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Synthesis and Characterization of Inorganic Acid-doped Conducting Polymer

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ABSTRACT

Conducting polymeric materials containing conjugated bonds has gained much focus in scientific and technological areas in recent years. The unique optical, electrical and chemical properties of these materials find their use in electronic displays, telecommunication, biosensors, anti-corrosion coatings, etc. Compared to polyaniline, poly ortho toluidine has attracted considerable attention, since they exhibit better solubility in a wide range of solvents. In this work, poly ortho toluidine (POT) has been synthesized by Chemical oxidative polymerization technique by using sulfuric acid as a protonation agent and ammonium peroxo disulfate (APS) as an oxidizing agent. The optical, structural and morphological properties and the size of the particles have been investigated. X-ray diffraction has shown that POT was a partially crystalline polymer due to doping of highly concentrated sulfuric acid. A flake-like feature was observed via scanning electron micrograph (SEM). The better protonation effect of POT was indicated by UV spectroscopy. The chemical structure of POT was investigated by FT-IR. Nanoparticle size analysis has revealed that the particle size was below 100 nm.

Keywords: POT; FT-IR; Optical and Structural properties; SEM; Particle size.

1. INTRODUCTION

Conducting polymer is also known as a conjugated organic polymer with the highly π-conjugated polymeric chains. It has been widely used in different areas such as chemical and biosensors, catalysts, photovoltaic cells, batteries, supercapacitors and energy storage device applications, due to its unique optical properties, electrochemical activity and biocompatibility. Different kinds of conducting polymers have been developed for different applications (Duong Nguyen Nguyen and Hyeonseok Yoon, 2016). The properties of polymers obtained from substituted anilines are somewhat different from those of polyaniline. Poly ortho toluidine (POT) is a derivative of polyaniline with a methyl group (-CH_3) attached in the ortho position at the aromatic ring (Salma Bilal *et al.* 2014).

Chemical, electrochemical and photo-induction are the techniques to initiate the polymerization. In the first case, chemical oxidants such as ferric chloride, Ammonium peroxo disulfate (APS) are used to oxidize the monomer. In the second case, the monomer is oxidized electrochemically; in the third technique, a light is required to oxidize the monomer. Poor reproducibility of bulk conducting polymer and difficulty to remove the grown film from the electrode surface are the drawbacks of electrochemical polymerization. Most of the conducting polymer in bulk form can be synthesized via oxidative chemical polymerization, which results in a more homogeneous morphology than the electrochemical route (Babu *et al.* 2009; Sezer *et al.* 1999; Gorey *et al.* 2014).

In general, conducting polymer exists in three different states classified as: leucoemaraldine, pernigraniline, and emeraldine; again, it exists in two forms namely, insulating and conducting states under the emeraldine form. The chemical route can generate nano-sized particles of POT in the conducting state by optimizing the concentration of monomer and oxidizing agent. Notably, sulphuric acid (H_2SO_4) used as a dopant (protonic acid) plays a vital role in developing the properties of polymers. The partially crystalline conducting polymer can be achieved by doping oxidizing agents and acids in the monomer solution.

Here we report a chemical oxidative polymerization pathway for the synthesis of nano-sized and pure emeraldine salt form of POT. In the present work, H_2SO_4 has been used as a dopant and APS as an oxidant. After the end of the reaction, two phases are completely separated. The organic phase consists of POT- H_2SO_4, whereas the aqueous phase consists of the reaction by-products such as unreacted H_2SO_4 and APS. Very pure POT- H_2SO_4 in powder form can be separated and washed several times with acetone to remove the impurities. After the separation of POT- H_2SO_4, the optical properties and particle size analysis of POT were found using Tetrahydrofuran (THF) as an organic solvent. The improved physicochemical and optical properties and particle size distribution at the nano-range can lead to many exciting potential applications.

2. EXPERIMENTAL DETAILS

2.1 Materials and Methods

O-toluidine (monomer, AR grade), sulphuric acid (H_2SO_4), ammonium peroxo disulfate (APS) and Millipore water were used to prepare aqueous solutions.

