Synthesis, characterization and photovoltaic property evaluation of poly (3-phenyl azomethine alkyl thiophene)s

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Abstract: Poly (3-phenyl ethyl azomethine thiophene) (PPAET) and poly (3-phenyl butyl azomethine thiophene) (PPABT) were synthesized by oxidative coupling method using $FeCl_3$ as oxidant. Study of concomitant optical and electrochemical properties of the polymers revealed that they possess excellent potentiality of being good photovoltaic materials. The electrochemical band gap of PPAET and PPABT were calculated to be 2.19 eV and 2.14 eV respectively. The absorption spectra showed broad absorption over the wavelength range of 350-590 nm with maximum absorption peak at 407 and 415nm (λ_{max}) respectively for PPAET and PPABT. The polymer photovoltaic cells based on blend of polymers and TiO_2 nanoparticles were fabricated and the power conversion efficiency (PCE) of the photovoltaic cells was measured to be 0.102% and 0.125% respectively for PPAET and PPABT.

Keywords: photovoltaic, polyazomethine, band gap, power conversion efficiency, thiophene.

I. INTRODUCTION

Conjugated polymers have dragged great research interest as they offer many possibilities in terms of their potential applications in light emitting diodes (LED), sensors, photovoltaic devices, actuators, electrochromic devices etc.[1-9] Extended π-conjugation along the polymer chain is pre-requisite condition for electronic applications for such polymers, but choice of suitable side chains also influences the properties like band gap, ionic conductivity, morphology and miscibility with other substances. Amidst different conjugated polymers, polythiophenes are enticing material owing to its good stability and ease of substitution for the design of functional materials. Poly(3-substituted thiophenes) with a variety of substituents such as alkyl, alkoxy, alkyl heteroatom-functionalized side chains have been studied extensively for bulk heterojunctions and hybrid organic/inorganic photovoltaic devices.[5,10-15] Hybrid solar cells involve the use of inorganic material especially metal oxides as the electron transporting components having higher electron mobility than organic counterpart and organic polymers as the donors. Hybrid device based on zinc oxide (ZnO) nanoparticles (5 nm) with MDMO-PPV polymer showed power conversion efficiency (PCE) of 1.1%.[16] The PCE reported for hybrid solar cells based blends of isotropic TiO_2 particles with P3HT and elongated TiO_2 rods with MEH-PPV were 0.42% and 0.49% respectively.[17-18] G. D. Sharma et al reported hybrid solar cell from poly(3-phenyl azomethine thiophene)PPHT: ZnO and dye-sensitized PPHT: ZnO thin films for photovoltaic application. The dependence of photovoltaic parameters on the weight fraction of ZnO in PPHT: ZnO was also investigated and found that the device with 45% of ZnO in both composites exhibits the best photovoltaic performance with PCE being 0.12% and 0.52% respectively.[19]

The absorption ability of p-type polymers can be intensified by introducing additional absorptive chromophores directly and conjugatively attached to the main chain backbone for better photovoltaic performance.[12] Li et al. developed a series of polythiophene derivatives having conjugated bi(thienylenevinylene) side chains and observed strong and broad absorption covering both the UV and visible regions from 350 to 650 nm due to extension of

conjugated side chain to the polythiophene main chain. In addition, improved PCE of 3.18% was reported to this polymer based bulk heterojunction (BHJ) solar cell using PCBM as the acceptor (1:1, w/w) and found superior to that of the device based on P3HT under the same conditions.[20] Therefore, an approach to synthesize efficient photovoltaic materials with conjugated side chain bearing imine chromophore has been made to receive improved absorption ability.

In this present paper, we have therefore, reported synthesis and characterization of poly(3-phenyl alkyl azomethine thiophene)s with conjugated azomethinic chromophore as the side chain. The photovoltaic properties of two poly(3-phenyl ethyl azomethine thiophene) and poly(3-phenyl butyl azomethine thiophene) polymers have been evaluated with hybrid organic/inorganic structure using TiO_2 as electron acceptor.

II. EXPERIMENTAL

2.1. Chemicals and Measurements

3-Thiophene carboxyldehyde (Aldrich), 4-ethyl aniline (Merck), 4-butyl aniline (Merck) and Iron(III) chloride (Aldrich), poly(ethylene-dioxy-thiophene):poly(styrene sulphonate) (PEDOT:PSS) (Aldrich), TiO_2 nanoparticles (Avg. Size 5 nm)(Aldrich) were commercial products and used as received. All the solvents were properly purified before use by standard methods.

