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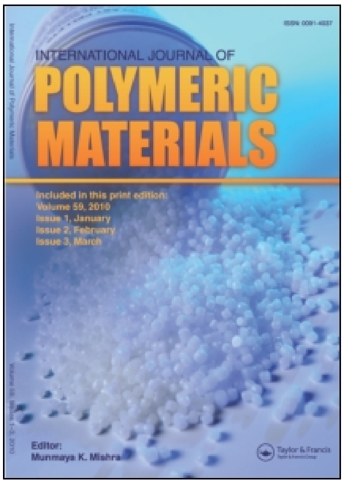

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Peroxosalts Initiated Graft Copolymerization of o-toluidine onto Rayon Fibre - A Kinetic Approach

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Graft copolymerization of o-toluidine (OT) onto Rayon fibre by using peroxy disulphate (PDS) and peroxomonosulphate (PMS) as an initiator in aqueous acidic medium under nitrogen atmosphere was carried out. Rate of homopolymerization, rate of grafting, % grafting and % efficiency were determined. Both rate of homopolymerization and rate of grafting showed first order dependence on [M], [I] and (amount of Rayon fibre). From the experimental results rate constants were evaluated. The modification of Rayon fibre in the form of chemical grafting was confirmed through FTIR, UV-Visible spectroscopy, Cyclic voltammetry, weight loss study and conductivity measurements. Probable mechanism has been proposed to explain the obtained experimental results.

Keywords: Grafting; Poly(o-toluidine); Peroxosalts; Rayon fibre; Rate constant and mechanism

INTRODUCTION

As the interest in graft copolymers has increased over the years, owing to their diversified applications in many different domains, a large variety of methods have been developed for their synthesis. Ionic living

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*Corresponding author.

processes have contributed extensively but they apply to a limited number of cases only. For more general are the methods derived from the polymerization which have been studied in great detail. Gopalan *et al.* [1–3] reported the graft co-polymerization of vinyl polymers onto PET and nylon 6 fibres. Recently Anbarasan and co-workers [4] communicated the results on the graft copolymerization of 4-vinyl pyridine onto wool and nylon 66 fibres.

In recent years conducting polymers with highly extended conjugated electron systems in their backbone have attracted great interest due to their electrical, electrochemical and optical properties [5]. However practical applications of the conducting polymers have been slow owing to certain deficiencies like insolubility, poor mechanical properties, environmental stability and thermal stability [6–8]. In order to ameliorate the above said deficiencies, conducting polymers have been grafted with various natural and synthetic fibres and hence the processability of conducting polymers have been improved. Conducting polymers can be synthesized by various methods. Among those methods chemical methods [9–11] are frequently used due to minimum side reactions. Peroxosalts initiated graft copolymerization of aniline onto nylon 6 fibre was reported by our active research team [12]. Anbarasan *et al.* [13] proved that the thermal stability of conducting polymers were improved by grafting with PET fibre. The conductivity of various natural and synthetic fibres was improved to some magnitude through graft copolymerization of conducting polymers onto their matrix [14, 15]. The thermal stability of poly (aniline)(PANI)/PMMA blend was reported by Yong *et al.* [16].

Abel and co-workers [17] published the results of solvent effect on the morphology of PMMA coated poly(pyrrole) (PPy) surfaces. Chemical grafting of aniline onto nylon 66 fibre in different media was reported and the nature of dopants was discussed on the basis of rate parameters [18]. Currently our dedicated research team communicated some kinetic results on the PMS initiated graft copolymerization of aniline and OT onto PET fibre [19]. Water soluble PANI/P(4-VP) complex was reported and its electrochemical behaviour was tested through cyclic voltammetric (CV) method [20]. Minto and co-workers [21] reported the morphology of PANI/PMMA blend and demonstrated the nature of interaction between the conducting polymer and the backbone matrix. Kinetic results on the chemical grafting of

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conducting polymer onto wool and nylon fibres were reported by Anbarasan and team [22, 23]. Our recent communications bring the report on the kinetics of graft copolymerization of conducting polymer onto PP and Rayon fibres [24, 25]. The conducting polymer coated or grafted textile fibres is used in the field of sensors [26] and corrosion inhibitors [27]. The above research papers, having some interesting experimental results, led us do investigate the grafting capability of poly(o-toluidine) (POT) onto insulating polymer backbone such as Rayon, and the effects of the preparation conditions such as amount of monomer, initiator and Rayon fibre.

EXPERIMENTAL

Materials and Methods

o-Toluidine (SRL 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 such. Rayon fibre (a gift sample from M/S. Madura coats, Madurai, India) was soxhlet extracted with acetone for 24 hours and dried at room temperature before used.

Procedure

A typical graft copolymerization study was conducted as described.

Rayon fibre (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 (o-toluidine) 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 (polymerization 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 hrs) and weighed to obtain its exact 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 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, POT, formed.

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Rate Measurements

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

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

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

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

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

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 OT.

FTIR SPECTROSCOPY

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

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Conductivity Measurements

Conductivity of both POT grafted and pure Rayon fibre was 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.

Cyclic Voltammetry

The POT grafted Rayon fibre (green coloured) was allowed to stand over night in 0.5 N aqueous ammonia solution (the fibre turns blue) then the fibre was washed well with acetone 2 to 3 times to remove any adhering materials which were absorbed on the surface of the fibre. The dried fibre was immersed in formic acid and made into a paste. The paste was dip coated onto a Pt micro working electrode (surface area $9.50 \times 10^{-2}\,\mathrm{cm}^2$). Cyclic voltammograms (CV's) were recorded (by using BAS 100 A Electrochemical Analyzer) for Rayon-g-POT 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

Given weights of the POT grafted Rayon fibre were treated with acetone (30 min) and dried to constant weight. Changes in weight were observed. The fibres were then treated with NMP solution for 4 hrs and removed from NMP, dried under vacuum and weighed. The POT grafted Rayon fibre was soaked with 0.5 N aqu. ammonia solution and isolated from the reaction condition and dried at room temperature. Some 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 recorded. Thus the total % weight loss was determined.

