# Synthesis and Characterization of Poly(1,4-bis((*E*)-2-(3-dodecylthiophen-2-yl)vinyl)benzene) Derivatives

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**ABSTRACT:** New amorphous semiconducting copolymers, poly(9,9-dialkylfluorene)-alt-(3-dodecylthienyl-divinylbenzene-3-dodecylthienyl) derivatives (PEFTVB and POFTVB), were designed, synthesized, and characterized. The structure of copolymers was confirmed by H NMR, IR, and elemental analysis. The copolymers showed very good solubility in organic solvents and high thermal stability with high  $T_g$  of 178–185 °C. The weight average molecular weight was found to be 107,900 with polydispersity of 3.14 for PEFTVB and 76,700 with that of 3.31 for POFTVB. UV–vis absorption studies showed the maximum absorption at 428 nm (in solution) and 435 nm (in film)

for PEFTVB and at 430 nm (in solution) and 436 nm (in film) for POFTVB. Photoluminescence studies showed the emission at 498 nm (in solution) and 557 nm (in film) for PEFTVB and at 498 nm (in solution) and 536 nm (in film) for POFTVB. The solution-processed thin-film transistors showed the carrier mobility of  $2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for PEFTVB-based devices and  $2 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for POFTVB-based devices. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 3942–3949, 2010

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**INTRODUCTION** Organic thin-film transistors (OTFTs) based on oligomers and polymers have recently received considerable attention because of their fundamental optoelectronic properties and potential applications for organic integrated circuit sensors, low-cost memories, smart cards, and driving circuits for large area display device applications such as active matrix flat panel liquid crystal displays, organic lightemitting diodes, and electronic paper displays.<sup>1-8</sup> To minimize the manufacturing costs, the field-effect transistor (FET) fabrication process should ideally include a solutionprocessable methods such as spin coating, stamping, and inkjet printing. Improvements in fabrication techniques have enhanced the performance of solution-processed polymer FETs to a point at which they are now approaching the inorganic amorphous silicon thin-film transistors (TFTs) with mobilities of 0.2–0.6  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and on/off current ratios greater than 10<sup>7,9,10</sup>

The conjugated polythiophenes (PTs) are one of the most promising materials due to their good solubility as well as high electrical performance.<sup>11</sup> In spite of these good characteristics, PT-based organic FETs (OFETs) have some disadvantages that hinder their use as replacements for Si transistors; for example, they have low field effect mobilities, high off-currents, poor oxidative stabilities, and low uniformity.<sup>12</sup> To overcome these limitations, a wide range of structural modifications has been tried.<sup>13–28</sup> Especially, stable amorphous polymers have been studied for annealing-free process in OTFT because additional chain alignment processes for high-ordered structure are hard to optimize and control.<sup>29</sup> Our group has reported the high field effect mobility using amorphous polymers containing fluorene and modified thiophene groups.<sup>30–33</sup> Recently, Ackermann et al.<sup>17,34</sup> reported oligothiophenes end-capped with styryl and divinylbenzene end-capped with oligothiophenes, which showed the high field-effect mobility with high stability. Our group has also reported divinylbenzene derivatives which showed not only good mobilities but also good oxidation stability.<sup>35,36</sup>

In the present study, we designed and synthesized the new amorphous semiconducting copolymers, poly(9,9-dialkylfluorene)alt-(3-dodecylthienyl-divinylbenzene-3-dodecylthienyl) derivatives (PEFTVB and POFTVB) for solution-processable OTFTs. The introduction of electron rich and structural rigid divinylbenzene end-capped with thiophene can lead increased interchain stacking. And the long alkyl groups substituted thienyl ring and fluorene can increase the solubility of polymer for solution process.

# EXPERIMENTAL

#### Materials

3-Bromothiophene, 1-bromododecane, *N*-bromosuccinimide (NBS), *n*-butyllithium, 2-isopropoxy-3,3,4,4-tetramethyl-1,3,2-

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dioxaborolane, 1,3-bis(diphenylphosphinopropane)-dichloronickel, *N*,*N*-dimethylformamide (DMF), xylylenebis(triphenylphosphonium bromide), sodium hydride, and tetrakis(triphenylphosphine)palladium (0) were purchased from Aldrich.

