

Synthesis, Characterization, and Optoelectronic Properties of Two New Polyfluorenes/ Poly(*p*-phenylenevinylene)s Copolymers

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Received 21 November 2005; accepted 18 January 2006

DOI 10.1002/app.24264

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two novel copolymers of polyfluorenes/ poly(*p*-phenylenevinylene)s copolymers with *p*-*tert*-butylphenylenemethylene groups in the C-9 position of alternating fluorene unit, poly[1,4-(2,5-dibutyloxy)-phenylenevinylene-*alt*-9-(*p*-*tert*-butylphenylenemethylene)fluorene] and poly[1,4-(2,5-dioctyloxy)-phenylenevinylene-*alt*-9-(*p*-*tert*-butylphenylenemethylene)fluorene], have been synthesized via the Heck polycondensation reaction. The synthesized polymers were characterized by FTIR, NMR, DSC, TGA, UV-vis, and PL spectra. The polymers showed high glass transition tempera-

tures and good thermal stability. A polymer light-emitting diode with the configuration ITO/PEDOT:PSS/P2/Ca/Al has been fabricated. The device emitted a yellow light with a peak wavelength of 578 nm similar to the PL spectra of the copolymer film. A maximal luminance of 534 cd/m² was obtained at a driving voltage of 24.5 V. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3955–3962, 2006

Key words: copolymer; electroluminescence; photoluminescence; polymer light-emitting diode (PLED); synthesis

INTRODUCTION

Since the discovery of poly(phenylenevinylene)-based light-emitting diodes (LEDs) in 1990,¹ considerable efforts have been made toward the development of new conjugated polymers and in the performance of their related LEDs.² The light-emitting conjugated polymers are attractive because of the flexibility available for fine-tuning their luminescence properties through the manipulation of their chemical structures and the feasibility of combining spin-coating or printing processes for preparing large area flat-panel displays. Blue-emitting conjugated polymers are of special use, because they could be used either as a blue light source in full-color displays or as the host material for generating other colors through energy transfer to lower-energy chromophores.³ Polyfluorenes (PFs) are among the most promising candidates for blue light-emitting polymers because of their high photoluminescence and electroluminescence efficiencies.⁴ However, the application of PFs in PLEDs was hampered because of an undesired long-wavelength emission band resulting from the color instability.^{5,6} Moreover, the emissions

of typical dialkylpolyfluorenes are located in the deep-blue region, where the human eye is not very sensitive.⁷ Recently, conjugated polymers that emit different colors (green, red) have been obtained by copolymerizing fluorene with diphenyl moieties,⁸ poly(*p*-phenylenevinylene) (PPV),⁹ and thiophenes.¹⁰ In addition, the facile process of functionalizing the C-9 position of the fluorene unit also provides the opportunity to improve the color stability and to tune up the optoelectronic properties of the resulting polymers.^{11,12}

In this article, we report on the synthesis and characterization of two new PFs/PPVs copolymers containing pendent *p*-*tert*-butylphenylenemethylene (PTBP) group. PTBP attached to the C-9 positions of fluorene unit may help prevent π -stacking between polymer chains and suppress the formation of excimers in the solid state.^{11,13} These copolymers have the advantage of permitting the incorporation of a high concentration of PTBP and can emit yellow fluorescence. The synthesized copolymers are highly soluble in common organic solvents and can be easily made for fabricating PLED devices by spin-coating.

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Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 50473045.

Journal of Applied Polymer Science, Vol. 102, 3955–3962 (2006)
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EXPERIMENTAL

Materials

2,7-Dibromofluorenone and terephthalaldehyde were purchased from Pacific Chemical Source

Company (China). Triphenyl phosphine, dichloride benzenylene, (*p-tert*-butyl)benzyl chloride, alkyl bromine were purchased from Shanghai Medical Company (China). All the solvents were commercially of analytical-grade quality and used as received.

Synthesis of monomers and copolymers

Synthetic routes of the monomers and polymers are showed in Scheme 1.