Isolation of POT Grafted Rayon Fibre from POT Homopolymer

The mixture (W_1 g) of the POT grafted Rayon fibre and POT, the homopolymer, was dedoped with 0.5 N aqu. ammonia solution and extracted with N-methyl pyrrolidone (NMP) solution 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 completed and was ascertained by a colourless filtrate. The fibre was dried in vacuum to reach a 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. This can be quantified with UV-Visible spectroscopy. Visible spectrum was recorded till the extract gives nil OD value.

UV-Visible Spectroscopy

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

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RESULTS AND DISCUSSION

Effect of [OT] on R_h and Graft Parameters

[OT] was varied during the graft copolymerization between 0.20 to 0.60 mol l^{-1} while keeping other experimental conditions constant. It is important to note that both R_h and R_g increased with increase in [OT]. It was observed that the R_h values are higher for PDS case whereas the R_g values are higher for PMS case in a given concentration of OT. The % grafting and % efficiency are shown in Table I.

The increase in R_h and R_g may be due to the formation of more and more monomer radical cations. A second reason is the auto

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

	% grafting		*% efficiency*	
[OT] mol l^{-1}	*A*	*B*	*A*	*B*
0.20	1.70	4.25	0.54	1.35
0.30	2.55	5.75	0.54	1.22
0.40	2.75	7.25	0.46	1.14
0.50	4.31	9.05	0.54	1.15
0.60	5.22	10.9	0.55	1.16

A: [PDS] = 0.01 mol l^{-1}, B: [PMS] = 0.02 mol l^{-1}.
A, B: Wt. of Rayon fibre = 0.20 g, HCl = 1.00 M.

acceleration effect caused by the homopolymer surface and POT grafted Rayon fibre surface.

The effect of [OT] on R_h and R_g was analysed kinetically for the PDS system. Plots of $\log R_h$ *vs.* log[OT] (Fig. 1A) and $\log R_g$ *vs.* log[OT] (Fig. 1B) were drawn and the slopes of both plots were found to be one. This indicates the first order dependence of both R_h and R_g on [OT]. The first order dependence was further confirmed by plotting R_h *vs.* [OT] (Fig. 1C) and R_g *vs.* [OT] (Fig. 1D). The linearity of these

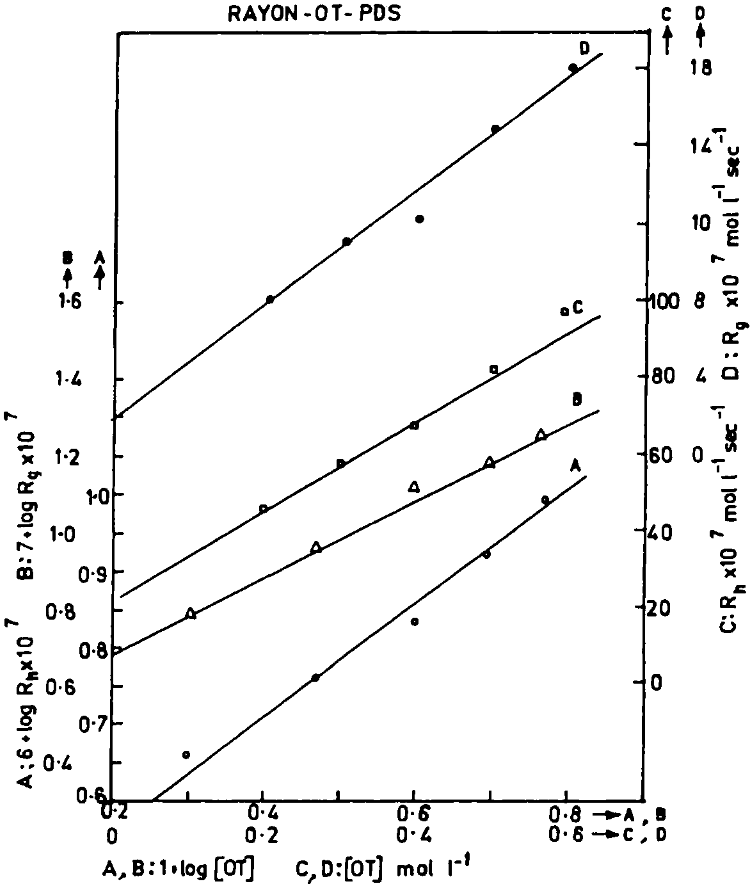

FIGURE 1 Effect of [OT] on R_h and R_g [PDS] = 0.01 mol l^{-1}, Weight of Rayon fibre = 0.20 g, [HCl] = 1.00 M.

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plots confirmed the first order dependence of R_h and R_g on [OT]. The intercept values were noted from the direct plots. The % grafting and % efficiency values are indicated in Table I.

Similar attempts were made for PMS system (Fig. 2). Here also the same first order dependence was noticed. The % grafting and % efficiency reveals the same trend (Tab. I).

