Novel 2,4-Divinyl-3-Alkylthiophene/1,3,4-Oxadiazole Alternating Conjugated Copolymer Synthesized by the Heck Coupling Method: Synthesis, Characterization, and Electronic and Optical Properties

Zheng-Jian Qi, Bin Wei, Chen Shi, Yan-Fang He, Jing Yu, Xue-Mei Wang, Feng Kang, Biao Jin, Yue-Ming Sun

Department of Chemistry and Chemical Engineering, Southeast University, Nan Jing 210096, People's Republic of China

ABSTRACT: A novel alternating copolymer with 3-alkyl-thiophene and oxadiazole (or pyridine) units in ordered arrangement was synthesized with vinyl as a bridge for the first time. The synthesis process included four steps: bromo-methylation, preparation of the ylide monomer, the formation of 2,4-divinyl-3-alkylthiophene, and Heck alternating copolymerization. The Fourier transform infrared spectroscopy, ^{1}H-NMR, and gel permeation chromatography measurements showed that all of the copolymers had the required structures. The weight-average molecular weights of the copolymers were in the range 5500–15,000 with a relatively low polydispersity index of 1.4–1.7. The solubility of the copolymers in common solvents (e.g., methylene chloride, chloroform, tetrahydrofuran) was excellent. The optical properties and bandgap of the copolymers was compared with corresponding poly(3-alkylthiophene) homopolymers. The photoluminescence quantum efficiency (QE) of the copolymers improved markedly in chloroform. The QEs of poly(2,4-divinyl-3-hexylthiophene-*alt*-2,5-diphenyl-1,3,4-oxadiazole) and poly(2,4-divinyl-3-octythiophene-*alt*-2,5-di-phenyl-1,3,4-oxadiazole) were 43.2 and 34.2%, respectively, which were about 20 and 21 times higher than those of the homopolymers, respectively. The ionization potential of the copolymers between 5.53 and 6.13 eV was appropriated to poly(3-alkylthiophene)s. The high electron affinity of the copolymers (2.71–2.95 eV) made the electrons inject from the cathode more easily. With excellent solubility, low bandgap energy, high QE, and both electron-transporting and hole-transporting abilities, the proposed copolymers might be excellent polymeric materials for applications in polymer light-emitting diodes, light-emitting electrochemical cells, and polymer solar cells. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1392–1399, 2010

Key words: copolymerization; light-emitting diodes (LED); luminescence

INTRODUCTION

Conjugated polymers have drawn much attention in recent years because of their promising applications in electrochromics,[1] biosensors,[2] electrochemical supercapacitors,[3] anticorrosion,[4] polymer thin-film transistors,[5–7] polymer light-emitting diodes,[8,9] polymer photodetectors and polymer solar cells,[10] and so

forth. Among π-conjugated polymers, soluble poly (3-alkylthiophene)s (P3ATs) are the most promising and frequently investigated conjugated systems as a result of their synthetic availability, stability in various redox states, widespread processability, and tunable electronic properties.[11,12] Moreover, it is solubility that enables the easy characterization and understanding of the physical and chemical structure and properties in great detail. The alkyl side-chain modification induces their easy color tuning.[13]

However, for the majority of P3AT derivatives developed so far, the injection and transport of electrons has been much less efficient than those of holes because of their low electron affinities.[14] Therefore, the development of P3AT derivatives with improved electron injection and transporting capability and a balance in the injection of electrons and holes into the emissive layers is necessary to obtain high-efficiency polymer light-emitting diode devices.[15] Materials, such as 1,3,4-oxadiazole or pyridine, with an electron-deficient heteroaromatic ring

always have lower barriers for electron injection from metal cathodes.[16] Thus, copolymers containing 1,3,4-oxadiazole or pyridine in the main chain or in the side groups have been found to be very efficient for increasing electron affinity and, therefore, enhancing their electron-transporting properties.[17]

Actually, in our early research, we prepared poly(3-dodecylthiophene) copolymers, such as poly(3-dodecylthiophene-co-2,5-diphenyl-1,3,4-oxadiazole) (P3DDT–OXD; Scheme 1), via the Grignard metathesis method;[18,19] the results show that P3DDT–OXD had a strong tendency to form a molecular assembly because of the intermolecular interactions and both p-type and n-type doping capabilities. Unfortunately, the yield of P3DDT–OXD was very low because the steric hindrance caused by the alkyl side groups of thiophene inhibited the formation of backbone bonds between the rigid thiophene ring and the 1,3,4-oxadiazole ring. Therefore, simple, high-yielding synthetic protocols for the preparation of conjugated 3-alkylthiophene-*alt*-(heteroaromatic ring) polymer with desired properties are required.

