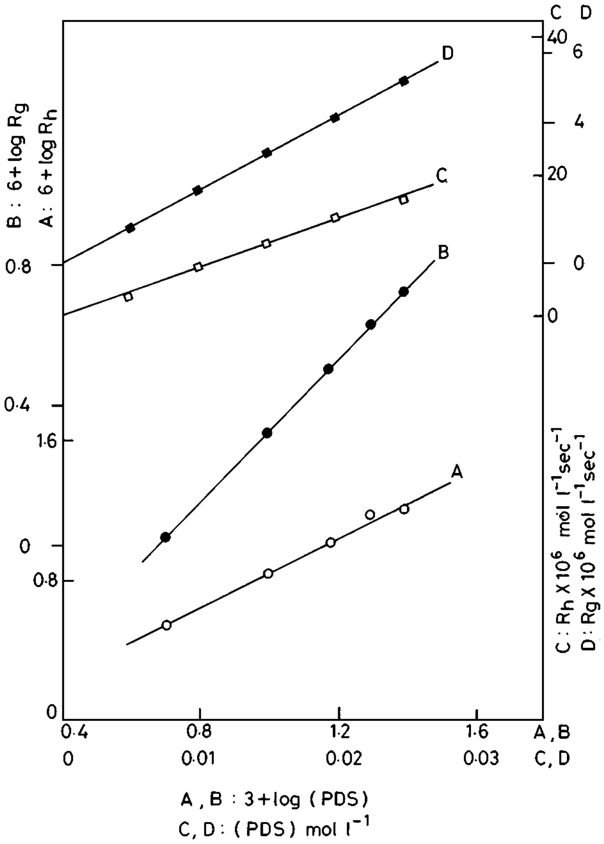

Figure 3 [ANI] = 0.30 mol l^{-1}, [HCl] = 1.00 M, weight of wool = 0.20 g.

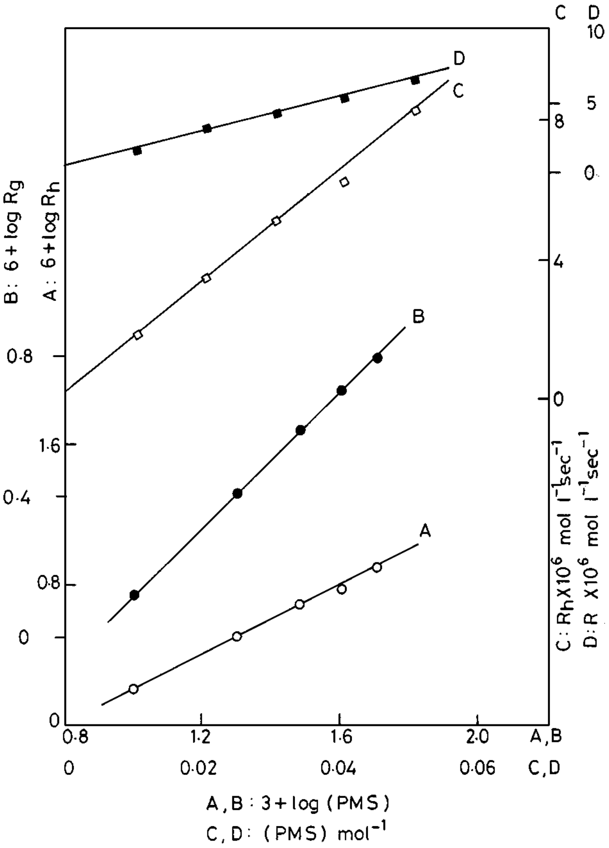

Figure 4 [ANI] = 0.30 mol l^{-1}, [HCl] = 1.00 M, weight of wool = 0.20 g.

(Fig. 3C) and R_g vs. [PDS] (Fig. 3D) were drawn. Then direct plots were found to be linear and passing through the origin. Fig. 3A and B indicates the first order dependence of R_h and R_g on [PDS]. The % grafting and % efficiency reveals the same trend (Table II).

Similar plots were made for PMS case also (Fig. 4). We found that the same first order dependence of R_h and R_g on [PMS]. The direct plots were found to be a straight line and passing through the origin.

3.3. Effect of amount of fibre on R_h and graft parameters

The effect of amount of fibre on R_h and graft parameters were studied under the conditions mentioned in Table III. The fibre weight was varied between 0.10 to 0.35 g while keeping other experimental conditions as constant. R_h and R_g increased with increase in amount of fibre. PDS system shows higher R_h value than the PMS system where the R_g value is higher for PMS system than the PDS case.