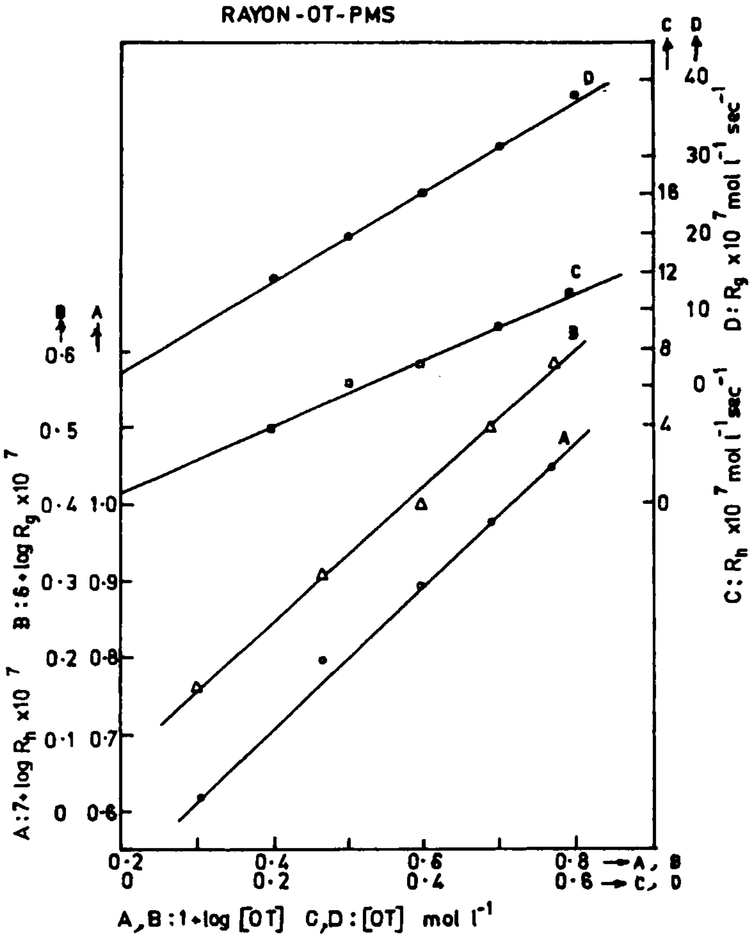

FIGURE 2 Effect of [OT] on R_h and R_g [PMS] = 0.02 mol l^{-1}, Weight of Rayon fibre = 0.20 g, [HCl] = 1.00 M.

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

Table II presents the effect of varying the [PDS] or [PMS] on graft parameters. The [PDS] was varied in the range of 0.005 to 0.025 mol l^{-1} while keeping other experimental conditions constant. The R_h and R_g values increased with increase in [PDS] or [PMS]. R_h values were found to be higher with PDS case and R_g values were higher for PMS system. The % grafting and % efficiency value reveals the same trend (Tab. II).

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

In order to quantify the order dependences the following plots were made. The plots of log R_h *vs.* log[PDS] (Fig. 3A), log R_g *vs.* log[PDS] (Fig. 3B), R_h *vs* [PDS] (Fig. 3C) and R_g *vs.* [PDS] (Fig. 3D) were drawn. The log-log plots indicate the first order dependence of R_h and R_g on [PDS]. The direct plots were linear and passed through the origin.

Similar plots were also drawn for PMS case (Fig. 4). We found first order dependence of R_h and R_g on [PMS]. The direct plots were found to be straight lines passing through the origin. The % grafting and % efficiency values are given in Table II.

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

The effect of amount of Rayon fibre on R_h and graft parameters were studied under the conditions mentioned in Table III. The Rayon fibre weight was varied between 0.10 to 0.35 g while keeping other

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	0.95	3.80	0.20	0.81
0.010	0.020	2.15	5.95	0.45	1.25
0.015	0.030	3.75	8.46	0.80	1.80
0.020	0.040	4.80	11.4	1.02	2.43
0.025	0.050	6.11	12.7	1.30	2.72

A, B: [OT] = 0.30 mol l^{-1}, Wt. of Rayon fibre = 0.20 g, HCl = 1.00 M.
A: [PDS], B: [PMS].

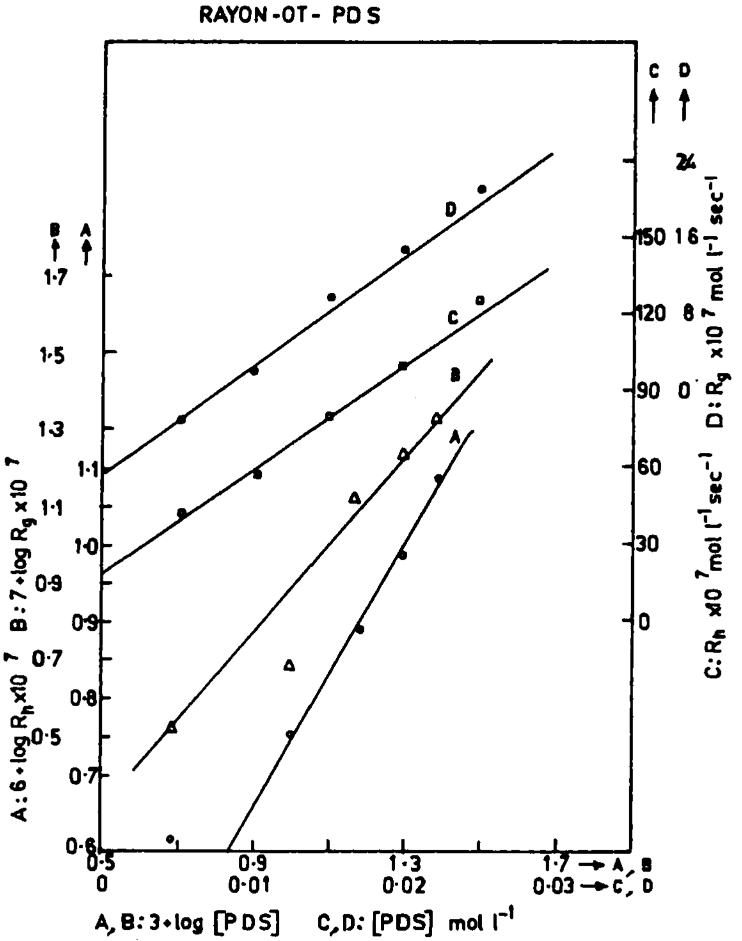

FIGURE 3 Effect of [PDS] on R_h and R_g [OT] = 0.30 mol l^{-1}, Weight of Rayon fibre = 0.20 g, [HCl] = 1.00 M.

experimental conditions constant. Both R_h and R_g showed greater proportion of increase with higher amount of Rayon fibre for both cases. PDS system showed higher R_h and the PMS system showed higher R_g value. The % grafting and % efficiency values are given in Table III.

On increasing the amount of fibre, large number of active sites are possible. These active sites enhance both homopolymerization and graft copolymerization through auto acceleration effect.

