Branched Poly(p-phenylenevinylene): Synthesis, Optical and Electrochemical Properties

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ABSTRACT: A series of poly(p-phenylene vinylene) (PPV) derivatives with phenylene vinylene side chains (branched PPVs), PPV0, PPV1, PPV2, and PPV3, were synthesized by the Heck coupling reaction and characterized by TGA, absorption spectra, photoluminescence (PL) spectra, and electrochemical cyclic voltammetry. The branched PPVs showed two absorption peaks in the UV–vis region, corresponding to the conjugated side chains (UV absorption) and the main chains (the visible absorption). Especially the absorption spectrum of PPV3 covers a broad wavelength range from 300 to 500 nm. Introducing the electron-donating alkoxy substituents on the PPV main chains and increasing the content of the alkoxy groups lead to bathochromic shift of both absorption and PL spectra from PPV1 to PPV2 to PPV3. The onset oxidation potential of the branched PPVs is lower by 0.1–0.2 V than that of PPV, indicating that the electron-donating ability of the branched PPVs enhanced in comparison with that of PPV. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1002–1008, 2008

Key words: conjugated polymers; PPV; conjugated side chains; absorption spectra

INTRODUCTION

Poly(p-phenylenevinylene) (PPV) and its soluble derivatives have received much attention since the discovery of electroluminescence of PPV in 1990,[1] because of their potential applications in polymer light-emitting diodes (PLEDs) and polymer solar cells (PSCs).[1–6] In recent years, the rapid development of PLEDs and PSCs has stimulated considerable interests in modulating molecular structures of PPV.[7–18]

Conjugated side chains have been introduced into poly(p-phenyleneethynylene) (PPE),[19,20] polythiophene,[21–29] and poly(thienylene vinylene)[30] for bandgap engineering and for modulating the absorption spectra of the polymers. The hole injection ability was improved[19] and the absorption spectra were broadened[25–30] for the polymers with the conjugated side chains. Moreover, hole mobility was improved for some polythiophenes derivatives by the conjugated side chains[28,29] or by crosslinking conjugated bridges.[31,32] In this work, we synthesized the branched PPV derivatives with conjugated phenylene vinylene side chains (see Scheme 1) for improving the absorption and electronic properties of PPVs.

EXPERIMENTAL

Materials

$Pd(AcO)_2$, $P(o\text{-tol})_3$, phenanthroline, 4-iodophenol, and diphenylamine were purchased from Aldrich Chemical, Methyltriphenylphosphonium bromide was obtained from Acros Chemical, and they were used as received. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Tributylamine (TBA), N,N-dimethylformamide (DMF), and N,N-dimethyl-acetamide (DMA) were dried over molecular sieves and freshly distilled prior to use. The N-bromosuccinimide (NBS) and other materials were common commercial chemicals and used as received.

Instruments

^{1}H-NMR spectra were measured on a Bruker DMX-300 spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV–vis spectrophotometer. Photoluminescence spectra were measured using a Hitachi F-4500 spectrophotometer. TGA measurement was performed on a Perkin-Elmer TGA-7 at a heating
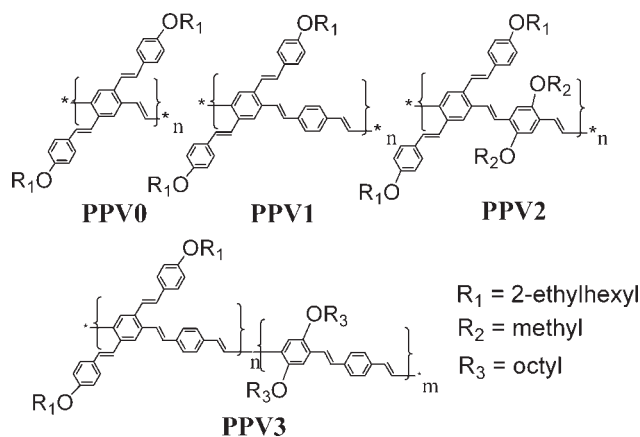
Scheme 1 Chemical structures of PPV0, PPV1, PPV2, and PPV3.

rate of 10°C/min under a nitrogen atmosphere at a flow rate of 60 cm^3/min, and the weight of the samples was ~ 5 mg. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard in chloroform. The electrochemical CV was conducted on a Zahner IM6e Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag$^+$ electrodes as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) acetonitrile solution.

Synthesis

The synthesis routes of the polymers are shown in Schemes 1–3. The detailed synthetic processes are as follows.

