

# Photophysical and Electrochemical Investigations on Photoconducting Poly(6-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine)

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**Summary:** Poly(6-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine) was synthesized by thermally activated cationic ring opening polymerization. The structure of the polymer was confirmed by spectral and thermal studies. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were estimated using cyclic voltammetry and optical absorption. Modulated photocurrent measurement technique was employed to study the spectral and field dependence of photocurrent. Photocurrent of the order of 1.5  $\mu\text{A}/\text{m}^2$  was obtained for polymer at a biasing electric field of 40 V/ $\mu\text{m}$ .

**Keywords:** conducting polymers; fluorescence; FT-IR; glass transition; UV-vis spectroscopy

## Introduction

Semiconducting polymers have attracted considerable attention as promising materials for electronic and optoelectronic applications.<sup>[1,2]</sup> The high flexibility, thermal stability, low cost and low density makes them suitable for fabrication of optoelectronic devices.<sup>[3–5]</sup> Various designing methods have been employed to achieve efficient semiconducting properties in polymers.<sup>[6,7]</sup> The charge transport and the semiconducting properties of these materials depend mainly on the structure and morphology of the polymer chains. In this article, we discuss the synthesis, characterization and electrochemical studies done on photoconducting polymer, poly(6-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine) along with the results of photoconductivity measurements. Benzoxazines are a class of heterocyclic compounds obtained by Man-

nich condensation of a phenol, formaldehyde and an amine.<sup>[8–11]</sup> The polymerization of benzoxazine monomers occurs through heterocyclic ring opening reaction at elevated temperatures.<sup>[12]</sup> The Mannich base bridge characterizes the structure of the polymer,<sup>[13]</sup> with the reaction taking place preferentially at the ortho position of free phenolic group.<sup>[14]</sup>

We have synthesized poly(6-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine), (P1), via thermally activated cationic ring opening polymerization. The thermally activated polymerization of benzoxazines with and without initiators or catalyst, in the presence and absence of solvent has been studied in detail.<sup>[12]</sup> The structure of P1 was confirmed by spectral and thermal analysis. The electrochemical and photophysical behavior of P1 was also discussed. The spectral and electric field dependence of photocurrent was studied using the lock-in technique described elsewhere.<sup>[15]</sup>

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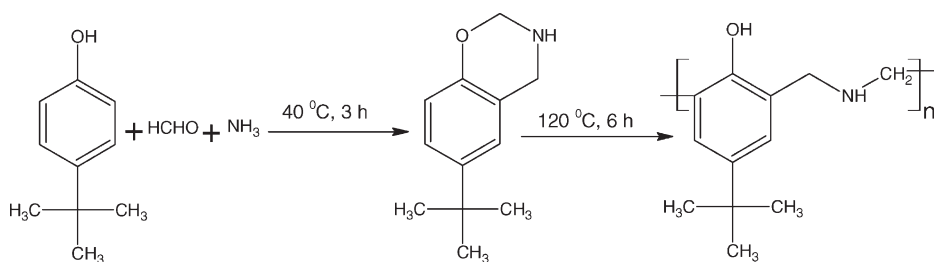
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## Experimental Part

### Materials

Toluene (Rankem, AR Grade) was dried over sodium and distilled before use. The



**Figure 1.**

Synthesis route of poly(6-tert-butyl-3,4-dihydro-2H-1,3-benzoxazine), P1.

following chemicals were used as received without further purification: 4-tertiary butyl phenol (97%, Acros Organics), dioctylphthalate (DOP) (98%, Alfa Aesar), formaldehyde solution (97%, Merck) (37–41% w/v), ammonia solution (AR, Merck) (25%), chloroform (99%, Merck, Spectroscopic Grade), toluene (98%, Merck, Spectroscopic Grade) and dimethylformamide (DMF), (98%, Merck, Spectroscopic Grade).

### Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded with Bruker Advance II NMR spectrometer operating at 400 MHz for <sup>1</sup>H and at 100 MHz for <sup>13</sup>C. Fourier transform-infrared (FT-IR) spectra of the samples were taken on a Bruker 550 spectrometer. Absorption spectra of the samples were recorded using a Jasco V-570 UV/VIS/NIR spectrophotometer. A Fluoromax-3 fluorimeter was used to record the fluorescence spectra of the samples. CHN estimations were taken from Elementar Vario EL III CHNSO elemental analyzer. The molecular weight of the synthesized polymers was determined by size exclusion chromatogram (SEC), (Waters 2414) using a column packed with polystyrene gel beads. The polymer was analyzed using toluene as eluent, at a flow rate of 0.5 mL/min at 25 °C. The molecular weight was calibrated using polystyrene standards. The molecular weight was further estimated with Jeol SX 102 mass spectrometer. Glass transition temperature was determined from differential scanning

calorimetre (DSC), (Q-100, TA Instruments) under nitrogen at heating rate of 10 °C/min. Thermal stability was determined from thermo gravimetric analyzer (TGA), (Q-50, TA Instruments) under nitrogen at a heating rate of 20 °C/min. Electrochemical measurements were performed in a three electrode BASi Epsilon electrochemical workstation.

### Polymer Synthesis

Polymerization was carried out as per the procedure described below. The structure is shown in Figure 1. A mixture of 4-tertiary butyl phenol (10.4 g, 69.0 mmol) and formaldehyde solution (11.02 mL, 175 mmol, 38%) were heated to 40 °C. Ammonium solution (5.49 mL, 80.6 mmol, 25%) was added drop wise to the above mixture. The solution was stirred at 120 °C for 6 h and then cooled to room temperature. The bright yellow solid product obtained was dissolved in chloroform (25 mL) and reprecipitated from methanol. The precipitated polymer was isolated by filtration, washed with distilled water and dried at room temperature. The polymer was further purified by soxhlet extraction with methanol. The purified polymer was dried under vacuum at 40 °C for 72 h. Yield: 86.5%. FTIR (KBr)  $\nu$  cm<sup>-1</sup>: 1483 (tetra-substituted benzene), 1121 (C-N-C ay st), 3320 (-NH st). <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>)  $\delta$ : 1.27 (s, 9H), 2.35 (s, 1H), 3.82 (2H), 4.23 (s, 2H), 4.29 (s, 2H), 4.35 (s, 4H), 4.63 (s, 2H), 5.23 (s, 2H), 6.75–7.15 (m, 2H). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>)  $\delta$ : 33.99, 43.53, 46.80, 49.72, 113.15–153.28.

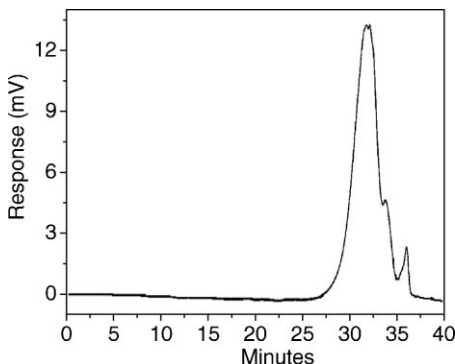
### Sample Preparation for Photoconductivity Measurements

The samples for photocurrent measurements were prepared by drop casting a 7.5 wt% solution of P1 and DOP (1 wt%) in chloroform. The solution was passed through a 0.45  $\mu\text{m}$  nylon filter and deposited on indium tin oxide (ITO) coated glass substrates. Overnight evaporation of the solvent at room temperature and subsequent drying of the films for 12 h in vacuum chamber (at  $10^{-2}$  Torr), resulted in good optical quality films of about 15  $\mu\text{m}$  thickness as measured using a Stylus profiler (Dektak 6M). Silver top contacts of 36–42  $\text{mm}^2$  active area were evaporated on the polymer films. Photoconductivity measurements were done using the modulated photocurrent technique, which has been described in detail previously.

