

# Peroxomonosulphate Initiated Graft Copolymerization of o-Toluidine onto Nylon 6 and Wool Fibers—A Kinetic Approach

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**ABSTRACT:** Chemical polymerization of o-toluidine (OT) in the presence of nylon 6 and wool fibers initiated by peroxomonosulphate (PMS) in an aqueous acidic medium was carried out under nitrogen atmosphere. During the polymerization process, graft copolymers were formed along with homopolymers of OT. A procedure is given for the separation of poly(o-toluidine) (POT) grafted fiber from the homopolymer. Rate of homopolymerization ( $R_h$ ), rate of grafting ( $R_g$ ), percentage grafting, and percentage grafting efficiency were determined. Rate constants were evaluated from the experimental results. The chemical grafting of POT onto nylon 6 and wool fibers was confirmed through Fourier transform infrared (FTIR) spectroscopy and electrical conductivity measurements. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2317–2326, 2002

**Key words:** graft copolymers; Fourier transform infrared spectroscopy; nylon 6; wool; conductivity; rate constant; mechanism

## INTRODUCTION

Chemical grafting of selected natural and synthetic fibers by electricity-conducting polymers is currently being studied in an attempt to impart significant conductivity and thermal properties to make them suitable for applications in EMI shielding,<sup>1</sup> rechargeable batteries,<sup>2</sup> and corrosion inhibitors.<sup>3</sup> Li et al.<sup>4,5</sup> reported the conducting polymer composites. Toppare et al.<sup>6,7</sup> prepared some conducting polymers based on composites, and they reported the conductivity values. Greg-

ory et al.<sup>8</sup> published the polyaniline (PANI) grafted nylon 6 and PET fibers. Various initiators such as AIBN,<sup>9</sup> Peroxydisulphate (PDS),<sup>10</sup> and peroxomonosulphate (PMS)<sup>11</sup> were used for this grafting purpose. However, these reports do not cover many of the kinetic aspects. Few reports are available that use PMS as an initiator for the graft copolymerization of conducting polymers onto various natural and synthetic fibers. At present, Anbarasan et al.<sup>12</sup> have reported that peroxosalts initiated graft copolymerization of aniline onto wool fiber. PDS-initiated graft copolymerization of aniline and o-toluidine (OT) onto PET,<sup>13</sup> nylon 6,<sup>14</sup> wool,<sup>15</sup> and nylon 66<sup>16,17</sup> fibers has also been reported. We reported the initiation of graft copolymerization of aniline onto rayon fiber by peroxosalts.<sup>18</sup> PMS-initiated graft

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copolymerization of aniline and OT onto polypropylene (PP)<sup>19</sup> and PET<sup>20</sup> fibers was recently reported by Anbarasan et al. Poly(o-toluidine) (POT) was grafted onto rayon fiber by using peroxosalts as initiators.<sup>21</sup> This article reports the analysis of the kinetic results on the graft copolymerization, initiated by PMS, of OT onto nylon 6 and wool fibers.

## EXPERIMENTAL

### Materials Used

OT (SRL AR) was used after distillation under vacuum. PMS (Merck), HCl (Fischer AR), and other chemicals were also used after such distillation. Nylon 6 fiber (a gift from M/S. Madura Coats, Madurai, India) and wool fiber (a gift from M/S. J. K. Synthetics, Rajasthan, India) were Soxhlet extracted with acetone for 24 hours and dried at room temperature before being used.

### Grafting Procedure

Wool or nylon 6 fiber ( $W_1$  g) was immersed in a 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 PMS (using standard solutions). The time of adding 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 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 hours, and weighed until the constant weight was obtained. This procedure gave the total weight of the grafted polymer along with the homopolymer ( $W_2$  g). The grafted wool or nylon 6 fiber 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 to get constant

weight ( $W_3$  g). The difference in ( $W_3 - W_1$ ) gives the weight of the grafted polymer.

### Rate Measurements

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

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

$$R_h = \frac{W_2 - W_3}{VtM} \times 1000$$

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

percentage grafting efficiency =

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

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

### Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FTIR) spectrum was recorded for wool-g-POT and the nylon 6-g-POT samples using a Bruker FTIR Equinox 55 model instrument by KBr pelletization method.

### Conductivity Measurements

Conductivity of both POT grafted and pure nylon 6 or wool fiber was measured by using Keithley 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.

### Isolation of POT Grafted Nylon 6 or Wool Fiber from POT, Homopolymer

The mixture ( $W_1$  g) of the POT-grafted nylon 6 or wool fiber and POT, the homopolymer, was deposed with 0.5 N aq. ammonia solution and extracted with N-methyl pyrrolidone (NMP) solvent 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 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 homopolymer formed.

