

The Substituent Effects on the Structure and Surface Morphology of Polyaniline

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ABSTRACT: In this work, poly(2-fluoroaniline), poly(2-chloroaniline), poly(2-methylaniline), and poly(*N*-ethylaniline) were prepared by a self-assembly method using an oxidizing system consisting of a dopant anion, *p*-toluene sulfonate with ammonium peroxydisulfate. The effects of substituents on the surface morphology, conductivity, molecular weight, spectral and thermal properties of the polymers were studied. SEM results revealed that the surface morphology of the resulting polymers changed from nanofiber to spherical structure by changing the substituent on the aniline monomers. The structure and properties of these conducting films were characterized by FTIR, UV-vis, ele-

mental analysis, TGA, conductivity, and cyclic voltammetry. The polymer films show electroactivity in monomer free solution. Molecular weight of the polymers was determined by gel permeation chromatography. The dry electrical conductivity values of the substituted-polyanilines were found to be lower than that of PANI. The results revealed that the molecular structures of the polymers were similar to those of the emeraldine form of polyaniline. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3024–3030, 2010

Key words: polyaniline; poly(2-fluoroaniline); poly(2-chloroaniline); poly(2-methylaniline); poly(*N*-ethylaniline)

INTRODUCTION

Conductive polymeric materials in the highly extended conjugated electron systems in the main chain have attracted much interest in scientific and technological areas in recent years.^{1–3} Until recently, it was commonly accepted that plastics were isolators. Now the electrically conducting plastics, so called synthetic metals or conducting polymers (CP), are becoming a part of our daily life. Polyaniline (PANI) is the first conducting polymers whose electronic properties can be reversibly controlled by protonation.⁴ PANI and some of its derivatives have been extensively studied because of their ease of preparation by chemical and electrochemical methods, good environmental stability, and also because their electrical properties can be modified by both the oxidation state of the main chain and by protonation. This versatility has made polyaniline attractive for numerous applications, including sensors, battery electrodes, display devices, anticorrosion coatings, and field effect transistors, etc.^{5–8} PANI is inherently brittle and poor in processibility due to its insolubility in common organic solvents. Its

applications are strongly limited by its poor processibility. The associated difficulty of PANI for the application due to restricted solubility in common organic solvents has been tried to overcome by several researchers by different approaches. One of the methods employed to improve the solubility of PANI is the use of sulfonic acids as dopants. Introducing a $-\text{SO}_3\text{H}$ group on the PANI chain affects the properties of parent PANI without substantially conductivity and is of specific interest for several reasons such as solubility, environmental stability, processibility, etc.^{9–16}

Substituted polyanilines are used to increase the processibility of the polymer. The substituent groups present in the units of the polymer chain cause decrease in the stiffness of the polymer chain and results better solvation. Several substituted polyanilines with electron-donating^{17–20} and electron-withdrawing groups as substituents were reported in the literature.^{21–25} These polymers are soluble in common solvents but exhibit lower electrical conductivity value than the unsubstituted polyaniline. These results indicate that the side-groups may markedly affect the polymerizability of anilines.

Recently, the nanostructures conducting polymer was synthesized by the template method, an external addition of dopant^{26,27} or the self-assembly process.^{28–30} However, the method in this study is very different from the methods of template and an external addition of dopant. Unlike the two methods,

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dopant molecule did not need to be removed after polymerization because it acted as a dopant and was linked in the polymer chains at the same time.³⁰ In fact, this belongs to a self-assembly process. The function of dopant and substituent demonstrated a key role in the formation of nanostructures of conducting polymers. Nanostructures of polyaniline (PANI) have been synthesized by self-assembly process in the presence of different dopants.^{30,31} However, the synthesis of poly(2-fluoroaniline) (PFANI), poly(2-chloroaniline) (PCIANI), poly(2-methylaniline) (PMANI), and poly(*N*-ethylaniline) (PNEANI) by self-assembly process were not encountered in the literature.

