

Synthesis, Characterization, and Photophysical Properties of Novel Poly(*p*-phenylene vinylene) Derivatives with Conjugated Thiophene as Side Chains

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ABSTRACT: Two novel poly(*p*-phenylene vinylene) (PPV) derivatives with conjugated thiophene side chains, P1 and P2, were synthesized by Wittig-Horner reaction. The resulting polymers were characterized by ¹H-NMR, FTIR, GPC, DSC, TGA, UV-Vis absorption spectroscopy and cyclic voltammetry (CV). The polymers exhibited good thermal stability and film-forming ability. The absorption spectra of P1 and P2 showed broader absorption band from 300 to 580 nm compared with poly[(*p*-phenylene vinylene)-alt-(2-methoxy-

5-octyloxy-*p*-phenylene vinylene)] (P3) without conjugated thiophene side chains. Cyclic voltammograms displayed that the bandgap was reduced effectively by attaching conjugated thiophene side chains. This kind of polymer appears to be interesting candidates for solar-cell applications. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 3387–3394, 2011

Key words: conjugated polymers; poly(*p*-phenylene vinylene); photophysics; synthesis

INTRODUCTION

Harvesting energy directly from sunlight using photovoltaic cells is a very important way to address growing global energy needs with a renewable resource. For this purpose, the polymer solar cells have received a great deal of attention based on their potential applications as flexible, low cost, lightweight and solution processable devices.¹ Poly(*p*-phenylene vinylene) (PPV) and its derivatives are one of the most promising classes of conjugated polymers for polymer solar cells due to their easy modification of chemical structures and good film-forming and optical properties. Recently, Zhang et al.² reported a bulk heterojunction solar cell based on poly(2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene) (MEH-PPV) and 6,6-phenyl C₆₁ butyric acid methyl ester (PCBM) with a power conversion efficiency (PCE) of 1.3%. To improve the device performance, many efforts have been done in optimizing device architectures and modifying chemical structures of PPVs.^{3,4} For chemical modification, works mostly focused on improving regioregularity,⁵ side chain functionalizations,⁶ and polymerization with other monomers.⁷ Recently, Li and coworkers demonstrated that conjugated side chains could

broaden the absorption spectrum and improve the hole mobility of polythiophene efficiently.^{8,9} But the effect of conjugated thiophene side chain structure on photophysical properties of PPVs is less studied.

To investigate the effect of conjugated side chains on the photophysical properties of PPVs and explore new photovoltaic materials, we synthesized two novel PPV derivatives with conjugated thiophene side chains, P1 and P2, using Wittig-Horner reaction. The thermal, photophysical, and electrochemical properties of the polymers were investigated in detail.

EXPERIMENTAL

Materials

1,4-Dibromo-*p*-xylene (98+%), tri-*n*-butyltin chloride (96%), and 1-bromooctane (CP) were purchased from Alfa Aesar and Shanghai Medical Company (China). Thiophene (98%), 2-formylthiophene (98%), and Pd(PPh₃)₄ (98%) were obtained from Pacific Chemical Source Company (China). Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. *N,N*-Dimethylformamide (DMF) was dried over molecular sieves and freshly distilled prior to use. The other materials were of common commercial grades and used as received.

Measurements

¹H-NMR spectra were collected on a Bruker AVANCE 400 spectrometer. FTIR spectra and ultraviolet-visible

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(UV-Vis) absorption spectra were obtained on Perkin-Elmer Spectra One and Lamada 25 spectrometer, respectively. The elemental analysis of all monomers and polymers were performed with a Perkin-Elmer 2400 analyzer for C, H, S determination. Differential scanning calorimetric measurements (DSC) of the polymers were performed under nitrogen at a heating rate of 10°C/min with PA DSCQ10 instrument. Thermogravimetric analyses (TGA) were performed under nitrogen at a heating rate of 20°C/min with WRT-3P analyzer. The weight-average molecular weights (\bar{M}_w) of the polymers were determined using Waters1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Photoluminescence (PL) spectra were obtained using Perkin-Elmer LS-50 luminescence spectrometer. The electrochemical cyclic voltammetry (CV) was conducted on an EG and G Princeton Applied Research Model 273 potentiostat/galvanostat equipped with electrochemical analysis system software. Platinum wires were used as both the counter and working electrodes, and saturated calomel electrode (SCE) was used as a reference electrode. Thin films of the polymers on platinum electrodes were prepared by dipping the electrode into a 0.2–1.0 wt % polymer solution. The measurements were conducted in a 0.1 mol L⁻¹ Bu₄NClO₄ acetonitrile solution at a scan rate of 50 mV/s at room temperature.

