

Effect of Dopant Type on the Properties of Polyaniline

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ABSTRACT: The comparative study on the effect of different type of dopants on the properties of polyaniline (PANI) is relative less although dopant has profound effect of the properties of PANI. So, the aim of the present work is to study the effect of different type of dopant, namely strong inorganic hydrochloric acid (HCl), organic and aromatic acids containing different aromatic substitution, namely *p*-toluene sulfonic acid (PTSA), dodecylbenzenesulfonic acid (DBSA), organic and aliphatic acids having long hydrocarbon chain, namely lauric acid (LA), on the properties of PANI. The PANI was prepared through oxidative polymerization methods and doped with HCl, PTSA, DBSA, and LA and then characterized through different methods like conductivity measurement, UV, X-ray,

DSC, TGA, and SEM. It was found that the properties of doped PANI depend on the type and molecular size of the dopant. With the increase in dopant chain length, the crystallinity is decreased, whereas the *d*-spacing, interchain separation, and solubility are increased. The bond formation of water molecules with the backbone nitrogen of the polymers is much less in presence of aromatic dopants when compared with those of inorganic or aliphatic dopants. All the doped polyanilines under investigation do not decompose up to 500°C. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3135–3140, 2009

Key words: conducting polymer; thermogravimetric analysis; differential scanning calorimetry; X-ray

INTRODUCTION

After the discovery of intrinsically conducting polymers (ICPs), a lot of application possibilities have been developed.¹ ICPs are inherently conducting in nature due to the presence of conjugated π electron system in their structure. ICPs have a low energy optical transition, low ionization potential, and high electron affinity. ICPs can be oxidized or reduced easily in the presence of charge transfer agents (dopants), and through doping they can achieve near metallic conductivity.² Widely known ICPs are polyacetylene, polypyrrole, polythiophene, polyaniline, polyparaphenylene, polyparaphenylene vinylene, and their derivatives.³ Among the ICPs, polyaniline (PANI) has attracted most attention and become important subject of research because of its interesting properties, potentiality for practical applications, good environmental stability, low cost, and ease of synthesis.^{4–14} Usually, PANI is synthesized from monomeric aniline by either oxidative polymerization or electro chemical polymerization. However, the chemical oxidation of aniline is the more feasible route for bulk production. However, the polymer obtained by this process is insoluble in common solvents with poor processibility. The processability of PANI can be improved by using

different dopants.^{15–22} The comparative study on the effect of different type of dopants on the properties of PANI is relative less.^{22–25}

The present study deals with the synthesis of PANI through the oxidative polymerization methods and doping with different dopant to investigate the effect of dopant type on the properties of PANI. Different dopants were judiciously chosen, for example, strong inorganic hydrochloric acid (HCl), organic and aromatic acids containing different aromatic substitution, namely *p*-toluene sulfonic acid (PTSA), dodecylbenzenesulfonic acid (DBSA), organic and aliphatic acids having long hydrocarbon chain, namely lauric acid (LA). Different properties like conductivity, band gap, crystal structure, solubility, and thermal properties of doped PANI samples were measured and compared.

EXPERIMENTAL

Materials

Aniline, ammonium peroxydisulphate (APS), *p*-toluene sulfonic acid (PTSA), toluene, and ammonia solution were obtained from S.D. Fine Chem., Mumbai, India. Dodecylbenzenesulfonic acid (DBSA) and lauric acid (LA) were purchased from Loba Chemie, Mumbai, India. Methanol was procured from SISCO Research Laboratories, Bombay, India. Hydrochloric acid (HCl) was obtained from Ranbaxy, India. All these chemicals are of AR grade. All the chemicals were used as received.

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Synthesis of doped Pani using different dopant

In a typical polymerization, 9.3 mL (0.1M) of aniline and 1-mL conc. HCl were added to 250 mL of toluene in a beaker. The reaction medium was kept at 0°C, and to start the polymerization reaction, an aqueous solution containing 22.8 g (0.1M) of APS in 20 mL of water was slowly added over a period of 10 min with constant stirring. The PANI prepared from this ratio of aniline to APS (1 : 1M/M) results in a good conductivity and productivity.⁴ The polymerization was carried out for 6 h, and the reaction was then terminated by adding 50 mL of methanol.⁴ The polymer thus obtained was taken in a beaker containing 100 mL of distilled water; an 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 a vacuum oven at room temperature to remove ammonia and to get undoped polymer. Different parts of undoped polymer were redoped with the 50 mol percentages of HCl, PTSA, DBSA, and LA. For redoping, different parts of the polymer was taken in a beaker separately containing 100-mL distilled water, required amount of dopant (polymer to dopant 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.

