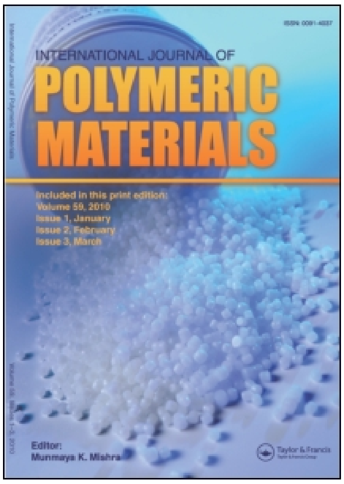

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Modification of Textile Fibers

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Modification of Textile Fibers into Electrically Conducting Ones

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Peroxy disulphate initiated graft copolymerization of aniline onto poly(ethylene-terephthalate) and nylon6 fibre was carried out under nitrogen atmosphere at various experimental conditions in aqueous acidic medium. Graft parameters such as % grafting, % efficiency and rate of graft copolymerization were determined. Grafting was always accompanied by homopolymer formation. The rate of homopolymerization was also followed in all experimental conditions. The chemical grafting was confirmed by FTIR spectroscopy, differential thermal analysis and conductivity measurements. Probable mechanism has been proposed to explain our experimental results.

Keywords: Chemical grafting; Poly(aniline); Synthetic fibers; Rate constant; Mechanism

1. INTRODUCTION

Graft copolymerization is a well known method for the modification of chemical and physical properties of polymeric materials. Various methods are used for the graft copoymerization technique. Among those, free radical initiated graft copolymerization by chemical method has been proven to be an excellent choice with minimum side reactions [1–4].

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Aniline (ANI) and various ring substituted anilines are polymerized by chemical [5, 6] and electrochemical [7, 8] methods. Graft copolymerization of conducting polymers onto natural and synthetic polymers have been performed by chemical methods [9, 10]. Graft copolymerization of aniline and o-toluidine onto wool and nylon6 fibre was reported by us [11, 12]. Recently Anbarasan and co-workers [13] communicated results on the peroxy disulphate (PDS) initiated graft copolymerization of aniline onto nylon66 fibre in different media. Peroxosalts initiated graft copolymerization of aniline and o-toluidine onto various natural and synthetic fibre was reported by us [14 – 17]. Currently Anbarasan *et al.*, communicated the results on the peroxosalts initiated graft copolymerization of aniline and o-toluidine onto rayon [18, 19] and polypropylene fibres [20 – 22]. Toppare and co-workers [23] grafted poly(pyrrole) (PPy) onto a synthetic backbone and they characterized it through FTIR, DSC, TGA and SEM analysis. Polyaniline (PANI) grafted poly(p-amino styrene) was reported by Suzhen Li and co-workers [24]. Yang and colleagues [25] grafted PANI onto chitosan fibre and they submitted FTIR, TGA and conductivity measurements as evidence for grafting. Such conducting polymer grafted textile fibres are used as EMI shielders [26].

The present work deals with the polymerization of aniline with PDS as a chemical initiator in the presence of PET and Nylon6 fibres. The rate parameters were evaluated and critically compared. The chemical grafting was confirmed through DTA, FTIR and conductivity measurements.

2. EXPERIMENTAL

2.1. Materials and Methods

Aniline (Fischer AR) was used after distillation under vacuum. Potassium peroxydisulphate (PDS) (CDH AR), HCI (Fischer AR) and other chemicals were used as such. PET and Nylon6 fibres (a gift samples from M/S.Madura coats, Madurai, India) were soxhlet extracted with acetone for 24 hours and dried at room temperature before used.

2.2. Procedure

A typical graft copolymerization study was conducted as follows.

PET or Nylon6 fibre (W_1 g) was immersed in definite concentration of HCI (to adjust acidity) in a polymer tube and thermostated for 30 min. The 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 (using standard solutions). The moment of adding PDS 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 stop further reactions.

The reaction mixture was filtered using a G4 sintered crucible and washed with 1 M HCl several times, dried (at 80°C for 4 hrs) and weighed to constant weight. This gives the total weight of the grafted polymer along with the homopolymer (W_2 g). The grafted PET or Nylon6 fibre was soxhlet extracted with NMP for several hours to remove the homopolymer (no colour changes were seen in the grafted fibre). The extraction was repeated until separation of the homopolymer from the grafted sample was completed. This was ascertained by drying the fibre in vacuum to 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.

2.3. Rate Measurements

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

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

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

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

$$R_h = \frac{W_2 - W_1}{\text{V.t.M.}} \times 1000$$

where $W_3 - W_1$ is weight of the grafted polymer, V is total volume of the reaction mixture, t is reaction time, $W_2 - W_3$ is weight of the homopolymer formed and M is molecular weight of aniline.

2.4. FTIR Spectroscopy

The FTIR spectrum was recorded for PET-g-PANI and Nylon6-g-PANI samples by using Bruker FTIR Equinox 55 model instrument by KBr pelletisation method.

2.5. Conductivity Measurements

Conductivity of both PANI grafted PET and Nylon6 fibres, and pure PET and Nylon6 fibres were measured by using Keithly 617 Programmable Electrometer Instrument. 1 cm length of the fibre sample was taken and its two ends were connected with two poles of the electrometer instrument. Current was passed through the poles and the conductivity was displayed on the display meter.

2.6. Weight Loss Study

Definite weight of the PANI grafted Nylon6 fibre was treated with acetone (30 min) and dried to constant weight. The change in weight was observed. Then treated with N-Methyl Pyrrolidone(NMP) solution for 4 hrs, removed from NMP, dried under vacuum and weighed. The PANI grafted Nylon6 fibre was soaked with 0.5 N aqu. ammonia solution and then dried at room temperature. An amount of weight loss was noticed due to dedoping process. It was once again treated with NMP solution for 4 hrs, dried under vacuum condition and weighed. Change in weight was inferred. Thus the total % weight loss was determined. The same procedure was repeated for the PET case too.