In this study, a novel alternating copolymer with 3-alkylthiophene and oxadiazole (or pyridine) units in an ordered arrangement was synthesized via a bridge of vinyl for the first time. The copolymerization reaction was improved because the distance between the thiophene ring and rigid heteroaromatic ring was extended by the vinyl and the steric hindrance was weakened. A critical length of the alkyls was needed for sufficient solubility and processability of the polymer from solution. The copolymer with hexyl or octyl side chains dissolved quickly in common organic solvents, such as chloroform ($CHCl_3$), tetrahydrofuran (THF), and toluene, at room temperature. On the other hand, the electron-injecting and transporting capability of the copolymer was improved efficiently by the incorporation of electron-accepting oxadiazole or pyridine into alkyl-substituted polythiophene. As a result, a high luminescence quantum yield was obtained.

EXPERIMENTAL

Materials

3-Bromothiophene (99%), 1-bromooctane (98%), 1-bromohexane (95%), $PdCl_2$, and [1,3-bis(diphenylphosphino)propane]dichloronickel(II) (98%) were purchased from Aldrich Chemical Co., Inc. (NJ). Tetrabutylammonium perchlorate (TBAP; 98%) and ferrocene
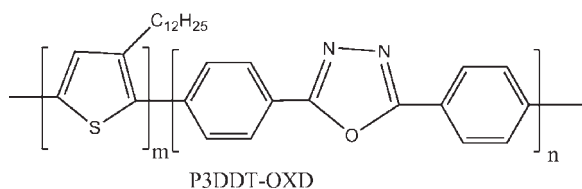
were purchased from Wanqin Chemical Co., Inc., Nanjing, China.

2,5-Bis(*p*-bromophenyl)-1,3,4-oxadiazole and the 2,6-pyridine monomer were synthesized according to literature methods.[20]

3-Hexylthiophene, 3-octylthiophene, poly(3-hexylthiophene) (P3HT), and poly(3-octylthiophene) (P3OT) were synthesized by our group according to literature methods.[21]

NMR

^{1}H-NMR spectra were recorded at 500 MHz on a Bruker DRX-500 (Ettlingen, Germany) with tetramethylsilane as an internal reference and with $CDCl_3$ or acetone-d_6 [$CO(CD_3)_2$] as the solvent.

High-resolution mass spectroscopy (HRMS)

HRMS measurements were taken with a JEOL JMS 700 spectrometer. (Tokyo, Japan).

High-performance liquid chromatography (HPLC)

HPLC was performed with a PerkinElmer Spheri-5 RP-18 column (Boston, MA) (4.6×50 mm i.d., 5 μm), and the compounds were eluted with methanol and detected with an ultraviolet–visible (UV–vis) spectrophotodetector at 254 nm.

Gel permeation chromatography (GPC)

GPC was performed with a PerkinElmer series 200 apparatus (a mixed 10-μm PS column with a length of 750 mm and a refractive-index detector). THF acted as the eluant at a flow rate of 1.0 mL/min at 40°C. The polymer solution was filtered through a 0.45-μm polytetrafluoroethylene filter before it was injected into the column. The calibration was conducted with polystyrene standards.

UV–vis and photoluminescence (PL)

UV–vis spectra of the polymers were recorded on a UV-2201 (Shimadzu, Japan) in a laboratory atmosphere at room temperature.

PL spectra were recorded on a Spex, FL-2T2(Spex, NJ).

Thermogravimetric analysis (TGA)

TGA was performed on a DuPont 9900 analyzer (DuPont Instrument, Wilmington, DE) at a heating rate of 5°C/min under a nitrogen atmosphere.

Cyclic voltammetry (CV)

CV studies were performed with a standard three-electrode cell. A platinum disk was used as a

Scheme 1 Structure of P3DDT–OXD.

counter electrode, and a 213 platinum slice was used as a working electrode. Ag/AgCl ($0.1M$ AgNO$_3$ in acetonitrile) was used as a reference electrode. TBAP (98%) was used as an electrolyte and was recrystallized three times from acetic ether and was dried *in vacuo* at 100°C before each experiment. All experiments were carried out in an air-sealed electrochemical cell. Before each experiment, the cell was purged with a high-purity inert gas for 15 min. Before the start of the measurement, the inert gas was turned to blanket mode. Measurements were recorded with a CHI660B CV voltametric analyzer (Chenhua, Shanghai, China) at a scan rate of 50 mV/s. The working electrode was cleaned before each experiment through sonication in 65% HNO$_3$, followed by subsequent sonication in absolute acetone. The samples were prepared by the dipping of the working electrode in a viscous 10 wt % CHCl$_3$ solution of the polymers and subsequent drying.