## RESULTS AND DISCUSSION

### Effect of [OT] on $R_h$ and Graft Parameters

The [OT] was varied between 0.20 and 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 the increase in [OT] (for the nylon 6 system). We observed that both  $R_h$  and  $R_g$  values were higher for wool than were those for nylon 6. To find out the order dependence, the following plots were made. The plots of  $\log R_h$  versus  $\log [OT]$  [Fig. 1(A)] and  $\log R_g$  versus  $\log [OT]$  [Fig. 1(B)] were drawn, and the slope of the plots was found to be close to unity, thus indicating the first order dependence of both  $R_h$  and  $R_g$  on [OT]. Furthermore, it was confirmed by plotting  $R_h$  versus [OT] [Fig. 1(C)] and  $R_g$  versus [OT] [Fig. 1(D)]. The plots were found to be linear, and the intercept values were noted. The percentage grafting and percentage grafting efficiency are indicated in Table I.

The increase in  $R_h$  and  $R_g$  can be explained as follows: The first reason for the increase might be the increase of monomer radical cations; the second reason is the auto acceleration effect caused by the formed active POT and POT-grafted wool or nylon 6 fiber surface.

The above-mentioned plots also were made for wool systems (Fig. 2). Here also we observed that both  $R_h$  and  $R_g$  showed first-order dependence on OT concentration. The percentage grafting and percentage grafting efficiency values increase with an increase in OT concentration (Table I).

### Effect of [PMS] on $R_h$ and Graft Parameters

[PMS] varied from 0.01 to 0.05 mol  $L^{-1}$  while keeping other experimental conditions constant. The experimental results showed that both  $R_h$  and  $R_g$  increase with an increase in [PMS].  $R_h$  is found to be higher for the nylon 6 system, whereas  $R_g$  is found to be higher for the wool system. The percentage grafting and percentage

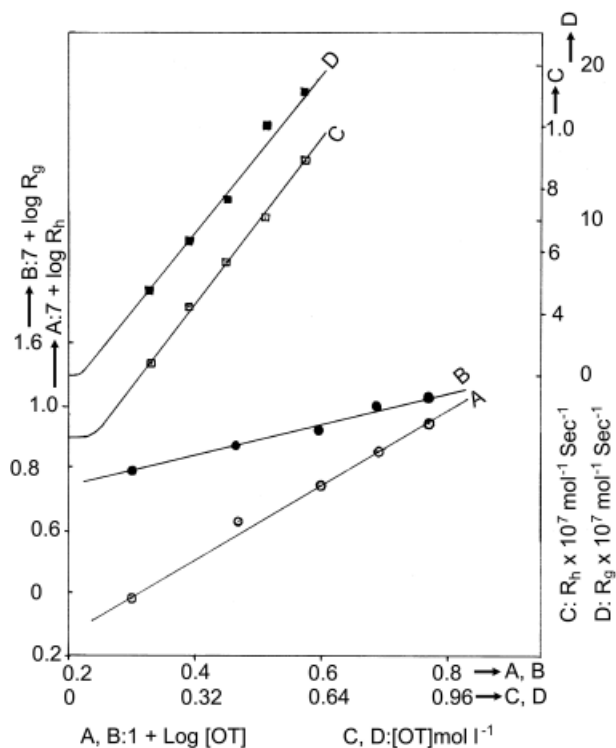
grafting efficiency values reveal the same trend (Table I).

The plots of  $\log R_h$  versus  $\log [PMS]$  [Fig. 3(A)] and  $\log R_g$  versus  $\log [PMS]$  [Fig. 3(B)] were drawn for the nylon 6 system. Figure 3(A,B) indicates the first-order dependence of  $R_h$  and  $R_g$  on [PMS]. The first-order dependence was further confirmed by plotting  $R_h$  versus [PMS] [Fig. 3(C)] and  $R_g$  versus [PMS] [Fig. 3(D)]. The direct plots are found to be linear and pass through the origin.

The increase in  $R_h$  and  $R_g$  can be ascribed to the formation of large number of active free radicals. Similar plots were made for the wool system (Fig. 4). The first-order dependence of  $R_h$  and  $R_g$  on PMS concentration is observed. The percentage grafting and percentage grafting efficiency values are given in Table I.

### Effect of Amount of Nylon 6 or Wool Fiber on $R_h$ and on Graft Parameters

The effect of amount of nylon 6 and wool fibers on  $R_h$  and on the graft parameters was studied under the conditions mentioned in Table II. The nylon 6 fiber weight was varied between 0.10 and 0.35 g while other experimental conditions were



**Figure 1** Effect of [OT] on  $R_h$  and  $R_g$ . [PMS] = 0.02 mol  $L^{-1}$ , weight of nylon 6 fiber = 0.20 g, [HCl] = 1.0M.

