Synthesis and Characterization of Poly(o-toluidine) Doped with Camphor Sulphonic Acid

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Abstract-**Among the conducting polymers, Polyaniline and its derivatives have been studied extensively in the last decade with improvements in processing having the key role in establishing the intrinsic electrical properties. In the present paper, the camphor sulphonic acid [CSA] doped Poly (o-toluidine) [POT] was prepared using chemical oxidative polymerization method. The prepared CSA doped POT was characterized using XRD, FTIR and UV-Vis analysis. The XRD pattern showed the amorphous nature of the Polymer. The FTIR pattern shows the various stretching and bending modes of POT. UV-Vis analysis exhibits emaraldine state of the polymeric system. Conductivity of the sample was studied by impedance spectroscopy.**

Keywords- conducting polymer; POT; CSA; XRD; FTIR; UV-Vis analysis

I. INTRODUCTION

Intrinsically conducting polymers[ICP] are inherently conducting in nature because of the presence of the conjugated π electrons in the system and having potential applications due to its low energy optical transition, low ionization potential and a high electron affinity[1,2]. Generally, there are various types of synthesis that have been done on ICP's, it is important to not only achieve a high degree of conductivity but also make them suitable for the processing either alone or in the matrix form of a suitable host polymer. The deficient processability of most of the conducting polymers has limited their advantages in commercial applications. Therefore, there is a generous scope for modifying the conductivity and processability of the ICP's through the suitable dopant or by changing the starting monomer [1,3].

These ICP's include polythiophene, polyacetylene, polyaniline and its derivatives [1]. Addition of dopant to these ICP's changes their magnitude of conductivity, from insulator to metal like conducting behaviour. Among these, Polyaniline[PANI] has been at the center of investigations due to the unique electrochemical, optical properties and its stability. This system can be obtained by both electrochemical and chemical oxidative polymerization of aniline in aqueous and nonaqueous media [4-6]. Poly(o-toluidine) [POT] is a derivative of polyaniline, which contains methyl group in its ortho position. Recently, POT was also found to have additional advantage with respect to PANI due to its faster switching time between the reduced and oxidized states [7-9].

The aim of our work is to synthesize and characterize the Camphor sulphonic acid[CSA] doped Poly(o-toluidine) by chemical oxidative polymerization. In order to investigate the properties of CSA doped POT, the sample has been characterized by XRD, FTIR, UV-vis and conductivity of the sample was studied by the impedance spectroscopy(Solatron 1260 impedance analyser) in the frequency range between 1Hz to 1MHz by mounting a pellet form of 8mm diameter between the silver electrodes.

II. MATERIALS AND METHODS

A. Materials:

The monomer o-toluidine (99%) was distilled under reduced pressure prior to use. Ammonium peroxydisulfate (98%), camphor-10- Sulphonic acid(98%) were all of AR grade and used without further purification.

B. Experimental Section:

POT was chemically sythesized by oxidation method. In a typical synthesis process 2.28 g of $(NH_4)_2S_2O_8$ as the oxidant was dissolved in 10 ml of distilled water. The polymerization was initiated by the dropwise addition of oxidizing agent in an 0.01M acidified(CSA) solution of monomer under constant stirring at 0-4˚C. The monomer to oxidizing agent ratio was kept as 1:1. After complete addition of oxidant, the reaction was kept under stirring for 12hr. The obtained greenish black precipitate was then washed with water several times followed by methanol and dried in an oven for 12hr.

III. RESULTS AND DISCUSSIONS

Figure(1) shows the X-ray diffraction pattern of CSA doped POT. In this the broad and weak diffraction peak appeared at 2θ ~24.8°. This obtained pattern is in good agreement with the literature on ICP's, according to which all the polymers have either semicrystalline or amorphous nature of the structure[1].

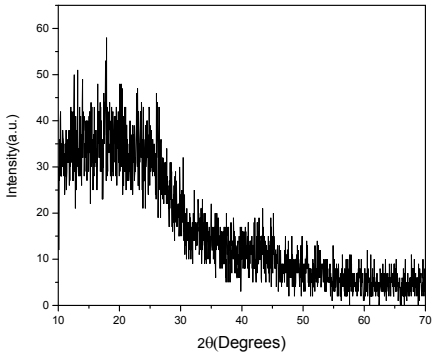

Figure 1: xrd pattern of CSA doped POT

The FT-IR spectrum of CSA doped POT is shown in figure (2). The presence of the characteristic peaks of polymeric material doped with CSA indicates the successful formation of the polymer. The broad peak appears around 3400 cm^{-1} corresponds to the interstitial water and hydroxyl groups. 3220 cm^{-1} indicates the NH_2^+ stretching mode and 2922 cm^{-1} is attributed to CH_3 stretching mode. Two peaks at 2357 cm^{-1} and 2337 cm^{-1} may be attributed to NH^+ stretching of amine group [10, 11]. Existence of peaks at 1597 cm^{-1} and 1498 cm^{-1} arises from C-C stretching and 1742 cm^{-1} for a C=O stretching mode of the system. In addition to this peak at 1379 cm^{-1} corresponds to the CH_3 bending mode. The band at 1318 cm^{-1} is assigned to the C-N stretching mode in the neighbourhood of quinonoid ring. –CH stretching mode was observed at 1151 cm^{-1} and 1111 cm^{-1}. The bands at 1032 cm^{-1} and 515cm^{-1} are due to S=O stretching which confirms the presence of CSA doping in this aniline derivative. Then, the absorption peak at 804 cm^{-1} is the -CH deformation mode present in the substituted benzene ring [12, 13].

