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ORIGINAL PAPER

Synthesis, characterization, and optical properties of a novel alternating 3-dodecyloxythiophene-co-pyridine copolymer

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Abstract A novel soluble alternating conjugated copolymer, comprised of 3-dodecyloxythiophene and pyridine moieties, was synthesized via the Heck Couple approach. Regioregular poly(3-dodecyloxythiophenel) synthesized by McCullough was also studied for comparison. The obtained polymers were characterized by 1H NMR, HR-MS, gel permeation chromatography, UV–Vis spectroscopy, photoluminescence and Cyclic voltammetry. The photoluminescence of the copolymer exhibited extraordinary bright blue. The electrochemical study shows that the new alternating copolymer does not merely have the properties of the two units that constitute it but has mutual hole and electron charge carrier properties which might be promising material for applications in high efficiency, single or low number layers functional devices.

Keywords 3-Alkoxylthiophene · Copolymerization · Donor–acceptor · Photoluminescence · LED

Introduction

Conjugated polymers have drawn much attention in recent years, due to their promising applications in electrochromics [1], biosensors [2, 3], electrochemical supercapacitors [4], anticorrosion [5], polymer thin film transistors [6–8], polymer light-emitting diodes (PLEDs) [9–12], polymer photodetectors and polymer solar cells (PSCs) [13–19], etc. Among π-conjugated polymers, soluble polythiophene derivatives (PTs) are the most promising and frequently investigated conjugated systems as a result of their synthetic availability, stability in various redox states,

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widespread processibility, and tunable electronic properties [20–22]. Moreover, it is solubility that enables the easy characterization and understanding of the physical and chemical structure and properties in great detail.

Polythiophenes with substituents other than alkyl groups have also been investigated, among which those with electron-donating alkoxy groups have displayed promising electronic and optical properties [23, 24]. Compared to P3ATs, the incorporation of an alkoxy group to the 3-position of the thiophene ring yields poly (3-alkoxythiophenes) (P3AOTs) with optical absorption maxima at longer wavelength. This may be attributed to both the electron-donating effect of the alkoxy group and the more coplanar conformation of the P3AOTs [25, 26]. Therefore, polymers and copolymers based on 3-alkoxythiophene may also have smaller band gaps than those based on P3ATs [27, 28] and will be another promising conjugated systems.

Recently, a large number of π-conjugated polymers containing pyridines have been synthesized and applied [29]. However, synthesis of POTs bearing pyridine units in the conjugated main chain has not been reported. We herein report the synthesis of 3-alkoxylthiophene-2,4-vinylene-co-pyridine copolymers (P3AOTVs) with mutual hole and electron charge carrier properties, which is highly sought after reducing the number of layers required for functional devices.

Actually, we also synthesized regioregular head-to-tail (HT) poly(3-dodecyloxythiophene) homopolymer via Grignard metathesis (GRIM) [30] method initially reported by McCullough et al. The newly synthesized poly(3-dodecyloxythiophene-2,4-vinylene) containing electron-donating thiophene unit and the electron-accepting pyridine unit, is expected to expand the scope of chemistry of POTs with such a charge-transferred (CT) structure.

In this paper we wish to report on the synthesis of p–n conjugated copolymer, an alternating 3-dodecyloxythiophene, ethylene and pyridine backbone, obtained by Heck Couple Method [31]. The electron donating and accepting groups on consecutive repeat units are introduced to stimulate intramolecular charge transfer along polymer chains.

Experimental

Materials

3-Bromothiophene (99%), dodecanol (98%), 2, 6-dibromopyridine [1, 3-bis (diphenylphosphino) propane] dichloronickel(II) (98%) (Ni(dppp)Cl_2), $PdCl_2$ were purchased from Aldrich Chemical Co., Inc.