1,4-Dibromo-phenyl-2,5-*bis*(methylene)phosphonic acid diethyl ester (**4**)

A mixture of **3** (15.0 g, 35.5 mmol), triethyl phosphite (11.8 g, 71 mmol), and DMA (100 mL) were stirred for 3 h at 160°C. After cooling to room temperature, the reaction mixture was filtered and the filtrate was washed with water twice, then the solution was extracted with methylene chloride, and evaporation of the organic layer under reduced pressure afforded **4** as an orange-red liquid without further purification.

1,4-Dibromo-2,5-*bis*((E)-4-(2′-ethylheptyloxy)styryl)-benzene (**5**)

In ice-water bath, 4-(2-ethylhexyloxy)benzaldehyde (5.15 g, 22 mmol) was added dropwise to the mixture of **4** (5.75 g, 20 mmol), sodium methylate (2.38 g, 44 mmol), and DMF (50 mL), after being stirred for 0.5 h, the reaction mixture was warmed up to room temperature slowly for 8 h. The solution was poured into water and then extracted with methyl-

ene chloride, the methylene chloride layer was washed with water twice and dried over anhydrous magnesium sulfate. After the removal of solvents, the crude product was purified by recrystallization and dried under vacuum to give **5** as a crystal-like yellow solid powder 7.66 g (11 mmol, yield 55%): GC-Ms: m/z = 696. ^{1}H-NMR (300 MHz, CDCl$_3$) 7.80 (s, 2H), 7.46–7.43(dd, J_1 = 11.28 Hz, J_2 = 6.8 Hz, 4H), 7.33–6.94 (m, 8H), 3.86 (d, J = 6 Hz, 4H), 1.72–1.40 (m, 18H), 0.91 (m, 12H). Calcd. for C$_{38}$H$_{48}$Br$_2$O$_2$: C = 65.52; H = 6.95. Found: C = 65.31; H = 6.91.

4-Dibromo-2,5-*bis*((E)-4-(2′-ethylheptyloxy)styryl)phenylaldehyde (**6**)

Under N$_2$, compound **5** (6.96 g, 10 mmol) was put into a well-dried flask, distilled THF (25 mL) was added by a syringe. The flask was cooled to −78°C
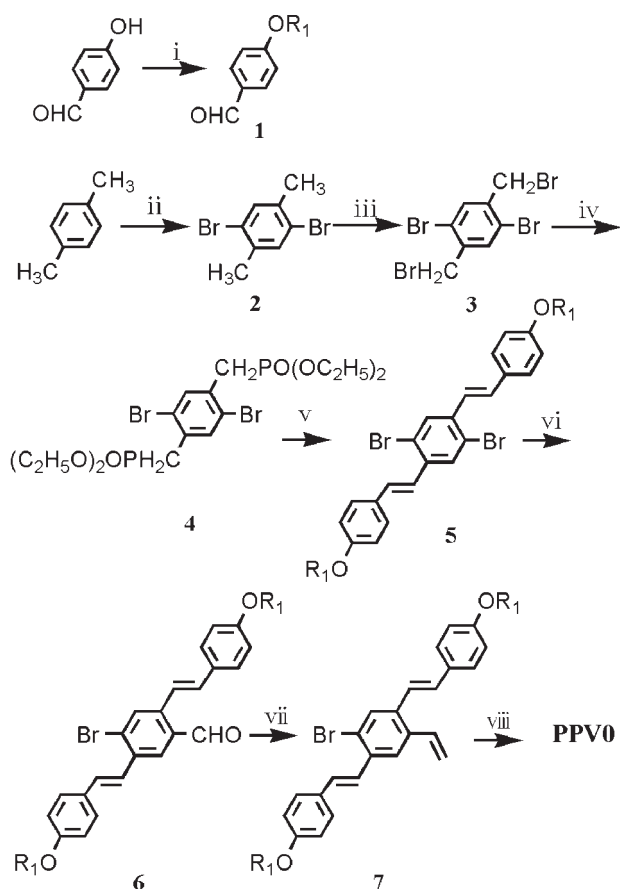
(i)2-ethylhexyl bromide, DMF, K$_2$CO$_3$, reflux; (ii) Br$_2$, CCl$_4$, r.t. ,5h; (iii)NBS, CCl$_4$,BPO, hv;(iv)P(OC$_2$H$_5$)$_3$, DMA, 160 ℃, 3h; (v) NaOCH3, DMF, 0℃ then r.t 8h;(vi) THF, n-BuLi, -78 ℃ ,1h, then N-carbaldehyde piperidine, r.t., 30min (vii)CH$_3$PPh$_3$Br; KOC$_4$H$_9$,THF, N$_2$, reflux, 4h;(viii)Pd(OAc)$_2$, Tri(o-tolyphosphine), Bu$_3$N, DMF, 24 h

