

Chemical Grafting of Polyaniline onto Nylon66 Fiber in Different Media

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ABSTRACT: Graft copolymerization of polyaniline (PANI) onto nylon 66 fiber was carried out in two different media, hydrochloric acid and *p*-toluene sulfonic acid (PTSA), using peroxodisulfate (PDS) as an initiator. Percentage grafting, percentage efficiency, and rate of grafting were determined. The grafting of PANI onto nylon 66 was confirmed through FTIR spectroscopy, cyclic voltammetry (CV), weight-loss study, and conductivity measurement. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1283–1296, 2001

Key words: grafting; PANI; nylon66; FTIR; cyclic voltammetry

INTRODUCTION

Chemical modification of conventional polymers, both natural and synthetic, can provide a potential route for altering their physical and chemical properties significantly. Graft copolymerization of vinyl monomers onto PET,¹ nylon6,² and jute³ fiber have been the subject of extensive studies. We know that nylon66 has poor dyeability and electrically insulating characteristics. Conducting polymers can be grafted onto nylon6 fiber and such studies have recently become an attractive field due to their wide applications in various electrical and electronic devices.^{4–6} Recently also, conducting polymers have been grafted with conventional polymers which are used in the fields of EMI shielding,⁷ gas sensors,⁸ and batteries.⁹

Peroxydisulfate (PDS)-initiated copolymerization of aniline onto PET fiber was reported.¹⁰ Polyaniline (PANI) was grafted onto wool fiber and the conductivity values were reported.¹¹ Nylon6 fiber was made into a conducting one by the

grafting of PANI.¹² Graft copolymerization of polythiophene onto poly(methyl methacrylate) was reported by Sunke et al.¹³ Tzou and Gregory¹⁴ published kinetic results on the chemical grafting of PANI onto nylon6 fiber. Li et al.¹⁵ grafted PANI onto the poly(amino styrene) backbone and they reported the conductivity values. Electro-initiated graft copolymerization of aniline onto various natural fibers was reported by Bhadani and coworkers.¹⁶ Poly(*o*-toluidine) was grafted onto nylon6 fiber and chemical grafting was confirmed by cyclic voltammetric results.¹⁷ The present investigation reports the kinetics of graft copolymerization of PANI onto nylon66 fiber and the grafting was confirmed through UV-visible spectroscopy, cyclic voltammetry (CV), and conductivity studies.

EXPERIMENTAL

Materials Used

Aniline (Fisher, AR) was distilled under a vacuum prior to use. PDS (CDH, AR, India), HCl (Fischer, AR, India), *p*-toluene sulfonic acid

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(PSTA; CDH, AR), *N*-methyl pyrrolidone (NMP; SRL, AR), acetone (Ranbaxy, AR), and other chemicals were used as such. Nylon66 fiber (a gift sample from M/S Madura Coats, Madurai) was used after 24 h Soxhlet extraction with acetone and drying at room temperature.

Preparation of Graft Copolymers

A graft copolymerization study was carried out as given below: Nylon66 (W_1 g) was immersed in a definite volume of 1.0M HCl or 1.0M PSTA in a polymer tube and thermostated for 30 min. The solution was deaerated by passing pure nitrogen gas for 30 min. A required amount of the monomer (aniline) was added and deaerated for another 15 min. The polymerization was initiated by the addition of calculated volumes of preaerated PDS (using standard solutions). The time of adding the oxidizing agent, PDS, 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 an added oxidant). This was ascertained by a separate experiment. The reaction mixture was found to turn green in color and a 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 nylon66 fiber (now green in color) and the homopolymer, PANI, were filtered from the reaction mixture using a G4 sintered crucible and washed well with 1.00M HCl or 1.00M PTSA several times. This was then treated with aqueous ammonia for several hours and the blue-colored powder with the fiber (blue color) was dried at 80°C for 4 h and weighed to get a constant weight. This gives the total weight of the grafted polymer with the homopolymer (W_2 g). The mixture of the grafted nylon66 along with the homopolymer, PANI, was then Soxhlet-extracted with NMP for

24 h to separate the homopolymer. The extraction was repeated until the separation of the homopolymer from the grafted sample was complete and this was ascertained by drying the fiber in a vacuum to get a constant weight (W_3 g). 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. All of the graft copolymerization study was carried out at 45°C for a polymerization time of 30 min.

The following trial experiments ensured that the weight changes noted in the present work were only due to grafting and homopolymerization. In one of the trial experiments, the fiber (same amount as maintained in the graft copolymerization) was kept in a medium containing an oxidant alone for the polymerization time at 45°C. In another experiment, the fiber (same amount as maintained in the graft copolymerization) was treated with aqueous ammonia for the same period used to treat the grafted fiber. Also, the fiber (same amount as maintained in the graft copolymerization) was kept in Soxhlet extraction condition with NMP for 24 h. In all the cases, after drying to get a constant weight, no difference in weight was noticed between the parent fiber and the fiber after treatment. These studies clearly demonstrated that the weight changes noticed were only due to grafting and homopolymerization.

Rate Measurements

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

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

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

Table I Effect of [ANI], [PDS], and Weight of Fiber on Percent Grafting and Percent Efficiency

[ANI] ^a (mol L ⁻¹)	Percent Grafting	Percent Efficiency	[PDS] ^b (mol L ⁻¹)	Percent Grafting	Percent Efficiency	Weight of Fiber ^c (g)	Percent Grafting	Percent Efficiency
0.20	9.4	2.02	0.005	7.0	1.00	0.10	13.5	0.96
0.30	11.1	1.58	0.010	12.6	1.81	0.15	10.9	1.17
0.40	12.6	1.35	0.015	14.9	2.14	0.25	11.9	2.13
0.50	15.1	1.29	0.020	16.8	2.42	0.30	14.7	3.17
0.60	18.4	1.31	0.025	21.2	3.03	0.35	15.2	3.81

^a [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; temperature = 45°C; [HCl] = 1.00 mol L⁻¹.

^b [ANI] = 0.30 mol L⁻¹; weight of nylon66 = 0.20 g; temperature = 45°C; [HCl] = 1.00 mol L⁻¹.

^c [ANI] = 0.30 mol L⁻¹; [PDS] = 0.010 mol L⁻¹; temperature = 45°C; [HCl] = 1.00 mol L⁻¹.

Table II Effect of [ANI], [PDS], and Weight of Fiber on Percent Grafting and Percent Efficiency

[ANI] ^a (mol L ⁻¹)	Percent Grafting	Percent Efficiency	[PDS] ^b (mol L ⁻¹)	Percent Grafting	Percent Efficiency	Weight of Fiber ^c (g)	Percent Grafting	Percent Efficiency
0.20	13.9	2.98	0.005	15.0	2.15	0.10	32.7	2.34
0.30	19.1	2.73	0.010	19.1	2.73	0.15	24.0	2.57
0.40	21.8	2.34	0.015	21.2	3.03	0.25	17.4	3.11
0.50	25.1	2.16	0.020	24.6	3.51	0.30	17.3	3.73
0.60	26.9	1.93	0.025	28.2	4.03	0.35	16.8	4.22

^a [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; temperature = 45°C; [PTSA] = 1.00 mol L⁻¹.

^b [ANI] = 0.30 mol L⁻¹; weight of nylon66 = 0.20 g; temperature = 45°C; [PTSA] = 1.00 mol L⁻¹.

^c [ANI] = 0.30 mol L⁻¹; [PDS] = 0.010 mol L⁻¹; temperature = 45°C; [PTSA] = 1.00 mol L⁻¹.

where W_4 is the weight of the monomer,

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

where $W_2 - W_3$ is the weight of the grafted polymer; V , the total volume of the reaction mixture; t , the reaction time; and M , the molecular weight of the monomer used.