In this work, the synthesis of PFANI, PCIANI, PMANI, and PNEANI by self-assembly process is reported for the first time in the literature. The results are compared with PANI. The effect of the substituents on the surface morphology, conductivity, molecular weight, spectral and thermal properties has been discussed.

EXPERIMENTAL

Chemicals and synthesis

Aniline, 2-fluoroaniline, 2-chloroaniline, 2-methylaniline, and *N*-ethylaniline were purchased from Aldrich and distilled repeatedly under vacuum until a colorless liquid was obtained, and kept under nitrogen in darkness at 4°C prior to use. Conducting polymer powders were prepared by a self-assembly method using an oxidizing system consisting of a dopant anion, *p*-toluene sulfonate (pTS, Aldrich) with ammonium peroxydisulfate (APS, Aldrich). APS and pTS were of analytical reagent grade and used without further purification. All solutions were prepared by using predistilled ($18M\Omega\text{ cm}^{-1}$) deionized water. The molar ratio of monomer to dopant was fixed at 1 : 1 and dissolved in 100 mL of distilled water, and then an aqueous solution of APS (0.57 g in 12.5 mL of distilled water) was added to the above mixture under stirring for 5 min. The polymerization was carried out in a stationary condition at 4°C during 24 h. Dark green-blue solid polymers were filtered and washed with water, methanol, and ether until a colorless liquid passed through the filter and then dried under vacuum for 24 h.

Instrumentation

UV-vis spectra of the polymer solutions in DMSO were recorded on a Shimadzu UV-3150 UV-vis-NIR spectrophotometer. The polymer structures were determined by Perkin Elmer Spectrum 100 FTIR spectrometer and KBr pellets of solid samples. Elemental composition of the polymers was determined

by Vario EL III Elementar system. Thermal gravimetric measurements from ambient temperature to 500°C at 10°C min⁻¹ were carried out by Setaram Labsys TGA-DTA 1600 model in argon atmosphere. Scanning electron micrograph (SEM) of the polymers was performed by using Field Emission Gun Scanning Electron Microscope (FEG-SEM) (Oxford Instruments-7430). The molecular weight of the polymers was determined by Agilent 1100 GPC system with a RI detector. The dry electrical conductivity values were measured using a four-probe technique at room temperature. Gold plated probes were used to avoid any errors that might arise from ohmic contacts. At least, 10 different current values were used in the measurement of the potential drop. Cyclic voltammeters (CV) were taken by using the Autolab PGSTAT 100 Potentiostat/Galvanostat with GPES 4.9 version conversion software (EcoChemie, The Netherlands). The electrochemical cell used was of the three-electrode type for the reference electrode (Ag/AgCl, sat.) and the counter electrode (Pt spiral). The working electrode for the cyclic voltammetric studies was an ITO (Indium doped Tin Oxide). Before each electrochemical measurement, the working electrode was washed with ethyl alcohol and with deionized water to eliminate the impurities after that dried. Working electrode was made by coating the polymer suspension onto an ITO electrode surface and allowing the solvent to evaporate.

RESULTS AND DISCUSSION

Surface morphology and its formation mechanism

Scanning electron micrographs of the polyaniline (PANI), poly(2-fluoroaniline) (PFANI), poly(2-chloroaniline) (PCIANI), poly(2-methylaniline) (PMANI), and poly(*N*-ethylaniline) (PNEANI) films are shown in Figure 1. Although the molar ratio of monomer to dopant was fixed in all polymerization process, the surface morphology of the polymer films were quite different. This difference indicates the effects of substituents on the surface morphology. Actually, it was found that the surface morphology strongly depended on the type of substituents.

