Peroxydisulfate Initiated Graft Copolymerization of Aniline onto Poly(propylene) Fiber—A Kinetic Approach

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ABSTRACT: A novel method for the preparation of electrically conducting fibers through chemical grafting of electrically conducting polymer onto poly(propylene) (PP) fiber is described. The graft copolymerization of aniline (ANI) was performed in aqueous acidic medium by using a chemical oxidant such as peroxydisulfate (PDS). Grafting occurred with simultaneous homopolymer formation. The content of polyaniline in the backbone fiber was found to vary by varying [monomer], [initiator], and amount of PP fiber. Various graft parameters such as rate of grafting (R_g), % grafting, and % grafting efficiency were evaluated. The rate of homopolymerization (R_h) was also determined. Both R_h and R_g showed first-order dependency on [ANI], [PDS], and amount of PP fiber variation. The chemical grafting was confirmed by use of cyclic voltammetry and conductivity measurements. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 3827–3834, 2003

Key words: graft copolymers; peroxydisulfate; rate constants; poly(propylene) (PP); conducting polymer

INTRODUCTION

During the last decade there has been increasing interest in the synthesis and characterization of conducting polymers. Polyanilines (PANI), which can be obtained in conducting form by chemical oxidation of anilines,[1–3] have been studied most extensively because of their high electrical conductivity and good environmental stability under ambient conditions. The principal problem encountered with the practical use of conducting polymers is their poor processability. Significant progress in the preparation of processable forms of polyanilines has been made in recent years.[1] Incorporating plastic or rubber with conducting polymers constitutes a promising method for improving processability. Various methods are used for this purpose; among them, chemical oxidation is an inexpensive and good method.[4–6] Laska and coworkers[7] blended PANI with conventional polymers. Kang et al.[8] reported the results on the graft copolymerization of PANI and polypyrrole (PPy) onto poly(acrylic acid) (PAA). In 1992 Gregory et al.[9] published some kinetic results on the graft copolymerization of aniline onto poly(ethylene terephthalate) (PET) and nylon-6 fibers. However, they failed to consider the rate of homopolymerization with reaction parameters. Based on this work, we carefully analyzed the rate of homopolymerization with reaction parameters and modified Gregory's rate equation. Recently Anbarasan and coworkers reported some kinetic results on conducting polymer grafted textile fibers by using peroxydisulfate (PDS) and peroxymonosulphate (PMS) as a lone initiator for the first time.[10–18] Conducting polymer grafted textile fibers are used in the electromagnetic irradiation (EMI) shielding technique[19] and in secondary batteries.[20] The present study directs attention to the systematic approach with respect to homopolymer formation during the graft copolymerization of PANI onto poly(propylene) (PP) fiber by using PDS as a single initiator and separation of the grafted polymer backbone from the homopolymer (PANI).

EXPERIMENTAL

Materials

Aniline (AR grade; Fischer, India) was used after distillation under vacuum. Potassium peroxydisulfate (PDS, AR grade; CDH), HCl (AR grade; Fisher), and other chemicals were used as received. PP fiber (a gift sample from M/S Madura coats, Madurai, India) was Soxhlet extracted with acetone for 24 h and dried at room temperature.

Procedure

A typical graft copolymerization study was conducted as now described. PP fiber (W_1, g) was immersed in a definite concentration of HCl (to adjust acidity) in a

polymer tube and thermostated at 45°C for 30 min. The required amount of monomer, aniline was added and deaerated for 15 min. Graft copolymerization was initiated by the addition of calculated volumes of PDS (using standard solutions). The time when PDS was added 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, as shown by a separate experiment. Formation of PANI was an exothermic reaction; thus liberated heat was absorbed by the PP fiber and activated itself for grafting. The liberated heat did not affect the system in any way and the reaction temperature was maintained at almost 45°C.[10,14–16] After a definite interval of time, the contents were filtered immediately.

The reaction mixture was filtered using a G4 sintered crucible and washed with 1M HCl several times, dried (at 80°C for 4 h), and weighed to constant weight. This gave the total weight of the grafted polymer along with the homopolymer (W_2, g). The grafted PP fiber was dedoped with 0.5N aqueous NH_3 and extracted with N-methyl pyrrolidone for several hours to remove the homopolymer (color changes, from green to blue, were seen in the grafted fiber). The extraction was repeated until the separation of homopolymer from the grafted sample was complete, as ascertained by drying the fiber in vacuum to constant weight (W_3, g). The difference ($W_3 - W_1$) gives the weight of the grafted polymer. The difference ($W_2 - W_3$) gives the weight of the homopolymer, PANI formed.

