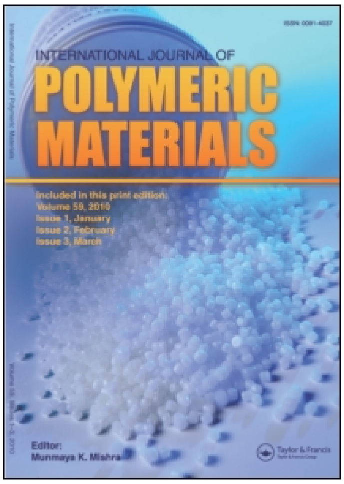

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Anbarasan, R. , Jayaseharan, J. , Sudha, M. , Nirmala, P. V. and Gopalan, A.(2001) 'Peroxy Disulphate Initiated Graft Copolymerization of o-toluidine onto Wool and Nylon6 Fibres -A Kinetic Approach', International Journal of Polymeric Materials, 49: 4, 379 — 406

To link to this Article: DOI: 10.1080/00914030108035873

URL: http://dx.doi.org/10.1080/00914030108035873

Intern. J. Polymeric Mater., 2001, Vol. 49, pp. 379-406
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Peroxy Disulphate Initiated Graft Copolymerization of *o*-toluidine onto Wool and Nylon6 Fibres – A Kinetic Approach

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(Received 2 January 2000; In final form 3 March 2000)

Graft copolymerization of *o*-toluidine (OT) onto wool and nylon6 fibres were carried out by using Peroxy disulphate (PDS) as a lone initiator in aqueous acidic medium under nitrogen atmosphere. Various graft parameters like % grafting, % grafting efficiency and rate of grafting were determined. Grafting occurs with simultaneous homopolymer formation. Rate of homopolymerization was also followed. The content of poly(*o*-toluidine) (POT) in the backbone fibres were found to vary while changing the [OT], [PDS], (amount of fibre). Chemical grafting was confirmed by FTIR spectroscopy, cyclicvoltammetry (CV) and conductivity measurements. Probable mechanism has been proposed to explain the experimental results obtained.

Keywords: Grafting; Poly(*o*-toluidine); Kinetics; FTIR; CV; Mechanism

INTRODUCTION

Nowadays natural and synthetic polymer backbones are modified suitably such that their inherent properties are improved and are thus

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tailor made for certain end use applications. Various methods are available for such modification. Among those methods graft copolymerization is one of the technique used by polymer chemists for modifying chemical [1] and mechanical [2] properties of the polymer backbones. A wide range of vinyl monomers have been graft copolymerized onto various natural and synthetic polymer backbones by using a number of redox initiating systems [3–6]. For the past few decades aniline and its derivatives were polymerized either chemically or electrochemically [8] in aqueous acidic medium. Among them, chemical method is of particular importance because it provides the most feasible route for the production of polyaniline(PANI) and its derivatives in large scale [7].

Aniline and its derivatives can be polymorized by using PDS [9], Peroxo monosulphate (PMS) [10], hydrogen peroxide [11], dichromate [12], chromyl chloride [13], ferric chloride [14], Ce(IV) sulphate [15], $KMnO_4$ [16], AsF_5 [17]. Unfortunately the processability of conducting polymer was unknown for long time due to its insolubility in common organic and inorganic solvents. Several approaches have been made to improve the processability of the conducting polymers. Among those blending of conducting polymer with conventional polymer is an important and economic method due to its ease of preparation. Changjiang *et al.* [18] made a transparent and conducting PANI-PET composite films and it was characterized by UV-visible and SEM analysis.

In order to improve the processability of the conducting polymer, several conventional polymer based blends have been synthesized by many researchers [19–25]. Recently Toppare and co-workers [26] prepared a conducting polymer composite and he reported that the composite showed good conductivity and air stability. In 1992, Gregory and colleagues [27] grafted PANI onto PET and nylon6 fibres. For the first time they proposed some kinetic equations. The possibililty of grafting between conducting polymer and an insulating polymer was studied *via* semi-empirical methods [28]. Hochfilzer and co-workers [29] grafted oligo(phenylene vinylene) onto polystyrene backbone. Li *et al.* [30], grafted PANI onto poly(amino styrene) backbone by using PDS as an initiator.

In the above mentioned literatures, there is no systematic kinetic approach available to study the graft copolymerization of conducting polymers onto textile fibres. For the first time our research team published comparative and systematic analysis of the kinetic results on the peroxosalts initiated graft copolymerization of aniline onto nylon6 [31] and wool fibres [32]. Anbarasan and co-workers [33] reported the PDS initiated graft copolymerization of aniline and *o*-toluidine onto PET fibre. Peroxosalts initiated graft copolymerization of aniline and *o*-toluidine onto poly(propylene) [34] and rayon [35, 36] fibres were reported by Anbarasan and colleagues. And also we communicated the peroxomonosulphate initiated graft copolymerization of OT onto PET [37] and poly(propylene) [38] fibres. Currently we reported some PDS and PMS initiated graft copolymerization of aniline and OT onto nylon66 [39], nylon6 [40], wool [41] and PET [42] fibres. Such type of conducting polymer grafted textile fibres are used in EMI shielding [43], electrochemical cells [44], secondary batteries [45] and sensors [46]. This research paper reports the analysis of the kinetic results on the graft copolymerization of OT onto nylon6 and wool fibres.

EXPERIMENTAL SECTION

Materials and Methods

OT (SRL AR) was used after distillation under vacuum. Potassium peroxydisulphate (PDS) (CDH AR), HCl (Fischer AR) and other chemicals were used as such. Nylon6 fibre (a gift sample from M/s. Madura coats, Madurai, India) and wool (a gift sample from M/s. J. K. Synthetics, Kota, Rajasthan) were soxhlet extracted with acetone for 24 hours and dried at room temperature before used.

Procedure

A typical graft copolymerization study was conducted as described.

Nylon6 or wool 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 (OT) was added and deaerated for another 15 min. Graft copolymerization was initiated by the addition of calculated volumes of PDS (using standard solutions). The time of adding 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 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 until get the constant weight. This gives the total weight of the grafted polymer along with the homopolymer (W_2 g). The grafted nylon6 or wool fibre was soxhlet extracted with NMP for several hours to remove the homopolymer (no colour changes were seen in the grafted fibre). The extraction was repeated until separation of the homopolymer from the grafted sample was completed. This was ascertained by drying the fibre in vacuum to constant weight (W_3 g). The difference in (W_3-W_1) gives the weight of the grafted polymer. The difference, in (W_2-W_3) gives the weight of the homopolymer, POT, formed.

Rate Measurements

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

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

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

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

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

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

Isolation of POT Grafted Nylon6 or Wool Fibre from POT, Homopolymer

The mixture (W_1 g) of the POT grafted Nylon6 or wool 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 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 homopolymer formed. This can be quantified with UV-visible spectroscopy. Visible spectrum was recorded till the extract gives nil OD value.

