

Photoluminescence, FTIR, and Electrical Characterization of Samarium(III) Chloride-Doped Polyaniline

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ABSTRACT: The synthesized polyaniline (PANI) is doped with different concentrations of Samarium(III) chloride (SmCl_3). The electrical conductivity of doped PANI samples has been measured in the temperature range (300–400K). It has been found that dc conductivity increases with the increase of dopant concentration. Different parameters, based on the conductivity, such as pre-exponential factor (σ_0) and activation energy (ΔE) have also been calculated. These parameters exhibit information about the nature and suitability of the dopant. Doped samples are characterized by FTIR and photoluminescence

studies, which show the interaction of dopant with PANI. Two sharp peaks of different intensities from PL spectra at 388 and 604nm have appeared in doped PANI, which might be due to the effect of SmCl_3 . It has been observed that SmCl_3 (dopant) shows noticeable changes in the electrical and spectroscopic properties of doped PANI. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2315–2319, 2009

Key words: conducting polymers; doping; photoluminescence; FTIR

INTRODUCTION

Conducting polymers contain π -electron backbone which is responsible for their electronic properties such as electrical conductivity, low energy optical transitions, low ionization potential, and high electron affinity.¹ Three major targets are important for these conducting polymers, i.e., high electrical conductivity, processability, and stability in air. The stability of conducting polymers is important for vital applications of synthesized materials. Stability is always a problem in polymers. Polymers stability in air refers to polymer's degradation with respect to atmosphere. Heat, oxygen, high energy radiations, ozone, and other atmospheric pollutions are the major factors that degrade the stability of polymers. Most of the reported conducting polymers are unstable in air except those containing nitrogen or sulfur atoms in the polymer backbone.^{2–7}

Polyaniline (PANI) is one of the most discussed conducting polymers. It has been an interest of investigations because of its straightforward polymerization, excellent environmental stability, and important electrical, electrochemical, and optical properties. It is inexpensive, simpler to synthesize and has various industrial applications such as in

static films for transparent packaging of electronic components, electromagnetic shielding, rechargeable batteries, light-emitting diodes, sensors for medicine and pharmaceuticals, nonlinear optical devices, and membranes for the separation of gas mixtures.^{8–10}

Organic polymers are either an insulator or a semiconductor, having small conductivity. Through doping they can be converted into a polymer, which are in metallic conducting regime. The controllable addition of known, usually small quantities, chemical species (dopant) results in drastic changes in the electrical, magnetic, optical, electronic, and structural properties of the polymer.¹¹

Electrical, thermal, and spectroscopic studies of Cu^{+1} , Sulfamic acid, and Te-doped^{12–14} PANI system have already been studied in our previous work but there is always a scope to search new dopants for conducting polymers. Literature survey reveals that only a few works on rare earth compounds is done, and thus we have considered Samarium(III) chloride (SmCl_3) as a dopant for PANI. The selection of SmCl_3 has been made on the basis of its exceptional qualities. It is a strong Lewis acid of light yellow-colored crystals. This dopant is stable in nature and has no hazardous effects.

Efforts are being made to study the electrical and spectroscopic behavior of SmCl_3 -doped PANI. The spectroscopic characterization is done by photoluminescence and Fourier transform infrared (FTIR) studies. FTIR characterization confirms the structural changes caused by the incorporation of dopant

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species into the polymeric chain. The concept of photoluminescence depends upon excitation of photons. The ability of a polymer to exhibit photoluminescence is associated with the presence of dopant, occurring relatively in small concentration in the polymeric chain.