Characterization

The "DC" conductivity of solid pellet samples was measured by a two-point probe method using "SCHLUMBERGER" computing multimeter (model SI-7071). Sample powder was compacted into a disk pellet with a diameter of 12.6 mm and thickness of about 1.0 mm under a pressure of 10 tons. All data presented are the average value of the measurements from at least five samples.

The UV analysis was carried out using a UV-visible Spectrophotometer, UV-1601, SHIMADZU CORPN. from JAPAN. The testing was carried out taking only the soluble portion of PANI in DMF, and 0.05% solution was prepared for each sample.

The band gap energy for the π - π^* transition was calculated from the following equation

$$\Delta E = \frac{hc}{\lambda_{\max}} \quad (1)$$

$$h = 6.625 \times 10^{-34} \text{ J.s, } c = 3 \times 10^8 \text{ m/s}$$

Here, ΔE is the band gap energy, h is the Plank's constant, c is the velocity of light, and λ_{\max} is the wave length of the absorption maxima corresponding to the first absorption band at 250–320 nm.

The XRD analysis of these polymers was carried out using a X Pert PRO, PANalytical instrument from USA, with copper target (Cu $K\alpha$) with a wave length of 1.54Å.

The XY (2*Theta versus Intensity) data obtained from this experiment was plotted using Origin 6.1. The curve smoothing was carried out by 15 points adjacent averaging method. Then a straight line was subtracted to make $Y = 0$. Finally, the Gaussian fit for multiple peaks was carried out to obtained areas of different peaks. The percentage of crystallinity of the samples was estimated from the ratio of crystalline peak area to total peak area.^{9,26}

The d -spacing (d) corresponding to different crystalline peaks was determined by the Debye-Scherrer (powder) method using the Bragg's relation.^{9,27}

$$n\lambda = 2d \sin\theta \quad (2)$$

Here, n is an integer, λ is the wavelength of the X-ray which is 1.54 Å for Cu target, and θ is the angle between incident and reflected rays.

The interchain separation (R) was determined from the relation given by Klug and Alexander.^{9,28}

$$R = \frac{5\lambda}{8 \sin\theta} \quad (3)$$

The differential scanning calorimetric study was carried out using a DSC, Q100 from TA Instruments, under a N_2 atmosphere from -150 to 350°C at the heating rate $10^\circ\text{C}/\text{min}$.

The thermo gravimetric analysis was carried out using a TGA, Q50 from TA Instruments. The experiment was carried out under a N_2 atmosphere from 30 to 500°C at a heating rate of $20^\circ\text{C}/\text{min}$.

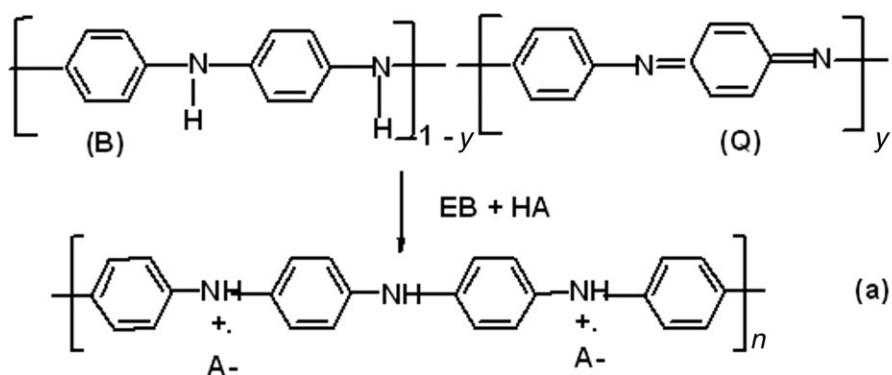
The morphological study was carried out from scanning electron microscopy (SEM) using a JSM 5800, JEOL, JAPAN. All the samples were coated with gold before test.