# Measurements

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker AM-200 spectrometer. Fourier transform infrared spectrometry (FT-IR) spectra were measured on a Bomen Michelson series FT-IR spectrometer. The melting points were determined with an Electrothermal Mode 1307 digital analyzer. The thermal analysis was performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 20  $^{\circ}$ C min $^{-1}$ . Differential scanning calorimeter was conducted under nitrogen on a TA instrument 2100 DSC. The sample was heated at 20 °C min<sup>-1</sup> from 30 to 250 °C. UV-vis absorption studies were carried out using Perkin-Elmer LAMBDA-900 UV/VIS/IR spectrophotometer. The photoluminescence (PL) spectra were measured on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Molecular weights  $(M_w s)$  and polydispersities of the copolymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (waters highpressure GPC assembly Model M515 pump, u-Styragel columns of HR4, HR4E, and HR5E, with 500 and 100 Å, refractive index detectors, solvent CHCl<sub>3</sub>). Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in a solution of Bu<sub>4</sub>NClO<sub>4</sub> (0.1 M) in acetonitrile at a scan rate of 100 Mv s<sup>-1</sup>. The polymer films were coated on a square Pt electrode  $(0.50 \text{ cm}^2)$  by dipping the electrode into the corresponding solvents and then drying in air. A Pt wire was used as the counter electrode, and an  $Ag/AgNO_3$  (0.1 M) electrode was used as the reference electrode.

#### **Fabrication of the OFET Devices**

Top-contacted OFETs were fabricated on a common gate of highly *n*-doped silicon with a 300-nm-thick thermally grown SiO<sub>2</sub> dielectric layer. Octadecyltrichlorosilane monolayer was treated in toluene solution for 2 h. Films of organic semiconductor were obtained using chlorobenzene solvent. Gold source and drain electrodes were evaporated on the top of semiconductor for the thickness of 100 nm. For all measurements, we used channel length (*L*) of 100  $\mu$ m and channel width (*W*) of 2000  $\mu$ m. The electrical characteristics of the fabricated FETs were measured in air using both Keithley 2400 and 236 source/measure units. Field-effect mobilities were extracted in the saturation regime from the slope of the source-drain current.

# Synthesis

# 3-Dodecylthiophene (1)

3-Dodecylthiophene was synthesized using the procedure reported elsewhere  $^{10}$  with yield of 70%; bp = 104  $^\circ\text{C}/$  1 mmHg.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.26 (s, 1H), 6.95 (m. 2H), 2.65 (t, 2H), 1.63–1.67 (m, 2H), 1.30–1.34 (m, 18H), 0.92 (t, 3H).

#### 2,5-Dibromo-3-didodecylthiophene (2)

NBS (14 g, 79.2 mmol) was added to a solution of compound 1 (10 g, 39.6 mmol) in tetrahydrofuran (THF; 250 mL) at 0 °C. The reaction mixture was stirred for 24 h and poured into water. After extracted with methylene chloride, the organic phase was separated and dried over magnesium sulfate. The product was obtained after a column chromatography using hexane as eluent.

Yield: 12 g (74%). FT-IR (KBr, cm<sup>-1</sup>): 2852–2952 (aliphatic CH<sub>2</sub>), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  6.77 (1H, s), 2.50 (t, 2H), 1.53 (m, 2H), 1.27 (m, 18H), 0.88 (t, 3H).

## 5-Bromo-3-dodecylthiophene-2-carbaldehyde (3)

Compound **2** (5 g, 12.1 mmol) was mixed with dry THF (150 mL). This mixture was added with *n*-butyllithium (4.8 mL, 2.5 M in hexane, 12.1 mmol) dropwise at -78 °C under nitrogen. After the addition was finished, the mixture was stirred for another 1 h and anhydrous *N*,*N*-DMF (0.98 g, 13.4 mmol) was added into solution. The mixture was slowly warmed to room temperature overnight and poured into 2 N HCl. The organic layer was extracted with ethyl acetate and dried over MgSO<sub>4</sub>. The product was purified by column chromatography using hexane and ethyl acetate.

Yield: 2.71 g (62%). FT-IR (KBr, cm<sup>-1</sup>): 2852–2959 (aliphatic CH<sub>2</sub>), 1747 (C=O), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  9.73 (s, 1H), 7.45 (s, 1H), 2.57 (t, 2H), 1.57–1.62 (m, 2H), 1.08–1.31 (m, 18H), 0.66–0.89 (t, 3H).