It is accepted that the first step in the development of a PANI-like structure is the oxidation of monomers to radical and/or dimeric cations (anilinium cations). These species are reactive toward most nucleophiles. Their reactions with monomers with or without eventual deprotonation, are responsible for film growth in the initial stages of polymerization. Fibril structure of PANI is shown in Figure1(a). Yang et al. explained the dendrite morphology.³⁰ pTS and anilinium cations first form micelles in aqueous solution. Micelles were regarded as the templates to further produce PANI nanofibers. At the addition of the oxidant

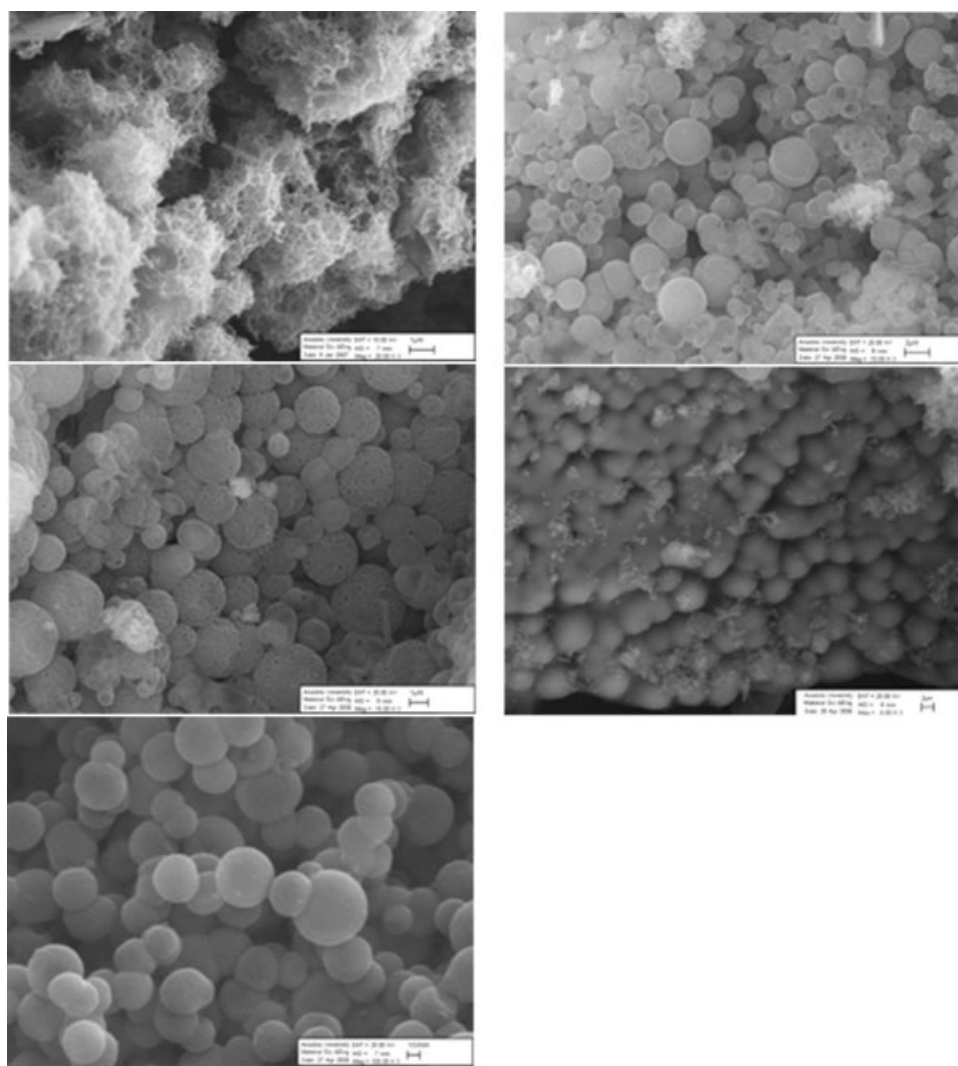


Figure 1 Scanning electron micrographs of (a) PANI, (b) PFANI, (c) PCIANI, (d) PMANI, and (e) PNEANI

