

# Synthesis and characterization of triphenylpyridine containing azo-linked polymer materials

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## Abstract

A 2, 4, 6-Tris (4-nitrophenyl) pyridine (TNPP) was synthesized from nitrobenzaldehyde and nitroacetophenone in glacial acetic acid and conformed. The TNPP monomer further reacted with diamines such as benzidine (TNPP-B) and phenylenediamine (TNPP-P) to obtain azo linked polymers for photochemical activity. These polymer structures were identified using different characterization techniques like FTIR, UV-visible spectroscopy, scanning electron microscope (SEM), fluorescence spectroscopy, cyclic voltammetry, DSC and TGA. The FTIR spectra of all the azo-linked functional group of polymers were observed at  $1592\text{ cm}^{-1}$  and  $1596\text{ cm}^{-1}$ . The TNPP-B based TNPP polymer exhibit high thermal decomposition temperature (Td) at  $403\text{ }^{\circ}\text{C}$ . UV/vis absorption spectra for TNPP-B and TNPP-P were absorbed in the region 300-375, 285-385 and 350-400 nm. These polymer materials could be used for optical and energy applications. Copyright © 2016 VBRI Press.

**Keywords:** Azo-linked, polymeric material, thermal stability, photochemical activity, energy.

## Introduction

In recent year some azo linked polymers were synthesized with hyper branched structure having high thermal stability, mass transport, photochemical and optical activity. The polymers containing azo-linked pyridine ring play a key role in biological activity [1]. Azobenzene based polymer show a wide range of applications such as dyes, optical switching [2], nonlinear optical devices and surface relief gratings and so on [3]. These polymer materials exhibit significant macroscopic mass transport under the mechanical effects and homogeneous irradiation and of photoisomerization cycling, thin films possess the well-known ability for variety of all optical material applications [4]. In a supramolecular assembly of cross linked (azo) based polymer showed a reversible isomerization on irradiation of UV light followed by a number of cycles and it has good cycling stability; azo polymer matrix leads to a macroscopic deformation by a controlling of polymer segments. These types of hyper branched polymers are partially soluble in organic solvents. Yong et al. have demonstrated the azo polymer material make adequate potential applications in capable of moving at a slow photoresponsive [5]. Azo linked materials have been considered as great potential for optical

data storage, electro-optical (EO) modulators because of the unique able to be turned the another way of cycle on photoisomerization between two isomers [6-7]. In the article, we report on the azo-bridged polymer prepared with terminal amino groups, through the direct coupling of aromatic nitro compounds and aromatic amines. In this type of polymer may be used as ligand. Herein, the new azo-containing polymers were synthesized from different monomer, which polymer were prepared through the co-polymerization process and obtain a solid like materials. These azo-linked polymers confirmed and identified it has poor solubility it could be used to electric device and energy storage application.

## Experimental

### Materials

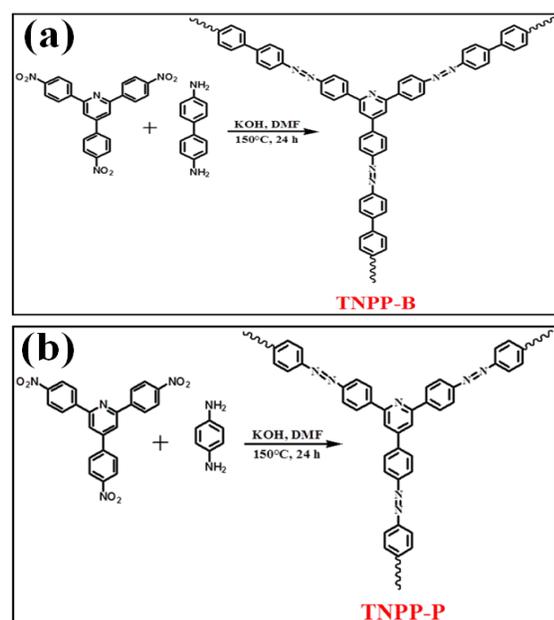
All the materials as 4-nitrobenzaldehyde, 4-nitroacetophenone, ammonium acetate, glacial acetic acid, benzidine, p-phenylenediamine. These materials are supplied by Sigma-Aldrich (USA) and used without purification. The solvents were used as HPLC grade for all the reactions.

### Preparation of 2,4,6-Tris(4-nitrophenyl) pyridine (TNPP)

TNPP was prepared by a mixture of 4-nitrobenzaldehyde (0.06mol), 4nitroacetophenone (0.06 mol), ammonium acetate (60 g) and glacial acetic acid (150 ml) was refluxed in round bottomed flask for 4 h. Upon cooling, the precipitated solid was filtered, washed with acetic acid and cold ethanol [6-7]. The crude product was recrystallized from DMF and then dried at 75 °C under vacuum and used for various analyses [8-9].