Synthesis procedure

The synthesis was carried out in four steps, as shown in Scheme 2: (1) 2,4-dibromomethyl-3-alkyl-thiophene was prepared by the bromomethylation of 3-alkylthiophene, (2) ylide monomer was prepared by the reaction of 2,4-dibromomethyl-3-alkylthiophene with triphenylphosphine, (3) 2,4-divinyl-3-alkylthiophene was prepared by the reaction of the ylide with formaldehyde in 20% NaOH, and (4) the title alternating copolymer was synthesized by the Heck coupling method[22] to polymerize 2,4-divinyl-3-
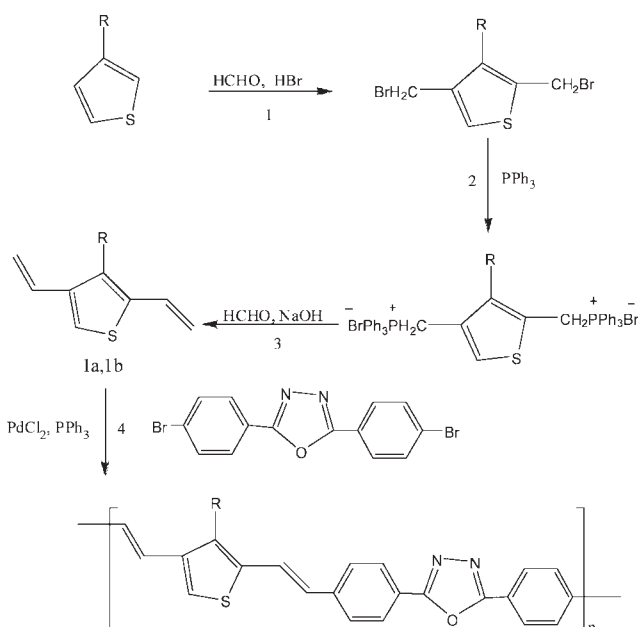
Scheme 2 Synthesis procedure for the monomers and copolymers.

alkylthiophene with 2,5-bis(*p*-bromophenyl)-1,3,4-oxadiazole or 2,6-dibromopyridine monomer.

Synthesis of 2,4-dibromomethyl-3-hexylthiophene

In a round flask that was degassed, 1.20 g of para-formaldehyde was dispersed in 20 mL of acetic acid, 4 mL of 90% phosphoric acid, and 4 mL of concentrated hydrobromic acid to form a white suspension; under a N$_2$ atmosphere, 3.02 g (18.0 mmol) of 3-hexylthiophene was added. The reaction was stirred at 60°C, and during the initial 2 h, about 6 mL of concentrated hydrobromic acid was dropped into it. After 14 h, the product was precipitated in ice water, filtered, and washed with pure water. After crystallization from isopropyl alcohol, a brown solid of 2,4-dibromomethyl-3-hexylthiophene was obtained (4.99 g, yield = 78.3%, purity = 94.5%, HPLC).
^{1}H-NMR (CDCl$_3$, δ): 0.88–0.95 (m, 3H), 1.31–1.40 (m, 6H), 1.55–1.65 (m, 2H), 2.46–2.60 (m, 2H), 4.60 (s, 2H), 4.64 (s, 2H), 7.42 (s, 1H). HRMS: $m/e = 354$ (Calcd: 354). ANAL. Calcd for C$_{12}$H$_{18}$Br$_2$S: C, 40.68%; H, 5.08%; S, 9.03%. Found: C, 40.72%; H, 5.13%; S, 9.07%.

Synthesis of 2,4-dibromomethyl-3-octylthiophene

2,4-Dibromomethyl-3-octyl thiophene was obtained from 3-octylthiophene following a procedure similar to that described for 2,4-dibromomethyl-3-hexylthio-phene. The yield of the brown solid 2,4-dibromo-methyl-3-octylthiophene was 78.0%. The purity (HPLC) was 91.4%.
^{1}HNMR (CDCl$_3$, δ): 0.86–0.90 (m, 3H), 0.93–1.17 (m, 10H), 1.45–1.61 (m, 2H), 2.89–2.99 (m, 2 H), 4.45–4.53 (m, 4H), 7.34 (s, 1H). HRMS: $m/e = 382$ (Calcd: 382). ANAL. Calcd for C$_{14}$H$_{22}$Br$_2$S: C, 43.98%; H, 5.76%; S, 8.38%. Found: C, 44.02%; H, 5.85%; S, 8.37%.

Synthesis of 2,4-divinyl-3-hexylthiophene (1a)

2,4-Dibromomethyl-3-hexylthiophene (3.45 g, 9.21 mmol), PPh$_3$ (5.16 g, 19.7 mmol), and toluene (30 mL) were charged into a dry 100-mL, three-necked, round-bottom flask, and the mixture was stirred at reflux for 4 h. After the mixture was cooled to ambient temperature, the precipitate was obtained and was dried *in vacuo*. The yield of 2,4-di(triphenyl-phosphinebromomethyl)-3-hexylthiophene was about 95%. In a 100-mL, three-necked, round-bottom flask, 8.58 g (9.77 mmol) of 2,4-di(triphenylphosphine-bromomethyl)-3-hexylthiophene, 27 mL of methylene chloride (CH$_2$Cl$_2$), and 7.2 mL of formalin were added. Under an ice–salt bath, 10 mL of 20% NaOH was added dropwise. The mixture was stirred overnight at ambient temperature. Then, the reactant

was poured into water, and the organic CH_2Cl_2 layer was collected, washed with saturated NaCl aqueous and water, dried with $MgSO_4$, and concentrated. After purification by column chromatography (silica, acetic ether/petroleum ether = 1/1), a red brown powder was obtained (1.26 g, yield = 58.6%). The purity (HPLC) was 94.2%.