**Table I** Effect of [OT], [PMS] on Percentage Grafting and Percentage Grafting Efficiency

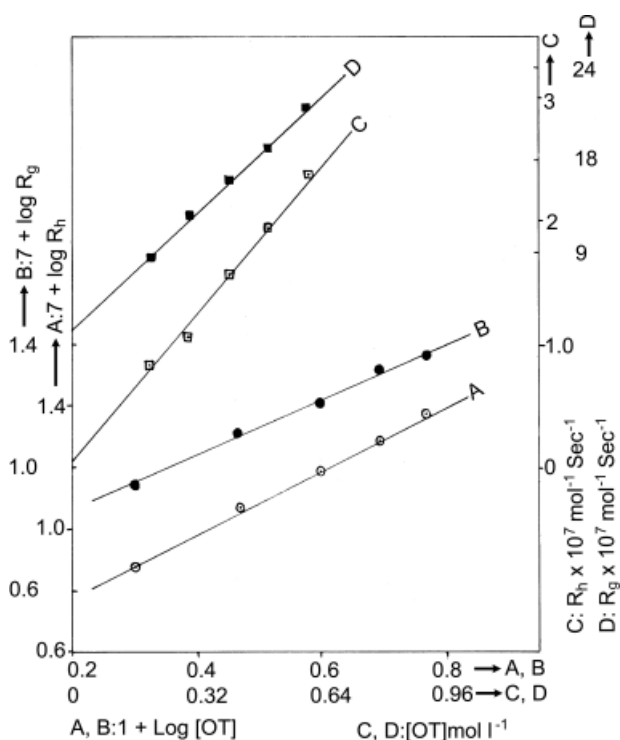
[OT] mol L <sup>-1</sup>	Percentage grafting		Percentage grafting efficiency		[PMS] mol L <sup>-1</sup>	Percentage grafting		Percentage Grafting Efficiency	
	A	B	A	B		C	D	C	D
0.20	2.79	4.23	0.52	0.79	0.01	1.60	3.51	0.20	0.44
0.30	4.15	6.12	0.52	0.76	0.02	3.90	7.01	0.49	0.88
0.40	5.57	7.95	0.52	0.75	0.03	6.65	10.1	1.21	1.26
0.50	7.79	10.1	0.58	0.75	0.04	7.91	14.3	1.98	1.77
0.60	8.74	11.1	0.54	0.70	0.05	10.6	17.9	2.32	2.24

A, B: [PMS] = 0.02 mol L<sup>-1</sup>, [HCl] = 1.0 M; C, D: [OT] = 0.30 mol L<sup>-1</sup>, [HCl] = 1.0 M; A, C: Weight Of nylon 6 fiber = 0.20 g; B, D: Weight of wool fiber = 0.20 g.

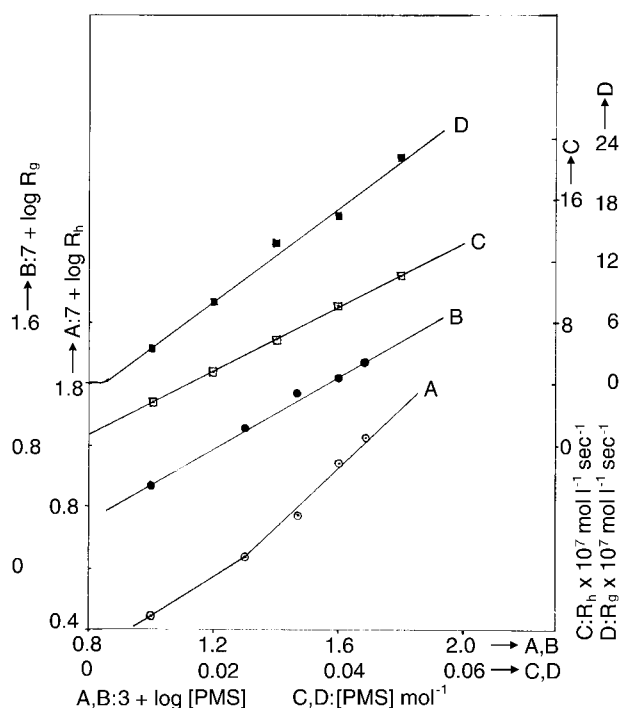
kept constant. Both  $R_h$  and  $R_g$  show a greater percentage increase with a larger amount of fiber for both systems. The  $R_h$  value is higher for the nylon 6 system than for the wool system, whereas the  $R_g$  value is slightly higher for the wool system than for the nylon 6 system. The percentage grafting and percentage grafting efficiency values are also given in Table II.

In an attempt to quantify the order dependence for the nylon 6 system, the plots of  $\log R_h$  versus