EXPERIMENTAL

Synthesis of PANI was done from oxidative polymerization by using ammonium peroxydisulfate in aqueous acid solution. Ammonium hydroxide (NH_4OH) was used to deprotonate the yielded green polymer powder (ES) to insulate dark blue PANI.¹⁵

Doping of PANI had been done chemically. Solutions of dopant (SmCl_3) in 0.02N HCl of different concentrations such as 0.5, 1.5, 2.5, 3.5, and 4.5% had been used to dope PANI. A separate solution of PANI EB (powder) dissolved in THF and water was also prepared. The dopant solutions of different concentrations were added to swollen PANI (swollen by the action of solvent) and were kept under constant mechanical stirring for about 30min. The doped PANI solution was then filtered and dried in an oven at about 40–60°C. The dried PANI was ground to make fine powder for making the samples (pellets).

Bulk samples in the form of pellets of diameter 1.01cm and thickness 0.016cm were prepared by grinding and compressing the powder under a pressure of $\approx 6.6\text{ton}$. These samples were placed between the two steel electrodes, situated inside a metallic sample holder for conductivity measurements. To avoid the effect of moisture absorption, annealing of these samples was done before conductivity measurements in vacuum of the order of 10^{-3} Torr. Conductivity was measured through Keithley electrometer (Model 617) by applying a voltage of 1.5 V across the samples.

The chemical structure of PANI and doped PANI samples were characterized by FTIR spectroscopy. FTIR spectra of PANI-KBr pellets were obtained by using Perkin-Elmer FTIR spectrometer in the range from 4000 to 400cm^{-1} at a resolution of 4cm^{-1} . Photoluminescence of all the doped PANI samples was studied by Perkin Elmer LS55, Luminescence Spectrometer in the range of 300–700 nm at an excitation of 500 nm.

RESULTS AND DISCUSSION

DC conductivity

The temperature dependence of dc conductivity for various samples of PANI doped with different concentrations of SmCl_3 is shown in Figure 1. The plots of $\ln\sigma$ versus $1000/T$ are straight lines, which indi-

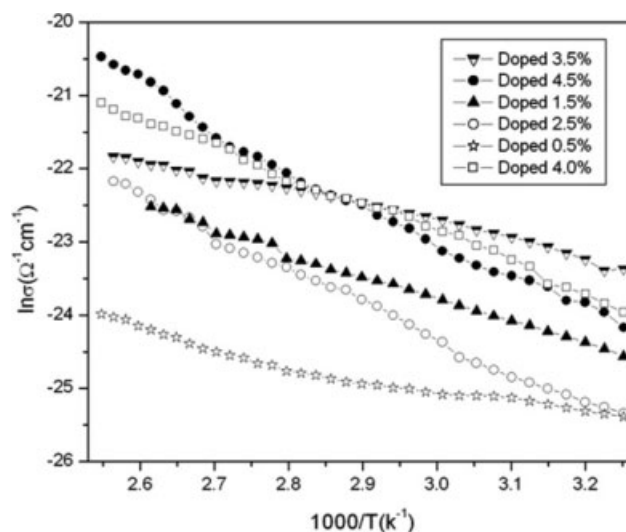


Figure 1 Variation of dc conductivity versus $1000/T$ for PANI doped with different concentrations of Samarium (III) chloride.

cate that conduction in these samples is through an activated process, having single activation energy in the temperature range (300–400K). The change in slope is responsible for the change in activation energy. The value of activation energy (ΔE) is calculated from the slope of the graph. As the slope of the graph increases with the dopant concentration, activation energy increases. Further, the slope of the graph explains the conductivity mechanism taking place in the doped PANI samples. The dc conductivity can, therefore, be expressed by the usual relation as follows¹⁶:

$$\sigma_{\text{dc}} = \sigma_0 \exp(-\Delta E/k_B T) \quad (1)$$

where k_B is the Boltzmann constant and σ_0 is the pre-exponential factor. The conductivity of PANI doped with 0.02N HCl has been found to be $2.708 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$, whereas the conductivity of undoped PANI is $3.62 \times 10^{-14} \Omega^{-1} \text{cm}^{-1}$. Doping introduces carrier into the electronic structure. The attraction of an electron in one repeated unit to the nuclei of the neighboring unit leads to carrier delocalization along the polymer chain. Thus, doping of PANI increases the conductivity by increasing the carrier concentration, which ultimately enhances the mobility of charge carrier. When PANI is doped with 4.5% SmCl_3 , sudden increase in conductivity and a sharp increase in the intensity of PL spectrum peak are observed. Thus, at this particular doping percentage, doped PANI can be used for sensors purposes.

