

CHEMICAL SYNTHESIS, SPECTRAL CHARACTERIZATION AND STABILITY OF SOME ELECTRICALLY CONDUCTING POLYMERS*

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Abstract The synthesis, characterization, thermal degradation and stability of polyaniline (PANI), poly(*m*-nitroaniline), poly(*m*-chloroaniline) and poly(*o*-methylaniline) were reported. Different properties were measured and compared with PANI to find out the effect of electron donating groups ($-\text{CH}_3$) and electron withdrawing groups ($-\text{Cl}$, $-\text{NO}_2$). It was found that the presence of any type of substitution in the benzene ring of aniline increased the solubility but reduced the yield, thermal stability and electrical conductivity. Two probe methods were used to measure the electrical conductivity of these polymers. The structural properties of these polymers were characterized by using FTIR and UV-Vis spectroscopic methods. Thermal degradation and stability of these polymers were explained by using thermogravimetric analysis (TGA) and conductivity measurements.

Keywords: Polyaniline; Electrical conductivity; Yield; Thermal degradation; Stability.

INTRODUCTION

Conducting polymers exhibit one of the most versatile behaviors of polymer materials. Knowledge of thermal degradation and stability of conducting polymers is important for their use in many practical applications while the synthesis, structure and redox properties of electro active polymers have been reported extensively. There have been only few systematic studies on their thermal aging and thermal degradation behavior. Polyaniline (PANI) has become an important representative of the class of conducting polymers because of its excellent stability in air.

Many studies are going on with PANI due to its ease of synthesis, novel properties and potential applications such as sensor, light emitting diodes, solar cells, actuator and organic batteries^[1–5].

One of the major problems with conducting polymers is the non-processibility by solvent or multitechniques. Most of them are insoluble in common solvents and undergo degradation before reaching the melting point. Also they have poor mechanical strength and are environmentally unstable. Many researchers have succeeded in overcoming these problems^[6–8] and are generating polymer composites and blends^[9–11] which can show better stability and mechanical strength.

The properties of the poly(substituted anilines) depend on the type of substitution like electron withdrawing, electron donating groups or less affecting groups like alkyl groups^[12–15]. This investigation reports that how different types of groups affect the synthesis and properties of poly(substituted anilines). The chemical oxidative method was used to synthesize PANI and different poly(substituted anilines) under similar conditions.

The preparation of PANI and poly(substituted anilines) with the above mentioned three different types of

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substitution and the detailed comparative studies are relatively much less. It will be interesting to study how different types of groups affect the synthesis and properties of poly(substituted anilines).

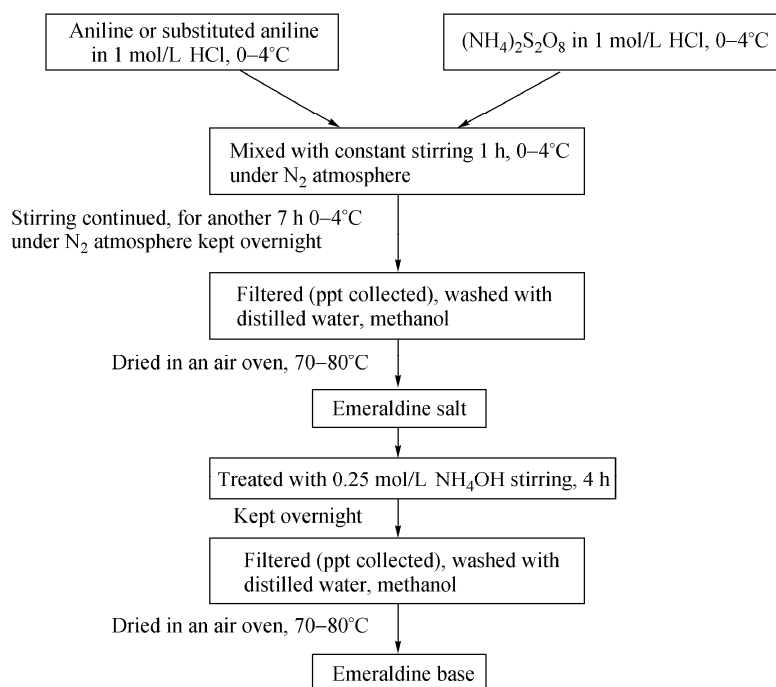
EXPERIMENTAL

Materials

Aniline: Ranbaxy Chemicals (distilled under reduced pressure). *m*-Chloroaniline was distilled twice prior to use. *m*-Nitroaniline (98%): SD Fine Chemicals (recrystallized from alcohol and then acetone). *o*-Methyl aniline: SD Fine Chemicals (distilled under reduced pressure). Ammonium persulphate (APS) (99%): CDH Chemicals, AR grade (used as received). Dimethyl sulfoxide (DMSO) (99%): Merck India (used as received). Dimethyl formamide (DMF) (99%): Fluka (used as received). Acetone (99%): Merck India, AR grade (used as received). Methanol (99%): Merck India (used as received). All the aqueous solutions were prepared using double distilled water.