Simultaneous Homopolymerization

The rate of grafting was determined as follows:

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

where $W_2 - W_3$ is the weight of the homopolymer formed.

Isolation of the Grafted Fiber From Homopolymer

The visible spectrum was recorded using a Shimadzu UV 2401 PC Model UV-visible spectrophotometer for the analysis of the PANI content at various Soxhlet extraction time intervals during the isolation of the grafted fibers. PANI-grafted nylon66 fiber was dedoped by treating it with a 0.5N aqueous solution of ammonia for 4 h. The fiber was removed from the ammonia solution and dried at 60°C for 4 h and treated with 30 mL of NMP (solvent) with vigorous stirring. After a definite interval of time, the Soxhlet extract was subjected to UV-visible spectra analysis. The visible spectrum was recorded for the Soxhlet extract for different time intervals.

FTIR Spectroscopy

The FTIR spectrum was recorded for the nylon66-g-PANI prepared in HCl and PTSA medium using

a Bruker FTIR Equinox55 Model instrument with KBr. For the sake of comparison, the FTIR spectrum of PANI in HCl and PTSA were also recorded.

Cyclic Voltammetric Study

The PANI-grafted nylon66 fiber (HCl- and PTSA-doped, green-colored) was allowed to stand overnight in a 0.5N aqueous ammonia solution (the fiber turns blue in color) and the fiber was then washed well with acetone two to three times to remove any adhering materials which were ab-

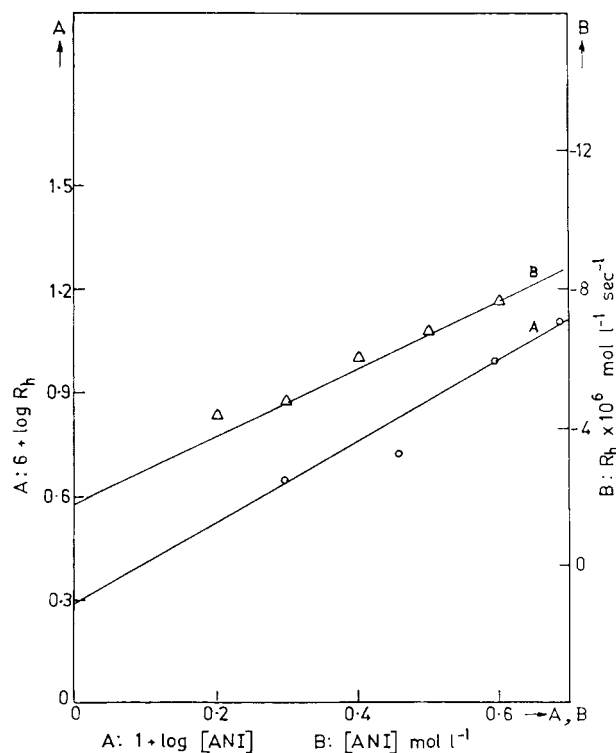


Figure 1 (A,B) [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; HCl = 1M; temperature = 45°C.

sorbed onto the surface of the fiber. The dried fiber was immersed in formic acid and made into a paste. The paste was dip-coated onto a Pt microworking electrode (surface area of $9.50 \times 10^{-2} \text{ cm}^2$). Cyclic voltammograms were recorded (using a BAS 100A electrochemical analyzer) for the nylon66-g-PANI by cycling the potential in the range of 0.00–0.90 V using Ag/AgCl as a reference electrode.

Conductivity Measurements

The conductivity of both grafted and parent fiber samples were determined by a Keithley 617 programmable electrometer instrument. A 1-cm length of the fiber was taken and its two ends were fixed at the two poles of the instrument and current was passed. The display meter directly showed the conductivity value.

RESULTS AND DISCUSSION

Effect of Aniline Concentration on R_h and Grafted Parameters

Aniline concentration was varied in the range of 0.20–0.60 mol L⁻¹ while keeping other experi-

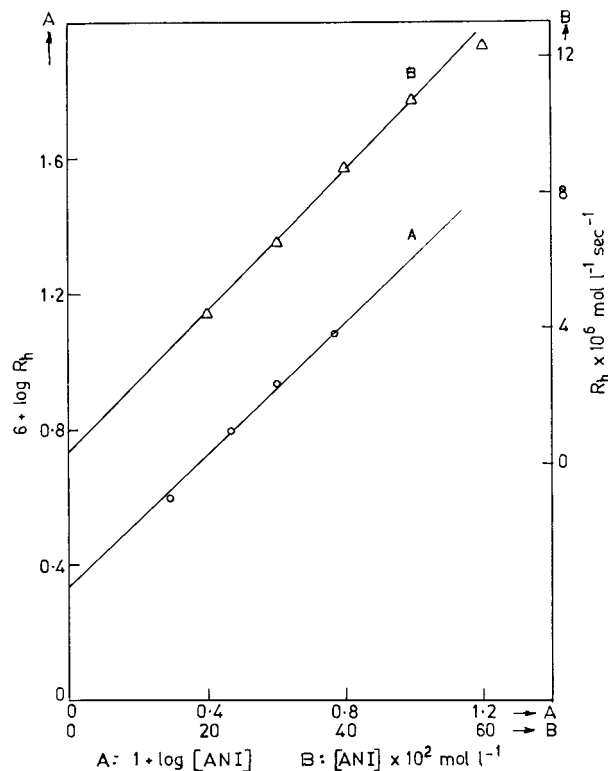


Figure 2 (A,B) [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; PTSA = 1M; temperature = 45°C.

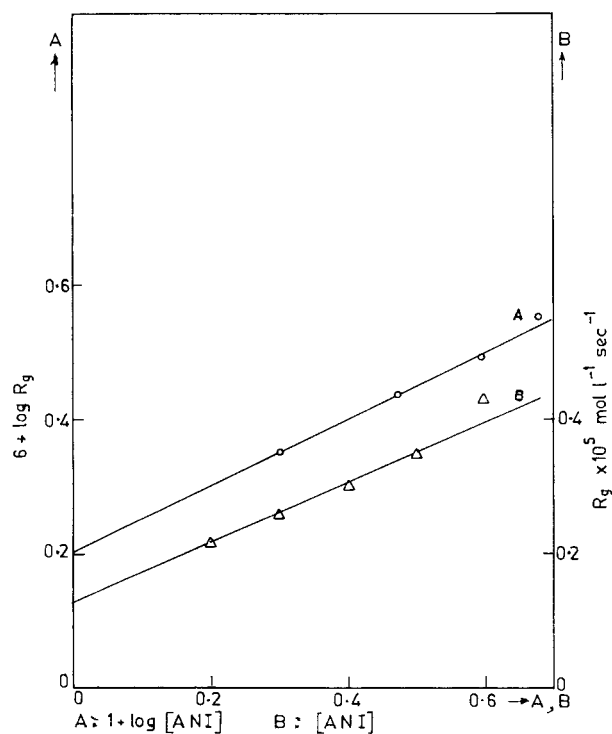


Figure 3 (A,B) [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; HCl = 1M; temperature = 45°C.

mental conditions constant. It is interesting to note that both R_h and R_g increase with increase in [ANI]. The R_h value was found to be lower with the PTSA medium than in the HCl medium in comparative conditions. The R_g value was found to be higher in all the above experimental conditions with the PTSA medium than in the HCl medium. This indicates that aniline could be better grafted onto nylon66 fiber using PTSA as a reaction medium. The percent grafting and percent efficiency values also reveal the same relationship (Tables I and II).