Instrumental measurements

^{1}H NMR spectra were recorded at 500 MHz on a Bruker DRX-500, in D-acetone at room temperature. FT-IR spectra of the synthesized polymers were recorded on a Nicolet 700 FT-IR spectrometer. High-resolution mass spectroscopy (HR-MS) measurements were taken with a JEOL-JMS 700 spectrometer. HPLC was performed by using an Perkin Elmer Spheri-5RP-18 column (4.6 × 50 mm i.d., 5 μm), and compounds were eluted with methanol and detected by a UV–Vis spectrophotodetector at 254 nm. Gel permeation chromatography (GPC) was performed with a Perkin Elmer series 200 apparatus (a mixed 10-μPS column with a length of 750 mm, refractive index detector). Tetrahydrofuran was acted as an eluant at a flow rate of 1.0 mL/min at 40 °C. Polymer solution was filtered through a 0.45 μm PTFE filter prior to injecting into the column. Calibration was conducted with polystyrene standards. Thermo-gravimetric analysis (TGA) was performed on a DuPont 9900 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. UV–Vis spectra of Chloroform solvent of the polymers were recorded on a UV-2201 (Japan) in a laboratory atmosphere at room temperature. Photoluminescence spectra were recorded on a Spex FL-2T2 (USA).

Cyclic voltammetry (CV) studies were performed using a standard three-electrode cell. Platinum disk was used as counter and 213 Platinum slice was used as working electrodes. Ag/AgCl (0.1 M $AgNO_3$ in acetonitrile) was used as a reference electrode. Tetrabutylammonium perchlorate (TBAP) 98% from Aldrich was used as electrolyte and recrystallized three times from acetic ether and dried in vacuum at 100 °C before each experiment. Ferrocene was provided by Aldrich and purified by beening recrystallized through cyclohexane before the experiments. All experiments were carried out in an air-sealed electrochemical cell. Before each experiment, the cell was being purged with high purity inert gas for 15 min. Before the start of the measurement the inert gas was turned to “blanket mode”. Measurements were recorded by using a CHI660B CV voltametric analyzer (China) at a scan rate of 50 mV/s. The working electrode was cleaned before each experiment through sonication in 65% HNO_3 and absolute acetone. Samples were prepared by dipping the working electrode in a viscous 20wt% chloroform solution of the polymers and then dried.

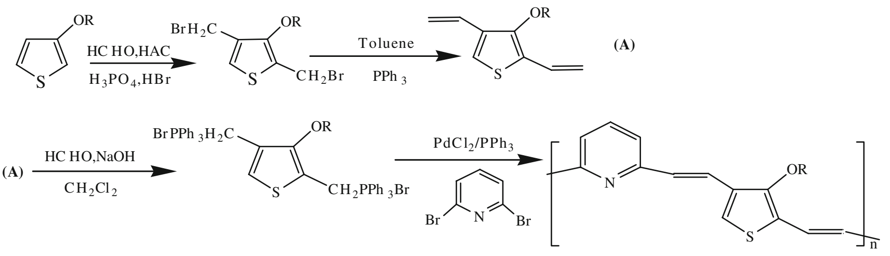
Preparation of monomers

Synthesis of 2, 4-bisbromomethyl-3-dodecyloxythiophene

A total of 20 mL ice acetic acid, 4 mL 90% phosphoric acid, 4 mL saturated bromine hydride, 1.2 g polyformaldehyde and 3.02 g (18.0 mmol) of 3-dodecyloxythiophene (performed according to the literature [32]) were added in a round and degassed flask under N_2 atmosphere. The reaction was stirred at 60 °C and after every 4 h, about 6 mL saturated bromine hydride was dripped. After 14 h the product was precipitated in ice water, filtrated and washed with pure water. After being recrystallized from isopropyl alcohol, a brown solid of 2,4-bisbromomethyl-3-dodeoxylthiophene was obtained (4.99 g, yield: 78.3%, purity: 94.5%, HPLC).