The Chemical oxidative polymerization of o-toluidine monomer was carried out at room temperature by the addition of 0.1 M of O-toluidine into 100 ml of an aqueous solution, which contain different molar concentrations of H_2SO_4 with continuous stirring for 45 minutes. 0.1 M of APS, which acts as an initiator, was dissolved in 25 ml of water and added dropwise into the polymerization bath. The polymerization solution was left for 5 h with continuous stirring. The supernatant was filtered and washed several times with millipore water followed by acetone to remove the excess of H_2SO_4 and APS. Then the sample was dried at 80 °C in an oven.

3. MATERIAL CHARACTERISATION

The X-ray diffraction studies of POT were performed on XPERT Diffractometer with Cu Kα X-ray (λ=1.54 A°). The morphology of POT was observed by Scanning Electron Microscopy (SEM). Zeta Sizer (Horiba, Japan) instrument was employed to find the size distribution of POT particles by dispersing the polymer in THF solvent with water. Optical properties of POT were characterized by UV-Visible spectrometer (DRS - Analytekjena, Germany). IR spectra were obtained by using ATR-FTIR, Germany.

4. RESULTS AND DISCUSSION

4.1 X-ray diffraction Analysis

Fig. 1 shows the XRD spectrum of POT. Both crystalline and amorphous regions exist in the POT spectrum in the range of 15-30°. XRD spectrum of the polymer depends on the dopants and method used in synthesis. Many of the literature reported that conducting polymers are amorphous in nature. It comes to crystalline nature when it is doped with strong protonic acids; in this work, sulphuric acid, a strong inorganic mineral acid, has been used as protonic acid. It is very difficult to fix the conducting polymer in crystalline nature. Based on acid doping, the state of the polymer was found to be partially crystalline in the range of 22° due to the presence of a rigid chain and ordered structure. Small peaks at 38°, 44°, 64° and 77° were also observed.

4.2 Morphological Analysis

The surface morphology of immaculate POT was studied by SEM analysis. Fig. 2 shows the uniform flaky-like feature with a few globular structures, revealing crystalline as well as amorphous regions. The crystalline region contained sharp-edged particles and lamellar side were found to be interposed in the amorphous regions with particles of no well-defined shapes. This morphological result has well-matched with SEM results of highly crystalline and soluble DBSA-doped Poly ortho toluidine (Sh M. Ebrahim *et al.* 2010).