Rate measurements

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

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

$$R_h = \frac{W_2 - W_1}{VtM} \times 1000$$

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

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

where ($W_3 - W_1$) is the weight of the grafted polymer, V is the total volume of the reaction mixture, t is reaction time, ($W_2 - W_3$) is the weight of the ho-

mopolymer formed, W_4 is the weight of monomer used, and M is molecular weight of aniline.

Conductivity measurements

Conductivities of PANI grafted and pure PP fiber were measured by using a Keithley 617 programmable electrometer instrument (Keithley Metrabyte, Taunton, MA). A 1-cm fiber sample was taken, the two ends of which were connected with the two poles of the electrometer instrument. Current was passed through the poles and the conductivity was displayed on the display meter.

Cyclic voltammetry

PANI grafted PP fiber (green colored) was allowed to stand overnight in 0.5N aqueous ammonia solution (the fiber turns blue), after which the fiber was washed well with acetone two to three times to remove any adhering materials that were absorbed on the surface of the fiber. The dried fiber was dissolved in formic acid and made into a paste. The paste was dip coated onto a Pt micro working electrode (surface area 9.50 $\times 10^{-2}$ cm^2). Cyclic voltammograms (CVs) were recorded (by using BAS 100 A electrochemical analyzer) for PP-g-PANI 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.

RESULTS AND DISCUSSION

Effect of [ANI] on R_h and graft parameters

The aniline concentration [ANI] was varied between 0.20 and 0.60 mol L^{-1}, while other experimental conditions were kept constant. Both R_h and R_g increased with an increase in [ANI]. This may be attributable to the formation of an increasing number of monomer radical cations. To determine the order of dependencies, plots of log R_h versus log[ANI] [Fig. 1(A)] and log R_g versus log[ANI] [Fig. 1(B)] were drawn. The slopes of the plots were found to be unity and thus showed first-order dependency of both R_h and R_g on [ANI]. It was further confirmed by plotting R_h versus [ANI] [Fig. 1(C)] and R_g versus [ANI] [Fig. 1(D)]. The plots were found to be linear and the intercepts were noted. Both % grafting and % grafting efficiency values, given in Table I, increased with an increase in [ANI].

Effect of [PDS] on R_h and graft parameters

As shown in Table I, [PDS] was varied between 0.005 and 0.025 mol L^{-1} while other experimental conditions were kept constant. It was observed that both R_h and R_g increased with an increase in [PDS]. This can
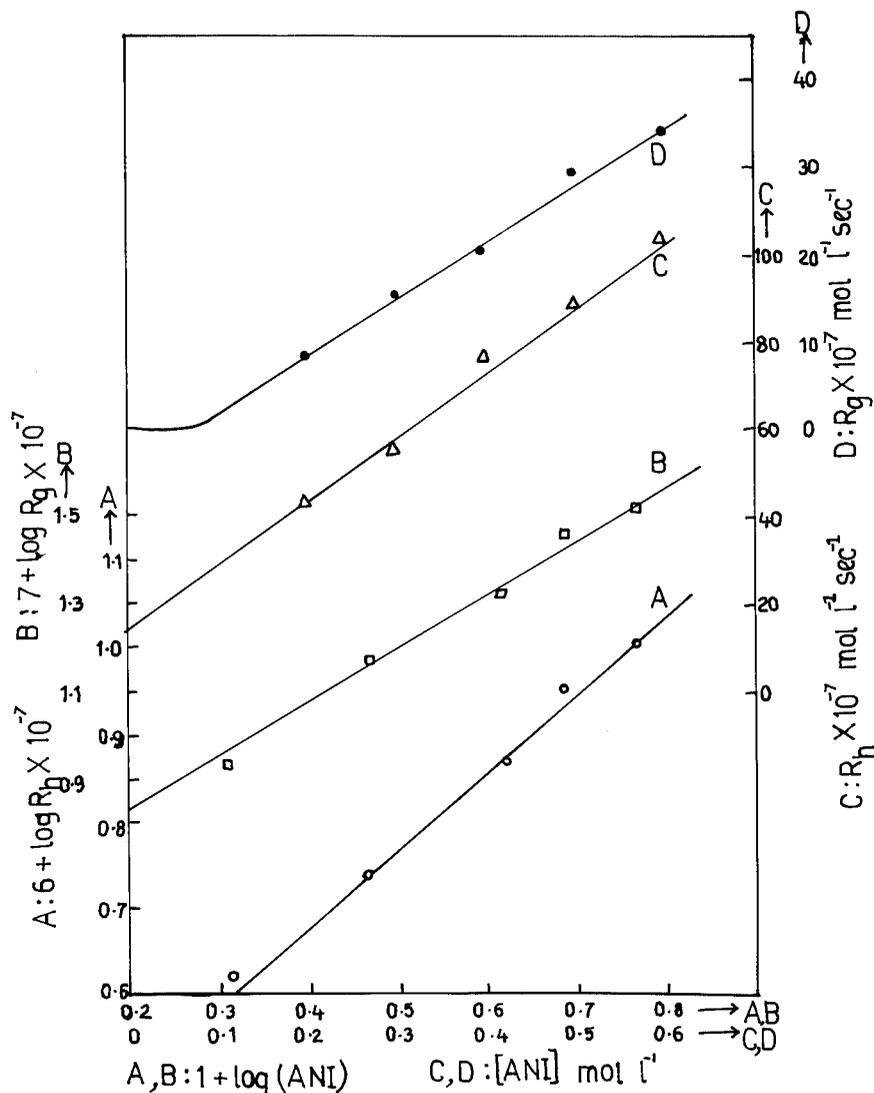
Figure 1 Effect of [ANI] on R_h and R_g: [PDS] = 0.01 mol L^{-1}, weight of PP fiber = 0.20 g, [HCl] = 1.00M, temperature = 45°C.

