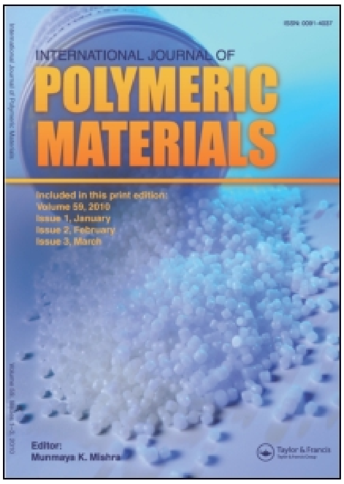

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Modification of Nylon6 into Conducting Fibre by Peroxosalts Initiated Graft Copolymerization – A Kinetic Approach

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Graft copolymerization of polyaniline (PANI) onto nylon6 fibre was carried out by using peroxo disulphate (PDS) and peroxo monosulphate (PMS) as a lone initiator separately under nitrogen atmosphere at various experimental conditions in aqueous HCl medium. The grafting of PANI onto nylon6 fibre was verified by recording cyclic voltammetry and conductivity measurements. The graft parameters such as % grafting, % efficiency and rate of grafting were followed. Grafting was always accompanied by homopolymerization. The rate of homopolymerization was also followed in all experimental conditions. A comparative account of all these parameters while initiated by PDS or PMS is made.

Keywords: Polyaniline; grafting; Nylon6; peroxosalts initiator; comparison

INTRODUCTION

Modification of natural [1] and synthetic [2] polymers through the attachments of foreign polymers by free radical graft copolymerization methods has been reported by several workers [1-3]. These modification make changes in physical [4] and chemical [5] properties of the backbone. Grafting of vinyl polymers [6-8] are proved to improve

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physical and chemical properties of the polymer backbone [9]. Modification was reported by graft copolymerization which can be initiated by irradiation [10], electrochemical [11], plasma treatment [12], using metal ion [13] and chemical methods [14]. Among these free radical initiated graft copolymerization by chemical method was proved to be an excellent choice with minimum side reactions.

Anilines and various ring substituted anilines are chemically polymerized by using variety of oxidizing agents [15–18]. In recent years much interest has been focused on graft copolymerization of aromatic conducting polymers through chemical initiation. Graft copolymerization of electrically conducting polymers onto natural and synthetic fibres have been done by electrochemical method [19, 20]. Elina *et al.* [21] carried out the graft copolymerization of polyaniline onto nitrile rubber and provided the spectroscopical evidences for grafting. Gregory *et al.* [22] grafted polyaniline and polypyrrole onto various textile fibres and they reported the conductivity values of modified polymers. Bhadani *et al.* [23] produced cyclic voltammograms of polyaniline grafted wool fibre in his article. Li and coworkers [24] grafted polyaniline onto the backbone of amino functionalised polystyrene by using ammonium persulphate as a lone initiator. Gregory *et al.* [25] proposed a kinetic equation for polyaniline grafted PET fibre.

In all, in the above set of studies the probability of simultaneous homopolymerization and isolation of grafted polymer backbone from the homopolymer have not been well accounted. The present study directs its attention to systematically approach the possibilities of homopolymer formation during grafting of PANI onto nylon6 fibre by using PDS or PMS as a lone initiator and separate the grafted polymer backbone from the homopolymer (PANI). A close comparison of graft parameters while using PDS or PMS as a lone initiator onto the same backbone under identical condition is made here.

EXPERIMENTAL

Aniline (Fischer AR), was used after distillation under vacuum. Potassium peroxodisulphate (PDS), (CDH AR) and potassium peroxomonosulphate (PMS), (MERCK) was used as such. Nylon6 fibre (a gift sample from Madura Coats, Madurai) was purified and used. Hydrochloric acid (HCl) (Fischer AR), *N*-methyl pyrrolidone, (NMP), (SRL, India), Acetone (Ranbaxy AR) and the other chemicals were used as such.

Procedure

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

Nylon6 (W_1g) was immersed in definite volume of 1M HCl (to adjust acidity) in a polymer tube and thermostated for 30 min. The solution was 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 preaerated 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 occurred in the absence of added oxidant). This was ascertained by separate experiment. The reaction mixture was found to turn green in colour and visible appearance of polymer formation was noticed. At the end of the reaction time, the reaction was arrested by blowing air into the polymer tube to freeze further reactions.