To determine the order dependence of [ANI] on R_h and R_g , plots of $\log R_h$ versus $\log[\text{ANI}]$ [Figs. 1(A) and 2(A)] and $\log R_g$ versus $\log[\text{ANI}]$ [Figs. 3(A) and 4(A)] were drawn and found to be straight lines with unit slopes, indicating the first-order dependence of R_h and R_g on [ANI]. Further, the order dependence was confirmed by plotting R_h versus [ANI] [Fig. 1(B) and 2(B)] and R_g versus [ANI] [Fig. 3(B) and 4(B)]. These plots were found to be linear. The plots of R_h versus [ANI] [Fig. 1(B) and 2(B)] give the intercept value.

Effect of Initiator Concentration on R_h and Graft Parameters

The [PDS] was varied between 0.005 to 0.025 mol L⁻¹ while keeping other experimental conditions

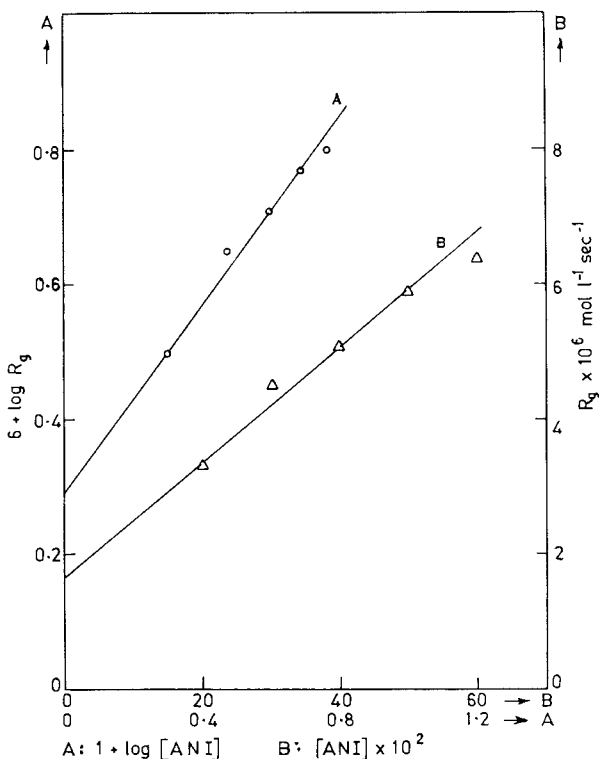


Figure 4 (A,B) [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; PTSA = 1M; temperature = 45°C.

constant. Here, again, the value of R_h was found to be higher with the HCl medium than with the PTSA medium. The rate of grafting, percent grafting, and percent efficiency values were found to be higher for the PTSA medium than for the HCl medium. The percent grafting and percent efficiency values are presented in Tables I and II.

The plot of $\log R_h$ versus $\log[\text{PDS}]$ [Fig. 5(A) and 6(A)] and $\log R_g$ versus [PDS] [Figs. 7(A) and 8(A)] were drawn and found to show first-order dependencies for R_h and R_g on [PDS]. This was further confirmed by plotting R_h versus [PDS] [Fig. 5(B) and 6(B)] and R_g versus [PDS] [Fig. 7(B) and 8(B)]. These plots were found to be straight lines and passing through the origin.

Effect of Amount of Fiber on R_h and Graft Parameters

As represented in Tables I and II, the amount of nylon66 fiber was varied between 0.10 to 0.35 g in both studies involving HCl and PTSA as a reaction medium. R_h and R_g show an increasing trend with increase in the amount of fiber in both cases. R_h was found to be higher for the PTSA medium than for the HCl case. The higher values of the

rate of the grafting, percent grafting, and percent efficiency in the PTSA medium also point this out.

The plot of $\log R_h$ versus $\log(\text{weight of nylon66})$ [Figs. 9(A) and 10(A)] and $\log R_g$ versus $\log(\text{weight of nylon66})$ [Fig. 11(A) and 12(A)] were drawn and found to have a first-order dependence of R_h and R_g on the weight of the fiber. The first-order dependence was further confirmed by drawing the plots R_h versus (weight of nylon66) [Fig. 9(B) and 10(B)] and R_g versus (weight of nylon66) [Fig. 11(B) and 12(B)].

Effect of Temperature on R_h and Graft Parameters

It was observed that both R_h and R_g values showed an increase initially to 323 K following by a decrease (in HCl medium). The percent grafting and percent efficiency also show the same trend. The R_h value was found to increase initially up to 323 K and, thereafter, showed a decrease, whereas the R_g value steadily increased with increase in temperature (in the PTSA medium).

The energy of activation (E_a) value was determined from the plot $\log R_h$ versus $1/T$ [Fig. 13(B) and 14(B)] and $\log R_g$ versus $1/T$ [Fig. 13(A) and 14(A)] as 1.50 and 9.15 K cal/mol, respectively (for the HCl medium), whereas for the PTSA medium the activation energy for homopolymerization

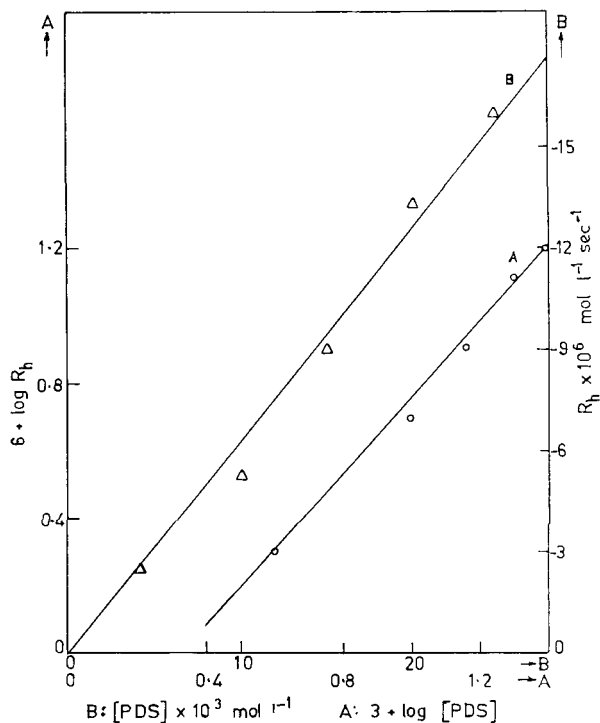


Figure 5 (A,B) [ANI] = 0.30 mol L⁻¹; weight of nylon66 = 0.20 g; HCl = 1M; temperature = 45°C.

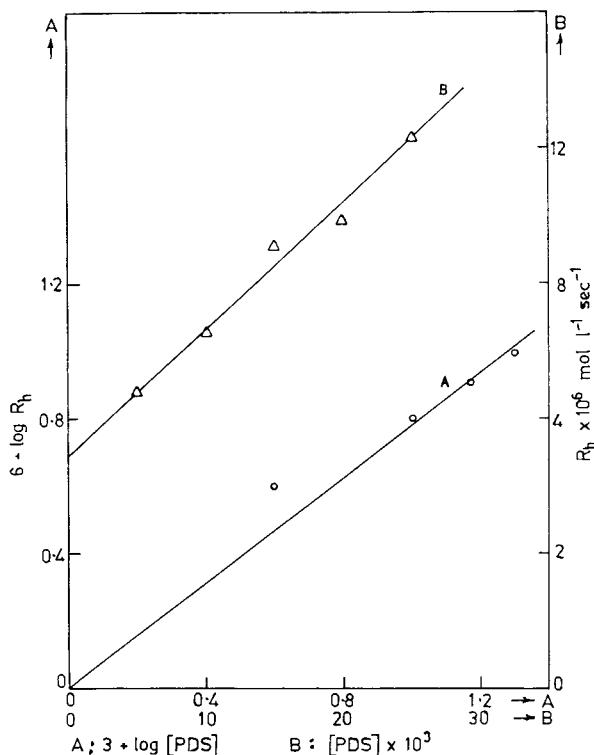


Figure 6 (A,B) $[ANI] = 0.01 \text{ mol L}^{-1}$; weight of nylon66 = 0.20 g; PTSA = 1M; temperature = 45°C.

was determined as 2.5 K cal/mol, and for graft copolymerization, as 2.7 K cal/mol. The decreasing trend of the rate at higher temperature can be visualized as due to the loss of the monomer and also due to the probable side reactions of the initiating reactive species. Such explanations are given to explain the decreasing trends of the rate of polymerization with temperature for the vinyl polymerization.