2.7. Isolation of PANI Grafted PET or Nylon6 Fibre from PANI, Homopolymer

The mixture (W_1 g) of the PANI grafted Nylon6 fibre and PANI, the homopolymer was dedoped with 0.5 N aqu. ammonia solution and extracted with NMP for 12 hours to separate the homopolymer from the reaction mixture. The extraction process was repeated until the separation of homopolymer from the grafted sample was complete and was ascertained by a colourless filtrate. The fibre was dried in vacuum to constant weight (W_2 g). This gives the weight of the grafted polymer. The difference between W_1 and W_2 gives the weight of homopolymer formed. The procedure was followed for PET case too.

2.8. Differential Thermal Analysis

Differential Thermal Analysis (DTA) was recorded for both grafted and ungrafted PET fibres by using Dupont 2000 Thermal Analyzer instrument.

3. RESULTS AND DISCUSSION

3.1. Effect of [ANI] on R_h and Graft Parameters

[ANI] was varied in the range of 0.30 to 0.70 mol l^{-1} keeping other experimental conditions constant. It is interesting to note that the R_h and R_g increased with increase in [ANI]. Both the R_h and R_g values were found to be low with PET system in comparison with Nylon6 system. This indicates that aniline could be better grafted onto Nylon6 fibres using PDS as an chemical initiator. The increase in R_h and R_g can be ascribed to the formation of more and more monomer radical cation and auto acceleration effect due to formed homopolymer, PANI, and PANI grafted PET or Nylon6 fibres.

In the case of Nylon6 system both R_h and R_g showed first order dependence on [ANI]. This can be confirmed by plotting $\log R_h$ *Vs.* log[ANI] (Fig. 1A) and $\log R_g$ *Vs.* log[ANI] (Fig. 1B). Furthermore the first order dependence was confirmed by drawing R_h *Vs.* [ANI] (Fig. 1C) and R_g *Vs.* [ANI] (Fig. 1D). These plots were found to be linear. The plots of R_h *Vs.* [ANI] (Fig. 1C) and R_g *Vs.* [ANI] (Fig. 1D) give some intercept values. The % grafting and % efficiency values are showed in Table I.

The same plots were made for PET fibre also (Fig. 2). The same first order dependence was noticed here.

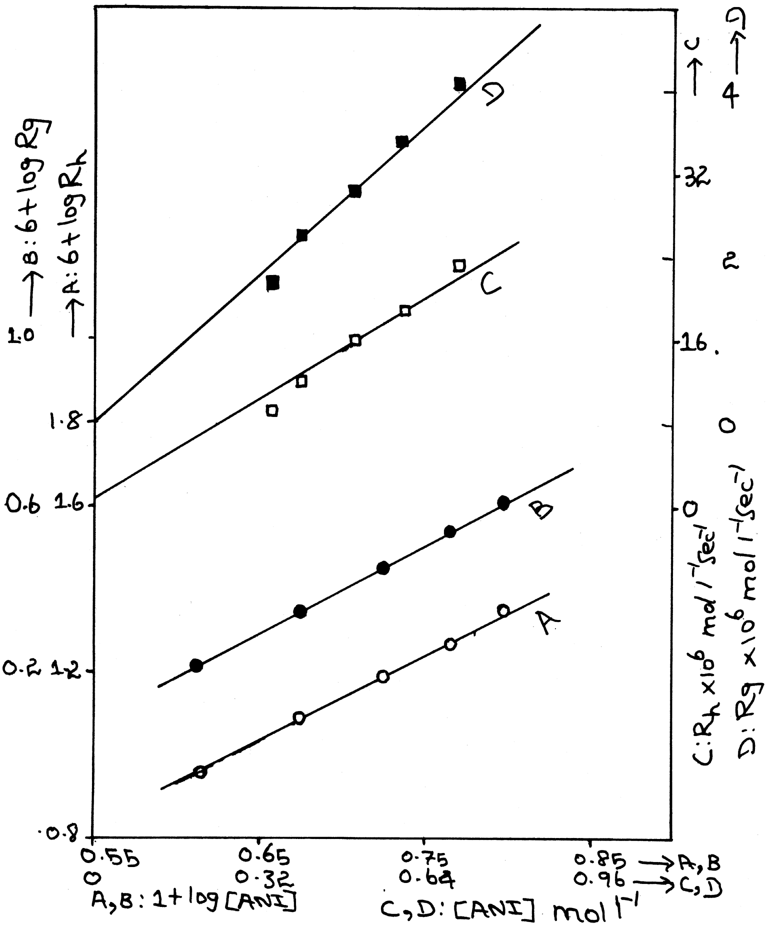

FIGURE 1 Effect of [ANI] on R_h and R_g [PDS] = 0.015 mol l^{-1}, Weight of Nylon6 fibre = 0.30 g, [HCl] = 1.00 M.

3.2. Effect of [PDS] on R_h and Graft Parameters

The [PDS] was varied from 0.005 to 0.025 mol l^{-1} while keeping other experimental conditions constant. Here again the R_h and R_g values were found to be higher with Nylon6 system. In order to find out the order dependency of both R_h and R_g on [PDS], plots of

TABLE I Effect of [ANI] on % grafting and % efficiency

[ANI]	*% grafting*		*% efficiency*	
mol l^{-1}	*A*	*B*	*A*	*B*
0.30	4.69	3.10	1.01	0.67
0.40	6.29	4.16	1.01	0.67
0.50	7.90	5.33	1.02	0.69
0.60	9.58	6.34	1.03	0.68
0.70	11.4	7.70	1.06	0.71

A, B: [PDS] = 0.015 mol l^{-1}, HCl = 1.00 M.
A: Wt. of Nylon6 = 0.30 g, B: Wt. of PET fibre = 0.30 g.