In an attempt to quantify the order dependences, the effect of amount of wool on R_h and graft parameters were studied under a set of different experimental conditions as specified in Figs 5 and 6. The pots of log R_h vs. log (weight of fibre) (Fig. 5A) and log R_g vs. log (weight of fibre) (Fig. 5B) were drawn. The slope values of the log-log plots were found to be close to one indicating first order dependence of R_h and R_g on weight of fibre. Further it was confirmed through plotting R_h vs. (weight of fibre) (Fig. 5C) and R_g vs. (weight of fibre) (Fig. 5D). These plots were found to be linear and passing through the origin. The linear plots support the clear first order dependence of R_h and R_g on backbone amount. The % grafting and % efficiency values are also given in Table III.

TABLE III Effect of (weight of wool) on R_h and graft parameters

	$R_h \times 10^7$		$R_g \times 10^7$					
Wt. of wool (g)	mol l^{-1}	s^{-1}	mol l^{-1}	s^{-1}	% grafting		% efficiency	
	a	b	a	b	c	d	c	d
0.10	16.1	9.40	1.07	10.0	4.57	12.4	0.39	1.06
0.15	24.3	12.5	1.62	15.8	4.56	12.6	0.49	1.35
0.25	40.9	20.7	12.7	26.4	4.34	12.3	0.65	1.86
0.30	48.9	23.6	3.42	33.4	4.40	12.3	0.76	2.13
0.35	56.5	38.7	3.91	36.7	4.51	12.6	0.87	2.45

a: [PDS] = 0.01 mol l^{-1}, b: [PMS] = 0.02 mol l^{-1}.
a, b: [ANI] = 0.30 mol l^{-1}, HCl = 1 M.
c: [PDS] = 0.015 mol l^{-1}, d: [PMS] = 0.03 mol l^{-1}.
c, d: [ANI] = 0.50 mol l^{-1}, HCl = 1 M.

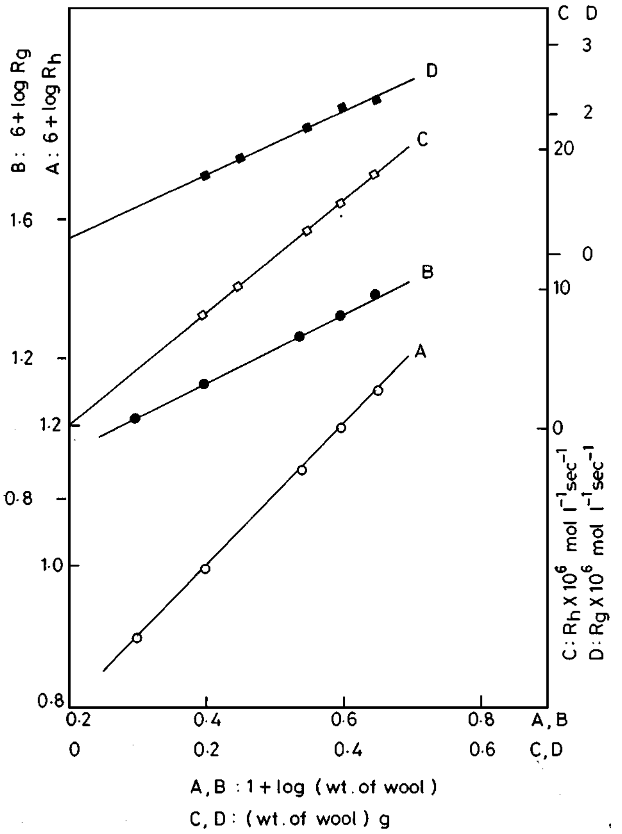

Figure 5 [ANI] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, [HCl] = 1.00 M.

