New bithiophene-containing electroluminescent polymer: Synthesis, characterization, optical and electrical properties

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ABSTRACT

A semi-conducting polymer, **P-DSBT**, based on distyryl-bithiophene π-conjugated sequences has been synthesized and characterized. The macromolecular material was soluble in volatile solvents and showed a good film quality; it exhibited an amorphous morphology with relatively high glass transition temperature. The absorption and photoluminescence properties of the polymer were studied in solution and as thin solid film, which showed an optical gap of 2.6 eV. The HOMO/LUMO energy levels were evaluated by cyclic voltammetry measurements and indicate a p-type semi-conducting material. The electrical properties of **P-DSBT** were investigated by the current-tension characteristic and modeled by the current space-charge-limited (SCLC) mechanism; charge carrier mobility higher than $10^{-6}\,cm^2\,V^{-1}\,s^{-1}$ was evaluated. A yellow-green electroluminescence was evidenced in a multilayer organic light-emitting diode with an [ITO/PEDOT:PPS/**P-DSBT**/BCP/Al] configuration.

1. Introduction

The π-conjugated semi-conducting polymers have received a great deal of attention as active layers in thin film electronic devices such as organic field-effect transistors (OFETs) [1–3], organic light-emitting diodes (OLEDs) [4–6], organic photovoltaic devices (OPVs) [7] and chemo- and biosensors [8–10]. Moreover, these polymeric organic semiconductors are recently emerged as highly versatile nanoparticles that can potentially exploited in various areas such as photonics, optoelectronics, bio-imaging, bio-sensing and nanomedicine [11–13]. In fact, as compared to the inorganic semiconductors typically used in electronics, the unique mechanical properties and film-forming quality of the π-conjugated polymers allow the fabrication of flexible electronic devices, while their solubility open the way to low-cost manufacturing techniques such as spin-coating, ink-jet printing and roll-to-roll printing processes. However, the major characteristic justifying the huge interest in polymeric semi-conducting materials is their tunable opto-electronic properties, benefiting from the richness of the organic synthesis and therefore from an adjustable macromolecular structure [14–16].

The oligothiophenes were among the most extensively investigated molecular skeletons in the design of polymeric

semiconducting materials [17,18]. In fact, these sulfur-rich macromolecules constitute an interesting class of π-conjugated compounds suitable in fabrication of OLEDs [19], OFETs [20] and especially in chemical sensors owing to their complex-forming ability [21,22]. However, for the application in electronics they require solubilizing end-group functionalization [23]. An alternative approach involves the design of π-conjugated systems in which oligothiophene moieties (bithiophene, terthiophene, etc.) are attached to central solubilizing units. Hence, by an appropriate selection of the central unit and the position of alkyl substituents, the optoelectronic properties of these organic materials can be tuned to a large extent [24,25].

Recently, Videlot-Ackerman et al. have reported that the end-substitution of oligothiophene by the less oxidable styryl groups enhance considerably its chemical stability [26]. A series of distyryl-oligothiophenes which combine the good electrical performances and exceptional stability were studied. In particular, the distyryl-bithiophene (DSBT) structure was exploited in OTFTs and sensors; nevertheless, due to their low solubility, the active DSBT layers could only be prepared by vacuum evaporation. Herein, we report the synthesis of a new polymer based on the DSBT π-conjugated sequences separated by isopropylidene flexible units as spacer and solubilizing groups. We also applied incorporation of the ethoxy groups on the DSBT moieties as an effective approach to increase the polymer solubility. The thermal, morphological, optical, electrical and electroluminescent behaviors of this organic semi-conducting material were investigated.

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2. Experimental

2.1. Synthesis of the monomers (M1; M2) and the π-conjugated polymer (P-DSBT)

The monomers 2,2-bis(4-ethoxy-3-triphenylphosphoniomethyl phenyl)propane dichloride (**M1**) and 5,5′-diformyl-2,2′-bithio phene (**M2**) were prepared according our previously reported procedures [27,28]. Tetrahydrofuran (THF) was dried over Na/benzophenone and freshly distilled before use and potassium tert-butoxide (t-BuOK) (Acros, 98%) was used as received.

The polymer **P-DSBT** was synthesized via the Wittig reaction as following: To a stirred equimolar mixture of the diphosphonium salt **M1** (1 mmol) and the bithiophene dialdehyde **M2** (1 mmol) in 10 mL of anhydrous THF, 10 mL of a 0.5 M t-BuOK/THF solution (5 mmol) was added dropwise at room temperature under an argon atmosphere. The reaction mixture was stirred for 24 h at room temperature, then at reflux (60 °C) for 2 h. The mixture was then acidified with 3% aqueous hydrochloric acid, poured into water and extracted with chloroform. The organic phase was washed with water, concentrated and then precipitated twice into methanol. The polymer was then filtered and dried under vacuum.