The variation of σ_{dc} and ΔE with concentration of dopant are shown in Figures 2 and 3. From Figure 3, the initial increase in activation energy with the increase of dopant concentration might due to the

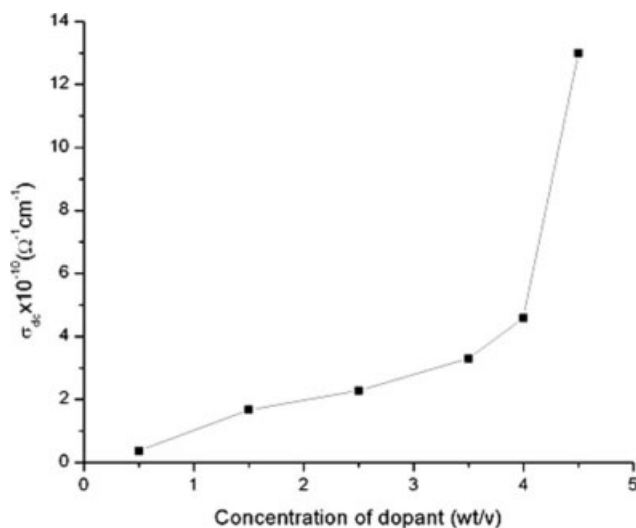


Figure 2 Variation of dc conductivity versus different concentrations of dopant (w/v).

increase of charge carrier concentration and the fermi level may change. The decrease in activation energy at 3.5% could be attributed to the increase of localized states. The increased dopant concentration facilitates the movement of charge carriers through the increased localized states.

Table I confirms that there are noticeable changes in the value of σ_0 . The conduction mechanism can be explained in terms of preexponential factor (σ_0) for conduction in the localized states. The value of σ_0 should be about $10^3 \Omega^{-1} \text{cm}^{-1}$, which is two to three orders smaller than those for conduction in the extended states and should become still smaller for the conduction in the localized states near the Fermi level.¹⁷ Hence, the magnitude of σ_0 in this work indicates that conduction is taking place by hopping process because of the wide range of localized states present near the Fermi level, and thus conduction through extended states is completely ruled out.

FTIR STUDIES

The FTIR characterizations have been done for undoped and all the SmCl_3 -doped samples. Here, we have given the IR spectra of undoped and 0.5,

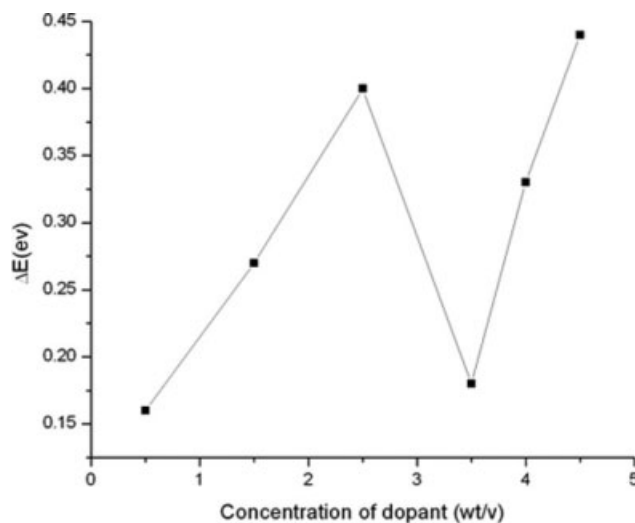


Figure 3 Variation of ΔE versus different concentrations of dopant (w/v).

3.5, and 4.5% SmCl_3 -doped PANI samples, which are presented in Figure 4(a–d), respectively.