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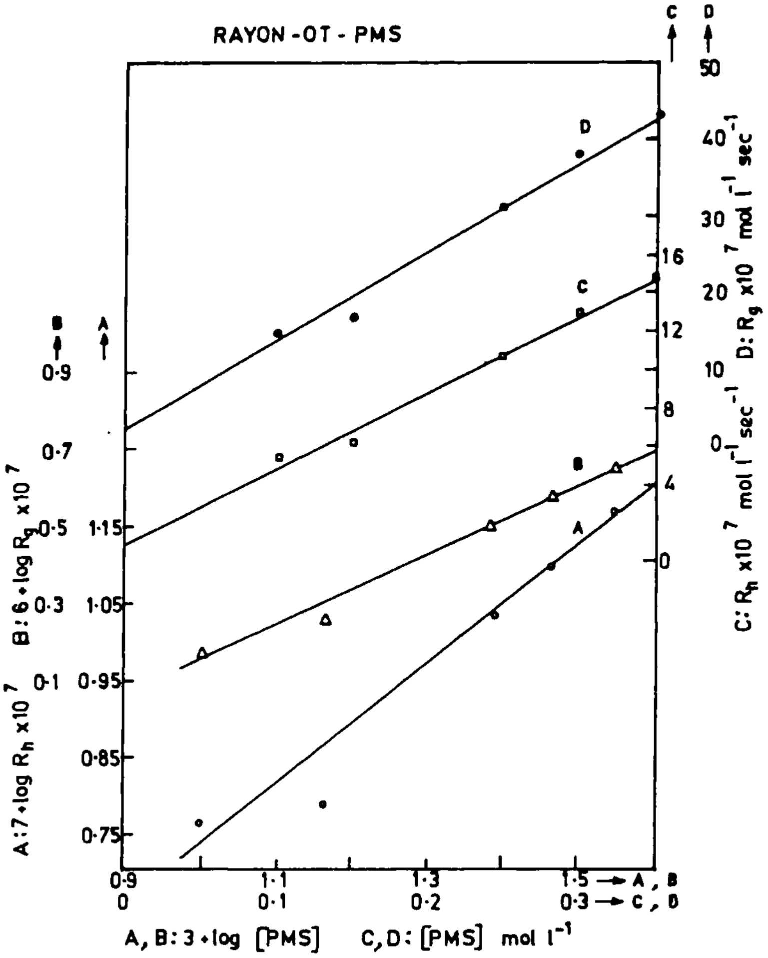

FIGURE 4 Effect of [PMS] on R_h and R_g [OT] = 0.30 mol l^{-1}. Weight of Rayon fibre = 0.20 g, [HCl] = 1.00 M.

TABLE III Effect of (amount of Rayon fibre) on % grafting and % efficiency

(*Amount of Rayon fibre*) (*g*)	% *grafting* *A*	*B*	% *efficiency* *A*	*B*
0.10	2.51	8.71	0.26	0.93
0.15	2.46	6.80	0.39	1.09
0.25	2.68	7.08	0.71	1.89
0.30	2.71	7.41	0.87	2.37
0.35	2.80	7.32	1.05	2.73

A: [PDS] = 0.01 mol l^{-1}, B: [PMS] = 0.02 mol l^{-1}.
A, B: [OT] = 0.30 mol l^{-1}, HCl = 1.00 M.

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In order to quantify the order dependencies for PDS system, plots of $\log R_h$ *vs.* log (amount of Rayon fibre) (Fig. 5A) and $\log R_g$ *vs.* log(amount of Rayon fibre) (Fig. 5B) were made and the slope values were found to be close to one indicating first order dependence of R_h and R_g on (amount of Rayon fibre). It was further checked through plotting R_h *vs.* (amount of Rayon fibre) (Fig. 5C) and R_g *vs.* (amount of Rayon fibre) (Fig. 5D). These plots were found to be linear and

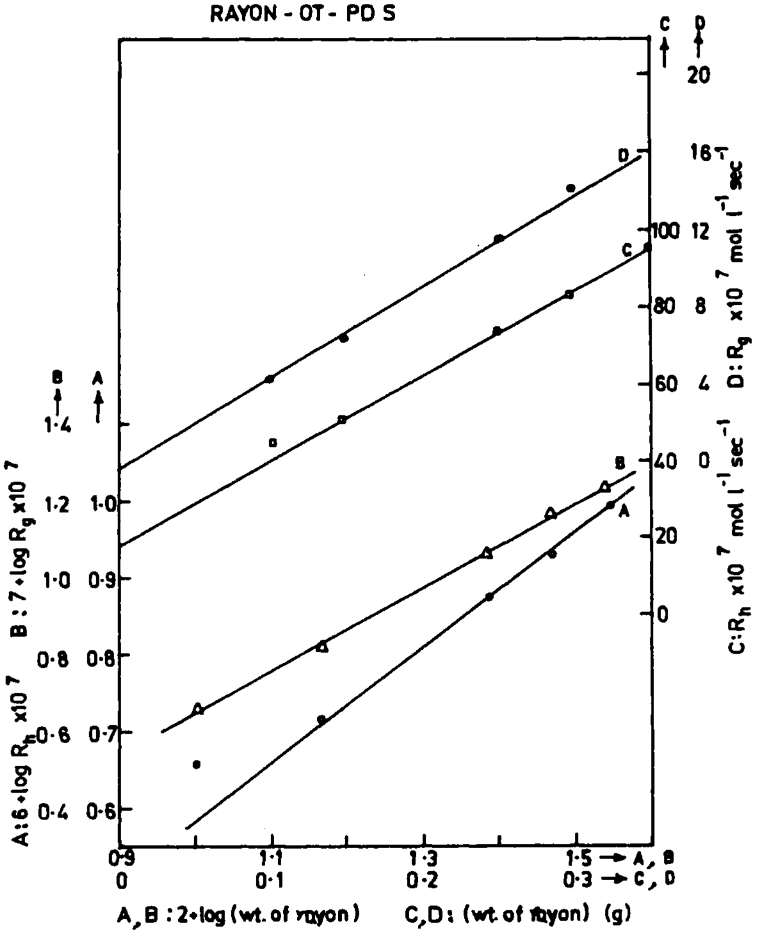

FIGURE 5 Effect of (amount of Rayon fibre) on R_h and R_g [OT] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, [HCl] = 1.00 M.

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passing through the origin. These linear plots support the first order dependence of R_h and R_g on backbone amount.