The grafted nylon6 fibre along with the homopolymer (PANI) were filtered from the reaction mixture using a G4 sintered crucible and washed well with 1M HCl for several times. This was then treated with aqueous ammonia for several hours and blue coloured powder with the fibre (blue colour) was dried (at 80°C for 4 hrs) and weighed till to get constant weight. This gives the total weight of the grafted polymer with the homopolymer (W_2g). The mixture of the grafted nylon6 along with the homopolymer (PANI) was soxhlet extracted with *N*-methyl pyrrolidone (NMP) for 24 hrs to separate the homopolymer. The extraction was repeated until the separation of the homopolymer from the grafted sample completed and this was ascertained by drying the fibre in vacuum till to get constant weight (W_3g) was obtained. The difference (W_3-W_1) gives the weight of the grafted polymer. The difference (W_2-W_3) gives the weight of the homopolymer (PANI) formed.

Rate Measurements

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

$$\%\ \text{grafting} = \frac{\begin{array}{c}\text{(dry weight of the grafted sample)}\\ -\ \text{(dry weight of the backbone)}\end{array}}{\text{Dry weight of the backbone}} \times 100$$

$$\%\ \text{efficiency} = \frac{\text{Weight of the grafted polymer}}{\text{Weight of monomer used } (W_4)} \times 100$$

$$= \frac{W_3 - W_1}{W_4} \times 100$$

$$\text{Rate of grafting} = \frac{(W_3 - W_1)}{V.t.M} \times 1000$$

where (W_3–W_1) = weight of the grafted polymer, V = total volume of the reaction mixture, t = reaction time and M = molecular weight of the monomer used.

Simultaneous Homopolymerization

Rate of homopolymerization was determined as follows:

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

where W_2–W_3 = weight of the homopolymer.

Cyclic Voltammetric Study

The PANI grafted (HCl doped, green coloured) nylon6 fibre was allowed to stand overnight in aqueous ammonia (the fibre turns blue) and the fibre was then 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 on to a Pt micro working electrode (surface area of $9.50 \times 10^{-2}\,\text{cm}^2$). Cyclic voltammograms were recorded (by using BAS 100A Electrochemical Analyzer) for the nylon6-g-PANI coated Pt electrode in 1M HCl as a background electrolyte by cycling the potential in the range 0.00 to 0.90 V using Ag/AgCl as a reference electrode.

Conductivity Measurement

Conductivity of both pure nylon6 and nylon6-g-PANI fibre was measured by using Keithley 617 Programmable Electrometer instrument.

RESULTS AND DISCUSSIONS

Graft copolymerization of aniline onto nylon6 fibre was performed under nitrogen atmosphere at various experimental conditions such as different concentrations of ANI, PDS or PMS and the fibre amount. In each case, while varying the concentration of one component, the other experimental conditions were kept constant.

It was found that the medium becomes green immediately on the addition of the initiator in all the experimental conditions and green particles of polyaniline was also found to precipitate during the course of the reaction. A systematic procedure was therefore adopted for following the course of grafting as well as the simultaneous homopolymerization of aniline as described in experimental section. The possibility of grafting PANI onto nylon6 fibre was checked by the following method.

The homopolymer (PANI) was separated from the grafted fibre and care was taken to remove the possible adherent particles of polyaniline on the nylon6 fibre by physical adsorption. This was done in a systematic experimental analysis of the grafted fibre. The grafted fibre (green colour) was allowed to stand in aqueous NH_3 for the conversion of the doped PANI to nuetral form (blue colour). This process converts both doped polyaniline in grafted as well as the physically adsorbed homopolymers (PANI) to neutral forms [26]. The grafted fibre was then dried and soaked with *N*-methyl pyrrolidone (NMP) to remove the possible adhered neutral polyaniline on the fibre surface.

The nylon6 fibre remains blue in colour even after the complete removal of the homopolymer of PANI and adds evidence for the chemical grafting of PANI onto nylon6 fibre. Grafting of PANI onto nylon6 fibre was further evident through recording cyclic voltammogram of the grafted fibre. The grafted fibre was treated with formic acid (to isolate the grafted polyaniline units from the backbone) and the filtered residue (grafted polyaniline) was made into a paste and was casted as film on Pt electrode by evaporation of NMP in vacuum.

