Chemical Oxidative Grafting of Conducting Poly(*N*-methyl aniline) onto Poly(ethylene terepthalate)

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ABSTRACT: Detailed studies on the peroxidisulfate (PDS) initiated graft copolymerization of *N*-methyl aniline (NMA) with poly(ethylene terepthalate) (PET) were carried out in *p*-tolene sulfonic acid medium under nitrogen atmosphere. Experiments were designed to follow the rate of formation R_h of the poly(*N*-methyl aniline (PNMA), simultaneously with the rate of grafting of PNMA onto PET. Effects of concentration of NMA, PDS, PET, time, and temperature on R_h and graft parameters were followed. Kinetic equations were deduced to correlate the changes in the rate with experimental conditions. Graft copolymers were isolated and grafting of PNMA onto PET was confirmed through FTIR, thermogravimetric analysis, and conductivity measurements. Tensile measurements showed that grafting of PNMA did not alter the tensile properties of PET. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 596–605, 2005

Key words: conjugated polymers; graft copolymers; kinetics (polym.); polyesters; thermogravimetric analysis (TGA)

INTRODUCTION

Grafting of vinyl polymers onto natural[1,2] or synthetic[3,4] fibers can be made through free-radical graft copolymerization. Grafting can be affected by high-energy radiation,[5] low-energy radiation in the presence or absence of stabilizers,[6] and chemical methods.[7–9] In general, grafting results from abstraction of the hydrogen atom from a hydroxyl group[1] or amino group[10] attached to the active carbon atom[11] in the polymer backbone. Initiation of grafting often occurs though a free-radical route and thus several free-radical–producing systems were tried for this purpose. The use of peroxosalts [potassium peroxodisulfate (PDS), potassium peroxomonosulfate (PMS), etc.] as initiator for free-radical initiation of vinyl polymerization and graft copolymerization has been exhaustively studied.[12–18]

For meeting specified applications, the properties of the textile fibers can be suitably modified by appropriate graft copolymerization. Kawahara and coworkers[19] reported the grafting of methacrylamide onto silk fiber to modify the mechanical properties and structure of the fiber. Mechanical and thermal properties of poly(ethylene terepthlate) (PET) fiber could be altered by graft copolymerization of various vinyl polymers onto PET fiber.[20,21] Poly(acrylonitrile) and poly-(methyl methacrylate) were grafted onto PET fiber by Gopalan and coworkers.[3,4]

Conducting polymers can be grafted onto various fibers and such studies have been the focus of much attention because they can provide wide applications in electrical and electronic devices.[22–24] Moreover, conducting polymers have been grafted with conventional polymers, which are used in the fields of EMI shielding, gas sensors,[25] and batteries.[26]

Chemical[27] and electrochemical[28] methods were used for the preparation of poly(aniline) (PANI) and its various ring-substituted derivatives. Processability of PANI has been improved by blending with other conventional polymers and also by grafting onto insulating materials.[29] Grafting of PANI onto polyamino styrene was reported by Li et al.[30] Yang and coworkers[31] grafted PANI onto chitosan backbone and provided evidences through thermal, spectroscopic, and conductivity measurements. Li et al.[32] could produce soluble PANI through grafting and the grafting was proved by morphology, spectroscopy, and electrical conductivity measurements. Abraham et al.[33] prepared a highly conducting blend of nylon 6/PANI film. Transparent PANI/nylon 6 composite film was prepared and the degradation kinetics of electrical conductivity was reported.[34] None of the above research articles details the kinetics of homopolymer formation. Our research team reported[35–42] few of the kinetic studies using peroxosalts as initiator for the graft copolymerization of aniline and *o*-toluidine onto PET, ny-

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lon 6, nylon 66, wool, polypropylene, and rayon fibers.

Toppare and coworkers[43] prepared a polypyrrole–polyamide composite by an electrochemical method and they provided spectroscopic evidence for the bonding between two polymers that resulted in grafting. Gregory and Tzou[44] grafted PANI onto PET fiber and they reported the kinetic results. Bhadani et al.[45] prepared a conducting fiber from natural fibers by an electrochemical method.

The present investigation reports the kinetics of graft copolymerization of poly(N-methyl aniline) (PNMA) onto PET in p-toluene sulfonic acid (p-TSA) medium. Detailed investigation on the kinetics of graft copolymerization and the simultaneous homopolymerization was made. Rate equations correlating the experimental parameters were deduced. Evidence for the grafting of PNMA onto PET was provided through UV–visible spectroscopy, thermogravimetry, and conductivity studies.

EXPERIMENTAL

Materials

N-Methyl aniline (NMA, Merck, Darmstadt, Germany), potassium peroxodisulfate (PDS, Merck), and p-toluene sulfonic acid (Merck) were used as received. PET was used after Soxhlet extraction with acetone to remove any adhering impurities and was dried at room temperature.

Grafting copolymerization

PET (W_1 g), a required amount of NMA, and water were charged to a polymer tube and thermostated at 40°C for 30 min. The solution was deaerated by passing pure nitrogen gas for 30 min. Polymerization was initiated by the addition of a calculated volume of preaerated PDS (using standard solution). The time of adding the oxidizing agent PDS was taken as the starting time for the reaction (polymerization conditions were selected in such a way that no polymerization occurred in the absence of the added oxidant). This was ascertained by a separate experiment. At the end of the reaction time, the reaction was arrested by immersing the reaction vessel in ice-cold water and blowing air into the reaction vessel. Graft copolymerization experiments were carried out at 40°C for 90 min.