The effect of added textile fiber on the chemical polymerization of aniline was studied by Tzou and Gregory.¹⁴ In this study, no correlation was tried to find the changes in the rate of homopolymerization with the experimental conditions. However, Wei and coworkers²¹ proposed an autoacceleration effect by the electrode surface in the electrochemical polymerization of aniline and they proposed a kinetic equation as

$$R_p = k[M][+ k'[M][P] \quad (1)$$

where k is the rate constant of formation of PANI on a bare Pt electrode surface, and k' , the rate constant on a PANI-coated Pt electrode surface. Shim et al.²² proposed a kinetic equation for the polymerization of aniline on a bare Pt electrode,

including the autoacceleration effect, and proposed the following type of equation:

$$R_p(ANI) = k_1[ANI][PDS] + k_2[ANI][TAS] \quad (2)$$

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

In the case of chemical polymerization of aniline, a 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 similar rate of homopolymerization dependence can be considered. The rate of PANI was monitored for different $[ANI]$, $[PDS]$ and the amount of the fiber and used to deduce such a relation. In the present study, the added fiber for grafting and the formed homopolymer and the grafted backbone may cause the autoacceleration effect.

The plot of $R_p(ANI)$ versus $[ANI]$ [Figs. 1(B) and 2(B)] is a straight line with a definite intercept, $R_p(ANI)$ versus $[PDS]$ [Figs. 7(B) and 8(B)]

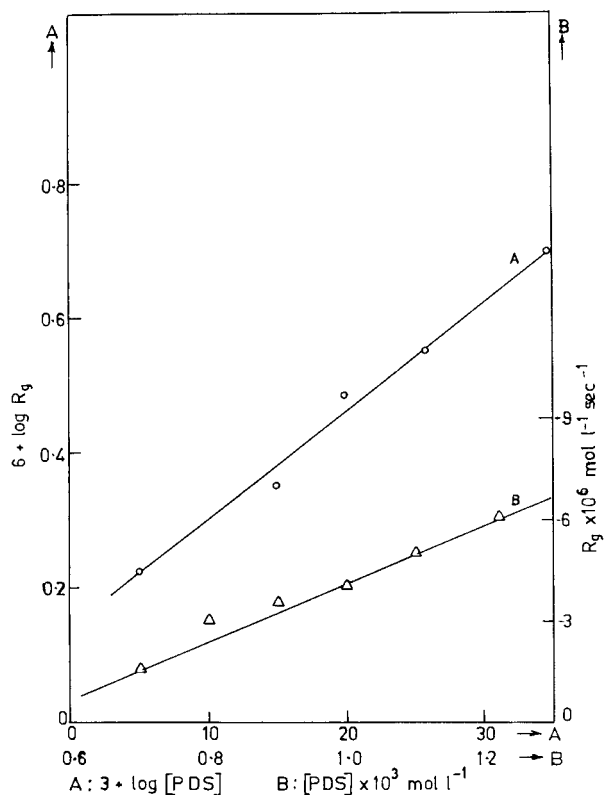


Figure 7 (A,B) $[ANI] = 0.30 \text{ mol L}^{-1}$; weight of nylon66 = 0.20 g; HCl = 1M; temperature = 45°C.

is a straight line and passes through the origin, and R_p (ANI) versus (amount of nylon66) [Figs. 9(B) and 10(B)] is a straight line with a definite intercept. These three combined facts necessitate the modification of eq. (2) as

$$R_h = k_{1h}[\text{ANI}][\text{PDS}] \text{ (amount of nylon66)} \\ + k_{2h}[\text{ANI}][\text{TAS}] + k_{3h} \quad (3)$$

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

The rate of grafting also shows the same trend: first-order dependencies of [ANI], [PDS], and (amount of nylon66). Hence, the following equation is proposed for R_g :

$$R_g = k_{1g}[\text{ANI}][\text{PDS}] \text{ (amount of nylon66)} \\ + k_{2g}\{\text{ANI}\}\{\text{TAS}\} + k_{3g} \quad (4)$$

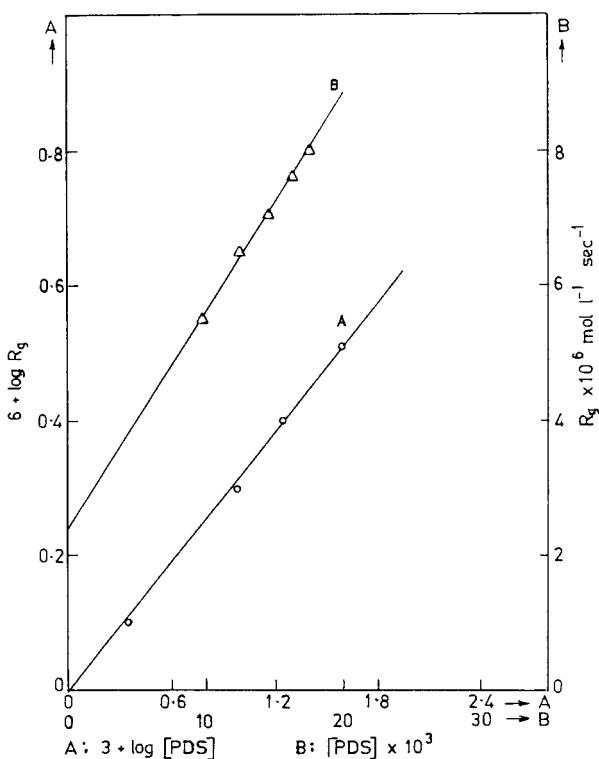


Figure 8 (A,B) [ANI] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; PTSA = 1M; temperature = 45°C.

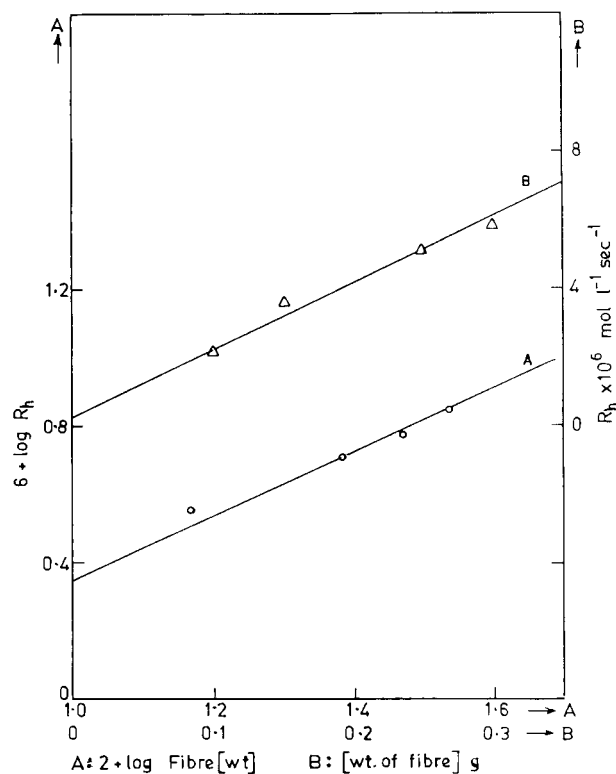


Figure 9 (A,B) [PDS] = 0.01 mol L⁻¹; [ANI] = 0.30 mol L⁻¹; PTSA = 1M; temperature = 45°C.