^{1}H-NMR (acetone-d_6, δ): 0.78–0.88 (m, 3H), 1.26–1.35 (m, 6H), 1.52–1.59 (m, 2H), 2.49–2.53 (m, 2H), 7.48 (s, 1H), 7.49–7.71 (m, 6H). HRMS: m/e = 220 (Calcd: 220). ANAL. Calcd for $C_{14}H_{20}S$: C, 76.36%; H, 9.09%; S, 14.55%. Found: C, 76.31%; H, 9.10%; S, 14.64%.

Synthesis of 2,4-divinyl-3-octylthiophene (**1b**)

1b was obtained from 2,4-dibromomethyl-3-octyl-thiophene following a procedure similar to that described for **1a.** The yield of the red brown solid was 54.3%. The purity (HPLC) was 95.2%.

^{1}H-NMR (acetone-d_6, δ): 0.85–0.88 (m, 3H), 1.20–1.46 (m, 12H), 2.89–2.92 (m, 2H), 7.47 (s, 1H), 7.56–7.73 (m, 6H). HRMS: m/e = 248 (Calcd: 248). ANAL. Calcd for $C_{16}H_{24}S$: C, 77.42%; H, 9.68%; S, 12.90%. Found: C, 77.45%; H, 9.58%; S, 13.98%.

Synthesis and characterization of the copolymer

The synthesis route of the poly(2,4-divinyl-3-alkyl-thiophene) derivatives (P3ATVs) alternating copolymers is shown in Scheme 3.

Poly[(2,4-divinyl-3-hexylthiophene)-*alt*-2,5-bisphenyl-1,3,4-oxadiazole] (P3HTV–OXD or **3aa**)

A 50-mL, three-necked, round-bottom flask was carefully degassed. Triphenylphosphine (PPh$_3$; 65.6 mg, 0.25 mmol), triethylamine (0.7 mL), and *N,N*-dimethylformamide (DMF; 5 mL) were added, and the mixture was stirred. **1a** (220 mg, 1.00 mmol), 2,5-bis(*p*-bromophenyl)-1,3,4-oxadiazole (380 mg, 1.00 mmol), and PdCl$_2$ (5.0 mg) were subsequently added. The reaction mixture was heated at 115°C for 12 h and 140°C for 2 h under a N$_2$ atmosphere. Next, the reactant was cooled and precipitated into an excess of methanol. The obtained polymer was dried *in vacuo* and extracted in a Soxhlet apparatus with hexane to remove short-chain oligomers. The final polymer was dissolved in CHCl$_3$, precipitated again with methanol, and dried *in vacuo*. The yield of the straw-brown solid P3HTV–OXD was 48.1%.

Fourier transform infrared (FTIR; KBr pellet, cm^{-1}): 3055, 2956, 2923, 2852, 1670, 1604, 1546, 1479, 1403, 1261, 1072, 1012, 829, 800, 733. ^{1}H-NMR (acetone-d_6, δ): 0.85–0.87 (m, 3H), 1.10–1.28 (m, 8H), 2.95–2.96 (m, 2H), 7.35 (s, 1H), 7.25–7.27 (m,2H), 7.56–7.59 (m, 2H), 8.01–8.08 (m, 4H), 8.20–8.23 (m, 2H), 8.32–8.34 (d, J = 8.31 Hz, 2H).
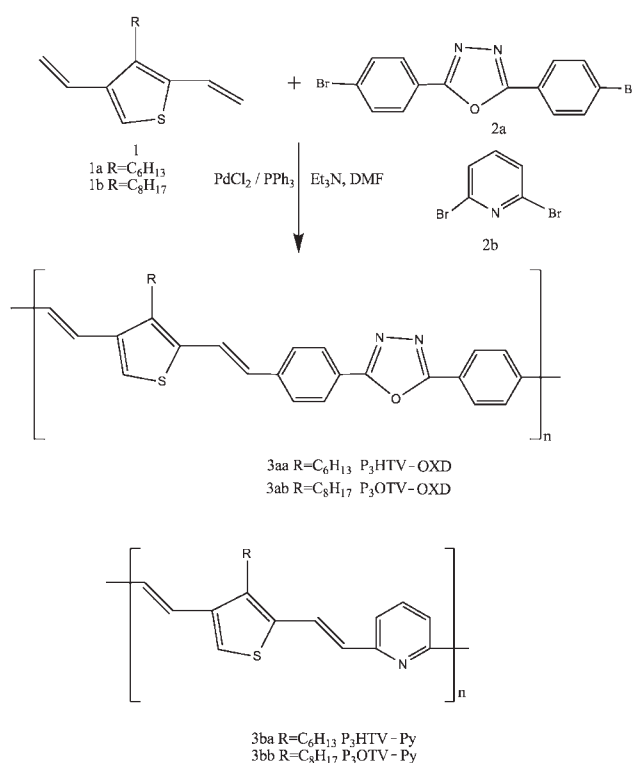
Scheme 3 Copolymerization reaction.