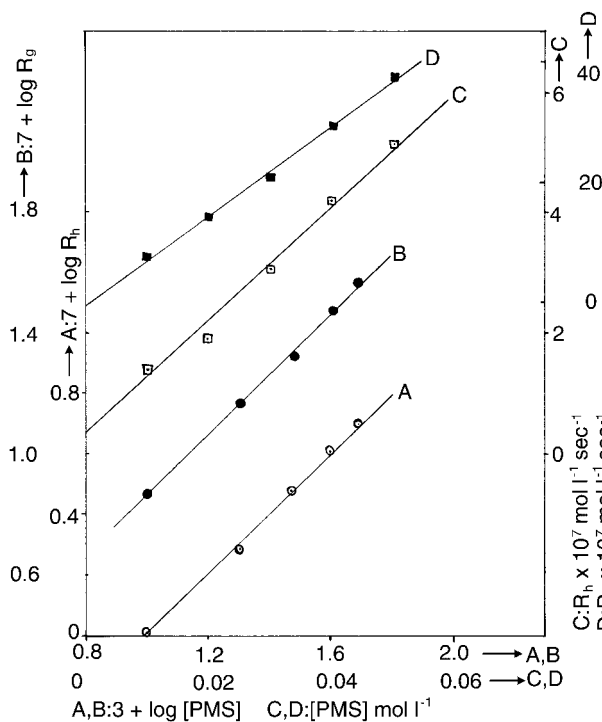
$\log$  (amount of nylon 6 fiber) [Fig. 5(A)] and  $\log R_g$  versus  $\log$  (amount of nylon 6 fiber) [Fig. 5(B)] were made, and the slope values were found to be unity, indicating the first-order dependence of  $R_h$  and  $R_g$  on the amount of nylon 6 fiber. The first-order dependence was further confirmed by plotting  $R_h$  versus the amount of nylon 6 fiber [Fig. 5(C)] and  $R_g$  versus the amount of nylon 6 fiber [Fig. 5(D)]. These plots were found to be linear and passed through the origin. These linear plots support the first-order dependence of  $R_h$  and  $R_g$  on the amount of nylon 6 fiber.



**Figure 2** Effect of [OT] on  $R_h$  and  $R_g$ ; [PMS] = 0.02 mol L<sup>-1</sup>, weight of wool fiber = 0.20 g, [HCl] = 1.0M.



**Figure 3** Effect of [PMS] on  $R_h$  and  $R_g$ ; [OT] = 0.30 mol L<sup>-1</sup>, weight of nylon 6 fiber = 0.30 g, [HCl] = 1.0M.



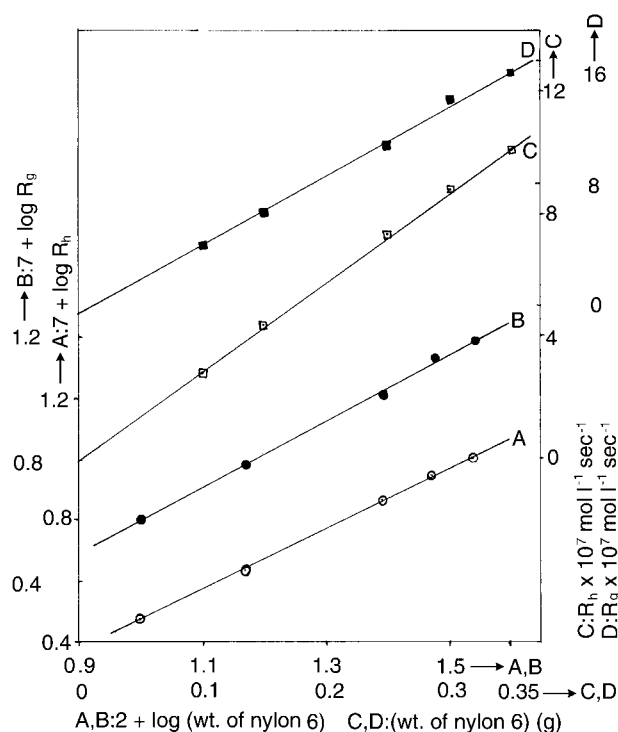
**Figure 4** Effect of [PMS] on  $R_h$  and  $R_g$ ; [OT] = 0.30 mol L<sup>-1</sup>, weight of wool fiber = 0.30 g, [HCl] = 1.0M.

Similar plots were made for the wool system (Fig. 6). Figure 6(A,B) shows the first-order dependence of  $R_h$  and  $R_g$  on the amount of wool fiber. The percentage grafting and percentage grafting efficiency values are given in Table II. By increasing the amount of nylon 6 or wool fiber, the active fiber surface—as well as the fiber macro radicals—is also increased. These active sites are present on backbone polymer enhanced by ho-

**Table II** Effect of Amount of Nylon 6 or Wool Fiber on Percentage Grafting and Percentage Efficiency

Weight of fiber (g)	Percentage Grafting		Percentage Grafting Efficiency	
	A	B	A	B
0.10	3.83	4.64	0.24	0.29
0.15	3.80	4.86	0.36	0.46
0.25	4.09	4.94	0.63	0.77
0.30	4.37	4.92	0.81	0.92
0.35	4.19	5.04	0.92	1.09

A, B: [OT] = 0.30 mol L<sup>-1</sup>, [PMS] = 0.02 mol L<sup>-1</sup>, [HCl] = 1.0 M; A: nylon 6 fiber; B: wool fiber.



**Figure 5** Effect of the amount of nylon 6 fiber on  $R_h$  and  $R_g$ ; [OT] = 0.30 mol L<sup>-1</sup>, [PMS] = 0.01 mol L<sup>-1</sup>, [HCl] = 1.0M.