### Results and Discussions

Poly(6-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine), was synthesized and characterization was done using spectral and thermal analysis. The route of polymer synthesis is depicted in Figure 1. The reaction was carried out in a single stage by reacting stoichiometric amounts of tertiary butyl phenol, formaldehyde and ammonia without isolating the benzoxazine monomer. At first, the temperature was maintained at 40  $^{\circ}\text{C}$  and stirring was continued for 3 h. The reaction temperature was then slowly raised and the reaction medium was refluxed for 6 h at 120  $^{\circ}\text{C}$ . The product was obtained as bright yellow solid with good transparency and solubility in organic solvents such as toluene, dimethylformamide, tetrahydrofuran and chloroform.

The molecular weight of P1 was determined using SEC. The chromatogram, shown in Figure 2, exhibited two peaks, a broad peak centred at 31.2 min with a shoulder peak at 33.5 min. The shoulder peak was assigned to closed-ring monomer species and the peak at 31.5 to open ring species. The number average molecular weight ( $M_n$ ) was 403 and the weight average

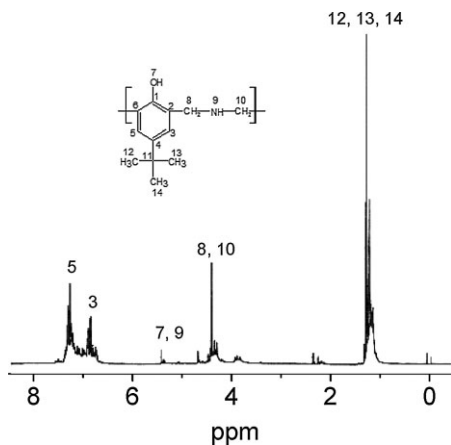


**Figure 2.**  
SEC of P1.

molecular weight ( $M_w$ ) was 1080. The polydispersity index ( $M_w/M_n$ ) was 2.67 indicating a broad distribution of molecular weights.

The  $^1\text{H}$  NMR spectrum of P1 is shown in Figure 3. The peak at 2.27 and 2.35 corresponds to the proton attached to the nitrogen atom in the oligomeric and oxazine ring structures. The resonance peaks at 3.82, 4.23, 4.29, 4.35 and 4.63 were assigned to methylene protons of oligomeric, oxazine ring and open bridge Mannich base compounds.

The resonance at 5.23 ppm was assigned to the protons attached to the nitrogen and hydroxyl groups. The intense resonance signal at 4.30 ppm indicated that both the methylene groups in the repeating unit

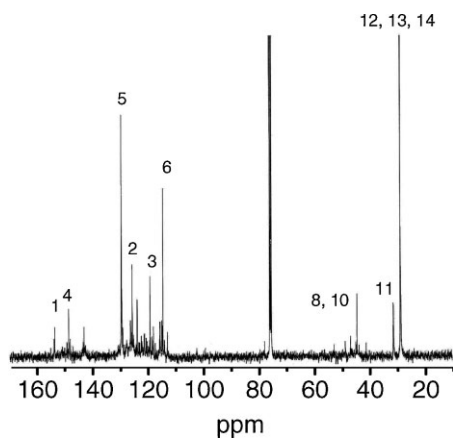


**Figure 3.**  
 $^1\text{H}$  NMR spectrum of P1.

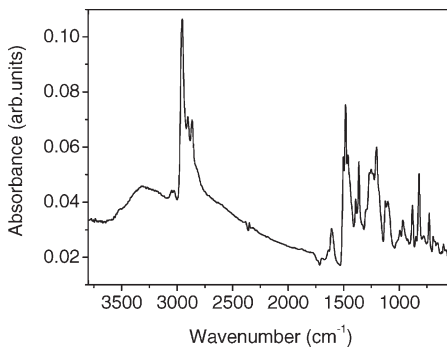
were chemically equivalent. Assignment of protons was done assuming that the two TBP units are connected with methylene-secondary amine-methylene linkage at the ortho-position as shown in the structure in Figure 1. Methyl protons of TBP unit resonate at 1.28 ppm. Aromatic signals of the TBP unit appear from 6.75 to 7.15 ppm.