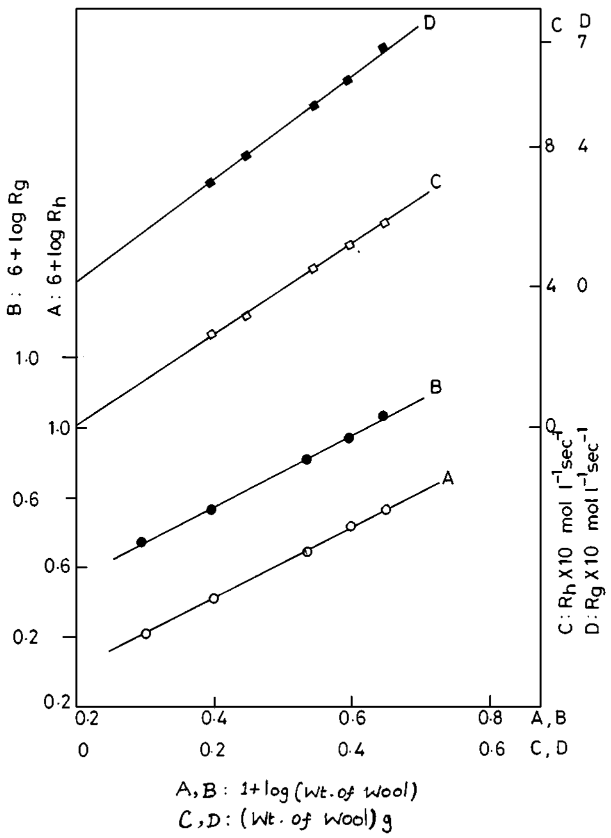

Figure 6 [ANI] = 0.30 mol l^{-1}, [PMS] = 0.02 mol l^{-1}, [HCl] = 1.00 M.

Similar plots were made for PMS system (Fig. 6). PMS system also showed first order dependence of R_h and R_g on (weight of fibre).

3.4. Effect of temperature on R_h and graft parameters

R_h and R_g measurements were carried out under the conditions given in Table IV. It was observed that both R_h and R_g values increased initially upto 323 °K followed by decrease. The energy of activation (E_a) were found out from the plot $1/T$ vs. log R_h (Fig. 7A) and $1/T$ vs. log R_g (Fig. 7B). As usual the R_h value is higher for PDS system and R_g value is higher for PMS system. Similar plots were made for PMS system also (Fig. 7C, D).

R_h and R_g values were determined under different set of experimental conditions as given in Table IV. It was found that both the R_h and R_g values show similar trend as noticed above. The average E_a value for the PDS initiated graft copolymerization of ANI was found to be 3.30 K cal/mol and 4.39 K cal/mol for the homopolymerization and graft copolymerization respectively. In the case of PMS initiated graft copolymerization of ANI, the E_a value for the homopolymerization was found to be 6.86 K cal/mol and for graft copolymerization as 3.95 K cal/mol respectively. The E_a values for homopolymerization of PDS system is lower than that of PMS case whereas the E_a value for graft copolymerization of PMS system is lower than that of PDS system. These values indicate that PDS give better homopolymer formation and PMS gives better grafting yield.

The decreasing trend of both R_h and R_g at higher temperature can be visualised as due to the loss of monomer and due to the probable side reactions of the initiating reactive species. Such an explanations are given for explaining the effect of temperature on R_p in the vinyl polymerization studies [26–28].

In 1992, Gregory and co-workers [24] studied the effect of added fibre on chemical polymerization of

TABLE IV Effect of temperature on R_h and graft parameters

	$R_h \times 10^6$		$R_g \times 10^7$					
	mol l^{-1}	s^{-1}	mol l^{-1}	s^{-1}	% grafting		% efficiency	
Temperature	a	b	a	b	a	b	a	b
305	33.18	1.50	0.85	6.69	0.35	2.80	0.05	0.40
313	3.46	2.01	1.07	8.30	0.45	3.48	0.06	0.51
323	4.19	2.89	1.43	22.4	0.60	9.35	0.08	1.34
328	3.84	2.62	1.90	19.5	0.80	8.15	0.11	1.17
333	3.21	2.01	1.73	15.2	0.70	6.35	0.10	0.91

a: [PDS] = 0.30 mol l^{-1}, b: [PMS] = 0.02 mol l^{-1}.
a, b: [ANI] = 0.30 mol l^{-1}, HCl = 1 M, Weight of wool = 0.20 g.