(APS), the polymerization initially performed on the surface of the micelles. The polymer chain acted like a template in the self-assembly of PANI nanofibers. Fiber structures are assembled by the micelles through aggregation and elongation depending on the local conditions. The aggregation of micelles may mainly affect the size of the resulting nanostructures. The morphology of PANI obtained shows an interconnected, branched network-like nanofibrous structure with the nanofiber diameters varying in the range of 50 to 80 nm. The wires can reach as long as several micrometers. The formation of micelles changed with the presence of substituents on the aniline unit. As a result, we observed the influence of substituents on the formation and morphology of the polymers (nanofiber or sphere). Similarity, it is accepted that micelles mentioned earlier also play template function in the formation of spherical structure; however, polymer interaction including π - π interaction, hydrogen bonding and ionic bonding

may be a driving force to form aggregated dendrite morphology of the spheres. Spherical micelles existed in the PFANI, PCIANI, PMANI, and PNEANI structures [Fig. 1(b–e), respectively], whereas the micelle spheres aggregated to form a spherical structure. These images clearly show that type of substituents greatly influence the surface morphology.

Structural characterization and conductivity

FTIR and UV–vis spectra were used to characterize the molecular structure of the resulting different polyanilines. To determine the degree of dopant (S/N ratio) the elemental compositions of the polymers were obtained using elemental analysis. Dry electrical conductivity values and molecular weight of the polymers were also measured.

The absorption of IR radiation at wavelength below 2000 cm^{-1} is rich in molecular signatory information. Because of this reason the IR peaks in the

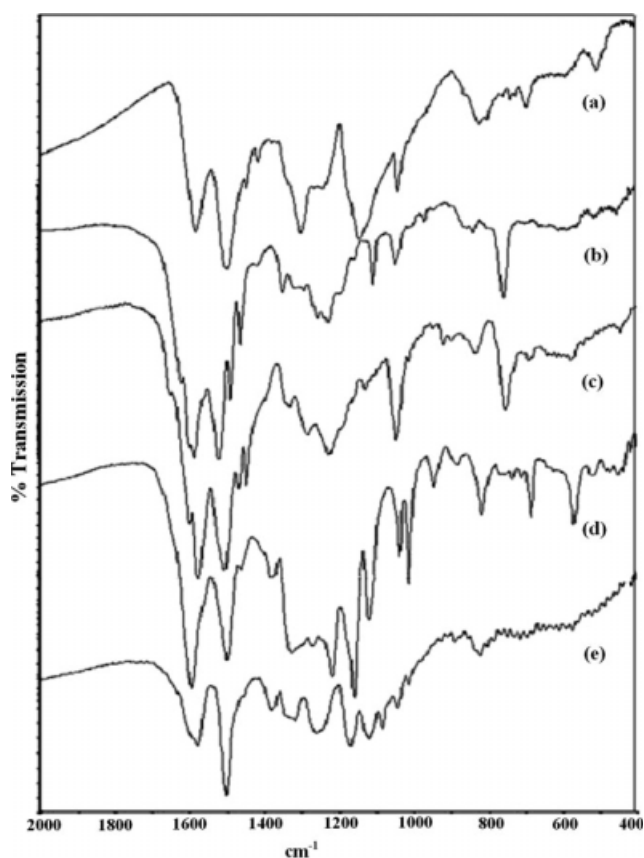


Figure 2 FTIR spectra, showing the 2000–400 cm^{-1} region, of (a) PANI, (b) PFANI, (c) PCIANI, (d) PMANI, and (e) PNEANI