Cyclic voltammogram (CV) curves of nylon6-g-PANI fibre film was recorded at different scan rates in the range of 200 to 1200 mV/s between 0.00 to 0.90 V *vs* Ag/AgCl in 1.00 M HCl show that there is no significant difference between PANI homopolymer film and nylon6-g-PANI film. This indicates that the insertion of PANI units onto nylon6 polymer matrix is a pure chemical grafting process. The CV's at various sweep rates are represented in Figure 1 (B-solid line). With an

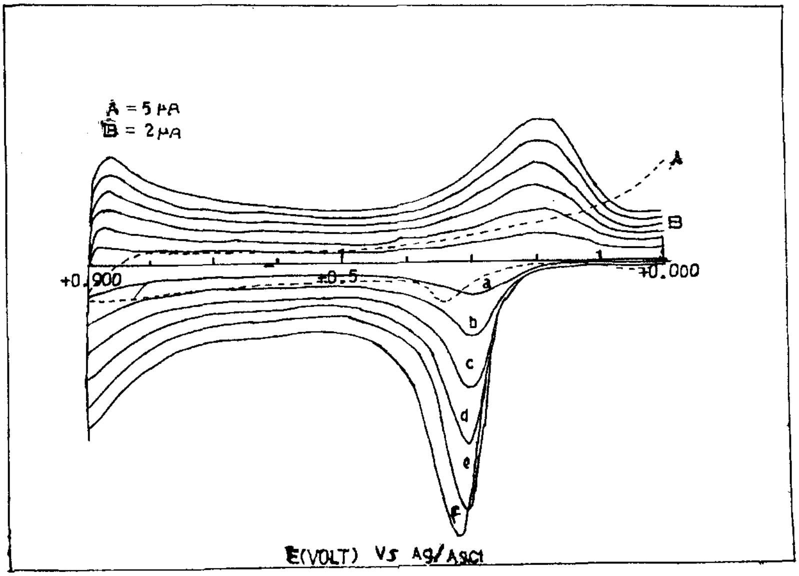

FIGURE 1 Cyclic voltammogram of nylon6-g-PANI fibre film (B-solid line) and PANI film (A-broken line at 200 mV/sec) on Pt working electrode in 1.00 M HCl as a background electrolyte using Ag/AgCl reference electrode at various sweep rate. (a) 200 mV/sec; (b) 400 mV/sec; (c) 600 mV/sec; (d) 800 mV/sec; (e) 1000 mV/sec; (f) 1200 mV/sec.

increase in scan rate the anodic peak current showed an increase and the peak potential was found to be slightly shifted towards more anodic direction. This may be due to the effect of non-conducting nylon6 polymer matrix. For the sake of comparison the CV of PANI film at 200 mV/s was shown in Figure 1 (A-broken line). Inorder to establish the stability of the grafted fibre (conducting), the plot peak current *vs* scan rate was drawn (Fig. 2, plot A and B). The linear nature of the plot indicates that the nylon6-g-PANI film is stable on the electrode surface as film.

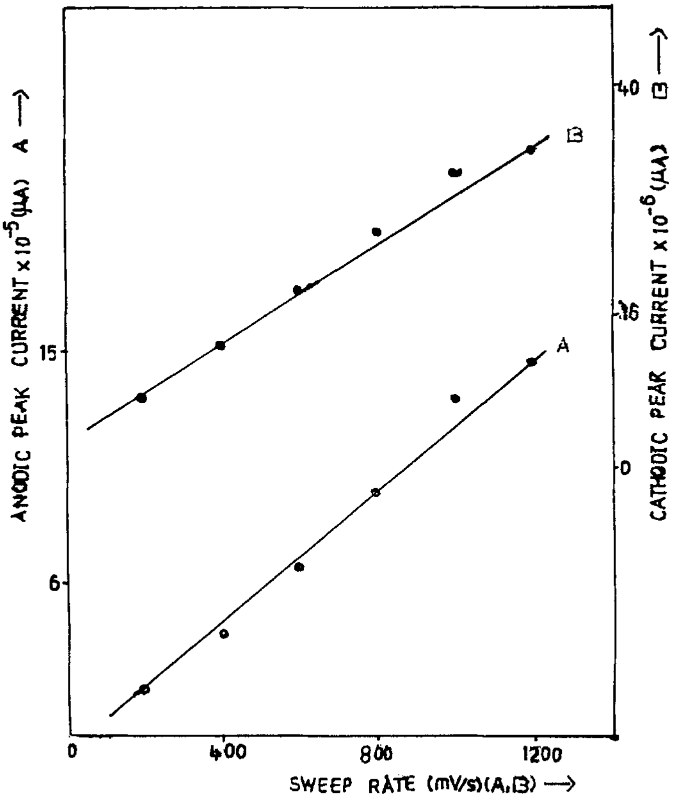

FIGURE 2 Plot A: Anodic peak current *vs* scan rate; Plot B: Cathodic peak current *vs* scan rate.

