



Picric Acid Doped Trimer of *o*-Phenylenediamine

P. Chitra, P. Kavitha A. Muthusamy*, S. Dineshkumar

Department of Chemistry, Sri Ramakrishna Mission Vidyalyaya College of Arts and Science, Coimbatore, TN, India.

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Abstract

Trimer of *o*-phenylenediamine was synthesized by in-situ polymerization method Ammonium persulphate as an oxidant. Ammonium persulphate in water was added drop wise into the solution over a period of 30 minutes with constant stirring. After complete addition of the oxidant, the reaction mixture was left stirring for about 6h at room temperature. The reddish brown coloured trimer formed was filtered and washed with deionized water and 2 M HCl solution until the washing liquid was colourless. Then the precipitate was dried at 60 °C overnight under vacuum oven to obtain the final product. It is further characterized by UV-Visible, FT-IR, ¹H NMR and ¹³C NMR spectral data conformed the structure of *o*-phenylenediamine and dopant present in the trimer of *o*-phenylenediamine.

Keywords: Ammonium persulphate; ¹H NMR and ¹³C NMR; Picric acid; Trimer.

1. INTRODUCTION

Polymers exhibiting a wide range of electrical properties from insulator or semi-conductor to metal. Phenylenediamines are a class of aniline derivatives having an extra "NH₂ group in the *o*-, *m*- or *p*-position. Although reports are available on polymerization of *m*- and *p*-isomers (Cataldo *et al.* 1996), *o*-phenylenediamine is the most frequently studied member. Poly (*o*-phenylenediamine) has apparently shown different characteristics of molecular structure and properties when compared to PANI (Li *et al.* 2002). It has a variety of suggested or already realized applications in the fields of electrochromism, sensors and biosensors (Deng *et al.* 1994), fuel cells, rechargeable batteries and corrosion Protection. Mostly Poly(*o*-phenylenediamine) has been reported to be a highly aromatic polymer containing 2, 3-diaminophenazine or quinoxaline repeat units and

exhibits unusually high thermo stability. A PANI like structure has also been proposed.

2. EXPERIMENTAL METHODS

2.1 Materials

o-Phenylenediamine (Hi-media), ammonium persulphate (sd fine), succinic acid (Hi-pure), tartaric acid (sd fine), 1, 5 cyclohexane dicarboxylic acid (Aldrich), acetone and methanol (AR grade) were used as received without further purification.

2.2 Chemical synthesis of trimer of *o*-phenylenediamine (OPDT)

Trimer of *o*-phenylenediamine was synthesized according to a procedure reported in literature (Sestrem *et al.* 2010) after some modifications. In a typical procedure, 5.298 g of *o*-phenylenediamine was dissolved in 70 ml of 2 M HCl under magnetic

*A. Muthusamy Tel: +919442002244
E-mail: amsamsrmv@gmail.com

stirring. After total dissolution, equal moles of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (oxidant) in water was added drop wise into the solution over a period of 30 minutes with constant stirring. After complete addition of the oxidant, the reaction mixture was left stirring for about 6 h at room temperature. The reddish brown coloured trimer formed was filtered and washed with deionized water and 2 M HCl solution until the washing liquid was colourless. Then the precipitate was dried at 60 °C overnight under vacuum oven to obtain the final product.

2.3 Chemical synthesis of picric acid doped trimer of *o*-phenylenediamine (PA-OPDT)

5.298g (0.049 moles) of *o*-phenylenediamine was dissolved in 70ml of 2M HCl containing 0.998 g of picric acid under magnetic stirring. After total dissolution, 9.787 g (0.0429 moles) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (oxidant) in water was added drop wise into the solution over a period of 30 minutes with constant stirring. After complete addition of the oxidant, the reaction mixture was left stirring for about 6 h at room temperature. The reddish brown coloured trimer formed was filtered and washed with deionized water and 2 M HCl solution until the washing liquid was colourless. Then the precipitate was dried at 60 °C overnight under vacuum oven to obtain the final product.

3. RESULTS & DISCUSSION

3.1 Characterization of trimers of *o*-phenylenediamine

3.1.1 UV-visible spectral analysis

UV-visible spectrum of trimer of *o*-phenylenediamine (OPDT) was recorded in SYSTRONICS Double Beam UV-visible spectrophotometer. Ethanol was used as a solvent. The spectrum shows two absorption band, one band in UV-region and other one band in visible region. The UV region absorption 262 nm is due to excitation of $(\pi \rightarrow \pi^*)\pi$ -electrons present in the aromatic ring system of the

trimer. The peak at 442 nm is due to $\pi \rightarrow \pi^*$ transition of the quinoid structure in trimer. The UV- visible spectrum of OPDT is shown in Fig.1a (Shenashen *et al.* 2011).