Poly[(2,4-divinyl-3-octylthiophene)-*alt*-(2,5-bisphenyl-1,3,4-oxadiazole)] (P3OTV–OXD or **3ab**)

P3OTV–OXD was obtained following a procedure similar to that described for P3HTV–OXD. The yield of the straw-brown solid was 41.4%.

FTIR (KBr pellet, cm^{-1}): 2923, 2854, 1635, 1382, 1265, 1074, 738. ^{1}H-NMR (acetone-d_6, δ): 0.85–0.87 (m, 3H), 1.25–1.29 (m, 12H), 2.81–2.82 (m, 2H), 7.37 (s, 1H), 7.19–7.21 (m, 2H), 7.63–7.66 (m, 2H), 8.01–8.07 (m, 4H), 8.20–8.23 (m, 2H), 8.32–8.35 (m, 2H).

Poly[(2,4-divinyl-3-hexylthiophene)-*alt*-2,6-pyridine] (P3HTV–Py or **3ba**)

P3HTV–Py was obtained following a procedure similar to that described for P3HTV–OXD, and 2,6-dibromopyridine was chosen instead of oxadiazole. The yield of the fawn powder P3HTV–Py was 33.2%.

FTIR (KBr pellet, cm^{-1}): 2923, 2853, 1658, 1565, 1423, 1382, 1263, 1078, 783. ^{1}H-NMR (acetone-d_6, δ): 0.87–0.88 (m, 3H), 1.02–1.34 (m, 8H), 3.05 (m, 2H), 6.57–6.88 (m, 4H), 7.37 (s, 1H), 7.56–7.71 (m, 3H).

Poly[(2,4-divinyl-3-octylthiophene)-*alt*-2,6-pyridine] (P3OTV–Py or **3bb**)

P3OTV–Py was obtained following a procedure similar to that described for P3HTV–Py. The yield of the fawn solid P3OTV–Py was 31.6%.

TABLE I
Solubility in Organic Solvents and Average Molecular Weights, PDIs, and DPs of the P3ATVs

Polymer	Solvent				GPC			
	CHCl$_3$	THF	Toluene	Xylene	M_w	M_n	DP	PDI
P3HTV–OXD	●	●	●	●	15,286	10,997	37	1.39
P3OTV–OXD	●	●	●	●	12,246	7,333	28	1.67
P3HTV–Py	●	●	●	●	5,864	3,910	22	1.51
P3OTV–Py	●	●	●	●	5,589	3,584	19	1.56

● = soluble; DP = degree of polymerization; M_w = weight-average molecular weight; M_n = number-average molecular weight; PDI = polydispersity index.

FTIR (KBr pellet, cm^{-1}): 2923, 2853, 1658, 1635, 1383, 1261, 1083, 800, 742. ^{1}H-NMR (acetone-d_6, δ): 0.86–0.88 (m, 3H), 1.03–1.33 (m, 12H), 2.95–2.97 (m, 2H), 6.55–6.82 (m, 4H), 7.34 (s, 1H), 7.51–7.82 (m, 3H).

RESULTS AND DISCUSSION

Physical properties

The solubility and molecular weights of the copolymers are shown in Table I. Four copolymers showed good solubility. The average molecular weights and polymerization degrees presented downward trends, attributed to the steric exclusion of the substitution in the side chains. All of the polymers had relatively narrow molecular weight distributions (polydispersity = 1.39–1.67).

In the TGA experiment, all of the polymers exhibited very good thermal stability, losing less than 5% of their weight on heating to approximately 250–310°C under a nitrogen atmosphere. We explained these results by assuming relatively high molecular weights and narrow molecular weight distributions. Obviously, the thermal stability of the polymers is adequate for application in TFTs, light-emitting diodes, and other photoelectronic devices.

Optical characterization

The copolymers were studied by UV–vis and PL spectroscopy. In conjugated polymers, the extent of conjugation directly affects the observed energy of the π–π* transition, which appears as the maximum absorption.[23] The π–π* transitions were exhibited by the absorption with maximum wavelength (λ_{max}) values around 316, 330, 264, and 299 nm for P3HTV–OXD, P3OTV–OXD, P3HTV–Py, and P3OTV–Py, respectively, in CHCl$_3$ solution (1×10^{-7} M), as shown in Figure 1(a). It was interesting to find that the absorption of the four copolymers showed the characteristics of oxadiazole and pyridine and the complete absence of the thiophene optical absorption. This implied that more electrons were leant to oxadiazole or pyridine moieties. The blueshifted λ_{max} absorption of the copolymers was attributed to a relatively low poly-

merization degree and a decreased effective conjugation length, which resulted in a relatively high optical bandgap energy (E_g) compared to that of homopolythiophene.