Effect of Monomer Concentration on Graft Parameters

Table I shows the % grafting, % efficiency, rate of grafting and rate of homopolymerization of ANI while varying [ANI] in the range of 0.20 mol l^{-1} to 0.60 mol l^{-1} by keeping other experimental conditions as constant. It is interesting to note that the R_h and R_g increases with increase in [ANI]. The R_h value was found to be low with PMS as an initiator in comparison with PDS initiated aniline polymerization. R_g value was found to be higher in all the above experimental conditions with PMS than when PDS was used as initiator. This indicates that aniline could be better grafted onto nylon6 fibre using PMS as an chemical initiator. The % grafting and % efficiency value also reveals the same (Tab. I).

Effect of Initiator Concentration on Graft Parameters

Table II presents the effect of varying the [PDS]/[PMS] on graft parameters. [PDS] was varied from 0.005 mol l^{-1} to 0.025 mol l^{-1} and the [PMS] was varied from 0.01 mol l^{-1} to 0.05 mol l^{-1} while keeping other experimental conditions as constant during such studies. Here again the value of R_h was found to be higher with PDS than PMS. R_g, % grafting and % efficiency values are found to be higher for PMS case and indicates the better initiating capacity for PMS.

TABLE I Effect of [ANI] of graft parameters

[ANI] *mol* l^{-1}	$R_h \times 10^7$ *mol* l^{-1}*sec*$^{-1}$		$R_g \times 10^7$ *mol* l^{-1}*sec*$^{-1}$		*% Grafting*		*% Efficiency*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
0.20	43.82	13.36	12.27	18.73	6.40	7.84	1.37	1.67
0.30	62.18	24.81	16.94	27.44	7.10	11.50	1.02	1.65
0.40	84.56	45.02	21.47	40.20	9.00	16.85	0.97	1.81
0.50	105.64	66.15	23.86	47.72	10.00	20.00	0.86	1.72
0.60	132.89	85.05	26.00	57.26	10.90	24.00	0.78	1.72

a = PDS; b = PMS.
[PDS] = 0.01 mol l^{-1}; Temperature = 45°C; [PMS] = 0.02 mol l^{-1}; Time = 30 min; [HCl] = 1.00 mol l^{-1}; Nylon6 = 0.20 g.

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

[PDS]/[PMS] *mol l*$^{-1}$	$R_h \times 10^7$ *mol l*$^{-1}$ *sec*$^{-1}$		$R_g \times 10^7$ *mol l*$^{-1}$ *sec*$^{-1}$		*% Grafting*		*% Efficiency*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
0.005/0.01	28.99	7.39	14.19	21.83	5.95	9.15	0.85	1.31
0.010/0.02	61.94	23.12	16.46	26.84	6.90	11.25	0.99	1.61
0.015/0.03	88.64	35.31	18.89	33.40	7.50	14.00	1.07	2.00
0.020/0.04	110.47	42.95	23.61	36.03	7.80	15.10	1.12	2.16
0.025/0.05	148.59	58.77	29.44	46.17	8.15	19.35	1.17	2.77

a = PDS; b = PMS.
[ANI] = 0.30 mol l^{-1}; Temperature = 45°C; [HCl] = 1.00 mol l^{-1}; Nylon6 = 0.20 g; Time = 30 min.

Effect of Amount of Fibre on Graft Parameters

As represented in Table III, the amount of nylon6 fibre was varied between 0.10 to 0.35 g in both studies involving PDS or PMS as an initiator. R_g and R_h shows an increasing trend with increase in the amount of fibre in both cases. R_h was found to be higher for PDS initiated aniline polymerization than PMS case. The higher values of R_g, % grafting and % efficiency in PMS initiated aniline polymerization also points out this. The effect of added PET fibre on the chemical polymerization of aniline was studied by Gregory *et al.* [25]. In his study no correlation was tried to relate the changes in the rate of homopolymerization with experimental conditions. Wei *et al.* [27] proposed an auto acceleration effect by the electrode surface in the electrochemical polymerization of aniline and they proposed a kinetic