Synthesis of monomers and polymers

The synthesis routes of the monomers and resulting polymers are shown in Scheme 1.

2,5-Dibromoterephthalaldehyde (1)

Compound 1 was synthesized according to the reported literature.¹⁰

IR (KBr, cm⁻¹): 3074 (ν_{CH}), 1688 ($\nu_{\text{C=O}}$), 1448 ($\nu_{\text{C=C}}$), 1342, 1158, 1060. ¹H-NMR (CDCl₃) δ : 10.34 (s, 2 H, -CHO), 8.16 (s, 2 H, benzene-H). Anal. Calcd. for C₈H₄Br₂O₂: C, 32.91%; H, 1.38%. Found: C, 32.60%; H, 1.52%.

(E)-1,2-Bis(2-thienyl)ethylene (2)

Compound 2 was synthesized by an adapted literature procedure.¹¹

IR (KBr, cm⁻¹): 3075 (ν_{CH}), 1433, 1281, 1216, 1182, 1073, 1038 (ν_{CS}), 943. ¹H-NMR (CDCl₃) δ : 7.18 (d, 2 H, thiophene-H), 7.05 (s, 2 H, -CH=CH-), 7.04 (d, 2 H, thiophene-H), 6.99 (m, 2 H, thiophene-H). Anal. Calcd. for C₁₀H₈S₂: C, 62.50%; H, 4.17%; S, 33.33%. Found: C, 62.27%; H, 4.09%; S, 33.06%.

2-((E)-2-(5-Octylthiophen-2-yl)-vinyl) thiophene (3)

8.0 mL (20 mmol) of *n*-BuLi (2.5M in hexane) was slowly dropped to a stirred solution of (E)-1,2-bis(2-

thienyl)ethylene (2) (3.84 g, 20 mmol) in 120 mL dry THF at -78°C under the protection of nitrogen. After stirring for 3 h, 1-bromooctane (3.86 g, 20 mmol) was added and allowed to warm to room temperature. After 24 h, the reaction mixture was poured into 200 mL cool water and extracted three times with 50 mL Et₂O. The organic phase was washed with water, dried with anhydrous MgSO₄, filtered, and concentrated. Purification was carried out via silica gel column chromatography, using petroleum ether (60–90°C) as the eluent. After concentration, a white solid of compound **3** was obtained (3.29 g, yield 54%, mp 49–50°C).

IR (KBr, cm⁻¹): 2955 (ν_{CH}), 2923 (ν_{CH}), 2850 (ν_{CH}), 1465, 1426, 1384, 1273, 1226, 1184, 938. ¹H-NMR (CDCl₃) δ : 7.16 (d, 1 H, thiophene-H), 7.00–6.94 (m, 4 H, thiophene-H and -CH=CH-), 6.90 (d, 1 H, thiophene-H), 6.65 (d, 1 H, thiophene-H), 2.80 (t, 2 H, -CH₂-), 1.69 (m, 2 H, -CH₂-), 1.44–1.28 (m, 10 H, -CH₂-), 0.90 (t, 3H, -CH₃). Anal. Calcd. for C₁₈H₂₄S₂: C, 71.05%; H, 7.90%; S, 21.05%. Found: C, 71.92%; H, 7.99%; S, 22.12%.

5-((E)-2-(5-Octylthiophen-2-yl)-vinyl)-2-tributylstannyl-thiophene (4)

A solution of 2-((E)-2-(5-octylthiophen-2-yl)-vinyl) thiophene (3) (1.52 g, 5 mmol) in dry THF (30 mL) was cooled to -78°C and then *n*-BuLi (2.2 mL, 5.5 mmol, 2.5M in hexane) was slowly added. After stirring at -78°C for 3 h, tri-*n*-butyltin chloride (1.80 g, 5.5 mmol) was added in one portion to the reaction mixture at the same temperature. The solution was stirred at -78°C for 30 min, slowly warmed to room temperature, stirred for 24 h, and then quenched by the addition of water. The reaction mixture was extracted with hexane, and the organic layer was dried over anhydrous MgSO₄ and filtered. The solvent was removed by evaporation under reduced pressure. The crude product was obtained in 90% yields as yellow oil and could be used for further reactions without any purification.

¹H-NMR (CDCl₃) δ : 7.10 (d, 1 H, thiophene-H), 7.04(d, 1 H, thiophene-H), 6.97 (s, 2 H, -CH=CH-), 6.82 (d, 1 H, thiophene-H), 6.64 (d, 1 H, thiophene-H), 2.79 (t, 2 H, -CH₂-), 1.70 (m, 2 H, -CH₂-), 1.39–1.29 (m, 28 H, -CH₂-), 0.90(m, 12 H, -CH₃).