Scheme 2 Synthesis routes of the monomers and polymer PPV0.
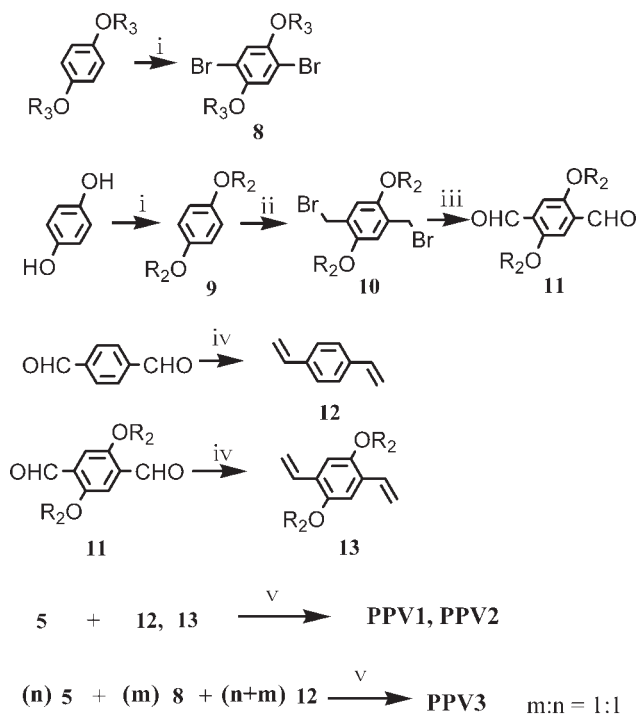
(i) Alkyl halide, DMF, K$_2$CO$_3$, reflux, 24h; (ii)HBr, (HClO)n, aceticacid, reflux, 12h(iii) 40 % fomalin,; sodium metabisulfite, HCl (iv)CH$_3$PPh$_3$Br; KOC$_4$H$_9$, THF, N$_2$, reflux,4h(v)Pd(OAc)$_2$,;Tri(o-tolyphosphine), Bu$_3$N, DMF, 24 h,

Scheme 3 Synthesis routes of the monomers and polymers PPV1-3.

by a liquid-nitrogen/acetone bath, and then *n*-butyllithium (3.8 mL, 2.88 mol/L solution in hexane, 11 mmol) was injected by a syringe. After being stirred for 1 h, *N*-carbaldehyde piperidine (2 mL) was added, and then the cooling bath was removed. After the temperature warmed up to room temperature, the solution was stirred for another 30 min and water (30 mL) was injected into the flask, then it was extracted by ether. The organic layer was washed with water twice and dried over anhydrous magnesium sulfate. After the removal of solvents, the crude product was purified by column chromatography (petroleum ether/acetic ethylester 30 : 1, v/v) and dried under vacuum to give **6** as a yellow solid powder 4.0 g (6.2 mmol, yield 62%): GC-Ms: *m/z* = 644. ^{1}H-NMR (300 MHz, CDCl$_3$) 10.04 (s, 1H), 7.65 (s, 1H), 7.54 (s, 1H), 7.46–7.43 (dd, J_1 = 11.28 Hz, J_2 = 6.8 Hz, 4H), 7.37–6.92 (m, 8H), 3.85 (d, J = 6 Hz, 4H), 1.72–1.41 (m, 18H), 0.91 (m, 12H). Calcd. for C$_{39}$H$_{49}$BrO$_3$: C = 72.54; H = 7.65. Found: C = 72.52; H = 7.61.