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

Tzou and Gregory¹⁴ determined the value of k_{1h} as 0.0008 min⁻¹. For the present case of PDS-initiated grafted copolymerization of aniline onto nylon66 fiber in the HCl medium, the value of the rate constants k_{1h} and k_{1g} are determined from the slopes of the plots R_h versus [ANI] [Fig. 1(B) and 2(B)] and R_g versus [ANI] [Figs. 3(B) and 4(B)] and using Eqs. (3) and (4), which are far higher than is the simple homopolymerization rate constant and augments the autoacceleration effect in the homopolymerization by TAS and grafting. The rate constant (k_{1h} , k_{3h} , k_{1g} , and k_{3g}) values are given in Table III.

On making similar attempts for the determination of the rate constant for the PTSA medium, the values were also obtained and are given in Table III. The rate constant values of the graft copolymerization of PANI in both the HCl and PTSA mediums were compared. The rate constant k_{1h} and k_{3g} have an almost equal value for the HCl and PTSA mediums. The k_{3h} value of the

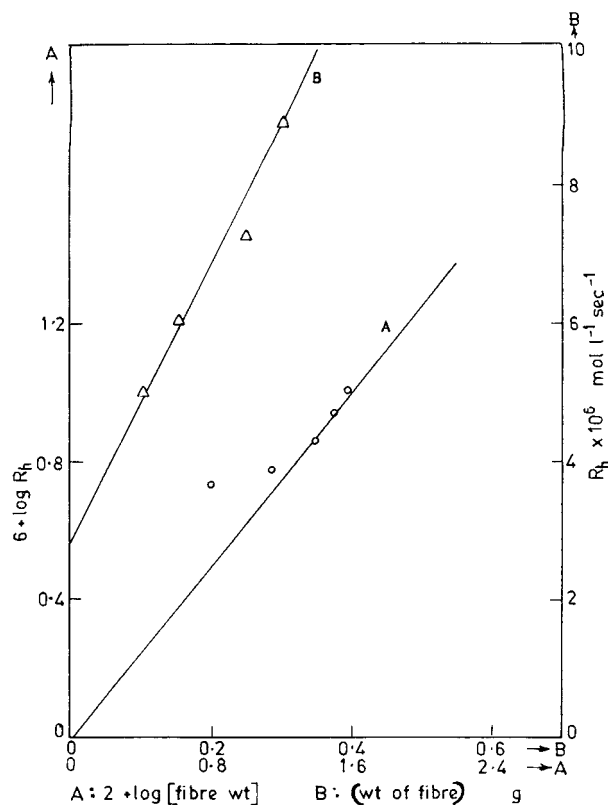


Figure 10 (A,B) $[PDS] = 0.01 \text{ mol L}^{-1}$; $[ANI] = 0.30 \text{ mol L}^{-1}$; $PTSA = 1M$; temperature = 45°C .

HCl medium is lower than that of the PTSA medium, whereas the k_{1g} value is higher for the HCl medium than for the PTSA medium (Table III).

Weight-loss Study

A definite weight ($X \text{ g}$) of the HCl- or PTSA-doped PANI grafted nylon66 fiber was treated with acetone and soaked in a $0.5N$ aqueous solution of ammonia for 4 h and removed from the reaction conditions and dried at room temperature to a constant weight ($Y \text{ g}$). The difference in weight ($X - Y$) is the change in weight due to the dedoping of HCl or PTSA from the PANI-grafted nylon66 fiber. It was once again treated with NMP for 4 h, taken out from the NMP solution, dried in a vacuum, and weighted. No weight loss was noticed in this case. These observations clearly indicate that physisorbed PANI was totally removed after treatment with NMP and the leftover weight beyond the parent fiber is due only to the presence of grafted side chains of PANI. This is shown in Table IV. From this weight-loss study, we come to the conclusion that the chemical grafting of PANI

occurred along with simultaneous homopolymerization during grafting studies in the selected media.

Isolation of PANI-grafted Nylon66 Fiber from Homopolymer

The PANI-grafted nylon66 fiber was removed from the homopolymer and dedoped with a $0.5N$ aqueous ammonia solution for 4 h and then Soxhlet-extracted with a NMP solution. After a definite interval of time, the fiber was removed from NMP, and the NMP extract was tested for the PANI content through UV-visible spectroscopy. Figure 15 shows the visible spectrum of PANI in the NMP solution for different Soxhlet-extraction time intervals. The visible spectrum shows a peak at the wavelength of 610 nm. From Figure 15, it was observed that the o.d. decreased with increase in the Soxhlet-extraction time. After 12 h of soxhlet extraction with NMP, the physisorbed PANI was completely removed. After 12 h of Soxhlet extraction with NMP, the visible spectrum showed no optical density value. The visible spectrum (after dedoping of the nylon66 fiber) of PANI synthesized in HCl and PTSA were compared. Both were found to have the peak at

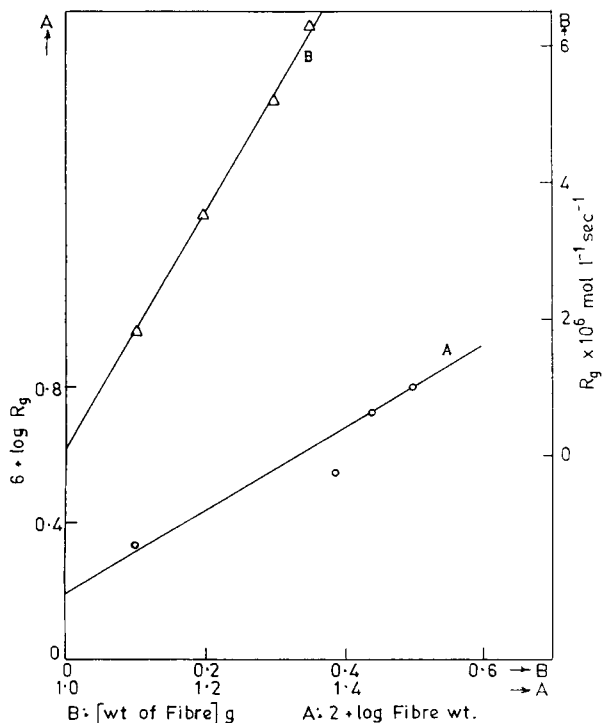


Figure 11 (A,B) $[PDS] = 0.01 \text{ mol L}^{-1}$; $[ANI] = 0.30 \text{ mol L}^{-1}$; $PTSA = 1M$; temperature = 45°C .