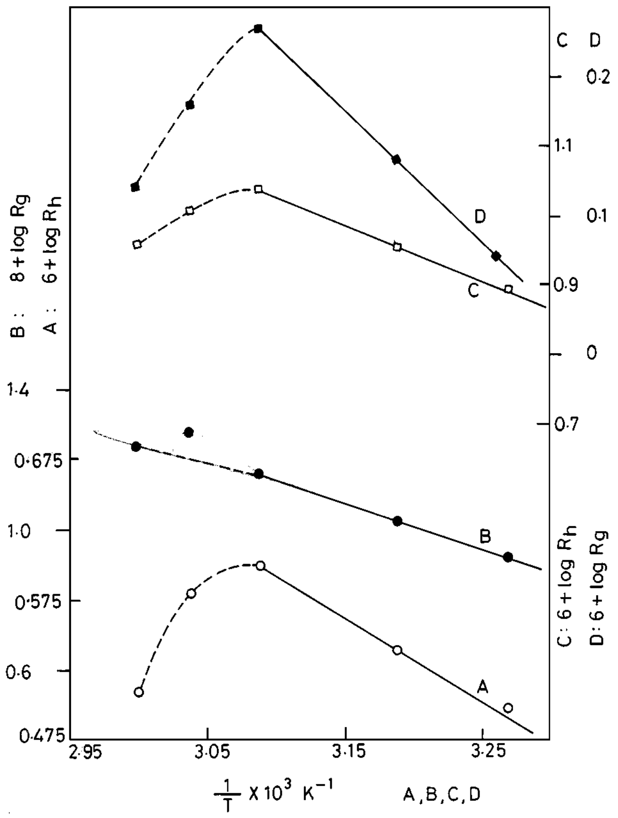

Figure 7 A, B: [ANI] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, weight of wool = 0.20 g; C, D: [ANI] = 0.30 mol l^{-1}, [PMS] = 0.02 mol l^{-1}, weight of wool = 0.20 g.

aniline in the presence and absence of PET fibre. In such a study, no correlation was tried to relate the changes in the rate of homopolymerization with reaction parameters. Wei *et al.* [29] proposed an auto acceleration effect in the electrochemical polymerization of aniline by electrode surface in an attempt to explain the changes in the induction time during the polymerization. A kinetic equation was proposed as follows.

$$R_p = k[M] + k'[M][P] \tag{1}$$

where k is the rate constant of formation of PANI on a bare Pt electrode and k' is the rate constant on PANI coated Pt surface. Shim and Park [30] proposed a kinetic equation for the polymerization of aniline on bare Pt electrode including the auto acceleration effect and proposed a type of the following equation as,

$$R_p(\mathrm{ANI}) = k_1[\mathrm{ANI}][\mathrm{PDS}] + k_2[\mathrm{ANI}][\mathrm{TAS}] \tag{2}$$

where k_1 and k_2 are the rate constant of formation of PANI on a bare Pt electrode surface and rate constant of PANI coated Pt electrode surface respectively. TAS is total available surface.

In the case of chemical polymerization of aniline similar consideration based on the above kinetic model may be considered including the additional effect due to the added oxidizing agent as well as the heterogeneous phase. For the present case, a simple rate of homopolymerization dependence was taken into consideration and the rate of PANI was monitored for different [ANI], [PDS] and amount of fibre. In the present study the added fibre for grafting and the formed homopolymer and the grafted backbone may cause the auto acceleration effect due to the presence of active sites in the backbone structure.

The plot of R_p (ANI) vs. [ANI] (Fig. 1C) was found to be a straight line with a definite intercept and R_p (ANI) vs. [PDS] (Fig. 2C) is a straight line and passing through the origin and R_p (ANI) vs. (amount of wool fibre) (Fig. 3C) is a straight line with and passing through the origin. These three combined facts necessiate the modification of Equation 2 as,

$$\begin{aligned} R_h(\mathrm{ANI}) = {} & k_{1h}\,[\mathrm{ANI}]\,[\mathrm{PDS}]\,(\text{weight of wool fibre}) \\ & + k_{2h}\,[\mathrm{ANI}]\,[\mathrm{TAS}] + k_{3h} \end{aligned} \tag{3}$$

where k_{1h} is the rate constant corresponding to homopolymer formation, k_{2h} and k_{3h} are rate constant for the homopolymer formation taking into account to the additional effects of available surface and probable change due to grafting. [TAS]—total available surface (which includes surface of homopolymer and grafted one on weight basis). The value of k_{3h} can be taken from the intercept of the plot of R_p (ANI) vs. [ANI] (Fig. 1C).

The rate of grafting also has the same trend {first order dependences of [ANI], [PDS] and (amount of wool)}. Hence the following equation is proposed for R_g as,

$$\begin{aligned} R_g\,(\mathrm{ANI}) = {} & k_{1g}\,[\mathrm{ANI}][\mathrm{PDS}]\,(\text{weight of wool fibre}) \\ & + k_{2g}\,[\mathrm{ANI}][\mathrm{TAS}] + k_{3g} \end{aligned} \tag{4}$$

where k_{1g} is the rate constant corresponding to the graft copolymer formation, k_{2g} and k_{3g} are the rate constants for the graft copolymer formation taking into account for the additional effects of available surface and probable changes due to grafting.