The grafted PET and the homopolymer (PNMA) were filtered from the reaction mixture using a G4 sintered crucible, washed thoroughly with distilled water several times, dried at 70°C (for 4 h), and weighed to a constant weight, giving the total weight of the grafted polymer with the homopolymer (W_2 g). The mixture of the grafted PET along with the ho-

mopolymer, PNMA, was Soxhlet extracted with acetone for 24 h to separate PNMA from the grafted PET.

After the separation of PNMA, the grafted PET was dried at room temperature and weighed to a constant weight (W_3 g). The difference between W_3 and W_1 gives the weight of NMA grafted onto PET. The difference between W_2 and W_3 gives the weight of the formed homopolymer, PNMA. The above experimental approach thus provides a way to follow the kinetics of both graft copolymerization and simultaneous homopolymerization.

Rate measurements

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

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

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

where W_4 is the weight of monomer used.

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

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

where V is the total volume of the reaction mixture, t is the reaction time in seconds, and M is molecular weight of the monomer.

UV–visible spectrophotometry analysis for the isolation of the grafted PET from PNMA

The visible spectrum was recorded using a UV-2401 PC UV–visible spectrometer (Shimadzu, Kyoto, Japan) for the analysis of the PNMA content at various Soxhlet-extraction time intervals during the isolation of grafted PET from the homopolymer. Grafted PET with PNMA (green in color) in the doped state was treated with aqueous ammonia and the blue colored mass was separated by filtration, dried at 60°C for 5 h, and again treated with N-methyl pyrrolidone (NMP) with constant stirring. For each time interval, the Soxhlet extraction was subjected to UV–visible spectra analysis.

FTIR spectrophotometry analysis

PNMA and PNMA-*grafted*-PET were pressed as a disk with KBr and FTIR spectra were recorded using an
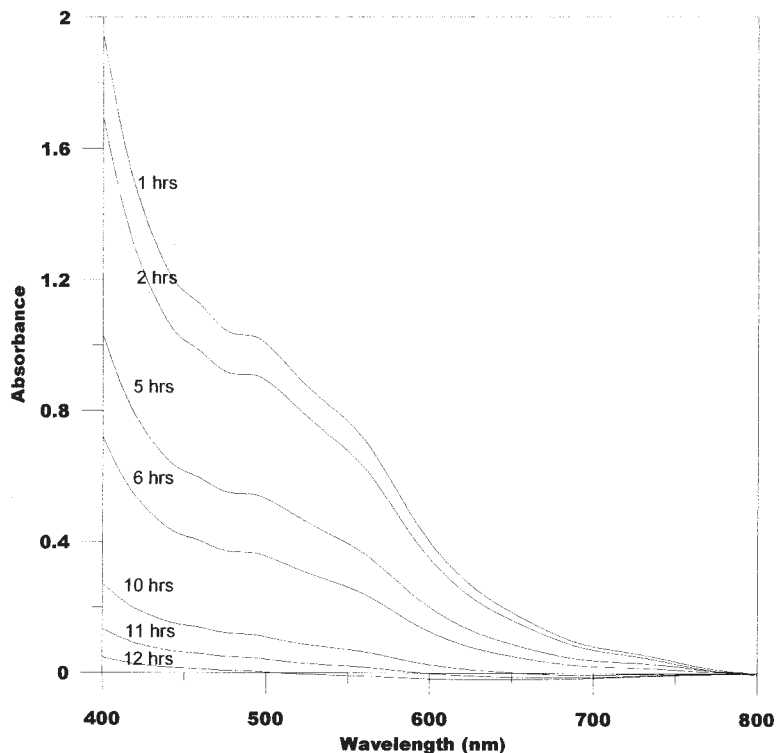
Figure 1 Visible spectra of PNMA in NMP at different Soxhlet-extraction times.

FTIR Rx 1 (Perkin–Elmer, Buckinghamshire, UK) at a resolution of 4 cm^{-1}, at a minimum of 32 scans, and were signal-averaged at room temperature.

Scanning electron microscopy (SEM)

SEM observation was carried out for PNMA-*grafted*-PET with Au-coated vacuum ion sputter by a liquid hydrogen method (JEOL 840 A, Tokyo, Japan). A rotating system was attached to the instrument and used for accurate measurements for various magnifications.

Tensile strength measurement

Tensile strength of the grafted and ungrafted PET samples was measured by using a tensometer (Type W 10,241, Monsanto, Poole, UK). A specimen length of 20 cm and a width of 3.3 cm were used to measure the tensile strength of grafted and ungrafted PET fibers.

Thermogravimetric analysis (TGA)

TGA of PET, PNMA-*grafted*-PET, and PNMA were made with a DuPont 2050 thermogravimetry analyzer (TA Instruments, New Castle, DE), using platinum crucibles with about 2 mg of the samples, under dynamic air atmosphere (30 mL/min) at a heating rate of 10°C min^{-1}.

Conductivity measurements

Conductivities of both grafted and ungrafted PET and PNMA were determined by a Keithley 617 electrometer (Keithley Metrabyte, Taunton, MA). A 1-cm length of the fiber was taken and its two ends were fixed at the two poles of the instrument and the current was passed. The meter directly showed the conductivity value.