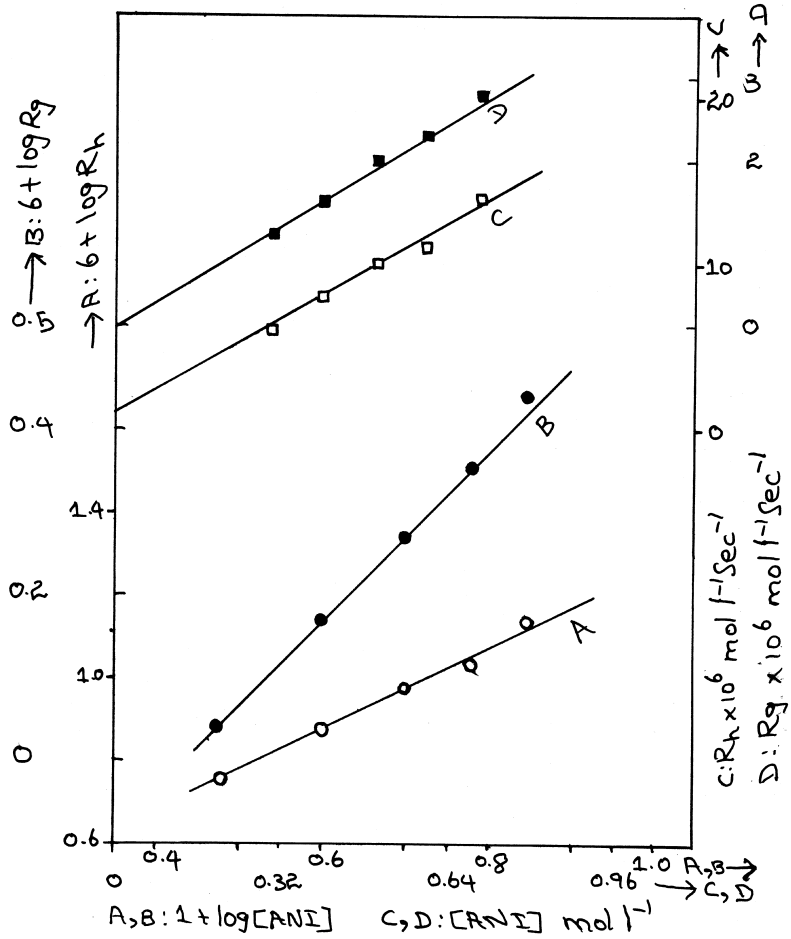

FIGURE 2 Effect of [ANI] on R_h and R_g [PDS] = 0.015 mol l^{-1}, Weight of PET fibre = 0.30 g, [HCI] = 1.00 M.

log R$_h$ *Vs.* log[PDS] (Fig. 3A) and log R$_g$ *Vs.* log[PDS] (Fig. 3B) were drawn and found to be straight lines with slope of unity. This confirms the first order dependence of both R$_h$ and R$_g$ on [PDS]. It was further confirmed by plotting R$_h$ *Vs.* [PDS] (Fig. 3C) and R$_g$ *Vs.* [PDS] (Fig. 3D). The increase in R$_h$ and R$_g$ can be explained as follows: On increasing the PDS concentration, more and more

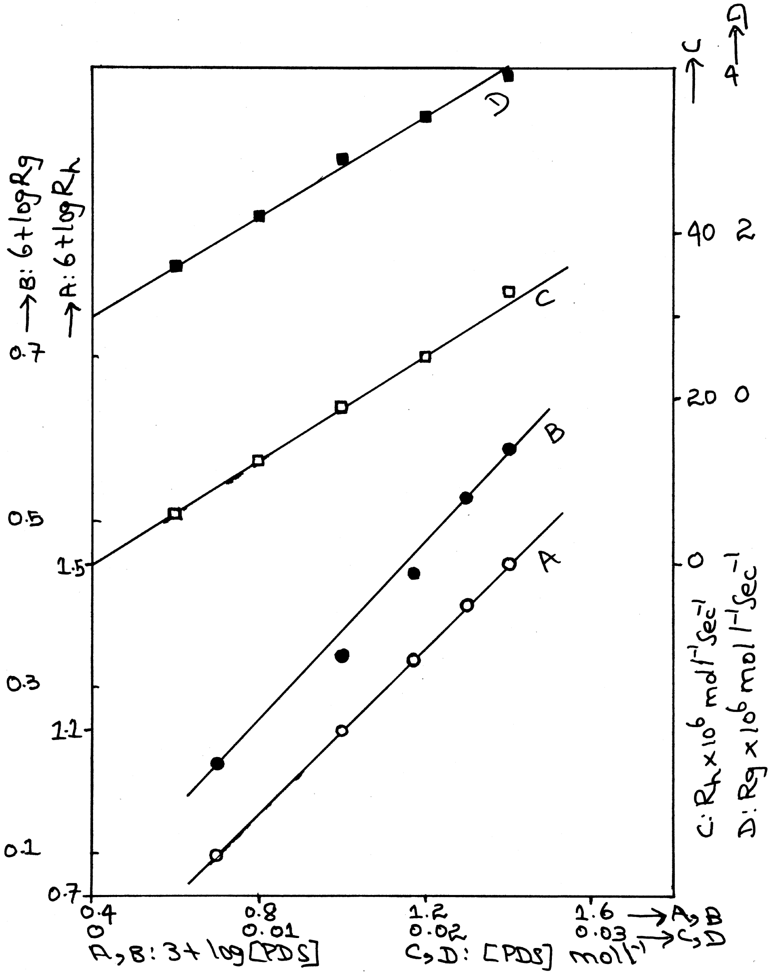

FIGURE 3 Effect of [PDS] on R$_h$ and R$_g$ [ANI] = 0.50 mol l^{-1}, Weight of Nylon6 fibre = 0.30 g, [HCl] = 1.00 M.

free radicals will form. These radicals can interact with the fibre matrix to form macroradicals which lead to graft copolymerization. The free radicals can also react with the monomer to form monomer radical cations and thus form the homopolymer, PANI. The % grafting and % efficiency values reveal the same trend (Tab. II).