Similar plots were made for PMS system too (Fig. 6). Figures 6A and B showed the first order dependence of R_h and R_g on (amount of Rayon fibre). The % grafting and % efficiency values are shown in Table III.

Gregory [28] and co-workers studied the effect of added fibre on chemical polymerization of aniline in the presence and absence of

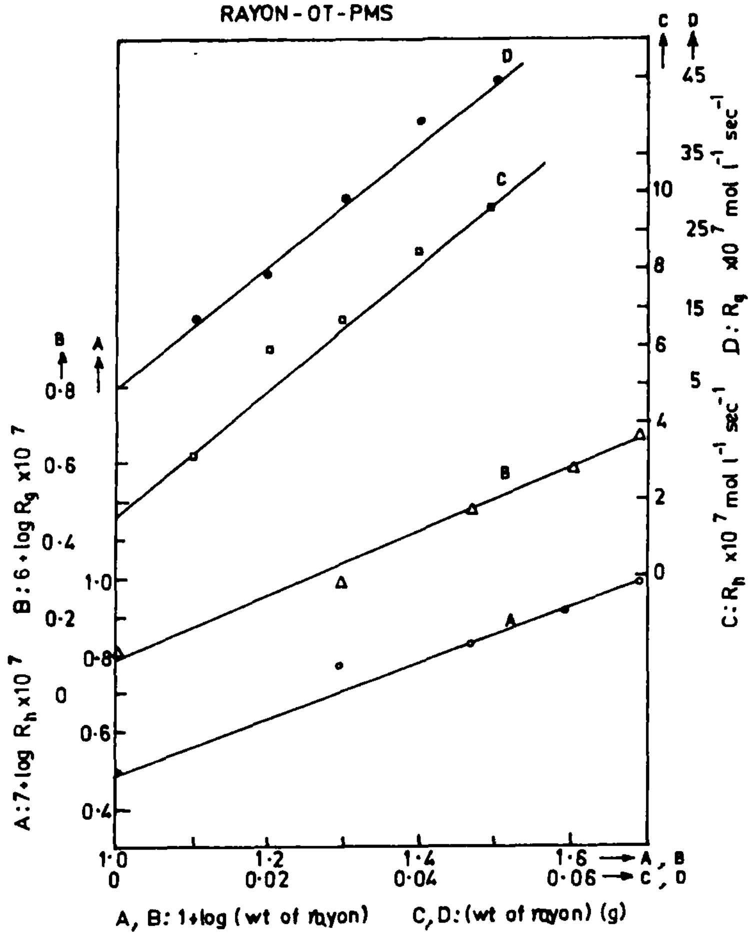

FIGURE 6 Effect of (amount of Rayon fibre) on R_h and R_g [OT] = 0.30 mol l^{-1}, [PMS] = 0.02 mol l^{-1}, [HCl] = 1.00 M.

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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.* [29] 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 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 [30] proposed a kinetic equation for the polymerization of aniline on bare Pt electrode including the auto acceleration effect and proposed a type of the following equation as,

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

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 OT 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 fibre for grafting and the formed homopolymer may cause the auto acceleration effect due to the active surface effect.

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

$$\begin{aligned} R_h(\mathrm{OT}) = {} & k_{1h}[\mathrm{OT}][\mathrm{PDS}](\text{amount of Rayon fibre}) \\ & + k_{2h}[\mathrm{OT}][\mathrm{TAS}] + k_{3h} \end{aligned} \tag{1}$$

where k_{1h} is the rate constant corresponding to homopolymer formation, k_{2h} and k_{3h} are rate constants for the homopolymer formation

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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 obtained from the intercept of the plot of R_h *vs.* [OT] (Fig. 1C).

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

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

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

Gregory *et al.* [28] determined the k_{1h} value as $0.0008\,\mathrm{min}^{-1}$. For the present case, PDS initiated graft copolymerization of OT onto Rayon fibre in aqueous HCl medium, k_{1h} and k_{1g} values are determined from the slope of the plots R_h *vs.* [OT] (Fig. 1C) and R_g *vs.* [OT] (Fig. 1D) using Eqs. (1) and (2) as $7.01 \times 10^{-3}\,\mathrm{g}^{-1}\mathrm{m}^{-1}\mathrm{sec}^{-1}$ and $7.14 \times 10^{-3}\,\mathrm{g}^{-1}\mathrm{m}^{-1}\mathrm{sec}^{-1}$ respectively. This value is far higher than that of the simple homopolymerization rate constant and reflects the auto acceleration effect in homopolymerization by TAS and grafting. The value of k_{3h} was found to be $2.30 \times 10^{-7}\,\mathrm{mol\,l}^{-1}\,\mathrm{sec}^{-1}$ whereas the value of k_{3g} was found to be $0.20 \times 10^{-7}\,\mathrm{mol\,l}^{-1}\,\mathrm{sec}^{-1}$. The above rate constant values indicate that k_{1h} and k_{1g} values are almost equal.

In the case of PMS initiated graft copolymerization of OT onto Rayon fibre, the rate constants were determined by modifying the Eqs. (1) and (2) as

$$\begin{aligned} R_h(\mathrm{OT}) = {} & k_{1h}[\mathrm{OT}][\mathrm{PMS}](\text{amount of Rayon fibre}) \\ & + k_{2h}[\mathrm{OT}][\mathrm{TAS}] + k_{3h} \end{aligned} \tag{3}$$

$$\begin{aligned} R_g(\mathrm{OT}) = {} & k_{1g}[\mathrm{OT}][\mathrm{PMS}](\text{amount of Rayon fibre}) \\ & + k_{2g}[\mathrm{OT}][\mathrm{TAS}] + k_{3g} \end{aligned} \tag{4}$$

The k_{1h} and k_{1g} values are found to be $0.57 \times 10^{-3}\,\mathrm{g}^{-1}\,\mathrm{m}^{-1}\,\mathrm{sec}^{-1}$ and $1.38 \times 10^{-3}\,\mathrm{g}^{-1}\,\mathrm{m}^{-1}\,\mathrm{sec}^{-1}$ respectively. Here the k_{3h} and k_{3g} values are

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found to be $0.8 \times 10^{-7}\,\mathrm{mol\,l^{-1}\,sec^{-1}}$ and $0.25 \times 10^{-7}\,\mathrm{mol\,l^{-1}\,sec^{-1}}$ respectively. In the case of PMS system the rate of grafting was found to be higher than that of the homopolymerization.