be ascribed to the formation of a large amount of initiator radicals. To determine the order of dependencies the following plots were made.

The plots of log R_h versus log[PDS] [Fig. 2(A)] and log R_g versus log[PDS] [Fig. 2(B)] were drawn that

confirmed the first-order dependency of R_h and R_g on [PDS]. R_h versus [PDS] [Fig. 2(C)] and R_g versus [PDS] [Fig. 2(D)] were also drawn to confirm further the first-order dependency of both R_h and R_g on [PDS]. Both % grafting and % grafting efficiency values,

TABLE I
Effect of [ANI] and [PDS] on % Grafting and % Grafting Efficiency

[ANI][a] (mol L^{-1})	% Grafting	% Grafting efficiency	[PDS][b] (mol L^{-1})	% Grafting	% Grafting efficiency
0.20	2.15	0.79	0.005	2.30	0.55
0.30	3.85	0.92	0.010	4.11	0.98
0.40	5.31	0.94	0.015	5.83	1.39
0.50	7.40	1.02	0.020	7.30	1.75
0.60	8.62	1.03	0.025	8.95	2.14

[a] [PDS] = 0.01 mol L^{-1}, amount of PP fiber = 0.20 g, HCl = 1.00M.
[b] [ANI] = 0.30 mol L^{-1}, amount of PP fiber = 0.20 g, HCl = 1.00M.
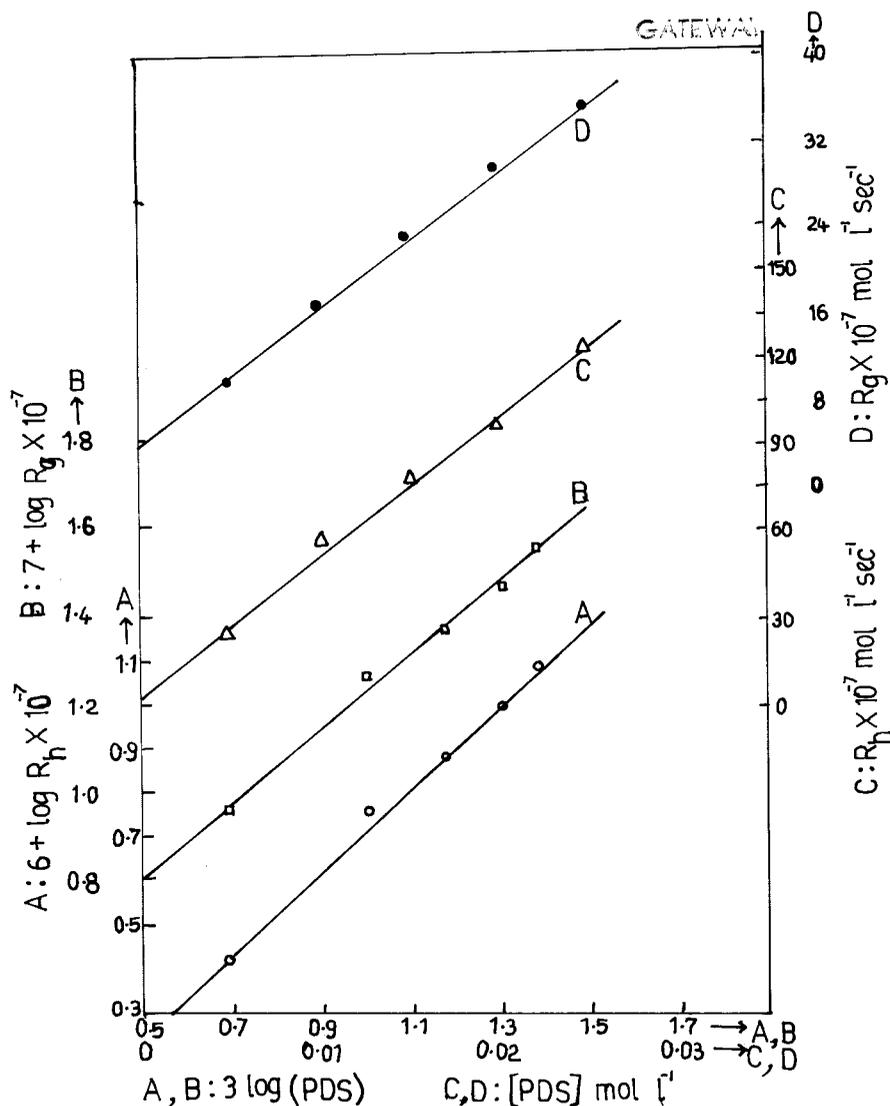
Figure 2 Effect of [PDS] on R_h and R_g: [ANI] = 0.30 mol L^{-1}, weight of PP fiber = 0.20 g, [HCl] = 1.00M, temperature = 45°C.