RESULTS

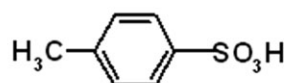
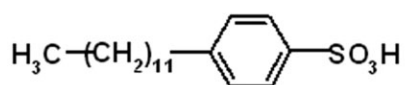
Depending upon the oxidation level, PANI has three basic structures, namely: (i) a fully reduced leucoemeraldine base (LEB), where all repeat units have benzenoid structure (B), (ii) a fully oxidized pernigraniline base (PNB), where all repeat units have quinoid structure (Q), and (iii) a partially oxidized ($\sim 50\%$) form is known as emeraldine base (EB) with the B to Q ratio ~ 1 (Fig. 1). The LEB and PNB are relatively insulating, whereas doped EB (emeraldine salt) [Fig. 1(a)] is generally conducting in nature.^{4,7}

Electrical conductivity

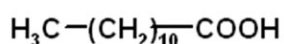
The DC conductivity of different PANI samples is presented in Table I. The good conductivity values



- (i) $y = 0$, Leucoemeraldine base (LEB) Fig (a) is emeraldine salt after doping, HA is dopant acid
(ii) $y = 1$, Pernigraniline base (PNB)
(iii) $y = 0.5$, Emeraldine base (EB)

(b) *p*-toluene sulphonic acid (PTSA)

(c) Dodecyl benzene sulphonic acid (DBSA)



(d) Lauric acid (LA)

Figure 1 Different structure of polyaniline, (a) emeraldine salt after doping, (b) *p*-toluene sulfonic acid (PTSA), (c) Dodecyl benzene sulfonic acid (DBSA), and (d) Lauric acid (LA).

of these polymers indicate that the sufficient EB form of PANI was formed during synthesis. The conductivity of different doped samples is in the order of PANI-HCl > PANI-PTSA > PANI-DBSA > PANI-LA. The net conductivity of doped PANI depends on the concentration and mobility of charge carriers, which in turn depends upon the type of dopant, method of preparation and the structure of the doped PANI.⁴⁻⁷

UV spectroscopy

Figure 2 presents the UV spectra of doped PANI samples. The π orbital produces the valance band and π^* forms the conduction band. The difference in energy between these two bands is called band gap, which

determines the optical properties of semi conducting polymers. Lower the band gap energy easier is the π - π^* electronic transition, and hence, higher is the conductivity. The UV spectra of doped PANI shows three characteristic absorption bands over the wavelength regions 250–320, 320–450, and 450–750 nm. The first absorption is due to the excitation of the nitrogen in the benzenoid segments (π - π^* transition), whereas the second and the third ones are ascribed to polaron/bipolaron transition that occurs in doped PANI.^{5,7} The band gap for the π - π^* transition corresponding to the first absorption band at 250–320 nm of doped PANI samples is presented in Table I. The order of conductivity is found to be just reverse of their band gap order. The band gap is in sound agreement with the conductivity of the PANI samples.

TABLE I
Properties of PANI Samples Doped With Different Dopant

Properties	PANI-HCl	PANI-PTSA	PANI-DBSA	PANI-LA
DC conductivity (S/cm)	1.6×10^{-1}	4.8×10^{-2}	3.4×10^{-2}	2.6×10^{-2}
Band gap (eV)	4.48	4.50	4.51	4.53
Crystallinity (%)	59	47	39	42
d-Spacing (Å)	3.49	3.50	3.55	3.53
Interchain separation (Å)	4.36	4.37	4.42	4.40
Solubility in DMF at RT (g/L)	3	11	16	13

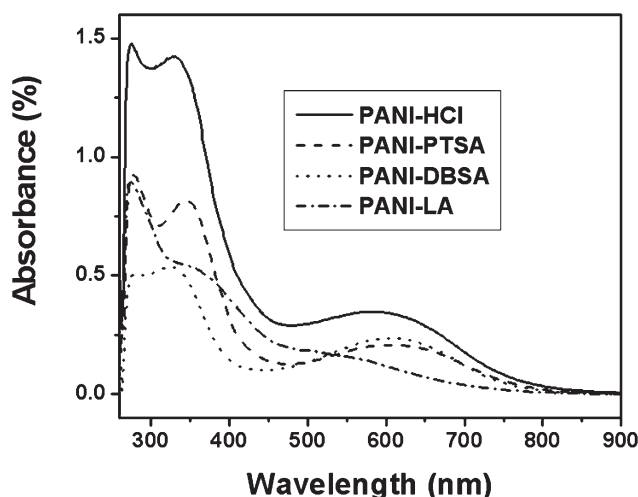


Figure 2 UV spectroscopy of doped PANI samples.