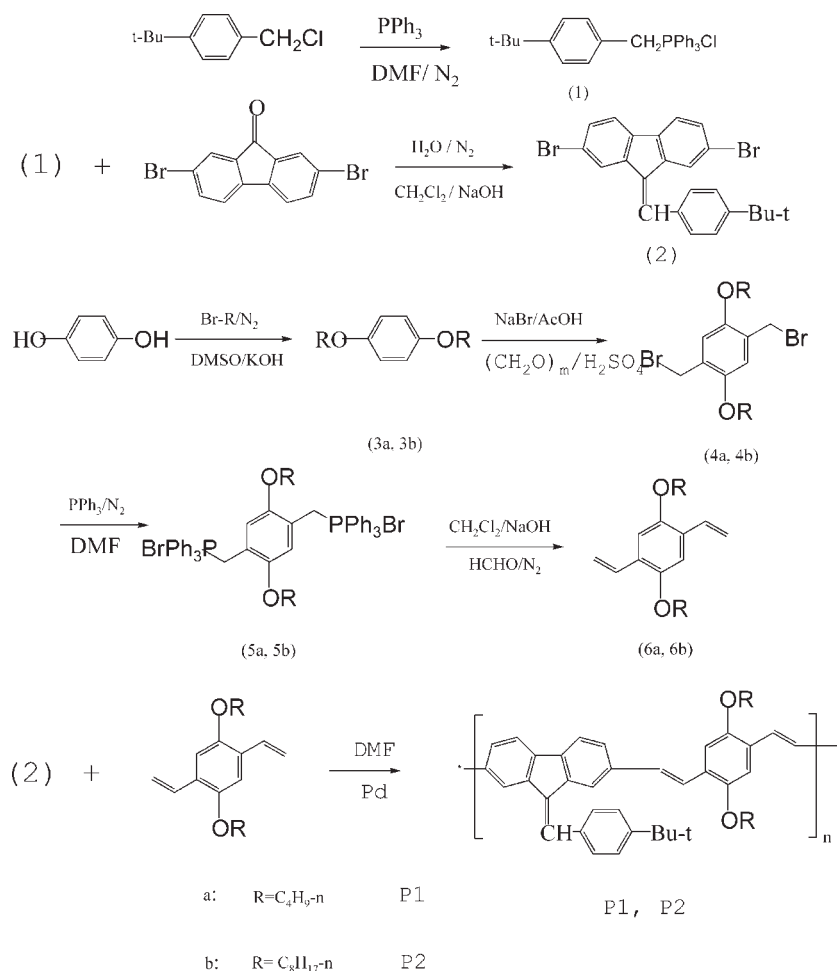
p-tert-Butylbenzyl triphenyl-phosphonium chloride (1)

A mixture of *p-tert*-butylbenzyl chloride (50.4 mmol, 9.20 g), triphenyl phosphine (55 mmol, 14.5 g), anhydrous toluene (50 mL) was heated at 110°C for 20 min under nitrogen, then an extra amount of anhydrous toluene (20 mL) was supplemented into the colorless solution. After 12 h, the mixture was cooled to room temperature, filtered, washed with anhydrous toluene for three times, and dried in vacuum to obtain a white powder. Yield: 91%; m.p., >200°C; FTIR (KBr, cm⁻¹):

753 (P—C st), 530 (P—Cl st); ¹H NMR (CDCl₃, ppm): δ 7.59 (d, 9H), 7.24 (m, 6H), 6.94 (t, 4H), 2.6 (s, 2H), 1.01 (s, 9H).

2,7-Di-bromo-9-(*p-tert*-butylphenylmethylene)-fluorene (2)¹⁴

To a 100 mL flask with compound 1 (1.85 mmol, 1.64 g) and 7 mL dichloromethane, 2,7-dibromofluorenone (1.85 mmol, 0.645 g) in 20 mL dichloromethane was added under nitrogen protection, then, 30 mL solution of sodium hydroxide (20 wt %) was dropped sequentially into the flask with ice salt bath. The mixture was stirred at room temperature for 3 h, and then heated for 24 h at 40°C. After that, 50 mL distilled water and 10 mL dichloromethane were added to the solution, the organic layer was collected and dried with anhydrous MgSO₄, then distilled through rotary evaporator. A faint yellow solid was obtained through chromatographic column using hexane as eluent. Yield: 56%; m.p., 136–137°C; FTIR (KBr, cm⁻¹): 1065 (Ar—Br), 690.6 (trans C=CH), 515 (Ar—Br); ¹H NMR (CDCl₃, ppm):



Scheme 1 Synthetic routes of the monomers and polymers.

δ 7.904 (s, 1H), 7.901 (s, 1H), 7.756 (s, 1H), 7.438 (m, 8H), 1.43 (s, 9H).

2,5-Dibutoxy benzene (3a)

To 100 mL distilled dimethyl sulfone, potassium hydroxide (28 g, 0.5 mol) was added with violent stirring for half an hour under nitrogen. Hydroquinone (16.53 g) and 1.7 g of cetyl trimethyl ammonium bromide as the phase transfer catalyst was added while stirring. Then *n*-butyl bromide (58.92 g, 0.43 mol) was added dropwise to the mixture. The reaction proceeded for 7 h, then the mixture was poured into plenty of distilled water, there was light-yellow solid at the above layer. The crude product was recrystallized by isopropyl after filtration, which was washed with distilled water, 10% sodium hydroxide in turn, dried under vacuum. A white sheet-like product was afforded. Yield: 93%; m.p., 44.5–45.2°C; FTIR (KBr, cm^{-1}): 1042 (Ar—O—), 935 (C—O—C); ^1H NMR (CDCl_3 , ppm): δ 0.92–1.00 (t, 6H), 1.40–1.72 (m, 8H), 3.75–3.8 (t, 4H), 6.76 (s, 4H).