### Synthesis of azo-linked polymer

2,4,6-Tris(4-nitrophenyl) pyridine (0.02 mole) monomer and three equivalent of benzidine (0.03 mole) were dissolved in DMF (100 ml) in a three-neck RB flask equipped with condenser, thermocouple and a magnetic stirrer, while the reaction was started after that 10 mole percentage of (5.61g) KOH was added in the reaction solution. The temperature of the reaction mixture was slowly increased up to 150 °C with constant vigorous stirring under nitrogen atmosphere condition and continued for 24 h. The colour of the solution was changed and followed by the formation of orange precipitate TNPP-B 63% obtains with NO<sub>2</sub> termination. The reaction mixtures were cooled at room temperature then added 100 ml of distilled water and continue by stirred for 1 h. The precipitate was filtered off and washed with warmed distil water (4 times), acetone (3 times) and THF (2 times). The orange color precipitate was dried at 100 °C under vacuum for 3 h. Same procedure was followed to the synthesis of polymer TNPP-P (yield 60%). Finally, all the azo-linked polymers TNPP-B and TNPP-P were successfully synthesized and confirmed.



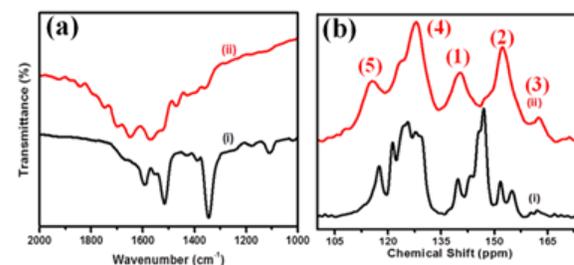
**Scheme 1.** Synthesis of azo-linked polymer (a) TNPP-B and (b) TNPP-P.

### Characterization

The azo-linked polymers were characterized by Fourier transform infrared spectroscopy (FTIR), ZASCOFTIR-4200, Canada. The spectra were collected from the range of 500 to 4000 cm<sup>-1</sup> with a resolution of 3cm<sup>-1</sup> by scans. The thermal studies of thermogravimetric analysis of (TGA), polymers were characterized by TA analysis Model Q50, TA instruments, Waters Private Limited, Bangalore, India, special capacity of heating rate at 10 °C per min from 25 °C to 600 °C under nitrogen atmosphere. The morphology analysis determined by using scanning electron microscope (SEM), model phenom pro SKV image. Absorption studies carrying by using varian Cary 50 Bio UV-Visible spectroscopy, emission properties studies using photoluminescence (PL) varian Cary eclipse fluorescence spectroscopy. Cyclic voltammetry band gap calculated from CH instruments CH1600D, with platinum working electrode. Differential scanning calorimetric (DSC) analysis were done by using NETZSCH-PROTEUS-TO-LNK, heating rate at 5 °C per min under nitrogen atmosphere from -70 °C to 600 °C.

### Results and discussion

The TNPP-B and TNPP-P polymers were successfully synthesized and characterised. The **Fig. 1(a)** shows the azo-linked polymers of TNPP-B and TNPP-P were analysed using FT-IR spectroscopy, the azo polymer (C=C stretching, aromatic) band observed at 1590-1560 cm<sup>-1</sup>, (N=N stretching) band observed between at 1530-1510 cm<sup>-1</sup> [10,11] because the N=N stretching vibration is overlapped with C=C stretching vibration of benzene ring, (-NO<sub>2</sub>) band at 1340 cm<sup>-1</sup>. From the **Fig. 1(b)** show the solid state <sup>13</sup>C NMR spectra and assignment of each chemical shift  $\delta$  = 115.05 (5), 128.32 (4), 140.49 (1), 151.84 (2), 162.54 (3) ppm.



**Fig. 1.** (a) FT-IR spectra of (i) TNPP-B and (ii) TNPP-P (b) Solid state <sup>13</sup>C NMR spectra of (i) TNPP-B and (ii) TNPP-P.

The solid state <sup>13</sup>C NMR chemical shift value indicates the position of the azo-linked polymeric materials. All the azo substituent occupying a specified position in a polymer material and were located in the same position but different backbone conceptual structure [12].