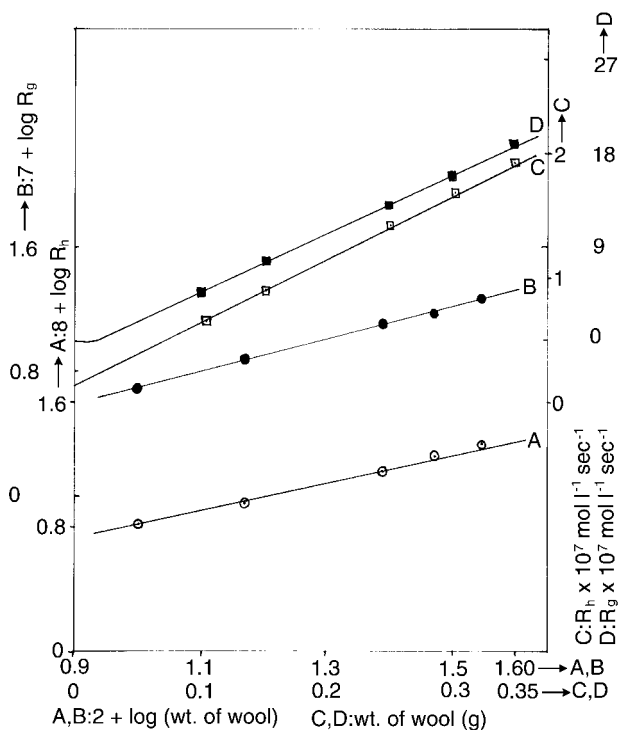
mopolymerization and graft copolymerization through an auto acceleration effect.

### Effect of Temperature on $R_h$ and $R_g$

$R_h$  and  $R_g$  were determined at different reaction temperatures. It was observed that both  $R_h$  and  $R_g$  values increase initially up to 323°K, followed by a decrease. The overall energy of activation ( $E_a$ ) values were calculated for nylon 6 system from the plot of  $1/T$  versus  $\log R_h$  [Fig. 7(A)] and  $1/T$  versus  $\log R_g$  [Fig. 7(B)].  $R_h$  values are found to be higher for the nylon 6 system, whereas the  $R_g$  values are higher for the wool system. Similar plots were made for wool system [Fig. 7 (C,D)].

The average  $E_a$  value for the nylon 6 case was found to be 5.95 Kcal/mol (for homopolymerization) and 8.24 Kcal/mol (for graft copolymerization). In the case of the wool system, the overall activation energy for the homopolymerization was found to be 8.70 Kcal/mol, and for graft copolymerization, it was 8.00 Kcal/mol. The  $E_a$  value for the (homopolymerization) nylon 6 system was found to be low, whereas the value for the graft copolymerization of both system was almost equal. The decreasing trend of both  $R_h$  and  $R_g$  at





**Figure 6** Effect of the amount of wool fiber on  $R_h$  and  $R_g$ ;  $[\text{OT}] = 0.30 \text{ mol L}^{-1}$ ,  $[\text{PMS}] = 0.01 \text{ mol L}^{-1}$ ,  $[\text{HCl}] = 1.0M$ .

higher temperature can be seen as a result of the depletion of monomer radical cations and of the probable side reactions of the initiator reactive species.<sup>12</sup>

Gregory and Tzou<sup>8</sup> studied the effect of added fiber on the chemical polymerization of aniline in the presence and absence of PET fiber. No correlation was attempted to relate the changes in the rate of homopolymerization with reaction parameter in their study. In the electrochemical polymerization of anilines, Wei and colleagues<sup>22</sup> proposed the existence of an auto acceleration effect on the electrode surface in an attempt to explain the changes in the induction time during the polymerization. A kinetic equation was proposed as follows:

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

where  $k$  is the rate constant for the formation of PANI on a bare Pt electrode surface,  $k'$  is the rate constant on the PANI-coated Pt surface,  $[M]$  is the concentration of monomer, and  $[P]$  is the amount of polymer formed. Shim and Park<sup>23</sup> proposed a kinetic equation for the polymerization of

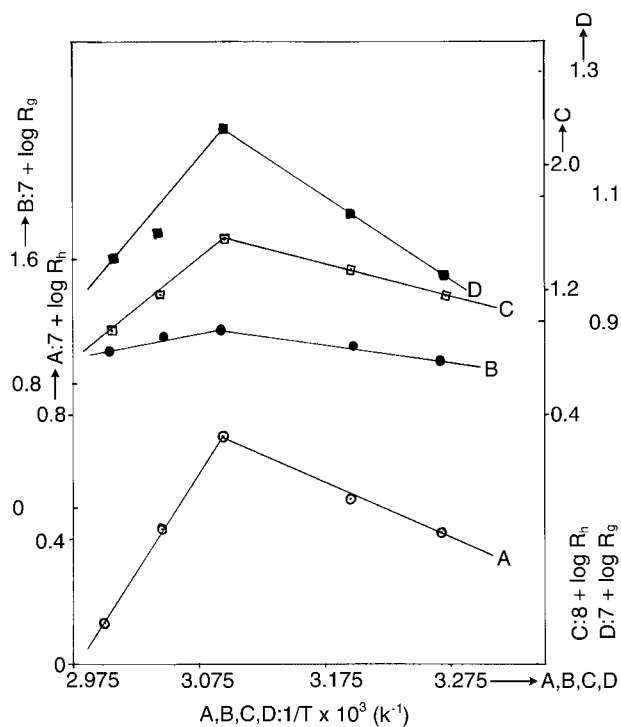
aniline on a bare Pt electrode, including the auto acceleration effect, and proposed the following equation:

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

where  $k_1$  and  $k_2$  are the rate constants of formation of PANI on a bare Pt electrode surface and a 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 caused by the added oxidizing agent, as well as the heterogeneous phase. In this case, the added fiber for grafting and the formed homopolymer may cause the auto acceleration effect as a result of the active surface effect.

