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Synthesis and characterization of polynitrosoaniline

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Abstract

We report the chemical synthesis and characterization of a new conducting polymer, polynitrosoaniline. The presence of nitroso moieties in the polymeric backbone results in a change in the conductivity behaviour of the polymer. The scanning electron micrographs of the polynitrosoaniline reveal an irregular globular pattern. The thermogravimetric analysis and differential scanning calorimetry studies of the polymer show degradation at 429°C. X-ray diffraction studies of the polymer indicate lesser crystallinity as compared with emeraldine base.

Keywords: Polynitrosoaniline; Scanning electron microscopy; X-ray diffraction

1. Introduction

Polyaniline is one of the most studied and interesting conducting polymers having many potential applications. These devices include electrochromic display, rechargeable battery, microactuators, biosensors and field-effect transistors (FETs), etc. [1–5]. Polyaniline has recently been studied extensively as a rather unique member of the conducting polymer family. It can be doped to the metallic conducting level by protonic acids [6] and has interesting electrochemical behaviour [7]. Moreover, it is known to exhibit a variety of features, such as number of oxidation states, flexibility in doping (protonation) levels, molecular conformation and presence of oligomeric impurities, which strongly affect its electric properties [8–11]. Doping level and conformational changes in the polyaniline backbone can be brought about by the substitution of a desired functional group in the polymeric backbone [12].

Processability is an important requirement in conducting polymers for their possible commercial use. Since most of the conducting polymers are not processable, much of the efforts made in this field have been directed towards circumventing this problem. To solve this problem, various approaches have been tried, including addition of side groups to the polymer backbone [13], grafting of polymers to a non-conducting polymer [14], direct polymerization of intractable polymers into the final desired shape, making a composite of blend of conducting polymers [15–17] and copolymerization [18,19], etc.

The observation that alkyl and alkoxy substituted derivatives of polythiophene and polypyrroles are solution processable has led to the idea of preparation of alkyl and alkoxy substituted derivatives of polyaniline. Undoped polyaniline is soluble only in some of the organic solvents, such as 1-methyl 2-pyrrolidone (NMP), dimethyl formamide (DMF), tetrahydrofuran (THF) and dimethyl sulphoxide (DMSO), whereas alkyl substituted polyanilines like poly(*o*-ethylaniline) are known to be soluble in a large number of organic solvents [20].

In the present paper, we report the synthesis and characterization of a new conducting polymer, polynitrosoaniline. The polymer was synthesized for obtaining enhanced processability.

2. Experimental

Aniline was procured from Sigma and used without further purification. Reagent grade ammonium persulphate (APS), hydrochloric acid (HCl) and methanol were also used as received. *N*-methyl 2-pyrolodine (NMP) of synthetic grade was procured from Merck. Aqueous solutions were prepared using doubly distilled, deionized water (Millipore RO 10 TS).

0.15 M solution of sodium nitrate (250 ml) was slowly added to the constantly stirred solution of 50 g emeraldine

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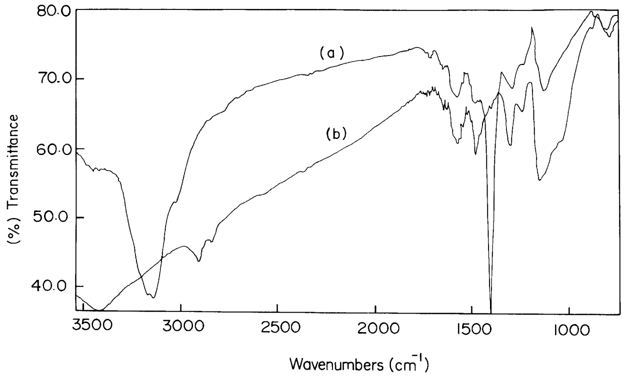

Fig. 1. FT-IR of doped (a) polynitrosoaniline and (b) polyaniline.

base in 250 ml con HCl at 0°C. The solution was maintained at 0°C by using JULABO water bath (model F10) and the rate of addition of sodium nitrate solution was kept at 1 ml min^{-1}. After about 24 h, the precipitate was collected on a buchner funnel using a vacuum filtration flask and a vacuum pump. The precipitate was washed with distilled water until the filtrate becomes colourless. The precipitate was dried under vacuum for about 4 h.