range 2000–400 cm^{-1} are shown in Figure 2. The spectra of all the polymers show the main bands. The peak at about 1580 cm^{-1} is due to the C=C double bond of quinoid (Q) rings, whereas the peak at 1500 cm^{-1} arises due to vibration of the C=C double bond associated with the benzenoid (B) ring.³² These bands indicate that all the polyanilines were in the emeraldine form. Although these bands were seen in all the IR spectra of the polyanilines, the intensity of Q and B peaks were different in the polymer structures. The intensity of Q was higher in the PMANI structure and the intensity of B was higher in the PANI and PNEANI structures. PFANI and PCIANI show the equal amount of benzenoid and quinoid units in their structures. The intensities of these two peaks are about equal showing that PFANI and PCIANI films are more doped than the other films. Aromatic C–N stretching is responsible for the clustering of peaks at 1285 cm^{-1} .³³ The band around 1070–1170 cm^{-1} is attributed to B⁻NH⁺=Q structure which is formed during the protonation process. The band at about 1140 cm^{-1} due primarily to CH in-plane deformation, has been used by Chiang and MacDiarmid as a measure of the extent of electron delocalization in the polymer. The peak

at 804–831 cm^{-1} is due to aromatic C–H bending.³⁴ We also investigated the IR spectra of pure 2-fluoroaniline, 2-chloroaniline, 2-methylaniline, and *N*-ethylaniline to see the specific peaks of substituent groups (not shown here). The new vibration bands found at around 1350, 1220, 980, and 740 cm^{-1} [Fig. 2(b)] is characteristic of fluoro group²³ in the structure of PFANI. This confirms the presence of the fluoro moieties in the polyaniline backbone. Three new bands were observed at 1350, 900–920, and 740 cm^{-1} in PCIANI spectrum [Fig. 2(c)]. These peaks were associated with the presence of chlorine groups in the polymer structure. PMANI shows the main IR bands when compared to the corresponding bands in the spectrum of the PANI [Fig. 2(d)]. The band between 1200 and 1100 cm^{-1} was split in the spectrum of PMANI. These sharp bands were explained as a measure of the extent of electron delocalization in the polymer by McDiarmid and coworkers.³⁴ Its increased intensity is congruent with the high electrical conductivity value, compared to those of PFANI and PCIANI, of the polymers caused by pure electron delocalization induced by the methyl groups. The new bands at about 1010, 940, and 560 cm^{-1} also indicate the effect of substituent group on the structure of PANI. The split of the peak between 1200 and 1100 cm^{-1} was also seen in the spectrum of PNEANI. The bands of PNEANI were broader than the other polymers. Although the bands between 1400 and 1200 were broader, the resolution was better than the others. Aromatic C–N stretching is responsible for the clustering of peaks between 1400 and 1200 cm^{-1} . The ethyl groups directly attached to nitrogen atoms affect the electron delocalization on the polymer chain.

The UV-vis spectra of the polymer solutions in DMSO recorded at room temperature were shown in Figure 3 and summarized in Table I. The spectra are dominated by two broad absorption bands for PANI, PFANI, PCIANI, and PMANI. However, three absorption bands were obtained for PNEANI.

According to the general practice of peak assignment, Peak 1 is attributed to the π - π^* transition of the benzenoid moieties in the PANI linear structure.³⁵ Peak 3 closely resembles the benzenoid-quinoid transition in the emeraldine form (middle oxidation state) of PANI.³⁶ An absorption band around 436 nm (Peak 2) appears in the PNEANI. This band attributed to the polaron transition of the PNEANI.³⁷ The appearance of the 436 nm polaron band is in agreement with the higher conductivity observed for the PNEANI as compared with that of the PFANI, PCIANI, and PMANI where this band has not been observed.