The same plots were also made for PET system (Fig. 4). Once again we found first order dependency of R_h and R_g on [PDS].

3.3. Effect of (Amount of PET or Nylon6 Fibre) on R_h and Graft Parameters

The amounts of Nylon6 and PET fibres were varied from 0.20 to 0.45 g while keeping other experimental conditions constant. Both R_h and R_g showed an increasing trend. It was found that the Nylon6 fibre system has higher value of R_h and R_g than PET system. On increasing the amount of fibre, the amount of macroradicals greatly increased. These active sites enhance both homopolymerization and graft copolymerization through auto acceleration effect.

In an attempt to quantify the order dependencies for Nylon6 fibre system, plots of log R_h *Vs.* log(amount of Nylon6 fibre) (Fig. 5A) and log R_g *Vs.* log(amount of Nylon6 fibre) (Fig. 5B) were made and the slope values were found to be close to unity indicating first order dependence of R_h and R_g on (amount of Nylon6 fibre). It was further checked by plotting R_h *Vs.* (amount of Nylon6 fibre) (Fig. 5C) and R_g *Vs.* (amount of Nylon6 fibre) (Fig. 5D). These plots were found to be linear and passing through the origin. These linear plots support the

TABLE II Effect of [PDS] on % grafting and % efficiency

[PDS]	*% grafting*		*% efficiency*	
mol l^{-1}	*A*	*B*	*A*	*B*
0.005	4.50	3.10	0.57	0.40
0.010	6.07	3.66	0.78	0.47
0.015	7.83	5.46	1.01	0.70
0.020	9.63	7.24	1.24	0.93
0.025	10.9	9.11	1.41	1.17

A, B: [ANI] = 0.50 mol l^{-1}, HCl = 1.00 M.
A: Wt. of Nylon6 or PET fibre = 0.30 g, B: Wt. of PET fibre = 0.30 g.

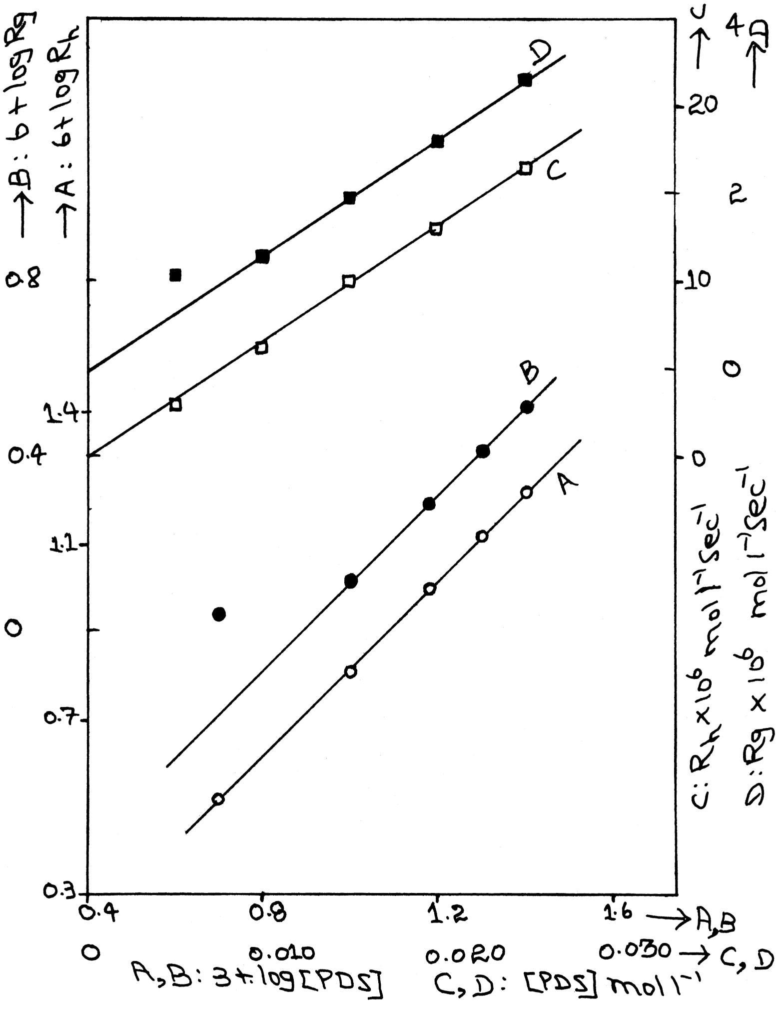

FIGURE 4 Effect of [PDS] on R_h and R_g [ANI] $= 0.50\,\mathrm{mol\,l^{-1}}$, Weight of PET fibre = 0.30 g, [HCI] = 1.00 M.

first order dependence of R_h and R_g on backbone amount. Table III showed the % grafting and % efficiency values.

Similar plots were made for PET fibre system also (Fig. 6). Figures 6A and B show the first order dependence of R_h and R_g on (amount of PET fibre).

