

Peroxosalts Initiated Graft Copolymerization of Aniline onto Rayon Fiber—A Kinetic Approach

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ABSTRACT: Oxidative chemical polymerization of aniline was carried out using peroxydisulphate and peroxomonosulphate as a lone initiator in an aqueous acidic medium in the presence of Rayon fiber. The Rayon fiber was tested for the chemical grafting of polyaniline onto it. The content of polyaniline (wt %) in the backbone was found to vary while varying the [M], [I], and (amount of Rayon fiber) during the polymerization of aniline. Various graft parameters like rate of grafting, % grafting, and % efficiency were calculated. Rate of homopolymerization was also followed for both cases. The chemical grafting was confirmed using FTIR spectroscopy, cyclic voltammetry, weight loss study, and conductivity measurements. Probable mechanism has been proposed to explain the experimental results obtained. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 468–478, 2001

Key words: graft copolymerization; aniline; peroxosalts; rayon fiber

INTRODUCTION

Chemical modification of conventional polymers, both natural and synthetic, can provide a potential route for significantly altering their physical and chemical properties. Such a modification can be made through graft copolymerization techniques. It is believed that the graft copolymerization occurs through the abstraction of hydrogen atom from the backbone polymer containing a hydroxyl group, an amino group, and an active carbon atom.^{1–4} Various initiators are used for the grafting technique. Among those, peroxosalts were proven to be an excellent choice, with minimum side products.⁵ The electrically conducting

polymers have recently become an active research field due to their ease of preparation, environmental stability, and applications in various electrical⁶ and electronic devices.⁷ Recently, the conducting polymers have been grafted with conventional polymers, which are used in the field of EMI shielding,⁸ gas sensors,⁹ and in secondary batteries.¹⁰ Toppare et al.¹¹ prepared some conducting polymer composites and reported the conductivity values. Chanjiang and coworkers¹² reported the conducting polymer composites. Poly(aniline) (PANI) was grafted onto PET and Nylon 6 fibers initiated by peroxydisulphate.¹³ PANI-grafted polyamino styrene was reported by Li et al.¹⁴ S. Yang and coworkers¹⁵ grafted PANI onto chitosan backbone, and they reported TGA, UV-Visible, FTIR spectroscopy and conductivity values as evidences. Suzhen Li and their research team¹⁶ synthesized soluble PANI through a graft-

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ing method, and they proved the grafting by SEM, WAXD, FTIR spectroscopy, electronic spectra, and electrical conductivity measurements. Highly conducting nylon 6/PANI film was reported by Abraham et al.¹⁷ Transparent PANI/Nylon 6 composite film was prepared, and the degradation kinetics of electrical conductivity were reported.¹⁸ But the above research articles did not mention anything about homopolymer formation. Recently, our active research team communicated some kinetic results on the peroxosalts-initiated graft copolymerization of aniline and *o*-toluidine onto PET,^{19,20} Nylon 6,²¹ wool,^{22,23} and Nylon 66²⁴ fibers. Peroxosalts-initiated graft copolymerization of aniline and *o*-toluidine onto polypropylene (PP)²⁵ and Rayon²⁶ fiber was reported by Anbarasan and coworkers.

In this article we reported the simple chemical modification of Rayon fiber through graft copolymerization of aniline initiated by PDS and PMS at a given concentrations. Various rate constants were evaluated from the experimental results. The chemical modification through graft copolymerization are supported by FTIR spectroscopy, cyclic voltammetry (CV), weight loss study, and conductivity measurements. To explain the experimental results obtained, a plausible mechanism has been proposed.

EXPERIMENTAL

Aniline (Fischer AR) was used after distillation under vacuum. Potassium peroxydisulphate (PDS) (CDH AR), potassium peroxomonosulphate (PMS) (E. Merck), HCl (Fischer AR), and other chemicals were used as received. Rayon fiber (a gift sample from M/S. Madura coats, Madurai, India) was soxhlet extracted with acetone for 24 h and dried at room temperature before use.

Procedure

A typical graft copolymerization study was conducted as described.

Rayon fiber (W_1 g) was immersed in definite concentration of HCl (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 or PMS (using standard solutions). The time of adding PDS or PMS was taken as the starting time for the reaction (poly-

merization conditions were selected in such a way that no polymerization occurred 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 1M HCl several times, dried (at 80°C for 4 h), and weighed until get the constant weight. This gives the total weight of the grafted polymer along with the homopolymer (W_2 g). The grafted Rayon was soxhlet extracted with NMP for several hours to remove the homopolymer (no color changes were seen in the grafted fiber). The extraction was repeated until separation of the homopolymer from the grafted sample was completed. This was ascertained by drying the fiber in vacuum until 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.

Rate Measurements

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

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

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

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

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

where $W_3 - W_1$ is the 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 the molecular weight of the aniline.