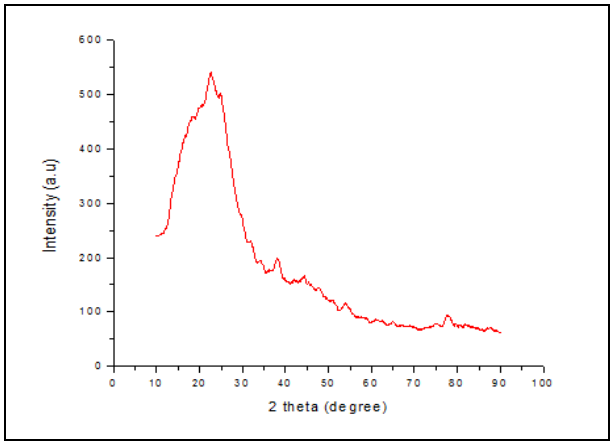

Fig. 1: XRD plot of POT – H_2SO_4

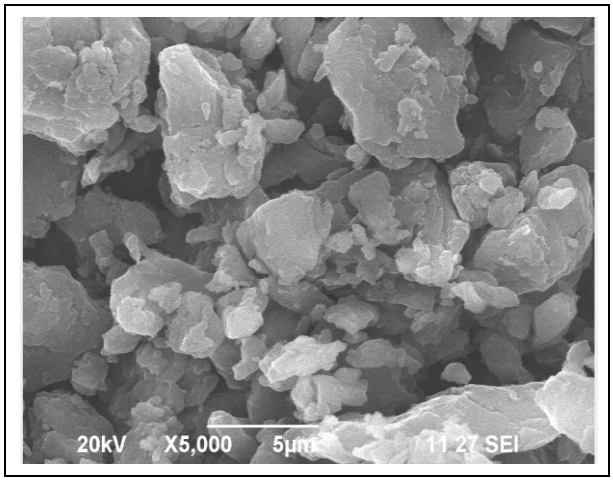

Fig. 2: SEM image of POT– H_2SO_4

4.3 Particle Size Analysis

During polymerization reaction, a particle growth of polymer will happen. Initially, the solution containing monomer is a clear liquid in which the size of the particles must be zero. But when the monomer is converted into the polymer during the polymerization reaction, a propagation process takes place; the growth of particles depends on reaction time. If the reaction time is increased long, a polymer molecule chain will be formed. The dynamic light scattering mechanism is involved in measuring the size of the particles. Fig. 3 shows that POT was having particles of size 42.3 nm, which is less than 100 nm, due to the fact that proton molecule only react

with a reactive molecule of POT without any molecular formation.

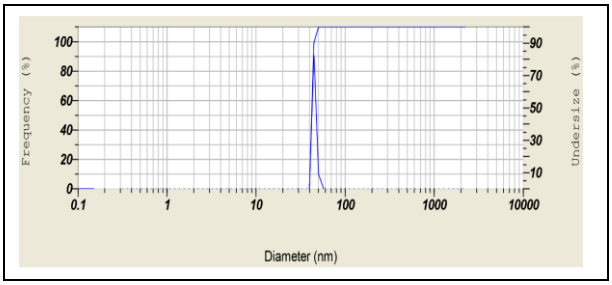

Fig. 3: Particle size analysis by Zeta Sizer

4.4 UV-Vis. Analysis

The UV-Vis. spectra of H_2SO_4-doped POT is shown in Fig. 4. The hypsochromic shift was observed at the peak of 326 nm, which corresponded to π-π^*electronic transition of benzenoid rings, representing the degree of conjugation between the adjacent benzenoid rings in the chain of polymer ((Salma Bilal *et al.* 2014). Instead of a redshift in the absorption spectra of POT, a blue shift occurred due to the steric effect of the methyl group, which reduced the degree of conjugation length in POT (Meixiang Wan and Jiping Yana, 1995). The absorption band located at 607 nm denoted the n- π^* transition of the quinoid unit (Kakarla Raghava Reddy *et al.* 2008). The peaks at 759 and 855 nm were stronger and can be assigned to the emeraldine salt state of conducting polymer POT (Salma Bilal *et al.* 2014).

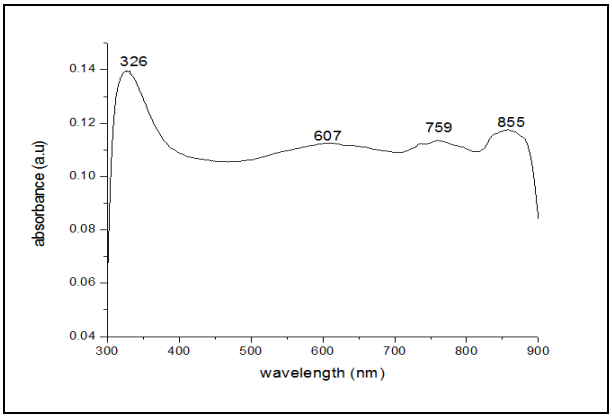

Fig. 4: UV-Vis. spectra of POT– H_2SO_4

4.5 FT-IR Analysis

Fig. 5 shows the FT-IR characteristic peaks of pure POT. The peaks at 1585 cm^{-1} and 1489 cm^{-1} have been assigned to C=C stretching of the quinoid and benzenoid rings. The peak at 1378 cm^{-1} can be attributed to the symmetric deformation of a methyl group at the ortho position. The peaks at 1206 cm^{-1} and 1152 cm^{-1} corresponded to C-C or C-N stretching and in-plane C-H bending modes. The band at 1099 cm^{-1} indicated the charge de-localization on the polymer backbone. The band at 1000 cm^{-1} and 934 cm^{-1} were assigned to C-H in-plane bending vibration of quinoid rings. The band located at 796 cm^{-1} represented the out-of-plane bending vibration of C-H. These observed peaks have well-matched with the literature reported earlier (Kakarla Raghava Reddy *et al.* 2008).