Cyclic Voltammetry

The POT grafted Nylon6 or wool fibre (HCl doped, green coloured) was allowed to stand over night in 0.5 N aqueous ammonia solution (the fibre turns into blue colour) then the fibre was washed well with acetone for 2–3 times to remove any adhering materials which were absorbed on the surface of the fibre. The dried fibre was immersed in formic acid and made into a paste. The paste was dip coated onto a Pt micro working electrode (surface area $9.50 \times 10^{-2} \text{cm}^2$). Cyclic voltammograms (CV's) were recorded (by using BAS 100 A Electrochemical Analyzer) for Nylon6-g-POT or Wool-g-POT films 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.

FTIR Spectroscopy

The FTIR spectrum was recorded for Nylon6-g-POT, Wool-g-POT samples by using Bruker FTIR Equinox 55 model instrument by KBr pelletisation method.

Weight Loss Study

Definite weight of the POT grafted Nylon6 or wool fibre was treated with acetone (30 min) and dried to constant weight. A change in weight was observed. Then treated with NMP for 4 hrs and removed from NMP, dried under vacuum and weighed. The POT grafted nylon6 or wool fibre was soaked with 0.5 N aqu. ammonia solution and isolated from the reaction condition and dried at room temperature. Some weight loss was noticed due to the dedoping process. It was once again treated with NMP for 4 hrs, dried under vacuum condition and weighed. Change in weight was inferred. Thus the total % weight loss was determined.

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.

Conductivity Measurements

Conductivity of both POT grafted and pure nylon6 and wool fibres were measured by using Keithly 617 Programmable Electrometer Instrument. 1 cm length of the fibre sample was taken and its two ends were connected with two poles of the electrometer instrument. Current was passed through the poles and the conductivity was displayed and recorded.

RESULTS AND DISCUSSION

Effect of [OT] on R_h and Graft Parameters

Experimental results obtained by changing the [OT] in the range from 0.20 to 0.60 mol l^{-1} using PDS as a lone initiator while keeping other experimental conditions constant. It is important to note that both R_h and R_g increased with increase in [OT]. The R_h values are higher for Nylon6 system than wool system. The R_g values of both systems are almost equal. The % grafting and % efficiency are shown in Table I.

In order to find out the order dependences for Nylon6 system, the plots of logR_h *vs.* log[OT] (Fig. 1A) and logR_g *vs.* log[OT] (Fig. 1B) were drawn and it showed a first order dependence of both R_h and R_g on [OT]. It was further confirmed by plotting R_h *vs.* [OT] (Fig. 1C) and R_g *vs.* [OT] (Fig. 1D). The linearity of these plots confirm the first order dependence of R_h and R_g on [OT]. The intercept values of the plots R_h *vs.* [OT] (Fig. 1C) and R_g *vs.* [OT] (Fig. 1D) were noted.

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

[OT]	*% grafting*		*% efficiency*		*[PDS]*	*% grafting*		*% efficiency*	
mol l^{-1}	*a*	*b*	*a*	*b*	*mol* l^{-1}	*c*	*d*	*c*	*d*
0.20	5.30	5.30	0.99	1.00	0.005	3.75	6.08	0.47	0.76
0.30	8.21	8.34	1.02	1.04	0.010	5.30	12.7	0.67	1.59
0.40	10.8	10.8	1.01	1.02	0.015	8.70	18.4	1.09	2.29
0.50	13.4	13.4	1.01	1.02	0.020	11.5	26.8	1.44	3.33
0.60	17.0	16.9	1.07	1.06	0.025	14.1	33.7	1.76	4.20

a,b: [PDS] = 0.01 mol l^{-1}; a,c: Wt. of nylon6 = 0.20 g; b,d: Wt. of wool fibre = 0.20 g; c,d: [OT] = 0.30 mol l^{-1}; a,b,c,d: HCl = 1.00 M, Temperature = 45°C.

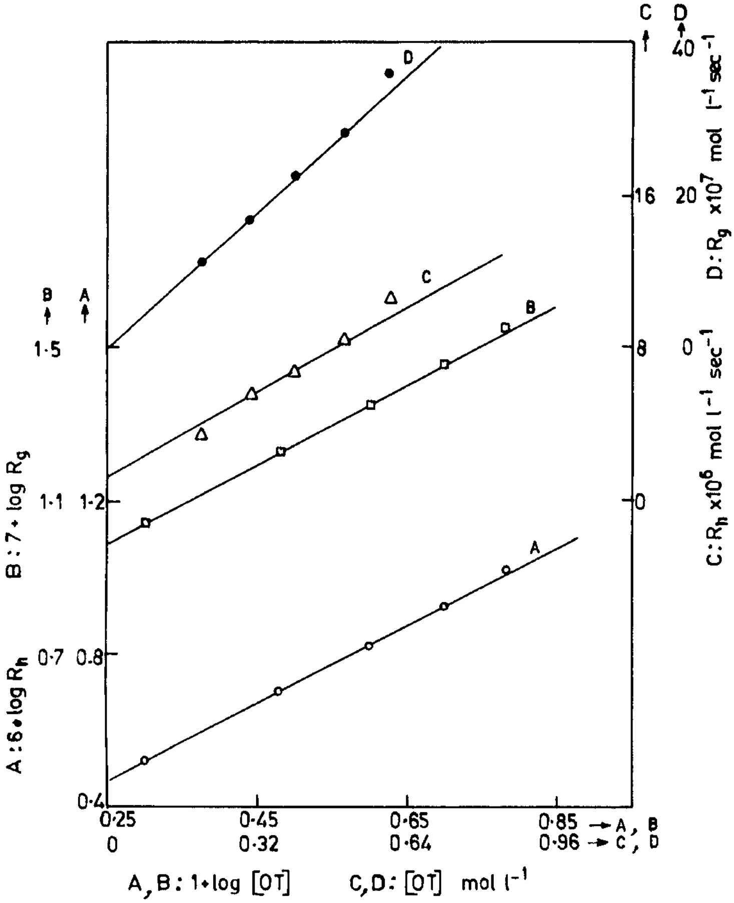

FIGURE 1 Effect of [OT] on R_h and R_g. [PDS] = 0.01 mol l^{-1}, Weight of Nylon6 fibre = 0.20 g, [HCl] = 1.00 M.

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 auto acceleration caused by the homopolymer surface and POT grafted Nylon6 or wool fibre's surface.

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

Effect of [PDS] on R_h and Graft Parameters

The [PDS] was varied from 0.005 to 0.025 mol l^{-1} while keeping other experimental conditions as constant. The R_h and R_g values increased

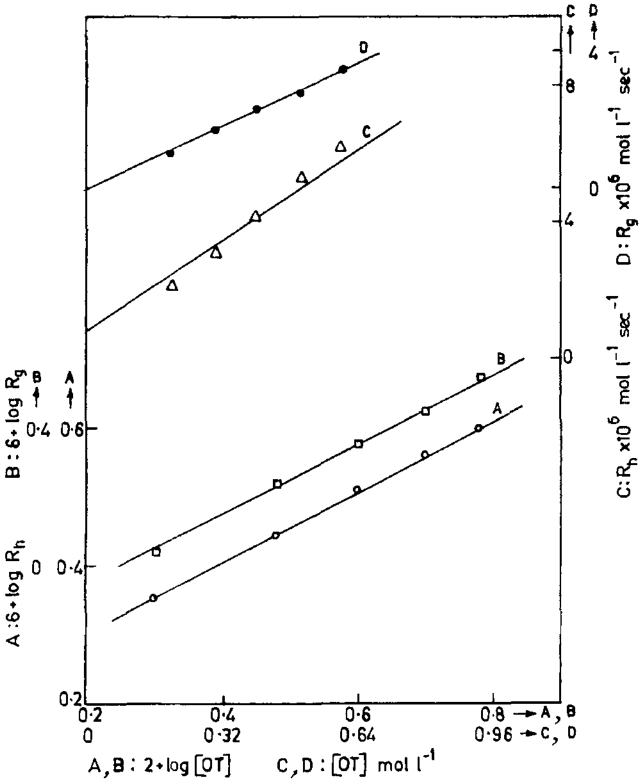

FIGURE 2 Effect of [OT] on R_h and R_g. [PDS] = 0.01 mol l^{-1}, Weight of Wool fibre = 0.20 g, [HCl] = 1.00 M.