FTIR Spectroscopy

The FTIR spectrum was recorded for Rayon-g-PANI sample by using Bruker FTIR Equinox 55 model instrument by KBr pelletisation method.

Conductivity Measurements

Conductivity of both PANI grafted and pure Rayon fiber was measured by using a Keithly 617 Programmable Electrometer Instrument. A 1-cm length of the fiber 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.

Cyclic Voltammetry

The PANI-grafted Rayon fiber (HCl doped, green colored) was allowed to stand over night in 0.5 *N* aqueous ammonia solution (the fiber turns into blue color); then the fiber was washed well with acetone for two to three times to remove any adhering materials that were absorbed on 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 9.50×10^{-2} cm²). Cyclic voltammograms (CVs) were recorded (by using BAS 100 A Electrochemical Analyzer) for Rayon-*g*-PANI film 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.

Weight Loss Study

Definite weight of the PANI-grafted Rayon fiber was treated with acetone (30 min) and dried until constant weight. When a change in weight was observed, it was treated with NMP solution for 4 h and removed from NMP, dried under vacuum, and weighed. The PANI-grafted Rayon fiber was soaked with 0.5 *N* aqu. ammonia solution, isolated from the reaction condition, and dried at room temperature. Some amount of weight loss was noticed due to the dedoping process. It was once again treated with NMP solution for 4 h, dried under a vacuum condition, and weighed. A change in weight was inferred. Thus, the total % weight loss was determined.

Isolation of PANI-Grafted Rayon Fiber from PANI, Homopolymer

The mixture (W_1 g) of the PANI-grafted Rayon fiber and PANI, the homopolymer, was dedoped with 0.5 *N* aqu. ammonia solution and extracted with *N*-methyl pyrrolidone (NMP) solution for 12 h to separate the homopolymer from the reac-

Table I Effect of [ANI] on % Grafting and % Efficiency

[ANI] mol L ⁻¹	% Grafting		% Efficiency	
	A	B	A	B
0.20	2.10	3.70	0.77	1.36
0.30	3.65	5.05	0.87	1.21
0.40	4.90	7.60	0.87	1.35
0.50	6.95	8.95	1.00	1.28
0.60	9.01	10.9	1.08	1.30

A: [PDS] = 0.01 mol L⁻¹, B: [PMS] = 0.02 mol L⁻¹.
A,B: Wt. of Rayon fiber = 0.20 g, HCl = 1.00M.

tion mixture. The extraction process was repeated until the separation of homopolymer from the grafted sample was completed and was ascertained by a colorless filtrate. The fiber was dried in vacuum to get the 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 the formed homopolymer. This can be quantified with UV-visible spectroscopy. A visible spectrum was recorded until the extract gave a nil OD value.

UV-Visible Spectroscopy

Visible spectrum was recorded by using a UV 2401 PC model spectrophotometer for NMP extract at different extraction time intervals, and the corresponding optical density (OD) values were noted.

RESULTS AND DISCUSSION

Effect of [ANI] on R_h and Graft Parameters

Experimental results were obtained by changing the [ANI] in the range from 0.20 to 0.60 mol L⁻¹ using PDS or PMS as a lone initiator while keeping other experimental conditions as constant. It is important to note that both R_h and R_g increased with an increase in [ANI]. The R_h values are higher for the PDS case, whereas the R_g values are higher for the PMS system. The % grafting and % efficiency are shown in Table I.

To find out the order dependences for the PDS system, the plots of $\log R_h$ vs. $\log[\text{ANI}]$ [Fig. 1(A)] and $\log R_g$ vs. $\log[\text{ANI}]$ [Fig. 1(B)] were drawn, and it showed the first-order dependence of both R_h and R_g on [ANI]. Further, it was confirmed by

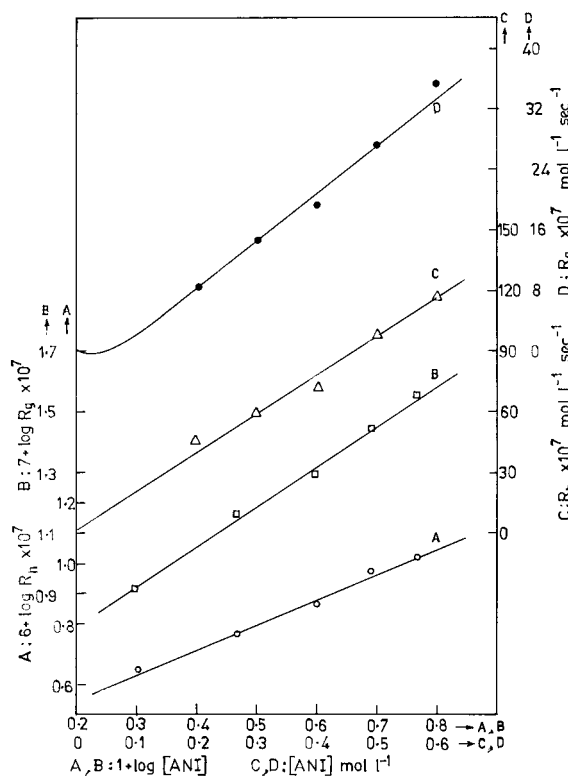


Figure 1 Effect of [ANI] on R_h and R_g : [PDS] = 0.01 mol L⁻¹, weight of Rayon fiber = 0.20 g, [HCl] = 1.00M.