For the copolymers in the solid state [Fig. 1(b)], the UV absorption peaks became broad, smooth, and redshifted to longer wavelengths compared to those
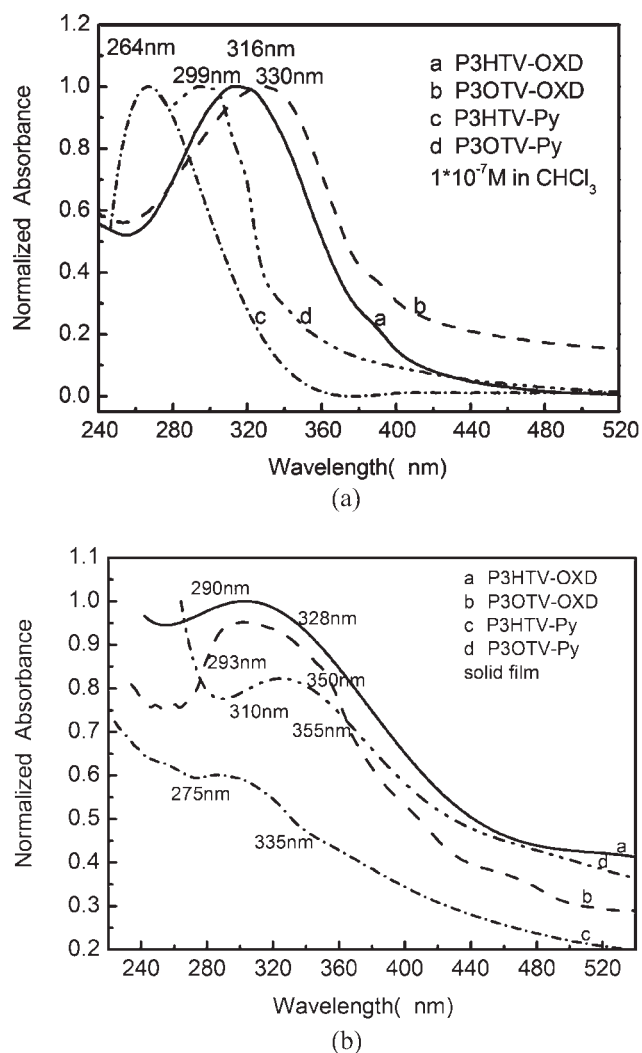

Figure 1 UV–vis absorption spectra of the copolymers (a) in CHCl$_3$ solutions and (b) as solid films.

TABLE II
Optical Data for the Polymers in CHCl$_3$ (1×10^{-7} M) and as Solid Films

| | UV–vis | | | | PL | | |
| | CHCl$_3$ solution | | Solid film | | CHCl$_3$ solution | | |
Polymer	λ_{max} (nm)	E_g (eV)	λ_{max} (nm)	E_g (eV)	λ_{max} for excitation (nm)	λ_{max} for emission (nm)	QE$_S$ (%)
P3HTV–OXD	316	3.30	290–328	2.80	393	402, 420	43.2
P3OTV–OXD	330	3.18	293–350	2.71	332	391	34.2
P3HTV–Py	264	3.62	275–335	2.90	360, 379, 385	410, 435, 460	6.03
P3OTV–Py	299	3.47	310–355	2.79	302, 327	365	2.25
P3HT[a]	371	2.80	438	2.11	372	435	2.17
P3OT[a]	382	2.63	465	1.86	380	443	1.60

[a] These data were taken from Feng.[32]

of the polymers in CHCl$_3$ solution. The results imply that the conformation of P3ATVs in solution would be that of a coil with a small effective conjugation length and that of the solid state would be a more extended structure with more extensive electronic delocalization.[24]

E_g was calculated according to the following formula:

$$\alpha h\nu = B(h\nu - E_g)^n$$

where α is the absorbance coefficient, h is Planck's constant, B is the constant related to the materials, ν is the frequency of light waves, and n is the transition type.[25] The value of n was 0.5 in the case of band transition directly, and the absorbance coefficient amounted to absorbance for the given sample, so the $(h\nu A)^2$–$h\nu$ (where A is absorbancy) curves of the polymers could be drawn. The linearity edge of absorbance was extended and intersected with the energy axis, and the bandgap energy was obtained. The comparison of E_g for the copolymer and corresponding homopolymer are summarized in Table II.
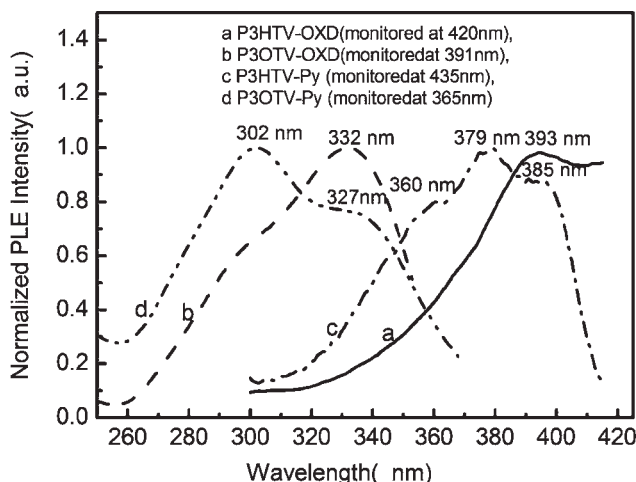
E_g of the copolymer increased because of a relatively low molecular weight and a short effective conjugated length compared with the P3ATs.