TABLE III Effect of weight of fibre on graft parameters

Weight of fibre (g)	$R_h \times 10^7$ *mol l*$^{-1}$ *sec*$^{-1}$		$R_g \times 10^7$ *mol l*$^{-1}$ *sec*$^{-1}$		*% Grafting*		*% Efficiency*	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*
0.10	49.24	10.28	12.64	12.76	10.60	10.70	0.76	0.77
0.15	57.00	17.12	15.27	20.40	8.53	11.40	0.92	1.22
0.25	70.39	28.22	18.13	30.87	6.08	9.68	1.09	1.73
0.30	82.01	33.59	22.42	39.00	6.27	9.50	1.35	2.04
0.35	85.00	42.11	28.87	47.70	6.91	9.03	1.73	2.26

a = PDS; b = PMS.
[ANI] = 0.30 mol l^{-1}; [PDS] = 0.01 mol l^{-1}; [HCl] = 1.00 mol l^{-1}; [PMS] = 0.02 mol l^{-1}; Temperature = 45°C; Time = 30 min.

equation as,

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

where k is rate constant of formation of PANI on a bare Pt electrode surface and k' is rate constant on PANI coated Pt electrode surface. Shim and Park [28] 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 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 work, a simple rate of homopolymerization dependence was taken into consideration and the rate of PANI was monitored for different [ANI] and [PDS]/[PMS]. 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. 3, plot A) is found to be linear with a definite intercept and R_p(ANI) *vs* [PDS] (Fig. 4, plot A) is a straight line and passing through the origin. These two combined facts necessiate the modification of Eq. (2) as

$$R_p(\mathrm{ANI}) = k_1[\mathrm{ANI}][\mathrm{PDS}] + k_2[\mathrm{ANI}][\mathrm{TAS}] + k_3 \tag{3}$$

where k_1 is the rate constant corresponding to homopolymer formation. k_2 and k_3 are rate constants for the homopolymer formation taking into account to the additional effects of available surface and probable change due to grafting. [TAS] – total available surface (includes homopolymer (weight basis) and grafted one). The value

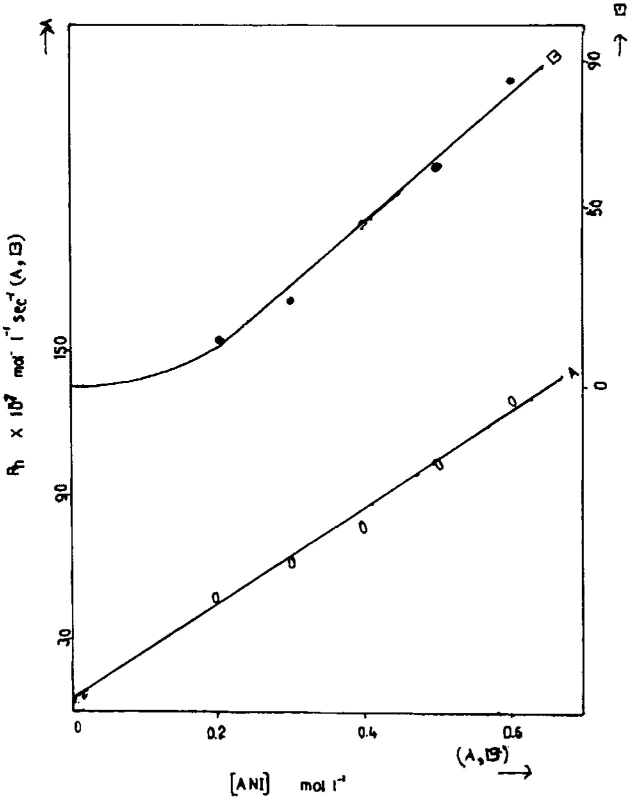

FIGURE 3 A, B: [ANI] = 0.30 mol l^{-1}; Time = 30 min.; Temperature = 45°C; Wt. of nylon6 = 0.20 g; HCl = 1.00 mol l^{-1}.

of k_3 can be taken from the intercept of the plot of R_p(ANI) *vs* [ANI].