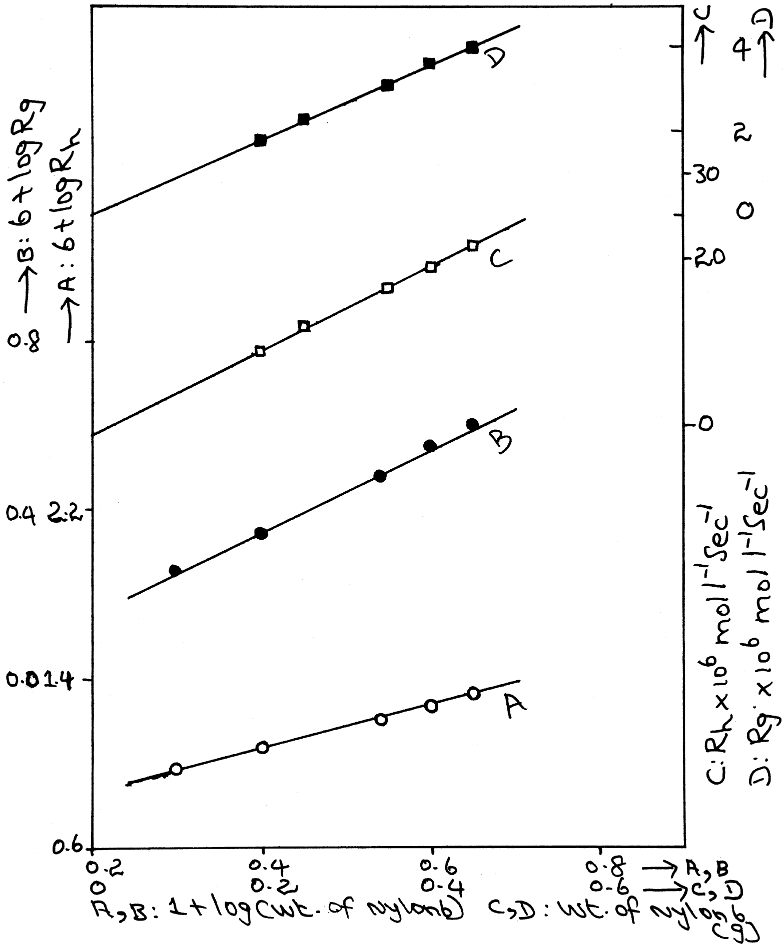

FIGURE 5 Effect of (amount of Nylon6 fibre) on R_h and R_g [ANI] = 0.50 mol l^{-1}, [PDS] = 0.015 mol l^{-1}. [HCl] = 1.00 M.

Gregory [27] and co-workers studied the effect of added fibre on the chemical polymerization of aniline in the presence and absence of PET fibre. No correlation was tried to relate the changes in the rate of homopolymerization in that study. In the electrochemical polymerization of anilines, Wei *et al.* [28] proposed an auto acceleration effect by the electrode surface in an attempt to explain the changes in the induction time during the polymerization. A kinetic equation was

TABLE III Effect of (amount of PET or Nylon6 fibre) on % grafting and % efficiency

(*Amount of fibre*) (*g*)	% *Grafting*		% *Efficiency*	
*PET or Nylon*6	*A*	*B*	*A*	*B*
0.20	7.67	6.29	0.65	0.54
0.25	7.60	6.17	0.82	0.66
0.35	7.42	6.00	1.12	0.64
0.40	7.54	6.10	1.30	1.05
0.45	7.49	5.96	1.45	1.15

A, B: [ANI] = 0.30 mol l^{-1}, HCl = 1.00 M, [PDS] = 0.01 mol l^{-1}.
A: Nylon6 fibre, B: PET fibre.

proposed consisting of two components:

$$R_p = k[M] + k'[M][P]$$

where k is the rate constant for the formation of PANI on a bare Pt electrode surface, k' is rate constant on the PANI coated Pt surface, [M] is concentration of monomer and [P] – amount of polymer formed. Shim and Park [29] 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,

$$R_p(ANI) = k_1[ANI][PDS] + k_2[ANI][TAS]$$

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

In the case of chemical polymerization of aniline a similar model may be considered based on the above kinetic model including the additional effect due to the added oxidizing agent as well as the heterogeneous phase. In the present case, the added fibre for grafting and the formed homopolymer may cause the auto acceleration effect due to the active surface effect.

The plot of R_h(ANI) *Vs*. [ANI] (Fig. 1C) was found to be a straight line with a definite intercept, R_h(ANI) *Vs*. [PDS] (Fig. 2C) is a straight line passing through the origin, and R_h(ANI) *Vs*. (amount of Nylon6 fibre) (Fig. 3C) is a straight line passing through the origin. These three combined facts necessiate the modification of the above

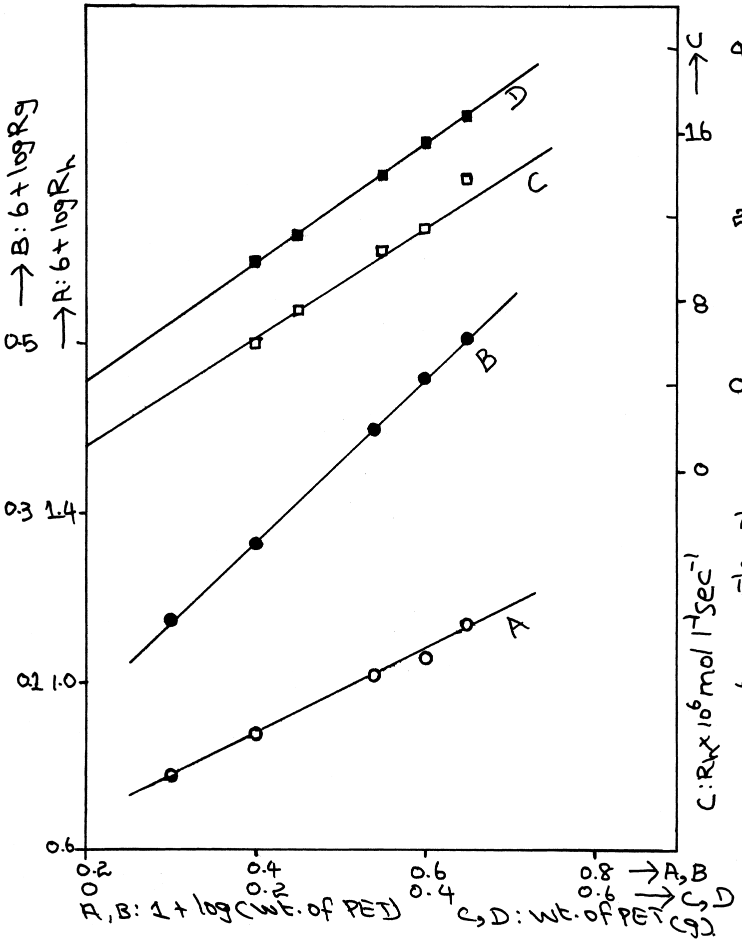

FIGURE 6 Effect of (amount of PET fibre) on R_h and R_g $[ANI] = 0.50\,mol\,l^{-1}$ $[PDS] = 0.015\,mol\,l^{-1}$, $[HCl] = 1.00\,M$.