X-ray diffractometry

The XRD plots of different PANI samples are presented in Figure 3. All PANI samples exhibit one crystalline peak at $\sim 25^\circ$ angles. The percentages of crystallinity, d -spacing, and interchain separation of these polymers are presented in Table I. It is found that, with the decrease in crystallinity and increase in d -spacing and interchain separation, conductivity is decreased. Higher the degree of regularity in arrangement or ordering of the polymer chains higher is the crystallinity. The regularity and organized structure which is defined in terms of crystallinity is a favorable factor mainly for intramolecular mobility of charged species along the chain and to some extent intermolecular hopping because of better and closer packing. Hence, the increase in the crystallinity is expected to increase the conductivity. Again, with the decrease in d -spacing and interchain separation, the probability of interchain hopping will increase and concurrently the conductivity is expected to increase. The net conductivity is not only due to the intrachain mobility of electron and hole but also the interchain mobility of the same.⁴⁻⁷ The decrease in conductivity is in the order of PANI-HCl > PANI-PTSA > PANI-DBSA > PANI-LA. However, the decrease in crystallinity is in the order of PANI-HCl > PANI-PTSA > PANI-LA > PANI-DBSA and the order of d -spacing and interchain separation is just opposite of this order. The size (length) of the dopants is in the order of HCl < PTSA < LA < DBSA [Fig. 1(b-d)]. The higher size dopant exerts more force against ordering and closing of the polymer chains leading to a lower crystallinity, a higher d -spacing, and a higher interchain separation, and hence, a lower conductivity. So, the conductivity of PANI-LA is expected to be a higher than that of PANI-DBSA. However, experimentally it is just reversed. This may be due to the difference in

strength of the dopant acid because DBSA (sulfonic) is stronger acid than LA (carboxylic).

Solubility

The solubility of different PANI samples is presented in Table I. Usually, the undoped PANI has very poor solubility due to strong intermolecular force of attraction which concurrently depends on high polarity and highly crystalline structure. After doping, the solubility of PANI is increased. It is found that greater the dopant size (length) lower is the crystallinity but higher is the solubility of the doped polymer (Table I). The greater the size of the dopant higher is the interchain separation, and hence, it becomes easier for the solvent molecules to penetrate into the cluster of the polymer chains isolating individual polymer chain from each other and solubilize the polymer. The higher the solubility of a polymer in an organic solvent, the better is the processability. Therefore, the dopant with higher chain length is expected to produce a PANI with better solution processability.

Differential scanning calorimetry (DSC)

Figure 4 presents the DSC plots of doped PANI samples. All samples show two endothermic peaks one at around $100\text{--}150^\circ\text{C}$ and another at around $200\text{--}350^\circ\text{C}$. The first endothermic peak may be due to the loss of loosely associated moisture and the second for the loss of relatively strongly bonded water molecules often termed as bound water, which acts as a secondary dopant.^{9,14} The second peak is stronger for PANI-HCl and PANI-LA but relatively weak for PANI-PTSA and PANI-DBSA. This indicates that the PANI-PTSA and PANI-DBSA contain less bound water when compared with those of PANI-HCl and

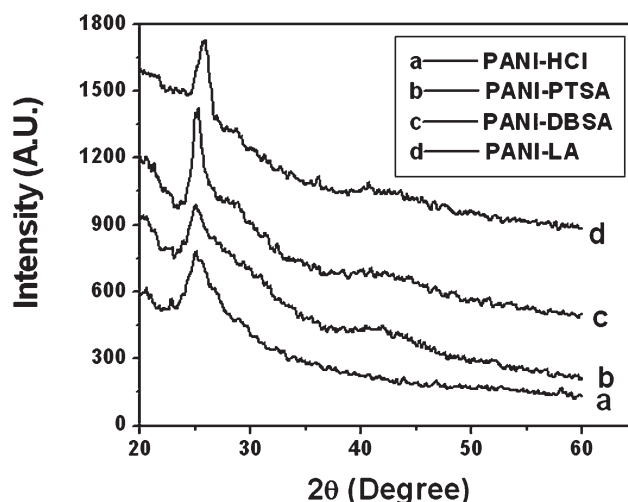


Figure 3 X-ray diffractogram of doped PANI samples.