2,5-Bis(5-((E)-2-(5-octylthiophen-2-yl)vinyl)thiophen-2-yl)terephthalaldehyde (5)

Tetrakis(triphenylphosphine) palladium(0) (0.05 g, 1.0 mol %) was added in one portion to a stirred solution of **1** (0.64 g, 2.2 mmol) and **4** (2.61 g, 4.5 mmol) in dry DMF (30 mL) under an atmosphere of nitrogen. After stirring at room temperature for 30 min, the mixture was heated to 80°C and stirred for 24 h, and then cooled to room temperature,

(m, 2 H), 1.45–1.27 (m, 10 H), 0.89 (t, 3H). Anal. Calcd. for $C_{44}H_{50}O_2S_4$: C, 71.54%; H, 6.77%; S, 17.34%. Found: C, 71.97%; H, 6.90%; S, 17.65%.

1-Methoxy-4-(octyloxy)benzene (6)

A solution of 4-methoxyphenol (2.48 g, 20 mmol), 1-bromooctane (3.86 g, 20 mmol), and potassium carbonate (3.04 g, 22 mmol) in DMF (60 mL) was stirred at 140°C overnight under the protection of nitrogen. The mixture was then poured into 200 mL distilled water after being cooled to room temperature. The crude product was washed several times with aqueous sodium carbonate solution and water then recrystallized from isopropanol. After filtration and drying in a vacuum oven, a white paste-like crystal was obtained (4.11 g, yield 87%, mp 34–35°C).

$^1\text{H-NMR}$ (CDCl_3) δ : 6.71 (s, 4 H, benzene-H), 3.80 (t, 2 H, $-\text{OCH}_2-$), 3.62 (s, 3 H, $-\text{OCH}_3$), 1.76 (m, 2 H, $-\text{CH}_2-$), 1.42–1.28 (m, 10 H, $-\text{CH}_2-$), 0.90 (t, 3 H, $-\text{CH}_3$).

1,4-Bis(bromomethyl)-2-methoxy-5-(octyloxy)benzene (7)

A mixture of 1-methoxy-4-(octyloxy)benzene (6) (2.36 g, 10 mmol), paraformaldehyde (1.05 g, 35 mmol), and sodium bromide (3.50 g, 34 mmol) in 15 mL glacial acetic acid was stirred for 30 min in an ice bath. Then a mixture of sulfuric acid (3.3 mL, 33 mmol) and isochoric glacial acetic acid (3.3 mL) was carefully added. After stirring at 70°C for 24 h, the resulting mixture was cooled to room temperature and then poured into water. The resulting gray precipitate was collected by filtration and washed with water. The product was obtained as white crystals after recrystallized from hexane (3.29 g, yield 78%, mp 82–83°C).

$^1\text{H-NMR}$ (CDCl_3) δ : 7.00 (s, 2 H, benzene-H), 4.72 (s, 4 H, $-\text{CH}_2\text{Br}$), 4.06 (t, 2 H, $-\text{OCH}_2-$), 3.84 (s, 3 H, $-\text{OCH}_3$), 1.80–1.64 (m, 2 H, $-\text{CH}_2-$), 1.38–1.25 (m, 10 H, $-\text{CH}_2-$), 0.90 (t, 3 H, $-\text{CH}_3$).

1,4-Bis(diethyl-phosphonate-methyl)-2-methoxy-5-(octyloxy)benzene (8)

A mixture of 1,4-bis(bromomethyl)-2-methoxy-5-(octyloxy)benzene (2.11 g, 5 mmol) and triethylphosphite (4.15 g, 25 mmol) was stirred at 150°C for 5 h. The excess triethylphosphite was then distilled off under reduced pressure. The product was obtained as a colorless sticky oil and used directly without further purification.

$^1\text{H-NMR}$ (CDCl_3) δ : 6.93 (s, 1 H, benzene-H), 6.90 (s, 1 H, benzene-H), 4.05 (m, 8 H, $-\text{OCH}_2-$), 3.93 (t, 2 H, $-\text{OCH}_2-$), 3.79 (s, 3 H, $-\text{OCH}_3$),

3.26–3.18 (m, 4 H, $-\text{CH}_2-$), 1.78–1.72 (m, 2 H, $-\text{CH}_2-$), 1.44–1.28 (m, 10 H, $-\text{CH}_2-$), 1.25 (t, 12 H, $-\text{CH}_3$), 0.90 (t, 3 H, $-\text{CH}_3$).