Synthesis of 2,4-bisvinyl-3-dodecyloxythiophene

A total of 3.45 g (9.73 mmol) 2,4-bisbromomethyl-3-dodecyloxythiophene, 5.16 g (21.4 mmol) PPh3 and 30 mL toluene were charged into a 100 mL dry three-neck



Scheme 1 Synthetic procedure of copolymers

and round-bottom flask. The mixture was being stirred at reflux for 4 h. After being cooled to ambient temperature, the obtained precipitate was dried under vacuum. The yield was about 95%. In a 100 mL three-neck and round-bottom flask, 1.62 g (1.85 mmol) 2,4-di (triphospheny bromomethyl)-3-dodecyloxythiophene, 27 mL CH_2Cl_2 and 7.2 mL formalin were added. Under an ice-salt bath, 10 mL 20% NaOH was added dropwise. The mixture was being stirred overnight at ambient temperature. Then the reactant was poured into water. Organic CH_2Cl_2 layer was collected and washed with saturated NaCl and water respectively, then dried with $MgSO_4$ and concentrated. After being purified by column chromatography (silica, acetic ether/petroleum ether 1/1), a red brown powder was obtained (1.26 g, yield: 58.9 %).

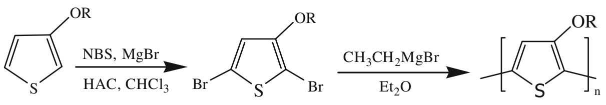
Results and discussion

The synthesis route of the donor–acceptor alternating polymer P3AOTVs is shown in Scheme 1.

Copolymer synthesis

Poly[(2,4-bisvinyl-3-dodecyloxythiophene)-co-pyridine] (P3DOTV-Py)

A total of 65.6 mg (0.272 mmol) PPh3, 0.7 mL triethylamine and 5 mL *N*,*N*-dimethylformamine were added in a 50 mL three-neck, round-bottomed and carefully degassed flask and stirred. 2, 4-bisvinyl-3-dodecyloxythiophene 220 mg (1.0 mmol), 2,6-dibromopyridine 380 mg (1.0 mmol) and 5.0 mg $PdCl_2$ were added subsequently. The reaction mixture was being heated at 115 °C for 12 h and 140 °C for 2 h under N_2 atmosphere. After then, the reactant was cooled and precipitated into an excess of MeOH. The obtained polymer was dried under vacuum and extracted in a Soxhlet apparatus by using hexane to remove short chain oligomers. The final reactant was dried under vacuum after being further purified by redissolving in Chloroform and precipitating into methanol. The yield of the straw brown solid P3DOTV-Py was 48.1%. ^1H NMR (D-acetone, δ): 0.89 (t, J = 6.8 Hz, 3H, CH_3); 2.0 (m, 18H, 9CH_2); 2.80 (q, J = 7.8 Hz, 2H, CH_2); 3.5 (t, J = 6.5 Hz, OCH_2); 6.05 (m, 4H) 7.37 (s, 1H); 7.80–7.97 (m, 3H). GPC (Mw: 24,940, Mn: 21,894, PDI: 1.14).



Scheme 2 Synthetic procedure of homopolymers

Homopolymer synthesis

The synthesis of regioregular polymer (P3DOTs) is shown in Scheme 2.

Regioregular poly(3-dodecyloxythiophene-2,5-diyl) (P3DOT)

A total of 50 ml aether and 0.12 g (5 mmol) disposed magnesium were putted in a 250 mL dry three-neck and round-bottom flask, and stirred under N_2 atmosphere. Bromoethane (5 mmol) was added in drops to the flask. 2,5-dibromo-3-dodecyloxythiophene (5 mmol) (in aether) would not be added to the flask until powdered magnesium was vanished entirely. After 1 h, Ni(dppp)Cl_2 (20 mg) was added. The reaction mixture was being stirred and gently refluxed for 20 h. The final reactant was obtained by following a similar procedure of the P3DOTV-Py. The yield of the straw brown solid P3DOT was 36.1%. ^{1}H NMR (D-acetone, δ): 0.89 (t, J = 6.8 Hz, 3H, CH3); 2.0 (m, 18H, 9CH2); 2.80 (q, J = 7.8 Hz, 2H, CH2); 3.5 (t, J = 6.5 Hz, OCH2); 6.9 (s, 1H). GPC (Mw: 5,017, Mn: 4,762, PDI: 1.05).