2.2. Measurements

NMR spectral data were obtained on a Bruker AV 300 spectrometer and the chemical shifts were referenced to the CHCl$_3$ signal (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). The FT-IR spectrum was acquired on a Perkin–Elmer BX FT-IR system spectrometer (0.5 cm^{-1} resolution), by dispersing samples in KBr disks. The Steric exclusion chromatography (SEC) was performed on an Agilent Technologies 1200 HPLC. The experiment was done at room temperature using THF as eluent with standard polystyrene calibration.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under ambient atmospheric conditions at a heating rate of 10 °C min^{-1}, using a Setaram TG-DTA 92-10 thermal analyzer and a Mettler Toledo DSC1, respectively. The atomic force microscopy (AFM) analysis of the polymer coated glass surface was carried out using a Nanoscope III (Digital Instruments, Santa Barbara, CA) operating in the tapping mode. Contact angle measurements with three different liquids (DI water, formamide and diiodomethane) were performed with Digidrop (GBX, France) contact angle instrument. The size and volume of the drops were kept constant and each contact angle represents an average of at least three separate drops on different areas of the given wafer.

The UV–vis absorption spectra were acquired on a Cary 2300 spectrophotometer. Fluorescence spectra were obtained on a Jobin-Yvon spectrometer HR460 coupled to a nitrogen-cooled Si Charged-Coupled Device (CCD) detector; samples were excited at the absorption maximum with a 450 W Xenon lamp. For optical solid-state measurements, the polymer films were spin-cast onto quartz substrates from chloroform solutions ($2 \cdot 10^{-2}$ M); the film thicknesses were measured using a mechanical profilometer Veeco Dek-tak150. In the fluorescence quantum yields measurements, absorbance of the sample solutions was kept below 0.05 to avoid inner filter effect. Both sample and reference solutions were excited at the same wavelength (366 nm).

The cyclic voltammetry (CV) was performed on an EG&G model 273 potentiostat/galvanostat (Princeton Applied Research) in a three-electrode cell using polymer film that was drop-cast onto an indium tin oxide (ITO) working electrode. The measurements were carried out at a scan rate of 50 mV s^{-1} and referenced to saturated calomel electrode (SCE), using 0.1 M tetrabutylammonium perchlorate ((n-Bu)$_4$NClO$_4$) in acetonitrile as supporting electrolyte. The measurements were performed at room temperature and the cell was briefly deoxygenated with argon before each reductive scan.

2.3. Elaboration and characterization of the organic diodes

Indium-tin oxide (ITO)-coated glass substrates with a size of 1.5×1.5 cm^2 and sheet resistance 50 Ω/square were supplied from Solems. They were cleaned successively in ultrasonic baths of RBS detergent for 20 min, de-ionized water for 5 min, acetone for 15 min, and de-ionized water for 5 min. The substrates were then dried in a nitrogen flow and in air at 60 °C for 1 h. To prepare the ITO electrodes, diagonal 1 mm stripes were etched according to a previously described photolithography process [29].

The single-layer device was fabricated as a sandwich structure between the aluminum cathode and ITO anode. The polymer solution (10 mg mL^{-1} in chloroform) was spin-cast (2000 rpm) onto ITO glass to obtain a film with a thickness of about 100 nm after annealing at 40 °C for 1 h. Finally, the 150 nm aluminum layer was deposited by thermal evaporation under $3 \cdot 10^{-6}$ Torr with a 1 nm s^{-1} rate through a shadow mask. Hence, an active zone of 1 mm^2 results from intersection of cathode and anode stripes.

In the multilayer device, the poly(ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) layer (30 nm) was spin-cast onto ITO at 3000 rpm from 0.14 wt.% aqueous suspension, and then dried at 60 °C for 12 h. The 55 nm bathocuproine (BCP) layer was thermally deposited through shadow mask under a vacuum of $2 \cdot 10^{-6}$ Torr at a rate of 0.1 nm s^{-1}.

The current–voltage (I–V) characteristics of the diodes were recorded with a digital oscilloscope Tektronix 5034. The EL spectrum was obtained using a cooled CCD camera attached to a JobinYvon Triax 190 spectrometer. All measurements were carried out under ambient temperature.

3. Results and discussion

3.1. Synthesis, structural and thermal characterization

The synthesis of the π-conjugated polymer **P-DSBT** was carried out via the Wittig polycondensation between the bisphenol A-based diphosphonium salt **M1** and the bithiophene dialdehyde **M2**, using the t-BuOK/THF system (Scheme 1a). The polymer was purified by successive precipitations from methanol and it was found to have good solubility in organic volatile solvents commonly used in spin-coating process, such as THF, chloroform and methylene chloride.

The macromolecular structure of **P-DSBT** was established by NMR spectroscopic analysis as illustrated in Fig. 1. The ^{1}H NMR spectrum reveals several peaks between 7.5 and 6.5 ppm assigned to aromatic and vinylene protons. The oxymethylene units (OCH$_2$) appear around 4.0 ppm and the methyl groups are between 1.2 and 1.8 ppm. The absence of aldehyde terminal groups was supported by the lack of the corresponding peak in the ^{1}H NMR spectrum (10 ppm) and the appearance of a weak signal at 2.1 ppm suggesting aromatic methyl end-groups (Ar-CH$_3$). By comparing the signal integration of these terminal groups to that of the OCH$_2$ units, the number-average molecular weight (M_n) of **P-DSBT** was estimated to be 9770 g mol^{-1}. The SEC analysis showed a low polydispersity index (Ip) around 1.2 for the polymer; nevertheless, the polymer weight was underestimated comparing to the NMR calculated value. In fact, contrary to NMR method which gives absolute exact weight, the SEC analysis is related to the macromolecular hydrodynamic volume and the obtained results depend on the nature of the polymer used as reference. Indeed, the conjugated polymer **P-DSBT**