Synthesis of P1

P1 was synthesized by a typical Wittig-Horner reaction.¹² In a 50-mL flask, compound 5 (0.37 g, 0.5 mmol), 8 (0.27 g, 0.5 mmol), and anhydrous THF (30 mL) were mixed under nitrogen. Potassium *tert*-butoxide (0.17 g, 1.5 mmol) was slowly added, and the solution was stirred at room temperature under nitrogen for 24 h. The resulting solution was poured into 100 mL of methanol and then the precipitate was filtered. The crude product was dried under vacuum and then fractionated in a Soxhlet apparatus using the following sequence of three solvents: methanol, hexane, and chloroform. The title polymer was recovered from the chloroform fraction by rotary evaporation. The solid was dried under vacuum for 24 h. 0.24 g P1 (yield 46%) was obtained.

IR (KBr, cm^{-1}): 3060 (ν_{CH} aromatic), 2955 (ν_{CH}), 2923 (ν_{CH}), 2851 (ν_{CH}), 1578 ($\nu_{\text{C}=\text{C}}$), 1411 ($\delta_{\text{C}-\text{H}}$), 966 (γ_{CH} *trans*-vinylene). $^1\text{H-NMR}$ (CDCl_3) δ : 7.74–7.70 (m, 4 H), 7.53–7.52 (m, 2 H), 7.25–6.82 (m, 14 H), 4.32–3.70 (m, 5 H), 2.87–2.77 (m, 4 H), 2.04–1.37 (m, 36 H), 1.04–0.87 (m, 9 H). Anal. Calcd. for $(\text{C}_{61}\text{H}_{74}\text{O}_2\text{S}_4)_n$: C, 75.77%; H, 7.66%; S, 13.25%. Found: C, 74.27%; H, 7.60%; S, 13.36%.

Synthesis of P2

P2 was synthesized from compounds 5, 8, and terephthalaldehyde by the similar procedure as that for the synthesis of P1 (yield 67%).

IR (KBr, cm^{-1}): 3060 (ν_{CH} aromatic), 2954 (ν_{CH}), 2924 (ν_{CH}), 2853 (ν_{CH}), 1581 ($\nu_{\text{C}=\text{C}}$), 1413 ($\delta_{\text{C}-\text{H}}$), 963 (γ_{CH} *trans*-vinylene). $^1\text{H-NMR}$ (CDCl_3) δ : 7.84–7.34 (m), 7.14–6.66 (m), 4.32–3.60 (m), 2.87–2.77 (m), 2.04–1.37 (m), 1.04–0.87 (m). Anal. Calcd. for $[(\text{C}_{61}\text{H}_{74}\text{O}_2\text{S}_4)_{0.4} + (\text{C}_{25}\text{H}_{30}\text{O}_2)_{0.6}]_n$: C, 75.91%; H, 7.64%; S, 8.22%. Found: C, 74.32%; H, 7.81%; S, 7.94%.

Synthesis of P3

Poly[*p*-phenylene vinylene]-alt-(2-methoxy-5-octyloxy-*p*-phenylene vinylene)] (P3) was synthesized from compound 8 and terephthalaldehyde by the similar procedure as that for the synthesis of P1 (yield 68%).

IR (KBr, cm^{-1}): 3060 (ν_{CH} aromatic), 2954 (ν_{CH}), 2924 (ν_{CH}), 2853 (ν_{CH}), 1580 ($\nu_{\text{C}=\text{C}}$), 1422 ($\delta_{\text{C}-\text{H}}$), 963 (γ_{CH} *trans*-vinylene). $^1\text{H-NMR}$ (CDCl_3) δ : 7.48–7.42 (m, 4 H), 7.13–7.03 (m, 6 H), 4.03–3.73 (m, 5 H), 1.85–1.16 (m, 12 H), 1.04–0.87 (m, 3 H). Anal. Calcd.

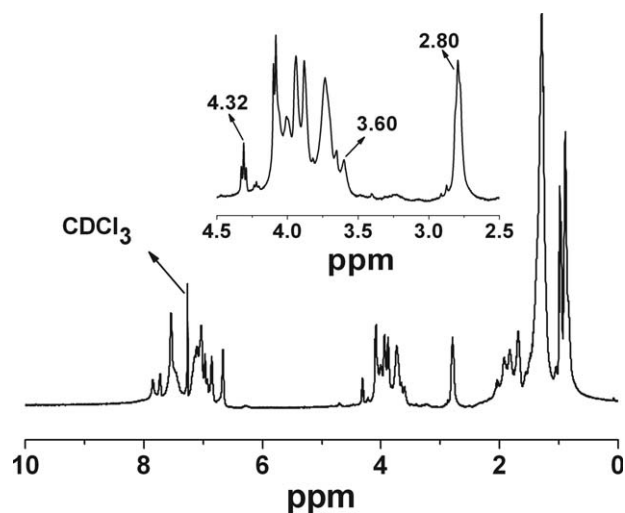


Figure 1 $^1\text{H-NMR}$ spectrum of the polymer P2 in CDCl_3 .