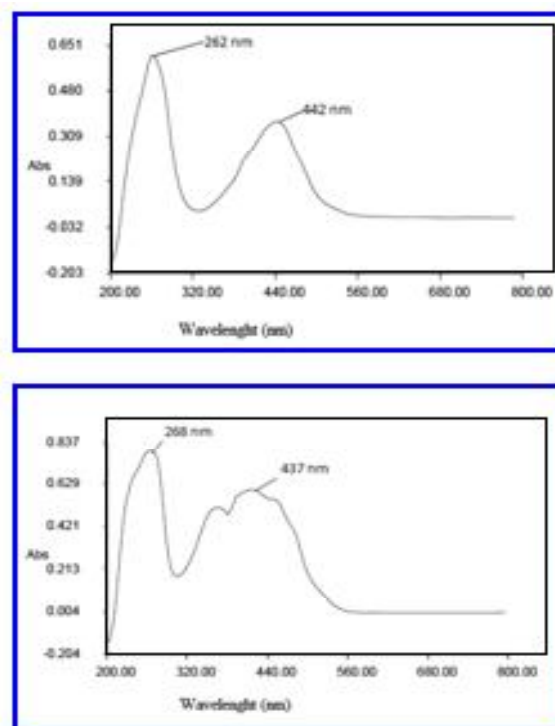


Fig. 1: UV-visible spectrum of OPDT and PA-OPDT

3.1.2 FT-IR spectral analysis

FT-IR spectroscopy is a vast tool to analysis the structure and end groups of the polymers and oligomers with great accuracy. The spectral data of various groups in trimers are shown in the figures.

An FT-IR spectrum of OPDT is shown in Fig 2a. A broad band at 3308 cm^{-1} due to the characteristic of N-H asymmetric stretching vibration and shoulder band at 3146 cm^{-1} corresponds to N-H symmetric stretching vibration. The band appears at 2910 and 2850 cm^{-1} might be due to C-H asymmetric

and symmetric stretching vibration on aromatic ring. The two peaks center at 1535 cm^{-1} and 1483 cm^{-1} are ascribed to the C=C stretching vibration in quinoid and benzoid rings, while the peaks at 1366 cm^{-1} and 1249 cm^{-1} are assigned to C-N stretching vibrations of quinoid and benzoid imine groups (Li, et al. 2001). The characteristic peak at 853 and 584 cm^{-1} are attributed to the C-H out of plane deformation. The peak at 607 cm^{-1} indicates C-C bending vibration and 755 cm^{-1} corresponds to 1, 2 substituted benzene ring (Li, et al. 2003).

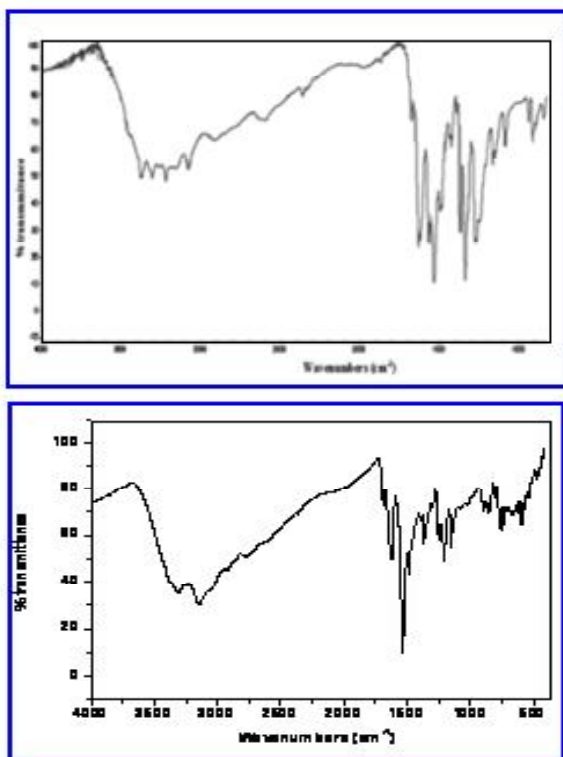


Fig. 2: FT-IR spectra of OPDT and PA-OPDT

The characteristic peaks of PA-OPDT located at 1633 , 1272 and 788 cm^{-1} indicates that PA has doped into OPDT. The peak at 1633 cm^{-1} corresponds to NO_2 stretching vibration. The peak at 1272 cm^{-1} attributed to C-O stretching vibration and the peak

assigned to NO_2 and N-H out of plane bending vibration. Most of the other characteristic peaks are similar absorption to the OPDT (Ahmed et al. 2000).

3.2 Nuclear Magnetic Resonance Spectroscopy

3.2.1 ^1H NMR of OPDT and PA-OPDT

The ^1H NMR spectrum of OPDT is shown in Fig.3a. The singlet peak appears at 7.04 ppm is assigned to H_1 and H_4 Protons. The NH Proton signal is found at 7.31 ppm . The multiplet peak appears from 7.72 to 7.75 ppm due to H_{14} and H_{15} Protons. The triplet signal occurs from 7.85 to 7.89 ppm is assigned to H_{11} proton. The multiplet peak appears from 8.03 to 8.13 ppm is due to $\text{H}_5, \text{H}_6, \text{H}_7$ and H_8 protons.