Synthesis of Polymers

The chemical oxidative polymerization of aniline, *m*-nitroaniline, *m*-chloroaniline and *o*-methylaniline was carried out at identical reaction conditions and procedure as shown in Scheme 1. At the start of the reaction, 0.1 mol/L aniline/0.1 mol/L substituted anilines were dissolved in 1 mol/L HCL solution. Polymerization reaction was started by drop wise addition of aqueous solution of APS (0.1 mol/L in 100 mL distilled water), and the reaction was carried out for 8 h at room temperature with constant stirring. The reaction mixture was then kept over a whole night at room temperature, after which the formed polymer precipitate was filtered and washed several times with 0.1 mol/L HCL, distilled water thoroughly followed by methanol to remove the low molecular weight oligomers (ammonia)^[16–18]. The ratio of monomer to oxidant 1:1 was taken because we found that with this ratio the productivity and conductivity of the resultant polymer were very good.



Scheme 1 Various steps involved in the polymerization process

Polymerization reaction of aniline is generally carried out for 2–6 h, but the productivity of poly(substituted aniline) after 5 h was very low. So, the polymerization time 8 h was set to produce all the polymers.

Characterization of the Polymers

FTIR spectra

The FTIR spectra of the polymers were recorded on an FTIR spectrophotometer Inter Spec-2020 (Spectra Lab U.K.) in KBr pellets.

UV analysis

The UV-analysis was carried out using an ELICO SL 177 scanning mini spectrophotometer with quartz cells of 1 cm optical path. 0.05% solution was prepared for each sample.

AC conductivity

The electrical conductivity of pressed pellets of polymers was measured by two-probe method using a Genard conductivity bridge (1659 RLC Digibridge, USA).

Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a DTG-60H simultaneous DTA-TGA apparatus, SHIMADZU CORP (00134). Polymer samples were heated under N₂ atmosphere from 90°C to 700°C at a heating rate of 20 K/min.

RESULTS AND DISCUSSION

Yield and Conductivity

Polyaniline (PANI), poly(*m*-nitro aniline), poly(*m*-chloro aniline) and poly(*o*-methyl aniline) were prepared from the respective monomers by using oxidative polymerization. The yield of the poly(substituted anilines) is much less than the yield of PANI because the presence of any substitution on benzene ring of aniline has significant effect on the rate of polymerization as well as the type of polymer formed as shown in Table 1. If the substituent controls the charge density on benzene ring, its size and its position with respect to amino group (—NH₂) also affect the polymerization process and properties of the final product formed^[19, 8].

Table 1. Yield & conductivity of polymers

Polymer	Yield (%)	Conductivity (S cm ⁻¹)
PANI	79.84	1.98×10^{-1}
Poly(<i>m</i> -nitro aniline)	20.00	1.02×10^{-7}
Poly(<i>m</i> -chloro aniline)	34.00	3.64×10^{-6}
Poly(<i>o</i> -methyl aniline)	48.00	6.56×10^{-4}

The AC conductivity of the pressed pellets of these polymers was measured by two-probe method at a frequency 10 kHz using a Genard conductivity bridge (1659 RLC Digibridge, USA). The AC conductivity of PANI is much higher compared to that of other polymers as shown in Table 1. It is because that in PANI, all the benzene rings and nitrogen are expected to be in the same plane where π electron delocalization is very high leading to high electrical conductivity. For poly(substituted anilines) the benzene rings may not be in the same plane and as a result the π electron delocalization is expected to be hindered leading to decrease in conductivity^[20–22]. The electrical conductivity of POMA is higher than that of PMNA and PMCLA because the methyl group has an electron donating effect. So it may increase the electron density in the polymer chain compared to PMNA and PMCIA.

FTIR Spectra

The structural characteristics of PANI and poly(substituted anilines) were investigated by FTIR spectroscopy in the range of 400–2000 cm⁻¹ as shown in Fig. 1.