equations as,

$$R_h(ANI) = k_{1h}[ANI][PDS](\text{amount of Nylon6 fibre}) + k_{2h}[ANI][TAS] + k_{3h} \tag{1}$$

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 the additional effects of available surface and probable change due to grafting. [TAS] – total available surface (include homopolymer(weight basis) and grafted one). The value of k_{3h} can be taken from the intercept of the plot of R_h *Vs*. [ANI] (Fig. 1C).

The rate of grafting also has the same trend (first order dependences of R_g on [ANI], [PDS] and (amount of Nylon6 fibre)). Hence the following equation is proposed for R_g as,

$$R_g(\mathrm{ANI}) = k_{1g}[\mathrm{ANI}][\mathrm{PDS}](\text{amount of Nylon6 fibre}) + k_{2g}[\mathrm{ANI}][\mathrm{TAS}] + k_{3g} \tag{2}$$

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 the additional effects of available surface and probable change due to grafting.

Gregory *et al.* [27] determined the k_{1h} value as $0.0008\,\mathrm{min}^{-1}$. For the present case, PDS initiated graft copolymerization of ANI onto Nylon6 fibre in aqueous HCI medium, k_{1h} and k_{1g} values are determined from the slope of the plots R_h *Vs*. [ANI](Fig. 1C) and R_g *Vs*. [ANI] (Fig. 1D) using Eqs. (1) and (2) as $9.62 \times 10^{-3}\,\mathrm{g}^{-1}\,\mathrm{m}^{-1}\,\mathrm{sec}^{-1}$ and $1.23 \times 10^{-3}\,\mathrm{g}^{-1}\mathrm{m}^{-1}\mathrm{sec}^{-1}$ respectively. This value is far higher than that of the simple homopolymerization rate constant and auguments the auto acceleration effect in homopolymerization by TAS and grafting. The value of k_{3h} was found to be $0.80 \times 10^{-7}\,\mathrm{mol\,l}^{-1}\,\mathrm{sec}^{-1}$ where as the value of k_{3g} was found to be nil. The above rate constant values indicate that k_{1h} is greater than k_{1g}.

In the case of PET fibre, the rate constants were determined by modifying Eqs. (1) and (2) as

$$R_h(\mathrm{ANI}) = k_{1h}[\mathrm{ANI}][\mathrm{PDS}](\text{amount of PET fibre}) + k_{2h}[\mathrm{ANI}][\mathrm{TAS}] + k_{3h} \tag{3}$$

$$R_g(\mathrm{ANI}) = k_{1g}[\mathrm{ANI}][\mathrm{PDS}](\text{amount of PET fibre}) + k_{2g}[\mathrm{ANI}][\mathrm{TAS}] + k_{3g} \tag{4}$$

The k_{1h} and k_{1g} values were found to be $6.33 \times 10^{-3}\,\mathrm{g}^{-1}\,\mathrm{m}^{-1}\,\mathrm{sec}^{-1}$ and $1.17 \times 10^{-3}\,\mathrm{g}^{-1}\,\mathrm{m}^{-1}\,\mathrm{sec}^{-1}$ respectively. Here the k_{3h} value was found to be $0.50 \times 10^{-6}\,\mathrm{mol\,l}^{-1}\,\mathrm{sec}^{-1}$ where as the k_{3g} value was found to be nil. In the case of PET system the rate of homopolymerzation was found to be higher than that of the rate of grafting.

The k_{1h}, k_{1g} and k_{3h} rate constant values of Nylon6 system are higher than PET case. This confirms that Nylon6 fibre is better grafted than PET fibre.

4. WEIGHT LOSS STUDY

The weight loss study of Nylon6-g-PANI is given in Table IV. The amount of % weight loss depends on various factors like the nature of monomer, initiator and fibre. Generally PDS favors the formation of homopolymer than graft copolymer. The maximum % weight loss was observed from the physisorbed homopolymers on the Nylon6 fibre surface.

The same study was carried out for PET-g-PANI fibre also (Tab. IV). Here also we observed almost the same % weight loss on each process. These results are in accord with our earlier publications [10, 12–14].

5. INFRARED SPECTROSCOPY

The FTIR spectrum of Nylon6-g-PANI is given in Figure 7. The peak at 1506 cm^{-1} indicates the ring stretch of benzene ring. The N-H

TABLE IV Weight loss study

Process	*% Wt. loss (approximately)*		
(*Treatment with*)	*A*	*B*	*Reason*
1. Acetone	2	2	Solubility of physisorbed monomer or dimer in acetone
2. NMP	3	3	Solubility of physisorbed HCl doped PANI
3. Ammonia	12–15	15	Removal of HCl from both physisorbed and grafted PANI
4. NMP	10–12	12	Solubility of all the dedoped physisorbed PANI

A: Nylon6-PDS-PANI.
B: PET-PDS-PANI.