The vibrational bands observed for undoped and doped PANI are explained on the basis of the normal modes of PANI. The broad medium band at 3126cm^{-1} is assigned to the N–H stretching vibration of aromatic ring, which shifts to 3428 , 3424 , and 3422cm^{-1} in 3.5, 4.5, and 0.5% doped PANI samples, respectively. The strong intensity band at 1118cm^{-1} (as in undoped PANI) is assigned to aromatic C–H in plane bending modes, which shifts to broad, splitted bands at 1054cm^{-1} in 0.5% doped, 1028cm^{-1} in 3.5% doped, and 1023cm^{-1} in 4.5% doped PANI samples. The absorption band at $\approx 600\text{--}700 \text{cm}^{-1}$ observed for undoped and doped PANI samples show characteristics peaks of the C–H out-of-plane bending vibration of the 1,4-disubstituted benzene ring.

The splitted band of higher intensity observed (in doped samples) around 1594cm^{-1} is the characteristic peak of nitrogen quinoid ring and is absent in undoped PANI sample. The presence of this band in doped samples is due to the substitution of SmCl_3 dopant in the PANI chain. On comparing the IR spectra of undoped, 0.5, 3.5, and 4.5% doped PANI

TABLE I
Electrical Parameters of PANI Doped with Different Concentrations of Samarium(III) chloride at Temperature 330 K

Samples	dc conductivity (σ_{dc}) ($\Omega^{-1} \text{cm}^{-1}$)	Pre-exponential factor (σ_0) ($\Omega^{-1} \text{cm}^{-1}$)	Activation energy (ΔE) $\times 10^{-2}$ (eV)
PANI doped with 0.02N HCl	2.70×10^{-13}	9.28×10^{-10}	20.50
PANI doped with 0.5% SmCl_3	3.70×10^{-11}	3.75×10^{-9}	16.19
PANI doped with 1.5% SmCl_3	1.67×10^{-10}	5.04×10^{-7}	27.22
PANI doped with 2.5% SmCl_3	2.28×10^{-10}	3.57×10^{-5}	40.74
PANI doped with 3.5% SmCl_3	3.30×10^{-10}	9.03×10^{-8}	18.60
PANI doped with 4.0% SmCl_3	4.59×10^{-10}	7.04×10^{-5}	33.93
PANI doped with 4.5% SmCl_3	1.30×10^{-9}	4.61×10^{-4}	44.18

samples, the small absorption band at 2926cm^{-1} in 3.5% doped and 2925cm^{-1} in 4.5% SmCl_3 -doped samples have been associated with the electrical conductivity and the high degree of electron delocalization in PANI. This band gets splitted and is of high intensity on increasing the SmCl_3 concentration. The splitting and increased intensity of the absorption band on increasing the SmCl_3 concentration [Fig. 4(c,d)] suggests the presence of higher extent of protonation in these samples when compared with that of samples in Figure 4(b). Similar characteristic peaks have been observed in other PANI samples doped with different concentrations of SmCl_3 . This interpretation also finds support from electrical measurements and photoluminescence studies.

PHOTOLUMINESCENCE STUDIES

Photoluminescent organic molecules are a new class of compounds with interesting properties. They undergo emission over a wide range from the violet to the red. They can also be combined in several different forms to produce white light. One category of organic material with photoluminescence properties is conjugated organic polymers. The photoluminescence spectroscopy (PL) of SmCl_3 -doped PANI has been performed and is shown in Figure 5. The PL spectra of 0.5, 1.5, 2.5, 3.5, and 4.5% doped sample show peaks at 388, 386, 604, and 609nm. The relative heights of the emission peaks alter with different dopant concentrations and nature of solvents (due to polarity). It has been noticed that the intensities of peak observed at 386 nm increases with the increase of dopant concentration, which may be due to the role played by interchain species. It is known that interchain species play an important role in the emission process of conjugated polymers. The