RESULTS AND DISCUSSION

Isolation of PNMA-*grafted*-PET fiber from homopolymer

The PNMA-*grafted*-PET (PNMA-*g*-PET) was removed from the homopolymer and dedoped with aqueous ammonia solution for 5 h and then Soxhlet-extracted in NMP. At each interval of time, the fiber was removed from NMP, and the NMP extract was tested for the PNMA content through UV–visible spectroscopy. Figure 1 shows the visible spectra of PNMA in NMP solution for different Soxhlet-extraction time intervals. The visible spectra have a broad band, around 550 nm, characteristic of neutralized PNMA. The absorbance at 550 nm decreased with increasing Soxhlet-extraction time and became nil after 12 h, clearly verifying that this process completely removes the physically adsorbed PNMA on the grafted fiber.
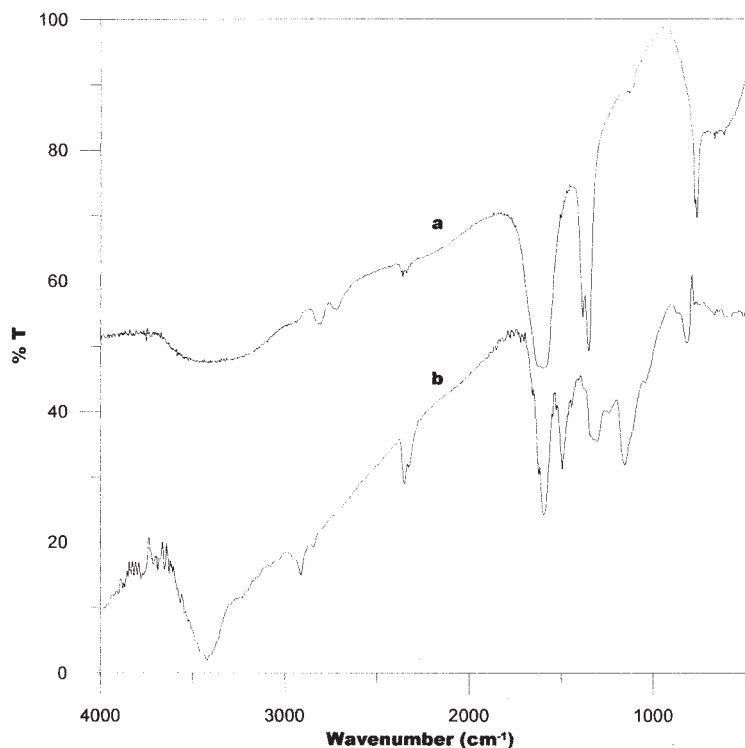
Figure 2   FTIR spectra of (a) PNMA and (b) PNMA-*grafted*-PET.

Evidences for grafting

FTIR spectroscopy

The FTIR spectra of PNMA and PNMA-*grafted*-PET are presented in Figure 2. The spectrum of PNMA-*grafted*-PET [Fig. 2(b)] shows peaks that are characteristic of PNMA besides the peaks corresponding to PET. This clearly confirms that PNMA is grafted as side chains in PET. The peaks at 1635 and 1353 cm^{-1} represent the stretching frequency of the C=N band. The broad band around 3375 cm^{-1} is attributed to the presence of –NH stretching of the aromatic amine. The C—H out-of-plane bending vibration of the substituted benzene ring appears at 826 cm^{-1}. The peaks at 1496 and 1602 cm^{-1} indicate the presence of the ring stretch of the benzenoid and quinoid form. The peak appearing at 1256 cm^{-1} is attributed to the C—H stretching of the aromatic secondary amine. The peaks at 890 and 772 cm^{-1} are attributed to the aromatic out-of-plane C—H bending stretch. These peaks are responsible for the presence of PNMA units in the fiber chain. The other peaks observed in the spectrum are attributed to the PET backbone polymer.

SEM topography

A scanning electron micrograph of PNMA-*grafted*-PET is presented in Figure 3 at a magnification of ×500. SEM topography shows the nature of grafting and it is obvious from the SEM topography that the PNMA was grafted onto PET fiber.

Tensile strength measurements

The results of tensile strength measurement of PNMA-*grafted*-PET and ungrafted PET (Table I) indicate that grafting does not influence the tensile strength of the fiber. The stress–strain curve (Fig. 4) justifies this.

Thermogravimetric analysis

Figure 5 presents the TGA curves of the PET, PNMA-*grafted*-PET fiber, and PNMA. The thermogram of PNMA [Fig. 5(iii)] shows two stages of weight loss.
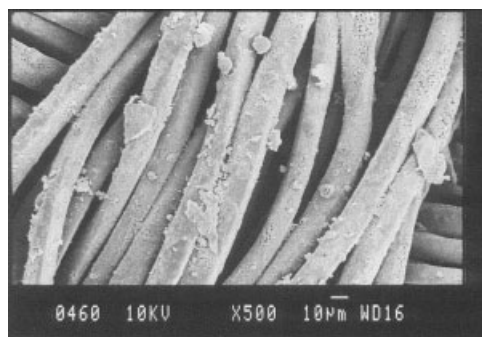

Figure 3   SEM microphotograph of PNMA-*grafted*-PET.