The plot of  $R_h(\text{OT})$  versus  $[\text{OT}]$  [Fig. 1(C)] was found to be a straight line with a definite intercept, and  $R_h(\text{OT})$  versus  $[\text{PMS}]$  [Fig. 2(C)] was a straight line that passed through the origin;  $R_h(\text{OT})$  versus the amount of nylon 6 fiber [Fig. 3 (C)] was a straight line that passed through the



**Figure 7** Effect of Temperature on  $R_h$  and  $R_g$ ;  $[\text{OT}] = 0.30 \text{ mol L}^{-1}$ ,  $[\text{PMS}] = 0.01 \text{ mol L}^{-1}$ , weight of fiber = 0.20 g,  $[\text{HCl}] = 1.0M$ .

origin. These three combined facts necessitate the modification of the above equation:

$$R_h(\text{OT}) = k_{1h}[\text{OT}][\text{PMS}](\text{amount of nylon 6 fiber}) + k_{2h}[\text{OT}][\text{TAS}] + k_{3h} \quad (1)$$

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 resulting from grafting. TAS is the total available surface, including the homopolymer (weight basis) and a grafted one. The value of  $k_{3h}$  can be taken from the intercept of the plot of  $R_h$  versus [OT] [Fig. 1 (C)].

The rate of grafting also has same trend (first-order dependence of [OT], [PMS], and [amount of nylon 6 fiber]). Hence, the following equation is proposed for  $R_g$ :

$$R_g(\text{OT}) = k_{1g}[\text{OT}][\text{PMS}](\text{amount of nylon 6 fiber}) + k_{2g}[\text{OT}][\text{TAS}] + k_{3g} \quad (2)$$

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 resulting from grafting.

Gregory et al.<sup>8</sup> determined the  $k_{1h}$  value to be 0.0008 min<sup>-1</sup>. For this case, PMS initiated graft copolymerization of OT onto nylon 6 fiber in aqueous HCl medium, and  $k_{1h}$  and  $k_{1g}$  values are determined from the slope of the plots  $R_h$  versus [OT] [Fig. 1(C)] and  $R_g$  versus [OT] [Fig. 1(D)] using eqs. (1) and (2) as  $4.25 \times 10^{-4} \text{ g}^{-1} \text{ m}^{-1} \text{ sec}^{-1}$  and  $7.30 \times 10^{-4} \text{ g}^{-1} \text{ m}^{-1} \text{ sec}^{-1}$ , respectively. This value is far higher than that of the simple homopolymerization rate constant and augments the auto acceleration effect in homopolymerization by TAS and grafting. The value of  $k_{3h}$  and  $k_{3g}$  was found to be nil. The above rate constant values indicate that the  $k_{1g}$  value is higher than that of the  $k_{1h}$  value.

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

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

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

The  $k_{1h}$  and  $k_{1g}$  values were found to be  $8.15 \times 10^{-4} \text{ g}^{-1} \text{ m}^{-1} \text{ sec}^{-1}$  and  $8.50 \times 10^{-4} \text{ g}^{-1} \text{ m}^{-1} \text{ sec}^{-1}$ , respectively. Here, the  $k_{3h}$  value was found to be  $0.10 \times 10^{-6} \text{ mol L}^{-1}$ , and the  $k_{3g}$  value was found to be zero.

The above kinetic results indicate that both homopolymerization and graft copolymerization values are higher for the wool system than for the nylon 6 system.