1,4-Bis(bromomethyl)-2,5-butoxybenzene (4a)^{15,16}

A mixture of 2,5-di-*n*-butyloxybenzene (10.08 g, 45 mmol), paraformaldehyde (4.7 g, 3.5 equiv.), sodium bromine (15.8 g, 0.153 mol), glacial acetic (85 mL) was added in a flask stirring for 1 h, then sulfuric acid (8.3 mL, 3.3 equiv.) and isochoric glacial acetic acid were dropped into the flask within 1 h. The system was stirring for 1 h at 25°C, after that it was slowly enhancing temperature to 60°C for 7 h. The system again enhanced temperature to 70°C for 1 h. The system is then cooled till 25°C and poured into beaker with 500 mL water, filtration washed with water till neutral point, the crude product was recrystallized from petroleum ether and dried under vacuum to give white powder of 14.6 g. Yield: 78.1%; m.p., 82–83°C; FTIR (KBr, cm^{-1}): δ 1661 (CH_2), 1042 (Ar—O—), 935 (C—O—C), 830 (γ , CH_2); ^1H NMR (CDCl_3): δ 7.00 (s, 2H, Ar—H), 4.50 (s, 4H), 4.00–3.98 (t, 4H), 1.76–1.45 (m, 8H), 0.9–0.87 (m, 6H).

2,5-Butoxy-1,4-xylylene-bis(triphenyl phosphonium bromine) (5a)^{17,18}

A mixture of compound 4a (2.04 g, 5 mmol), triphenyl phosphine (3.93 g, 15 mmol), and 10 mL of freshly distilled DMF was heated to 95°C, and reaction proceeded under the temperature while stirring for 24 h. The resulting mixture was poured into diethyl ether. The white solid was filtered, washed with diethyl ether repeatedly to remove the byproducts, dried under vacuum to afford a white powder. Yield 91%; m.p., >200°C; FTIR (KBr, cm^{-1}): 530 (P—Br, st); ^1H NMR (CDCl_3 , ppm): δ 0.9 (t, 6H), 1.30–0.95 (m, 8H), 3.94 (d, 4H), 5.02 (d, 4H), 6.70 (s, 2H), 7.87–7.54 (m, 30H).

2,5-Dibutoxy-1,4-divinyl-benzene (6a)¹⁹

A mixture of 2,5-butoxy-1,4-xylylene-bis(triphenyl phosphonium bromide) (5a) (1.76 g, 1.85 mmol), dichloromethane (27 mL), and formalin (7.2 mL) was added into 100 mL flask, then 20% sodium hydroxide was slowly dripped the flask at 0°C for 1 h dripping over. The reaction proceeded for 24 h at 25°C. Pouring the reaction mixture into a beaker with 50 mL water and 20 mL dichloromethane, the organic layer was collected, dried with anhydrous MgSO_4 , and distilled through rotary pressure distillation. The crude product was recrystallized two times from 20% ethanol to give 0.29 g of white crystals. Yield 54.2%; m.p., 42–43°C; FTIR (KBr, cm^{-1}): 966 (trans —HC=CH₂); ^1H NMR (CDCl_3 , ppm): δ 1.01 (t, 6H), 1.48–1.61 (m, 4H), 1.77–1.86 (m, 4H), 4.00 (t, 4H), 5.28 (dd, 2H), 5.76 (dd, 2H), 7.01 (s, 2H), 7.10 (dd, 2H).

2,5-Dioctyloxy benzene (3b)

Compound 3b was prepared according to the procedure described for 3a except that *n*-octyl-bromide instead of *n*-butyl-bromide. Yield: 93%; m.p., 44.5–45.2°C, FTIR (KBr, cm^{-1}): 1045 (Ar—O—), 933 (C—O—C); ^1H NMR (CDCl_3 , ppm): δ 6.81 (s, 4H), 3.88–3.91 (t, 4H), 1.72–1.77(m, 8H), 1.28–1.43 (t, 16H), 0.88–0.90 (t, 6H).