The doped polynitrosoaniline obtained by this method was in its doped form and was further undoped by treating it with aqueous ammonium solution (pH 12) for about 36 h with constant stirring. The powder was then collected on a buchner funnel and washed with distilled water several times. The resulting powder was partially dried in vacuum for about 15 min and subsequently dried at 80°C for about 4 h. To characterize polyaniline and polynitrosoaniline, the undoped powders were treated with 1 M HCl and constantly stirred for about 24 h. The doping levels of polynitrosoaniline and polyaniline were found 36.6 and 42.6%, respectively.

The conductivity measurements were performed using a four-points-probe set-up. The UV–Vis measurements were carried out using UV–Vis spectrophotometer (Shimadzu 160A). A Nicolet 510 P was used for recording the FT-IR spectra. Perkin Elmer DSC-7 and Mettler TA 3000 system were used for carrying out thermal measurements. Scanning electron microscopy (SEM) studies were carried out using LEO 440. X-ray diffraction studies were conducted using X-ray diffractometer (XRD) (Philips PW, Model 3020). Molecular weight was estimated using GPC/HPLC (Waters) with polystyrene samples as standard.

3. Results and discussion

The molecular weight of polynitrosoaniline by gel permeation chromatography (GPC), after using the polystyrene samples as standard, was observed to be about 46,000. The molecular weight of the polyaniline used for the synthesis of polynitrosoaniline was about 68,000.

The value of room temperature electrical conductivity for doped and undoped polynitrosoaniline obtained by four-points-probe technique was found to be 5.0×10^{-1} and 1.98×10^{-8} S cm^{-1}, respectively. The value of electrical conductivity of the doped polynitrosoaniline is found to be lower than that of doped polyaniline (1.2 S cm^{-1}) [21]. The decrease in the electrical conductivity of the polynitrosoaniline may be attributed to the presence of nitroso moieties in the polymeric chain as well as the reduction of the conjugation length.

FT-IR spectroscopic studies shown in Fig. 1(a) and (b) correspond to the doped polynitrosoaniline and polyaniline. Fig. 1(a) shows characteristic vibration bands at 3133, 1574, 1402, 1302, 1136 and 796 cm^{-1}. The peak at 3133 cm^{-1} is due to the aromatic C–H stretching while the peak at 1574 cm^{-1} is due to the C=C bond of quinoid rings. The presence of the peak at 1402 cm^{-1}, which corresponds to nitroso group, confirms the attachment of this group in the polyaniline chain. It can be seen from Fig. 1(b) that the peak of secondary amine is not present in the FT-IR spectra of polyaniline. The complete absence of secondary amine (N–H) peak and the appearance of the 1402 cm^{-1} peak corresponding to N–NO in the FT-IR spectra of polynitrosoaniline (Fig. 1(a)) suggests a complete replacement of N–H group by N–NO group. The vibration band at 1136 cm^{-1} is attributed to the presence of C–N bond.

The results of UV–Vis studies conducted on polynitrosoaniline and polyaniline at room temperature are shown in Fig. 2(a). The spectra were obtained after dissolving the polymer powder samples in NMP. The reference cell was filled with NMP. In this case, absorption peaks at 305 and 581 nm are attributed to π–π^* transition and n–π^* transition, respectively. A blue shift is obtained in the absorption of polynitrosoaniline as compared to polyaniline (Fig. 2(b)).

The plot of $(\alpha h\nu)^{-2}$ versus photon energy ($h\nu$) shows the value of the energy band gap for polynitrosoaniline as 2.4 eV, which is higher than that of polyaniline [22–24]. These results can be attributed to the lower doping level.

