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## Effect of aromatic substitution in aniline on the properties of polyaniline

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## ABSTRACT

Substitution in aniline has tremendous effect in the synthesis of poly(substituted anilines) as well as in their properties. In this investigation polyaniline (PANI), poly(*m*-nitro aniline) (PMNA), poly(*m*-amino phenol) (PMAP) and poly(*o*-ethyl aniline) (POEA) were synthesized by oxidative polymerization under identical conditions. Different properties were measured and compared with PANI to find out the presence of electron donating –OH group, electron withdrawing –NO<sub>2</sub> group and less effecting ethyl group on the properties of poly(substituted anilines). It was found that presence of any type of substitution in the benzene ring of aniline increases the solubility of the resulted polymer but reduces the yield, degree of polymerization, thermal stability, electrical and thermal conductivity. The colors, bulk density, particle size, percentage of crystallinity vary considerably depending on the nature of substitution.

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## 1. Introduction

Among the intrinsically conducting polymers polyaniline (PANI) has most potential applications in multidisciplinary fields like gas separation, actuator, sensor, light emitting diodes, conductive adhesive, solar cells, organic batteries, electrodes, switch, etc. [1–12]. Extensive studies are going on the PANI because of its ease of synthesis, novel properties and potential applications [13–19]. But the main problem for practical application of PANI lies in its inadequate processability because of poor solubility [20,21]. Inorganic or organic acids are generally used as dopant for PANI to improve its conductivity as well as its solubility [22–24]. Alternatively, the solubility of PANI is improved by using different substitutions in the benzene ring of aniline. 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. Electron withdrawing group decreases the electron density in aniline, electron donating

group increases the electron density in the phenyl ring of aniline, whereas alkyl group may not affect much to the electron density in aniline only some mild positive inductive effect (+I) may increase electron density. But it will increase the solubility of PANI leading to easier processing of the material. The preparation of PANI and poly(substituted anilines) with the above mentioned three different types of substitution and the detailed comparative studies on their properties is relatively much less [25]. So it will be interesting to study how different types of group affect the synthesis and the properties of poly(substituted anilines).

This investigation reports the synthesis of polyaniline (PANI) and different poly(substituted anilines) by oxidative polymerization under similar conditions and the detailed comparative study of their different properties like yield, bulk density, solubility, conductivity, thermal properties, molecular weight and particle size. In this case different substituted anilines were judiciously chosen like *m*-nitro aniline having a strong electron withdrawing –NO<sub>2</sub> group (–R effect), *m*-amino phenol having a strong electron donating –OH group (+R effect) and *o*-ethyl aniline having a less affecting (weak +I effect) ethyl group.

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## 2. Experimental

### 2.1. Materials

Aniline, ammonium peroxy disulphate (APS), toluene (Merck Ltd., Mumbai, India), *m*-nitro aniline, *m*-amino phenol (Loba Chemie Pvt. Ltd., Mumbai 400 005, India), *o*-ethyl aniline (Alfa Aesar, Shore Road, Heysham, Lancaster, UK), *p*-toluene sulphonic acid (PTSA), ammonia solution (S.D. Fine Chem. Ltd., Mumbai, India), methanol (SISCO Research Laboratories Pvt. Ltd., Bombay, India), hydrochloric acid (Ranbaxy, India).

All materials used are AR grade. Aniline and *o*-ethyl aniline were distilled and other materials were used as received.

### 2.2. Synthesis of polyaniline and poly(substituted anilines)

The polymerizations of aniline, *m*-nitro aniline, *m*-amino phenol and *o*-ethyl aniline were carried out at identical reaction conditions and procedure.

At the start of the reaction 0.1 M monomer (9.3 ml aniline/13.8 g *m*-nitroaniline/10.9 g *m*-aminophenol/12.1 ml *o*-ethylaniline) and 0.05 M (2 ml) HCl were taken in a beaker containing 50 ml toluene. Polymerization reactions were started by drop wise addition of aqueous solution of APS {0.1 M (22.8 g) APS in 100 ml distilled water} and the reactions were carried out for 12 h at room temperature with constant stirring. Polymerizations were stopped by addition of 50 ml methanol. The polymer particles were filtered and thoroughly washed with water to remove unreacted chemicals. The polymers thus obtained were taken in a beaker containing 100 ml of distilled water, excess ammonia solution was added until basic and then stirred for 24 h with a magnetic stirrer to remove HCl. The polymer was then filtered, washed several times with distilled water and dried in vacuum over at room temperature to remove ammonia and get undoped polymer. The undoped polymers were redoped with 50 mol% of *p*-toluene sulphonic acid (PTSA). For redoping, each polymer was taken in a beaker separately containing 100 ml distilled water, required amount of PTSA (polymer to PTSA mole ratio 2:1) was added to it and then stirred for 24 h with a magnetic stirrer. Then the mass was filtered, washed several times with distilled water and finally dried under vacuum at room temperature. Polyaniline is designated as PANI, poly(*m*-nitro aniline) as PMNA, poly(*m*-amino phenol) as PMAP and poly(*o*-ethyl aniline) as POEA.