4-Dibromo-2,5-*bis*((E)-4-(2′-ethylheptyloxy)styryl) vinylbenzene (7)

Under N$_2$, a mixture of methyltriphenylphosphonium bromide (2.15 g, 6 mmol) and potassium *tert*-

butoxide (0.672 g, 6 mmol) and THF (50 mL) was refluxed. After the mixture was stirred for 10 min, a solution of compound **6** (3.23 g, 5 mmol) and THF (10 mL) was injected by syringe and refluxed for 4 h at 70°C. After being cooled to room temperature, the white mixture was filtered and the filtrate was distilled to remove solvent. The remaining crude product was purified by column chromatography (petroleum ether) and dried under vacuum to obtain **7** as a light yellow solid power 1.35 g (2.1 mmol, yield 42%): GC-Ms: *m/z* = 644. ^{1}H-NMR (300 MHz, CDCl$_3$) 7.78 (s, 1H), 7.70 (s, 1H), 7.50–7.43(dd, J_1 = 11.28 Hz, J_2 = 6.8 Hz, 4H), 7.33–6.90 (m, 9H, Ar—H and CH=C), 5.74–5.68 (d, J = 18 Hz, 2H), 5.45–5.41 (d, J = 12 Hz, 2H), 3.88 (d, J = 6 Hz, 4H), 1.76–1.38 (m, 18H), 0.91 (m, 12H). Calcd. for C$_{40}$H$_{51}$BrO$_2$: C = 74.63; H = 7.99. Found: C = 74.52; H = 7.87.

2,5-Bimethoxyterephthalaldehyde (11)

Compound **11** was synthesized by the method as reported in literature[33] (yield 48%). GC-Ms: *m/z* = 194. ^{1}H-NMR (300 MHz, CDCl$_3$) 10.51(s, 2H), 7.46 (s, 2H), 3.93 (s, 6H).

p-Divinylbenzene (12)

Under N$_2$, a mixture of methyltriphenylphosphonium bromide (7.2 g, 20 mmol) and potassium *tert*-butoxide (2.3 g, 20 mmol) and THF (150 mL) was refluxed. After the mixture was stirred for 10 min, a solution of terephthalaldehyde (1.34 g, 10 mmol) and THF (20 mL) was injected by syringe and refluxed for 4 h at 70°C. After being cooled to room temperature, white mixture was filtered and the filtrate was distilled to remove solvent. The remaining crude product was purified by column chromatography (petroleum ether) and dried under vacuum to obtain **12** as a colorless oil 0.7 g (5.2 mmol, yield 52%). GC-Ms: *m/z* = 130. ^{1}H-NMR (300 MHz, CDCl$_3$) 7.38 (s, 4H), 6.77–6.67 (dd, J_1 = 10.95 Hz, J_2 = 6.6 Hz, 2H), 5.79–5.73 (d, J = 17.58 Hz, 2H), 5.27–5.24 (d, J = 10.92 Hz, 2H). Calcd. for C$_{10}$H$_{10}$: C = 92.26; H = 7.74. Found: C = 92.21; H = 7.69.

1,4-Dimethoxy-2,5-divinylbenzene (13)

Compound **13** was synthesized by the same procedure as that for the synthesis of **12** (yield 55%). GC-Ms: *m/z* = 190. ^{1}H-NMR (300 MHz, CDCl$_3$) 7.06–6.99 (dd, J_1 = 11.36 Hz, J_2 = 6.6 Hz, 2H), 6.99 (s, 2H), 5.75–5.71 (d, J = 17.76 Hz, 2H), 5.28–5.25 (d, J = 11.24 Hz, 2H), 3.84 (s, 6H). Calcd. for C$_{12}$H$_{14}$O$_2$: C = 75.76; H = 7.42. Found: C = 75.75; H = 7.39.

Poly{2,5-*bis*((E)-4-(2'-ethylheptyloxy)styryl)-*p*-phenylenevinylene} (PPV0)

Polymer PPV0 was synthesized by a typical Heck coupling reaction. Under N_2, the mixture of **7** (1.29 g, 2 mmol), $Pd(OAc)_2$ (18.0 mg, 0.08 mmol) and P(*o*-tol)$_3$ (148 mg, 0.48 mmol) was put into a flask. After 10 min of flushing with nitrogen, 15 mL of DMF and 6 mL of tributylamine were added. After being flushed with nitrogen for another 20 min, the mixture was reacted firstly at 90°C for 24 h and then at 110°C for 24 h under a nitrogen atmosphere. After 50 mL of methanol was added and stirred for 5 min, the scarlet precipitate was filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and THF. The polymer of PPV0 was recovered from the THF fraction by rotary evaporation. The solid was dried under vacuum for 1 day. After dried, 0.377 g PPV0 (yield 39%) was obtained. ^{1}H-NMR (300 MHz, $CDCl_3$) 7.85–7.70 (br, 2H), 7.51–7.29 (br, 4H), 7.21–6.71 (m, 10H), 3.82–3.65 (br, 4H), 1.70–1.30 (m, 18H), 0.89 (br, 12H). Calcd. for $C_{40}H_{50}O_2$: C = 85.36; H = 8.95. Found: C = 85.66; H = 8.72.