TABLE I
Tearing Strength for Grafted and Ungrafted Samples

Polymer	Grafted with	Maximum load applied (kg)	Tearing strength from graph (cm)	True extension (cm)	Percent elongation (%)	Stress (%)	Strain (%)
100% PET	—	17	9.2	2.375	25	617.05	43.7
100% PET	NMA	14	8.8	2.200	25	510.94	35.4

The weight loss at lower temperature (115°C) is attributed to the loss of the counteranion. The first weight loss is about 15%, which begins from 115°C and continues up to 370°C. The second stage weight loss, which starts from 465°C, corresponds to the decomposition of the polymer backbone. The existence of thermal degradation around 370°C, characteristic of PNMA in the grafted fiber, adds evidence for the grafting of PNMA onto PET. A variation in weight loss and temperature of decomposition could be noticed between simple PNMA and grafted PET. In PNMA-*grafted*-PET, decomposition starts around 370°C and this can be assigned to the removal of dopants and subsequent decomposition of the structural units in PNMA. It can be seen that the mass retained beyond 450°C was higher for the grafted fiber compared to that of simple PET. This shows that the presence of PNMA in the grafted PET makes the fiber more stable than PET beyond 450°C.

Conductivity measurements

The NMA-*grafted*-PET showed an improved conductivity over that of the ungrafted one (Table II). It was found that the conductivity value increased with increasing percentage of grafting. This also confirms the grafting of PNMA onto PET fiber.
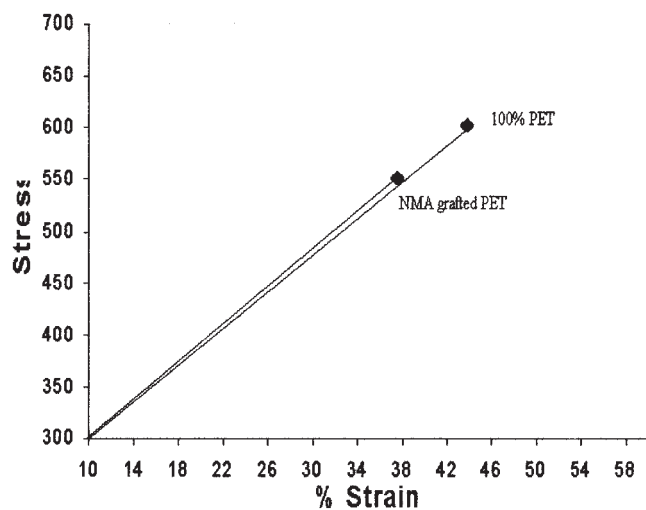

Figure 4 Stress–strain curve for PNMA-*grafted*-PET.

Kinetics of graft copolymerization and homopolymerization

Experiments were performed under different conditions to follow the kinetics of graft copolymerization and homopolymerization.

Effect of time on R_h and graft parameters

R_g, R_h, and graft parameters were determined at various time intervals while keeping other experimental conditions constant, as given in Table III. R_g and R_h increased initially up to 90 min and then decreased with an increase in time. To follow the kinetics of graft copolymerization, a reaction time of about 90 min was selected. This is based on the fact that homopolymer formation was higher than graft copolymer formation beyond 90 min. Steady increases in % grafting and % grafting efficiency were witnessed up to 90 min (Table III).

Effect of [NMA] on R_h and graft parameters

Experimental results were obtained by changing [NMA] in the range of 0.12 to 0.27 mol L^{-1} by keeping other experimental conditions constant. R_g and R_h values increase with an increase in [NMA] [Fig. 6(a) and (b)]. It is noted that % grafting increases steadily with increasing concentration of NMA. % Grafting efficiency remains unaffected for a change in concentration of NMA (Table IV).

To determine the order dependency of [NMA] on R_g and R_h, plots of R_g versus [NMA] [Fig. 6(a)] and R_h versus [NMA] [Fig. 6(b)] were drawn. These plots were found to be straight lines, indicating a first-order dependency of R_g and R_h on [NMA].

Effect of [PDS] on R_h and graft parameters

[PDS] was varied between 0.036 and 0.098 mol L^{-1}, while other experimental conditions were kept constant. R_g and R_h showed an increasing trend with increasing [PDS]. % Grafting and % grafting efficiency were also found to increase with [PDS] (Table V.)

The straight line plots of R_g versus [PDS] [Fig. 7(a)] and R_h versus [PMS] [Fig. 7(b)], passing through the
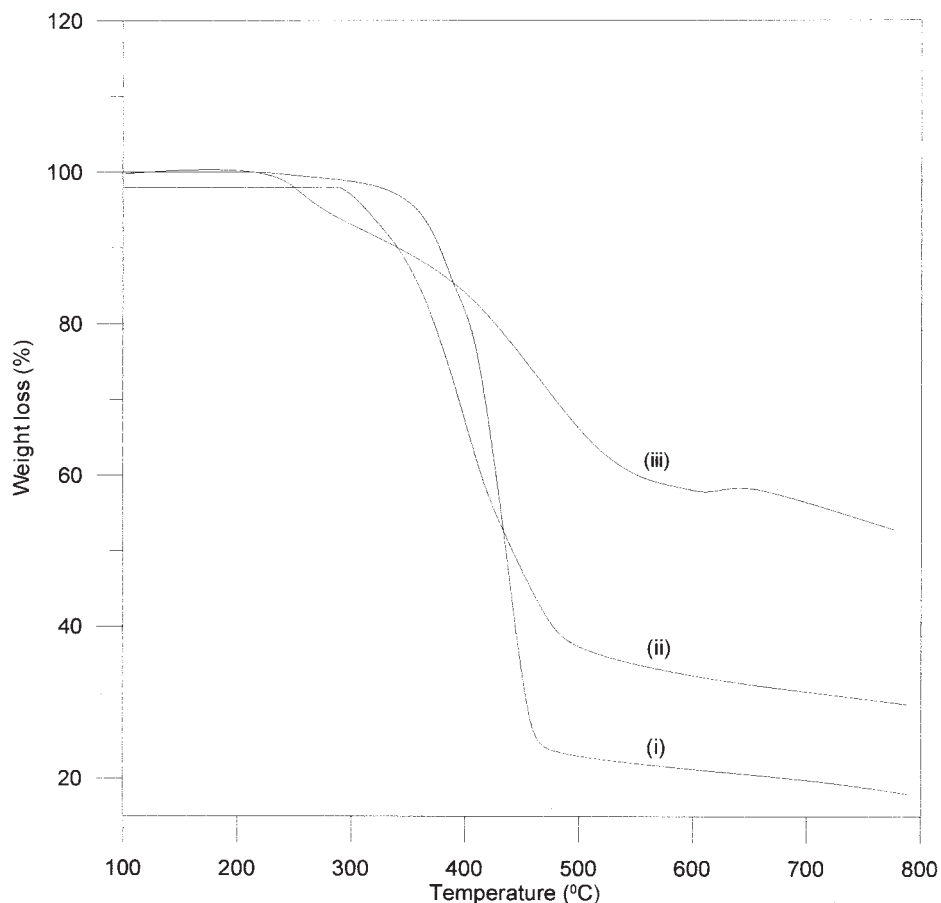
Figure 5 Thermogram of (i) PET fiber, (ii) PNMA-*grafted*-PET fiber, and (iii) PNMA.