given in Table I, also increased with an increase in [PDS].

Effect of amount of PP fiber on R_h and graft parameters

The amount of PP fiber was varied between 0.10 to 0.35 g while other experimental conditions were kept constant. The experimental results indicated that both R_h and R_g increased with an increase in the amount of PP fiber, attributed to the availability of the large number of macroradicals.

To study the effect of amount of PP fiber on R_h and R_g, plots of log R_h versus log(amount of PP fiber) [Fig. 3(A)] and log R_g versus log(amount of PP fiber) [Fig. 3(B)] were drawn. It was found that the slope of the plots was very close to unity, which indicated the

first-order dependency of both R_h and R_g on the amount of PP fiber. The first-order dependency was further confirmed by plotting R_h versus (amount of PP fiber) [Fig. 3(C)] and R_g versus (amount of PP fiber) [Fig. 3(D)], whose plots were found to be linear. Both % grafting and % grafting efficiency values, given in Table II, increased with an increase of the amount of PP fiber.

In the electrochemical polymerization of aniline on a bare Pt electrode, Shim and Park[21] proposed a kinetic equation including the autoacceleration effect. The equation is 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
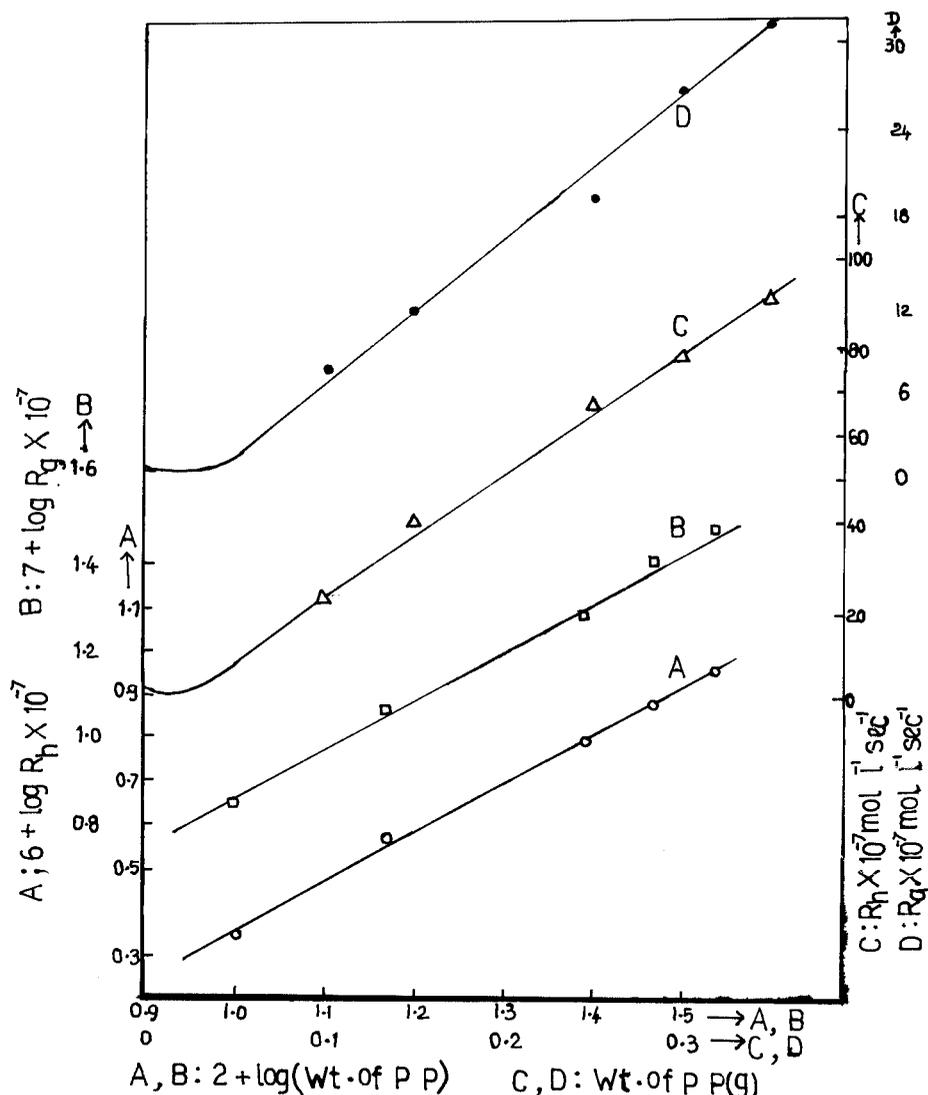
Figure 3 Effect of amount of PP fiber on $R_{h\ and}\ R_g$: [ANI] = 0.30 mol L^{-1}, [PDS] = 0.02 mol L^{-1}, [HCl] = 1.00M, temperature = 45°C.