The ratio of monomer to oxidant 1:1 and polymer to dopant is 1:0.5 was taken because we found that with these ratios productivity and conductivity of the resultant polymer is very good [13]. Polymerization reaction of aniline is generally carried out for 2–6 h [13,14]. But productivity of PMNA and PMAP after 6 h of polymerization was very low. So, the polymerization time 12 h was set to produce all the polymers.

### 2.3. Characterization of the polymers

#### 2.3.1. Molecular weight

The molecular weight and molecular weight distribution of the soluble portion of the undoped PANI and

poly(substituted anilines) were determined by size exclusion chromatography (SEC) at ambient temperature using a Viscotek GPC equipped with a Viscotek solvent pump (model VE 1122), a refractive index detector (model VE3580) and a set of two ViscoGEL GPC columns GMHHR-H and GMHHR-M connected in series. Undoped polymer solutions were prepared using GPC grade THF having solution concentration 1 mg/ml. The THF was used as the eluent at a flow rate of 1.0 ml/min and calibration was carried out using narrow polydispersity polystyrene standards. Data acquisition and processing were performed using Viscotek OMNI-01 software.

#### 2.3.2. Morphology

The morphology and particle size was determined using a scanning electron microscope (SEM), JSM 5800, JEOL, JAPAN. All samples were gold coated prior to analysis by SEM.

#### 2.3.3. DC conductivity

The DC conductivity was measured with the Milli-Ohm Meter, GOM 802, GW Instek, Taiwan. Sample was prepared in the pellet form from polymer powders by a Perkin Elmer hydraulic device using 15 tons pressure. The pellet was placed in between the sample holder and reading was recorded from the display. It is a two probe method.

#### 2.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was carried out using a TGA, Q50, TA Instruments, USA. Polymer samples were heated under N<sub>2</sub> atmosphere from 35 °C to 800 °C at a heating rate of 20 °C/min.

#### 2.3.5. Differential scanning calorimetric (DSC)

The differential scanning calorimetric (DSC) analysis was carried out on a DSC, Q100, TA Instruments, USA by heating the polymer samples under N<sub>2</sub> atmosphere from –20 °C to 550 °C at a heating rate of 10 °C/min.

#### 2.3.6. X-ray analysis

The XRD analysis was carried out on an X Pert PRO, PANalytical instrument, USA, with a Cu detector using 1.54 Å wavelength of the X-ray.

#### 2.3.7. UV analysis

The UV analysis was carried out using UV–Visible Spectrophotometer, UV-1601, SHIMADZU CORPN. JAPAN. Testing was carried out taking only the soluble portion of PANI in DMF. 0.05% solution was prepared for each sample.

The band gap energy is calculated from the following equation:

$$\Delta E = \frac{hc}{\lambda}, \quad h = 6.625 \times 10^{-34} \text{ J s}, \quad c = 3 \times 10^8 \text{ m/s},$$

where  $\Delta E$  is band gap energy,  $h$  is Planck's constant,  $c$  is velocity of light and  $\lambda$  is wave length of the UV ray.

## 3. Results and discussion

Polyaniline (PANI), poly(*m*-nitro aniline) (PMNA), poly(*m*-amino phenol) (PMAP) and poly(*o*-ethyl aniline)

(POEA) were prepared from the respective monomer by using oxidative polymerization under similar reaction conditions using APS as an oxidant. The yield of PANI is 80% after 12 h of reaction at room temperature (Table 1). The yields of other polymers are 20%, 15% and 55% for PMNA, PMAP and POEA, respectively, which are much less compared to PANI. The reasons for this can be found out from the polymerization mechanism as shown in Fig. 1. Aniline to polyaniline formation in presence of APS goes through oxidative polymerization through the formation of cation radicals by the reaction of aniline with sulphate anion rad-

ical (generated from APS in presence of acid). These cation radicals get rearranged and propagation process takes place via head-to-tail addition of two cation radicals at its *para* position to form first dimer after release of protons. The formation of dimer leads to formation of trimer through addition of aniline and so on. This process continues to form polymer. Like all other polymerization process reaction conditions affect the rate and degree of polymerization as well as the type of polymer formed. The molecular weight distribution, especially the presence of some low molecular weight oligomers significantly affects the