origin, imply first-order dependency of both R_g and R_h on [PDS].

Effect of (amount of PET) on R_h and graft parameters

Weight of PET was varied from 0.20 to 0.456 g, while keeping other experimental conditions constant. It was observed that both R_g and R_h values increased steadily with increasing weight of PET fiber (Table VI). It is interesting to note that both % grafting and % grafting efficiency were found to increase steadily.

Plots of R_g versus (amount of PET) [Fig. 8(a)] and R_h versus (amount of PET) [Fig. 8(b)] indicated the first-order dependency of R_g and R_h on the amount of PET.

Effect of temperature on R_h and graft parameters

R_g and R_h values obtained for the experiments with different temperatures (from 35 to 60°C) are given in Table VII. R_g and R_h increase initially up to 45°C and

TABLE II
Conductivity Measurements

Polymer	% of Grafting	Conductivity $(\Omega^{-1}\,cm^{-1})$
PET	—	0.95 G
PNMA	—	39.57 K
PNMA-*grafted*-PET	2.56	11.25 K
	6.45	14.56 K
	9.25	19.28 K

TABLE III
Effect of Time on R_h, R_g, Percent Grafting, and Percent Efficiency[a]

Time (s)	$R_h \times 10^6$ (mol L^{-1})	$R_g \times 10^7$ (mol L^{-1})	Percent grafting	Percent efficiency
900	0.65	1.56	0.65	0.45
1800	0.95	3.98	0.98	0.56
3600	1.55	5.64	1.12	0.78
5400	2.28	7.20	1.26	1.12
7200	2.00	6.23	1.13	1.01
9000	1.87	5.23	1.00	0.85

[a] [PDS] = 0.036 mol L^{-1}; [NMA] = 0.12 mol L^{-1}; wt. of PET = 0.2000 g; [*p*-TSA] = 1.0 mol L^{-1}; temperature = 313 K.

(a)

TABLE V
Effect of [PMS] on R_h, R_g, Percent Grafting, and Percent Efficiency[a]

[PMS] (mol L^{-1})	$R_h \times 10^6$ (mol L^{-1})	$R_g \times 10^7$ (mol L^{-1})	Percent grafting	Percent efficiency
0.036	2.28	7.20	1.26	1.12
0.048	2.9	9.23	2.98	1.56
0.061	3.58	10.90	5.23	2.99
0.073	4.47	13.08	6.27	3.87
0.090	5.67	15.23	9.25	5.06
0.098	6.13	18.00	10.25	5.73

[a] [NMA] = 0.12 mol L^{-1}; wt. of PET = 0.2000 g; temperature = 313 K; [p-TSA] = 1.0 mol L^{-1}.
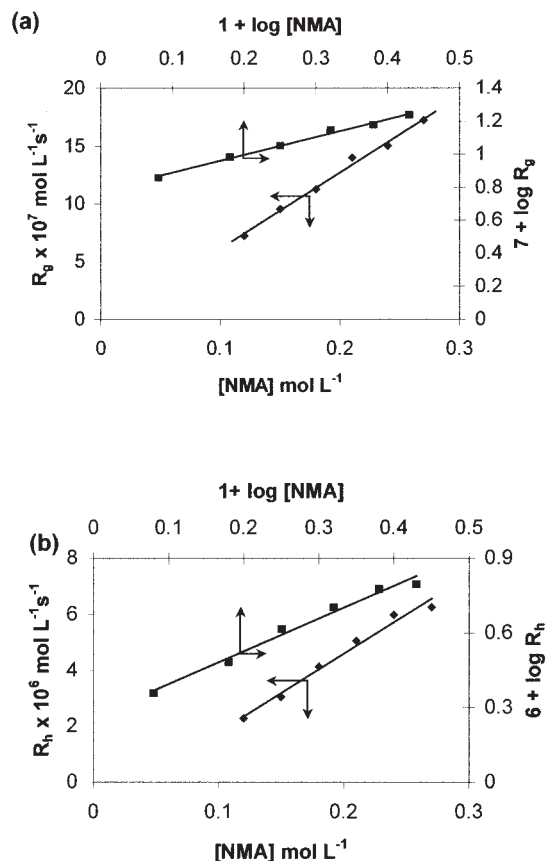
(b)