with increase in [PDS]. Here also both R_h and R_g increased with increase in [PDS]. At lower concentration of PDS both systems are having almost same R_h values whereas at higher [PDS], the nylon6 system showed higher values of R_h. Wool system showed greater values of R_g than nylon6 system. The % grafting and % efficiency values are given in Table I.

The plots of logR_h *vs.* log[PDS] (Fig. 3A), logR_g *vs.* log[PDS] (Fig. 3B), R_h *vs.* [PDS] (Fig. 3C) and R_g *vs.* [PDS] (Fig. 3D) were drawn for nylon6 system. Figures 3A and 3B 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.

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

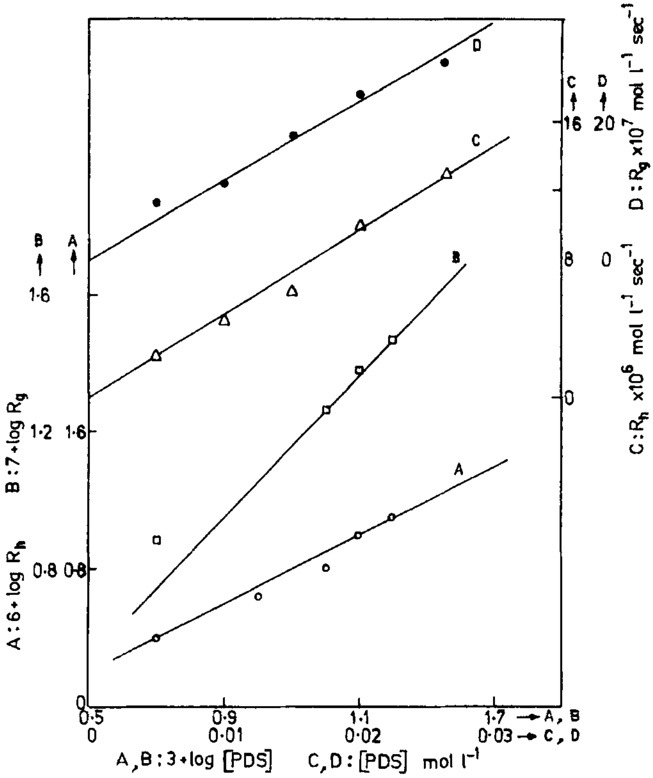

FIGURE 3 Effect of [PDS] on R_h and R_g. $[OT] = 0.30\,mol\,l^{-1}$, Weight of Nylon6 fibre = 0.20 g, [HCl] = 1.00 M.

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

Effect of (Amount of Nylon6 or Wool Fibre) on R_h and Graft Parameters

The effect of amount of Nylon6 fibre on R_h and graft parameters were studied under the conditions mentioned in Table II. The nylon6 fibre weight was varied between 0.10 to 0.35 g while keeping other experimental conditions as constant. Nylon6 showed higher R_h values

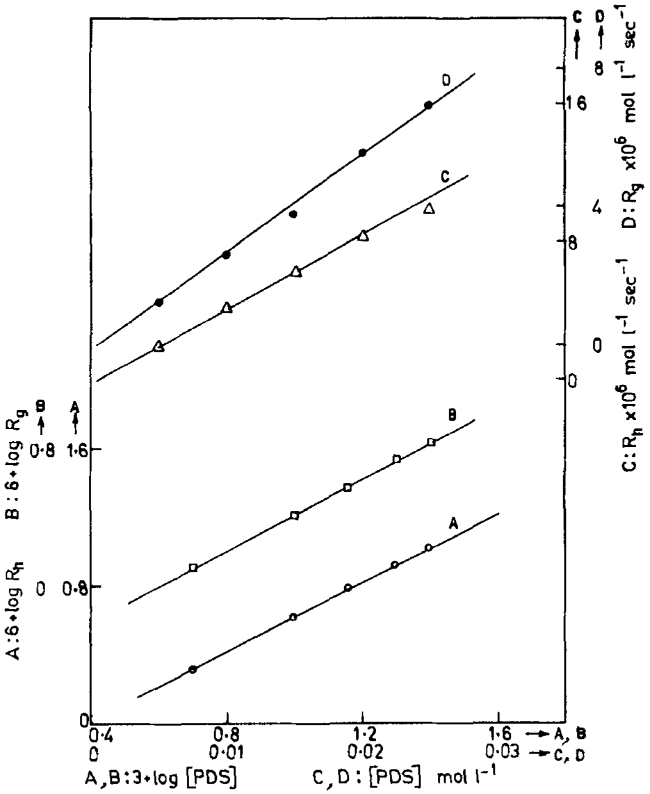

FIGURE 4 Effect of [PDS] on R_h and R_g. [OT] = 0.30 mol l^{-1}, Weight of Wool fibre = 0.20 g, [HCl] = 1.00 M.

TABLE II Effect of (weight of fibre) on % grafting and % efficiency

Wt. of fibre	*% grafting*		*% efficiency*	
(*g*)	*a*	*b*	*a*	*b*
0.10	4.20	7.90	0.26	0.49
0.15	4.28	8.10	0.44	0.76
0.25	4.47	7.95	0.70	1.24
0.30	4.44	7.90	0.83	1.49
0.35	4.38	7.83	0.95	1.70

a,b: [OT] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, HCl = 1 M; a: Nylon6 fibre; b: Wool fibre.

where wool system showed higher R_g values. The % grafting and % efficiency values are also given in Table II.

In an attempt to quantify the order dependences for Nylon6 system, the plots of logR_h *vs.* log(amount of nylon6 fibre) (Fig. 5A) and logR_g *vs.* log(amount of nylon6 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 nylon6 fibre). Further it was checked through plotting R_h *vs.* (amount of nylon6 fibre) (Fig. 5C) and R_g *vs.* (amount of nylon6 fibre) (Fig. 5D). These plots were found to be linear and passing through the origin. These linear plots support the first order dependence of R_h and R_g on backbone amount.

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

On increasing the amount of fibre, the amount of macroradicals also increased. These active sites enhance both homopolymerization and graft copolymerization through auto acceleration effect.