**Table 1**

Different properties of PANI and poly(substituted anilines)

Sl. no.	Properties	PANI	PMNA	PMAP	POEA
1	Yield <sup>a</sup> (%)	80	20	15	55
2	Color	Deep green	Deep brown	Gray	Deep blue
3	Solubility <sup>b</sup> (gm/L)	0.55	11.0	0.75	2.2
4	Molecular weights <sup>c</sup>				
	$\bar{M}_n$ (Da)	70,300	55,249	33,971	56,144
	$\bar{M}_w$ (Da)	315,167	296,722	234,009	238,401
	PDI ( $\bar{M}_w/\bar{M}_n$ )	4.5	5.4	6.9	4.2
5	Particle size <sup>d</sup> ( $\mu\text{m}$ )	$\sim 1$	$< 1$	$> 1$	$\ll 1$
	Particle shape <sup>d</sup>	Spherical	Spherical	Rod like	Spherical
6	Crystallinity <sup>e</sup> (%)	45	25	60	5
7	DC conductivity (S/cm)	$4.4 \times 10^{-4}$	$5.5 \times 10^{-7}$	$8.4 \times 10^{-7}$	$6.8 \times 10^{-7}$
8	Decomposition peak temperature <sup>f</sup> ( $^{\circ}\text{C}$ )	510	370, 540	360	405

<sup>a</sup> Polymerization reaction was carried out at room temperature for 12 h.

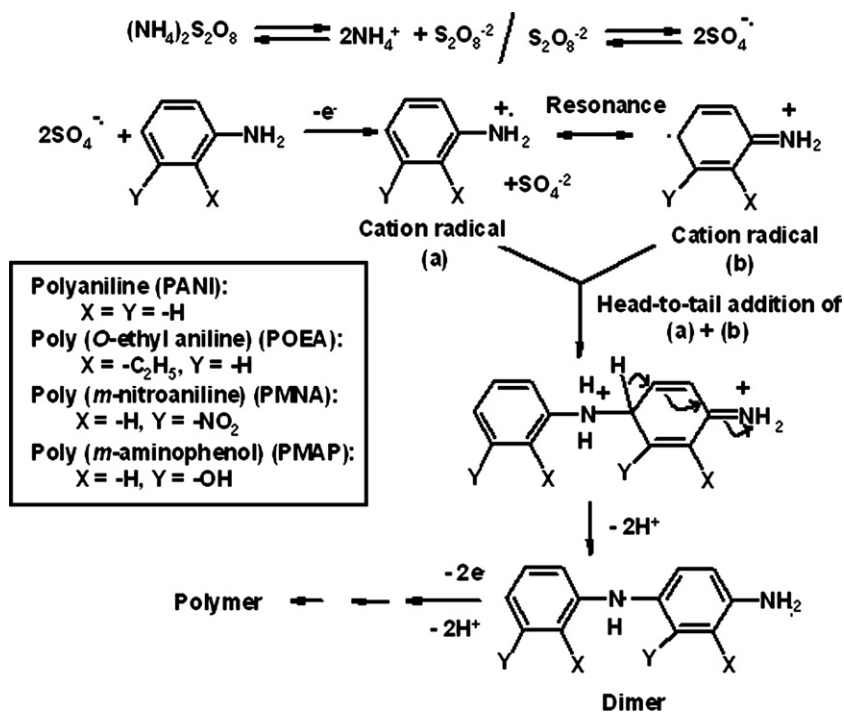
<sup>b</sup> Solubility was measured in tetrahydrofuran (THF) at room temperature.

<sup>c</sup> Molecular weight was obtained from GPC.

<sup>d</sup> Particle size and shape were determined from SEM.

<sup>e</sup> Percentage of crystallinity was estimated from XRD plots after multiplying the ratio of crystalline peak area to total peak area by 100.

<sup>f</sup> Decomposition temperature was determined from TGA.