PL spectra can provide a good deal of information on the electronic structures of conjugated polymers. The excitation curves of P3OTV–OXD (332 nm) and P3OTV–Py (302, 327 nm) in CHCl$_3$ (1×10^{-7} M) shown in Figure 2 were close to their UV absorption curves. However, the excitation curves of P3HTV–OXD (393 nm) and P3HTV–Py (360, 379, and 385 nm) displayed a characteristic property of the thiophene moiety. This may have been because of the energy transferring from oxadiazole or pyridine moieties to the thiophene backbone, which resulted in the predominant effect of the thiophene moiety under the high-energy laser.

PL emission spectra were recorded by excitation at the excited maximum. Figure 3 shows that the emission maxima of P3HTV–OXD, P3OTV–OXD, P3HTV–Py, and P3OTV–Py were at 420 (402), 391, 435 (410, 460), and 365 (450) nm, respectively, emitting bright blue and blue green. The emission maxima of the copolymers were blueshifted compared
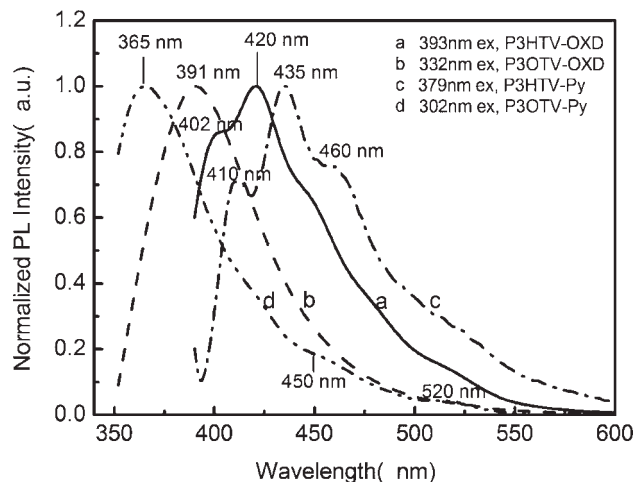

Figure 2 Photoluminescence excitation (PLE) curves of P3ATVs in CHCl$_3$ solutions (1×10^{-7} M).

Figure 3 PL emission curves of P3ATVs in CHCl$_3$ solutions (1×10^{-7} M).
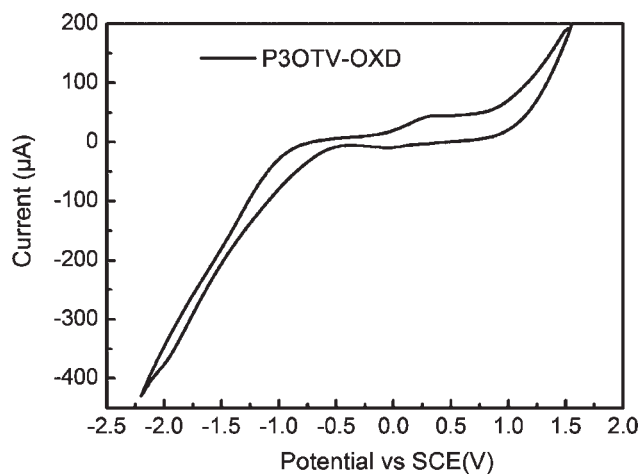
Figure 4 Cyclic voltammogram of P3HTV–OXD in THF (scan: 50 mV/s and 25°C).

with the corresponding homo-P3AT. This result agrees with the experimental conclusion of the UV–vis spectroscopy of the P3ATVs. Stoke's shift of the copolymer was in the range 27–63 nm.

The PL quantum efficiency (QE) is another important feature of the optical properties of conjugated polymers. The elative PL QE[26] of a polymer can be calculated with the following relation:

$$QE_S = QE_R(A_S \times I_S \times \eta_S^2)/(A_R \times I_R \times \eta_R^2)$$

where I is the intensity of the luminescence, A is the absorbency of the intersection point of UV absorptive curves, η is the refractive index, and the subscripts S and R represent the sample and standard materials, respectively. Here, with quinine sulfate (a 10^{-5} M solution in $0.5M$ H_2SO_4) with QE (55.0%) as a standard solution, the PL QE values of the four copolymers and their homopolymers were calculated according to a literature method[27] and are summarized in Table II.