The broad band, Peak 3, shifted to smaller wavelengths by the presence of fluorine and chlorine units in PFANI and PCIANI [Fig. 3(b and c)]

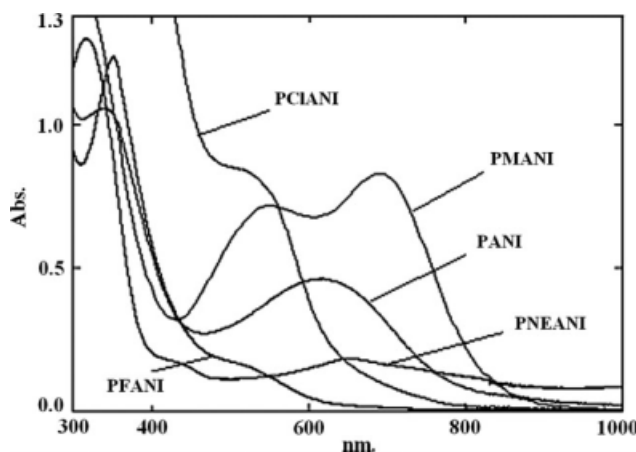


Figure 3 UV-vis spectra of PANI, PFANI, PCIANI, PMANI, and PNEANI in DMSO.

according to PANI. The absorption band shows a hypsochromic (blue) shift. The electron-withdrawing character of fluorine and chlorine units restrict the effective dispersion of electrical charge in the conjugated polymeric system, resulting in more locally oxidized polymeric units. Peak 3 shifted to longer wavelengths by the presence of electron-donating character of methyl and ethyl groups in PMANI and PNEANI, respectively. The absorption band shows a bathochromic (red) shift. It was concluded that the substituent effect on the structure of the polyanilines can be easily seen in the UV-vis spectra of the polymers.

Elemental analysis results give the structural information of the polymers to determine the sulphur to nitrogen ratio (S/N). The mole numbers of the elements, S and N, were found with their atomic weight percentage ratio. The molar S/N ratio of the polymers was then calculated by using the mole numbers and given in Table II. These results suggest that approximately one dopant molecule is substituted for every five aniline groups in the PANI, PFANI, PMANI, and PNEANI and one dopant is substituted for every ten aniline groups in PCIANI.

Studies reported in literature on poly(*N*-alkylaniline) claim that no protons are involved in the two step electrochemical processes.^{38–41} The structural units containing PNEANI are shown in Scheme 1. The electrochemistry of PNEANI is less complex

TABLE I
UV-Vis Absorption Band Values of PANI, PFANI, PCIANI, PMANI, and PNEANI in DMSO Solution

Polymer	Peak 1 (nm)	Peak 2 (nm)	Peak 3 (nm)
PANI	342	–	619
PFANI	351	–	529
PCIANI	389	–	532
PMANI	–	–	550 and 690
PNEANI	318	436	647

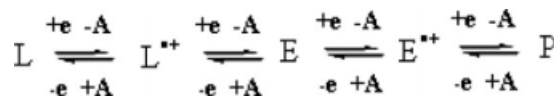
TABLE II
The Doping Degree and Dry Electrical Conductivity of PANI, PFANI, PCIANI, PMANI, and PNEANI at Room Temperature

Polymers	[S]/[N]	σ (S/cm)
PANI	0.18	6.6×10^{-1}
PFANI	0.19	9.2×10^{-4}
PCIANI	0.12	8.4×10^{-4}
PMANI	0.20	1.6×10^{-3}
PNEANI	0.17	8.7×10^{-3}

than for PANI because the acid–base reaction is hindered by the N substituents.⁴² The positive charges introduced through the electro-oxidation are neutralized by counter ions (A) in the structure. The relative amounts of these various forms depend on the potential applied to the electrode.

The dry conductivity values of the films, pressed pellets, are listed in Table II. The effect of substituent on the conductivity of polyanilines was seen from this table. The electron-withdrawing effect of fluorine and chlorine can be seen in the conductivity of the PFANI and PCIANI films. As the halogen content of electron-withdrawing species increases, the conductivity of the PFANI and PCIANI films decreases. The observed decrease in the conductivity of the PFANI, PCIANI, PMANI and PNEANI with respect to PANI can be attributed to the incorporation of the substituent moieties into the PANI chain. The PMANI and PNEANI exhibit higher dry electrical conductivity values than the PFANI and PCIANI films and lower values than PANI. The dry electrical conductivity values of the substituted-polyanilines were found to be lower than that of PANI. The lowered conductivity is caused by the decreased inter-chain diffusion of the charge carriers. This is induced by increased separation of the polymer chains due to the presence of side groups.