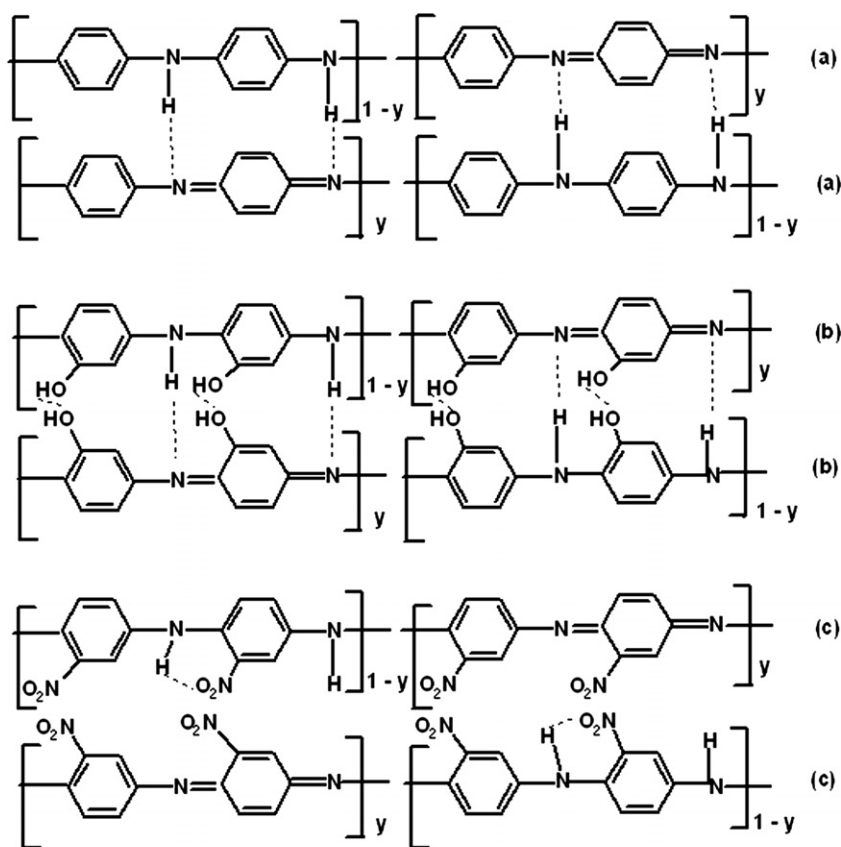
**Fig. 1.** Polymerization mechanism for poly(substituted anilines).

bulk conductivity of polyaniline. Presence of high degree of polarity, crystallinity and inter-chain H-bonding in polyaniline has made the polymer mostly insoluble and infusible in nature. Presence of any substitution on benzene ring of aniline has significant effect on rate of polymerization, as well as on the type of polymer formed. The nature of substituent if controls the charge density on benzene ring and its size and position with respect to amine group ( $-\text{NH}_2$ ) also affect the polymerization process and properties of final polymer formed.

In the present study three substituted anilines along with neat aniline were subjected to oxidative polymerization under identical conditions. The rate of polymerization again depends on the reactivity of the species taking part in the reaction process as well as any hindrance to propagation of reaction. The rate of reaction affects yield. The nitro group in *m*-nitroaniline and hydroxyl group in *m*-aminophenol present at the *meta* position ( $Y = -\text{OH}$  or  $-\text{NO}_2$  in Fig. 1) with respect to amine group exert steric hindrance to the approach of any moiety at the *para* position

where the polymer formation or propagation takes place. As a result, the reaction process gets slower in both the cases and it is reflected in the decrease of yield for both PMNA and PMAP compared to PANI. Whereas, the steric hindrance exerted by ethyl group is relatively less compared to other two substituents as the ethyl group is in *ortho* position ( $X = -\text{C}_2\text{H}_5$  in Fig. 1) and polymer formation progresses at *para* position. It is expected that higher the accessibility of the reactive species higher is the degree of polymerization and higher is the yield. The yield of POEA is higher than PMNA and PMAP.

The polymer formed have different color (Table 1) because of presence of different chromophores like  $-\text{NH}-$  or  $=\text{N}-$ ,  $-\text{NO}_2$ ,  $-\text{OH}$ . However, color of the polymer formed changes with oxidation level. Dry PANi exhibits deep green color, which indicates it is in almost half oxidized/half reduced emeraldine form, whereas deep blue color of POEA indicates that it contains more quinoid rings compared to that of benzenoid rings (Fig. 2) [13]. The deep brown color of PMNA and gray color of PMAP is due to presence of extra



For all figures when

$y = 0$ , Leucoemeraldine base

$y = 0.5$ , Emeraldine base

$y = 1$ , Pernigraniline base

Dotted line between two atoms indicates hydrogen bond

(a) is PANI, (b) is PMAP, (c) is PMNA

Fig. 2. Schematics of H-bonding in (a) PANI, (b) PMAP and (c) PMNA.

chromophores  $-\text{NO}_2$  and  $-\text{OH}$ , respectively, along with  $-\text{NH}-$  or  $=\text{N}-$ . These different colors of PANI and substituted PANIs may be efficiently used to produce different colored anticorrosive paints.