Figure 6 Effect of [NMA] on (a) R_g and (b) R_h. [PDS] = 0.036 mol L^{-1}, wt. of PET = 0.2000 g, temperature = 313 K, [p-TSA] = 1.0 mol L^{-1}.

the present work. The observed dependencies of rate of graft copolymerization and homopolymerization on the experimental parameters were found to be different in many respects. Earlier, Gregory and co-workers[44] studied the effect of added fiber on chemical polymerization of aniline in the presence of PET fiber and no correlation was attempted to relate the changes in the rate of homopolymerization with reaction parameters. Wei et al.[45] proposed an autoacceleration effect in the electrochemical polymerization of aniline by electrode surface in an attempt to explain
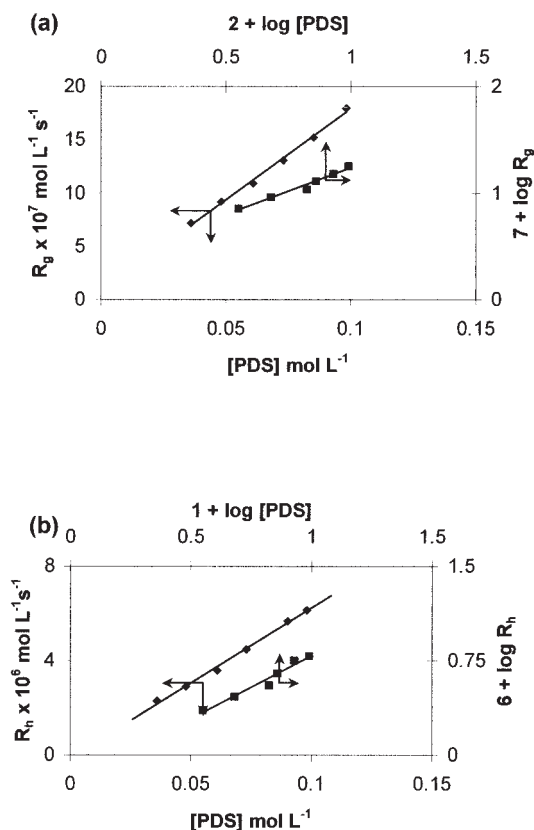
decrease thereafter (Table VII). % Grafting and % grafting efficiency also follow a similar trend. The decrease in R_h and graft parameters at higher temperatures may be attributable to the depletion of monomer concentration as a result of evaporation. Arrhenius plots, log R_g versus $1/T$ and log R_h versus $1/T$ (Fig. 9), were drawn. The plots showed an initial increasing trend with a subsequent decreasing trend.

It is pertinent to note that simultaneous measurements of homopolymerization were also followed in

(a)

(b)

Figure 7 Effect of [PDS] on (a) R_g and (b) R_h. [NMA] = 0.12 mol L^{-1}, wt. of PET = 0.2000 g, temperature = 313 K, [p-TSA] = 1.0 mol L^{-1}.

TABLE IV
Effect of [NMA] on R_h, R_g, Percent Grafting, and Percent Efficiency[a]

[NMA] (mol L^{-1})	$R_h \times 10^6$ (mol L^{-1})	$R_g \times 10^7$ (mol L^{-1})	Percent grafting	Percent efficiency
0.12	2.28	7.2	1.26	1.12
0.15	3.05	9.56	2.13	1.09
0.18	4.12	11.23	4.96	1.15
0.21	5.06	13.98	5.23	1.17
0.24	5.98	15.01	7.25	1.20
0.27	6.25	17.23	8.56	1.15

[a] [PDS] = 0.036 mol L^{-1}; wt. of PET = 0.2000 g; temperature = 313 K; [p-TSA] = 1.0 mol L^{-1}.

TABLE VI
Effect of Weight of Fiber on R_h, R_g, Percent Grafting, and Percent Efficiency[a]

Wt. of fiber (g)	$R_h \times 10^6$ (mol L^{-1})	$R_g \times 10^7$ (mol L^{-1})	Percent grafting	Percent efficiency
0.200	2.28	7.20	1.26	1.12
0.252	3.00	11.25	2.56	1.28
0.290	3.90	14.23	4.28	1.98
0.352	4.52	17.80	6.45	2.56
0.403	5.26	21.37	7.21	3.12
0.456	7.01	25.23	9.25	4.32

[a] [NMA] = 0.12 mol L^{-1}; [PDS] = 0.036 mol L^{-1}; temperature = 313 K; [p-TSA] = 1.0 mol L^{-1}.