plotting R_h vs. [ANI] [Fig. 1(C)] and R_g vs. [ANI] [Fig. 1(D)]. The linearity of these plots confirm the first-order dependence of R_h and R_g on [ANI]. The intercept values of the plots R_h vs. [ANI] [Fig. 1(C)] and R_g vs. [ANI] [Fig. 1(D)] were noted.

Similar attempts were made for PMS-initiated graft copolymerization of ANI onto Rayon fiber (Fig. 2). Here also the same first-order dependence was noticed. The % grafting and % efficiency reveals the same trend (Table I).

The increase in R_h and R_g may be due to the formation of more and more monomer radical cations. The second effect is the autoacceleration caused by the homopolymer surface and PANI grafted Rayon fiber surface.

Effect of [PDS] or [PMS] on R_h and Graft Parameters

The [PDS] was varied from 0.005 to 0.025 mol L⁻¹ while keeping other experimental conditions as constant. The R_h and R_g values increased with an increase in [PDS]. [PMS] was varied from 0.01 to 0.05 mol L⁻¹ while keeping other experimental conditions as constant. Here also both R_h and R_g increased with an increase in [PMS]. R_h values

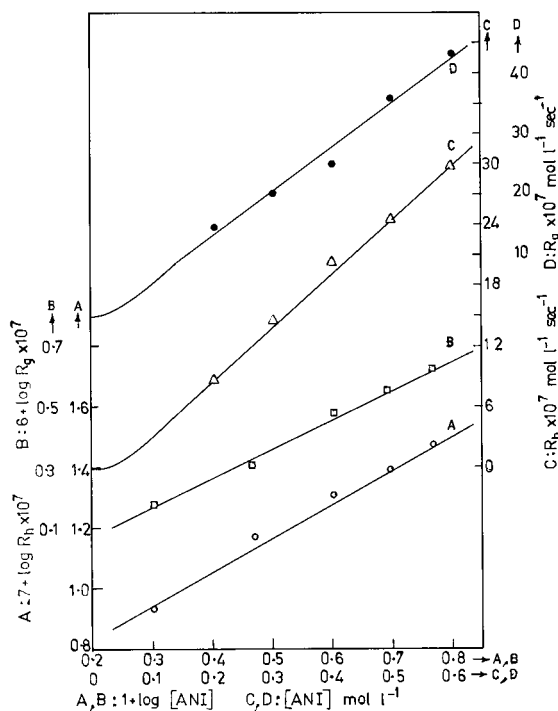


Figure 2 Effect of [ANI] on R_h and R_g : [PMS] = 0.02 mol L⁻¹, weight of Rayon fiber = 0.20 g, [HCl] = 1.00M.

were found to be higher with the PDS case, and R_g values were higher for the PMS system. The % grafting and % efficiency values are given in Table II.

The plots of $\log R_h$ vs. $\log [PDS]$ [Fig. 3(A)], $\log R_g$ vs. $\log [PDS]$ [Fig. 3(B)], R_h vs. [PDS] [Fig. 3(C)] and R_g vs. [PDS] [Fig. 3(D)] were drawn. Figure 3(A) and (B) indicates the first-order dependence of R_h and R_g on [PDS]. The direct plots were found to be linear, and passed through the origin.

Table II Effect of [PDS] or [PMS] on % Grafting and % Efficiency

[PDS] or [PMS] mol L ⁻¹		% Grafting		% Efficiency	
A	B	A	B	A	B
0.005	0.010	1.52	2.15	0.36	0.51
0.010	0.020	3.80	5.35	0.91	1.28
0.015	0.030	6.24	7.45	1.48	1.78
0.020	0.040	9.75	8.95	2.32	2.14
0.025	0.050	10.9	12.1	2.63	2.90

A,B: [ANI] = 0.30 mol L⁻¹, wt of Rayon fiber = 0.20 g, HCl = 1.00M.