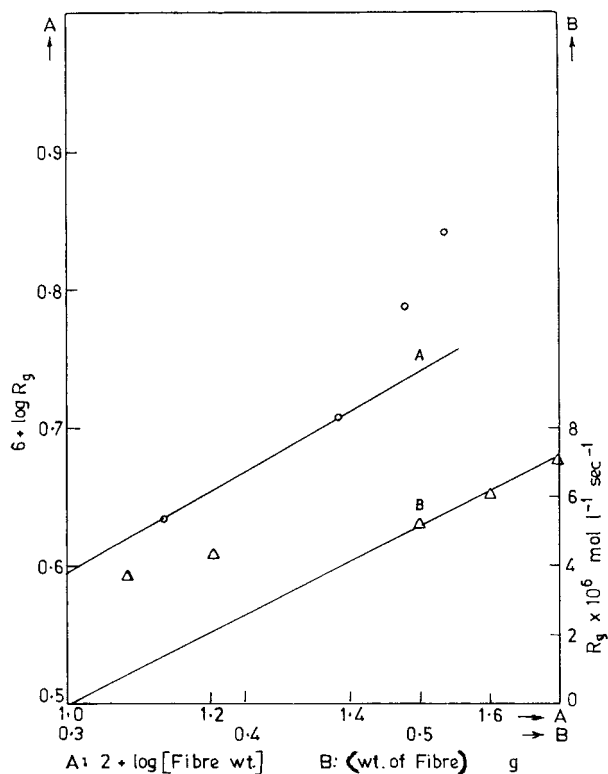


Figure 12 (A,B) [PDS] = 0.01 mol L⁻¹; [ANI] = 0.30 mol L⁻¹; PTSA = 1M; temperature = 45°C.

the same wavelength similar to that reported for the PANI spectrum.¹¹

Cyclic Voltammetric Study

The PANI-grafted nylon66 fiber (synthesized in both HCl and PTSA mediums) was dedoped with a 0.5N aqueous ammonia solution and dissolved in formic acid and made into a paste. The paste was dip-coated onto a Pt micro working electrode. The cyclic voltammeteries (CVs) were recorded between 0.00 and 0.900 V at various sweep rates.

The CVs of nylon66-g-PANI · HCl (Fig. 16) are found to have one anodic (0.62 V) and one cathodic (0.36 V) peak. HCl was used as a background electrolyte during the recording of the CV. For the sake of comparison, the CV of the homopolymer, PANI film, was recorded in a HCl electrolyte (Fig. 17). It gives one anodic (0.398 V) and one cathodic (0.76 V) peak. The peak current increases with increase in the sweep rate. The CV of nylon66-g-PANI and the PANI film in HCl were compared. The anodic peak of nylon66-g-PANI was found to be shifted in comparison with that of the parent PANI film. This shifting may be due to

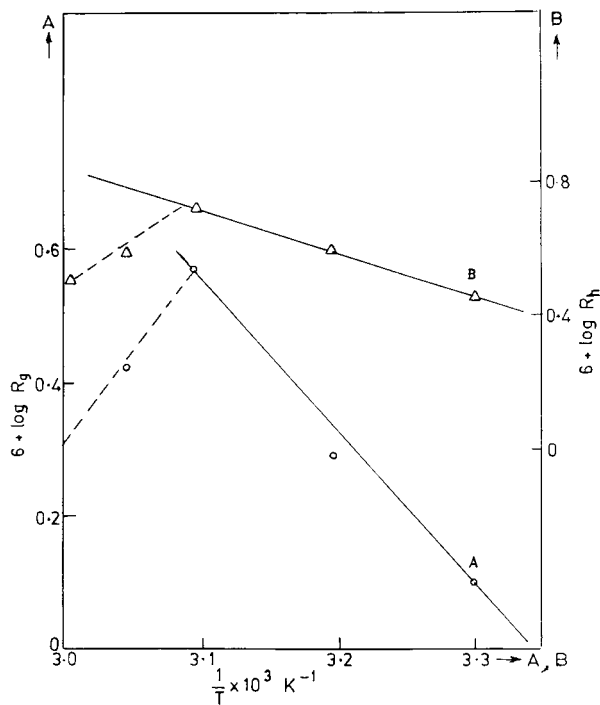


Figure 13 (A,B) [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; HCl = 1M; [ANI] = 0.30 mol L⁻¹.

the presence of a nonconducting fiber matrix (nylon66) in the case of PANI-grafted nylon66 fiber film.

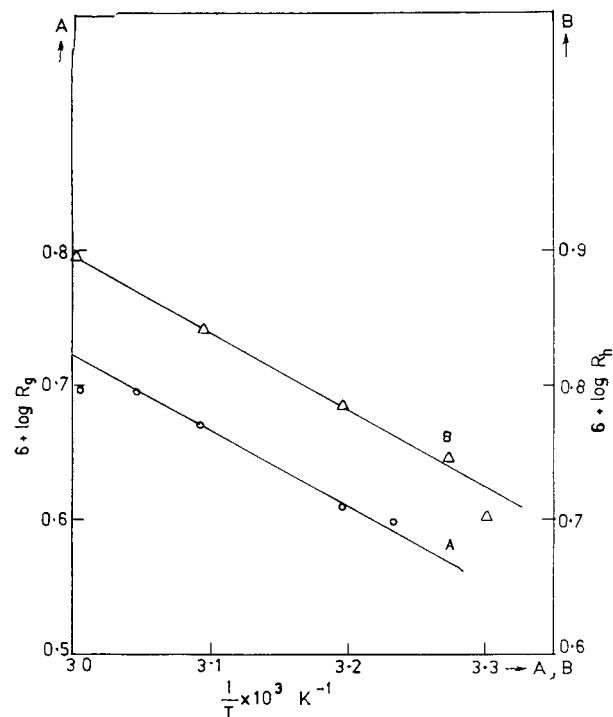


Figure 14 (A,B) [PDS] = 0.01 mol L⁻¹; weight of nylon66 = 0.20 g; PTSA = 1M; [ANI] = 0.30 mol L⁻¹.

Table III Rate Constant Values

Reaction Medium	Rate Constant	Value	Unit
HCl	k_{1h}	0.15	$\text{min}^{-1} \text{g}^{-1}$
	k_{3h}	1.08×10^6	$\text{mol L}^{-1} \text{s}^{-1}$
	k_{1g}	22.0×10^4	$\text{s}^{-1} \text{g}^{-1}$
	k_{3g}	0.12×10^5	$\text{mol L}^{-1} \text{s}^{-1}$
	k_{1h}	0.11	$\text{min}^{-1} \text{g}^{-1}$
	k_{3h}	3.00×10^6	$\text{mol L}^{-1} \text{s}^{-1}$
PTSA	k_{1g}	4.33×10^4	$\text{s}^{-1} \text{g}^{-1}$
	k_{3g}	1.75×10^6	$\text{mol L}^{-1} \text{s}^{-1}$

The CV was recorded for nylon66-*g*-PANI · PTSA film in a PTSA electrolyte at various sweep rates (Fig. 18). The CVs show one anodic (0.53 V) and one cathodic (0.43 V) peak. Here, the peak current sharply increases with increase in the sweep rate. No degradation was observed even at a higher sweep rate. For the sake of comparison, the CV of PANI-PTSA film in the PTSA electrolyte (Fig. 19) was recorded at various sweep rates. Here, also, both the anodic and cathodic peaks show a sharp increase in the peak current while the sweep rate was increased. The CV shows one anodic (0.62 V) and one cathodic (0.53 V) peak. The CVs of the nylon66-*g*-PANI film and the PTSA-doped PANI film are compared. The CV of nylon66-*g*-PANI-PTSA has an anodic peak at a lower oxidation potential than in the HCl-doped PANI film. The electroactivity of these two films differ. This may be attributed to the surface changes of the nylon66 fiber due to the nature of the dopant. Figure 20 shows the linear nature of the both anodic and cathodic peak current values against the sweep rates for the Pt electrode modified with nylon66-*g*-PANI · HCl and nylon66-*g*-PANI · PTSA fiber films.

Table IV Weight-loss Study

Process	Weight of Nylon66- <i>g</i> -PANI Fiber, HCl-doped (g)	Weight of Nylon66- <i>g</i> -PANI Fiber, PTSA-doped (g)
Before treatment		
with NH ₃	0.20 0.25 0.30 0.35 0.40	0.20 0.25 0.30 0.35 0.40
After treatment		
with NH ₃	0.16 0.19 0.24 0.27 0.31	0.17 0.20 0.25 0.26 0.32
After treatment		
with NMP	0.16 0.19 0.24 0.27 0.31	0.17 0.20 0.25 0.26 0.32

[ANI] = 0.30 mol L⁻¹; [PDS] = 0.010 mol L⁻¹; temperature = 45°C.