# 1,4-Bis((E)-2-(5-bromo-3-dodecylthiophen-2-yl) vinyl)benzene (4)

Sodium hydride [0.2 g (8.3 mmol)] was added to the solution of xylylenebis(triphenyl-phosphonium bromide) (2.98 g, 3.7 mmol) in THF (100 mL). The mixture was stirred at room temperature for 3 h and then compound **3** (3 g, 8.3 mmol) was added into this solution. After the mixture was refluxed for 24 h, it was poured into water and extracted with chloroform following drying with MgSO<sub>4</sub>. The solvent was removed via rotary evaporation and the residue was purified by column chromatography (25% CHCl<sub>3</sub> in hexane as eluent). The monomer was recrystallized by ethanol.

Yield: 0.93 g (32%). MS (EI) m/z: 788 (M<sup>+</sup>). FT-IR (KBr, cm<sup>-1</sup>): 3000 (aromatic C—H), 2846–2916 (aliphatic CH<sub>2</sub>),<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.39 (s, 4H), 7.25–7.10 (d, 2H), 6.78–6.72 (d, 2H), 6.74 (s, 2H), 2.53–2.48 (t, 4H), 1.57–1.54 (m, 4H), 1.30–1.11 (m, 36H), 0.90–0.85 (m, 6H). 13C NMR (300 MHz, CDCl<sub>3</sub>, ppm): 142.7, 142.3, 136.2, 127.8, 127.0, 126.6, 121.3, 108.1, 77.4, 76.9, 76.5, 31.9, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.1, 22.6, 14.0 Anal Calcd. for C<sub>42</sub>H<sub>60</sub>Br<sub>2</sub>S<sub>2</sub>:C, 63.96%; H, 7.62% Found: C, 63.90%; H, 7.59%.

# 2,7-Dibromo-9H-fluorene (5)

Bromine (1.23 mL, 24.06 mmol) was added slowly to a mixture of 9H-fluorene (2 g, 12.03 mmol), iodine, and dichloromethane (40 mL) over 30 min at 0 °C in the dark. The mixture was stirred at 0 °C for 1 h and then at room temperature for 2 h. An aqueous Na<sub>2</sub>CO<sub>3</sub> solution (10%) and then water were added to quench the reaction. The organic phase was separated and the aqueous phase was extracted



FIGURE 1 Synthetic scheme of the monomer, PEFTVB and POFTVB.

with dichloromethane. The combined organic phases were dried over  $MgSO_4$  and evaporated under reduced pressure to give a crude solid. The product was washed with ethanol.

Yield: 3.5 g (90%). <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ , ppm):  $\delta$  7.67–7.49 (m, 6H), 3.86 (s, 2H).

## 2,7-Dibromo-9,9-diethyl-9H-fluorene (6)

Compound **5** (5 g, 15.43 mmol) was added to a mixture of 50 mL dimethyl sulfoxide (DMSO) and 12 mL aqueous 50% sodium hydroxide in a round-bottom flask. The reaction mixture quickly turned purple. A catalytic amount of benzyltriethylammonium chloride was added to the reaction mixture followed by addition of 1-bromoethane (5.88 g, 54 mmol). A mechanical stirrer was attached and the reaction mixture was allowed to stir overnight. The resulting mixture was washed with 1 M HCl and water and then dried over MgSO<sub>4</sub>. After the solvent was removed under reduced pressure, the resulting yellow oil was purified by column chromatography using hexane as the eluent.

Yield: 4.1 g (70%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.54–7.44 (m, 6H), 2.02–1.95 (m, 4H), 0.38–0.28 (m, 6H).

# 2,2'-(9,9-Diethyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7)

*n*-Butyllithum (9.26 mL, 23.15 mmol, 2.5 M in hexane) was added over 30 min to a stirring solution of compound **6** (4 g, 10.52 mmol) in dry THF (80 mL) under nitrogen at -78 °C.

The reaction mixture was stirred for another 30 min at -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5.3 mL, 26.30 mmol) was added dropwise to the resulting mixture and stirred overnight at room temperature. The solution was then quenched with water, and the THF was evaporated and then, the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase was washed with water, dried over MgSO<sub>4</sub>, filtered, and the filtrate was washed with hexane.

Yield: 2.49 g (50%). FT-IR (KBr, cm<sup>-1</sup>): 2847–2973 (aliphatic CH<sub>2</sub>), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.00–7.71 (m, 6H), 2.11–2.04 (q, 4H), 1.38 (s, 24H), 0.27–0.22 (t, 6H).