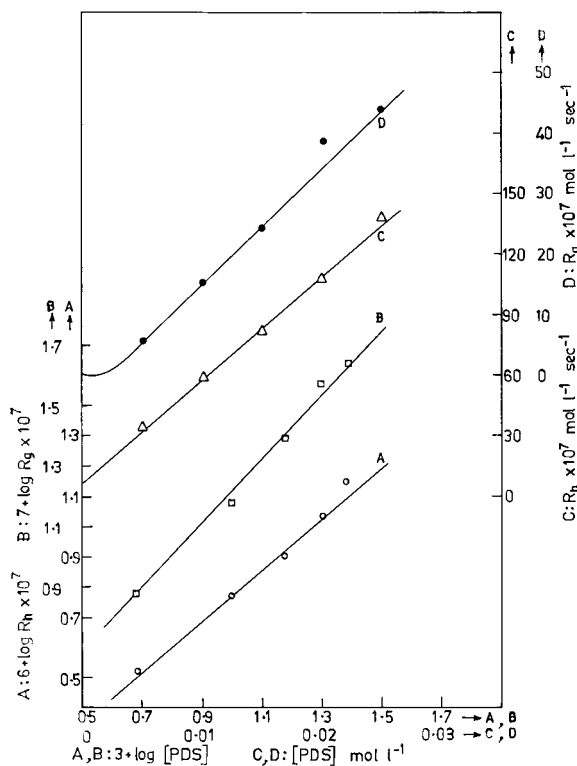


Figure 3 Effect of [PDS] on R_h and R_g : [ANI] = 0.30 mol L⁻¹, weight of Rayon fiber = 0.20 g, [HCl] = 1.00M.

Similar plots were also drawn for PMS case (Fig. 4). We found first order dependence of R_h and R_g on [PMS]. The % grafting and % efficiency values are given in Table II.

Formation of larger amounts of active free radicals are responsible for the increase of R_h and R_g for both systems.

Effect of (Amount of Rayon Fiber) on R_h and Graft Parameters

The effect of amount of Rayon fiber on R_h and graft parameters were studied under the conditions mentioned in Table III. The Rayon fiber weight was varied between 0.10 to 0.35 g while keeping other experimental conditions as constant. Both R_h and R_g showed a greater proportion of increase with higher amounts of Rayon fiber for both cases. The PDS system showed higher R_h , and the PMS system showed higher R_g values. The % grafting and % efficiency values are also given in Table III.

In an attempt to quantify the order dependences for PDS system, the plots of $\log R_h$ vs. $\log(\text{amount of Rayon fiber})$ [Fig. 5(A)] and $\log R_g$ vs. $\log(\text{amount of Rayon fiber})$ [Fig. 5(B)] were

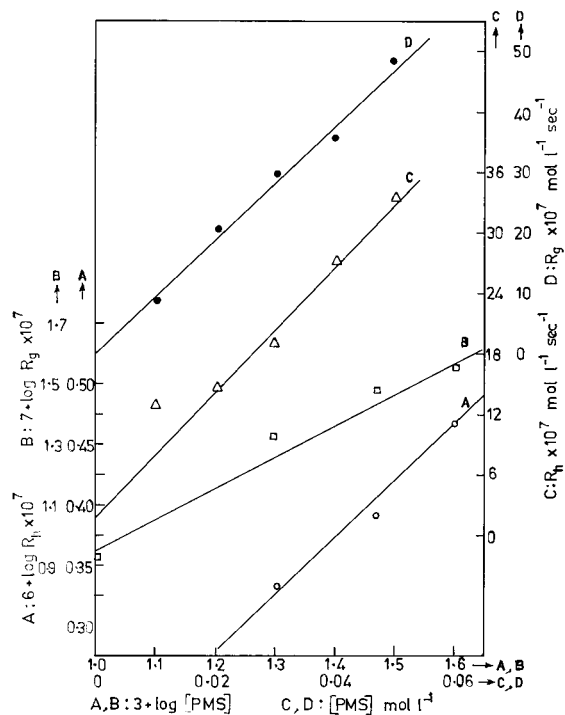


Figure 4 Effect of [PMS] on R_h and R_g : [ANI] = 0.30 mol L⁻¹, weight of Rayon fiber = 0.20 g, [HCl] = 1.00M.

made, and the slope values were found to be close to 1, indicating first-order dependence of R_h and R_g on (amount of Rayon fiber). Further, it was checked through plotting R_h vs. (amount of Rayon fiber) [Fig. 5(C)] and R_g vs. (amount of Rayon fiber) [Fig. 5(D)]. These plots were found to be linear and passing through the origin. These linear plots support the first-order dependence of R_h and R_g on the backbone amount.

Similar plots were made for the PMS system also (Fig. 6). Figure 6(A) and (B) showed the first-order dependence of R_h and R_g on (amount of

Table III Effect of (Amount of Rayon Fiber) on % Grafting and % Efficiency

(Amount of Rayon Fiber) (g)	% Grafting		% Efficiency	
	A	B	A	B
0.10	5.22	5.40	0.62	0.64
0.15	4.21	5.51	0.75	0.99
0.25	5.28	4.64	1.58	1.39
0.30	5.63	6.60	2.01	2.37
0.35	5.90	6.21	2.50	2.62

A: [PDS] = 0.01 mol L⁻¹, B: [PMS] = 0.02 mol L⁻¹.
A,B: [ANI] = 0.30 mol L⁻¹, HCl = 1.00M.