Gregory [27] and co-workers studied the effect of added fibre on the chemical polymerization of aniline in the presence and absence of PET fibre. No correlation was found in that study to relate the changes in the rate of homopolymerization. In the electrochemical polymerization of anilines, Wei *et al.* [47] 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:

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

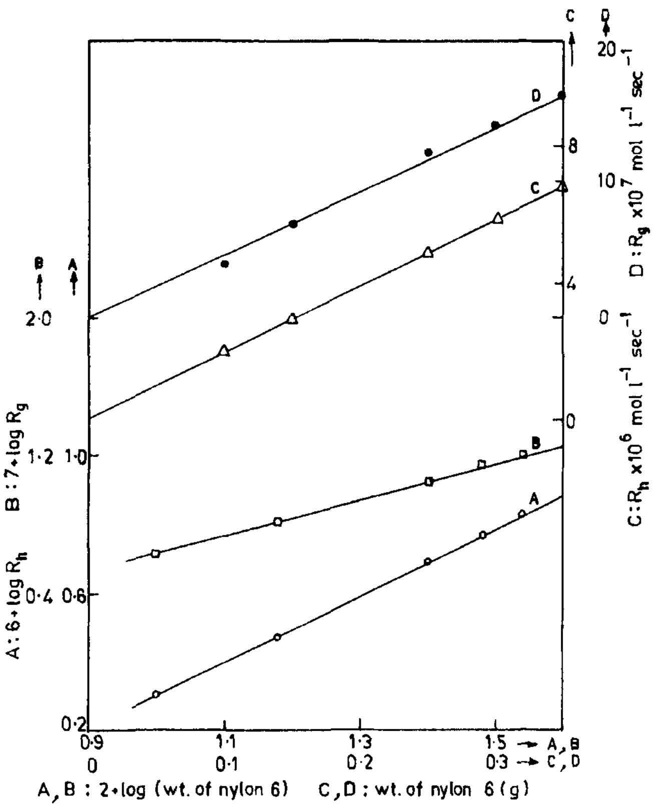

FIGURE 5 Effect of (amount of Nylon6 fibre) on R_h and R_g. [OT] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, [HCl] = 1.00 M.

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 [48] 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

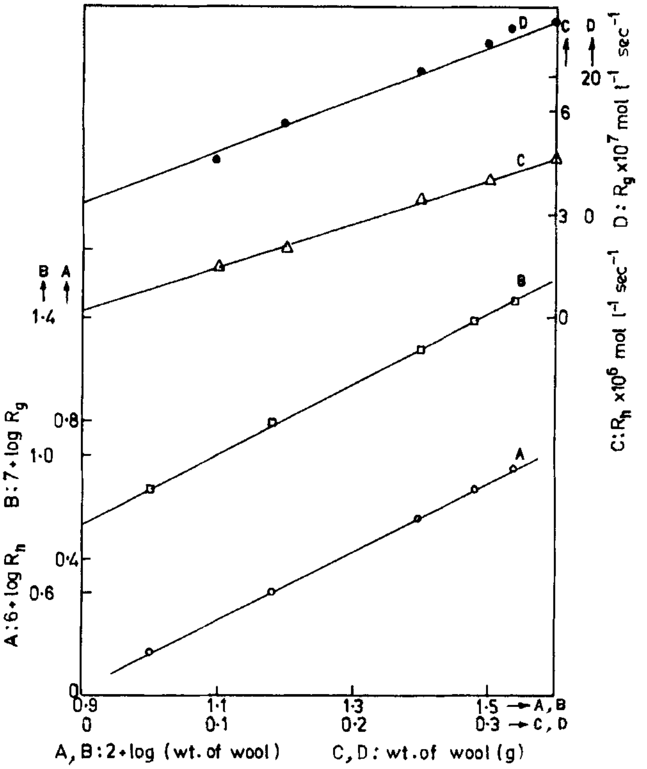

FIGURE 6 Effect of (amount of Wool fibre) on R_h and R_g. $[\mathrm{OT}] = 0.30\,\mathrm{mol\,l^{-1}}$, $[\mathrm{PDS}] = 0.01\,\mathrm{mol\,l^{-1}}$, $[\mathrm{HCl}] = 1.00\,\mathrm{M}$.

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 $R_h(\mathrm{OT})$ *vs.* [OT] (Fig. 1C) was found to be a straight line with a definite intercept and $R_h(\mathrm{OT})$ *vs.* [PDS] (Fig. 2C) is a straight line and passing through the origin and $R_h(\mathrm{OT})$ *vs.* (amount of Nylon6 fibre) (Fig. 3C) is a straight line and passing through the origin. These three combined facts necessitate the modification of the above equations as,

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

where k_{1h} is the rate constant corresponding to homopolymer formation, k_{2h} and k_{3h} are rate constants for the homopolymer formation taking into account for the additional effects of available surface and probable change due to grafting. [TAS] – total available surface (include homopolymer (weight basis) and grafted one). The value of k_{3h} can be taken from the intercept of the plot of R_h *vs.* [OT] (Fig. 1C).

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

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

where k_{1g} is the rate constant 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.* [27] determined the k_{1h} value as $0.0008\,\mathrm{min}^{-1}$. For the present case, PDS initiated graft copolymerization of OT onto nylon6 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 $6.03 \times 10^{-3}\,\mathrm{g}^{-1}\,\mathrm{m}^{-1}\,\mathrm{l}\,\mathrm{sec}^{-1}$ and $1.62 \times 10^{-3}\,\mathrm{g}^{-1}\,\mathrm{m}^{-1}\,\mathrm{l}\,\mathrm{sec}^{-1}$ respectively. This value is far higher than that of the simple homopolymerization rate constant and augumenting the auto acceleration effect in homopolymerization by TAS and grafting. The value of k_{3h} was found to be $1.20 \times 10^{-6}\,\mathrm{mol}\,\mathrm{l}^{-1}\,\mathrm{sec}^{-1}$ 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 wool fibre, the rate constants were determined by modifying the Eqs. (1) and (2) as

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

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

The k_{1h} and k_{1g} values are found to be $3.83 \times 10^{-4} g^{-1} m^{-1} l\ sec^{-1}$ and $1.73 \times 10^{-3} g^{-1} m^{-1} l\ sec^{-1}$ respectively. Here the k_{3h} value was found to be 0.40×10^{-6} mol l^{-1} sec^{-1} where as the k_{3g} value was found to be nil.

The kinetic results indicated that homopolymerization was encouraged by nylon6 system and grafting was encouraged by wool system.

In order to study the effect of added reductant like Ferrous Ammonium Sulphate (FAS) and Ascorbic Acid (AH_2) on R_h and R_g a separate experiment was carriedout.