Poly{2,5-*bis*((E)-4-(2'-ethylheptyloxy)styryl)-*p*-phenylenevinylene-alt-phenylene} (PPV1)

The polymer was synthesized by Heck reaction from **5** and **12** with the similar procedure as that for the synthesis of PPV0, and 0.41 g PPV1 was obtained (yield 44%). ^{1}H-NMR (300 MHz, $CDCl_3$) 8.01–7.75 (br, 2H), 7.70–7.29 (br, 8H), 7.25–6.82 (m, 12H), 3.87–3.78 (br, 4H), 1.73–1.33 (m, 18H), 0.91 (br, 12H). Calcd. for $C_{48}H_{56}O_2$: C = 86.70; H = 8.49. Found: C = 88.11; H = 8.72.

Poly{2,5-*bis*((E)-4-(2'-ethylheptyloxy)styryl)-*p*-phenylenevinylene-alt-2,5-bismethoxyphenylene} (PPV2)

The polymer was synthesized by Heck reaction from **5** and **13** by the similar procedure as that for the synthesis of PPV0, and the 0.28 g PPV2 was obtained (yield 62%). ^{1}H-NMR (300 MHz, $CDCl_3$) 8.01–7.80 (br, 2H), 7.65–7.31 (m, 8H), 7.18–6.82 (m, 10H), 3.93–3.74 (m, 10H), 1.74–1.32 (m, 18H), 0.91 (br, 12H). Calcd. for $C_{50}H_{60}O_4$: C = 82.83; H = 8.34. Found: C = 82.66; H = 8.72.

Poly{2,5-*bis*((E)-4-(2'-ethylheptyloxy)styryl)-*p*-phenylenevinylene-alt-2,5-bisoctanoxyphenylene} (PPV3)

The polymer was synthesized by Heck reaction from **5**, **8**, and **12** by the similar procedure as that for the synthesis of PPV0, and 0.31 g PPV3 was obtained (yield 37%). ^{1}H-NMR (300 MHz, $CDCl_3$) 8.02–7.73 (br, 4H), 7.51–6.92 (br, 28H), 4.07–3.81 (m, 8H), 1.87–1.25 (m, 42H), 0.89(br, 18H). Calcd. for $[(C_{48}H_{56}O_2)_{0.5}$

$+(C_{32}H_{44}O_2)_{0.5}]$: C 85.22, H 9.24; Found: C 83.76, H 9.84.

TABLE I
Molecular Weights and Thermal Property of the Polymers

Polymer	M_w[a] (10^4)	M_n[a] (10^4)	PDI[a] (M_w/M_n)	T_d[b] (°C)
PPV0	2.62	1.28	2.05	274
PPV1	2.29	0.85	2.69	339
PPV2	0.42	0.27	1.59	343
PPV3	1.89	1.07	1.77	341

[a] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in $CHCl_3$.
[b] The 5% weight-loss temperatures, represent the onset degradation temperatures.

RESULTS AND DISCUSSION

Synthesis

The general synthetic routes of the monomers and polymers are outlined in Schemes 1–3. **3** was synthesized by NBS free radical bromination and recrystallization from methanol in 31% yield. **5** was synthesized via the Wittig–Horner–Emmons reaction by coupling of **4** and **1** in 55% yield. The ^{1}H-NMR spectrum of **5** indicates that it is all *trans*-isomer. After the Sommelet reaction in the synthesis of **11**, **13** was synthesized by methyltriphenylphosphonium bromide in strong basic solution. To avoid polymerization of styrene, **12** and **13** must be quickly reacted with **5** by Heck coupling reaction with $Pd(OAc)_2$ and P(*o*-tol)$_3$ as catalysts and tributylamine as a base in DMF to obtain PPV1, PPV2, and PPV3. Additionally, to increase the solubility, 1-bromooctane was introduced to replace iodomethane in monomer **8**, which was copolymerized randomly with monomer **5**. The molecular weight of the polymers is listed in Table I.