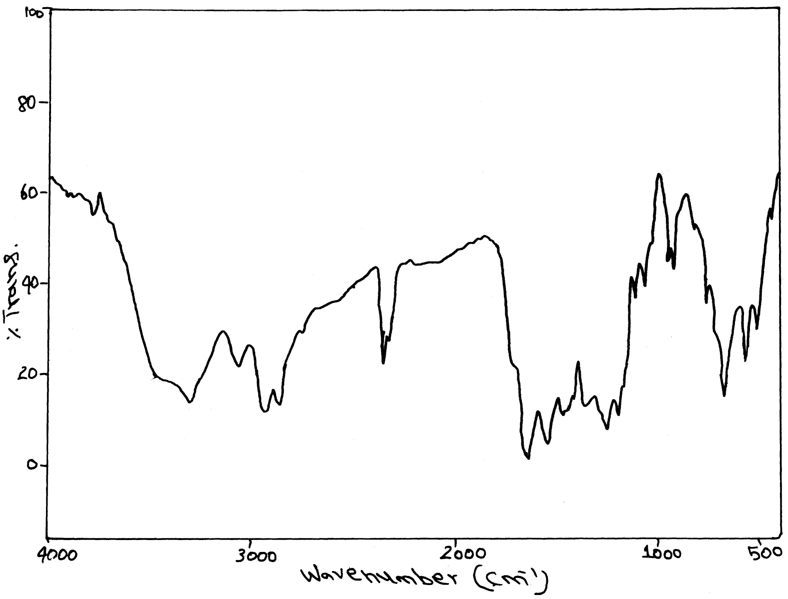

FIGURE 7 FTIR spectroscopy of Nylon6-g-PANI fibre.

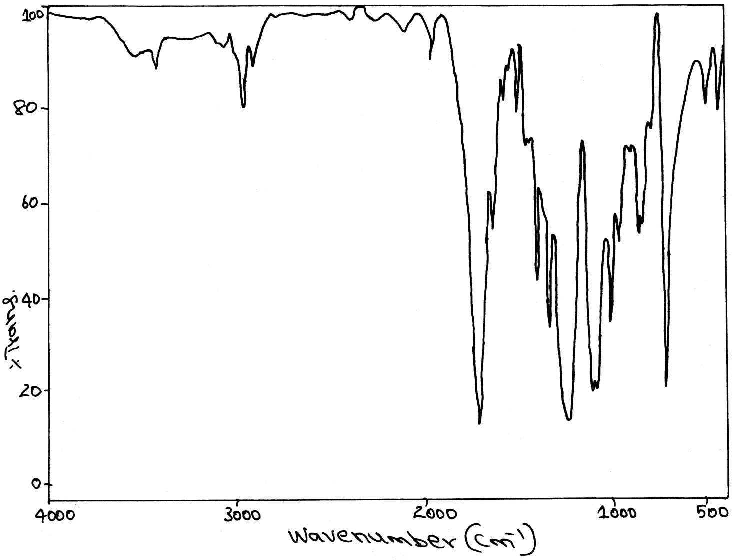

FIGURE 8 FTIR spectroscopy of PET-g-PANI fibre.

stretch of aromatic amine can be seen by the peak at 3300 cm^{-1}. The presence of chloride ion and p-linked PANI are evident by the peaks at 1251 and 846 cm^{-1} respectively. The peaks corresponding to C=N stretches appear at 1636, 1506 and 1344 cm^{-1}. The peak at 793 cm^{-1} can be assigned for C—N out of plane bending vibration of the para substituted benzene ring. The other peaks present in the figures are due to the backbone fibre.

The FTIR spectrum of PET-g-PANI is also shown in Figure 8. The above said peaks for PANI appear here too.

6. DIFFERENTIAL THERMAL ANALYSIS

DTA was recorded for PET-g-PANI fibre (Fig. 9B). It shows three endothermic peaks (162, 254 and 428°C) and one exothermic peak (at 613°C). The peak at 613°C indicates the thermal decomposition of PANI side chain. The increase in thermal stability of PANI may be due to the backbone PET fibre and crosslinks of PANI side chains. This result coincides with Kitani's report [30].

For the sake of comparison the DTA of PET fibre is also given in Figure 9A. Here we found two endothermic peaks (at 254 and 426°C). This indicates that the thermal stability of PET fibre was retained on grafting with PANI.

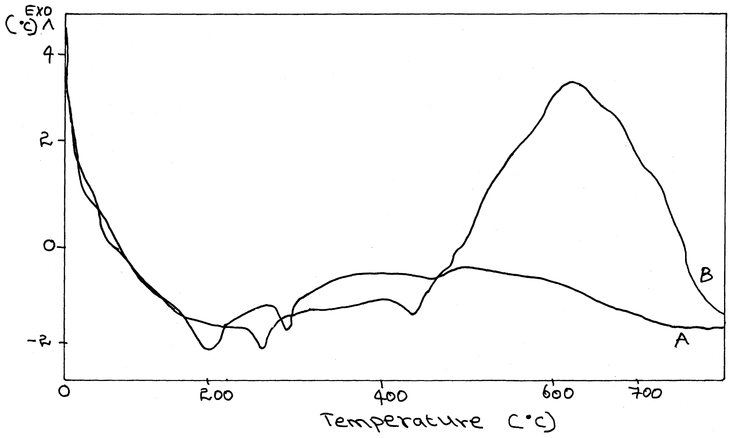

FIGURE 9 A: DTA of pure PET fibre, B: DTA of PET-g-PANI fibre.

7. CONDUCTIVITY MEASUREMENTS

The conductivity value of PANI grafted Nylon6 and PET fibre increased with % grafting (Tab. V). The conductivity value is higher for Nylon6 -g-PANI system than PET-g-PANI case. This confirms the better grafting nature of Nylon6 fibre.