Effect of [AH_2] on R_h and Graft Parameters

As mentioned in Figure 7 AH_2 concentration was varied from 0.0050 to 0.0250 mol l^{-1} while keeping other experimental conditions as

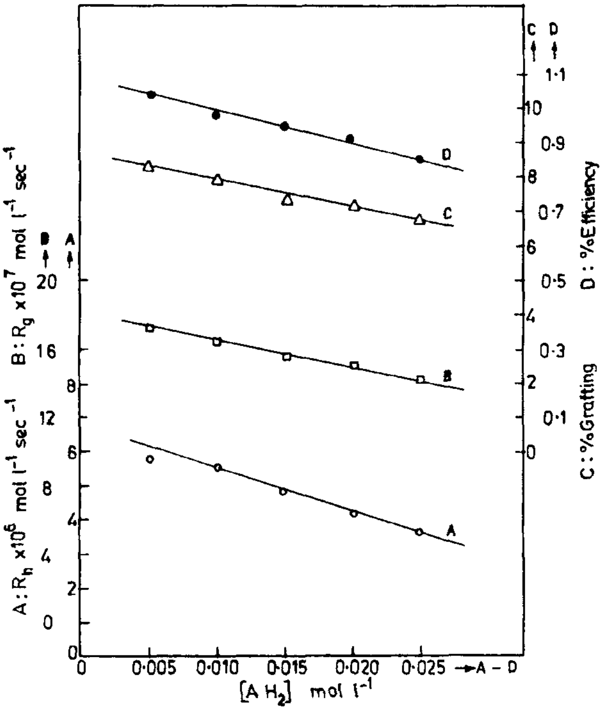

FIGURE 7 Effect of [AH_2] on R_h and graft parameters. [OT] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, Wt. of Nylon6 fibre = 0.20 g.

constant (nylon6 system). It was found that both R_h and R_g decreased with increase in AH_2 concentration (for both nylon6 and wool system). This is due to scavenging nature of ascorbate anion. This is in accordance with our earlier communications on the redox initiated polymerization of aniline and *o*-toluidine [10]. Figure 7 indicated the effect of $[AH_2]$ on R_h, R_g, % grafting and % efficiency. Similar plots were made for wool system also (Fig. 8).

Effect of [FAS] on R_h and Graft Parameters

Figures 9 and 10 showed the effect of added Fe^{2+} ion on R_h, R_g,, % grafting and % efficiency. Here the Fe^{2+} ion concentration was varied

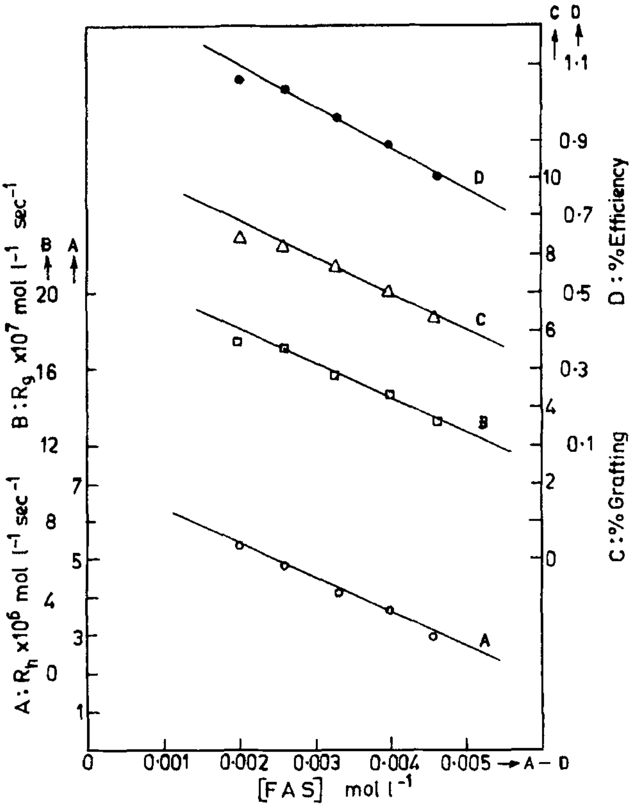

FIGURE 8 Effect of [FAS] on R_h and graft parameters. [OT] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, Wt. of Nylon6 fibre = 0.02 g.

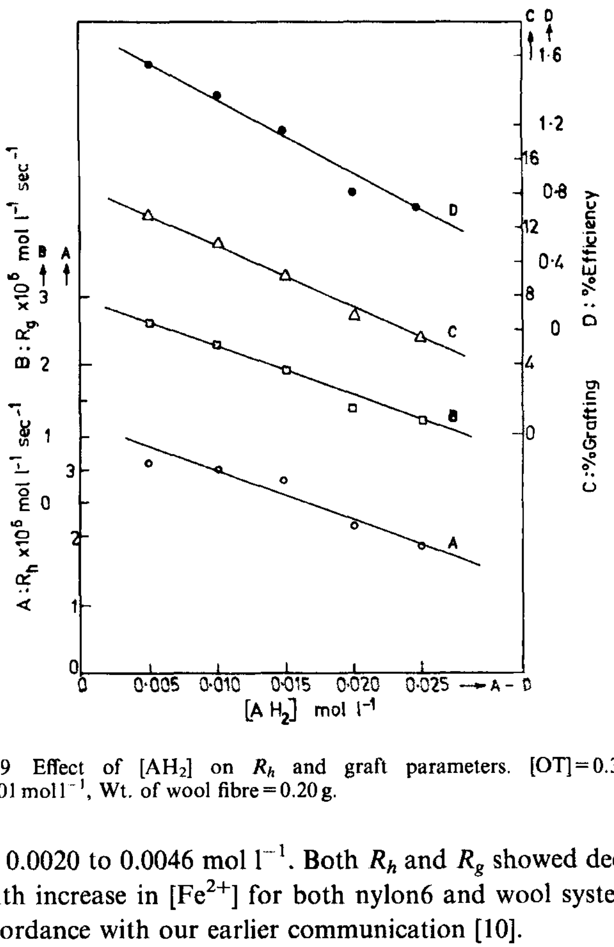

FIGURE 9 Effect of [AH$_2$] on R_h and graft parameters. [OT] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, Wt. of wool fibre = 0.20 g.

between 0.0020 to 0.0046 mol l^{-1}. Both R_h and R_g showed decreasing trend with increase in [Fe^{2+}] for both nylon6 and wool system. This is in accordance with our earlier communication [10].

Cyclic Voltammetry

Cyclic voltammogram (CV) was recorded for Nylon6-g-POT film at various sweep rates and showed in Figure 11. At lower sweep rates the CV showed one anodic peak (at 445 mV) and one cathodic peak (at 620 mV). At higher sweep rates the CV showed two anodic peaks (445 and 615 mV) and two cathodic peaks (380 and 620 mV). On increasing the sweep rates the anodic peak slightly shifted towards more anodic direction. 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