The inherent viscosity (η_{inh}) was determined using an Ubbelohde viscometer in DMAc at 30 ± 0.1^0C with 0.5 gm/dL polymer solution. UV-visible absorption spectra were taken on a Shimadzu UV-2500 spectrophotometer. The electrochemical cyclic voltammetry was conducted on a Sycopel AE-W2-10 electrochemical workstation with ITO coated glass, pt and Ag/Ag^+ as working electrode, counter electrode and reference electrode, respectively, in a 0.1M lithiumperchlorate ($LiClO_4$) acetonitrile solution. Molecular weights of polymers were measured by gel permeation chromatography using 410 Waters differential refractometer with the Flow rate of 1ml /min. The solvent used in gel permeation chromatography was tetrahydrofuran and polystyrene was used as standard.

2.2. Fabrication and characterization of polymer solar cell

Solar cells were fabricated with the structure of ITO/PEDOT:PSS/Polymer:TiO_2 nanoparticles/Al. A thin layer PEDOT:PSS was spin cast on pre-cleaned ITO coated glass from a PEDOT:PSS (Aldrich) aqueous solution and dried in vacuum oven at 120^0C for 20 min. The thickness of PEDOT:PSS layer was 60 nm. The photosensitive blend layer of polymer and TiO_2 nanoparticles dispersed in tetrahydrofuran (THF) (1:2. w/w) was spin-coated with polymer concentration of 10mg/ml on the ITO/PEDOT:PSS electrode and dried at 75^0C for 30 min. The thickness of the photosensitive layer was 90 nm which was spin cast at the rotating speed of 1200 rpm for 60 seconds. Then the metal cathode of Al was deposited on the polymer layer by vacuum evaporation under (4×10^{-5} Pa). The effective area of one cell is about 3 mm^2. The current-voltage (I - V) measurements of the device were conducted on a computer-controlled Keithley 2420 Source Measure Unit. A Xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm^2.

2.3. Synthesis of polymers

The monomer containing thiophene ring and azomethine linkages within the chain with full conjugated structure was synthesized by condensation reaction between p-alkylaniline and thiophene-3-carboxyldehyde in 1:1 ratio. Chemical oxidative polymerization method is employed to synthesize the polymers PPAET and PPABt using anhydrous $FeCl_3$ as oxidant. The synthesis of monomers and polymers is outlined in Scheme 1.
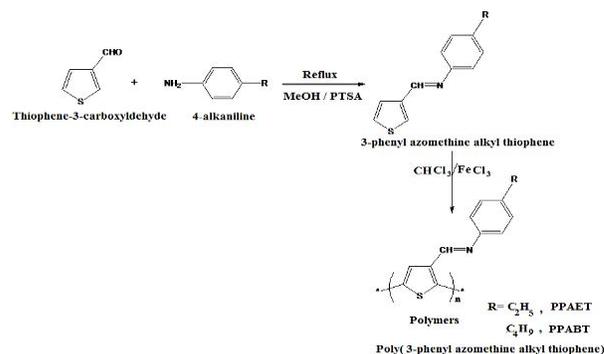
Scheme1. Synthetic outline of monomers and polymers

III. RESULTS AND DISCUSSION

The inherent viscosity of the polymers, PPAET and PPABT was found to be 0.19 and 0.23 dL/g respectively. Some of the physical properties of the polymers are listed in Table 1. Unlike other polyazomethines, the interesting feature of the synthesized polymer is their good solubility in some organic solvents like DMF, DMAc, DMSO and THF resulted due to the presence of alkyl groups as the side chain in the polymer.

Table. 1. Physical Properties of polymers

Polymer	η_{inh} (dLg^{-1})	M_n	M_w	M_w/M_n (PDI)	Yield (%)
PPAET	0.19	4256	4591	1.10	54
PPABT	0.23	4821	5074	1.05	57

3.1 Electrochemical Analysis

Cyclic Voltammeter was employed to investigate the redox behaviour of the polymer, PPAET and to estimate their HOMO and LUMO energy levels. The polymer films were spin–coated onto ITO electrodes and scanned positively and negatively at a scan rate of 50 mV/S in a 0.1M solution of Lithium Perchlorate ($LiClO_4$) in anhydrous acetonitrile. From the onset oxidation potentials (φ_{ox}) and the onset reduction potentials (φ_{red}) of the polymers, HOMO and LUMO energy levels as well as the energy gap (E_g^{ec}) of the polymer were calculated according to the equation.[21,22]

$$\text{HOMO} = -(\varphi_{ox} + 4.71) \text{ (eV)}; \dots\dots\dots\dots\dots \quad (1)$$

$$\text{LUMO} = -(\varphi_{red} + 4.71) \text{ (eV)}; \dots\dots\dots\dots\dots \quad (2)$$

$$E_g^{ec} = (\varphi_{ox} - \varphi_{red}) \text{ (eV)} \dots\dots\dots\dots\dots\dots \quad (3)$$