Optical characterization

The polymers were studied by UV–Vis and photoluminescence spectroscopy. Among conjugated polymers, the extent of conjugation directly affects the observed energy of the π–π^* transition, which appears as the maximum absorption [33, 34]. Their π–π^* transitions are exhibited by the absorption with maximum wavelength (λ_{max}) at around 279 and 296 nm for P3DOT and P3DOT-Py in $CHCl_3$ solution as shown in Fig. 1a. Upon examining the UV–Vis spectrum, it can be seen the complete absence of the thiophene optical absorption in the P3DOT while the thiophene character can be observed by an additional shoulder at 335 nm albeit weak for P3DOTV-Py in intensity in $CHCl_3$, as well as an weak shoulder peak at 330 nm in solid film. It is also interesting to find the maximum absorption of P3DOT-Py is 17 nm red-shifted comparing to its homopolymer P3DOT in solution. The results imply that the conformation of P3DOT-Py in solution would be a more extended structure with more extensive electronic delocalization attributed to rigid pyridine ring conducing to the planarity of thiophene backbone.

Examining the polymers in the solid state (Fig. 1b), peaks can be seen at 314 and 302 nm for P3DOT and P3DOTV-Py. The UV–Vis absorption maxima of films are red-shifted to longer wavelengths in comparison to the polymers in solution. An unexpected phenomenon is observed that the λ_{max} of P3DOTV-Py is 12 nm blue-shifted compared to that of homopolymer, being different from that in $CHCl_3$ solution. The results suggest that the planarity of copolymer has been disturbed

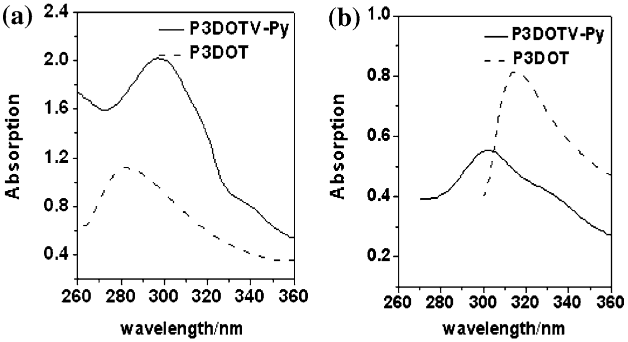


Fig. 1 UV–Vis spectra of polymer in $CHCl_3$ (**a**) and in solid film (**b**)

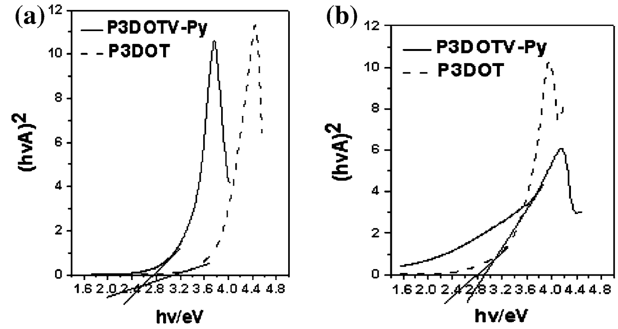


Fig. 2 The $(h\nu A)^2 - h\nu$ curves of copolymer in $CHCl_3$ (**a**) and in solid film (**b**)

because of the increasing polarity of copolymer during assembling, resulting in a reduction of the effective conjugated length.

The optical band-gap energy is calculated according to the following formula: $\alpha h\nu = B(h\nu - Eg)^n$ where α is the absorbance coefficient, h is the Planck constant, Eg is the optical band-gap energy and n is the transition type, respectively [35–37]. The value of n is 0.5 in case of band transition directly, and the absorbance coefficient amount to absorbance for the given sample, so the $(h\nu A)^2 - h\nu$ curves of the polymers can be drawn as shown in Fig. 2. The linearity edge of absorbance is extended and intersected with energy axis, and then the band-gap energy is obtained. The comparison of optical band-gap energy for the copolymer and homopolymer is listed in Table 1.