# 2,2'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (8)

This synthesis was carried out by synthetic method used for the synthesis of 2,2'-(9,9-diethyl-9H-fluorene-2,7-diyl)-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (7).

Yield: (50%). FT-IR (KBr, cm<sup>-1</sup>): 2847–2973 (aliphatic CH<sub>2</sub>), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.00–7.71 (m, 6H), 2.11–2.04 (t, 4H), 1.38 (s, 24H), 1.2 (m, 24H), 0.27–0.22 (t, 6H).

# Poly[5-(9,9-diethyl-7-methyl-9H-fluoren-2-yl)-3-dodecyl-2-(4-((E)-2-(3-dodecyl-5-methylthiophen-2-yl)vinyl)styryl) thiophene] (PEFTVB)

Monomer 4 (0.5 g, 0.63 mmol) and compound 7 (0.3 g, 0.63 mmol) were dissolved in 20 mL dry toluene and then a



FIGURE 2 <sup>1</sup>H NMR spectra of PEFTVB (top) and POFTVB (bottom).

solution of 2 M K<sub>2</sub>CO<sub>3</sub> (5 mL) was added to it, and the mixture was purged under nitrogen for 30 min. Afterward, 10 mol % (0.073 g) tetrakis(triphenyl-phosphine) palladium (0) were added into the reaction mixture. The reaction mixture was at 80 °C for 72 h under N<sub>2</sub>. The reaction mixture was then poured into a solution of 5% HCl and MeOH. After column chromatography using toluene as eluent, the polymer was precipitated and purified by soxhlet extraction (methanol and toluene).

Yield: 0.11 g (20%). FT-IR (KBr, cm<sup>-1</sup>): 3000 (aromatic C—H), 2853–2980 (aliphatic CH<sub>2</sub>), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  7.69–7.49 (m, 4H), 7.39–7.36 (m, 7H), 7.18–7.12 (s, 1H), 6.92–6.71 (m, 4H), 2.60 (b, 4H), 2.01 (b, 4H), 1.17 (b, 40H), 0.80–0.78(m, 6H), 0.38–0.30(m, 6H). ELEM. ANAL Calcd. for C<sub>59</sub>H<sub>76</sub>S<sub>2</sub>:C, 83.43%; H, 9.01%. Found: C, 83.07%; H, 9.36%.

# Poly[3-dodecyl-2-(4-((E)-2-(3-dodecyl-5-(7-methyl-9,9dioctyl-9H-fluoren-2-yl)thiophen-2-yl)vinyl)styryl)-5methylthiophene] (POFTVB)

Monomer 4 (0.5 g, 0.63 mmol) and 9,9-dioctyl-9H-fluorene-2,7-diyldiboronic acid (0.3 g, 0.63 mmol) were dissolved in 20 mL dry toluene, and a solution of 2 M K<sub>2</sub>CO<sub>3</sub> (4 mL) was added to it. The mixture was then purged under nitrogen for 30 min. Afterward, 10 mol % (0.073 g) tetrakis(triphenylphosphine) palladium (0) were added into the reaction mixture. The reaction mixture was at 80 °C for 72 h under N<sub>2</sub>. The reaction mixture was then poured into a solution of 5% HCl and MeOH. After column chromatography using toluene as eluent, the polymer was precipitated and purified by soxhlet extraction (methanol and toluene).

Yield: 0.48 g (75%). FT-IR (KBr, cm<sup>-1</sup>): 3000 (aromatic C—H), 2815–2923 (aliphatic CH<sub>2</sub>), <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,

ppm):  $\delta$  7.8–7.75 (m, 3H), 7.48–7.36 (m, 8H), 7.02–6.96 (m, 1H), 6.93–6.81 (m, 4H), 2.70 (b, 2H), 2.02 (b, 2H), 1.66 (b, 4H), 1.27–1.11 (m, 60H), 0.90–0.82(m, 16H). ELEM. ANAL Calcd. for C<sub>71</sub>H<sub>100</sub>S<sub>2</sub>:C, 83.98%; H, 10.23%.