for $(\text{C}_{25}\text{H}_{30}\text{O}_2)_n$: C, 76.14%; H, 7.61%. Found: C, 76.27%; H, 7.66%.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic routes to the monomers and the corresponding polymers were illustrated in Scheme 1. Compound **1** was synthesized in 40% yield by oxidation of 2,5-dibromo-*p*-xylene. Monomer **2** was synthesized via McMurry coupling, then followed by reaction with *n*-butyl lithium and 1-bromooctane to give the compound **3**. Monomer **5** was synthesized by using **4** and **1** via Stille coupling reaction in 45% yields. The basic strategy employed for the synthesis of the polymers was based on Wittig-Horner reaction. To investigate the effect of conjugated thiophene side chains on photophysical and electrochemical properties, P3 without conjugated thiophene side chains was also synthesized under the same condition.

The chemical structures of the polymers were characterized by $^1\text{H-NMR}$ and FTIR (detailed data shown in the experimental section). The disappearance of carbonyl vibration peak around 1670 cm^{-1} in IR and aldehyde spectral signature around 10 ppm in $^1\text{H-NMR}$ suggested the successful polymerization via Wittig-Horner reaction. FTIR revealed that all the polymers gave a sharp peak at 966 cm^{-1} assigned to the *trans*-vinylene out-of-plane stretch, which suggested that the configuration of *trans*-vinylene was dominant among the newly formed vinylene double bonds. The composition ratio of polymer P2 was estimated by the integration area of the peaks from the $^1\text{H-NMR}$. As shown in Figure 1, the peaks from 4.32 to 3.60 ppm were attributed to the protons of $-\text{OCH}_3$ and $-\text{OCH}_2-$ connected to benzene units and the peak around 2.80 ppm

TABLE I
Average Molecular Weights and Thermal Properties of the Polymers

	$\bar{M}_n [\times 10^3]$	$\bar{M}_w [\times 10^3]$	PDI	T_g [$^{\circ}\text{C}$]	T_m [$^{\circ}\text{C}$]	T_d^a [$^{\circ}\text{C}$]
P1	4.5	10.0	2.22	72	128	414
P2	4.6	10.6	2.30	72	124	396
P3	3.8	9.3	2.45	62	–	378

^a Temperature resulting in 5% weight loss based on initial weight.

was attributed to the protons of $-\text{CH}_2-$ connected to thiophene units. The area ratio for P2 was 3.22 and the calculated content of monomer **5** was 20%, which was quite consistent with the monomer feed ratios. Elemental analysis also confirmed the above calculated result with 7.94% content of Sulfur. The obtained polymers are soluble in common organic solvents, such as chloroform, THF, and chlorobenzene. The weight-average molecular weights (\bar{M}_w) of the polymers were 10,000, 10,600, and 9300 g/mol for P1, P2, and P3, respectively. The detailed data were listed in Table I. To improve product purity, the crude products were Soxhlet extracted with methanol and hexane to remove the unreacted monomers and oligomers.

Thermal analysis

The thermal stabilities of conjugated polymers are important for device performance. Figure 2 shows the DSC curves of the polymers. The first heating scans of P1 and P2 displayed only melting transitions and no glass transitions were observed. Meanwhile, the cooling scans of the polymers displayed only crystallization peaks. This indicated that P1 and P2 have highly crystalline structures. For further investigation, P1 and P2 were heated up to 160°C under nitrogen atmosphere rapidly followed quenched by liquid nitrogen,

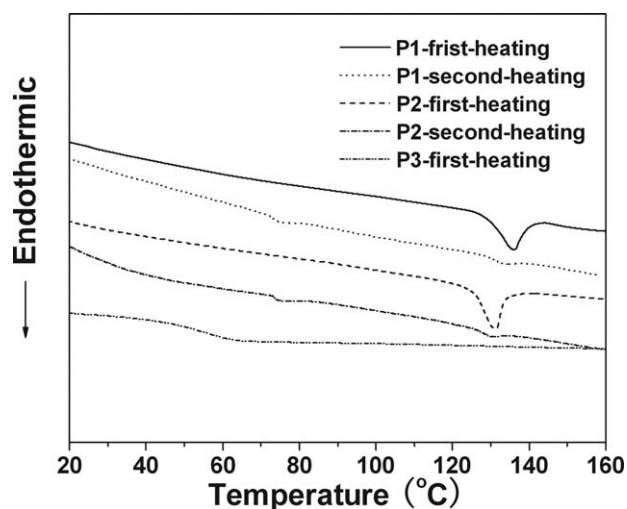


Figure 2 DSC thermograms of the polymers with a heating rate of $10^{\circ}\text{C}/\text{min}$.