In the case of PDS both R_h and R_g values are almost equal. This can be evidenced by the k_{1h} and k_{1g} values. The higher k_{1g} values of PMS system indicates higher value of R_g than R_h. When we compare the PMS and PDS system, the k_{1h} value of the PDS system was found to be higher than that of PMS system. The k_{1g} value for PMS system should be higher than that of PDS case due to the calculation factor, however, the k_{1g} values were found to be very low. {[PDS] = $0.01\,\mathrm{mol\,l^{-1}}$, [PMS] = $0.02\,\mathrm{mol\,l^{-1}}$}.

Cyclic Voltammetry

Cyclic voltammogram (CV) was recorded for Rayon-g-POT film at various sweep rates. The CV showed two anodic peaks (at 410 and 620 mV) and two cathodic peaks (at 300 and 600 mV) (Fig. 7). This is similar to that of CV of POT film at various sweep rates. The CV of POT film showed two anodic peak at 405 and 660 mV and two cathodic peaks at 685 and 267 mV. On increasing the sweep rate both anodic and cathodic peak currents of Rayon-g-POT film showed linear trend. On comparing the CV of Rayon-g-POT film showed some shift in the peak potential value. This may be due to the non-conducting

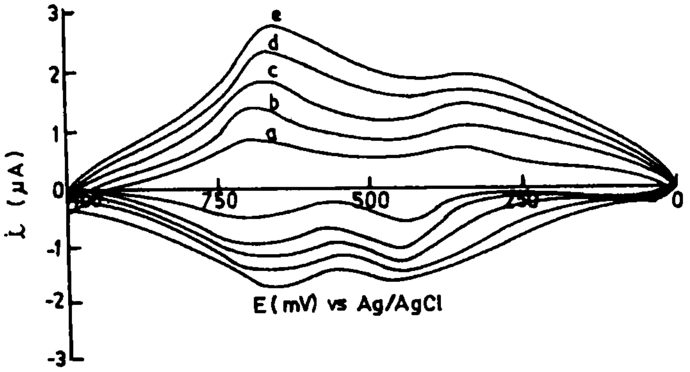

FIGURE 7 Cyclic Voltammogram of Rayon-g-POT film at various sweep rates (a) 100 mV/s, (b) 200 mV/s, (c) 300 mV/s, (d) 400 mV/s, (e) 500 mV/s.

Rayon fibre backbone. These results are in accordance with our earlier communications [13].

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

Weight Loss Study

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

The case of polyanilines methyl substituted at the ortho position leads indirectly to the formation of quinoid form. The bulky methyl substituent present in the ortho position disturbs the stereo regularity. As a result of this disturbance there is a chance to enhance the formation of quinoidal structure. Kang *et al.* [31] reported that during the chemical polymerization of aniline there will be a formation of 50% amino form and 50% imino form. They also 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 PET-g-PANI system [13].

TABLE IV Weight loss study

Process	*% Wt. loss (approximately)*		
(treatment with)	*A*	*B*	*Reason*
Acetone	1	2	Solubility of physisorbed monomer or dimer in acetone
NMP	4	2	Solubility of physisorbed HCl doped POT
Ammonia	12–15	20	Removal of HCl from both physisorbed and grafted POT
NMP	15–17	5	Solubility of all the dedoped physisorbed POT

A: Rayon-PDS-POT.
B: Rayon-PMS-POT.

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Strong oxidizing agents like PMS lead to the quinoidal structure due to over oxidation. Consequently the weight loss is larger. The R_g value showed that there is a complex forming between oxidant and fibre. In this situation, a weight loss from the grafted POT is observed.

(The complex formation between oxidant and fibre was confirmed through PDS or PMS analysis method. Graft copolymerization was carried out in the absence of monomer for different concentration of oxidant at 45°C. After 30 min the unreacted oxidant was estimated by volumetric method. The results indicates there is no unreacted oxidant. That means all the oxidant molecules are broken into active free radicals. Subsequently these free radicals activate the Rayon fibre backbone through direct interaction with the reactive sites present on the Rayon fibre backbone).

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

Regarding the backbone used, Rayon contains many active functional groups and substituents that causes the physisorbtion of POT onto the surface of the backbone. The physisorption takes place between fibre and monomer or polymer through secondary forces. Here, the secondary bond formation is possible only between hetero atom of the backbone and benzenoid structure of the POT unit. In the case of PP fibre the amount of physisorbed POT was found to be very low due to the absence of hetero atom on the PP backbone. From our earlier communications, it was observed that the natural fibre showed higher % weight loss than the synthetic backbone [13, 14, 18, 19]. Here, PDS showed weight loss from the homopolymer and PMS showed weight loss from the graft copolymer in different processes.

INFRA RED SPECTROSCOPY

The FTIR spectrum of Rayon-g-POT is given in Figure 8. The peak at $1269\,cm^{-1}$ is due to C—N stretching of the secondary amines. The peak for the symmetry bending of —CH_3 group appears at