the PANI-coated Pt surface, [M] is the concentration of monomer, and [P] is the amount of polymer formed.

In the electrochemical polymerization of aniline, the rate constant depends on the electrode potential and

TABLE II
Effect of Amount of PP Fiber on % Grafting and % Grafting Efficiency[a]

Weight of PP fiber (g)	% Grafting	% Grafting efficiency
0.10	3.50	0.42
0.15	3.81	0.69
0.25	3.92	1.16
0.30	4.36	1.57
0.35	4.40	1.87

[a] [ANI] = 0.30 mol L^{-1}, [PDS] = 0.01 mol L^{-1}, HCl = 1.00M.

electrode surface area. Similarly in the chemical polymerization of aniline, the rate constant depends on the amount of added oxidant and the number of available surface grafting sites (surface area).

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

where k_1 and k_2 are the rate constants of formation of PANI on a bare Pt electrode surface and PANI-coated Pt electrode surface, respectively. TAS is the total available surface.

In the case of chemical polymerization of ANI, a similar consideration based on the above kinetic model may be considered including the additional effect attributed to the added oxidizing agent as well as the heterogeneous phase. In the present case, the added fiber for grafting and the formed homopolymer

may cause the autoacceleration arising from the active surface effect.

The plot of R_h(ANI) versus [ANI] [Fig. 1(C)] was found to be linear with a definite intercept; R_h(ANI) versus [PDS] [Fig. 2(C)] is a straight line passing through the origin; R_h(ANI) versus (amount of PP fiber) [Fig. 3(C)] is also a straight line passing through the origin. These three combined facts necessitate modification of the above equations to give

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

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

where k_{1h} is the rate constant corresponding to homopolymer formation attributed to the added initiator, k_{2h} is the rate constant for homopolymer formation attributed to autoacceleration and surface effects, and k_{3h} is the individual rate constant for homopolymer formation and infers the initiator efficiency toward the homopolymer formation; k_{1g} is the rate constant for graft copolymer formation attributed to added initiator, k_{2g} is the rate constant for graft copolymer formation attributed to autoacceleration and surface effects, and k_{3g} is the individual rate constant that explains the initiator efficiency toward graft copolymer formation.

The values of k_{3h} and k_{3g} can be taken from the intercepts of the plot of R_h versus [ANI] [Fig. 1(C)] and R_g versus [ANI] [Fig. 1(D)], respectively. For the present case, PDS initiated graft copolymerization of aniline onto PP fiber in aqueous HCl medium; k_{1h} and k_{1g} values were determined from the slopes of the plots R_h versus [ANI] [Fig. 1(C)] and R_g versus [ANI] [Fig. 1(D)] using eqs. (1) and (2) as 8.00×10^{-3} and 2.30×10^{-3} g^{-1} m^{-1} s^{-1}, respectively. This value is far
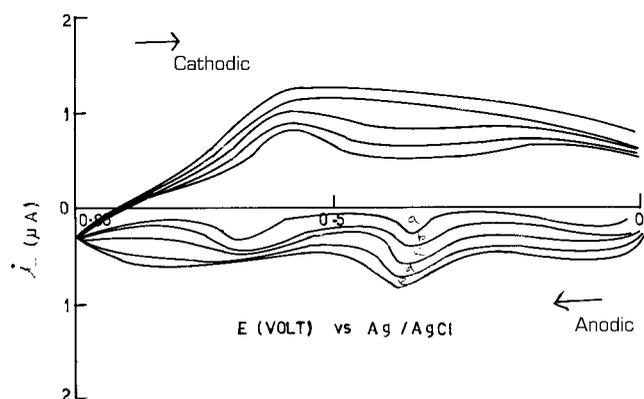
Figure 4 Cyclic voltammogram of PP-g-PANI film at various sweep rates (in mV/s): (a) 100, (b) 200, (c) 300, (d) 400, (e) 500.