From **Fig. 2(a)** & **2(b)**, the different monomer accompanied with TNPP to get the various azo-linked polymer materials terminate with nitro group;

the spectral study of copolymers exhibit interesting features on the absorption and fluorescence spectra of TNPP-B and TNPP-P. The characteristic absorption band in the range of 300 to 500 nm, this range indicates that azo groups contain in the polymers. Further these polymer exhibit one strong band located in the spectra and another one broad band located due to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  electron transitions of the (-N=N-) band [13-14], belongs to the  $\pi$ -conjugation in the material, respectively. The azo containing polymers TNPP-B and TNPP-P has absorption band located at 310 and 320 nm, with the broad shoulder at 365 and 370 nm.

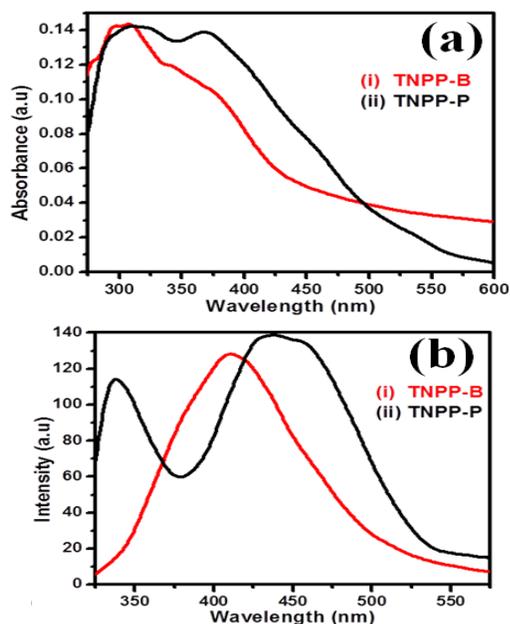


Fig. 2. (a) Absorption spectra of (i) TNPP-B and (ii) TNPP-P (b) Fluorescence spectra of (i) TNPP-B and (ii) TNPP-P.

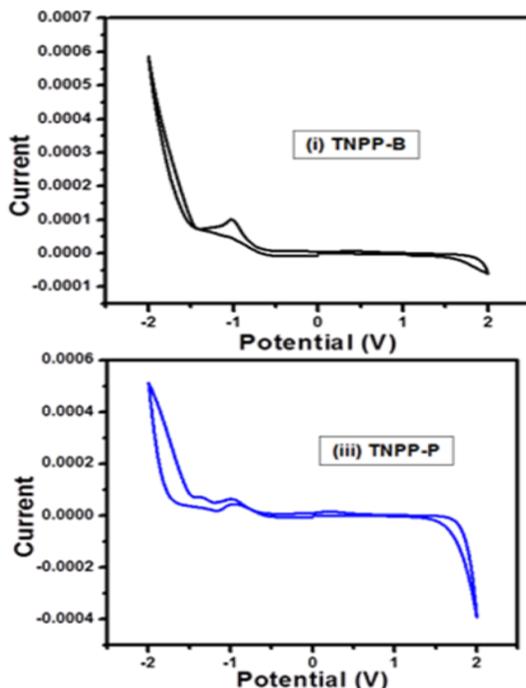


Fig. 3. Cyclic voltammetry for (i) TNPP-B and (iii) TNPP-P.

The exact absorption location of the TNPP based polymer depends on the type of azo chromophore. The fluorescence spectra of the azo polymers TNPP-B and TNPP-P intensity band located at 410 and 340 nm [15]. The emission spectra were recorded in chloroform, its emission spectra shift value in a smaller extent. The cyclic voltammetry investigation of some compounds could be used for photovoltaic applications.

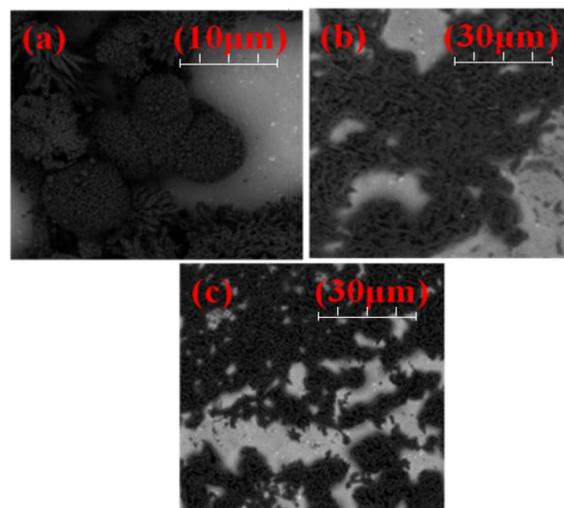


Fig. 4. SEM morphology analysis of (a) TNPP (b) TNPP-B and (c) TNPP-P.