The solubility of these polymers in appropriate solvent strongly depends on factors like crystallinity, polarity, possibility of inter-chain or intra-chain H-bonding and also H-bonding with solvent. The existence of strong inter-molecular electrostatic interaction and inter-chain H-bonding into these polymer systems prevent solvent molecules to penetrate in cluster of polymer chains, there by solvent can not isolate individual polymer chain from each other and solubilize the polymer. The position of different groups may also give rise to some intra-chain H-bonding. If there is higher tendency of intra-chain H-bonding then it is expected that the polymer will have higher solubility and lower crystallinity due to chain kinking. PMAP has slightly higher solubility than that of PANI (Table 1), which may be due to small tendency of intra-chain H-bonding. However, for PMNA the possibility of intra-chain H-bonding is much more prominent and this is also reflected in its lower crystallinity. Due to the formation of more intra-chain H-bonding in PMNA solvent molecules can some what penetrate the assembly of polymer chains and isolate larger number of chains from each other and thereby increasing solubility. The inter-chain H-bonding of PANI and PMAP and the intra-chain H-bonding of PMNA is schematically presented in Fig. 2. The solubility of POEA is higher than PANI and PMAP but lower than PMNA. Presence of ethyl group leads to some steric hindrance and also increase inter-chain distance and this leads to increase in solvent penetration. Thus the presence of ethyl group on the repeat chain has some increasing effect on solubility. The molecular weight and molecular weight distribution have also significant effect on solubility.

The soluble fraction of PANI is expected to be mainly lower molecular weight fraction, where inter-chain and inter-molecular force of attraction is less mainly due to lower surface area and hence solvent molecules can solvate polymer chains relatively easily. Thus higher fraction of low molecular weight species in substituted polyanilines may be present leading to higher solubility compared to PANI.

The knowledge on molecular weight of intrinsically conducting polymers (ICP) is important to understand its degree of polymerization, conductivity and processability [26,27]. The molecular weights (MW) of the soluble portion of the polymers were measured by GPC as shown in Fig. 3 and Table 1. The results show that PANI has the highest molecular weight (MW) whereas PMAP has the lowest MW. The polydispersity index (PDI) values (Table 1) indicates that PMNA and PMAP have broad MW distribution compared to that of PANI and POEA. Fig. 3 shows that PMNA has bimodal distribution in the GPC traces of this polymer. Bimodal distribution in PMNA clearly indicates that there are two types of species leading to the broader PDI than PANI and POEA. High PDI in PMAP indicates that there may be small low molecular weight fragment. That is why; in spite of very high crystallinity in PMAP, its solubility is slightly higher compared to PANI.

The particle size of the polymers was determined from scanning electron microscope (SEM) as shown in Fig. 4 [13,15,16]. The shape of PANI, PMNA and POEA is almost spherical, whereas PMAP is rod like. The size of the particles are PANI  $\sim 1 \mu\text{m}$ , PMNA  $< 1 \mu\text{m}$ , PMAP  $> 1 \mu\text{m}$  and POEA  $\ll 1$  (Table 1). The PANI and POEA have higher tendency for cluster formation, whereas the PMAP has lesser tendency and PMNA has least tendency for the same.

Fig. 5 represents the X-ray diffractogram (XRD) of all the polymers under investigation. There are different