1,4-Bis(bromomethyl)-2,5-octyloxybenzene (4b)

Compound 4b was prepared according to the procedure described for 4a. Yield: 78.1%; m.p., 82–83°C; FTIR (KBr, cm^{-1}): δ 1665 (CH_2), 1042 (Ar—O—), 931 (C—O—C), 865 (γ , —CH₂—); ^1H NMR (CDCl_3): δ 7.00 (s, 2H, Ar—H), 4.52 (s, 4H), 3.97–4.00 (t, 4H), 1.80–1.83 (m, 4H), 1.49–1.54 (m, 8H), 1.32–1.35 (m, 16H), 0.87–0.91 (t, 6H).

2,5-Octyloxy-1,4-xylylene-bis(triphenyl phosphonium bromine) (5b)

Compound 5b was prepared according to the procedure described for 5a. Yield: 91%; m.p., >200°C; FTIR (KBr, cm^{-1}): 535 (P—Br st); ^1H NMR (CDCl_3 , ppm): δ 7.86–7.57 (m, 30H), 6.78 (s, 1H), 6.54 (s, 1H), 5.12 (s, 1H), 4.97 (s, 4H), 3.04–3.12 (t, 4H), 2.80 (s, 6H), 1.30–0.97 (m, 24H), 0.85–0.83 (t, 6H).

2,5-Di-octyloxy-1,4-divinyl-benzene (6b)

Compound 6b was prepared according to the procedure described for 6a. Yield: 54.2%; m.p., 42–43°C; FTIR (KBr, cm^{-1}): 962 (trans —HC=CH₂); ^1H NMR (CDCl_3 , ppm): δ 7.08–6.99 (t, 4H), 5.75–5.71 (d, 2H), 5.26–5.24 (d, 2H), 3.99–3.96(m, 4H), 1.82–1.76 (m, 4H), 1.57–1.48 (m, 24H), 1.32–1.29 (t, 6H).

Poly[1,4-(2,5-dibutyloxy)-phenylenevinylene-*alt*-9-(*p*-*tert*-butyl phenylenemethylene)fluorene] (P1)^{20–22}

The polymerization as shown in Scheme 1 was carried out under nitrogen atmosphere employing the Heck reaction. A mixture of compound **2** (1.46 mmol, 0.666 g), compound **6a** (1.46 mmol, 0.564 g), palladium(II) dichloride (0.0472 mg), and 0.248 g of tri-*o*-tolylphosphine was added to 12 mL of DMF via a syringe. After a homogeneous solution was obtained, 1.2 mL of triethylamine was added to the reaction solution. The reaction mixture was stirred vigorously for 48 h at 90°C. The vinyl chain ends due to the excess feeding of the divinylbenzene were capped with 0.5 mL of bromotoluene in 10 mL of DMF at the end of the polymerization for 6 h at 100°C and then poured slowly into an excess amount of methanol (200 mL). The precipitated material was recovered by filtration. The polymer was redissolved by chloroform and microfiltered followed by precipitation again into methanol. Filtration and drying under vacuum for 24 h at 40°C, the polymer was purified by continuous extraction with methanol, the polymer was dried under vacuum at 40°C for 24 h to give 1.78 g of light-yellow solid (yield 86.5%); FTIR (KBr, cm⁻¹): 3057 (Ar–H, st), 2950 (C–H, st), 960 (trans HC=CH); ¹H NMR: δ 0.77 (br, 16H, –CH₂ and –CH₃), 1.08 (br, 24H, –CH₂), 2.05 (br, 8H, R–CH₂), 4.00 (br, 4H, –OCH₂), 6.51–7.78 (br, m, 12H, vinyl and aromatic).

Poly[1,4-(2,5-dioctyloxy)-phenylenevinylene-*alt*-9-(*p*-*tert*-butyl-phenylenemethylene)fluorene] (P2)

The synthetic method of P2 was similar to P1. Finally, it afforded a yellow solid. Yield: 82.5%; FTIR (KBr, cm⁻¹): 3024 (Ar–H, st), 2932 (C–H, st), 960 (trans HC=CH); ¹H NMR: δ 0.77 (br, 20H, –CH₂ and –CH₃), 1.08 (br, 36H, –CH₂), 2.05 (br, 8H, R–CH₂–), 4.00 (br, 4H, –OCH₂), 6.53–7.78 (br, m, 12H, vinyl and aromatic).