TABLE III
Conductivity Measurements

Polymer	% Grafting	Conductivity (Ω^{-1} cm^{-1})
Polypropylene	—	1.15 G
PP-g-PANI	8.60	1.36 M
	34.3	6.59 M

higher than that of the simple homopolymerization rate constant and augments the autoacceleration effect in homopolymerization and graft copolymer formation by TAS. The value of k_{3h} was found to be 14.0×10^{-7} mol L^{-1} s^{-1}, whereas k_{3g} was found to be zero. The above rate constants indicate that k_{1h} is higher than k_{1g}. This confirms that rate of homopolymerization is higher than that of grafting.

Cyclic voltammetry

Cyclic voltammograms (CVs) of PP-g-PANI film, recorded at various sweep rates and shown in Figure 4, showed two anodic peaks at 400 and 670 mV and one cathodic peak at 550 mV. At a higher sweep rate the anodic peak at 670 mV disappeared. On cycling the potential with various sweep rates, the peak current was found to increase with an increase in sweep rates. The film was not degraded even at higher applied potential, thus confirming the chemical grafting of PANI onto the PP fiber matrix.

Conductivity measurements

The conductivities of ungrafted PP fibers and PANI grafted fibers at various % grafting were measured. The PP-g-PANI showed a conductivity that is higher than that of pure PP fiber. The conductivity increases linearly with % grafting (Table III), confirming the chemical grafting of PANI onto the PP fiber matrix.

MECHANISM

Among the polyolefins, PP is a versatile polymer from a commercial standpoint, but the lack of a functional group has limited many of its potential applications. To solve such issues, the graft copolymerization of PP with polar monomer was investigated. However, the mechanism of the reactions in PP matrices are not yet well understood because of multiple competing side reactions like crosslinking, chain scission, and carbonylation,[22–24] the relative contributions of which are determined by, for example, the nature of the polymer and the peroxide type and concentrations. We report here a probable mechanism for the PDS initiated graft copolymerization of aniline onto PP fiber in aqueous acidic medium based on our earlier reports.[25,26]

It is believed that in PP, grafting takes place through the abstraction of hydrogen from the $>$C—H group because of its greater reactivity than that of –CH$_2$ and –CH$_3$ groups. Grafting of ANI onto PP takes place through a free-radical path. We know that the free-radical reaction proceeds through three steps: initiation, propagation, and termination.

Initiation

$$PDS(aq.) \rightarrow 2SO_4^{\bar{\cdot}}(R^\cdot)$$

$$PDS + ANI \rightarrow Complex\ C_1 \qquad (Step\ I)$$

$$C_1 \rightarrow ANI^{+\cdot} + SO_4^{2-} + SO_4^{\bar{\cdot}}$$

$$ANI^{+\cdot} \rightarrow Resonance\ stabilization$$

$$PP + PDS \rightarrow Complex\ C_2$$

$$C_2 \rightarrow PP^\cdot + HSO_4^- + SO_4^{\bar{\cdot}}$$

$$C_2 + ANI \rightarrow Complex\ C_3 \qquad (Step\ II)$$

$$C_3 \rightarrow ANI^{+\cdot} + PP^\cdot + HSO_4^- + SO_4^{2-}$$
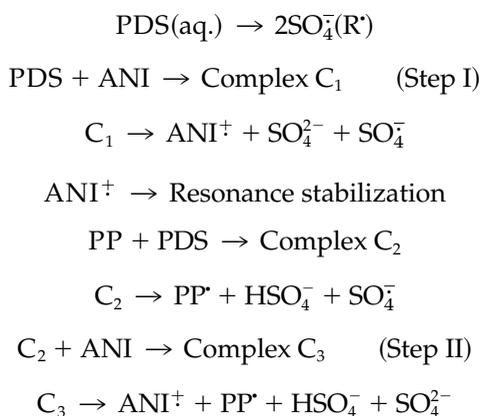
Step I was explained by Hunkeler et al.,[27] that a nitrogen-containing monomer can form a complex with a sulfate-containing initiator. Step II was explained by our research team.[28]