Molecular weight of the polymers was determined by size exclusion chromatography (GPC). Tetrahydrofuran (THF) was used as the solvent and eluent in the GPC analysis. The polymers with a high a molecular weight were not dissolved completely in THF. For this reason, NH_3 was passed through the solution to reduce the polymers to increase the solubility. The final oxidation products typically contain both oligomeric and polymeric components. M_n and



Scheme 1 The redox mechanism of PNEANI prepared with mobile counter anion (A). The leucoemeraldine, leucoemeraldine cation radical, emeraldine, emeraldine cation radical and pernigraniline-like forms are indicated as L, L^{*+} , E, E^{*+} , P, respectively.

TABLE III
 M_n and M_w Values of the PANI, PFANI, PCIANI, PMANI, and PNEANI Obtained from their Size Exclusion Chromatograms

Polymer	M_n	M_w
PANI	$8.94 \times 10^2 - 1.62 \times 10^6$	$8.72 \times 10^2 - 1.63 \times 10^6$
PFANI	$2.95 \times 10^2 - 8.66 \times 10^4$	$3.03 \times 10^2 - 8.73 \times 10^4$
PCLANI	$3.46 \times 10^2 - 1.17 \times 10^5$	$3.74 \times 10^2 - 1.35 \times 10^5$
PMANI	$2.92 \times 10^2 - 8.65 \times 10^4$	$3.12 \times 10^2 - 8.75 \times 10^4$
PNEANI	$2.85 \times 10^2 - 7.62 \times 10^4$	$2.93 \times 10^2 - 8.90 \times 10^4$

M_w values of the polymers obtained from their size exclusion chromatograms were given in Table III. Being of the oligomer products in the samples collected in the end of the polymerization process indicates that oligomers have not been converted to polymers but only accompany them. We have attempted to separate them by extraction of the oligomeric fraction with methanol. Although some oligomers were removed from the solutions, some of them are still entrapped in the methanol-insoluble fraction.

Thermal properties

Thermogravimetric curves for PANI, PFANI, PCIANI, PMANI, and PNEANI doped with pTSA are given in Figure 4. There are four major stages of weight loss for all the polymers. The first thermal transition could be attributed to the moisture evaporation and perhaps out gassing of unknown small molecules. The second thermal transition is related to removal of dopant molecule. The third thermal transition corresponds to the loss of low molecular weight oligomers or side products (hydroquinone or quinone) and the final transition is due to the degradation of backbone units of PANI, PFANI, PCIANI, PMANI, and PNEANI. The percent of weight losses at the selected temperatures (corresponding to mois-

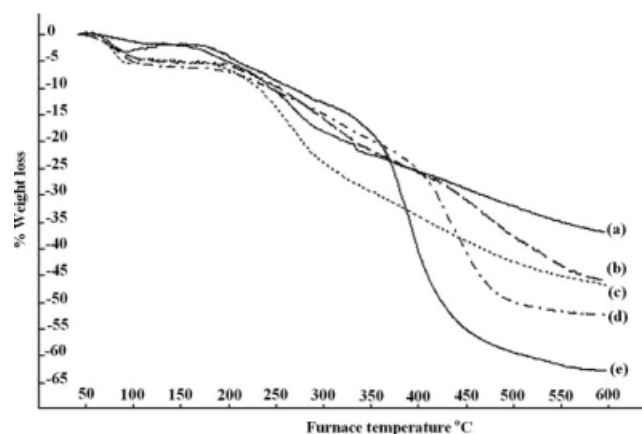


Figure 4 Thermal gravimetric analysis of (a) PANI, (b) PFANI, (c) PCIANI, (d) PMANI, and (e) PNEANI

ture evaporation, dopant removal, loss of oligomers, and main chain degradation) are listed in Table IV. Glass transitions (T_g) of the polymers are also observed by DTA curves (not given here). Table IV shows T_g data for PANI, PFANI, PCIANI, PMANI and PNEANI. The T_g order of PMANI < PANI < PCIANI < PNEANI < PFANI was observed in this work. Comparatively, the PFANI have more thermal stability in opposition to the other polymers.