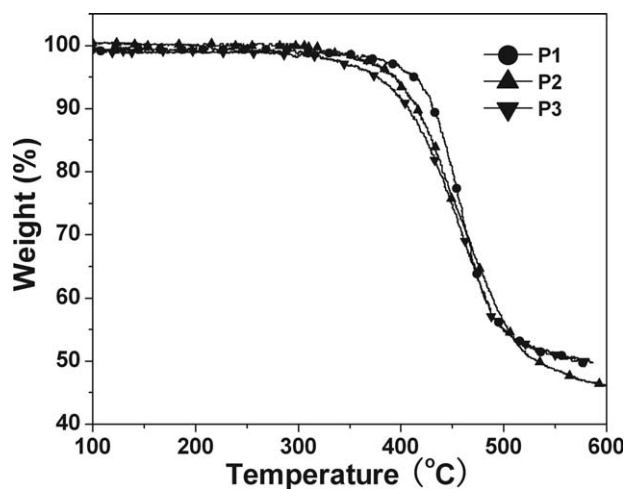


Figure 3 TGA plots of the polymers with a heating rate of 20°C/min.

and then the second heating scans of the polymers were taken. As shown in Figure 3, P1 and P2 showed the same glass transition temperature (T_g) at 72°C, which was higher than that of P3 at 62°C. The TGA curves revealed that the 5% weight loss temperature of P1, P2, and P3 were 414, 396, and 378°C, respectively. The higher glass transition temperature and decomposition temperature (T_d) of P1 and P2 compared with that of P3 should be due to the more contents of rigid side chains. The results indicate that introducing conjugated thiophene side chains into PPVs can be benefited to the improvement of the thermal stability. The stability of the polymers is adequate for the fabrication processes of the polymer solar cell devices.

Photophysical properties

The UV-Vis absorption spectra can provide a good deal of information on the electronic structures of the conjugated polymers. Figure 4 shows the absorption spectra of compound 5 and the polymers in chloroform solution. It can be seen that there are two maximum absorption peaks for compound 5, which is similar to the monomer reported by Demarille and coworkers.¹³ The two peaks at 385 and 450 nm may be assigned to the π - π^* transition of thienylene units and the whole molecule, respectively. Although absorption spectra of PPV derivatives with conjugated side chain of bulky diphenylstyryl groups showed two absorption peaks in the range of 300–500 nm reported by Shin and coworkers,¹⁴ only one broad single band could be observed to polymers P1 and P2 in the same wavelength range. This can probably be caused by the spectral overlap of the conjugated thiophene side chains with the PPV main chains. The absorption of P1 showed a sharp peak at 406 nm and blue-shifted by 50 nm compared with that of P3, which should

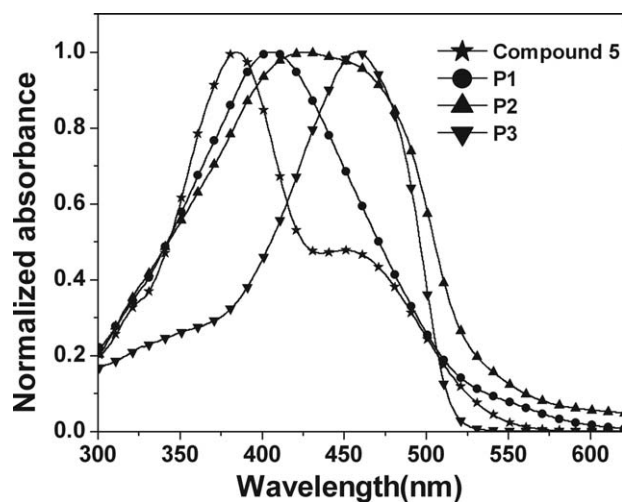


Figure 4 Normalized UV-Vis absorption of compound 5 and the polymers in chloroform.

be owing to the steric hindrance of the side chains making the polymer main chains distorted in solution.¹⁵ To decrease the steric hindrance of the polymer chains, we designed and synthesized copolymer P2 containing another constitutional unit without conjugated thiophene side chains. In comparison with P1, the maximum absorption peak of P2 red-shifted by 18 nm and the full width at half-maximum increased by 28% from 127 nm to 163 nm. The full width at half-maximum of P1 and P2 were broadened compared with that of P3 (90 nm), which should be owing to the additional absorption of the conjugated thiophene side chains.