In Table 1, the Eg for P3DOTV-Py is 0.32 eV lower in solution and 0.12 eV higher in solid state than that of P3DOT. As it is expected, the introduction of the pyridine rings in the main chain of P3AOT, disturbs the planarity of the homopolythiophene and results in a reduction of the effective conjugated length. It means that the turn-on voltage of the new P3AOTV copolymer should be increased in the same PLEDs of configuration of P3AOTs.

Table 1 The comparison of optical band-gap energy for the copolymer and homopolymer

Sample	Eg (eV) (in $CHCl_3$)	Eg (eV) (in solid film)
P3DOT-Py	2.78	2.92
P3DOT	3.10	2.80

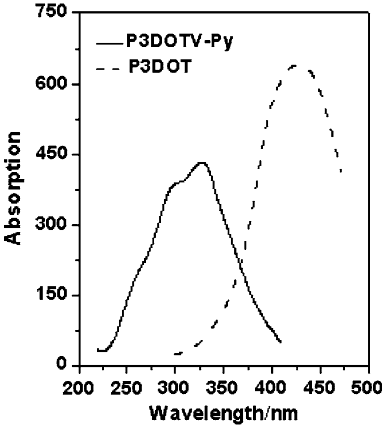


Fig. 3 The excitation curves of the polymers in $CHCl_3$ solution

Photoluminescence (PL) spectra can provide a good deal of information on the electronic structures of the conjugated polymers. Figure 3 shows the excitation curves of polymers P3DOT (425 nm) and P3DOTV-Py (302, 335 nm) in $CHCl_3$, while P3DOTV-Py (302, 335 nm) shows characteristic of thiophene which might be attributed to the predominant effect of thiophene moieties under high-power laser, and energy transfer from the pyridine moieties to the thiophene backbone takes place [38]. The shoulder peak also can been seen in the excitation curve of P3DOTV-Py.

Photoluminescence spectra were recorded by excitation at the absorption maximum. Figure 4a shows that the emission maximum of P3DOTV-Py is at 361 and 408.5 nm in solution. Compared to P3DOT (368 nm), the emission of P3DOTV-Py has an additional shoulder at 408.5 nm, meaning a new conjugation, and the absorption maximum and conjugated length are longer than that of polythiophenes. While examining polymers in the solid state, the emission maximum of P3DOTV-Py is at 412 and 520 nm, with a large additional shoulder than that of in solution. The results imply that the energy transfer from pyridines to thiophenes becomes more distinct in the solid state than that in solution. All of these are consistent with UV–Vis spectra.

Electrochemical study

Cyclic voltammetry was employed to investigate the redox behavior of the polymers and to estimate the HOMO and LUMO energy levels. The Ag/AgCl electrode was connected to the electrochemical cell through a salt bridge and was calibrated before

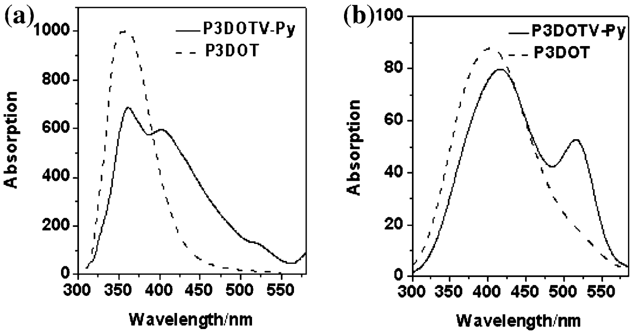


Fig. 4 PL spectra of P3DOTV-Py and P3DOT in $CHCl_3$ (**a**) and in solid film (**b**)