Thermal stability

Thermal stability of the conjugated polymers is important for the applications in polymer optoelectronic devices. Figure 1 shows the TGA plots of PPV0, PPV1, PPV2, and PPV3. The plots of PPV1, PPV2, and PPV3 show similar onset decomposition temperatures (T_d) at ∼ 340°C, and that of PPV0 is at ∼ 274°C. We can see the T_d of PPV0 is lower than that of PPV1, PPV2, and PPV3, which is probably due to that the more content of styryl as pendant groups lowered the thermal stability but the thermal stability of the polymers is enough for the optoelectronic applications.
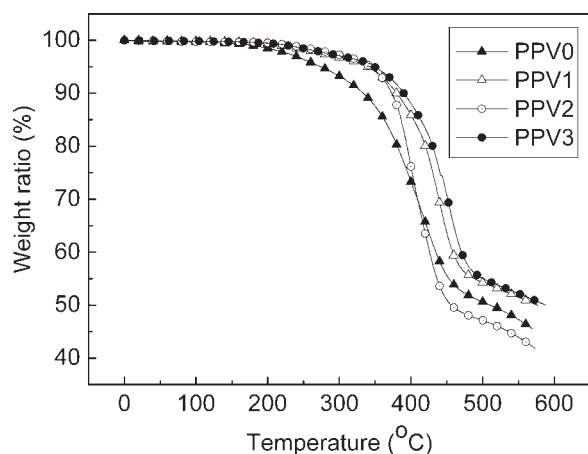
Figure 1 TGA plots of the polymers with a heating rate of 10°C/min under a nitrogen atmosphere.

Optical properties

The spectroscopic characteristics of the polymers were investigated by ultraviolet-visible (UV–vis) absorption and photoluminescence (PL) spectra of the polymer chloroform solutions with the concentration of 5×10^{-2} mol/L and the polymer films spin-coated on a quartz substrate. Figure 2 shows the absorption spectra of monomer **5** and the branched PPVs. It can be seen that the branched PPVs display broad absorption band in the UV–vis region. In comparison with the absorption peak of monomer **5**, the UV absorption peak of the branched PPVs could be ascribed to the conjugated side chains of the PPV derivatives because of the similar peak positions with that of monomer **5**, and the visible absorption should result from the PPV main chains of the polymers. The weak visible absorption of PPV0 could be due to the steric effect of its big pendant groups. Obviously, the visible absorption increased by copolymerization with the PPV units without the conjugated side chains. Interestingly,
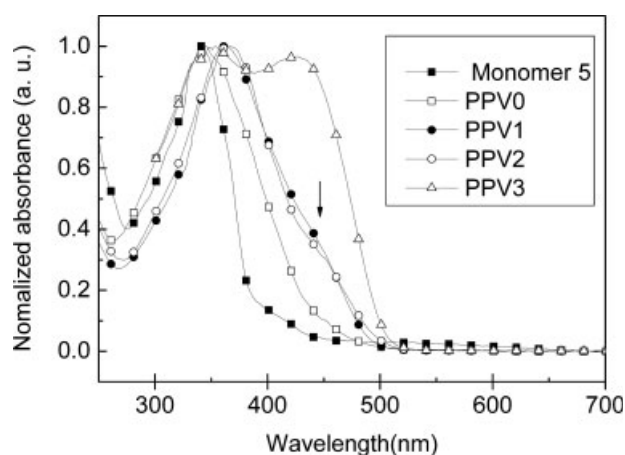

Figure 2 Absorption spectra of monomer **5** and the polymers in chloroform solution.
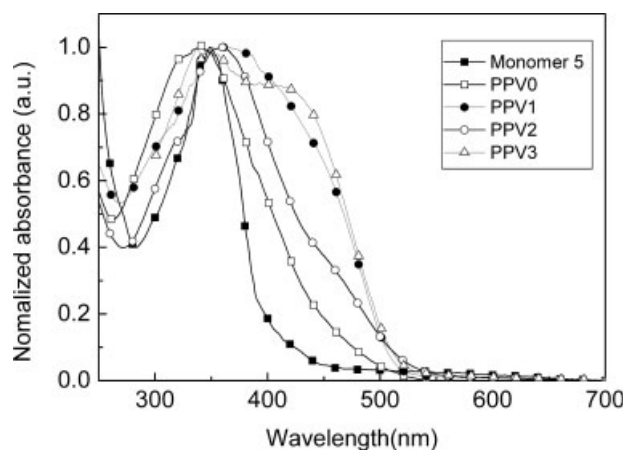
Figure 3 Absorption spectra of monomer **5** and the polymers films

PPV3 showed a broad and strong absorption band covering from 300 to 500 nm. The two absorption peaks of PPV3 partially overlaped so that it showed a broaden absorption peak from UV to visible reigon. The characteristics of absorption spectra of the branched PPVs are the same with that for the side chain conjugated polythiophenes.[25–29]