Measurements

¹H NMR spectra were obtained on a Bruker AVANCE 400 spectrometer, with reference to tetramethylsilane (TMS) as an internal standard. FTIR spectra were recorded by a Perkin–Elmer Spectra One spectrometer on KBr pellets. UV–visible absorption and photoluminescence (PL) spectra were measured on a Perkin–Elmer Lamada 25 UV–vis spectrometer and a Perkin–Elmer LS-55 fluorescence spectrometer at room temperature. Thermogravimetric analysis (TGA) was performed under nitrogen at a heating rate of 20°C/min with a Netzsch TG 209 analyzer. Differential scanning calorimetry (DSC) of the polymers was performed under nitrogen at a heating rate of 10°C/min with a Perkin–Elmer DSC-7 instrument. The average molecular weight and polydispersity (PDI) of the polymers

were determined using a Waters1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as internal standard. The electroluminescence (EL) spectra were recorded on an Instaspec 4 CCD spectrophotometer (Oriel). The current–voltage–brightness characteristics of the device were measured in a Keithley 236 source measure unit.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis routes of the monomers and polymers were outlined in Scheme 1. All steps were facile and can be well controlled. The monomer **2** was prepared by a Wittig reaction of *p*-*tert*-butyl-benzyl triphenyl-phosphonium chloride with 2,7-dibromofluorene. Monomer **6a** was prepared in four steps from hydroquinone through Williamson reaction, followed by conversion to the chloromethylation and thereafter conversion to the triphenylphosphonium salt, 2,5-dibutoxy-1,4-divinyl-benzene was obtained finally by a Wittig reaction. The polymerization between monomer **2** and **6a** or **6b** was carried out by a typical Heck coupling reaction with good yield. After the polymerization for 48 h, bromobenzene was added as the end-capper. The polymers structures were characterized with ¹H NMR and FTIR. Figure 1 shows the FTIR spectra of polymers. For P1, the absorption at 3057 and 3024 cm⁻¹ are assigned to the Ar–C–H stretching bands, 1595 cm⁻¹ is characteristic peak of Ar–C–C. About 1700 cm⁻¹ is the characteristic peak of C=C stretching bands, which is relatively weak in FTIR spectra. The absorption at 727 cm⁻¹ is assigned to the C–(CH₂)₂–C groups of side chains. The absorption at 1500 cm⁻¹ is assigned to the Ar–C–O stretching bands. Meanwhile, a sharp absorbance peak at 960 cm⁻¹ appeared, corresponding to the out of plane bending mode of the *trans*-vinylene

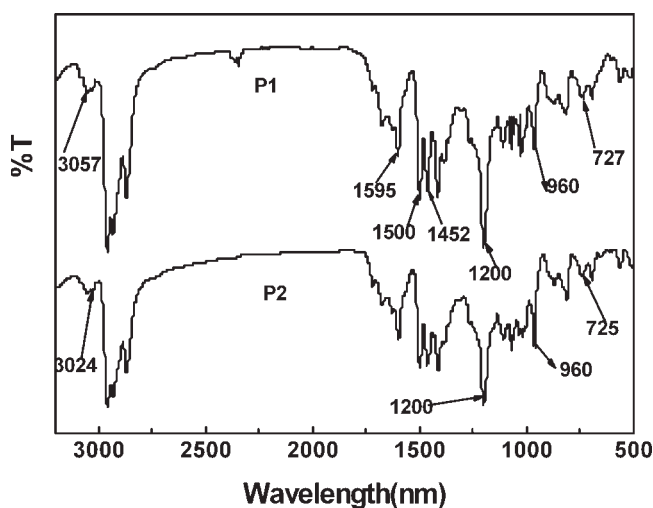


Figure 1 The FTIR spectra of polymers.

groups in the polymer. The FTIR spectrum of **P2** is similar to the spectra of **P1**. For ^1H NMR spectra of the polymers, the vinylene proton peaks appeared at around 6.5–7.0 ppm. The results from ^1H NMR and FTIR were accorded with the structures of **P1** and **P2** shown in Scheme 1. The obtained polymers are soluble in common organic solvents such as chloroform, dichloromethane, toluene, and tetrahydrofuran (THF). Thus, they can be spin-coated onto various substrates to give homogeneous transparent thin films. The average molecular weight and polydispersity index (PDI) of polymers were determined by gel permeation chromatography (GPC) with polystyrene as the standard and THF as the eluent. The results are listed in Table I. It can be seen the average molecular weights (both M_n and M_w) of the polymers prepared by Heck coupling were usually low.²³

Thermal properties

The thermal property of the synthesized polymer was evaluated by means of TGA and DSC under nitrogen atmosphere. The DSC thermograms were obtained from the second heating of the polymers. As shown in Figure 2, a glass transition temperature (T_g) at 118°C for **P1** and 106°C for **P2**, respectively, were detected by DSC. It can be seen that the polymer with the shorter alkyl chain exhibits stronger endothermic peaks at glass transition temperature. The T_g decreases with an increase of alkyl chain length, the dependence of T_g on the length of the alkyl substituent was interpreted in terms of the steric effect of alkyl chains.²⁴ No additional melting transition was observed for the two polymers, indicating that both two polymers are amorphous. The TGA thermogram curves (Fig. 3) measured under nitrogen atmosphere show that **P1** and **P2** have good thermal stability with no weight loss up to 350 and 300°C, respectively. The loss-weight of **P1** and **P2** are less than 5% on heating to 420 and 400°C, respectively. This indicated that the two polymers possessed good thermal stability but the thermal properties became inferior with increase in side chain length.