Results of the differential scanning calorimetry (DSC) studies conducted on chemically synthesized doped polynitrosoaniline and polyaniline are shown in Fig. 3(a) and

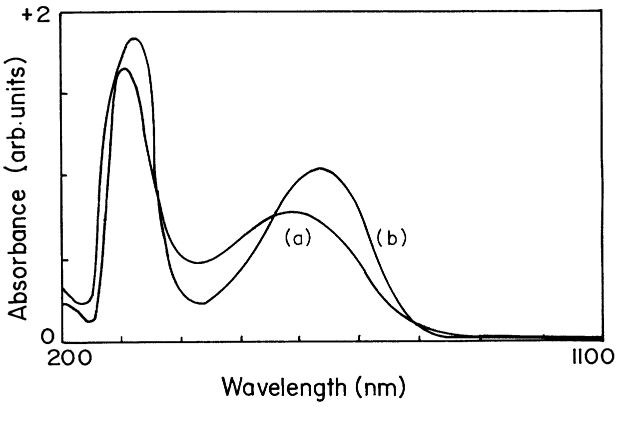

Fig. 2. UV–Vis spectra of doped (a) polynitrosoaniline and (b) polyaniline.

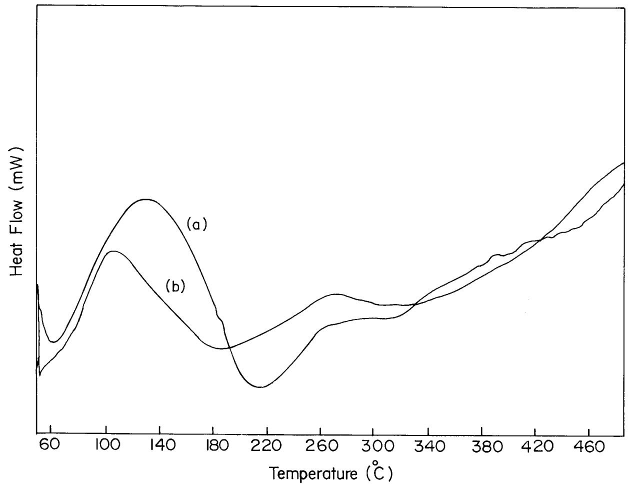

Fig. 3. DSC thermogram of doped (a) polynitrosoaniline and (b) polyaniline.

(b). In the case of polynitrosoaniline, endothermic peaks at 126 and 284°C, and an exothermic peak at 210°C are observed. The endothermic peak at 126°C is understood to arise from the removal of water molecules attached to the polymer matrix. The shift of this peak towards higher temperature may be attributed to the fact that it forms hydrogen bonding with the adsorbed water molecules, which require higher energy resulting in the creation of the intermolecular hydrogen bond. The 284°C peak has been associated with the removal of Cl^- dopants from the polymeric backbone. The 210°C peak is attributed to the interchain cross-linking [25–27]. The peak at 429°C is associated with the polymer degradation.

To further confirm the above results obtained for doped polynitrosoaniline and polyaniline, thermal gravimetric analysis (TGA) has been carried out in inert (nitrogen) atmosphere at 20°C min^{-1} and the results are shown in Fig. 4(a) and (b). It can be seen (Fig. 4(a)) that in the case of doped polynitrosoaniline, 5% weight loss occurs between 50 and 100°C and about 10% weight loss occurs between 100 and 200°C. Further weight loss of about 7.5% found between 200 and 300°C is due to the removal of Cl^- ions. The 3% weight loss has been found between 300 and 400°C. A huge weight loss of about 32% between 400 and 500°C shows that the degradation starts above 400°C in polynitrosoaniline. The total weight loss of polynitrosoaniline up to 500°C is about 58%, whereas in the case of doped polyaniline, the weight loss is only about 29% (Fig. 4(b)) in the same temperature range.