Where the units of φ_{ox} and φ_{red} are V vs Ag/AgCl. The calculation is based on ferrocene / ferrocenium (Fc/Fc$^+$) redox standard in CH_3CN. The values obtained are listed in Table.2 and cyclic voltammograms (CV) are shown in the Fig.1. From the cyclic voltammograms, it is observed that the polymers showed single irreversible oxidation and reduction peaks. The turn-on potential for the p-doping (onset oxidation potential) for the polymers PPAET and PPABT are very low compared to the turn-on potential of the n-doping (onset reduction potentials) which in turn indicates that the polymers possess very good donor ability. The electrochemical band gap for the polymers was calculated to be 2.23 and 2.13 eV respectively for PPAET and PPABT.
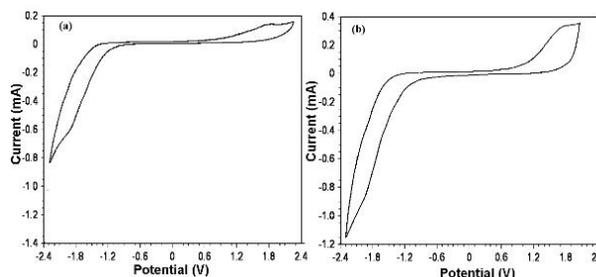

Fig.1. Cyclic Voltammogram of (a) PPAET and (b) PPABT films on ITO coated glass at a scanning rate of 50 mV/S.

Table.2. Electrochemical onset potentials and band-gap of the polymer films

Polymers Ag/Ag$^+$/ (eV)^a	φ_{ox} E_g^{ec} (V vs Ag/Ag$^+$)/ (eV) E_{HOMO} (eV)	φ_{red} E_g^{opt} (V vs E_{LUMO} (eV)
PPAET	0.98/-5.69 2.19	-1.21/-3.50 2.25
PPABT	0.91/-5.62 2.14	-1.23/-3.48 2.17

^{a} The optical band gap was obtained from empirical formula, $E_g = 1240/\lambda_{edge}$, in which λ_{edge} is the onset value of the absorption spectrum in the longer wavelength direction.

3.2. Optical Properties

The UV-vis absorption spectra of the 0.05% polymer solutions in THF are shown in the Fig.2. The absorption spectra showed broad absorption over the wavelength range of 350-590 nm with maximum absorption peak at 407 and 415 nm (λ_{max}) respectively for PPAET and PPABT. This is resulted due to the electronic transition throughout the whole conjugated molecule including both aromatic rings and azomethine (-CH=N-) linkage i.e. π- π^* and n- π^* conjugation. The onset of absorption of the polymers were 549 nm and 569 nm which lead to the optical band gap of 2.25 eV and 2.17 eV respectively for PPAET and PPABT which matches with calculated electrochemical band gap values.
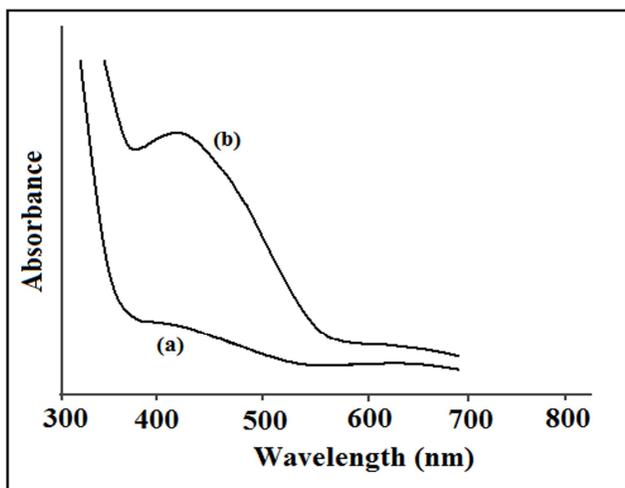

Fig.2. UV-visible absorption spectrum of 0.05% polymer solutions in THF.