Similar equation can be proposed for the PMS initiated graft copolymerization of ANI onto wool fibre as,

$$\begin{aligned} R_h\,(\mathrm{ANI}) = {} & k_{1h}\,[\mathrm{ANI}][\mathrm{PMS}]\,(\text{weight of wool fibre}) \\ & + k_{2h}\,[\mathrm{ANI}][\mathrm{TAS}] + k_{3h} \end{aligned} \tag{5}$$

$$\begin{aligned} R_g(\mathrm{ANI}) = {} & k_{1g}\,[\mathrm{ANI}][\mathrm{PMS}]\,(\text{weight of wool fibre}) \\ & + k_{2g}\,[\mathrm{ANI}][\mathrm{TAS}] + k_{3g} \end{aligned} \tag{6}$$

Gregory and co-workers [29] determined the value of k_{1h} as 0.0008 min^{-1}. For the present case, PDS initiated graft copolymerization of aniline onto nylon6 fibre in aqu. HCl medium, the value of rate constant k_{1h} and k_{1g} are determined from the slope of the plots R_h vs. [ANI] (Fig. 1C) and R_g vs. [ANI] (Fig. 1D) and using Equations 3 and 4, which is far higher than the simple homopolymerization rate constant and augumenting the auto acceleration effect in homopolymerization by TAS and grafting. The rate constant (k_{1h}, k_{3h}, k_{1g} and k_{3g}) values are given in Table V.

On making similar attempts for the determination of the rate constant for the PMS initiated graft

TABLE V Rate constant values

System	Rate constant	Value	Unit
PDS	k_{1h}	5.88×10^3	g^{-1} mol^{-1} 1 s^{-1}
	k_{3h}	0.50×10^6	mol l^{-1} s^{-1}
	k_{1g}	4.16×10^4	g^{-1} mol^{-1} 1 s^{-1}
	k_{3g}	—	mol l^{-1} s^{-1}
PMS	k_{1h}	8.66×10^4	g^{-1} mol^{-1} 1 s^{-1}
	k_{3h}	0.50×10^6	mol l^{-1} s^{-1}
	k_{1g}	9.3×10^4	g^{-1} mol^{-1} 1 s^{-1}
	k_{3g}	—	mol l^{-1} s^{-1}

TABLE VI Conductivity measurements

Polymer	% grafting	Conductivity (Ohm^{-1} cm^{-1})
Wool	—	1.20 G
Wool-g-PANI	0.67	0.12 K
	1.98	0.30 K

copolymerization of aniline onto wool fibre, the values are given in Table VI. The k_{1h} value for PDS system is higher than that of PMS system and the k_{1g} value is higher for PMS system. Both PDS and PMS systems are having the same k_{3h} value. k_{3g} value for both system was found to be negligible.

4. FTIR spectroscopy

The FTIR spectrum of wool-g-PANI fibre was recorded with KBr and presented in Fig. 8B. The stretching vibration of the C=N band are indicated by the peaks at 1635 and 1353 cm^{-1}. The peak at 3274 cm^{-1} is due to the presence of N-H stretching of the aromatic amine. The C-H out of plane bending vibration of the para substituted benzene ring appears at 826 cm^{-1}. The above peaks are responsible for PANI structure units in the fibre side chain. The other peaks observed in the spectrum are due to the wool backbone polymer. This confirms the chemical grafting of PANI units onto the woo fibre matrix. For the sake of comparison the FTIR spectrum of PANI is given in Fig. 8A. The peaks at 1496 and 1602 cm^{-1} indicate the presence of ring stretch of bezenoid and quinoid form. The peak appearing at 1256 cm^{-1} is due to the C-H stretch of aromatic secondary amine. The peak at 3274 cm^{-1} can be assigned due to the N-H stretch of aromatic amine. The peak at 815 cm^{-1} is due to the para linked benzene ring. The presence of dopant, Cl^- peak is evident from the peak at 1307 cm^{-1}. The peaks at 890 and 772 cm^{-1} are due to the aromatic out of plane C-H bending stretch. These assignments are in close agreement with earlier reports of FTIR studies of PANI.

5. Cyclic voltammetry

Cyclic voltammogram (CV) of wool-g-PANI fibre film was recorded for various sweep rates and shown in Fig. 9A. Two anodic peaks (0.42 and 0.68 V) and one cathodic peak (0.67 V) can be seen. On cycling the potential with various sweep rates, the peak current was found to increase with increase in sweep rate. The film was not degraded even at higher sweep rates. This was evident from the unchanged changes of the redox peaks at different sweep rates. The presence of PANI electroactivity for grafted fibre points out grafting of PANI onto wool fibre.

For the sake of comparison the CV of PANI, homopolymer film is given in Fig. 9B. It shows one anodic (0.32 V) and one cathodic (0.76 V) peak. The CV of the homopolymer film and wool-g-PANI film were critically compared. The CV of wool-g-PANI shows slight shifting towards more anodic direction. The cathodic peak was shifted to less cathodic direction. This shifting is due to non-conducting wool fibre matrix.