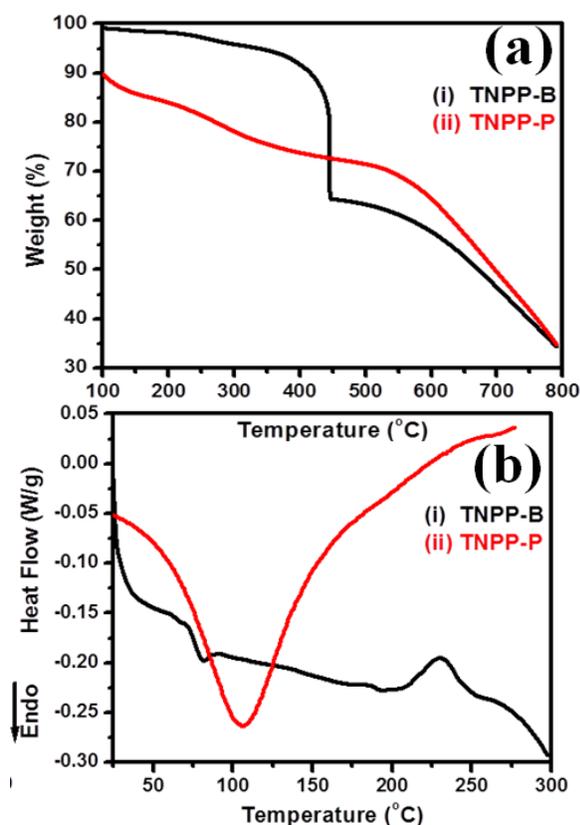
The scanning electron microscope was used to analyse the morphology of the polymeric materials. The TNPP monomer material without addition of diamine the morphology shows like a three dimensional microcapsule structure see Fig. 4 (a), the polymer materials TNPP-B and TNPP-P morphology being three dimensional polymerized structures shown in the Fig. 4 (b) & (c). However, the azo-linked polymers morphology could be identified like a fibre structure. Oxidation and reduction of all azo-linked materials were measured under the same experimental condition to approximately calculate both the energy of the HOMO (highest occupied molecular orbital) and the energy of LUMO (lowest unoccupied molecular orbital). HOMO level of azo polymers TNPP-B and TNPP-P were 1.07 eV and 1.53 eV LUMO level of 0.78 eV and 0.68 eV [16-18].

Table 1. Thermal transition temperature of azo-linked polymers.

Sample code	TGA( $T_d$ °C)		DSC	
	I	II	( $T_g$ )°C	$\Delta C_p^*$ (J/(g*K))
TNPP-B	387	447	81	1.457
TNPP-P	321	535	110	2.464

The Cyclic Voltammetry was performed to determine the band gap of the azo containing conjugated polymers were 1.8 eV and 2.2 eV. The CV data is shown in the Fig. 3. TNPP-P azo polymer

materials has high band gap compare with others materials, this could be used to semiconducting materials in photovoltaic applications [19]. Thermal stability of the azo-linked polymer was studied with TGA (Thermo Gravimetric Analysis) and DSC (Differential Scanning Calorimetry) [20], **Table 1.** shows the thermal degradation temperature ( $T_d$ ) of azo containing polymer having two stage decomposition transition temperature, the first degradation temperature corresponding to the loss of water and the second decomposition temperature was observed for the amine unit from the azo polymeric materials [12-15]. In all the azo materials were thermally stable the maximum weight loss of all the materials occurred at around 450 °C, TNPP-P material has high glass transition temperature compare with other polymeric materials, T-B has softening temperature, using the heat capacity ( $\Delta C_p^*$ ) to determine the enthalpy of all the azo materials **Fig 5 (a) & (b).**



**Fig. 5.** (a) Thermal analysis of TGA (i) TNPP-B and (ii) TNPP-P (b) DSC of azo-linked polymer (i) TNPP-B and (ii) TNPP-P.

## Conclusion

In conclusions the azo-linked polymers were prepared by one pot synthesized co-polymerization reaction. These polymers were prepared from 2,4,6-Tris(4-nitrophenyl)pyridine (TNPP) with different diamine monomers. Azo-containing polymers TNPP-B and TNPP-P were verified and confirmed by

various analysis, FT-IR, Solid state  $^{13}\text{C}$  NMR, scanning electron microscope, Cyclic voltammetry, UV-visible absorption, emission spectroscopy and thermal analysis. The high performance of azo-containing polymers can potentially may be used for applications such as optical, photosensitization of electric device and energy applications.

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