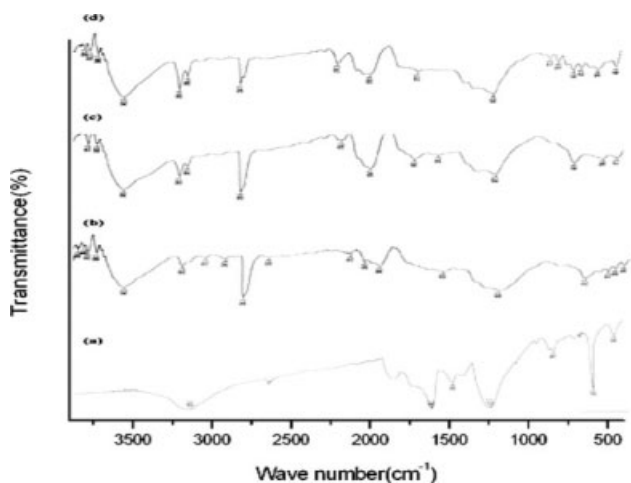


Figure 4 (a–d) FTIR spectra of (a) undoped PANI, (b) 0.5% doped PANI, (c) 3.5% doped PANI, and (d) 4.5% doped PANI.

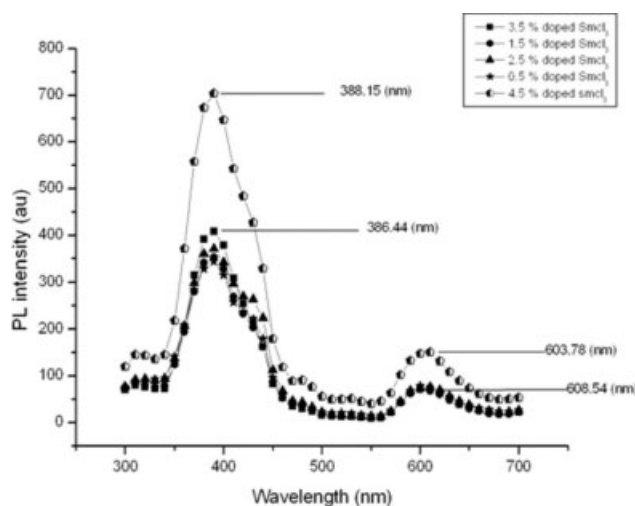


Figure 5 Photoluminescence spectra of PANI doped with different concentrations of Samarium(III) chloride.

observed reduced height of the photoluminescence emission intensity peaks (noticed at 609 and 604nm) might due to the possibility of atoms/molecules of dopant (SmCl_3) forming aggregation in the polymer chain. Overall, it is clear that the nature of conjugated polymer aggregation depends upon many factors, including the polymer coil size, the nature of polymer–solvent and polymer–dopant interactions and the degree of chain overlap.

The PL spectra of SmCl_3 -doped PANI samples may be significantly different with different ways of doping. The PL spectra of the samples have the same general shape, which indicates that it is an efficient way to tune the intensities of the peak by employing dopant at different concentration levels.

CONCLUSION

We have done electrical and spectroscopic characterizations of SmCl_3 -doped PANI. The dc conductivity of the SmCl_3 -doped sample increases with dopant concentration because of the delocalization of charge carriers along the PANI chain. Through electrical and photoluminescence studies, it is suggested that doped PANI can be used for sensors purposes when it is doped with 4.5% SmCl_3 . The calculated values of σ_0 indicate that conduction is taking place by hopping process because of the wide range of localized states near the Fermi level. The confirmation of increase in the extent of protonation with a slight increase in the concentration of dopant is done by FTIR studies. Photoluminescence studies of the doped samples indicate that the photoluminescence emission intensity peak increases with the increase of dopant concentration, which might due to interchain species present in the polymeric chain.

Conclusively, SmCl_3 has a prominent effect on electrical and spectroscopic properties of PANI.

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