FTIR Spectroscopy

The FTIR spectrum of HCl-doped PANI is given in Figure 21(A). The peak at 1481 cm⁻¹ indicates the C—C aromatic stretching vibration. The peaks at 1250 and 1566 cm⁻¹ correspond to C—N bond and C=N bond, respectively. The band at 805 cm⁻¹ is due to the C—H out-of-plane bonding vibration of the *para*-substituted benzene ring. The presence of the Cl⁻ ion can be identified from the peak at 1290 cm⁻¹. The vibration band of nitrogen quinone can be seen at 1169 cm⁻¹.

Figure 21(B) shows the FTIR spectrum of PTSA-doped PANI. Here, also, the above said peaks are observed except at 1290 cm⁻¹. Additional peaks observed are due to the stretching vibration of S=O in the sulfonate group at 1210, 1124, 1035, and 1008 cm⁻¹. The FTIR spectrum of nylon66-*g*-PANI (HCl-doped) and nylon66-*g*-PANI (PTSA-doped) are shown in Figure 22(A) and (B). The peaks observed are similar to those of Figure 21(A,B). Here, some additional peaks are also observed due to the nylon66 backbone. These facts confirm the chemical grafting of PANI units onto the nylon66 fiber in both HCl and PTSA mediums.

Conductivity Measurements

Conductivity values were determined for both grafted and ungrafted nylon66 fibers as per the procedure described in the Experimental section. The conductivity values were found for the PANI-grafted fiber prepared with different media under identical conditions. The results show that PANI-grafted nylon66 fiber synthesized in the PTSA medium has a higher conductivity value than that of the one synthesized in the HCl medium. But the pure backbone has a very low conductivity value. The conductivity value increases with increase in the percent grafting of PANI onto the

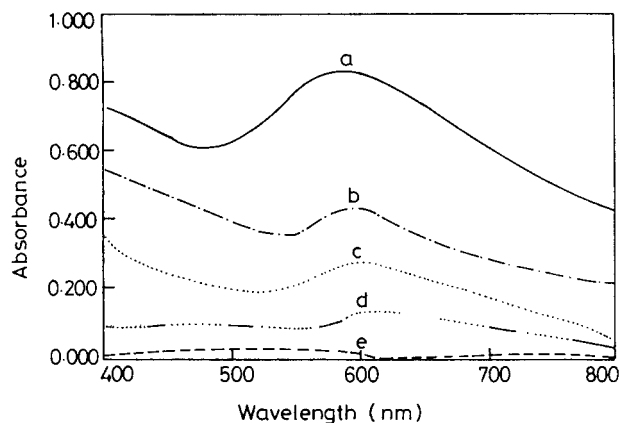


Figure 15 Visible spectrum of PANI in NMP: (a) 1 h; (b) 3 h; (c) 5 h; (d) 10 h; (e) 12 h.

backbone fiber, which may be due to relative changes in the dopant ions. The conductivity values are given in Table V.

Probable Mechanism for the Chemical Grafting of PANI onto Nylon66 Fiber

The mechanism suggested for the graft copolymerization of PANI onto nylon66 fiber in the present study is based on the mechanism proposed by two research groups. The first research team explained the formation of the homopolymer, PANI, which proceeds through the radical cations²¹ and the second research team explained the formation of the graft copolymer through oligomer formation.¹⁶

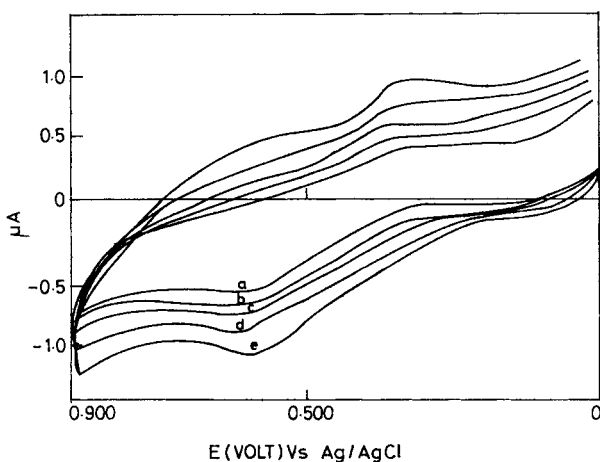


Figure 16 CV of nylon6-g-PANI (HCl-doped) film at various sweep rates: (a) 100 mV/s; (b) 200 mV/s; (c) 300 mV/s; (d) 400 mV/s; (e) 500 mV/s.

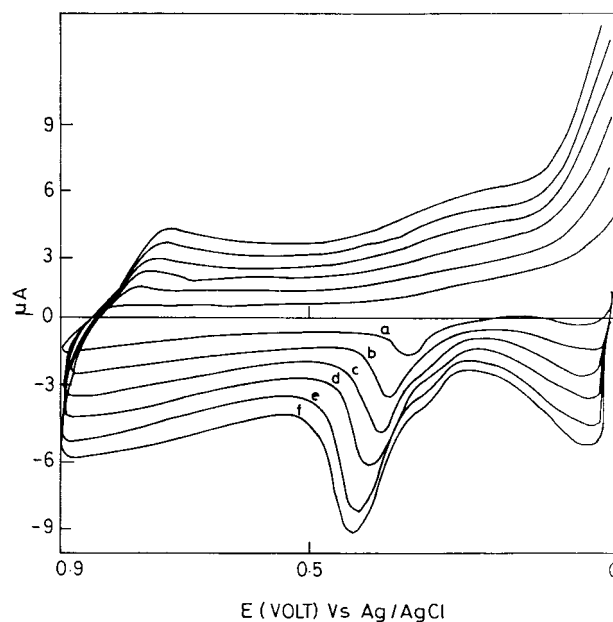
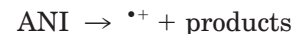


Figure 17 CV of PANI (HCl-doped) film at various sweep rates: (a) 100 mV/s; (b) 200 mV/s; (c) 300 mV/s; (d) 400 mV/s; (e) 500 mV/s.

Primary Reactions

ANI + PDS (in HCl or PTSA)



PDS (in HCl or PTSA) \rightarrow $2\text{SO}_4^{\bullet-}(\text{R}^{\bullet}) + \text{products}$

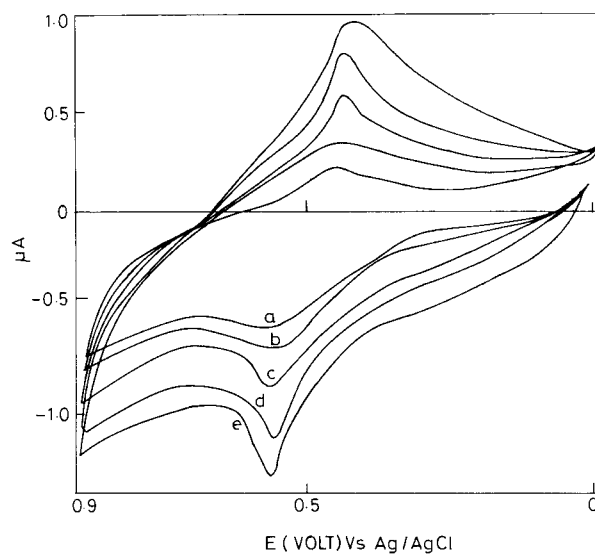


Figure 18 CV of nylon66-g-PANI (PTSA-doped) film at various sweep rates: (a) 100 mV/s; (b) 200 mV/s; (c) 300 mV/s; (d) 400 mV/s; (e) 500 mV/s.