### FTIR Spectroscopy

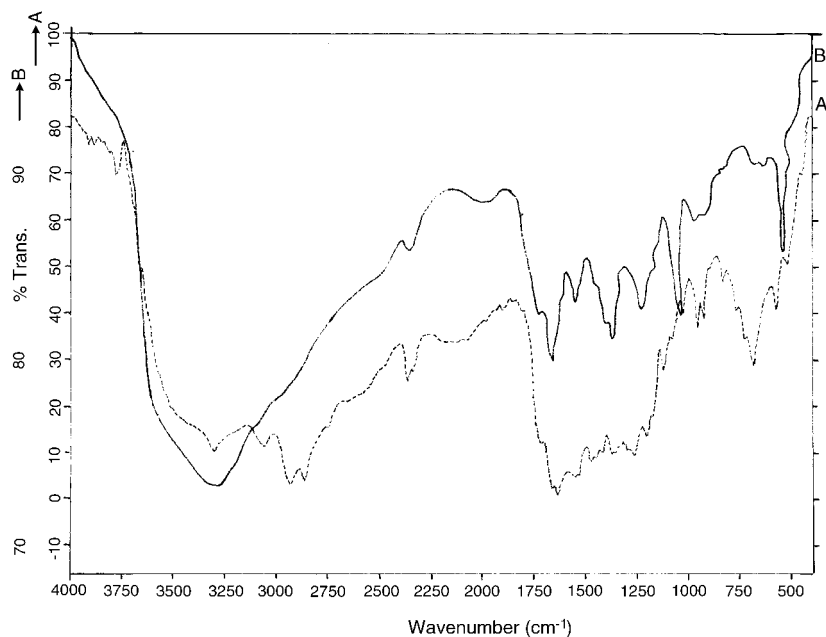
FTIR spectrum was recorded for both the POT grafted nylon 6 [Fig. 8 (A)] and wool [Fig. 8(B)] fibers. The peaks at 810 and 1265 cm<sup>-1</sup> correspond to the C–H bending vibration of the ortho-substituted aromatic ring and the C–N stretching of the aromatic secondary amines, respectively. The peak for the symmetric bending of the –CH<sub>3</sub> group appears at 1373 cm<sup>-1</sup>. The peaks at 2959 and 3300 cm<sup>-1</sup> are attributed to the C–H stretch of the –CH<sub>3</sub> group and the N–H stretch of the aromatic amines, respectively. The 1635, 1469, and 1373 cm<sup>-1</sup> peaks correspond to the C–N bond. The peaks at 1470 and 800 cm<sup>-1</sup> are attributed to the C–C aromatic stretching and the C–H out-of-plane bending vibration of the para-substituted benzene ring. The 1562 and 1488 cm<sup>-1</sup> peaks are responsible for quinoid and benzenoid ring forms. The other peaks correspond to the backbone polymer. The presence of benzenoid and quinoid absorption peaks in the grafted fiber as evident from spectral data confirms the incorporation of POT units onto backbone matrices.

### Conductivity Measurements

Conductivity was measured for both POT grafted and pure nylon 6 and wool fibers at different percentage grafting. For the sake of comparison, the conductivity value of pure backbone of wool or nylon 6 is also given in Table III. In general, the conductivity value of the conducting polymer-grafted textile fibers depends on the nature of the monomer, initiator, fiber, dopant, and experimental conditions like temperature. The POT-grafted wool fiber shows higher conductivity value than nylon 6 fiber at various percentages grafting. This may be a result of the nature of the fiber.

### Mechanism

The grafting of nylon 6 was reported to be initiated by the production of the nylon 6 radical by



**Figure 8** A: Fourier transform infrared (FTIR) spectrum of nylon 6-g-POT fiber; B: FTIR spectrum of wool-g-POT fiber.

the abstraction of a proton from the  $\text{-NH-}$  groups in the backbone polymer. The experimental results (both  $R_h$  and  $R_g$  showed first-order dependence on [Monomer], [initiator], and [weight of nylon 6 fiber] variations) confirmed the unimolecular termination and that one mole of oxidant is required to oxidize one mole of monomer. Here the initiation is affected in two ways, namely, by PMS addition and by the auto acceleration caused by the active surface of nylon 6 fiber, POT, and POT-grafted nylon 6 fiber surface.

We proposed the mechanism for the peroxy-salts-initiated graft copolymerization of conducting polymers onto various natural and synthetic fiber backbone.<sup>12,17,19,21</sup> A probable mechanism is proposed here to explain the experimental results obtained. The mechanism suggested in this

article for the graft copolymerization of POT onto nylon 6 fiber is based on the mechanism proposed by three research teams. Wei et al.<sup>22</sup> explained the formation of homopolymer via radical cation, and Bhadani et al.<sup>24</sup> proposed a mechanism for the graft copolymerization of PANI onto various natural backbones by electrochemical methods. They also explained that graft copolymerization proceeds through oligomerization.<sup>24</sup> Chevalier et al.<sup>25</sup> reported the molecular weight distribution for substituted and unsubstituted polyanilines. They proved experimentally that there exist polymer chains with different oxidation states. This is in accordance with Macdiarmid's report.<sup>26</sup> The degree of polymerization ( $D_p$ ) was found to decrease when the alkyl chain length as a substituent on the nitrogen atom of the aniline was increased.<sup>27</sup> The presence of increasingly bulky substituents induces additional deformations along the polymer backbone because of increasing steric hindrance. As a consequence, the degree of conjugation decreases markedly and the oxidation potential increases. Roy et al.<sup>27</sup> also reported that the conductivity of the chemically synthesized substituted polyanilines do not depend on their doping level. Taking the above three mechanisms as a basis, a probable mechanism to explain the modification of nylon 6 fiber through chemical grafting of POT is