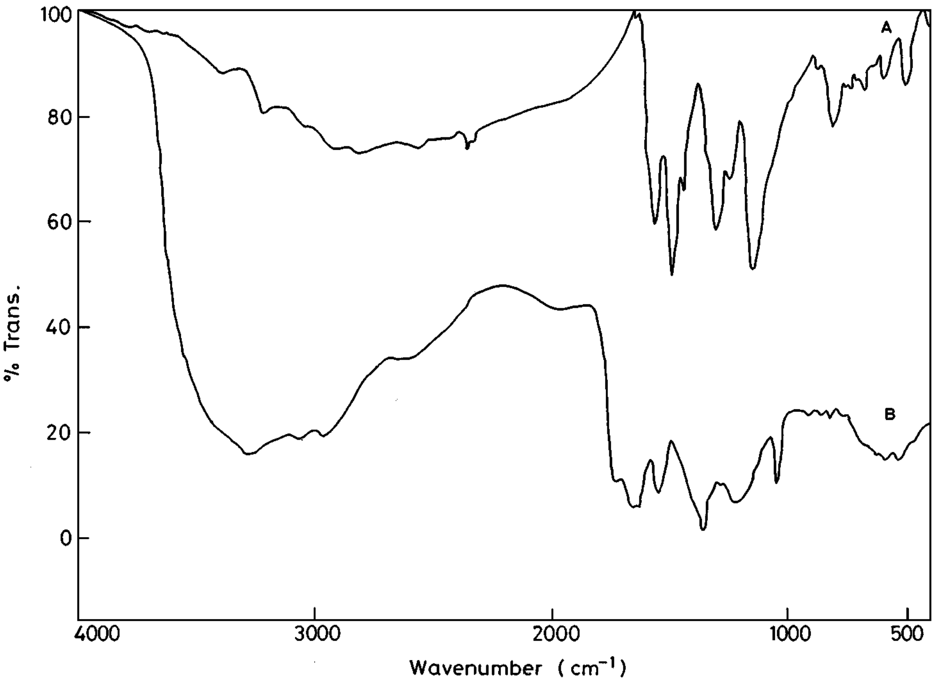

Figure 8 A: FTIR spectrum of PANI; B: FTIR spectrum of wool-g-PANI.

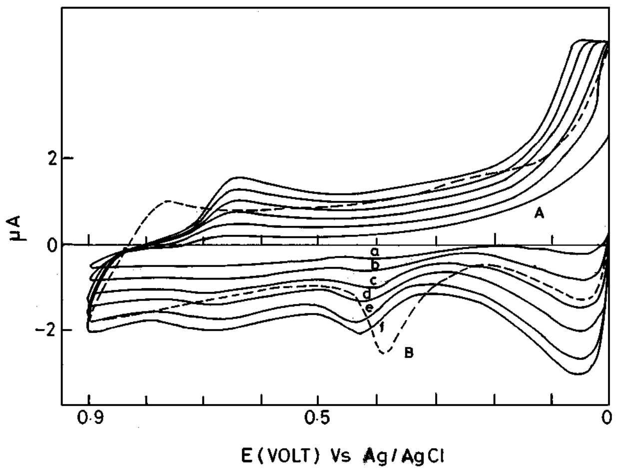

Figure 9 A: CV of wool-g-PANI film at various sweep rates a) 100 mV/s b) 200 mV/s c) 300 mV/s d) 400 mV/s e) 500 mV/s f) 600 mV/s; B: CV of PANI film at 200 mV/s.

6. Conductivity measurements

The conductivity of both grafted and ungrafted wool fibres were measured. The wool-g-PANI showed a good conductivity value than that of pure wool fibre. It was found that the conductivity values increased with increase in % grafting (Table VI). This confirms the chemical grafting of PANI onto wool fibre matrix.

7. Mechanism

A probable mechanism is proposed here to explain the experimental results obtained. The mechanism suggested for graft copolymerization of PANI onto wool fibre in this paper is based on the mechanism proposed by two research groups. Wei and coworkers [30] explains the formation of homopolymer via radical cation and Bhadani and Kumari [25] proposed a mechanism for the graft copolymerization of PANI onto various natural backbones by electrochemical method. And also they explained that the graft copolymerization proceeds through oligomerization. Taking the above two mechanisms as basis, a probable mechanism is suggested here to explain the modification of wool fibres through chemical grafting.

Probable mechanism for PDS initiated graft copolymerization of ANI onto wool fibre.