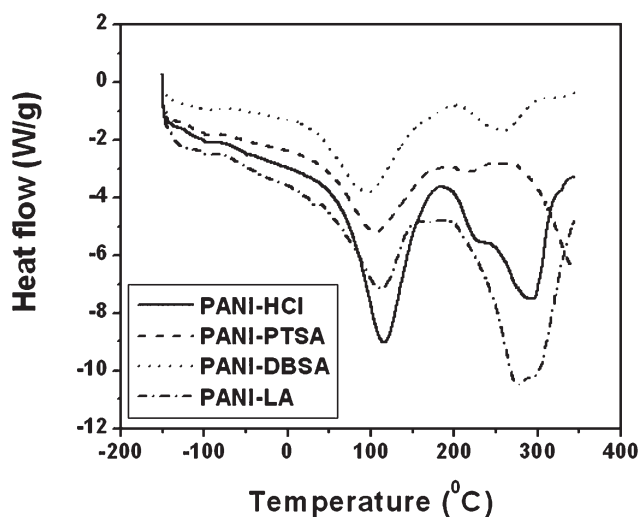


Figure 4 DSC plots of doped PANI samples.

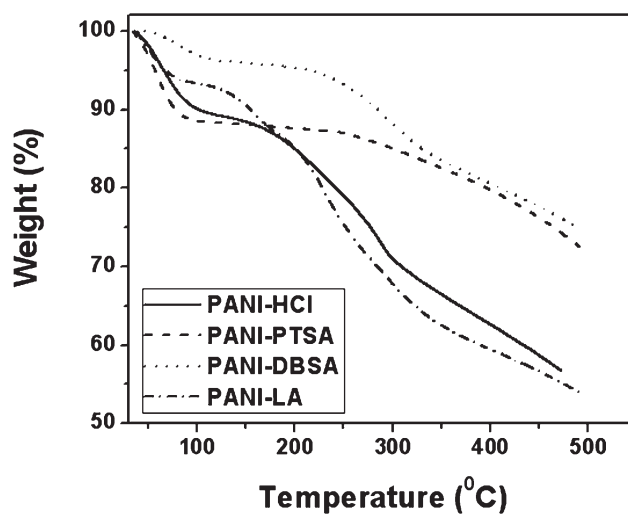


Figure 5 TGA plots of doped PANI samples.

PANI-LA. The result reflects that in presence of aromatic dopants bond formation of water molecules with the backbone nitrogen of the polymers is much less when compared with those of inorganic or aliphatic dopants. This may be due to the bulky size of the aromatic dopants (benzene ring), which prevents the bond formation of water molecule with the backbone nitrogen, present on the polymer.

Thermogravimetric analysis (TGA)

The TGA plots of doped PANI samples are presented in Figure 5. For all the doped PANI samples, two steps of weight loss occur; first at around 50–110°C, second over the temperature range 150–350°C. The first step of weight loss is due to the loss of moisture and the second step of weight loss is for bound water,