**Table III** Conductivity Measurements

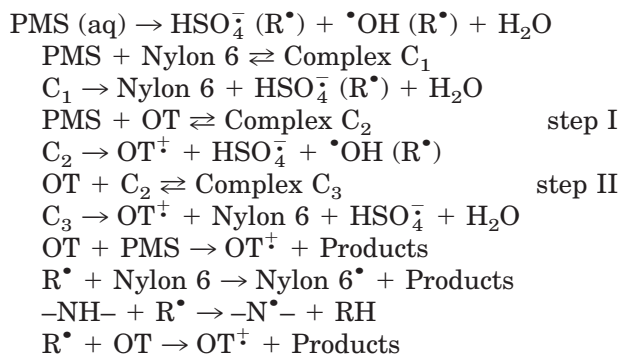
System	Percentage grafting	Conductivity Giga Ohm <sup>-1</sup> cm <sup>-1</sup>
Wool	—	1.20
Wool-g-POT	5.30	2.34
	16.9	6.27
Nylon 6	—	1.03
Nylon 6-g-POT	5.50	1.64
	11.2	2.85



suggested here. Our earlier article clearly indicated that both homopolymerization and graft copolymerization proceeded through condensation-type polymerization and that the molecular weight distributions in homopolymer and graft copolymers were based on the interaction between different possible cation radicals.<sup>12</sup> The molecular weight distributions of homopolymer and graft copolymers are under investigations.

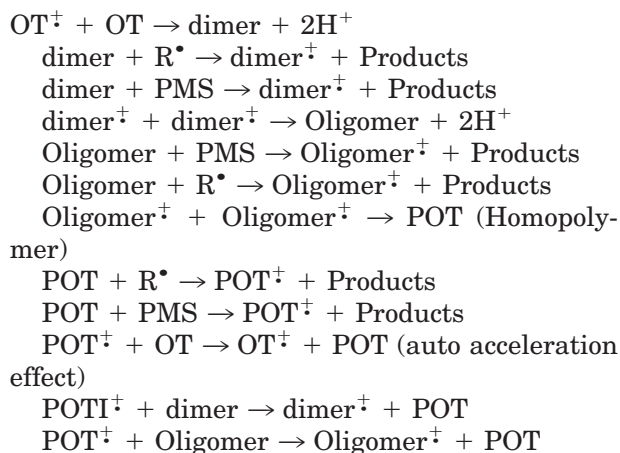
The probable mechanism for PMS-initiated graft copolymerization of OT onto nylon 6 fiber is as follows.

### Primary Reactions

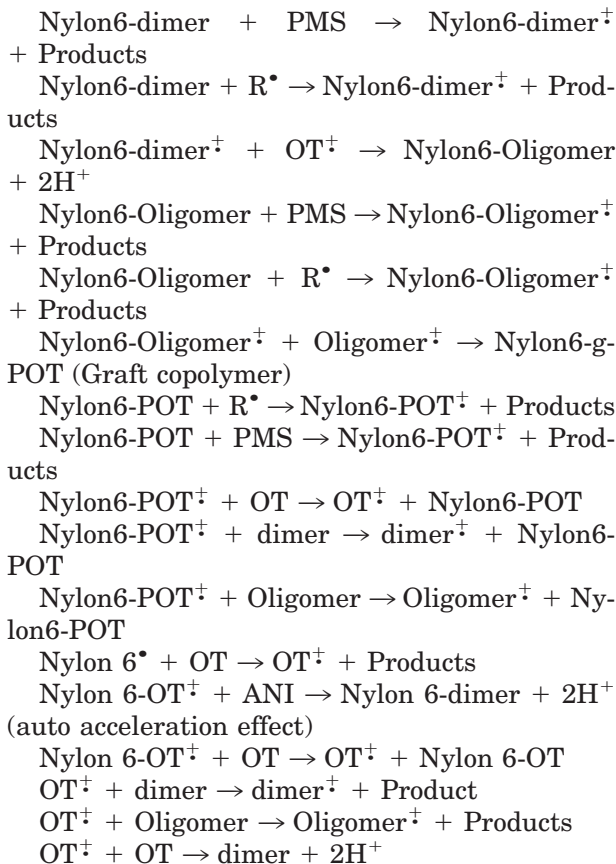
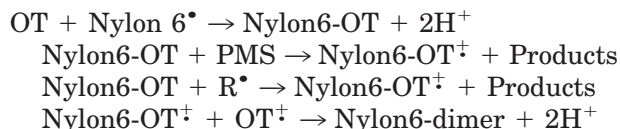


Step I, the formation of complex between the sulphate-containing initiator and the nitrogen-containing monomer, was proposed by Hunkeler et al.<sup>28</sup> Step II was explained by our research team.<sup>29</sup>

### Homopolymerization



### Graft Copolymerization



This mechanism explains the experimental results obtained. The mechanism in the case of the wool is similar to that of the nylon 6 system.

### CONCLUSIONS

From this study, we arrived at the following conclusions: 1) during the polymerization of OT in the presence of wool or nylon 6 fibers, chemical grafting occurred with simultaneous formation of POT, the homopolymer; 2) the higher grafting nature of wool fiber was confirmed through the evaluation of rate constants such as  $k_{1h}$  and  $k_{1g}$ ; 3) the conductivity value of the POT-grafted wool and nylon 6 fiber showed a higher value than the ungrafted ones; 4) the chemical grafting was confirmed by seeing the green color of the POT-grafted fibers, the weight changes during the monomer, the initiator, the amount of fiber variations, and finally, by the FTIR spectroscopy.

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