Primary reactions

$$\mathrm{ANI + PDS} \longrightarrow \mathrm{ANI^{+\bullet} + Products}$$

$$\mathrm{PDS} \longrightarrow \mathrm{2SO_4^{-\bullet}\,(R^{\bullet})}$$

$$\mathrm{R^{\bullet} + Wool} \longrightarrow \mathrm{Wool^{\bullet}}$$

$$\mathrm{R^{\bullet} + ANI} \longrightarrow \mathrm{ANI^{+\bullet}}$$

Homopolymerization

$$\mathrm{ANI^{+\bullet} + ANI^{+\bullet}} \longrightarrow \mathrm{dimer + 2H^{+}}$$

$$\mathrm{dimer + R^{\bullet}} \longrightarrow \mathrm{dimer^{+\bullet} + Products}$$

$$\mathrm{dimer + PDS} \longrightarrow \mathrm{dimer^{+\bullet} + Products}$$

$$\mathrm{dimer^{+\bullet} + dimer^{+\bullet}} \longrightarrow \mathrm{Oligomer + 2H^{+}}$$

$$\mathrm{Oligomer + PDS} \longrightarrow \mathrm{Oligomer^{+\bullet} + Products}$$

$$\mathrm{Oligomer + R^{\bullet}} \longrightarrow \mathrm{Oligomer^{+\bullet} + Products}$$

$$\mathrm{Oligomer^{+\bullet} + anymer^{+\bullet}} \longrightarrow \mathrm{Oligomer}$$

$$\mathrm{Oligomer^{+\bullet} + Oligomer^{+\bullet}} \longrightarrow \mathrm{Homopolymer\ (PANI) + 2H^{+}}$$

$$\mathrm{PANI + R^{\bullet}} \longrightarrow \mathrm{PANI^{+\bullet} + Products}$$

$$\mathrm{PANI + PDS} \longrightarrow \mathrm{PANI^{+\bullet} + Products}$$

$$\mathrm{PANI^{+\bullet} + ANI} \longrightarrow \mathrm{ANI^{+\bullet} + PANI\ (auto\ acceleration)}$$

Graft copolymerization

$$\mathrm{ANI + Wool^{\bullet}} \longrightarrow \mathrm{Wool\text{-}ANI^{+\bullet}}$$

$$\mathrm{Wool\text{-}ANI^{+\bullet} + ANI} \longrightarrow \mathrm{Wool\text{-}dimer + 2H^{+}}$$

$$\mathrm{Wool\text{-}dimer + R^{\bullet}} \longrightarrow \mathrm{Wool\text{-}dimer^{+\bullet}}$$

$$\mathrm{Wool\text{-}dimer + PDS} \longrightarrow \mathrm{Wool\text{-}dimer^{+\bullet} + Products}$$

$$\mathrm{Wool\text{-}dimer^{+\bullet} + ANI^{+\bullet}} \longrightarrow \mathrm{Wool\text{-}Oligomer + 2H^{+}}$$

$$\mathrm{Wool\text{-}Oligomer + R^{\bullet}} \longrightarrow \mathrm{Wool\text{-}Oligomer^{+\bullet}}$$

$$\mathrm{Wool\text{-}Oligomer + PMS} \longrightarrow \mathrm{Wool\text{-}Oligomer^{+\bullet} + Products}$$

$$\mathrm{Wool\text{-}Oligomer^{+\bullet} + Oligomer^{+\bullet}} \longrightarrow \mathrm{Graft\ copolymer\ (Wool\text{-}POT) + 2H^{+}}$$

$$\mathrm{Wool + R^{\bullet}} \longrightarrow \mathrm{Wool^{\bullet} + Products}$$

$$\mathrm{Wool^{\bullet} + ANI} \longrightarrow \mathrm{ANI^{\bullet} + Products}$$

(acceleration for homopolymerization)

$$\mathrm{ANI^{+\bullet} + ANI} \longrightarrow \mathrm{dimer + 2H^{+\bullet}}$$

Here the first two steps are established in our laboratory [1, 2]. This mechanism explains the experimental results obtained.

Probable mechanism for PMS initiated graft copolymerization of ANI onto wool fibre.