$^{13}\text{C}$  NMR spectrum of P1 is shown in Figure 4. The resonance at 33.99 ppm is assigned to methyl carbons. The resonance at 46.80 ppm is assigned to methylene carbon of the open Mannich base.<sup>[16]</sup> The resonances between 113.15, 124.28, 125.24, 127.90, 145.15 and 153.28 ppm are assigned to the aromatic carbons. The resonance around 43.53, 46.80 and 49.72 ppm are assigned to methylene carbons of oligomeric and oxazine ring compounds. Thus it appeared that the final product contained trace amount of dimers and closed ring compounds, which could be due to the fact that the reaction was carried out without isolating the monomer.

Figure 5, shows the FT-IR spectra of the purified polymer. Vibrational assignments of similar benzoxazine substituted polymers have been reported earlier.<sup>[16]</sup> The band centred at  $966\text{ cm}^{-1}$  associated with the oxazine ring indicating the presence of oxazine ring compounds. The  $1123\text{ cm}^{-1}$  band is assigned to C–N–C asymmetric stretching vibration.



**Figure 4.**  
 $^{13}\text{C}$  NMR spectrum of P1.

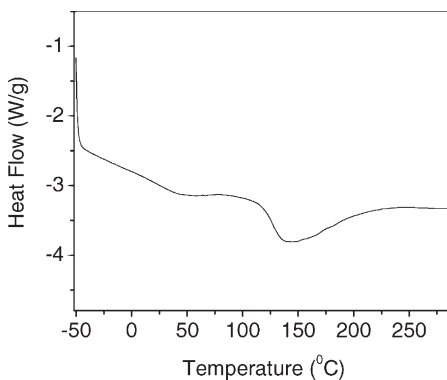


**Figure 5.**  
FT-IR spectrum of P1.

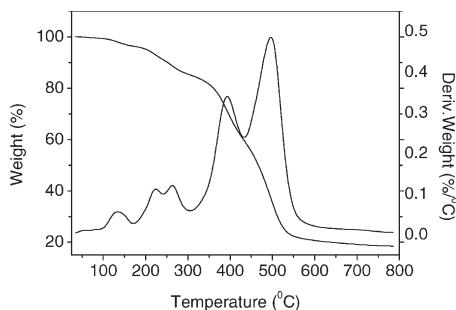
The band at  $1481\text{ cm}^{-1}$  is attributed to tetra substituted benzene ring with methylene-amine-methylene bridge at the ortho position. The band at  $1251\text{ cm}^{-1}$  is assigned to aromatic C–O stretching frequency of phenols. The broad peak centred at  $3324\text{ cm}^{-1}$  is attributed to hydrogen bonded hydroxyl groups.<sup>[17]</sup>

The glass transition temperature ( $T_g$ ) of P1 was  $46.49\text{ }^\circ\text{C}$ . The polymer showed well defined melting point at  $144.66\text{ }^\circ\text{C}$ , shown in Figure 6. The second DSC heating curve was not attempted because of the degradation of P1 in the melt state.

The thermal degradation behavior of P1 was examined by TGA and the derivative thermogram is shown in Figure 7. Four well resolved degradation peaks were found in the derivative thermogram. The first and second degradation process appeared



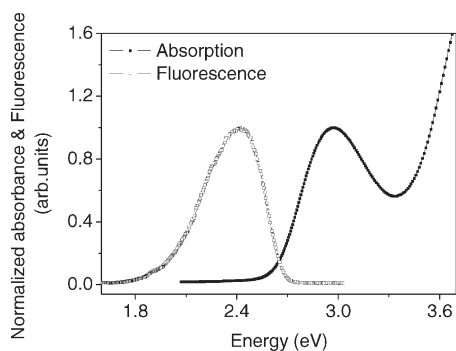
**Figure 6.**  
DSC curve of P1.