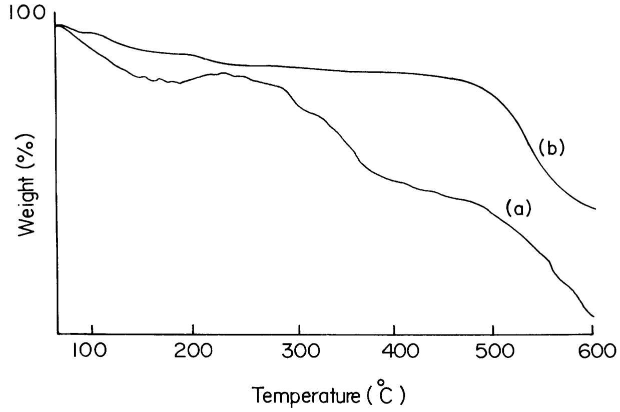

Fig. 4. TGA thermogram of doped (a) polynitrosoaniline and (b) polyaniline.

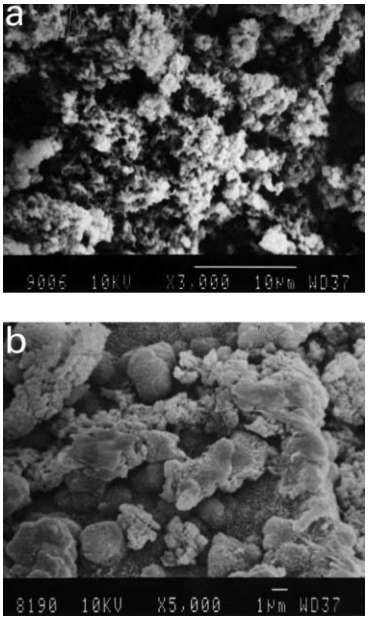

Fig. 5. SEM micrographs of doped (a) polynintrosoaniline and (b) polyaniline.

Fig. 5(a) and (b) shows the SEM photographs of doped polynitrosoaniline and polyaniline, respectively. It has been observed that the polynitrosoaniline shows an irregular globular pattern with an amorphous character. This is in contrast to polyaniline, which exhibits a complete regular pattern. The X-ray diffraction curve of polynitrosoaniline (Fig. 6(a)) shows a broad peak in the range $2\theta = 15$–30°, indicating the amorphous nature of the sample. However, in the case of emeraldine base (Fig. 6(b)), sharp peaks between $2\theta = 10$–30° are observed, revealing its crystalline nature.

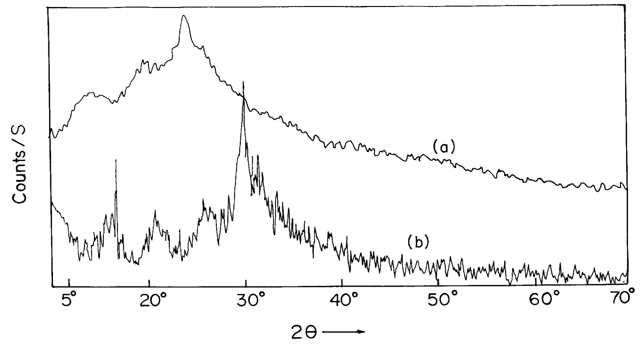

Fig. 6. X-ray diffraction pattern of doped (a) polynintrosoaniline and (b) polyaniline.

The solubility of polynitrosoaniline in undoped and doped states has been experimentally investigated. It is found that in its undoped form, it is soluble in NMP, DMF, THF and DMSO at room temperature, whereas polyaniline is less soluble in these solvents. However, doped polynitrosoaniline has been found to be partially soluble in NMP, DMF, THF and DMSO, whereas doped polyaniline is insoluble in these solvents.

4. Conclusions

The characterization of the chemically prepared polynitrosoaniline has been carried out using DSC, TGA, FT-IR, UV–Vis, SEM and X-ray diffraction pattern. The observed lower value of the electrical conductivity of the polynitrosoaniline has been attributed to the incorporation of nitroso moieties in polymer chains. In order to have a better understanding of the electrical behaviour, it should be interesting to quantitatively estimate the degree of the nitroso group per unit aniline ring using XPS measurements. However, the observed solubility of polynitrosoaniline common organic solvents indicates its potential for technological applications.

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