## **RESULTS AND DISCUSSION**

#### Synthesis and Characterization

The synthetic scheme of monomer and polymers are given in Figure 1. 1,4-Bis((*E*)-2-(5-bromo-3-dodecylthiophen-2yl)vinyl)benzene was prepared with Witting reaction of xylenebis(triphenyl-phosphonium bromide) and 5-bromo-3dodecylthiophene-2-carbaldehyde, which was obtained by selective formylation on 2-position of 2,5-dibromo-3-didodecylthiophene. Diboronic ester monomers were prepared by the boration of 2,7-dibromo-9,9-diethyl fluorene and 2,7dibromo-9,9-dioctylfluorene after lithiation. After polymerization, end-capping was carried out with bromobenzene following benzene boronic acid. The structure of synthesized copolymers was confirmed by <sup>1</sup>H NMR, IR, and elemental analysis. Figure 2 shows <sup>1</sup>H NMR spectra of polymers PEFTVB and POFTVB. The structure was confirmed by the aliphatic methylene protons of fluorene at 2.0 ppm and thiophene at 2.7 ppm as well as the integration ratio of aromatic protons and aliphatic protons.

The obtained copolymers PEFTVB and POFTVB are good soluble in common organic solvents such as chloroform and toluene. The good solubility of the synthesized polymers facilitates to make the solution processed thin films for electronic and optoelectronic applications. The  $M_{\rm w}$ s and polydispersity indexes of the polymers were determined with GPC using polystyrene as the standard. The weight average  $M_{\rm w}$  of PEFTVB and POFTVB were found to be 107,900 with polydispersity of 3.14 and 76,700 with that of 3.31 as shown in Table 1.

The thermal stability of the polymers was investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry under the nitrogen atmosphere. As shown in the Figure 3, the 5% weight loss was observed at 404 °C for PEFTVB and 414 °C for POFTVB. The glass transition temperatures ( $T_g$ ) of the copolymers were found to be 183 °C for PEFTVB and 178 °C for POFTVB. This shows that PEFTVB and POFTVB have not only amorphous nature but also good thermal stability.

TABLE 1	Photophysical	Properties	of the	Polymers
PEFTVB	and POFTVB			

Polymers	Yield (%)	<i>M</i> <sub>n</sub> <sup>a</sup>	<i>M</i> <sub>w</sub> <sup>a</sup>	PDI	T <sub>d</sub> (°C) <sup>I</sup>
PEFTVB	20	34,300	107,900	3.14	404
POFTVB	75	23,200	76,700	3.31	414

<sup>a</sup> Determined by GPC, relative to polystyrene standards.

<sup>b</sup> Temperature resulting in 5% weight loss based on initial weight.



FIGURE 3 TGA of PEFTVB and POFTVB.

# **Photochemical Properties of the Polymers**

UV-vis absorption and PL spectra of the polymers PEFTVB and POFTVB were recorded both in solution (chloroform) and in film state and shown in the Figure 4. From the absorption studies, the maximum absorption was observed



**FIGURE 4** UV-vis absorption and PL spectra of (a) PEFTVB and (b) POFTVB in solution and in film.

TABLE 2 Photochemical Properties and Energy Levels of Polymers PEFTVB and POFTVB

	Solution, $\lambda_{max}$ (nm) <sup>a</sup>		Film, $\lambda_{max}$ (nm) <sup>b</sup>		
Polymers	Absorption	PL Emission	Absorption	PL Emission	( <i>E</i> g <sup>e</sup> ) (eV)
PEFTVB	428	498	435	557	5.35/3.04 (2.31)
POFTVB	430	496	436	536	5.40/3.05 (2.35)

<sup>a</sup> Measured in chloroform solution.

<sup>b</sup> Measured in thin film onto quartz plates.

<sup>c</sup> Calculated using the empirical equation:  $I_{P}$  (HOMO) =  $-(E_{onset,ox} + 4.8)$  (eV).

<sup>d</sup> Calculated from the HOMO level and optical band gap.

 $^{\rm e}$  The optical band gap,  $E_{\rm g}$ , is taken as the absorption onset (value in parentheses) of the UV-vis spectrum of the polymer film.

at 428 nm (in solution) and 435 nm (in film) for PEFTVB and at 430 nm (in solution) and 436 nm (in film) for POFTVB. It is observed that the absorption spectra of the polymers are redshifted and broadened than that of solution, which is attributed to planarization of backbone and intermolecular  $\pi$  stacking between polymer chains. In the PL spectra, the PL maximum was observed at 498 nm (in solution) and 557 nm (in film) for PEFTVB and at 496 nm (in solution) and 536 nm (in film) for POFTVB. It is observed that PL emission of PEFTVB containing diethyl fluorene shows the large Stoke's shift than that of the POFTVB containing dioctyl fluorene, resulting in difference of geometrical structures in the ground state and the excited state. Moreover, the large redshift in PL emission was observed in film for PEFTVB, which may be attributed to enhanced intermolecular interaction of planar excited state.