TABLE VII
Effect of Temperature on R_h, R_g, Percent Grafting, and Percent Efficiency[a]

Temperature (K)	$R_h \times 10^6$ (mol L^{-1})	$R_g \times 10^7$ (mol L^{-1})	Percent grafting	Percent efficiency
308	1.57	3.00	1.03	0.95
313	2.28	7.20	1.26	1.12
318	3.70	9.01	2.95	2.18
323	3.26	10.20	4.00	1.89
328	2.50	8.56	3.28	1.52
333	1.88	7.26	2.97	1.21

[a] [NMA] = 0.12 mol L^{-1}; [PDS] = 0.036 mol L^{-1}; wt. of PET = 0.2000 g; [p-TSA] = 1.0 mol L^{-1}.

the changes in the induction time during the polymerization. A kinetic equation was proposed as

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

where k is the rate constant of formation of PANI on a bare Pt electrode and k' is the rate constant on PANI-coated Pt surface. Shim and Park[46] proposed a kinetic

equation for the polymerization of aniline on a bare Pt electrode including the autoacceleration effect and proposed a type of the following equation as

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

where k_1 and k_2 are the rate constants of formation of PANI on a bare Pt electrode surface and the rate constant of PANI-coated Pt electrode surface, respectively. *TAS* is the total available surface. In the study by Shim and Park,[46] the influence of the amount of added fiber on the rate of formation of homopolymer or rate of grafting was not considered.

In the present study, a kinetic model including the additional effects resulting from the added oxidizing agent as well as the heterogeneous phase is envisioned. The rate of PNMA formation was specifically monitored for different [NMA], [PDS], and the amount of PET fiber, while graft copolymerization simultaneously occurred. To highlight the role of the amount of fiber on the autoacceleration effect (resulting from the presence of active sites in the backbone structure), the rate changes were correlated with the amount of fiber.
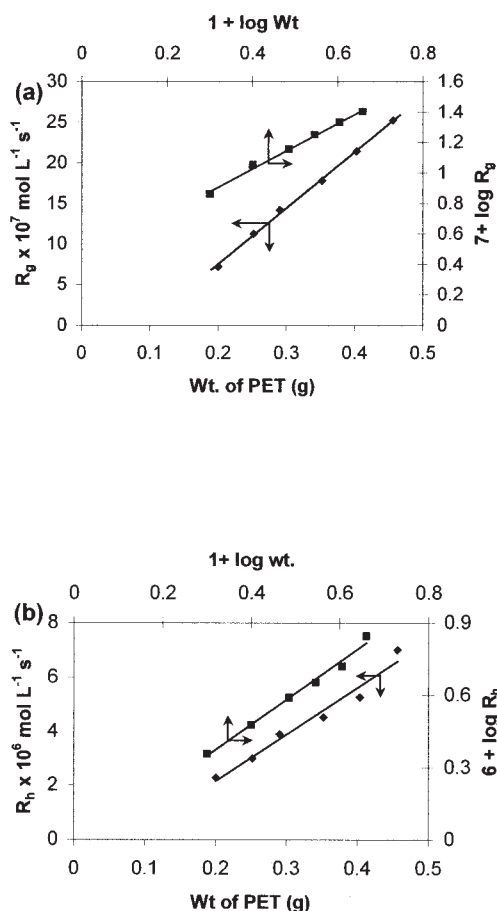

Figure 8 Effect of weight of fiber on (a) R_g and (b) R_h. [NMA] = 0.12 mol L^{-1}, [PDS] = 0.036 mol L^{-1}, temperature = 313 K, [p-TSA] = 1.0 mol L^{-1}.
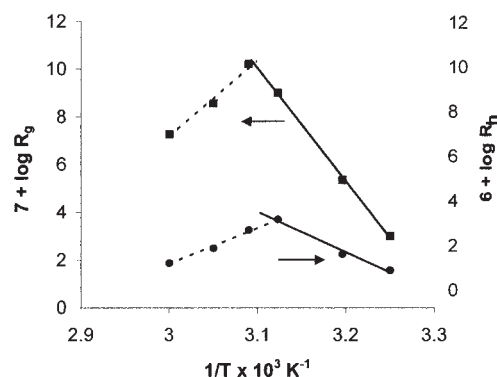
Figure 9 Effect of temperature on R_g and R_h. [NMA] = 0.12 mol L^{-1}, [PDS] = 0.036 mol L^{-1}, wt. of fiber = 0.2000 g, [p-TSA] = 1.0 mol L^{-1}.

TABLE VIII
Rate Constants Values

Rate constant	Value
k_{1h}	$23.20 \times 10^4 \text{ s}^{-1} \text{ g}^{-1}$
k_{3h}	$1.52 \times 10^6 \text{ mol L}^{-1} \text{ s}^{-1}$
k_{1g}	$65.95 \times 10^4 \text{ s}^{-1} \text{ g}^{-1}$
k_{3g}	$1.95 \times 10^6 \text{ mol L}^{-1} \text{ s}^{-1}$

On knowing the dependencies of various experimental parameters on R_p (NMA) and information that plots of R_p (NMA) versus [NMA] [Fig. 6(b)] and R_p (NMA) versus [PDS] [Fig. 7(b)] are straight lines, and R_p (NMA) versus wt. of fiber [Fig. 8(b)] is a straight line with definite intercepts, a modified representation of eq. (2) is proposed here:

$$R_h(\text{NMA}) = k_{1h}[\text{NMA}][\text{PDS}] \text{ (wt. of fiber)}$$
$$+ k_{2h}[\text{NMA}][TAS] + k_{3h} \quad (3)$$

where k_{1h} is the rate constant corresponding to homopolymer formation; and k_{2h} and k_{3h} are the rate constants for the homopolymer formation, taking into account the additional effects of available surface and probable change attributed to grafting. TAS includes the surface of homopolymer and grafted on a weight basis. The value of k_{3h} can be obtained from the intercept of the plot of R_p (NMA) versus [NMA] [Fig. 6(b)].