In our previous work, the PL QE of P3HT was lower than 3% in $CHCl_3$ solution. Here, it was very interesting, with the introduction of the electron-transporting moiety of 1,3,4-oxadiazole, the PL QE of P3HTV–OXD increased evidently, a 43.2% QE

was obtained, which was about 20 times higher than that of P3HT in $CHCl_3$ solution. Similarly, a 34.2% QE of P3OTV–OXD was gained, which was about 21 times higher than that of P3OT. The results imply that the formation of a bifunctional copolymer effectively compatibilized the immiscible pair of the two homopolymers, and the donor conjugated polymers being combined with the electron-accepting phases may provide the paths for both hole and electron transporting.[28] The equilibrium of charge transfer along the polymer's backbone took a crucial role in luminescence efficiency. Moreover, a small increased QE of P3HTV–Py and P3OTV–Py was made, only 2.8 and 1.4 times higher than that of P3HT and P3OT, respectively. This indicated that the electron injection and transporting capability of oxadiazole was more efficient than that of pyridine.

Electrochemical study

CV was used to investigate the redox behavior of the polymers and to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. The Ag/AgCl electrode was connected to the electrochemical cell through a salt bridge and was calibrated before each experiment by CV measurement in a ferrocene-containing solution. The potential obtained with Ag/AgCl was converted to it against a saturated calomel electrode. The energy levels were calculated with the following empirical equations:[29]

$$|E_{HOMO}| = E_{onset}^{ox} + 4.68 \text{ eV},$$
$$|E_{LUMO}| = E_{onset}^{red} + 4.68 \text{ eV}$$
$$E_g = E_{LUMO} - E_{HOMO} = E_{onset}^{ox} - E_{onset}^{red}$$

where E_{HOMO} is the highest occupied molecular orbital energy level, E_{LUMO} is the lowest unoccupied molecular orbital energy level, E_{onset}^{ox} is the onset oxidation potential, and E_{onset}^{red} is the onset reduction potential.

Examining the voltammogram of the copolymer P3OTV–OXD (Fig. 4), we observed an increase in the

TABLE III
Orbital Energy Levels and Bandgaps for the P3ATVs

Polymer	E_{onset}^{ox} (V)	E_{HOMO} (eV)	I_p	E_{onset}^{red} (V)	E_{LUMO} (eV)	E_a (eV)	E_g^{el} (eV)	$E_{g,film}$ (eV)	$E_{g,solution}$ (eV)
P3HTV–OXD	1.45	−6.13	6.13	−1.73	−2.95	2.95	3.18	2.80	3.30
P3OTV–OXD	0.85	−5.53	5.53	−1.94	−2.74	2.74	2.79	2.71	3.18
P3HTV–Py	1.15	−5.83	5.83	−1.75	−2.93	2.93	2.90	2.90	3.62
P3OTV–Py	0.95	−5.63	5.63	−1.97	−2.71	2.71	2.92	2.79	3.47
P3HT[a]	1.03	−5.71	5.71	—	—	—		2.11	2.80

I_p = ionization potential; E_a = electron affinity; E_g^{el} = electrochemical band-gap energy of materials; $E_{g,film}$ = optical band-gap energy of materials in solid film; $E_{g,solution}$ = optical band-gap energy of materials in $CHCl_3$ solutions.
  [a] These data were taken from Feng.[32]

oxidation current with an onset at 0.85 V, which corresponded to an ionization potential of 5.53 eV. The corresponding reduction process displayed a small peak related to an n-doping process at -1.97 V with an onset at -1.94 V. This suggested an electron affinity energy level of 2.74 eV, and the electrochemical bandgap of P3OTV–OXD was 2.79 eV. The HOMO and LUMO energies and bandgap for P3HTV–OXD, P3HTV–Py, and P3OTV–Py are shown in Table III. The electrochemical band-gap energy value (E_g^{el}) of materials obtained with the CV method was about 0.00–0.38 eV larger than that obtained with the optical method ($E_{g,film}$) in solid film. Because the charges transferred through the polymer film might have consumed more energy during electrochemical determination.[30] The difference between E_g^{el} and $E_{g,film}$ was in fairly good agreement with the theoretical error (<0.5 eV).[31]

CONCLUSIONS

Using vinyl as a bridge, we successfully synthesized a novel alternating donor–acceptor conjugated copolymer with 3-alkylthiophene and oxadiazole (or pyridine) units in ordered arrangement. The synthesis approach included four steps: bromomethylation, preparation of the ylide monomer, formation of 2,4-divinyl-3-alkylthiophene, and Heck copolymerization. The copolymers were studied with respect to their optical and electrochemical properties. Energy transfer from the heteroaromatic moieties to the polythiophene backbone was suggested. A n-doping process revealed that the alternating copolymer was capable of electron transfer. A remarkable increase in the PL QEs of P3HTV–OXD and P3OTV–OXD compared to their homopolymers indicated that the equilibrium of charge transfer along the polymer backbone took on a crucial role in the luminescence efficiency. On the basis of these results, this novel copolymer with both electron-transporting and hole-transporting abilities might be a promising material for applications in high-efficiency, single- or low-number-layer thin polymer light-emitting diodes.

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