There are similar absorption characteristics for PPV0, PPV1, PPV2, and PPV3 films with those of their solutions, as shown in Figure 3. In comparison with the absorption spectra of polymer solutions, those of the polymer films are further broadened and bathochromic shifted due to the interchain interaction of the polymer films. The optical band-gaps (E_g^{opt}) estimated from the onset position of the UV–vis absorption spectra of the polymer films are 2.46 eV, 2.40 eV, 2.30 eV, and 2.35 eV for PPV0, PPV1, PPV2, and PPV3, respectively. The absorption maxima ($\lambda_{\mathrm{max,abs}}$) and the optical-bandgap (E_E^{opt}) of the polymers are summarized in Table II.

Figure 4 shows the photoluminescent (PL) spectra of the polymers in chloroform solution. All the PL spectra were obtained under excitation at the wavelength (356 nm) of the main absorption peak except of PPV3 which was excited at two wavelengths of 356 and 426 nm corresponding to the two absorption peaks of the polymer. The PL peak wavelengths of monomer **5**, PPV0, PPV1, PPV2, and PPV3 in dilute chloroform solutions are ∼ 455, 495, 503, 513, and 510 nm, respectively. The PL peaks of the polymers are obviously different from that of the monomer **5**, indicating that the PL emission of the polymers are mainly from the conjugated PPV main chains, not from the conjugated side chains. The same PL peak positions of PPV3 excited at 356 and 426 nm (see Fig. 4), imply that energy transfer from the conjugated side chains to the main chains occurred on the branched PPVs, so that only the PL emission from the conjugated main chains was observed. The same

TABLE II
Optical Properties of the Branched PPVs

| Polymer | Solution Abs (nm)[a] | | Film Abs (nm) | | PL[a] | | |
	λ_{max}	λ_{onset}	λ_{max}	λ_{onset}	λ_{max}	Φ_f[b]	E_g^{opt} (eV)[c]
Monomer **5**	341	438	349	448	455	–	–
PPV0	346	477	341	503	495	0.51	2.46
PPV1	363	492	362	516	503	0.53	2.40
PPV2	367	501	359	538	513	0.83	2.30
PPV3	356/426	510	353/411	527	510	0.67	2.35

[a] In CHCl$_3$ solution.
[b] Quinine sulfate as a standard.
[c] Calculated from the onset of the absorption band of the copolymers in solid thin films, $E_g = 1240/\lambda_{edge}$.

phenomenon was observed on the side chain conjugated polythiophenes.[24–29] The PL quantum yields (Φ_f) were calculated using quinine sulfate as standard under the same conditions for the branched PPVs, which are also listed in Table II. PPV2 has the highest PL quantum yields of 0.83, probably due to more alkoxy side chains connected to PPV main chains in PPV2.

Electrochemical properties

The electrochemical redox behavior of the branched PPVs was investigated by cyclic voltammetry (CV). Figure 5 shows the cyclic voltammograms of PPV0, PPV1, PPV2, and PPV3 films on a Pt electrode in a 0.1 mol/L Bu$_4$NPF$_6$ acetonitrile solution, and the CV data are listed in Table III. It can be seen that there are reversible n-doping/dedoping (reduction/reoxidation) processes at negative potential range for PPV1, PPV2, and PPV3, and irreversible p-doping/dedoping (oxidation/re-reduction) processes at positive potential range for all the polymers. The reversible oxidation/re-reduction at positive potential range and reversible reduction/reoxidation at nega-

tive potential range are common phenomena for PPVs,[34] which are corresponding to the oxidation and reduction of the conjugated main chains of the polymers.