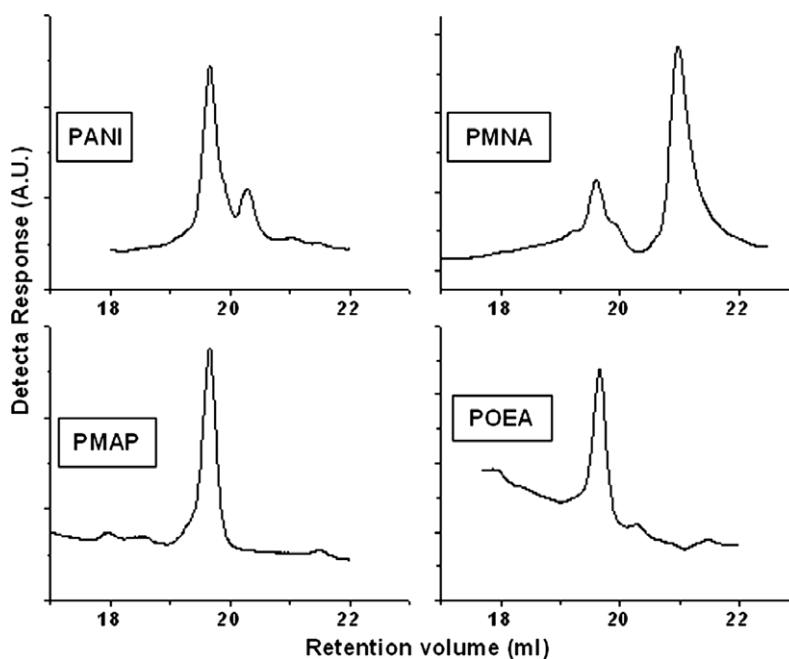


Fig. 3. GPC traces of PANI, PMNA, PMAP and POEA.



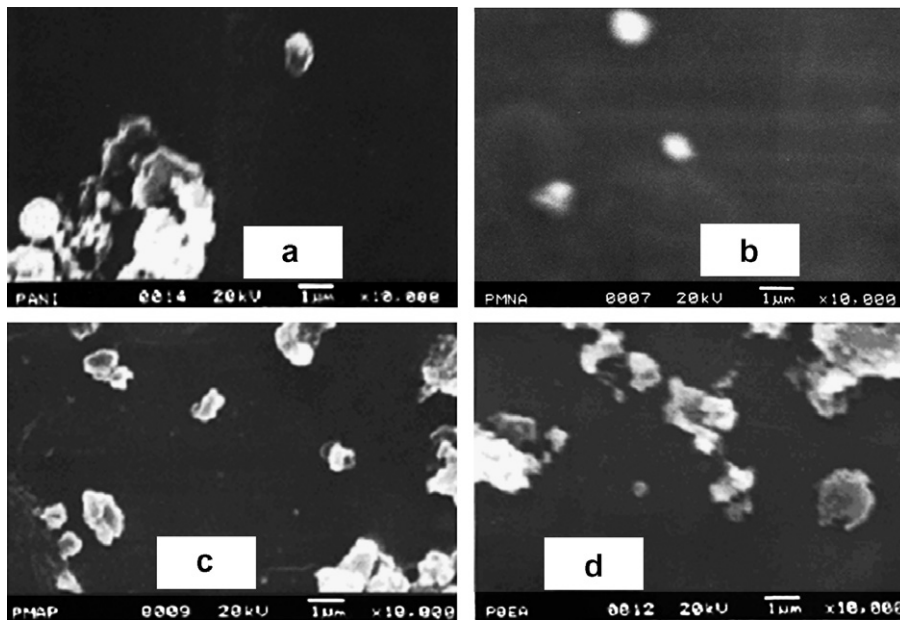


Fig. 4. Scanning electron microscope (SEM) picture of (a) PANI, (b) PMNA, (c) PMAP and (d) POEA.

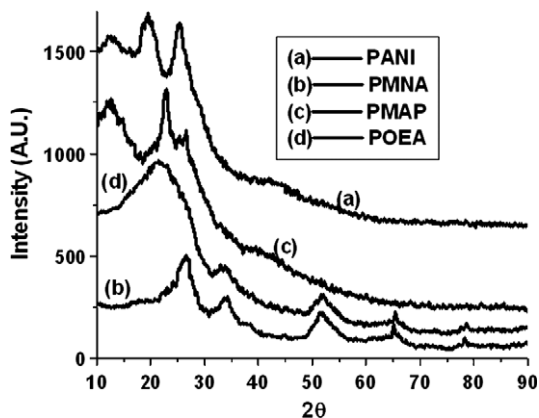


Fig. 5. X-ray diffractogram of all the polymers under investigation.

crystalline peaks for different polymers. The total percentage of crystallinity of all these polymers are calculated from their respective XRD plots and shown in Table 1 [15,16]. The percentage of crystallinity in PANI and PMAP is much higher compared to that of PMNA and POEA. Higher the degree of regularity in arrangement or ordering of the polymer chains higher is the crystallinity. This again depends on the inter-chain hydrogen bonding or electrostatic interaction existing among adjacent polymer chains. The higher degree of crystallinity or more ordered structural pattern in PANI and PMAP is due to the more inter-chain hydrogen bonding or electrostatic interaction (through both amine and/or phenolic group) compared to PMNA and POEA as mentioned earlier (Fig. 2). Bulky ethyl substitution in POEA hinders the ordering of the macromolecular chains, hence crystallinity is very low. Lower crystallinity of PMNA compared to that of PANI and PMAP

may also be due to the intra-chain hydrogen bonding between amine proton and nitro oxygen leading to marginal tilting of the backbone. The higher degree of crystallinity for PMAP compared to that of PANI indicates that the system contains highly ordered polymer chains. This may be due to the presence of stronger inter-chain hydrogen bonding as well as electrostatic (dipole–dipole) interactions involving both amine and phenolic groups present on PMAP compared to PANI where H-bonding and dipole–dipole interactions takes place only among amine groups.