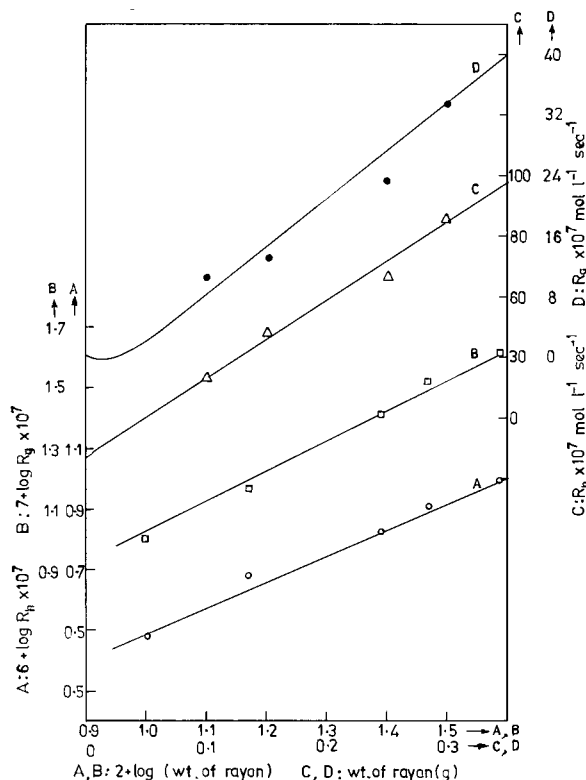


Figure 5 Effect of (amount of Rayon fiber) on R_h and R_g : $[ANI] = 0.30 \text{ mol L}^{-1}$, $[PDS] = 0.01 \text{ mol L}^{-1}$, $[HCl] = 1.00M$.

Rayon fiber). The % grafting and % efficiency values are shown in Table III.

On increasing the amount of fiber, the amount of macroradicals are also increased largely. These active sites enhance both homopolymerization and graft copolymerization through an autoacceleration effect.

Gregory²⁷ and coworkers studied the effect of added fiber on the chemical polymerization of aniline in the presence and absence of PET fiber. 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 autoacceleration effect by the electrode surface in an attempt to explain the changes in the induction time during the polymerization. A kinetic equation was 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

the concentration of monomer, and $[P]$ the amount of polymer formed. Shim and Park²⁹ proposed a kinetic equation for the polymerization of aniline on bare Pt electrode including the autoacceleration 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 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. In the present case, the added fiber for grafting and the formed homopolymer may cause the autoacceleration effect due to the active surface effect.

The plot of $R_h(ANI)$ vs. $[ANI]$ [Fig. 1(C)] was found to be a straight line with a definite intercept and $R_h(ANI)$ vs. $[PDS]$ [Fig. 2(C)] is a straight line and passing through the origin and $R_h(ANI)$ vs. (amount of Rayon fiber) [Fig. 3(C)] is

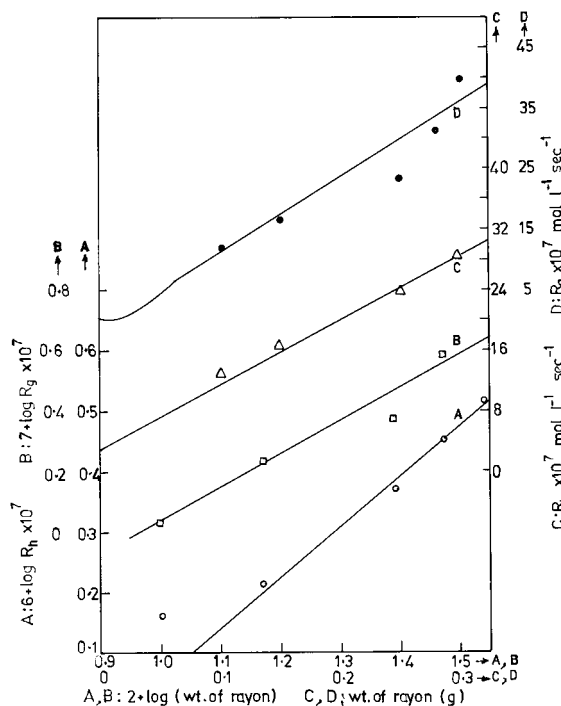


Figure 6 Effect of (amount of Rayon fiber) on R_h and R_g : $[ANI] = 0.30 \text{ mol L}^{-1}$, $[PMS] = 0.02 \text{ mol L}^{-1}$, $[HCl] = 1.00M$.

a straight line and passing through the origin. These three combined facts necessitate the modification of the above equations as,

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

where k_{1h} is the rate constant corresponding to homopolymer formation, k_{2h} and k_{3h} are rate constants for the homopolymer formation taking into account the additional effects of available surface and probable change due to grafting. [TAS] is the 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. 1(C)].