Propagation

$$2ANI + PDS \rightarrow 2ANI^{+\cdot} + 2SO_4^{2-}$$

$$ANI + R^\cdot \rightarrow ANI^{+\cdot} + SO_4^{2-}$$

$$ANI^{+\cdot} + ANI^{+\cdot} \rightarrow$$

$$Dimer\ (head–head,\ head–tail,\ tail–tail) + 2H^\cdot$$

$$dimer + R^\cdot \rightarrow dimer^{+\cdot}$$

$$dimer^{+\cdot} + dimer^{+\cdot} \rightarrow oligomer$$

$$oligomer + R^\cdot \rightarrow oligomer^{+\cdot}$$

$$2H^\cdot + 2SO_4^{\bar{\cdot}} \rightarrow 2HSO_4^-$$
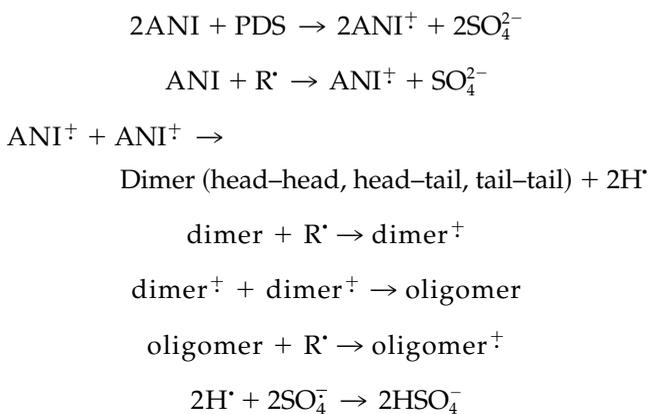
Dimerization occurs in three ways. Diphenyl hydrazine is formed as a result of head–head addition; *p*-amino diphenyl amine is formed as a result of head–tail addition; benzidine is also formed as a result of tail–tail addition as a third possible product. Formation of these products depends on (1) the pH of the medium, (2) reaction temperature, (3) initiating efficiency of the initiator, (4) reaction time, and (5) oxidation potential of the monomer.

Termination

$$HCl(aq.) \rightarrow H^+ + Cl^-$$

$$H^\cdot + SO_4^{\bar{\cdot}} \rightarrow SO_4^{2-} + H^+$$

$$H^\cdot + SO_4^{\bar{\cdot}} \rightarrow HSO_4^-$$

$$HSO_4^- + H^+ \rightarrow H_2SO_4$$

$$H_2SO_4 \rightarrow HSO_4^- + H^+$$

$$SO_4^{2-} + H^+ \rightarrow HSO_4^-$$

$$dimer^{+\cdot} + dimer^{+\cdot} \rightarrow oligomer$$

$$oligomer^{+\cdot} + oligomer^{+\cdot} \rightarrow PANI$$

$$PANI \cdot HCl + HSO_4^- + H^+ \rightarrow$$
$$PANI \cdot (HSO_4^-)(H^+) + HCl\ (doping)$$

$$PP–PANI \cdot HCl + HSO_4^- + H^+ \rightarrow$$
$$PP–PANI(HSO_4^-)(H^+) + HCl\ (doping)$$
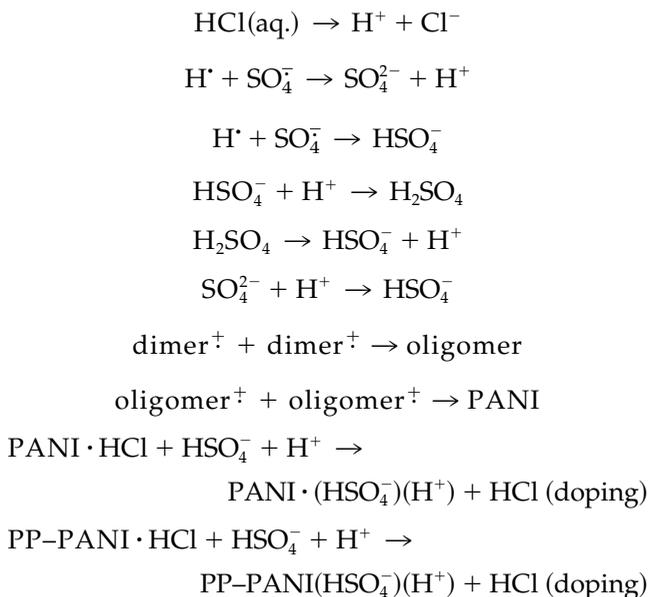
Autoacceleration effect