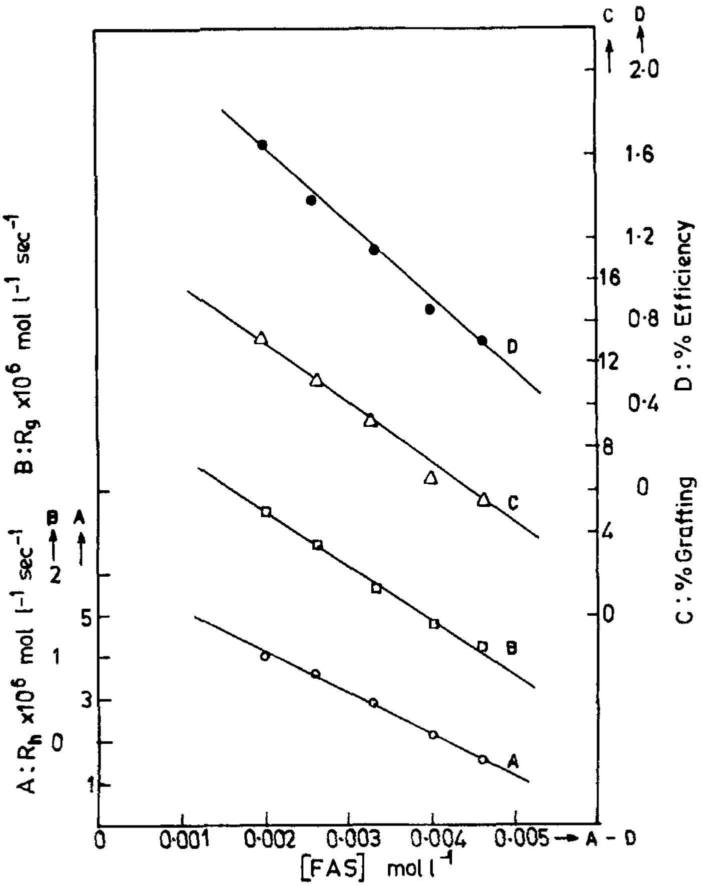

FIGURE 10 Effect of [FAS] on R_h and graft parameters. [OT] = 0.30 mol l^{-1}, [PDS] = 0.01 mol l^{-1}, Wt. of wool fibre = 0.20 g.

the unchanged redox peak at different sweep rates. This is similar to that of CV of POT film at various sweep rates [10]. On increasing the sweep rate both anodic and cathodic peak currents of Nylon6-g-POT film showed linear trend. The presence of POT electroactivity for grafted fibre points out the chemical grafting of POT onto nylon6 fibre.

The linear trend of peak current with the sweep rates confirm the chemical grafting of POT onto Nylon6 fibre. This shift in the peak potential value also add further evidence for the chemical grafting of POT onto Nylon6 fibre. For the sake of comparison the CV of

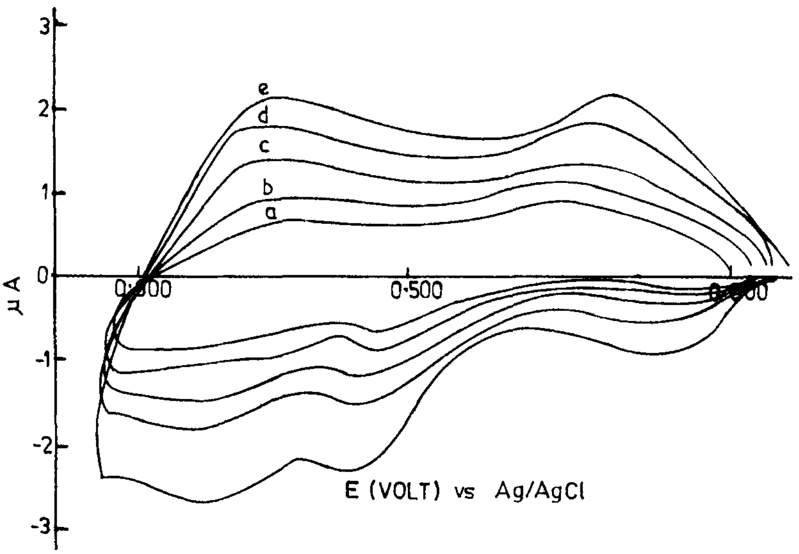

FIGURE 11 Cyclic Voltammogram of Nylon6-g-POT film at various sweep rates. (a) 200 mV/s, (b) 400 mV/s, (c) 600 mV/s, (d) 800 mV/s, (e) 1000 mV/s.

ungrafted and pure nylon6 fibre was recorded, the CV did not show any peak even at lower sweep rates.

CV was also recorded for wool-g-POT film at various sweep rates (Fig. 12). There are two anodic peaks (0.39 and 0.68 V) and two cathodic peaks (0.30 and 0.68 V). On increasing the sweep rates from 0.20 to 1.2 mV/s, the peak current showed increasing trend. The film was found to be stable at higher sweep rate as identified by the charges associated with CV for various sweep rates. The charge was found to be the same. This indicates the stable nature of the polymeric film against the applied potentials. The existence of POT in the grafting fibre adds evidence for chemical grafting of POT onto wool fibre.

Weight Loss Study

Table III indicates the % weight loss of Nylon6-g-POT fibre under different chemical process. The % weight loss of Nylon6-g-POT and wool-g-POT under each process depends on many experimental factors like nature of monomer, initiator and fibre used. The % weight loss is similar to that of our earlier communications [32–34].

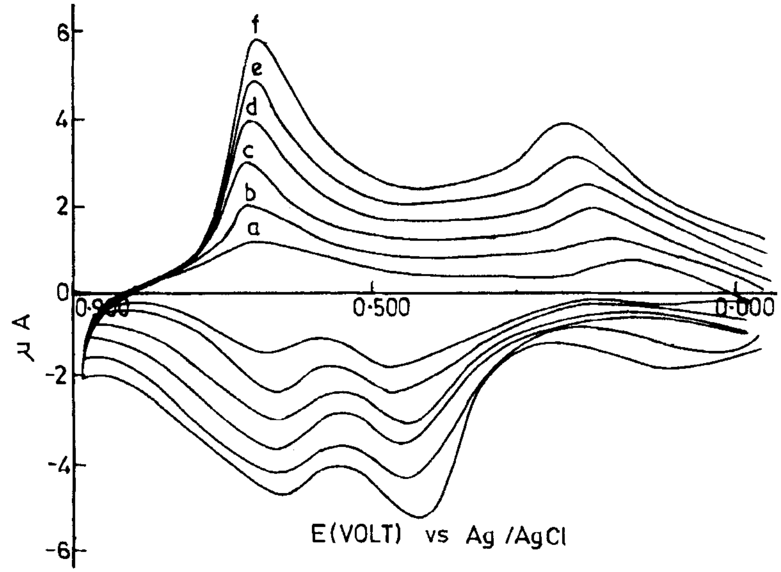

FIGURE 12 Cyclic voltammogram of Wool-g-POT film at various sweep rates. (a) 200 mV/s, (b) 400 mV/s, (c) 600 mV/s, (d) 800 mV/s, (e) 1000 mV/s, (f) 1200 mV/s.

TABLE III Weight loss study

Process	*% Wt. loss (Approximately)*		
(Treatment with)	*A*	*B*	*Reason*
1. Acetone	1	2	Solubility of physisorbed monomer or dimer in acetone
2. NMP	1	3	Solubility of physisorbed HCl doped POT
3. Ammonia	8–10	12	Removal of HCl from both physisorbed and grafted POT
4. NMP	10	14–16	Solubility of all the dedoped physisorbed POT

A: Nylon6-g-POT fibre; B: Wool-g-POT fibre.

Kang *et al.* [49] reported that during the chemical polymerization of aniline there will be a formation of 50% amino form and 50% imino form. And 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 PET-g-PANI system [33].

This indicates that the substituted polyanilines give the quinoid structure rather than the benzenoid structure.

(The complex formation between oxidant and fibre was confirmed through PDS or PMS analysis method [3–6]. 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 indicate that there is no unreacted oxidant. That means all the oxidant molecules are broken into active free radicals. Subsequently these free radicals activate the Nylon6 fibre backbone through the direct interaction with the reactive sites present on the Nylon6 fibre backbone).