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

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

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 min^{-1} . For the present case, PDS initiated graft copolymerization of ANI onto Rayon fiber in aqueous HCl medium, k_{1h} and k_{1g} values are determined from the slope of the plots R_h vs. [ANI] [Fig. 1(C)], and R_g vs. [ANI] [Fig. 1(D)] using eqs. (1) and (2) as $8.01 \times 10^{-3} \text{ g}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ and $3.33 \times 10^{-3} \text{ g}^{-1} \text{ m}^{-1} \text{ s}^{-1}$, respectively. This value is far higher than that of the simple homopolymerization rate constant and augmenting the autoacceleration effect in homopolymerization by TAS and grafting. The value of k_{3h} was found to be $7.50 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$, whereas the value of k_{3g} was found to be nil. The above rate constant values indicate that k_{1h} is greater than that of k_{1g} .

In the case of PMS-initiated graft copolymerization of ANI onto Rayon fiber, the rate constants were determined by modifying eqs. (1) and (2) as

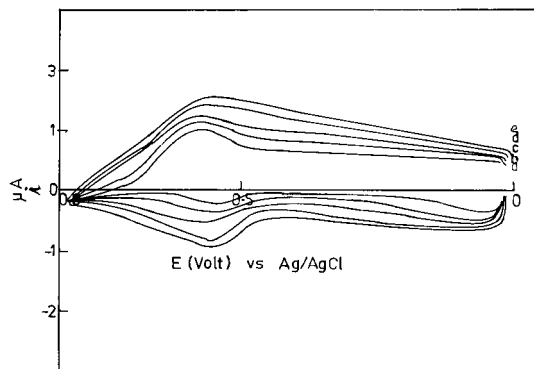


Figure 7 Cyclic voltammogram of Rayon-g-PANI film at various sweep rates: (a) 100 mV/s, (b) 200 mV/s, (c) 300 mV/s, (d) 400 mV/s, (e) 500 mV/s.

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

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

The k_{1h} and k_{1g} values are found to be $1.01 \times 10^{-3} \text{ g}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ and $1.66 \times 10^{-3} \text{ g}^{-1} \text{ m}^{-1} \text{ s}^{-1}$, respectively. Here, the k_{3h} and k_{3g} values were found to be nil. In the case of the PMS system the rate of grafting was found to be higher than that of the rate of homopolymerization.

At a given concentrations of PDS and PMS the rate constants were compared. Both k_{1h} and k_{1g} values for PDS system was found to be higher than that of PMS system.

Cyclic Voltammetry

Cyclic voltammogram (CV) was recorded for Rayon-g-PANI film at various sweep rates, and shown in Figure 7. The CV showed one anodic peak (at 590 mV) and one cathodic peak (at 620 mV) on cycling the potential with various sweep rates. The peak current was found to be increase with increase in sweep rates. The CV diagram indicates that the film was not degraded even at higher sweep rates. This was evident from the unchanged redox peak at different sweep rates. This is similar to that of CV of PANI film at various sweep rates. On increasing the sweep rate both anodic and cathodic peak currents of Rayon-g-PANI film showed a linear trend. The presence

Table IV Weight Loss Study

Process (Treatment with)	% Wt. Loss (Approximately)		Reason
	A	B	
1. Acetone	1	2	Solubility of physisorbed monomer or dimer in acetone
2. NMP	3	2	Solubility of physisorbed HCl doped PANI
3. Ammonia	10–13	20	Removal of HCl from both physisorbed and grafted PANI
4. NMP	15–17	5	Solubility of all the dedoped physisorbed PANI

A: Rayon–PDS–PANI.

B: Rayon–PMS–PANI.

of PANI electroactivity for grafted fiber points out the chemical grafting of PANI onto Rayon fiber.

The linear trend of peak current with the sweep rates confirm the chemical grafting of PANI onto Rayon fiber. This shift in the peak potential value also add further evidence for the chemical grafting of PANI onto Rayon fiber.

Weight Loss Study

Table IV indicates the % weight loss of Rayon-*g*-PANI fiber under different chemical process. The % weight loss of Rayon-*g*-PANI under each process depends on many experimental factors like the nature of monomer, initiator, and fiber used.