8. MECHANISM

A probable mechanism is proposed here to explain the experimental results obtained. The mechanism suggested for graft copolymerization of PANI onto Nylon6 fibre in this paper is based on the mechanism proposed by two research teams. Wei and co-workers [28] explains the formation of homopolymer *via* radical cation and Bhadani *et al.* [31] proposed a mechanism for the graft copolymerization of PANI onto various natural backbones by electrochemical method. They also explained that the graft copolymerization proceeds through oligomerization. Taking the above two mechanisms as a base, a probable mechanism is suggested here to explain the modification of Nylon6 fibre through chemical grafting of PANI.

Probable mechanism for PDS initiated graft copolymerization of ANI onto Nylon6 fibre is as follows:

8.1. Primary Reactions

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

$$\mathrm{PDS} \longrightarrow 2\mathrm{SO}_4^{\dot{-}}(\mathrm{R}^{\cdot})$$

$$\mathrm{R}^{\cdot} + \mathrm{Nylon6} \longrightarrow \mathrm{Nylon6}^{\cdot} + \mathrm{Products}$$

$$\mathrm{R}^{\cdot} + \mathrm{ANI} \longrightarrow \mathrm{ANI}^{\dot{+}} + \mathrm{Products}$$

TABLE V Conductivity measurements

Polymer	*% Grafting*	*Conductivity Ohm^{-1} cm^{-1}*
Nylon6	–	1.03 G
Nylon6-g-PANI	4.69	5.21 K
	11.4	9.06 K
PET	–	0.88 G
PET-g-PANI	3.10	3.49 M
	7.70	5.98 M

8.2. Homopolymerization

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

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

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

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

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

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

$$\mathrm{Oligomer}^{+\cdot} + \mathrm{Oligomer}^{+\cdot} \longrightarrow \mathrm{PANI}\ (\mathrm{Homopolymer})$$

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

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

$$\mathrm{PANI}^{+\cdot} + \mathrm{ANI} \longrightarrow \mathrm{ANI}^{+\cdot} + \mathrm{PANI}\ (\text{auto acceleration effect})$$

$$\mathrm{PANI}^{+\cdot} + \mathrm{dimer} \longrightarrow \mathrm{dimer}^{+\cdot} + \mathrm{PANI}$$

$$\mathrm{PANI}^{+\cdot} + \mathrm{Oligomer} \longrightarrow \mathrm{Oligomer}^{+\cdot} + \mathrm{PANI}$$

8.3. Graft Copolymerization

$$\mathrm{ANI} + \mathrm{Nylon6}^{\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{ANI} + 2\mathrm{H}^{+}$$

$$\mathrm{Nylon6} - \mathrm{ANI} + \mathrm{PDS} \longrightarrow \mathrm{Nylon6} - \mathrm{ANI}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{ANI} + \mathrm{R}^{\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{ANI}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{ANI}^{+\cdot} + \mathrm{ANI}^{+\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{dimer} + 2\mathrm{H}^{+}$$

$$\mathrm{Nylon6} - \mathrm{dimer} + \mathrm{PDS} \longrightarrow \mathrm{Nylon6} - \mathrm{dimer}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{dimer} + \mathrm{R}^{\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{dimer}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{dimer}^{+\cdot} + \mathrm{ANI}^{+\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{Oligomer} + 2\mathrm{H}^{+}$$

$$\mathrm{Nylon6} - \mathrm{Oligomer} + \mathrm{PDS} \longrightarrow \mathrm{Nylon6} - \mathrm{Oligomer}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{Oligomer} + \mathrm{R}^{\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{Oligomer}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{Oligomer}^{+\cdot} + \mathrm{Oligomer}^{+\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{g} - \mathrm{PANI}\ (\text{Graft copolymer})$$

$$\mathrm{Nylon6} - \mathrm{PANI} + \mathrm{R}^{\cdot} \longrightarrow \mathrm{Nylon6} - \mathrm{PANI}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{PANI} + \mathrm{PDS} \longrightarrow \mathrm{Nylon6} - \mathrm{PANI}^{+\cdot} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{PANI}^{+\cdot} + \mathrm{ANI} \longrightarrow \mathrm{ANI}^{+\cdot} + \mathrm{Nylon6} - \mathrm{PANI}$$

$$\mathrm{Nylon6} - \mathrm{PANI}^{+\cdot} + \mathrm{dimer} \longrightarrow \mathrm{dimer}^{+\cdot} + \mathrm{Nylon6} - \mathrm{PANI}$$

$$\mathrm{Nylon6} - \mathrm{PANI}^{+\cdot} + \mathrm{Oligomer} \longrightarrow \mathrm{Oligomer}^{+\cdot} + \mathrm{Nylon6} - \mathrm{PANI}$$

$$\mathrm{Nylon6} + \mathrm{ANI} \longrightarrow \mathrm{ANI}^{\dot{+}} + \mathrm{Products}$$

$$\mathrm{Nylon6} - \mathrm{ANI} + \mathrm{ANI} \longrightarrow \mathrm{Nylon6} - \mathrm{dimer} + 2\mathrm{H}^{+}$$

$$\mathrm{ANI}^{\dot{+}} + \mathrm{dimer} \longrightarrow \mathrm{dimer}^{\dot{+}} + \mathrm{Product}$$

$$\mathrm{ANI}^{\dot{+}} + \mathrm{Oligomer} \longrightarrow \mathrm{Oligomer}^{\dot{+}} + \mathrm{Products}$$

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

This mechanism explains the experimental results obtained [12, 15, 16]. Probable mechanism for PET system is similar to that of Nylon6 system.

9. CONCLUSION

From the above kinetic study the following conclusions were made. 1) Graft copolymerization occured with simultaneous homopolymer formation. 2) Both R_h and R_g showed first order dependence on [ANI], [PDS] and (amount of Nylon6 or PET fibre). 3) DTA, FTIR spectral study, weight loss study and conductivity measurements confirmed the chemical grafting of aniline onto Nylon6 or PET fibres. 4) The mechanism is consistent with the experimental results obtained.

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