Because the rate of grafting also has a similar trend, an equation similar to eq. (3) is proposed to explain the grafting:

$$R_g(\text{NMA}) = k_{1g}[\text{NMA}][\text{PDS}] \text{ (wt. of fiber)}$$
$$+ k_{2g}[\text{NMA}][TAS] + k_{3g} \quad (4)$$

where k_{1g} is the rate constant corresponding to graft copolymer formation; and 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 attributed to grafting.
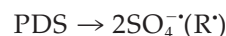
The values of the rate constants appearing in eqs. (3) and (4) were determined and are presented in Table VIII. It is important to note that the rate constant for homopolymer formation was comparatively higher ($23.20 \times 10^{-4} \text{ s}^{-1} \text{ g}^{-1}$) than that reported for aniline polymerization (0.0008 min^{-1}).[44] Further, the rate constant for grafting ($65.95 \times 10^{-4} \text{ s}^{-1} \text{ g}^{-1}$) was higher than that for homopolymerization, signifying the dominance of grafting over homopolymerization.
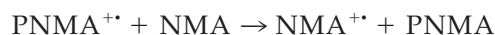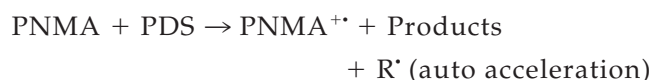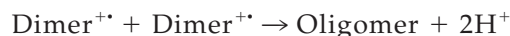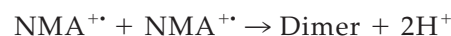
Mechanism

A probable mechanism explaining the simultaneous homopolymerization, along with grafting and autoacceleration effect by the presence of fiber, is presented here based on our experimental results and earlier literature[35–42] on grafting of PANI onto textile fibers. We envisage direct interaction of the monomer (NMA) and initiator (PDS) as the initiation step in these polymerization reactions.
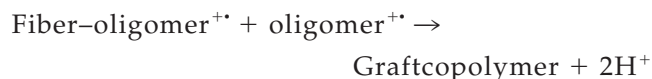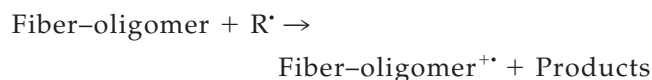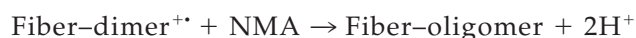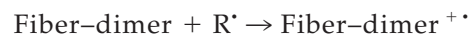
Primary reactions

$$\text{NMA} + \text{PDS} \rightarrow \text{NMA}^{+\bullet} + \text{products}$$

$$\text{PDS} \rightarrow 2\text{SO}_4^{-\bullet}(\text{R}^\bullet)$$

$$\text{R}^\bullet + \text{Fiber} \rightarrow \text{Fiber}^\bullet + \text{Products}$$

$$\text{R}^\bullet + \text{NMA} \rightarrow \text{NMA}^{+\bullet} + \text{Products}$$

Homopolymerization

$$\text{NMA}^{+\bullet} + \text{NMA}^{+\bullet} \rightarrow \text{Dimer} + 2\text{H}^+$$

$$\text{Dimer} + \text{R}^\bullet \rightarrow \text{Dimer}^{+\bullet} + \text{Products}$$

$$\text{Dimer} + \text{PDS} \rightarrow \text{Dimer}^{+\bullet} + \text{Products}$$

$$\text{Dimer}^{+\bullet} + \text{Dimer}^{+\bullet} \rightarrow \text{Oligomer} + 2\text{H}^+$$

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

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

$$\text{Oligomer}^{+\bullet} + \text{Oligomer}^{+\bullet} \rightarrow \text{PNMA} + 2\text{H}^+$$

$$\text{PNMA} + \text{PDS} \rightarrow \text{PNMA}^{+\bullet} + \text{Products}$$
$$+ \text{R}^\bullet \text{ (auto acceleration)}$$

$$\text{PNMA}^{+\bullet} + \text{NMA} \rightarrow \text{NMA}^{+\bullet} + \text{PNMA}$$

Graft copolymerization

$$\text{NMA} + \text{Fiber}^\bullet \rightarrow \text{Fiber–NMA}^{+\bullet}$$

$$\text{Fiber–NMA}^{+\bullet} + \text{NMA} \rightarrow \text{Fiber–dimer} + 2\text{H}^+$$

$$\text{Fiber–dimer} + \text{R}^\bullet \rightarrow \text{Fiber–dimer}^{+\bullet}$$

$$\text{Fiber–dimer} + \text{PDS} \rightarrow \text{Fiber–dimer}^{+\bullet} + \text{Products}$$

$$\text{Fiber–dimer}^{+\bullet} + \text{NMA} \rightarrow \text{Fiber–oligomer} + 2\text{H}^+$$

$$\text{Fiber–oligomer} + \text{R}^\bullet \rightarrow$$
$$\text{Fiber–oligomer}^{+\bullet} + \text{Products}$$

$$\text{Fiber–oligomer}^{+\bullet} + \text{oligomer}^{+\bullet} \rightarrow$$
$$\text{Graftcopolymer} + 2\text{H}^+$$

$$\text{Fiber} + \text{R}^\bullet \rightarrow \text{Fiber}^\bullet + \text{Products}$$

Fiber$^\bullet$ + NMA $\rightarrow$ NMA$^{+\bullet}$ + Products

(acceleration for homopolymerization)

NMA$^{+\bullet}$ + NMA $\rightarrow$ Dimer + 2H$^+$
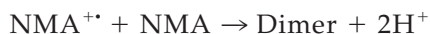
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