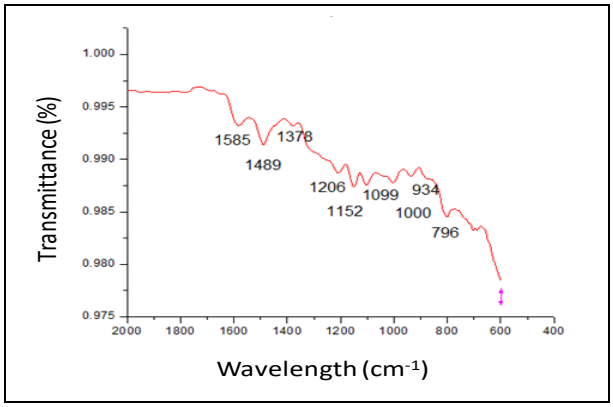

Fig. 5: FT-IR of POT– H_2SO_4

5. CONCLUSION

A Zeta Sizer was used to measure the particle size distribution of POT. The protonated POT salts were synthesized by Chemical oxidative polymerization. SEM micrograph has revealed that all the particles of POT were flakes with few globular structures. The properties such as surface area, reactivity, dissolution, and stability in suspension may be enhanced due to the nano-size of particles of POT suitable for a variety of potential applications such as catalysts, paints and environment-friendly products.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

REFERENCES

Babu, K. F, Senthil Kumar, R., Noel, M. and Kulandhainathan, M. A., Polypyrrole microstructure deposited by chemical and electrochemical methods on cotton fabrics, *Synth. Met*., 159(13), 1353-1358(2009). https://doi.org/10.1016/j.synthmet.2009.03.005

Duong Nguyen Nguyen and Hyeonseok Yoon, Recent Advances in Nanostructured Conducting polymers: from synthesis to practical applications, *Polymers*, 8(4), 118, (2016). https://doi.org/10.3390/polym8040118

Gorey, B., Smyth, .M. R., White, B. and Morrin, A., Fabrication of homogenous three-dimensionally ordered conducting polymer-polystyrene opal structure in microfluidic channels, *J. Mater. Chem.* C, 2, 6004-6009(2014). https://doi.org/10.1039/C4TC00402G

Kakarla Raghava Reddy, Kwang-Pill Lee, Youngil Lee, Anantha Iyengar Gopalan, Facile synthesis of conducting polymer-metal hybrid nanocomposite by in situ chemical oxidative polymerization with negatively charged metal nanoparticles, *Mater. Lett*., 62(12-13), 1815-1818(2008). https://doi.org/10.1016/j.matlet.2007.10.025

Meixiang wan and Jiping Yana, Studies on the structural and electrical properties of poly (o-toluidine). *Synth. Met*., 73(3), 201-204(1995). https://doi.org/10.1016/0379-6779(95)80016-6

Salma Bilal, Shehna Farooq, Anwar –ul-Haq Ali Shah and Rudolf Holze, Improved solubility, conductivity, thermal stability and corrosion protection properties of poly (o-toluidine) synthesized via chemical polymerization, *Synth. Met*., 197, 144-153(2014). https://doi.org/10.1016/j.synthmet.2014.09.003

Sezer, E., Ustamehmetoglu, B. and Sezai Sarac, A., Chemical and electrochemical polymerization of pyrrole in the presence of N-substituted carbazoles. *Synth. Met*., 107, 7-17(1999). https://doi.org/10.1016/S0379-6779(99)00114-9

Sh. M. Ebrahim, Gad, A. and Morsy, A., Highly crystalline and soluble dodecylbenzene sulfonic acid doped poly (o-toluidine), *Synth. Met*., 160(23-24), 2658-2663(2010). https://doi.org/10.1016/j.synthmet.2010.20.021