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

Regarding the backbone used, wool contains many active functional groups and substituents that causes the physisorbtion of POT onto the surface of the backbone. The physisorbtion takesplace between fibre and monomer or polymer through the 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 nylon6 fibre the amount of physisorbed POT was found to be low due to the lesser number of hetero atom on the backbone. From our earlier communications, it was observed that the natural fibre showed higher % weight loss than the synthetic backbone [35, 39, 43].

Infra Red Spectroscopy

FTIR spectrum was recorded for both grafted and ungrafted nylon6 and wool fibres. The POT grafted nylon6 fibre (Fig. 13) and wool (Fig. 14) fibre shows additional peaks other than corresponding to the backbones. The peaks at 810 and 1265 cm^{-1} correspond to C—H bending vibration of the ortho substituted aromatic ring and C—N stretching of the aromatic secondary amines respectively. The peak for symmetric bending —CH_3 group is appeared at 1373 cm^{-1}. The peaks at 2959 and 3300 cm^{-1} is attributed to C—H stretch of the —CH_3 group and N—H stretch of the aromatic amines respectively. 1635, 1469 and 1373 cm^{-1} peaks are corresponding to the C—N bond. The

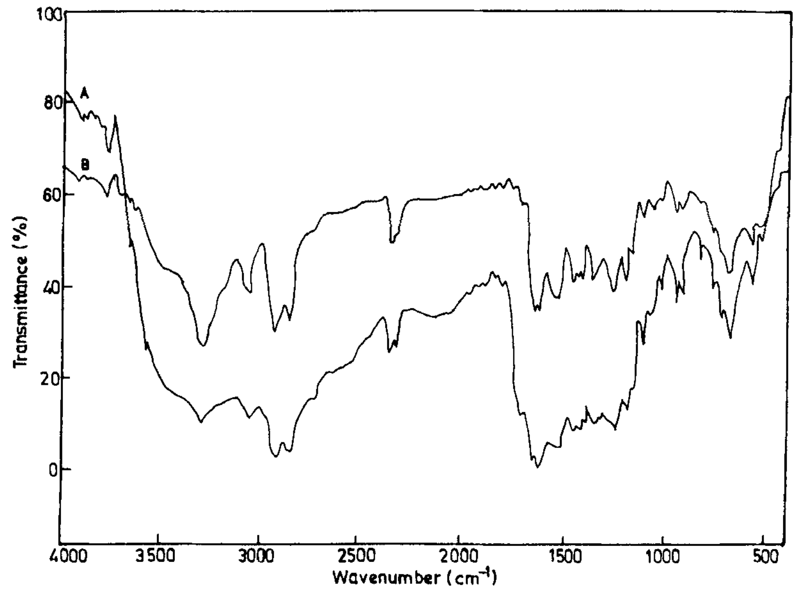

FIGURE 13 (A) FTIR spectroscopy of Nylon6-g-POT fibre. (B) FTIR spectrum of pure nylon6 fibre.

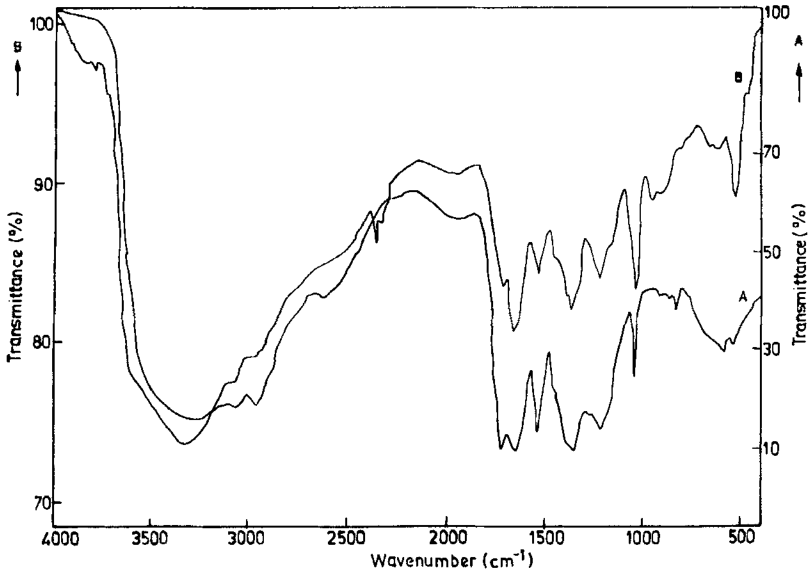

FIGURE 14 (A) FTIR spectrum of Wool-g-POT fibre. (B) FTIR spectrum of pure wool fibre.

peaks at 1470 and 800 cm^{-1} is attributed to C—C aromatic stretching and C—H out of plane bending vibration of the para substituted benzene ring. 1562 and 1488 cm^{-1} peaks are responsible for quinoid and benzenoid ring form. The other peaks are corresponding to the backbone polymer. The presence of POT structure in the grafted fibre as evident from spectral data confirms the incorporation of POT units onto backbone matrices.

UV-visible Spectroscopy

POT shows two absorption peak (Fig. 15) at 310 nm and 580 nm are similar to that of PANI. On the basis of assignments done for PANI it may be said that the 310 nm band is due to Pi ⟶ Pi* transition and is related to the extend of conjugation between the adjacent phenyl rings in the polymer chains. The hypsochromic shifts of this peak here as compared to the PANI spectrum can arise from the decreased conjugation because of the steric influence of the methyl groups in the POT backbone. This seems to well with the finding on the lowered electrical conductivity values as shown in our earlier communication [42]. The second broad band near 580 nm is a measure of the extended

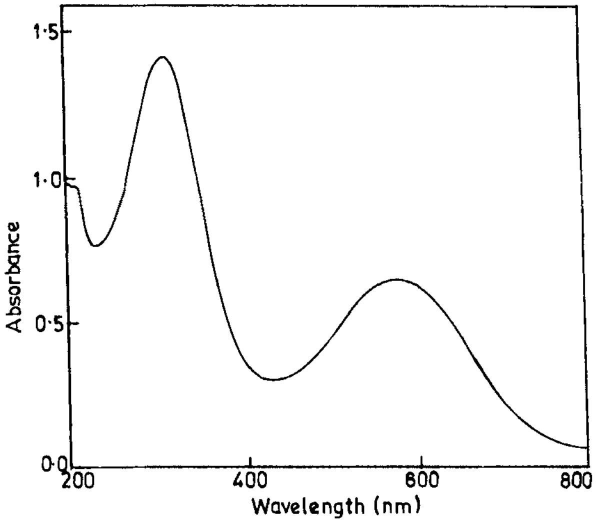

FIGURE 15 UV-visible spectrum of POT in NMP.

conjugation corresponding to the excitation transitions caused by inter-chain and intra-chain charge transfer. Here again it is noteworthy that 634 nm band assigned for PANI is appearing here at a lower wavelength. This is also a measure of the decreased conjugation and the hypsochromic effect for this band has perhaps the same significance. Visible spectrum of extract at various time intervals are shown in Figure 16. This also shows the same peak in the visible region similar to that of POT spectrum.

Visible spectrum was recorded for the extract at various extraction time intervals. The spectrum showed that the OD was decreased with increase in extraction time intervals. After 12 hrs, the spectrum showed nil OD value. It indicates that after 12 hrs extraction with NMP all the physisorbed POT units were removed from the fibre surface.