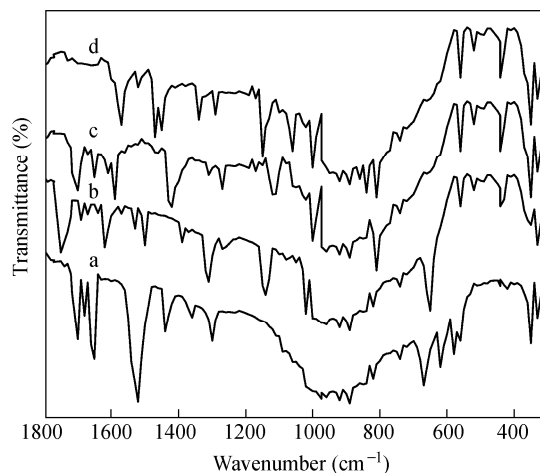


Fig. 1 FTIR spectra of (a) PANI, (b) poly(*m*-chloro aniline), (c) poly(*o*-methyl aniline) and (d) poly(*m*-nitro aniline)

In the FTIR spectra of PANI, the peaks at about 1650 and 1570 cm^{-1} are due to C=C double bonds of the quinoid rings. The absorption at 1296 and 1120 cm^{-1} corresponds to the C—N stretching and C—H bending modes^[23, 20].

In the FTIR spectra of poly(*m*-chloroaniline), the band at 1750 and 1618 cm^{-1} are assigned to the quinoid and benzenoid phenyl rings. A very intense band at 650 cm^{-1} is characteristic for C—Cl stretching.

In the FTIR spectra of poly(*o*-methyl aniline), the peaks at 1705 and 1544 cm^{-1} are assigned to the quinoid and benzenoid phenyl rings. The peak at 1396 cm^{-1} has been attributed to a C—N banding. Peaks at 1111–1113 cm^{-1} are due to the C—H vibration modes. The peak at 820 cm^{-1} appears due to —CH₃ groups in the phenyl rings.

In the FTIR spectra of poly(*m*-nitroaniline), the peaks at 1570 and 1450 cm^{-1} are assigned to the quinoid and benzenoid phenyl rings. The peak observed at 1340 cm^{-1} is ascribed to symmetric N=O stretching vibrations due to —NO₂ groups. The bands at 1320 and 1279 cm^{-1} are ascribed to C—N stretching vibrations.

UV-Vis Spectra

There are two main absorption bands in the electronic spectra of PANI, PMCIA, PMNA and POMA in DMSO and DMF^[12, 13]. The corresponding bands are given in Table 2. The band around 280 to 380 nm is assigned to the π - π^* (band gap) electronic transition in the phenyl ring in the polymer backbone, and the peak above 570 nm is due to inter band charge transfer associated with excitation of the benzenoid to the quinoid moieties. The π - π^* bands of polymers in different solvents also show a hypsochromic shift with increase in dielectric constant of the solvent. Ghose and Kalpakam^[24] tried to explain such shift on the basis of dielectric constant of the solvents. A polymer in solvent of high dielectric constant may exist in coil-like conformation (decrease in conjugation), and a less polar solvent provides thermodynamically more stable chain conformation and restricts the polymer in a lower energy high planar state. Such shift may increase the conjugation of the system which yields a lower energy transition, red shift^[25]. The exciton band produced by the inter/intra chain charge transfer is due to an absorption from the highest occupied molecular orbital (HOMO) band centered on the benzenoid units to the lowest unoccupied molecular orbital (LUMO) band centered on the quinoid units. These local charges reflected by exciton transition are sensitive to chain conformation related process since solvatochromism is observed in transition.

Table 2. UV-Vis peak positions (nm) of polymers in DMSO and DMF

Polymers	DMSO		DMF	
	$\pi-\pi^*$ (nm)	$n-\pi^*$ (nm)	$\pi-\pi^*$ (nm)	$n-\pi^*$ (nm)
PANI	322	620	324	608
Poly(<i>m</i> -nitro aniline)	302	407	304	410
Poly(<i>m</i> -chloro aniline)	302	586	296	578
Poly(<i>o</i> -methyl aniline)	320	590	270	600

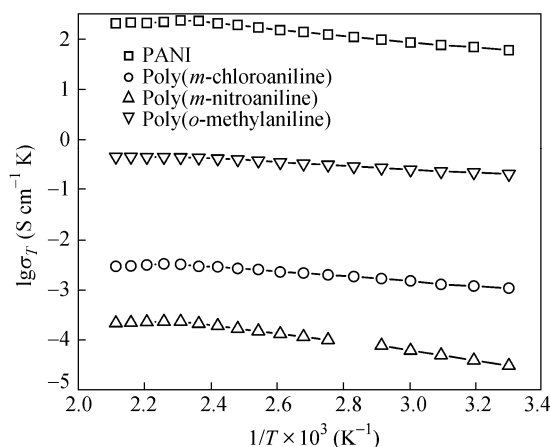
Electrical Conductivity and Charge Transport Studies

The temperature dependent electrical conductivity studies revealed a thermally activated conduction phenomenon in all these conducting polymers^[19, 20]. The electrical conductivity increased linearly with increase in temperature in the whole temperature range studied^[8, 22].