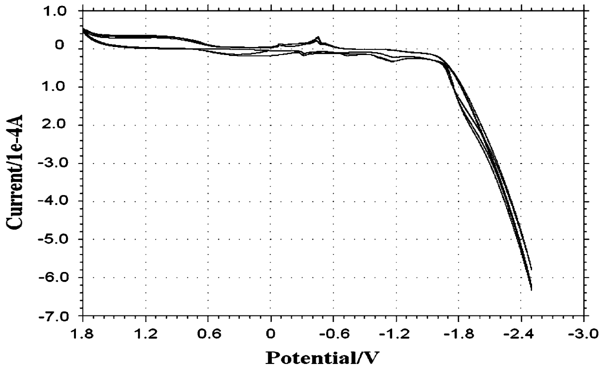


Fig. 5 Cyclic voltammogram of P3DOTV-Py

each experiment by running cyclic voltammetry on ferrocene. The potential values obtained vs Ag/Ag^+ were converted versus saturated calomel electrode (SCE). The energy levels were calculated by using the following empirical equations [35, 36]: $E_{\mathrm{HOMO}} = E^{\mathrm{ox}}_{\mathrm{onset}} + 4.68$, $E_{\mathrm{LUMO}} = E^{\mathrm{red}}_{\mathrm{onset}} + 4.68$, $\mathrm{Eg} = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}} = E^{\mathrm{ox}}_{\mathrm{onset}} - \mathrm{E}^{\mathrm{red}}_{\mathrm{onset}}$.

Examining the voltammogram of copolymer P3DOTV-Py (Fig. 5), an irreversible oxidation process is seen at 1.55 V with an onset at 1.20 V yielding an ionization potential of 5.88 eV. The electrochemical band gap at 2.75 eV is lower than 3.10 eV that can be calculated from the optical spectra. The cyclic voltammogram (Fig. 6) displays quasi-reversible oxidation processes for the homopolymer. The determined band gap (Eg) of the homopolymer (3.10 eV) is derived from its $(h\nu\mathrm{A})^2 - h\nu$ curve of in $CHCl_3$ as Fig. 2a shows and then the LUMO energy level can be deduced by the equation: $\mathrm{Eg} = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$.

Some interesting remarks can be seen from cyclic voltammogram of the copolymer. First of all, the oxidation and reduction process were revealed, suggesting that the new alternating type copolymer does not merely have the properties of two moieties that constitute it but has mutual hole and electron charge

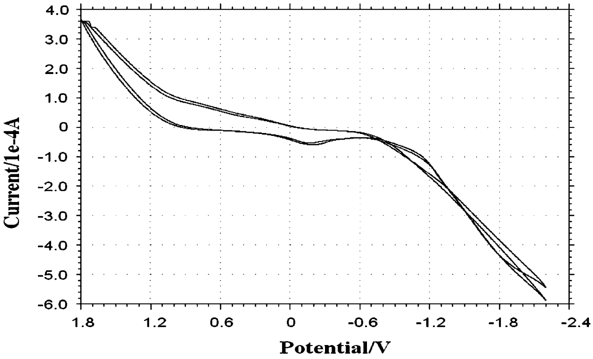


Fig. 6 Cyclic voltammogram of P3DOT

Table 2 The HOMO, LUMO and band gap of P3DOT, P3DOTV-Py

Sample	$E_{\mathrm{ons}}^{\mathrm{ox}}$	$E_{\mathrm{onset}}^{\mathrm{red}}$	HOMO (eV)	LUMO (eV)	Eg (eV)
P3DOT	1.00	–	5.68	2.58	3.10
P3DOTV-Py	1.20	−1.55	5.88	3.13	2.75

carrier properties. The copolymer displays a partly reversible n-doping process which is something that was not observed in the thiophene homopolymer [39]. From the Table 2, we can see the LUMO for P3DOTV-Py is lower than that of P3DOT, which will greatly facilitate the electron injection and excitation. The n-doping/dedoping processes suggest that copolymer could be used as an electron acceptor as an electron donator.

Conclusion

The copolymer was studied with respect to its optical and electrochemical properties. Energy transfer from the heteroaromatic moieties to the polythiophene backbone is suggested. The optical properties investigations show a new conjugation, and the absorption maximum and conjugated length are longer than that of homopolymer. The electrochemical study shows that the new alternating copolymer does not merely have the properties of the two units that constitute it but has mutual hole and electron charge carrier properties. On the basis of these results, the novel p/n doping alternatively copolymer with capability of both reversible oxidation and reduction might be promising material for applications in high efficiency, single or low number layers thin OLED devices.

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