Optical properties

Figure 4 shows the UV–vis and PL spectra of the polymers. The optical properties of the polymers are sum-

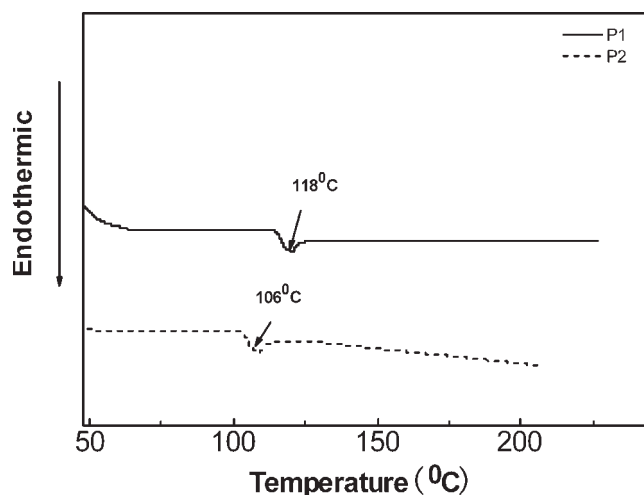


Figure 2 DSC thermograms of polymers with a heating rate of 10°C/min.

marized in Table II. The UV–vis spectra of the two polymers are highly similar in shape with the peak of the π – π^* absorption band occurring at 354 nm (2.08 eV) for **P1** and at 345 nm (2.29 eV) for **P2**. The difference is that the electron-donating long side chain makes the backbone of the polymers twisting, consequently reduces the effective conjugated length and causes the blue shift of the absorption and emission in dilute solution. The maximum absorption peaks of the polymers blue shifted were 60–80 nm as compared with that of PPV.²⁶ The results could be explained that the phenyl substituent at vinyl bridge inhibited the main chain coplanarity and lead to blue shift of maximum absorption peak. However, the butyloxy and octyloxy substituents at side chain are electron donating groups and leads to red shift of the maximum absorption peak. Meanwhile, the absorption band is broader in the solid state than in the solution, which means that there are more energy

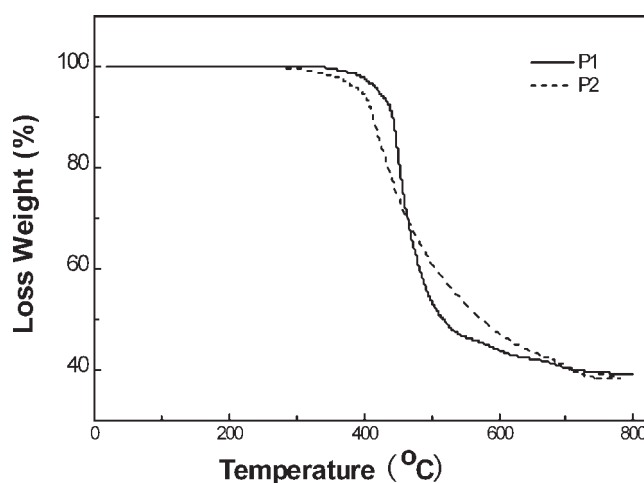


Figure 3 TGA thermograms for polymers.

TABLE I
Average Molecular Weight and Thermal Properties of Polymers

Polymers	Yield (%)	M_n	M_w	PDI	T_g (°C)	T_d^a (°C)
P1	86	7,120	20,648	2.9	118	420
P2	82	7,530	22,590	3.0	106	400