The temperature dependent conductivity data obtained in the temperature range from 303 K to 473 K can be fitted to the Arrhenius equation of conductivity.

$$\sigma_T = A \exp(-E_a/kT) \quad (1)$$

The plot as shown in Fig. 2 of $\lg \sigma_T$ versus $10^3/T$ gives a straight line whose slope $(-E_a/2.303R)$ gives the value of activation energy given in Table 3.

**Fig. 2** Arrhenius plot of $\lg \sigma_T$ versus $1/T \times 10^3$ (K^{-1})**Table 3.** Activation energy (eV) of polymers of aniline and substituted aniline

Copolymers	Activation energy (eV)
PANI	0.10303
Poly(<i>m</i> -nitro aniline)	0.14899
Poly(<i>m</i> -chloro aniline)	0.08240
Poly(<i>o</i> -methyl aniline)	0.06277

Thermal Gravimetric Analysis

When all these polymers are subjected to continuous heating, they exhibit several steps of loss in weight at different temperatures as shown by TGA curves in Fig. 3 and Fig. 4. The general observation from TGA curves is that the oxidative degradation of polymer backbone takes place after the removal of trapped water followed by dopants and low molecular weight oligomers^[26–28].

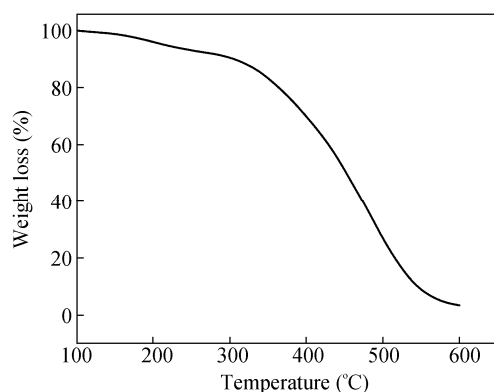


Fig. 3 TGA curve of PANI

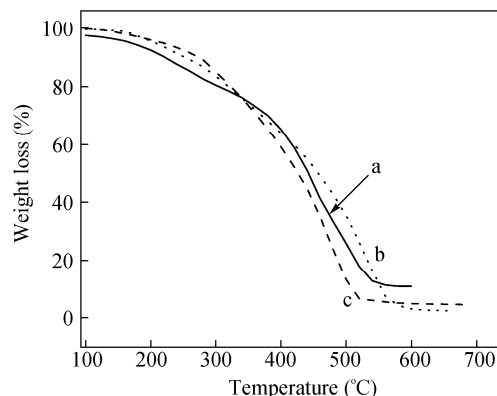


Fig. 4 TGA curves of (a) poly(*o*-methyl aniline), (b) poly(*m*-nitro aniline) and (c) poly(*m*-chloro aniline)

Thermogram of PANI shows three distinct regions of weight loss. The initial weight loss of (*ca.* 1.6%) by 160°C is attributed to the loss of water molecules. The weight loss of about 7.4% by 250°C corresponds to the loss of HCL. Beyond 250°C, the rate of decomposition is found to be maximum at 500°C.

The maximum decomposition of PMNA occurs at 460°C, which occurs at 440°C for POMA and 480°C for PMCLA.

During the degradation of polymer backbones, compounds such as ammonia, aniline and *p*-phenylenediamine are reported to be formed.

From thermogravimetric analysis, we conclude that PANI shows the maximum thermal stability among the polymers under investigation. The order of thermal stability PANI > POMA > PMNA > PMCLA is in accordance with the weight loss percentage under continuous heating. The rate of degradation is much faster in PMNA and PMCLA than that in PANI and POMA.

CONCLUSIONS

The presence of substituents on the benzene ring of aniline reduces the yield and increases the solubility depending on the type of substituents. The difference in the conductivity of poly(substituted anilines) is due to electron donation and withdrawing capability of different substituents.

This study reveals that PANI shows the maximum thermal stability among the polymers under investigation. The order of thermal stability is PANI > POMA > PMNA > PMCLA.

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