Figure 5 shows the UV-Vis absorption spectra of the polymer films on quartz plate. The maximum absorption peaks ($\lambda_{\text{max}}^{\text{abs}}$) of the polymer films were 416, 476, and 451 nm for P1, P2, and P3, respectively. In comparison with the absorption spectra of the polymer solutions, the absorption peaks of films

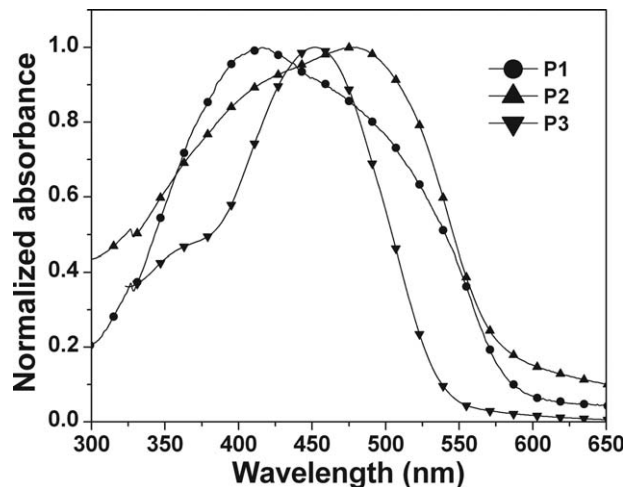


Figure 5 UV-Vis absorption spectra of the polymer films on quartz plates.

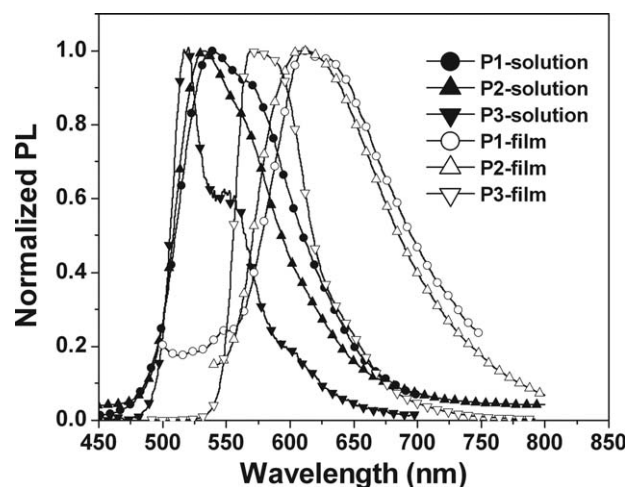


Figure 6 PL spectra of the polymers in chloroform solution and solid films.

red-shifted by 10 and 52 nm for P1 and P2, respectively. The results suggest a significant increase in the conjugation length in the solid state, and this is mostly due to the more planar conformation resulting from π -stacking/aggregation in the solid state.¹⁶ But no red shift was observed for the absorption spectrum of P3 film, which suggested that P3 film have similar electronic state with that of solution. The absorption band edges ($\lambda_{\text{onset}}^{\text{abs}}$) of the polymer films were 580, 578, and 534 nm for P1, P2, and P3, respectively. The red-shifted absorption band edges of P1 and P2 should be attributed to the reduced band gap caused by the electron-donating and conjugation effects of conjugated thiophene side chains.¹⁷ The full width at half-maximum of P1, P2, and P3 films were 198, 225, and 124 nm, respectively. These results indicated that absorption spectra of conjugated polymers in solid state could be red-shifted and broadened by introducing suitable content of conjugated thiophene side chains into the polymer backbones.

PL spectra of the polymers were shown in Figure 6. The polymers were excited at the wavelength corresponding to the maximum absorption of the π - π^* transition. The PL spectra, both in solutions and as thin films, all consisted of a typical vibronically structured band comprising a maximum, a shoulder, and a tail, which is associated with the rigid and well-defined backbone in the excited state.¹⁸ The emission peaks of P1, P2, and P3 films red-shifted by 73, 76, and 50 nm in comparison with that of solutions, respectively, which due to the stronger interactions between conjugated segments. P1 and P2 with conjugated thiophene side chains showed red-shifted emission peaks and broader emission regions compared with P3 both in solution and solid state, which implied that excitons formed in higher energy structures migrate to lower energy

TABLE II
Optical Properties of the Synthesized Polymers

	$\lambda_{\text{max}}^{\text{abs}}$ (nm)		$\lambda_{\text{onset}}^{\text{abs}}$ (nm)	$\lambda_{\text{max}}^{\text{em}}$ (nm)		$E_{\text{g}}^{\text{opt}}$ (eV)
	Solution	Film		Solution	Film	
P1	406	416	580	539	612	2.14
P2	424	476	578	532	607	2.15
P3	456	451	534	520	570	2.32

structures containing conjugated thiophene side chain units. The photophysical properties of the obtained polymers were summarized in Table II.