**Figure 7.**  
TGA curve of P1.

around 125 and 162 °C and reached its maximum rate of 0.05%/°C and 0.12%/°C at 132 and 220 °C. These peaks could be due to the degradation of Mannich base.<sup>[18]</sup> The third major weight loss process due to the degradation of phenolic linkage appeared at 295 °C with a maximum rate of 0.34%/°C at 389 °C. These degradation peaks were reported to be due to the primary decomposition products obtained from the cleavage of C–C, C–N and C–O linkages present in the polymer.<sup>[13,18]</sup> The fourth weight loss started at 425 °C with maximum rate (0.49%/°C) of degradation at 498 °C was reported to be due to secondary decomposition products which are not present in the polymer structure.<sup>[13]</sup>

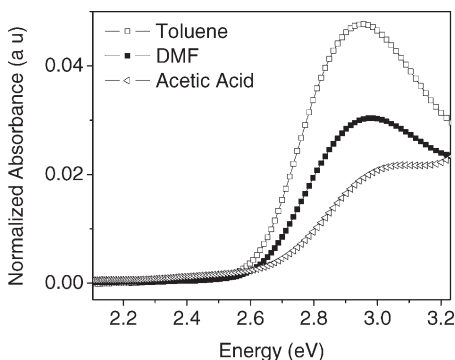
The fluorescence spectrum and optical absorption spectra of P1 are shown in Figure 8. The fluorescence studies were carried out in chloroform solution. The excitation wavelength was selected near the band edge. The emission maximum for



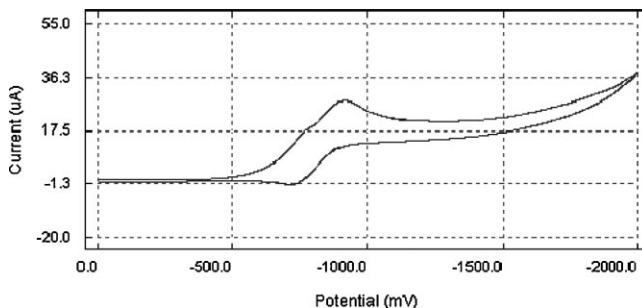
**Figure 8.**  
Optical Absorption and Fluorescence Spectra of P1.

P1 was observed at 2.42 eV with a shoulder peak at 2.25 eV.

A stoke's shift of 97 nm was observed between the absorption and emission maxima. This shift may possibly be due to interchain or intrachain interactions.<sup>[19]</sup> P1 exhibited maximum absorption at 2.96 and 3.80 eV. The band at the low energy region corresponds to  $n-\pi^*$  transition and the band in the high energy region corresponds to  $\pi-\pi^*$  transition. To distinguish  $n-\pi^*$  transition from  $\pi-\pi^*$  transition, Kasha<sup>[20]</sup> and McConnell<sup>[21]</sup> suggested the general solvation hypothesis and the specific hydrogen bonding hypothesis to explain the blue shift phenomenon observed in the absorption spectrum with the nature of solvent. An  $n-\pi^*$  transition involves excitation of  $n$  electrons present in the non-bonding molecular orbital of the hetero atom to the  $\pi^*$  anti-bonding molecular orbital of the conjugated ring. In order to prove the presence of  $n-\pi^*$  in the polymer sample, we followed the specific hydrogen bonding hypothesis proposed by Kasha et al. The specific hydrogen bonding of solvent with solute plays an important role in shift of  $n-\pi^*$  transitions on changing solvent from hydrocarbon to hydroxylic one. The hydroxylic solvents in comparison with hydrocarbon solvents favor hydrogen bond formation with solute molecule containing lone pair of electrons. The lone pair of electrons on the oxygen and nitrogen atom present in P1 is responsible for  $n-\pi^*$ .



**Figure 9.**  
UV-Vis spectrum of P1 showing the blue shift with change of solvent, indicating the transition to be  $n-\pi^*$ .



**Figure 10.**

Cyclic voltammogram of P1.