The UV-vis spectra of CSA doped POT is shown in Figure (3).The absorption peaks of the emaraldine form of the CSA doped POT in DMSO reveals absorption maxima at 315 and 617 nm initiating the π-π* and n- π* interband transition. This implies the half oxidized emaraldine state of the POT[7].

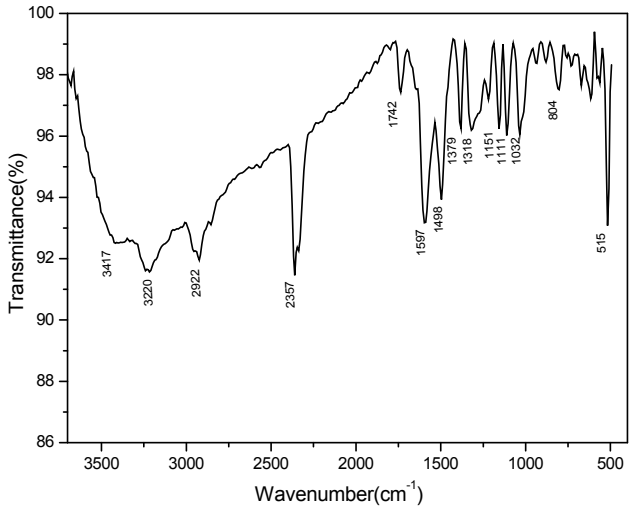

Figure 2: FTIR spectrum of CSA doped POT

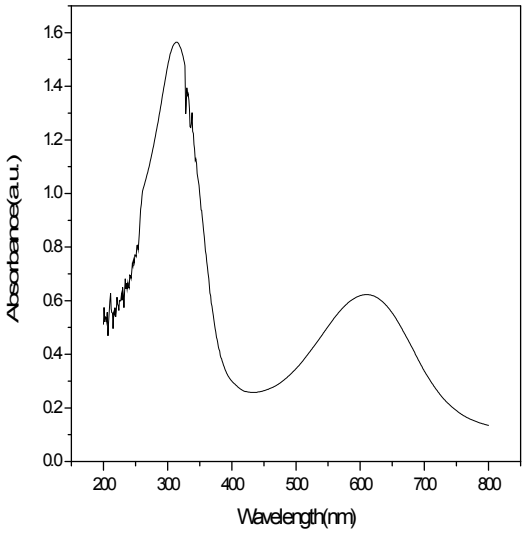

Figure 3: UV-vis spectrum of CSA doped POT

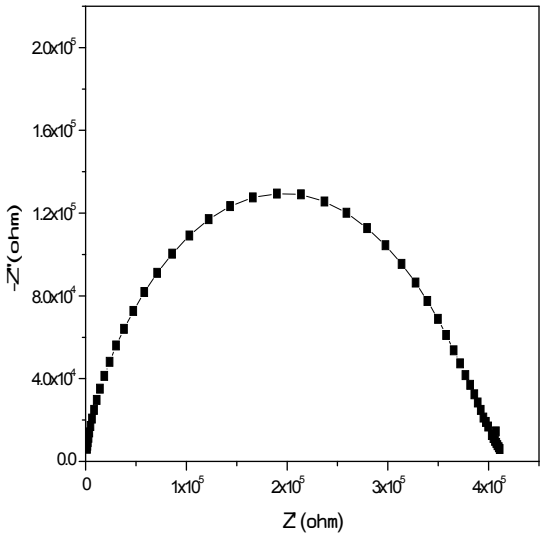

Figure 4: Nyquist plot

Solid state electrical conductivity at the room temperature was measured and the impedance plot is given in Figure (4). It exhibits semicircle behaviour for the given 100mV. The measured value of conductivity for CSA doped POT was found to be 0.482E-6 S/cm which is higher than the HCl doped POT [8]. The lesser conductivity of the doped POT related to polyaniline is caused by the presence of bulky methyl group present in the polymer [1]. The steric effect of the methyl substituent at the ortho position of the benzene ring is the predominant reason for the decrease in the extent of the π-electron conjugation which influences additional distortion along the polymer chain.

IV. CONCLUSION

POT doped with CSA was synthesized by chemical oxidative polymerization method. The doping process leads to chemical changes in the system, which changes the electrical and optical properties of the system. The XRD pattern shows the amorphous nature of the polymer. The FTIR pattern shows the various stretching and bending modes of CSA doped POT. UV-Vis reveals the conducting phase of the system. The impedance measurement suggests conducting property of the CSA doped POT. The conductivity measurements of CSA doped POT shows better conductivity compared to HCl doped POT. Thus, on the basis of our fundamental materials characterization a suitable doped conducting polymer is being suggested for the various fields of applications like optoelectronics, sensors and photocatalysts.

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