Electrochemical properties

The CV was widely employed for determining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the conjugated polymers. The polymer films dip-coated on a Pt electrode were scanned positively and negatively separately. The cyclic voltammograms of the polymer thin films were shown in Figure 7, and the electrochemical data were summarized in Table III. It can be seen that there were reversible *p*-doping/dedoping (oxidation/reduction) processes at positive potential range and *n*-doping/dedoping (reduction/reoxidation) processes at negative potential range for all the polymers. The onset oxidation potential ($E_{\text{onset}}^{\text{ox}}$) of the polymers P1, P2, and P3 are 0.80, 0.72, and 1.03 V (versus SCE), respectively. The $E_{\text{onset}}^{\text{ox}}$ of P1 is higher than that of P2 $\times 0.08$ V, probably due to the stronger steric hindrance of the side chain groups. The $E_{\text{onset}}^{\text{ox}}$ of P1 and P2 are lower by 0.23 and 0.31 V than that of P3, which should be ascribed to electron-donating conjugated thiophene side chains. The onset reduction

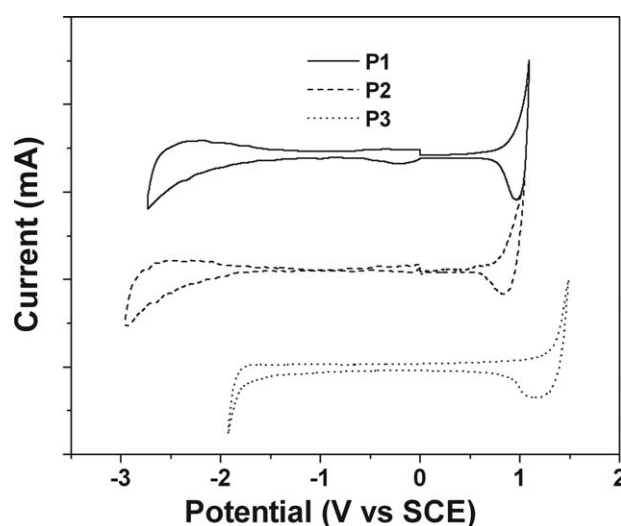


Figure 7 Cyclic voltammograms of the polymer films on platinum plates in acetonitrile solution containing 0.1 mol/L Bu_4NClO_4 at a scan rate of 0.05 V/s.

TABLE III
Electrochemical Properties of the Polymer Films

	$E_{\text{onset}}^{\text{ox}}$ (V)	$E_{\text{onset}}^{\text{red}}$ (V)	HOMO (eV)	LUMO (eV)	E_g^{EC} (eV)
P1	0.80	-1.61	-5.20	-2.79	2.41
P2	0.72	-1.64	-5.12	-2.76	2.36
P3	1.03	-1.51	-5.43	-2.89	2.54

potential ($E_{\text{onset}}^{\text{red}}$) of the polymers P1, P2, and P3 are -1.61, -1.64, and -1.51 V, respectively. From the onset oxidation potentials and reduction potentials of the polymers, HOMO and LUMO energy levels as well as the electrochemical energy gap (E_g^{EC}) of the polymers were calculated according to the equations:

$$\text{HOMO} = -e(E_{\text{onset}}^{\text{ox}} + 4.40) \text{ (eV)},$$

$$\text{LUMO} = -e(E_{\text{onset}}^{\text{red}} + 4.40) \text{ (eV)},$$

$$E_g^{\text{EC}} = e(E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}) \text{ (eV)}$$

where the units of $E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{red}}$ are V versus SCE.¹⁹ The calculated energy levels were shown in Table III. The optical bandgap (E_g^{opt}) was estimated from the absorption band edge ($\lambda_{\text{onset}}^{\text{abs}}$) of the films ($1240/\lambda_{\text{onset}}^{\text{abs}}$).

CONCLUSIONS

Two novel PPV derivatives with conjugated thiophene side chains, P1 and P2, were prepared by Wittig-Horner reaction. The effect of conjugated thiophene side chains on the photophysical and electrochemical properties of the PPV derivatives was investigated. The absorption spectra of the polymers with conjugated thiophene side chains were broadened and red-shifted effectively in 300–580 nm. Electrochemical measurement displayed that the *p*-doping/dedoping and *n*-doping/dedoping processes of P1 and P2 were reversible and the band gap of the polymers was reduced by attaching conju-

gated thiophene side chains. These results suggest that adding conjugated thiophene side chains on polymer main chain is an effective way to alter the photophysical and electrochemical properties of the conjugated polymers.

The applications of these polymers in polymer solar cells are currently in progress in our laboratory and will be reported in due course.

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