Kang et al.³⁰ reported that during the chemical polymerization of aniline there will be a formation of 50% amino form and 50% imino form. Also, they reported that the imino nitrogen atom present in the polyaniline chain is responsible for the doping–dedoping process. On increasing the quinoidal structure the amount of weight loss is also increased. Our earlier communications reported that PET-*g*-POT showed slightly higher % weight loss than the PET-*g*-PANI system.¹³ This indicates that the substituted polyanilines give the quinoidal structure rather than the benzenoidal structure.

The strong oxidizing agents like PMS leads to the quinoidal structure due to over oxidation; consequently, the weight loss is increased. The R_g value showed that there is a complex formation between oxidant and fiber. In this situation, the weight loss from grafted PANI is observed.

(The complex formation between oxidant and fiber was confirmed through the PDS or PMS analysis method. Graft copolymerization was carried out in the absence of monomer for different concentrations of oxidant at 45°C. After 30 min the unreacted oxidant was estimated by the volu-

metric method. The results indicate there is no unreacted oxidant. That means all the oxidant molecules are broken into active free radicals. Subsequently, these free radicals activate the Rayon fiber backbone through the direct interaction with the reactive sites present on the Rayon fiber backbone).

In the case of PDS, a mild oxidizing agent leads to the formation of homopolymer through the benzenoidal structure. Here, the weight loss from physisorbed PANI was observed rather than grafted PANI on various treatments, because PDS enhances the homopolymer formation rather than graft copolymer formation.

Regarding the backbone used, Rayon contains many active functional groups and substituents that causes the physisorbition of PANI onto the surface of the backbone. The physisorbition takes place between fiber and monomer or polymer through the secondary forces. Here, the secondary bond formation is possible only between the hetero atom of the backbone and the benzenoid structure of the PANI unit. In the case of PP fiber, the amount of physisorbed PANI was found to be very low due to the absence of the hetero atom on the PP backbone. From our earlier communications, it was observed that the natural fiber showed higher % weight loss than the synthetic backbone.^{19,21,23} Here, PDS showed weight loss from the homopolymer, and PMS showed weight loss from the graft copolymer in different processes.

Infrared Spectroscopy

The FTIR spectrum of Rayon-*g*-PANI is given in Figure 8. The stretching vibration of the C—N band are indicated by the peaks at 1645 and 1373 cm^{-1} . The C—H out of plane bending vibration of the *para*-substituted benzene ring appears at 894 cm^{-1} . The peak appeared at 1269 cm^{-1} is due to

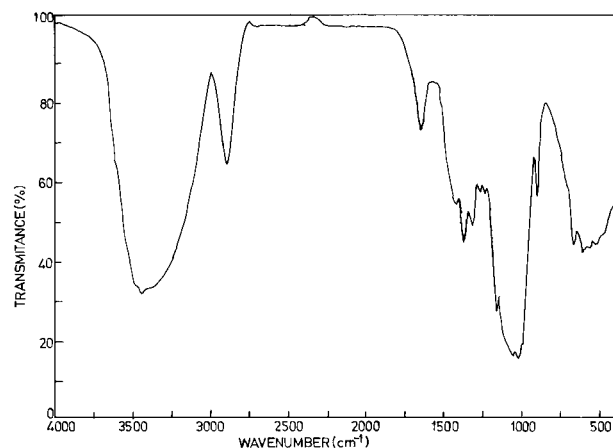


Figure 8 FTIR spectroscopy of Rayon-g-PANI fiber.

the C—H stretch of aromatic secondary amine. The presence of a dopant, Cl^- ion peak is evident from the peak at 1315 cm^{-1} . The other peaks appeared in the spectrum are due to the Rayon backbone. Although these assignments are in close agreement with earlier reports of FTIR studies of PANI, some of the aromatic peaks were disappeared due to Rayon backbone.

Isolation of PANI-Grafted Rayon Fiber from Homopolymer

The PANI-grafted Rayon fiber was removed from the homopolymer and dedoped with 0.5 *N* aqu. ammonia solution for 4 h, and it was extracted with NMP solution. After a definite interval of time, the fiber was removed from the NMP solution, and the extract was tested for PANI content through UV-visible spectroscopy. Visible spectrum (figure not included) was recorded for different extraction time intervals. The visible spectrum showed a peak at the wavelength of 630 nm. This is due to excitation transition caused by interchain and intracharge transfer. It can be seen that the OD value was decreased with an increase in extraction time. After 12 h of extraction with NMP, all the physisorbed PANI was completely removed. The visible spectrum of PANI at various extraction time intervals for the PDS and PMS system were critically compared. The PDS system showed a peak at 630 nm, whereas the PMS system showed the peak at 585 nm. There is a difference in the wavelength of the peak observed, which is due to the difference in the degree of oxidation. It is quite interesting to note that even after the removal of the homopolymer, the fiber was found to be a blue color. This strongly favors

definite modification in the form of chemical grafting of PANI onto Rayon fiber. To supplement the chemical grafting of PANI, further studies have also been made.