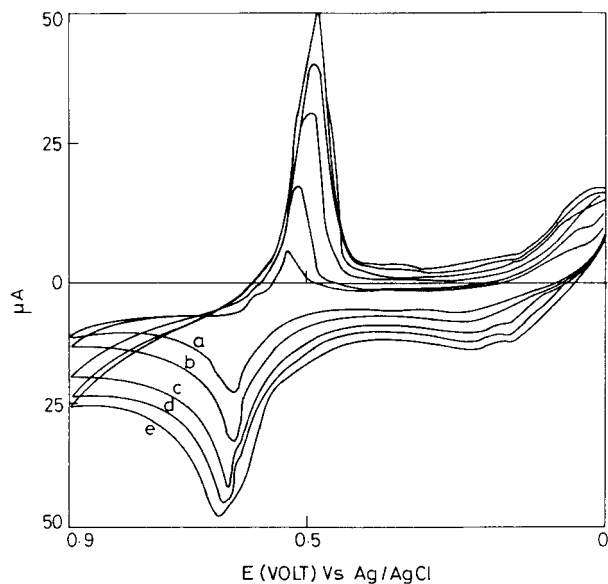
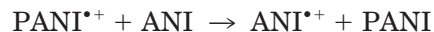
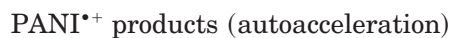
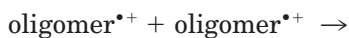
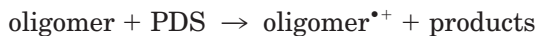
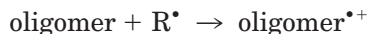
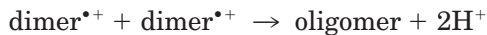
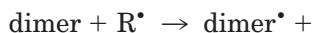
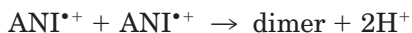


Figure 19 CV of PANI (PTSA-doped) film at various sweep rates: (a) 100 mV/s; (b) 200 mV/s; (c) 300 mV/s; (d) 400 mV/s; (e) 500 mV/s.



Homopolymerization



Graft Compolymerization

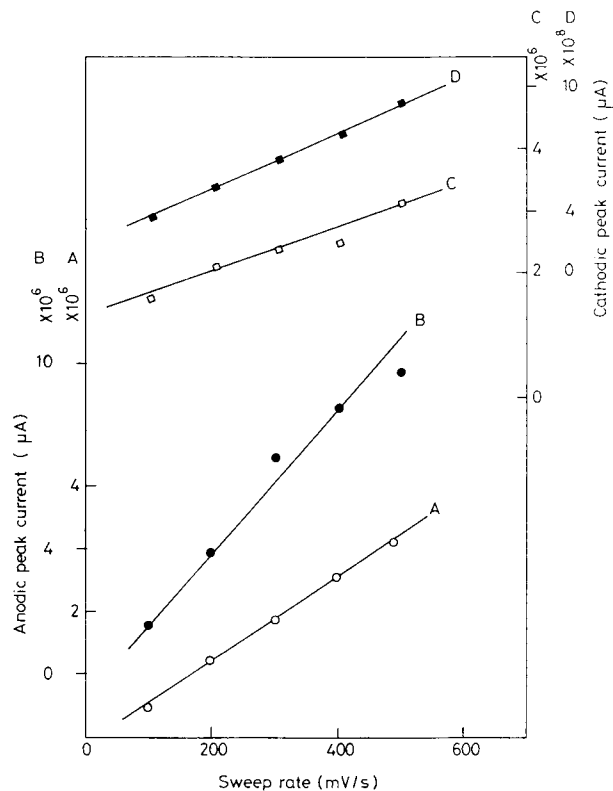
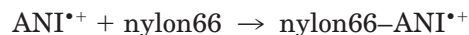


Figure 20 (A) Anodic peak current versus sweep rate (HCl medium); (B) anodic peak current versus sweep rate (PTSA medium); (C) cathodic peak current versus sweep rate (HCl medium); (D) cathodic peak current versus sweep rate (PTSA medium).

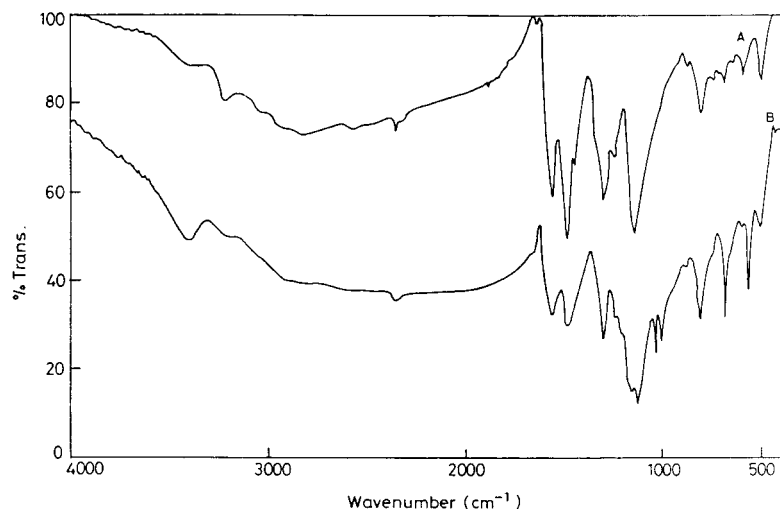


Figure 21 (A) FTIR spectrum of HCl-doped PANI; (B) FTIR spectrum of nylon66-g-PANI (HCl-doped).

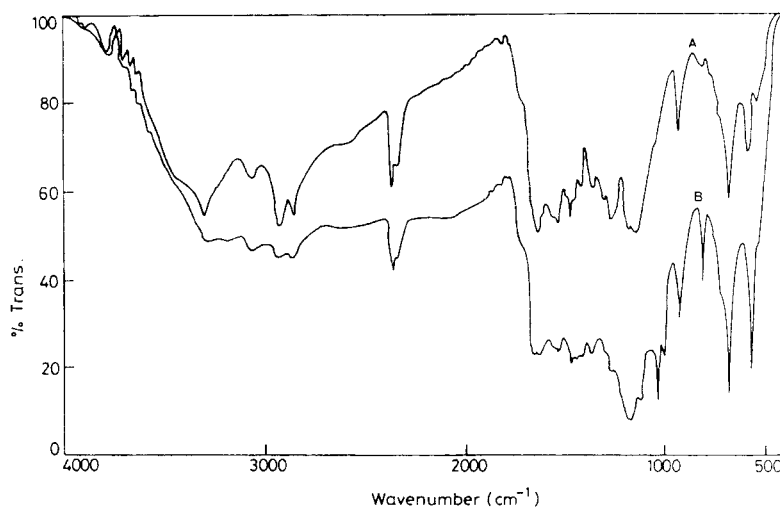
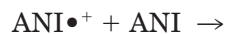
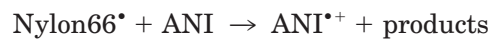
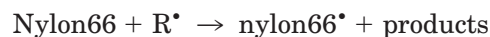


Figure 22 (A) FTIR spectrum of PTSA-doped PANI; (B) FTIR spectrum of nylon66-g-PANI (PTSA-doped).

Table V Conductivity Measurements

Polymer	Percent Grafting	Medium	Conductivity (Ohm ⁻¹ cm ⁻¹)
Nylon66	—	—	0.88G
Nylon66- <i>g</i> -PANI	13.5	HCl	8.51M
	15.2	HCl	10.3M
Nylon66- <i>g</i> -PANI	15.0	PTSA	14.3K
	28.2	PTSA	19.6K

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