The DC conductivity of PANI is much higher compared to that of other polymers (Table 1). The reason for lower conductivity of PMNA, PMAP and POEA may be due to the presence of different substitution at the benzene ring. In PANI all the benzene rings and nitrogen are expected to be on the same plane where  $\pi$ -electron delocalization is very high leading to high electrical conductivity. For poly(substituted anilines) the benzene rings may not in same plane and as a result the  $\pi$ -electron delocalization is expected to be hindered leading to decrease in conductivity. In case of poly(substituted anilines) the conductivity is in the order PMAP > POEA > PMNA. The –OH group in PMAP increases the electron density in the main chain because of its +R effect [26]. Hence its conductivity is higher than that of POEA and PMNA. The electrical conductivity of POEA is bit higher than that of PMNA because ethyl group has +I effect [26]. So, it has some what positive influence in increasing electron density in polymer chain compared to PMNA, where –NO<sub>2</sub> group withdraw electron density because of its –R effect [26].

The difference in energy between  $\pi$ -orbital (valance band) and  $\pi^*$ -orbital (conduction band) is called the band gap, which determines the optical properties of semi-conducting polymers. Band energy may be calculated from UV

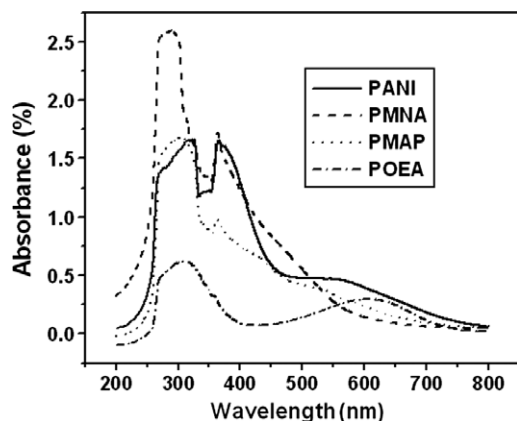


Fig. 6. UV absorption spectra of PANI, PMNA, PMAP and POEA.

absorption spectra. Fig. 6 shows the UV absorption spectra of all the polymers under investigation. The UV spectra of all these polymers show three characteristic absorption bands: (1) 250–350, (2) 350–450, and (3) 450–750 nm. The first absorption is due to the excitation of the nitrogen in the benzenoid segments ( $\pi-\pi^*$  transition) while the second and the third ones are ascribed to polaron–bipolaron transition that occurs in doped PANI [15,16]. All three bands for PANI are very sharp, whereas for PMNA the first and second bands are strong enough but third band is quite feeble. For PMAP the first band is sharp but second and third bands are quite faint and for POEA the first and third bands are intense but second band is difficult to detect. The transition energy corresponding to these bands of all these polymers are presented in Table 2. PANI shows lower band energy both for  $\pi-\pi^*$  transition and polaron–bipolaron transition leading to easier charge transport and hence higher conductivity compared to those of substituted polyanilines.

The wave length of visible light is 400–700 nm and wave length corresponding to the third absorption band for all these polymers are found to well within the visible range. The region of absorption band for violet, blue, green, yellow, orange and red colored materials are 400–424, 425–491, 491–575, 575–585, 585–647 and 647–700 nm,

Table 2

Peak position of different band and corresponding band energy of all the polymers under investigation

Polymers	Peak position of different band (nm)	Band energy of the corresponding peak (eV)
PANI	325	3.82
	365	3.40
	565	2.20
PMNA	286	4.34
	363	3.42
	481	2.58
PMAP	303	4.10
	361	3.44
	529	2.35
POEA	304	4.09
	610	2.04

respectively [27]. The third absorption band for PANI ranges from 485–725 nm and it exhibits deep green color, whereas PMNA has deep brown color when its third band occurs over wave length 430–575 nm. For gray colored PMAP the third band appeared over 500–680 nm and for deep blue colored POEA it is in the region 420–750 nm.