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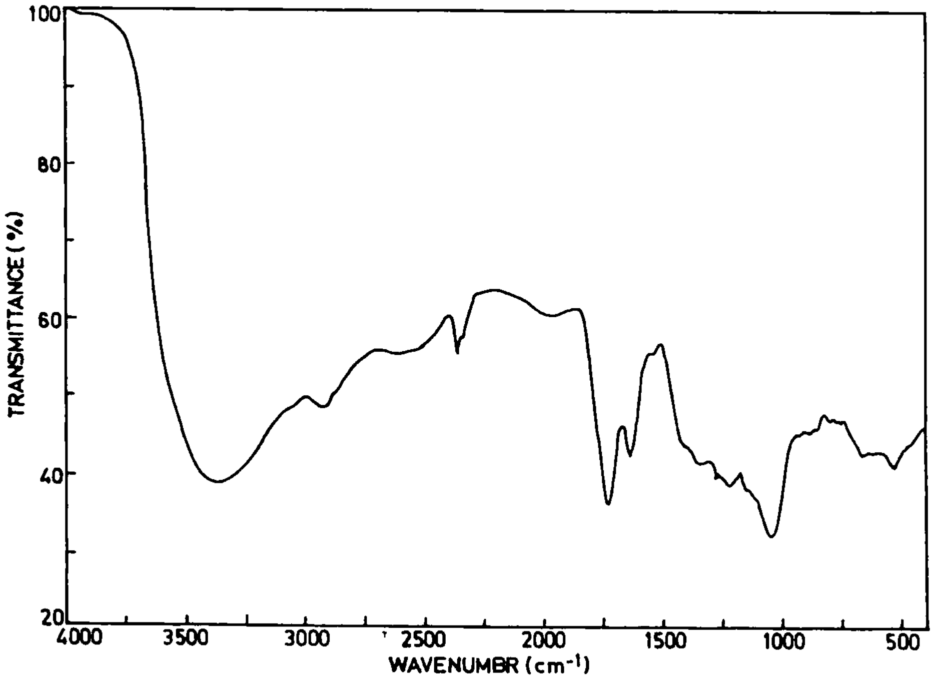

FIGURE 8 FTIR spectroscopy of Rayon-g-POT fibre.

$1373\,cm^{-1}$. The 1645, 1423 and $1373\,cm^{-1}$ peaks correspond to C—N bond. The other peaks correspond to the Rayon backbone fibre. The presence of POT structure in the grafted fibre as evident from spectral data, confirms the incorporation of POT units onto Rayon backbone matrix.

Isolation of POT Grafted Rayon Fibre from Homopolymer

The POT grafted Rayon fibre was removed from the homopolymer and dedoped with 0.5 N aqu.ammonia solution for 4 hrs and then extracted with NMP solution. After a definite interval of time, the fibre was removed from the NMP solution, and the extract was tested for POT 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 580 nm. This is due to excitation transition caused by interchain and intra charge transfer. It can be seen that the OD value was decreased with increase in extraction time. After 12 hrs of extraction with NMP, all the physisorbed POT was completely removed. The visible spectrum of POT at various extraction time intervals for PDS and PMS system were critically compared. The PDS system showed a peak at 580 nm whereas PMS system showed the peak at 562 nm. There is difference in the wavelength of the peak which is due to the difference in the degree of oxidation of the initiator. It is noteworthy that 624 nm band for PANI appears now for POT at a lower wavelength (580 nm). This is due to the decrease in conjugation length and due to the methyl substituent which causes steric effect. This blue shift has been earlier attributed to structural changes resulting in an increase in oxidation state or decrease in conjugation [32].

It is quite interesting to note that even after the removal of the homopolymer, the fibre was found to be blue in colour. This strongly favours definite modification in the form of chemical grafting of POT onto Rayon fibre. To supplement the chemical grafting of POT further studies have also been made.

Conductivity Measurements

The conductivity value of POT grafted Rayon fibre was increased with % grafting (Tab. V). But when compared with PANI grafted

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TABLE V Conductivity measurements

Polymer	*% grafting*	*Conductivity Ohm^{-1} cm^{-1}*
Rayon	–	2.31 G
Rayon-g-POT	8.91	4.12 G
(PDS)	18.9	5.86 G
Rayon-g-POT	14.9	3.13 G
(PMS)	25.3	3.80 G

Rayon fibre, it showed very low conductivity value. This is because of the bulky methyl group present in the ortho position that leads to a steric repulsion. As a result, the structural regularity of POT was disturbed and thus the resonance stabilization reduced. Due to this reason the conductivity values of POT grafted Rayon fibre were found to be very low when compared with PANI grafted Rayon fibre. This confirms that the substituent present on the ring will reduce the conductivity value.

The conductivity value of the POT grafted Rayon fibre also depends on the nature of initiator used. Here PMS is a stronger oxidizing agent than PDS, that leads to the formation of quinoidal structure rather than benzenoidal structure due to over oxidation. This PMS initiated system showed very low conductivity value when compared with a system where PDS was used as an initiator. Yoke *et al.* [33] reported that at higher [Ce^{4+}], the conductivity was found to decrease.

Temperature was found to be another one important factor which affects the conductivity of the conducting polymer. Here the graft copolymerization temperature was maintained at 45°C and definitely that should reduce the conductivity value. Jiping *et al.* [34] 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 such as concentration of oxidant, exposure time to aniline and HCl vapours, and concentration of HCl to PANI content. The above explanation may be applied to our system too.

MECHANISM

A probable mechanism is proposed here to explain the experimental results obtained. The mechanism suggested for graft copolymerization

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of POT onto Rayon fibre in this paper is based on the mechanism proposed by two research teams. Wei and co-workers [29] explains the formation of homopolymer *via* radical cation and Bhadani *et al.* [35] proposed a mechanism for the graft copolymerization of PANI onto various natural backbones by electrochemical method. They further 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 PP fibre through chemical grafting of POT.

Probable mechanism for PDS initiated graft copolymerization of OT onto Rayon fibre is as follows:

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Primary Reactions

$$\mathrm{OT} + \mathrm{PDS} \rightarrow \mathrm{OT}^{\overset{+}{\bullet}} + \mathrm{Products}$$

$$\mathrm{PDS} \rightarrow 2\mathrm{SO_4}^{\bar{\bullet}}(\mathrm{R}^{\bullet})$$

$$\mathrm{R}^{\bullet} + \mathrm{Rayon} \rightarrow \dot{\mathrm{R}}\mathrm{ayon} + \mathrm{Products}$$

$$\mathrm{R}^{\bullet} + \mathrm{OT} \rightarrow \mathrm{OT}^{\overset{+}{\bullet}} + \mathrm{Products}$$

Homopolymerization

$$\mathrm{OT}^{\overset{+}{\bullet}} + \mathrm{OT} \rightarrow \mathrm{dimer} + 2\mathrm{H}^{+}$$

$$\mathrm{dimer} + \mathrm{R}^{\bullet} \rightarrow \mathrm{dimer}^{\overset{+}{\bullet}} + \mathrm{Products}$$

$$\mathrm{dimer} + \mathrm{PDS} \rightarrow \mathrm{dimer}^{\overset{+}{\bullet}} + \mathrm{Products}$$