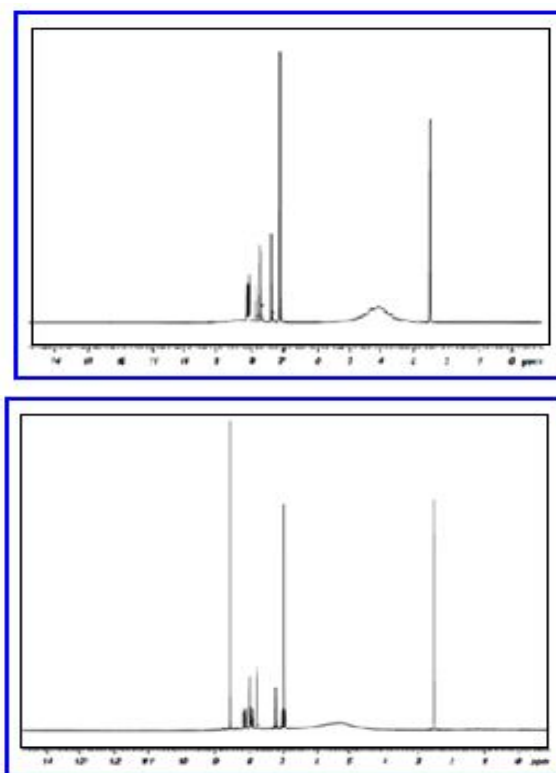


Fig. 3: ^1H NMR spectrum of OPDT and PA-OPDT

3.2.2 ^{13}C NMR spectrum of OPDT and PA-OPDT

The ^{13}C NMR spectrum of OPDT and PA-OPDT is shown in Fig.4a & Fig.4b. The important information of ^{13}C NMR spectrum of the trimer is the high number of peaks indicating that an open trimer with low symmetry was obtained. The assignment of peaks for OPDT is 91.85, 97.14, 106.66, 118.75, 123.27, 127.75, 128.60, 129.12, 132.12, 134.45, 137.57, 139.36, 145.28, 149.38 and 153.73 ppm. And the peaks for PA-OPDT are 91.82, 97.31, 106.77, 113.11, 118.69, 120.87, 123.50, 124.78, 125.66, 127.81, 129.31, 132.36, 142.25, 145.39, 149.14, 153.81 and 161.167 ppm. By comparing PA-OPDT with OPDT the number of peaks gets increased. This indicates that PA has doped OPDT (Sestrem *et al.* 2009).

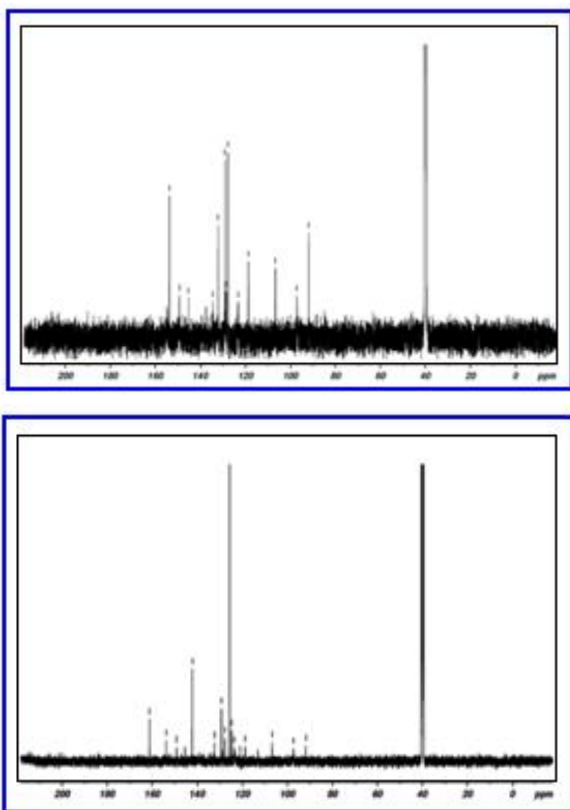


Fig.4. ^{13}C NMR spectrum of OPDT and PA-OPDT

4. CONCLUSION

Different acids doped trimers were prepared by chemical oxidation method by using ammonium persulphate as oxidizing agent. The synthesized samples were characterized by FT-IR, UV-vis and NMR spectroscopic techniques. The presence of the various characteristic absorptions in the trimers and doped trimers were assigned through FT-IR spectral analysis. The variation of bathochromic shift in doped trimers indicates that the dopant present in the trimers. The different kinds of protons and carbons present in the trimers and doped trimers were confirmed by NMR spectroscopic techniques.

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