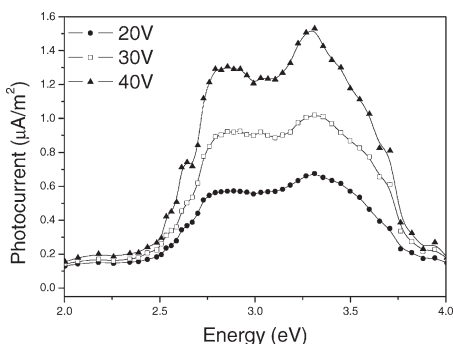
The absorption spectra of P1 were recorded in toluene, acetic acid and dimethylformamide solution. The spectrum of P1 showing  $n-\pi^*$  transition is shown in Figure 9. P1 shows an absorption band with maximum at 2.93 eV, in toluene. On changing the solvent from toluene to acetic acid to dimethylformamide, it was observed that the absorption band of P1 shifted towards higher energy region indicates  $n-\pi^*$  transition.

The electrochemical behavior of P1 was studied using cyclic voltammetry. The cyclic voltammogram of P1 is shown in Figure 10. The measurement was carried out at 25 °C in acetonitrile solution containing 0.1 M tetrabutylammonium chloride as supporting electrolyte with a glassy carbon working electrode. Ag/AgCl was used as the reference electrode. The experiment was calibrated with the standard ferrocene/ferrocenium redox system. The potential

was cycled between 0 to –2 V at a constant sweep rate of 25 mVs<sup>-1</sup>.

P1 showed the onset of reduction at –0.54 eV. The onset potential was used to calculate the LUMO level, according to the equation,  $E_{\text{LUMO}} = [E_{\text{red}} (\text{onset}) + 4.4 \text{ eV}]$ .<sup>[22]</sup> The LUMO energy level of the polymer was estimated as 3.86 eV. The HOMO energy level was estimated as 6.27 eV by adding the optical gap calculated from the absorption edge to the LUMO energy. The values were calculated based on 4.4 eV for ferrocenium redox system with respect to zero vacuum level.<sup>[23]</sup> P1 exhibited a band gap of 2.95 eV much lower than the well known photoconductor, poly(vinylcarbazole) (4.1 eV).<sup>[24]</sup>

Photocurrent action spectra of P1 at an electric field of 20, 30 and 40 V/ $\mu\text{m}$  with ITO biased positive is shown in Figure 10. The maximum photocurrent in the visible region was observed near the band edge.



**Figure 11.**

Photocurrent action spectrum of P1 at 20, 30 and 40 V/ $\mu\text{m}$ .

The photocurrent spectrum showed two peaks, one in the low energy region (2.8 eV) and the other in the higher energy region (3.3 eV). Maximum photocurrents of 0.56 (2.8 eV) and 0.67  $\mu\text{A}/\text{m}^2$  (3.3 eV) were obtained at an electric field of 20 V/ $\mu\text{m}$ . The photocurrent values were highly dependent on the electric field and reversible, which indicated that the increase in conductivity on exposure to light was not due to any photochemical reactions. At an electric field of 40 V/ $\mu\text{m}$ , the maximum photocurrents observed were 1.29  $\mu\text{A}/\text{m}^2$  (2.8 eV) and 1.52  $\mu\text{A}/\text{m}^2$  (3.3 eV).

The photoconductive sensitivity, defined as the change in electrical conductivity per unit incident light intensity,<sup>[25]</sup> of P1 was found to be  $28 \times 10^{-14}$  S.cm/W at 440 nm.

## Conclusions

Poly(6-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine) was synthesized by the Mannich condensation of 4-tertiary butyl phenol, formaldehyde and ammonia. The structure of the polymer was characterized by FT-IR and NMR spectral analysis. The reaction yielded a polymer of relatively low molecular weight exhibiting broad molecular weight distribution. Photocurrent of the order of 1  $\mu\text{A}/\text{m}^2$  was obtained for P1 at a biasing electric field of 40 V/ $\mu\text{m}$ . P1 showed photocurrents in the visible region without any sensitizers, which may be useful when fabricating photorefractive composites using P1. This can further reduce chances of phase separation. Work is in progress to determine the exact mechanism of charge carrier generation in P1.

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