When all these polymers are subjected to continuous heating, they exhibit several steps of loss in weight at different temperatures as shown in TGA and DTG curves (Fig. 7). The initial weight loss at around 40–150 °C may be due to the loss of moisture and volatile matters [14,16], the weight loss over the temperature range 150–350 °C may be due to the loss of dopant, bound water or oligomers [14,28,29]. The weight loss within 350–650 °C is due to the loss of polymer [14–16]. The maximum decomposition of PANI occurs at 510 °C, which occurs at 370 and 540 °C for PMNA, at 360 °C for PMAP and at 405 °C for POEA (Table 1). The PANI shows maximum thermal stability among the polymers under investigation. This may be due to the compact structure and higher molecular weight of PANI. The order of thermal stability (PANI > POEA > PMNA > PMAP) of all the polymers is in accordance with their molecular weight (Table 1). The two distinct decomposition temperatures (maximum decomposition at 370 °C) of PMNA may be due to the presence of large number of oligomers present in the polymers which decomposes at lower temperature. The solubility result is also in agreement with this statement. GPC also shows a distinct bimodal peak in PMNA (Fig. 3).

Some observations about transient heat flow behavior through different polymers may be made from their DSC plots. For that almost identical sample weight of all the polymers was taken. The relative value of heat flow at different temperature through different polymers may be considered as their temperature dependent or transient thermal conductivity (TDTC) [17]. DSC plots showed some endothermic and exothermic peaks for removal of different materials, crystalline melting, recrystallization and polymer decomposition [18]. All these phenomena occurred after 150 °C. From 0 °C to 150 °C curves are almost smooth. So, the TDTC of all the polymers were compared over the temperature range 0–150 °C (Fig. 8). The order of TDTC of

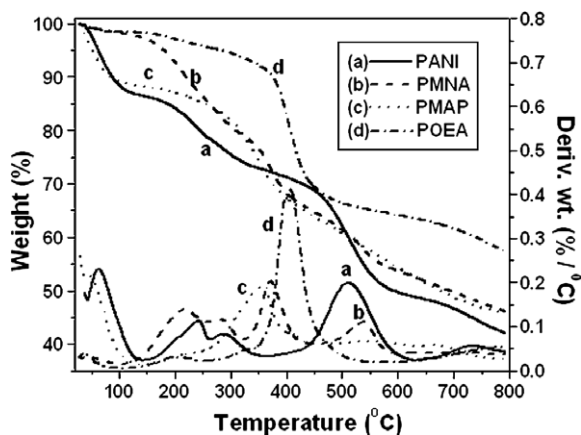


Fig. 7. Results of TGA analysis of different polyanilines.

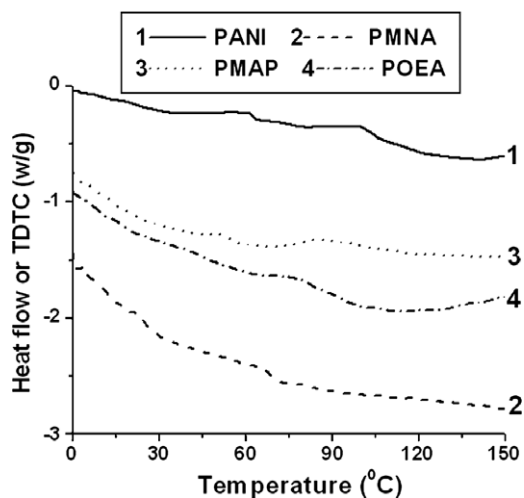


Fig. 8. Temperature dependent/transient thermal conductivity (TDTC) as a function of temperature for all the polymers obtained from DSC.

all polymer is PANI > PMAP > POEA > PMNA, which is same as their order of electrical conductivity (Table 1). It is expected because better electrical conductors are also better thermal conductor like metals when compared with ceramics.

#### 4. Summary and conclusion

The presence of substituents on the benzene ring of aniline reduces the yield and molecular weight (MW) of polymer formed. However, presence of substituents on the benzene ring of polyaniline increases the solubility depending on the type of substituents.

The large decrease of conductivity in presence of substituents is due to the loss of planarity of the polymer chain. The difference in conductivity of poly(substituted anilines) is due to electron donating and withdrawing capability of different substituents. The order of electrical and thermal conductivity of different polymer are found to be as polyan-

iline (PANI) > poly(*m*-aminophenol) (PMAP) > poly(*o*-ethylaniline) (POEA) > poly(*m*-nitroaniline) (PMNA).

The color, particle size, percentage of crystallinity largely varies due to the presence of different substituents. The percentage of crystallinity in PANI and PMAP is very high due to inter-chain H-bonding whereas, lower crystallinity in PMNA is due to more intra-chain H-bonding.

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