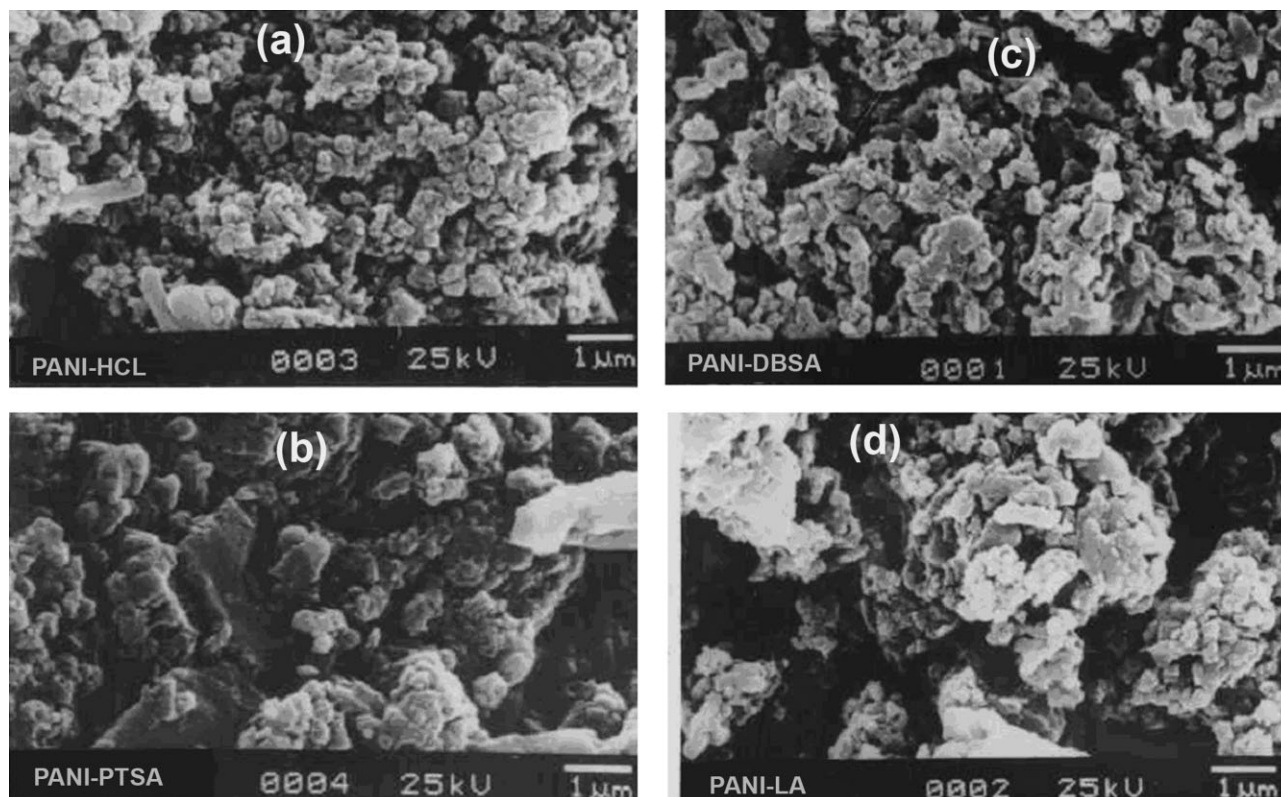


Figure 6 SEM images of (a) PANI-HCl, (b) PANI-PTSA, (c) PANI-DBSA, and (d) PANI-LA.

which is also observed in DSC.^{9,14} After the loss of secondary dopant (water) the loss of primary dopant may occur. Hence, a continuous loss in weight is observed in all samples over the temperature range 300–500°C. The TGA results show that the bound water (second weight loss) is much less in PANI-PTSA and PANI-DBSA when compared with PANI-HCl and PANI-LA. The TGA results are in well agreement with the DSC results. Crosslinking chemical decomposition followed by carbonation generally observed to occur beyond 450–500°C.^{5–7} As the heating is not continued beyond 500°C, these changes are not apparent in the given plots.

Morphology

The SEM images of all these doped polymers are presented in Figure 6. All PANI particles are agglomerated. Therefore, it is difficult to predict the actual morphology of a single particle. All PANI samples show irregular morphology with granular shape. The PANI-DBSA [Fig. 6(c)] has little rod like shape. The diameter of the particles ranges from 0.05 μm to 0.5 μm . The morphology of PANI depends on the method of synthesis, solvent or medium.²⁹ Huang et al. dissolved aniline in organic solvent like benzene, toluene, CS_2 , CCl_4 , and aqueous solution of APS and camphor sulfonic acid was added in it to obtain PANI nanofiber.²⁹ The present synthesis method is similar to their method of synthesis, however, the morphology of the resulted PANI samples are different. This may be due to use of different dopants.

CONCLUSIONS

The properties of doped polyaniline (PANI) depend on the type and molecular size of the dopant. The solubility of doped PANI depends on the molecular size of the dopant. With the increase in the dopant chain length, the solubility is increased. With the increase in dopant size, the crystallinity is decreased, whereas the d -spacing and interchain separations are increased. This reduces the charge carriers' mobility along a polymer chain as well as across the chains resulting in decrease in conductivity. However, all these structural changes favor the solubility of the doped PANI. Aromatic dopants reduce the bound water content in PANI when compared with inorganic and aliphatic doants.

A particular dopant cannot provide all excellent properties. For example, if one wants a PANI with high conductivity and high crystallinity, then the small inorganic dopant like HCl is suitable. If one

wants a PANI with high solubility, then the organic aliphatic acid with long chain length like lauric acid is effective. To reduce the moisture absorption of PANI, aromatic organic acids like DBSA or PTSA may be used. The dopant with the longer chain length is expected to produce a PANI with better solution processability.

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