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

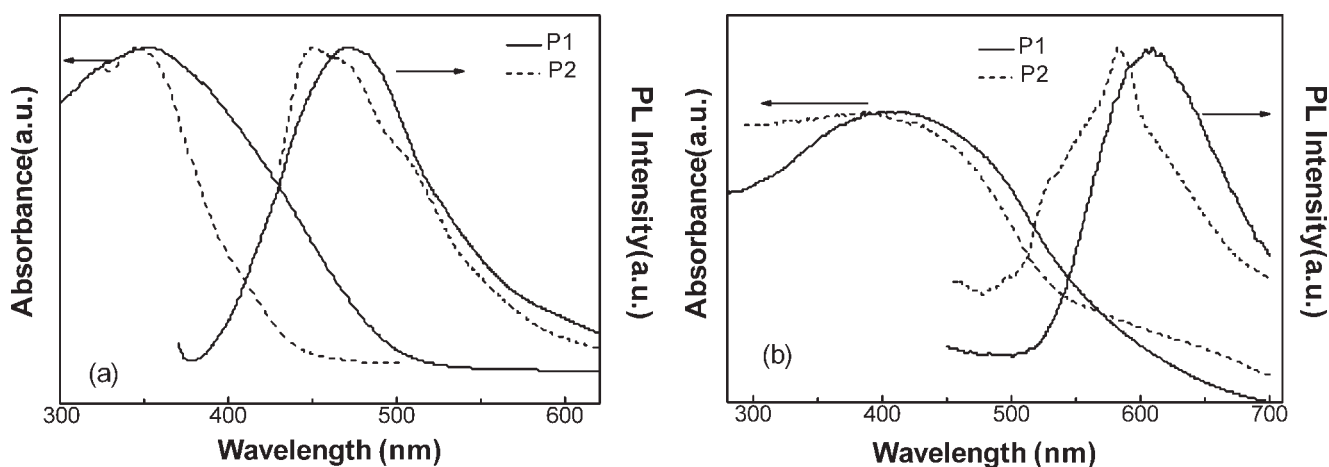


Figure 4 Absorption and PL spectra of polymers in chloroform solution (a) and solid film (b).

levels in solid state corresponding to the π - π^* transition for the polymers.

Photoluminescence (PL) spectra of the polymer solutions and films are recorded as shown in Figure 4. The solutions of the polymers exhibit PL emission maxima at 472 nm for **P1** and at 452 nm for **P2** when they are excited with the maximum excitation wavelength. The films of the polymers **P1** and **P2** show PL emission maxima at 590 and 582 nm, respectively. The PL spectra of solid films show broad peak and are red-shifted of about 130 nm compared to those of the polymer solution, which suggest that interchain interactions have an important effect on the excited state emission mechanisms of polymers. Usually, π - π^* interactions or aggregation of π -conjugated polymer chains in solid states lead to a red shift in the emission spectrum relative to the solution state, resulting in a higher conjugation length in the solid polymers.²⁷ Moreover, it probably results from more planar conformations of conjugated chains in the solid state than in solution. The intermolecular interactions in the solid state might favor coplanar arrangements of the aromatic rings in the polymer chain and may be responsible for the observed enhanced conjugation.²⁸ Meanwhile, conjugation of these polymers was enhanced, which results from that the introduction of the *p*-*tert*-butyl-phenylenemethylene (PTBP) moieties onto C-9 position of every fluo-

rene unit help prevent π -stacking between polymer chains and suppress the formation of excimers in the solid state.

Electrochemical characterization

The HOMO and the LUMO are measured by electrochemical cyclic voltammetry (CA). When Ag/AgCl electrode is used as the reference electrode, the correlation can be expressed as²⁹

$$E_{\text{HOMO}} = -|\text{IP}| = -|eE_{\text{ox}} + 4.37|$$

$$E_{\text{LUMO}} = -|\text{EA}| = -|eE_{\text{red}} + 4.37|$$

$$E_g = |\text{IP}| - |\text{EA}| = E_{\text{LUMO}} - E_{\text{HOMO}}$$

E_{ox} and E_{red} are onset potentials of the oxidation and reduction process, respectively. As for the **P1** and **P2**, the onset potential of oxidation occurs at 1.13 and 1.22 eV, so the HOMO levels are calculated as -5.50 eV and -5.59 eV, respectively. The band gap (E_g) of the **P1** and **P2** are estimated as 2.08 and 2.29 eV from the UV-vis absorption spectrum. The LUMO levels are calculated as -3.42 eV and -3.30 eV, respectively.

TABLE II
Optical Properties of the Polymers

Polymers	UV _(solution) (nm)	UV _(film) (nm)	PL _(solution) (nm)	PL _(film) (nm)	Stoke's shift ^a (nm)	Φ_{pl} ^b	E_g^c (eV)
P1	354	422	472	590	168	0.486	2.08
P2	345	401	452	582	181	0.478	2.29

^a Stoke's shift = PL_(film) - UV_(film) (in nanometers).

^b Relative values of Φ_{pl} ²⁵ in chloroform determined with a dilute quinine sulfate in 1N H₂SO₄ as the standard (<10⁻⁴M; Φ_{pl} = 0.55).

^c Band gap estimated from the onset wavelength of the optical absorption.