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

$$\mathrm{Oligomer} + \mathrm{PDS} \rightarrow \mathrm{Oligomer}^{\overset{+}{\bullet}} + \mathrm{Products}$$

$$\mathrm{Oligomer} + \mathrm{R}^{\bullet} \rightarrow \mathrm{Oligomer}^{\overset{+}{\bullet}} + \mathrm{Products}$$

$$\mathrm{Oligomer}^{\overset{+}{\bullet}} + \mathrm{Oligomer}^{\overset{+}{\bullet}} \rightarrow \mathrm{POT}\ (\mathrm{Homopolymer})$$

$$\mathrm{POT} + \mathrm{R}^{\bullet} \rightarrow \mathrm{POT}^{\overset{+}{\bullet}} + \mathrm{Products}$$

$$\mathrm{POT} + \mathrm{PDS} \rightarrow \mathrm{POT}^{\overset{+}{\bullet}} + \mathrm{Products}$$

$$\mathrm{POT}^{\overset{+}{\bullet}} + \mathrm{OT} \rightarrow \mathrm{OT}^{\overset{+}{\bullet}} + \mathrm{POT}\ (\text{auto acceleration effect})$$

$$\mathrm{POT}^{\overset{+}{\bullet}} + \mathrm{dimer} \rightarrow \mathrm{dimer}^{\overset{+}{\bullet}} + \mathrm{POT}$$

$$\mathrm{POT}^{\overset{+}{\bullet}} + \mathrm{Oligomer} \rightarrow \mathrm{Oligomer}^{\overset{+}{\bullet}} + \mathrm{POT}$$

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Graft Copolymerization

$$\text{OT} + \dot{\text{R}}\text{ayon} \rightarrow \text{Rayon-OT} + 2\text{H}^{+}$$

$$\text{Rayon-OT} + \text{PDS} \rightarrow \text{Rayon-OT}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-OT} + \text{R}^{\bullet} \rightarrow \text{Rayon-OT}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-OT}^{\overset{+}{\bullet}} + \text{OT}^{\overset{+}{\bullet}} \rightarrow \text{Rayon-dimer} + 2\text{H}^{+}$$

$$\text{Rayon-dimer} + \text{PDS} \rightarrow \text{Rayon-dimer}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-dimer} + \text{R}^{\bullet} \rightarrow \text{Rayon-dimer}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-dimer}^{\overset{+}{\bullet}} + \text{OT}^{\overset{+}{\bullet}} \rightarrow \text{Rayon-Oligomer} + 2\text{H}^{+}$$

$$\text{Rayon-Oligomer} + \text{PDS} \rightarrow \text{Rayon-Oligomer}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-Oligomer} + \text{R}^{\bullet} \rightarrow \text{Rayon-Oligomer}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-Oligomer}^{\overset{+}{\bullet}} + \text{Oligomer}^{\overset{+}{\bullet}} \rightarrow \text{Rayon-g-POT (Graft copolymer)}$$

$$\text{Rayon-POT} + \text{R}^{\bullet} \rightarrow \text{Rayon-POT}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-POT} + \text{PDS} \rightarrow \text{Rayon-POT}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-POT}^{\overset{+}{\bullet}} + \text{OT} \rightarrow \text{OT}^{\overset{+}{\bullet}} + \text{Rayon-POT}$$

$$\text{Rayon-POT}^{\overset{+}{\bullet}} + \text{dimer} \rightarrow \text{dimer}^{\overset{+}{\bullet}} + \text{Rayon-POT}$$

$$\text{Rayon-POT}^{\overset{+}{\bullet}} + \text{Oligomer} \rightarrow \text{Oligomer}^{\overset{+}{\bullet}} + \text{Rayon-POT}$$

$$\text{Rayon} + \text{OT} \rightarrow \text{OT}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{Rayon-OT}^{\overset{+}{\bullet}} + \text{OT} \rightarrow \text{Rayon-dimer} + 2\text{H}^{+} \text{ (auto acceleration effect)}$$

$$\text{Rayon-OT}^{\overset{+}{\bullet}} + \text{OT} \rightarrow \text{OT}^{\overset{+}{\bullet}} + \text{Rayon-OT}$$

$$\text{OT}^{\overset{+}{\bullet}} + \text{dimer} \rightarrow \text{dimer}^{\overset{+}{\bullet}} + \text{Product}$$

$$\text{OT}^{\overset{+}{\bullet}} + \text{Oligomer} \rightarrow \text{Oligomer}^{\overset{+}{\bullet}} + \text{Products}$$

$$\text{OT}^{\overset{+}{\bullet}}\ \text{OT} \rightarrow \text{dimer} + 2\text{H}^{+}$$

This mechanism explains the experimental results obtained. Probable mechanism for PMS initiated graft copolyemrization of OT onto Rayon fibre is as follows.

Primary Reactions

$$\mathrm{OT} + \mathrm{PMS} \rightarrow \mathrm{OT}^{\stackrel{+}{\bullet}} + \mathrm{Products}$$

$$\mathrm{PMS\ (aqu)} \rightarrow \mathrm{HSO_4}^{\bar{\bullet}} + \dot{\mathrm{O}}\mathrm{H}(\mathrm{R}^{\bullet}) + \mathrm{H_2O}$$

$$\mathrm{R}^{\bullet} + \mathrm{Rayon} \rightarrow \dot{\mathrm{R}}\mathrm{ayon} + \mathrm{Product}$$

$$\mathrm{R}^{\bullet} + \mathrm{OT} \rightarrow \mathrm{OT}^{\stackrel{+}{\bullet}} + \mathrm{Product}$$

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

CONCLUSIONS

From the above kinetic results the following conclusions were made.

1. During the graft copolymerization, simultaneous homopolymerization also took place.
2. Both R_h and R_g showed first order dependence on $[M]$, $[I]$ and (amount of Rayon fibre).
3. The chemical grafting was confirmed through FTIR spectroscopy, cyclic voltammetric methods and conductivity measurements.

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