Conductivity Measurements

Conductivity was measured for both POT grafted wool and nylon6 fibres at different % grafting. For the sake of comparison the conductivity value of pure backbones are also given in Table IV. The POT

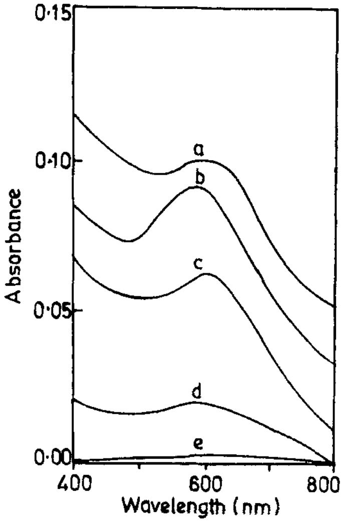

FIGURE 16 Visible spectrum of POT film at different extraction time intervals. (a) 1 hr, (b) 3 hr, (c) 5 hr, (d) 9 hr, (e) 12 hr.

TABLE IV Conductivity measurements

Polymer	*% grafting*	*Conductivity* $Ohm^{-1}\ cm^{-1}$
Nylon6		1.03 G
Nylon6-g-POT	5.30	1.64 G
	17.0	11.2 G
Wool-g-POT	5.30	2.34 G
	16.9	6.27 G
Wool	–	1.20 G

grafted wool fibre shows higher conductivity value than nylon6 fibre at various % grafting.

Mechanism

A probable mechanism is proposed here to explain the experimental results obtained. The mechanism suggested for graft copolymerization of POT onto Nylon6 fibre in this paper is based on the mechanism proposed by two research teams. Wei and co-workers [47] explain the formation of homopolymer *via* radical cation and Bhadani *et al.* [50] proposed a mechanism for the graft copolymerization of PANI onto various natural backbones by electrochemical method. They also explained that the graft copolymerization proceeds through oligomerization. Taking the above two mechanisms as basis a probable mechanism is suggested here to explain the modification of Nylon6 fibre through chemical grafting of POT. {The experimental results indicated the first order dependence of both R_h and R_g on [OT], [PDS] and (amount of fibre). And also indicates one mole of oxidant is required to oxidize one mole of monomer and the unimolecular termination}.

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

Primary reactions

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

$$\mathrm{PDS} \longrightarrow 2\mathrm{SO_4}^{-\cdot}\ (R^{\cdot})$$

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

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

Homopolymerization

$$\text{OT}^{+\cdot} + \text{OT} \longrightarrow \text{dimer} + 2\text{H}^{+}$$

$$\text{dimer} + R^{\bullet} \longrightarrow \text{dimer}^{+\cdot} + \text{Products}$$

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

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

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

$$\text{Oligomer} + R^{\bullet} \longrightarrow \text{Oligomer}^{+\cdot} + \text{Products}$$

$$\text{Oligomer}^{+\cdot} + \text{Oligomer}^{+\cdot} \longrightarrow \text{POT} \quad (\text{Homopolymer})$$

$$\text{POT} + R^{\bullet} \longrightarrow \text{POT}^{+\cdot} + \text{Products}$$

$$\text{POT} + \text{PDS} \longrightarrow \text{POT}^{+\cdot} + \text{Products}$$

$$\text{POT}^{+\cdot} + \text{OT} \longrightarrow \text{OT}^{+\cdot} + \text{POT} \quad (\text{auto acceleration effect})$$

$$\text{POT}^{+\cdot} + \text{dimer} \longrightarrow \text{dimer}^{+\cdot} + \text{POT}$$

$$\text{POT}^{+\cdot} + \text{Oligomer} \longrightarrow \text{Oligomer}^{+\cdot} + \text{POT}$$

Graft copolymerization

$$\text{OT} + \text{Nylon6}^{\bullet} \longrightarrow \text{Nylon6} - \text{OT} + 2\text{H}^{+}$$

$$\text{Nylon6} - \text{OT} + \text{PDS} \longrightarrow \text{Nylon6} - \text{OT}^{+\cdot} + \text{Products}$$

$$\text{Nylon6} - \text{OT} + R^{\bullet} \longrightarrow \text{Nylon6} - \text{OT}^{+\cdot} + \text{Products}$$

$$\text{Nylon6} - \text{OT}^{+\cdot} + \text{OT}^{+\cdot} \longrightarrow \text{Nylon6} - \text{dimer} + 2\text{H}^{+}$$

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

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

$$\text{Nylon6} - \text{dimer}^{+\cdot} + \text{OT}^{+\cdot} \longrightarrow \text{Nylon6} - \text{Oligomer} + 2\text{H}^{+}$$

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

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

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

$$\text{Nylon6} - \text{POT} + R^{\bullet} \longrightarrow \text{Nylon6} - \text{POT}^{+\cdot} + \text{Products}$$

$$\text{Nylon6} - \text{POT} + \text{PDS} \longrightarrow \text{Nylon6} - \text{POT}^{+\cdot} + \text{Products}$$

$$\text{Nylon6} - \text{POT}^{+\cdot} + \text{OT} \longrightarrow \text{OT}^{+\cdot} + \text{Nylon6} - \text{POT}$$

$$\text{Nylon6} - \text{POT}^{\dot{+}} + \text{dimer} \longrightarrow \text{dimer}^{\dot{+}} + \text{Nylon6} - \text{POT}$$

$$\text{Nylon6} - \text{POT}^{\dot{+}} + \text{Oligomer} \longrightarrow \text{Oligomer}^{\dot{+}} + \text{Nylon6} - \text{POT}$$

$$\text{Nylon6}^{\cdot} + \text{OT} \longrightarrow \text{OT}^{\dot{+}} + \text{Products}$$

$$\text{Nylon6} - \text{OT}^{\dot{+}} + \text{OT} \longrightarrow \text{Nylon6} - \text{dimer} + 2\text{H}^{+} \quad \text{(auto acceleration effect)}$$

$$\text{Nylon6} - \text{OT}^{\dot{+}} + \text{OT} \longrightarrow \text{OT}^{\dot{+}} + \text{Nylon6} - \text{OT}$$

$$\text{OT}^{\dot{+}} + \text{dimer} \longrightarrow \text{dimer}^{\dot{+}} + \text{Product}$$

$$\text{OT}^{\dot{+}} + \text{Oligomer} \longrightarrow \text{Oligomer}^{\dot{+}} + \text{Products}$$

$$\text{OT}^{\dot{+}} + \text{OT} \longrightarrow \text{dimer} + 2\text{H}^{+}$$

This mechanism explains the experimental results obtained. Probable mechanism for Wool system is similar to that of nylon6 system. This is in accordance with our earlier communications. [34, 39, 47, 51].

CONCLUSION

From the above kinetic study the following conclusions were made. (1) Graft copolymerization occurs with simultaneous homopolymer formation. (2) Both R_h and R_g showed first order dependence on [OT], [PDS] and (amount of fibre). (3) Homopolymerization was encouraged by nylon6 system whereas graft copolymerization was encouraged by wool system. (4) The mechanism explained the experimental results obtained.

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