Electroluminescence properties

A PLED was fabricated in the configuration: ITO/PEDOT:PSS (30 nm)/P2 (97 nm)/Ca (10 nm)/Al (180 nm). The electroluminescence (EL) spectrum from such a device is shown in Figure 5. The EL spectrum of the device based on *p*-*tert*-butyl-phenylenemethylene (PTBP) shows a very broad emission peak from 417 to 810 nm with a maximum at 578 nm. Similar to PL emission in the solid state, EL emission consists exclusively of PTBP unit emission, indicating that intrachain and/or interchain energy transfer from phenyleneethynylene segments to PTBP units occurred. As a result, the generated excitons are efficiently confined and recombined on *p*-*tert*-butyl-phenylenemethylene sites, and copolymer emits exclusively emission of PTBP component.⁸

The typical current–voltage–brightness curves of this device are shown in Figure 6. The current–voltage–brightness characteristics of the device revealed an excellent diode behavior. The current and the intensity of the emitting light increased linearly with the increase of applied voltage after surpassing the turn-on voltage (15.2 V). The high turn-on voltage of the copolymer is probably because of the bigger electron injection barrier between the cathode (Ca–Al) and the copolymer. The HOMO levels of the copolymers facilitate hole transport and are suitable to the work function of ITO-glass. However, the LUMO levels of the copolymers would not favor electron injection and act as an electron trap, which might affect the performance of the single-layer device.³⁰ The maximum brightness of the device was 535 cd/m² at a voltage of 24.3 V. The external quantum efficiency of 0.04% at a voltage of 15.91 V and a current density of 323.6 mA/cm² was obtained, which is slightly low, indicating that a relatively high energy barrier exists for hole injection in this case. It seems that the single-layer device of the copolymer is not opti-

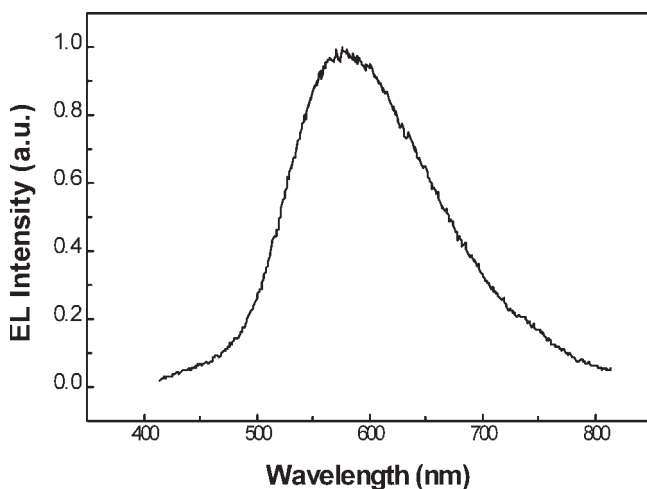


Figure 5 EL spectrum of ITO/PEDOT:PSS/P2/Ca/Al device.

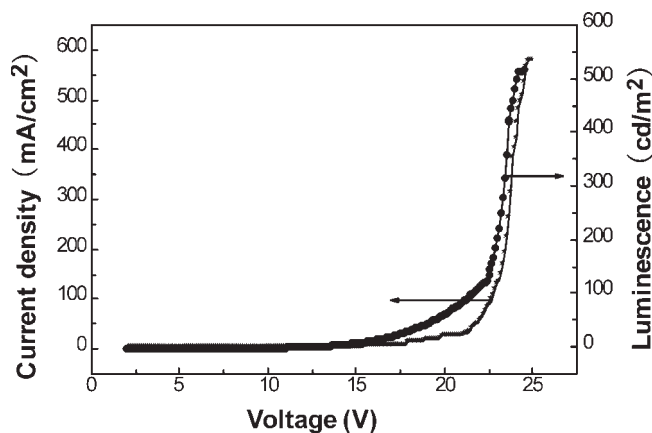


Figure 6 Current–brightness–voltage characteristics of an ITO/PEDOT:PSS/P2/Ca/Al device.

mized in terms of electron injection at cathode.³¹ Further optimization will require determination of the LUMO position to select the best cathode and the electron injection.³²

CONCLUSIONS

Two new conjugated PFs/PPVs copolymers containing the pendant (*p*-*tert*-butyl-phenylenemethylene) group in the C-9 position of fluorene unit were prepared. The amorphous conjugated polymers showed high glass transition temperatures and good thermal stability. These copolymers are highly soluble in common organic solvents. The PLED of ITO/PEDOT:PSS/P2/Ca/Al emits yellow light exhibiting a single peak at 578 nm with turn on voltage of 15.2 V. A maximum brightness of 535 cd/m² was obtained at a driving voltage of 24.3 V. The work here provides us with better understanding in the molecular design of C-9-functionalized fluorene-based conjugated copolymers for fine-tuning of optoelectronic and thermal properties.

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