Primary reactions

$$\begin{aligned}
\mathrm{ANI} + \mathrm{PMS} &\longrightarrow \mathrm{ANI}\\
\mathrm{PMS(aqu.)} &\longrightarrow \mathrm{HSO}_4^{-\bullet} +^{\bullet} \mathrm{OH}(\mathrm{R}^\bullet) + \mathrm{H_2O}\\
\mathrm{R}^\bullet + \mathrm{Wool} &\longrightarrow \mathrm{Wool}^\bullet + \mathrm{Products}\\
\mathrm{R}^\bullet + \mathrm{ANI} &\longrightarrow \mathrm{ANI}^{+\bullet} + \mathrm{Products}
\end{aligned}$$

Homopolymerization

$$\begin{aligned}
\mathrm{ANI}^{+\bullet} + \mathrm{ANI}^{+\bullet} &\longrightarrow \mathrm{dimer} + 2\mathrm{H}^+\\
\mathrm{dimer} + \mathrm{R}^\bullet &\longrightarrow \mathrm{dimer}^{+\bullet} + \mathrm{Products}\\
\mathrm{dimer} + \mathrm{PMS} &\longrightarrow \mathrm{dimer}^{+\bullet} + \mathrm{Products}\\
\mathrm{dimer}^{+\bullet} + \mathrm{dimer}^{+\bullet} &\longrightarrow \mathrm{Oligomer} + 2\mathrm{H}^+\\
\mathrm{Oligomer} + \mathrm{PMS} &\longrightarrow \mathrm{Oligomer}^{+\bullet}\\
&\qquad + \mathrm{Products}\\
\mathrm{Oligomer} + \mathrm{R}^\bullet &\longrightarrow \mathrm{Oligomer}^{+\bullet}\\
&\qquad + \mathrm{Products}\\
\mathrm{Oligomer}^{+\bullet} + \mathrm{anymer}^{+\bullet} &\longrightarrow \mathrm{Oligomer}^{+\bullet}\\
\mathrm{Oligomer}^{+\bullet} + \mathrm{Oligomer}^{+\bullet} &\longrightarrow \mathrm{Homopolymer}\\
&\qquad \mathrm{(PANI)} + 2\mathrm{H}^+\\
\mathrm{PANI} + \mathrm{R}^\bullet &\longrightarrow \mathrm{PANI}^{+\bullet} + \mathrm{Products}\\
\mathrm{PANI} + \mathrm{PMS} &\longrightarrow \mathrm{PANI}^{+\bullet} + \mathrm{Products}\\
\mathrm{PANI}^{+\bullet} + \mathrm{ANI} &\longrightarrow \mathrm{ANI}^{+\bullet} + \mathrm{PANI}\\
&\qquad \text{(auto acceleration)}
\end{aligned}$$

Graft copolymerization

$$\begin{aligned}
\mathrm{ANI} + \mathrm{Wool}^\bullet &\longrightarrow \mathrm{Wool\text{-}ANI}^{+\bullet}\\
\mathrm{Wool\text{-}ANI}^{+\bullet} + \mathrm{ANI} &\longrightarrow \mathrm{Wool\text{-}dimer} + 2\mathrm{H}^+\\
\mathrm{Wool\text{-}dimer} + \mathrm{R}^\bullet &\longrightarrow \mathrm{Wool\text{-}dimer}^{+\bullet}\\
\mathrm{Wool\text{-}dimer} + \mathrm{PMS} &\longrightarrow \mathrm{Wool\text{-}dimer}^{+\bullet}\\
&\qquad + \mathrm{Products}\\
\mathrm{Wool\text{-}dimer}^{+\bullet} + \mathrm{ANI} &\longrightarrow \mathrm{Wool\text{-}Oligomer}\\
&\qquad + 2\mathrm{H}^+\\
\mathrm{Wool\text{-}Oligomer} + \mathrm{R}^\bullet &\longrightarrow \mathrm{Wool\text{-}Oligomer}^{+\bullet}\\
\mathrm{Wool\text{-}Oligomer} + \mathrm{PMS} &\longrightarrow \mathrm{Wool\text{-}Oligomer}^{+\bullet}\\
&\qquad + \mathrm{Products}
\end{aligned}$$

$$\begin{aligned}
\mathrm{Wool\text{-}Oligomer}^{+\bullet} + \mathrm{Oligomer}^{+\bullet} &\longrightarrow \text{Graft copolymer}\\
&\qquad \text{[poly(wool-co-}\\
&\qquad \text{POT)]} + 2\mathrm{H}^+
\end{aligned}$$

$$\begin{aligned}
\mathrm{Wool} + \mathrm{R}^\bullet &\longrightarrow \mathrm{Wool}^\bullet\\
&\qquad + \mathrm{Products}\\
\mathrm{Wool}^\bullet + \mathrm{ANI} &\longrightarrow \mathrm{ANI}^{+\bullet}\\
&\qquad + \mathrm{Products}
\end{aligned}$$

(acceleration for homopolymerization)

$$\mathrm{ANI}^{+\bullet} + \mathrm{ANI} \longrightarrow \mathrm{dimer} + 2\mathrm{H}^+$$

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