3.3. Photovoltaic properties

The reason behind synthesis of this copolymer is to look for new conjugated polymers for use in photovoltaic devices. The photovoltaic properties of the synthesized polymers were studied by fabricating the device with the structure of ITO/PEDOT:PSS/Polymer:TiO$_2$ nanoparticles (1:2 w/w)/ Al where the PPAET and PPABT polymers were used as electron donor and TiO$_2$ nanoparticle was used as the electron acceptor. The exciton formation upon absorption of photon is the primary process which is followed by ultrafast electron transfer from LUMO of donor to acceptor. Thus electrons are collected at Al electrode through acceptor

and holes are collected at ITO via hole injecting PEDOT: PSS layer thereby causing voltage difference in two electrodes. Fig.3 shows the J–V curve of the PSC under the illumination of AM 1.5, 100mW/cm^2, and photovoltaic properties obtained from the J–V curve are listed in Table 3. The device parameters were calculated using the following equations:

$$FF = I_p . V_p / I_{SC} . V_{OC} \dots\dots\dots\dots\dots\dots\dots\dots (4)$$
$$\eta \,(\%) = FF \, I_{SC} . V_{OC} \,(V) / P_{in} \times 100 \dots\dots\dots\dots (5)$$

where V_{OC} is the open-circuit voltage, I_{SC} is the short-circuit current, FF is the fill factor, η_e is the power conversion efficiency, Pin is the intensity of the white light and V_P and I_P are the voltage and the current at the maximum power point of the J–V curve.

Table.3. Summary of photovoltaic performances of PPAET and PPABT based devices

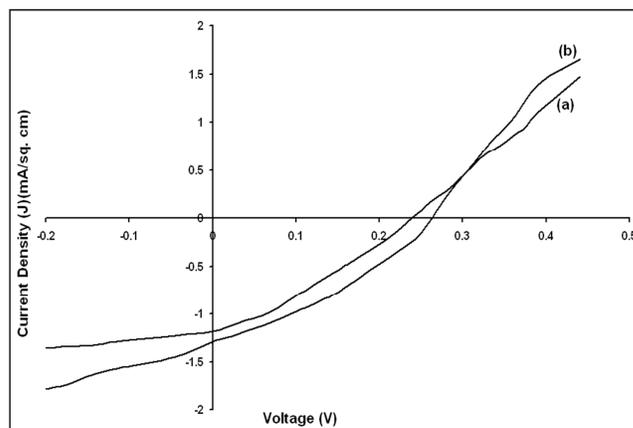| Photoactive layer (mA/cm^2)	FF	V_{OC} (V)	I_{SC} PCE, η_e (%)
PPAET: TiO$_2$ nanoparticles 1.16	0.36	0.24	0.102
PPABT: TiO$_2$ nanoparticles 1.29	0.37	0.26	0.125

Fig.3. J-V characteristics of photovoltaic devices of the structures (a) (ITO/PEDOT:PSS/PPAET:TiO$_2$ nanoparticles (1:2 w/w)/ Al) and (b) (ITO/PEDOT:PSS/PPABT: TiO$_2$ nanoparticles (1:2 w/w)/ Al)

The fabricated photovoltaic devices based on the synthesized polymers, PPAET and PPABT showed power conversion efficiency (PCE) (η_e) of 0.102% and 0.125% respectively. I_{SC}, V_{OC} and FF exhibited by the device based on PPAET were 1.16 mA/cm^2, 0.24 V and 0.36 while the same parameters exhibited by the device based on PPABT were 1.29 mA/cm^2, 0.26 V and 0.37. PPABT polymer based photovoltaic device showed higher power conversion efficiency compared to the device based on PPAET even though the devices were fabricated in similar environment and keeping the polymer to acceptor proportion same. This is attributed to higher donor ability of PPABT than PPAET as revealed in electrochemical study resulting easier exciton formation. Moreover, lower band gap of PPABT facilitates higher absorption of irradiated radiation thereby affecting improvement of PCE. The power conversion efficiency solar cell may be increased to manifold by optimization. Polymer purity, polymer to acceptor ratio, use of processing additives, solvent annealing are the some of the factors which affects the efficiency (η_e) of the PSC.[25-28]

IV. CONCLUSIONS

Poly(3-phenyl azomethine alkyl thiophene) polymers PPAET and PPABT were synthesized employing oxidative polymerization of condensation product resulted from the reaction of p-alkyl aniline and thiophene-3-carboxyldehyde. The polymers bear good solubility in common organic solvents. The conjugated azomethine linkage containing side chains possessed by these polymers attributes wide absorption range of 350-590 nm. The optical and electrochemical properties of the polymers PPAET and PPABT revealed that they are suitable for photovoltaic application. These polymers were investigated as donor for the hybrid photovoltaic cells using TiO$_2$ nanoparticles as acceptor. PPAET and PPABT based hybrid cells showed power conversion efficiency of 0.102% and 0.125% respectively. Higher donor ability, low band gap and matching HOMO energy levels with hole injecting layers of PPABT facilitates improved I_{SC} and power conversion effiecieny in comparision to PPAET. The device performance could be improved by multiparametric optimization so that polymeric solar cells find the new realm of application for clean and renewable energy.

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