Electrochemical behavior of the polymer films

Working electrode was made by coating the polymer suspension onto an ITO electrode surface and allowing the solvent to evaporate. The thickness of final film samples for conductivity measurement was around 10 μm . The electrochemical behavior of PANI, PFANI, PCIANI, PMANI, and PNEANI films were investigated on ITO electrode in acetonitrile solution containing 0.1M TBAP and 10 mM HClO_4 (monomer free solution). The cyclic voltammogram of the substituted polyanilines are essentially identical with that of parent polyaniline. The polymer films exhibit one broad oxidation and one broad reduction peak in the monomer free solution. The electroactivity of the films were seen in the acidic solution of acetonitrile. The oxidation and reduction peak potentials of the polymer films were summarized in Table V. The substituent effect can be seen especially on the oxidation peak potential of the

TABLE IV
 Thermal Properties of PANI, PFANI, PCIANI, PMANI, and PNEANI

Polymers	Weight loss in		Glass transition
	$T^a - T^b$ ($^\circ\text{C}$)	% weight loss	T_g ($^\circ\text{C}$)
PANI	50–120	5.1	164.5
	120–200	–	
	200–350	17.3	
	350–600	24.3	
PFANI	50–90	3.4	191.1
	90–155	–	
	155–250	8.2	
PCIANI	250–600	25.1	165.1
	50–115	5.7	
	115–195	–	
	195–320	20.4	
PMANI	320–600	21.4	162.7
	50–120	5.7	
	120–170	–	
	170–380	14.6	
PNEANI	380–600	31.5	171.2
	50–115	2.1	
	115–170	–	
	170–330	12.7	
	330–600	48.1	

^a Onset temperature of first thermal event.

^b Onset temperature of second thermal event.

TABLE V
The Oxidation and Reduction Peak Potentials of the
PANI, PFANI, PCIANI, PMANI, and PNEANI
Films in Acetonitrile Solution

Polymers	$E_{ox.}$ (V)	$E_{red.}$ (V)
PANI	+1.20	-0.08
PFANI	+0.52	-0.16
PCIANI	+0.73	+0.06
PMANI	+1.11	+0.17
PNEANI	+0.90	+0.35

polymers. For all the substituted polyanilines the oxidation peak occurs at a lower potential than in the parent polyaniline. This shows that the oxidation of the polysemiquinone with simultaneous deprotonation occurs more easily in the substituted polyanilines than in the parent polyaniline.⁴³ This may be caused by formation of imine nitrogens with a wider angle to release the steric strain,⁴⁴ leading to lower oxidation potentials. The oxidation peak potentials order of PFANI < PCIANI < PNEANI < PMANI < PANI was observed in this work.

CONCLUSION

Nanofibers of PANI, with a diameter of 80–100 nm, quite smooth spheres of PNEANI, with a diameter of 200–600 nm, a bunch of grapes shape of PMANI, nanoholes inside the spheres of PCIANI and stuck spheres of PFANI were successfully synthesized by a self-assembly process. Spectroscopic results (FTIR and UV–vis) were affected by electron-withdrawing and -donating characters of the substituents. The dry electrical conductivity values of the substituted-polyanilines were found to be lower than that of PANI. It was found that the surface morphology, spectroscopic, thermal and electrochemical properties strongly depended on the type of substituents. This innovative self-assembly method may open a new route to synthesize functional nanofibers and nanospheres of conducting polymers.

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