#### **Electrochemical Properties**

The electrochemical properties of the polymers PEFTVB and POFTVB were investigated through CV studies. The CV measurements were carried out using ferrocene (4.8 eV below the vacuum level) as the standard and the results are listed in Table 2. From the oxidation process, the highest occupied molecular orbital (HOMO) energy levels of PEFTVB and POFTVB were estimated to be 5.35 and 5.40 eV, respectively, which is about 0.4 eV higher than that of regioregular P3HT, thus showing a greater stability against the oxidation doping. The lowest unoccupied molecular orbital (LUMO) energies of



FIGURE 5 The typical transfer and output curves of OTFT devices based on (a), (b) PEFTVB and (c), (d) POFTVB.

 TABLE 3
 The Device Characteristics of Solution-Processed

 OTFTs
 Based on the Polymers

Polymer	Surface Treatment	Solution-Processed			
		$\mu$ (cm²/V s)	I <sub>on</sub> /I <sub>off</sub>	<i>V</i> <sub>t</sub> (V)	
PEFTVB	ODTS	$2 \times 10^{-4}$	200	-20	
POFTVB	ODTS	$2   imes  10^{-5}$	50	-20	

these copolymers were estimated from the optical band gaps (taken as the absorption onsets of the UV-vis spectra of the polymer films) and the HOMO energies. The estimated optical band gaps of PEFTVB and POFTVB were 2.31 and 2.35 eV, respectively.

# FET (OTFT) Characteristics

OTFTs based on PEFTVB and POFTVB were fabricated by solution process. Substrates were modified with ODTS (octadecyltrichloride). The films of organic semiconductors were spincoated at 2000 rpm from 0.5 wt % chlorobenzene solution. On top of the thin-film surface, gold was deposited through a shadow mask to give the source and drain. The OTFT characteristics were determined under the normal ambient. All the OTFTs based on the polymers PEFTVB and POFTVB were found to exhibit typical p-channel characteristics. Figure 5 shows the typical transfer and output curves of the OTFT devices based on these polymers under the normal ambient. The carrier mobility was calculated in the saturation regime from the slope of a plot of the square root of the drain current versus the gate voltage  $(V_{\rm G})$  by fitting the data to the following equation:  $I_{\rm DS} = (WC_i/2L)\mu(V_{\rm G}-V_{\rm th})^2$  where  $I_{\rm DS}$  is the drain current,  $\mu$  is the carrier mobility and  $V_{\rm th}$  is the threshold voltage. The hole mobility was found to be  $2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with the on/off ratio of 200 for PEFTVB-based devices and 2  $\times~10^{-5}~\text{cm}^2~\text{V}^{-1}~\text{s}^{-1}$  with the on/off ratio of 50 for POFTVBbased devices as shown in Table 3. Because the films of PEFTVB and POFTVB were very homogeneous and possessed no ordered crystal domains, the low mobility of polymers may be resulted from the amorphous nature of the molecular design and/or improper optimization of device conditions.<sup>30</sup> OTFTs based on PEFTVB with diethylfluorene showed slightly increased hole mobility than the devices based on POFTVB with dioctylfluorene. This can be explained by the large redshift in the emission of PEFTVB film due to enhanced intermolecular interaction of planar excited state.

#### CONCLUSIONS

We developed new amorphous copolymers PEFTVB and POFTVB via Pd-catalyzed Suzuki coupling reaction. The obtained polymers have good solubility and high thermal stability with high  $T_{\rm g}$  of 178–185 °C. The polymers have HOMO levels of -5.35 to -5.40 eV, resulting in good oxidation stability. The solution-processed OFETs based on PEFTVB and POFTVB were fabricated and characterized. The as-prepared OFET with PEFTVB as the active layer showed a hole mobility of  $2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, while POFTVB-based device showed that of  $2 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>; the low mobil-

ity of device may be resulted from amorphous nature of the obtained polymers. OTFT based on PEFTVB with diethylfluorene showed slightly increased hole mobility than that of the device based on POFTVB with dioctylfluorene, resulted from the enhanced intermolecular interaction of planar excited state.

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