The onset oxidation potential (E_{ox}) of the polymers is 0.44 V versus Ag/Ag$^+$ for PPV0, 0.42 V for PPV1, 0.33 V for PPV2, 0.40 V for PPV3, respectively. The lower oxidation potential of PPV2 should be ascribed to more electron-donating alkoxy substituents on its main chain. The onset oxidation potential of PPV3 is higher than that of PPV2 by 0.07 V, probably due to the steric effect of the longer alkoxy group of PPV3. The onset oxidation potential of all the branched PPVs are lower by 0.1–0.2 V than that of PPV.[35] Indeed, the styryl as pendant groups of P0–P4 extended the π-conjugated and then reduced the onset oxidation potential of the branched PPVs. The onset reduction potential (E_{red}) of the polymers is −2.01 V versus Ag/Ag$^+$ for PPV0, −1.90 V for PPV1, −1.87 V for PPV2 and −1.93 V for PPV3, respectively. From the onset oxidation potentials (E_{ox}) and the onset reduction potentials (E_{red}) of the polymers, HOMO and LUMO energy levels as well as the energy gap of the polymers are calculated
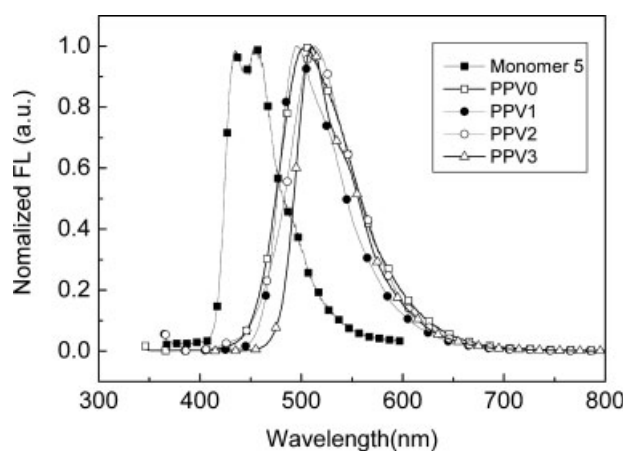

Figure 4 PL spectra of monomer **5** and the branched PPVs in chloroform solutions with the concentration of 5×10^{-2} mol/L.
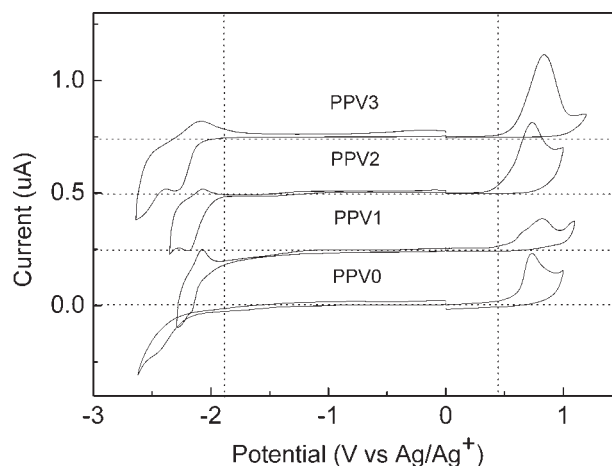

Figure 5 Cyclic voltammograms of PP0-PP3 films on platinum electrode in acetonitrile solution containing 0.1 mol/L Bu$_4$NPF$_6$ at a scan rate of 20 mV/s.

	E_{ox} (V vs. Ag/Ag$^+$)	E_{red} (V vs. Ag/Ag$^+$)	HOMO (eV)	LUMO (eV)	E_g^{ec} (eV)	E_g^{opt} (eV)
PPV0	0.44	−2.01	−5.15	−2.70	2.45	2.46
PPV1	0.42	−1.90	−5.13	−2.81	2.32	2.40
PPV2	0.33	−1.87	−5.04	−2.84	2.20	2.30
PPV3	0.40	−1.93	−5.11	−2.78	2.33	2.35

according to the equations LUMO $= -e(E_{red} + 4.71)$ (eV), HOMO $= -e(E_{ox} + 4.71)$ (eV),[36] and $E_g^{ec} = e(E_{ox} - E_{red})$, where the units of E_{ox} and E_{red} are V versus Ag/Ag$^+$. The energy levels calculated are shown in Table III.

CONCLUSION

We synthesized a series of branched PPV derivatives, PPV0, PPV1, PPV2, and PPV3, by the Heck coupling reaction. The polymers were characterized by TGA, UV–vis absorption spectra, PL spectra and electrochemical cyclic voltammetry. The absorption spectrum of PPV3 showed a broad absorption band covering from 300 to 500 nm, which included the UV absorption from the conjugated side chains and the visible absorption from the PPV main chains. Introducing and further increasing the content of the electron-donating alkoxy substituents on the PPV main chains lead to bathochromic shift both in absorption and PL spectra from PPV1 to PPV2 to PPV3. Cyclic voltammograms of the branched PPVs revealed that the onset oxidation potentials of the branched PPVs are lower by 0.1–0.2 V than that of PPV, indicating that the electron-donating ability of the branched PPVs enhanced in comparison with that of PPV. The polymers can find applications in polymer light-emitting diodes and polymer photovoltaic devices.

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