Any radical cation can initiate another neutral monomer species and form its corresponding radical cation (monomer radical cation) but at the same time a radical cation will not combine with the neutral monomer species.[8]

$$PANI^{+\cdot} + ANI \rightarrow PANI + ANI^{+\cdot}$$

$$PANI^{+\cdot} + dimer \rightarrow PANI + dimer^{+\cdot}$$

$$PANI^{+\cdot} + oligomer \rightarrow PANI + oligomer^{+\cdot}$$

$$PP–ANI^{+\cdot} + ANI \rightarrow PP–ANI + ANI^{+\cdot}$$

$$PP–dimer^{+\cdot} + ANI \rightarrow PP–dimer + ANI^{+\cdot}$$

$$PP–oligomer^{+\cdot} + ANI \rightarrow PP–oligomer + ANI^{+\cdot}$$
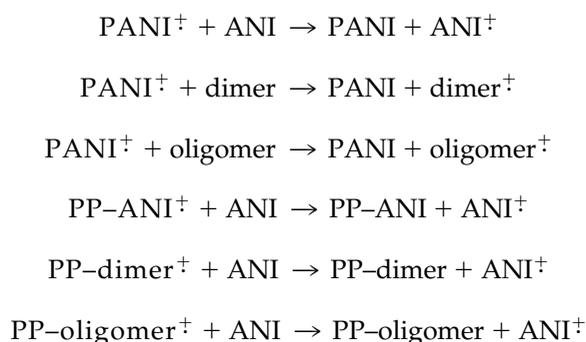
The above mechanism explains the experimental results obtained, that is, first-order dependency of both R_h and R_g on [ANI], [PDS], and amount of PP fiber variations. It also indicates that 1 mol of oxidant is required to oxidize 1 mol of monomer and one active site is required to oxidize 1 mol of monomer.

Important and interesting reactions other than grafting in the case of PP are crosslinking, β-scission, and carbonylation. The reactions are explained as follows:

$$\sim\sim CH_2—CH(CH_3)\sim + SO_4^{\bar{\cdot}} \rightarrow$$
$$\sim\sim CH_2—\overset{\cdot}{C}(CH_3)\sim + HSO_4^-$$

$2 \sim\sim CH_2 - \overset{\cdot}{C}(CH_3)\sim \; \rightarrow$

$\sim\sim CH_2 - C(CH_3)\sim$

$|$ (crosslinking)

$\sim CH_2 - C(CH_3)\sim$
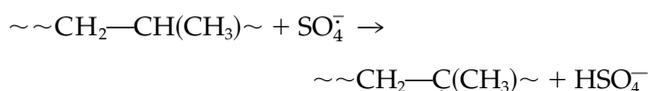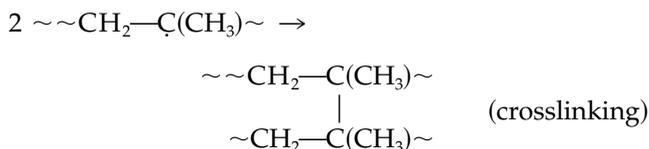
These reactions are similar to those reported by Ok-tern et al.[23] at higher temperature by use of organic peroxides:

$$\sim CH_2 - CH(CH_3) - CH_2 - CH(CH_3)\sim \xrightarrow{\text{Peroxide}}$$

$$\sim CH_2 - \overset{\cdot}{C}(CH_3) - CH_2 - CH(CH_3)\sim \; \rightarrow$$

$$\sim CH_2 - C(CH_3) = CH_2 + \overset{\cdot}{C}H(CH_3)\sim \quad (\beta\text{-scission})$$
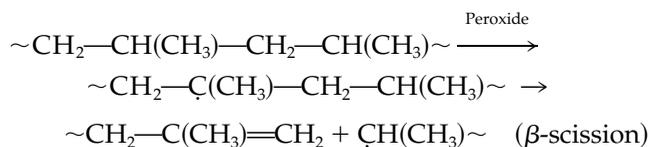
This kind of reactions is reported by Bettini and Ag-nelli[30] at higher temperature by use of organic perox-ides. At higher temperature the other expected prod-uct is ketone, attributed to the presence of hydroper-oxides.[31]

Our aim in this study was not to focus on determi-nation of % crosslinking, β-scission, and amount of carbonyl group formation. Our research team is cur-rently investigating the functionalization of polyeth-ylene (PE) and PP that will find an expanded range of industrial applications.

CONCLUSIONS

From this study the following conclusions were drawn.

1. During graft copolymerization simultaneous ho-mopolymerization also occurs.
2. Both R_h and R_g showed first-order dependency on [monomer], [initiatior], and amount of PP fi-ber.

3. Conductivity measurements and cyclic voltam-metry confirm the chemical grafting of PANI onto the PP fiber matrix.

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