Gregory *et al.* [25] determined the value of rate constant k_1 in the chemical polymerization of aniline in the presence of PET fibre as 0.0008 min^{-1}. For the present case of PDS initiated aniline polymerization in the presence of nylon6 fibre, the value of rate constant k_1 is determined from the slope of the plot R_p *vs* [PDS] (Fig. 3, plot A) and using Eq. (3) as 0.120 min^{-1} which is far higher than the simple homopolymerization rate constant and augumenting the auto acceleration effect in homopolymerization by TAS and grafting. The value of rate constant k_3 can also be obtained from the intercept of the plot

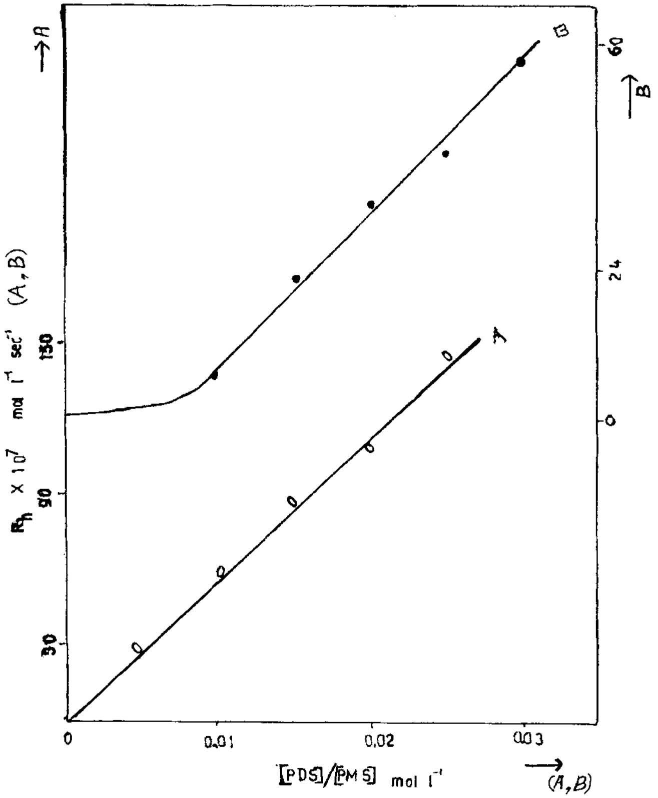

FIGURE 4 A, B: Temperature = 45°C; Time = 30 min.; Wt. of nylon6 = 0.20 g; HCl = 1.00 mol l^{-1}. A: [PDS] = 0.01 mol l^{-1}; B: [PMS] = 0.01 mol l^{-1}.

R_p(ANI) *vs* [ANI] (Fig. 4, plot A) as 0.045×10^{-4} mol l^{-1} min l^{-1}. This k_3 can now be taken as contribution to the surface changes due to chemical grafting.

On making similar attempts for the determination of the rate constant for the system with PMS as an initiator, the observed facts of the plot R_p(ANI) *vs* [PMS] (Fig. 4, plot B) passing through the origin and R_p(ANI) *vs* [ANI] (Fig. 3, plot B) is a straight line with an auto acceleration effect in the initial stage are taken into account. Hence the following equation was proposed.

$$R_p(\text{ANI}) = k_4[\text{ANI}][\text{PMS}] + x \tag{4}$$

TABLE IV Conductivity measurement

Polymer	*% Grafting*	*Conductivity*
Nylon6	–	$1.03\,\mathrm{G\,Ohm^{-1}}$
Nylon6-g-PANI	7.84	$6.88\,\mathrm{K\,Ohm^{-1}}$
	24.00	$7.80\,\mathrm{K\,Ohm^{-1}}$

[ANI] = 0.20 mol l^{-1}; [HCl] = 1.00 mol l^{-1}; Nylon6 = 0.20 g; [PDS] = 0.01 mol l^{-1}; Temperature = 45°C; Time = 30 min.

where k_4 is the rate constant for the homopolymer formation and x is a composite function of [TAS], [PMS] and [ANI] and the rate constant for the surface effect and due to grafting. From the above equation k_4 was determined from the slope of R_p *vs* [PMS] as $0.048\,\mathrm{min}^{-1}$. This value is found to be much lower in comparison with k_1 which also favours better grafting in the case of PMS.

Table IV shows the conductivity values of nylon6 and PANI grafted nylon6 fibres. The PANI grafted nylon6 fibre shows higher conductivity value than the ungrafted fibre. The conductivity value also increases with increase in % grafting. This can also be taken as added evidence for chemical grafting of PANI onto nylon6 fibre.

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