Conductivity Measurements

The conductivity value of PANI-grafted Rayon fiber was increased with % grafting (Table V). The conductivity value of the PANI-grafted Rayon fiber also depends on the nature of initiator used. Here, PMS is a stronger oxidizing agent than PDS, which leads to the formation of a quinoidal structure rather than a benzenoid structure due to over oxidation. This PMS-initiated system showed very low conductivity value when compared with PDS when used as an initiator. Yoke et al.³¹ reported that at higher $[\text{Ce}^{4+}]$, the conductivity was found to be decreased.

The another important factor that affects the conductivity of the conducting polymer was found to be temperature. Here, the graft copolymerization temperature was maintained at 45°C , and definitely should reduce the conductivity value. Jiping et al.³² reported the PPy/PP composite synthesized at higher temperature showed very low conductivity value. According to them, the conductivity value of the composite depends on various experimental conditions like concentration of oxidant, exposure time to aniline and HCl vapors, and concentration of HCl-to-PANI content. The above explanation may be applied to our system also.

Mechanism

A probable mechanism is proposed here to explain the experimental results obtained. The mechanism suggested for graft copolymerization of PANI onto Rayon fiber in this article is based on the mechanism proposed by two research teams. Wei and coworkers²⁸ explains the formation of homopolymer via radical cation, and Bhadani et

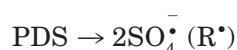
Table V Conductivity Measurements

Polymer	% Grafting	Conductivity $\text{Ohm}^{-1}\text{ cm}^{-1}$
Rayon		2.31 G
Rayon-g-PANI (PDS)	2.11	15M
	9.00	25M
Rayon-g-PANI (PMS)	2.15	3.25M
	12.1	8.90M

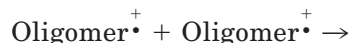
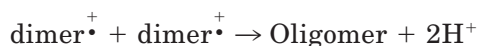
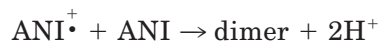
al.³³ proposed a mechanism for the graft copolymerization of PANI onto various natural backbones by the electrochemical method. Also, they explained that the graft copolymerization proceeds through oligomerization. Taking the above two mechanisms as a basis, a probable mechanism is suggested here to explain the modification of Rayon fiber through chemical grafting of PANI.

A probable mechanism for PDS-initiated graft copolymerization of ANI onto Rayon fiber is as follows:

Primary reactions



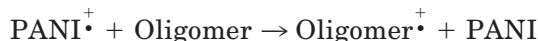
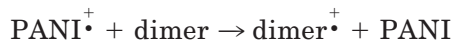
Homopolymerization



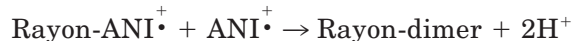
PANI (Homopolymer)



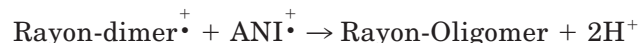
+ PANI (auto acceleration effect)



Graft Copolymerization



Rayon-dimer^{·+} + Products



Rayon-Oligomer^{·+} + Products



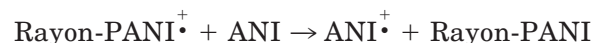
Rayon-Oligomer^{·+} + Products



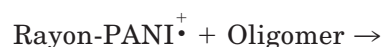
Rayon-g-PANI (Graft copolymer)



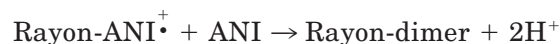
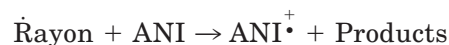
Rayon-PANI^{·+} + Products



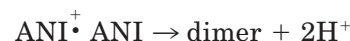
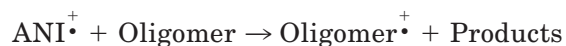
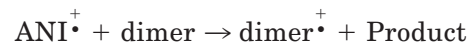
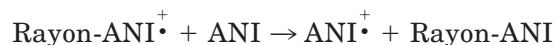
dimer^{·+} + Rayon-PANI



Oligomer^{·+} + Rayon-PANI



(auto acceleration effect)



This mechanism explains the experimental results obtained. A probable mechanism for PMS-initiated graft copolymerization of aniline onto Rayon fiber is as follows.

Primary Reactions



The mechanism of homopolymer and graft copolymer formations are similar to that of PDS with the interchange of PDS by PMS.

CONCLUDING REMARKS

From the above kinetic study the following conclusions are made. (1) Graft copolymerization occurs with simultaneous homopolymer formation. (2) Both R_h and R_g showed first-order dependence on [ANI], [PDS], or [PMS] and (amount of Rayon fiber). (3) Cyclic voltammetric study, FTIR spectral study, weight loss study, and conductivity measurements confirm the chemical grafting of aniline onto Rayon fiber. (4) A probable mechanism has been proposed to explain the experimental results obtained.

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