

Synthesis and Characterization of New Blue-Photoluminescent Copolymer Derived from Bisphenol A

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ABSTRACT: A new copolymer with short alternating conjugated and nonconjugated blocks, derived from bisphenol A (BPAEt₂-PPV) containing separated phenylenevinylene (PV) units has been synthesized by Wittig condensation. The copolymer is fully soluble in common organic solvents and has a number-average molecular weight of 3200 with a polydispersity index of 1.53. The structure of the polymer was confirmed by ¹H NMR, ¹³C NMR, FTIR and Raman spectroscopic analysis. Thermogravimetric analysis and differential scanning calorimetry indicate that BPAEt₂-PPV is stable up to 400°C in air and displays a glass transition

temperature of 107°C. The fluorescence spectrum of the polymer film shows an emission in the blue region (428, 456, and 488 nm). The band-gap energy, estimated from the edge absorption of the film, is about 2.9 eV. A single-layer diode device of the configuration ITO/BPAEt₂-PPV/Al has been fabricated and has a relatively low turn-on voltage of 3.7 V. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 2997–3004, 2006

Key words: bisphenol A (BPA); wittig polycondensation; conjugated polymers; luminescence; light-emitting diodes (LED)

INTRODUCTION

The field of polymeric light-emitting diodes (PLEDs) has attracted considerable interest from both academic and industrial laboratories, and significant progress has been made since the initial discovery of conjugated polymer electroluminescence in 1990.¹ Such light-emitting polymers have several potential advantages over electroluminescent inorganic materials or organic small-molecule materials in that single-polymer-layer devices that exhibit low operating voltage, high emission quantum yield, mechanical strength, low weight, large display area, and color tunability can be fabricated.² Moreover, device fabrication can be simplified by the use of spin-coating or ink-jet printing techniques.^{3,4}

In this regard, many conjugated polymers have been recently designed and synthesized to develop blue, green, and red light-emitting devices. Although all three primary colors have been demonstrated in PLEDs, only green and red ones currently meet the

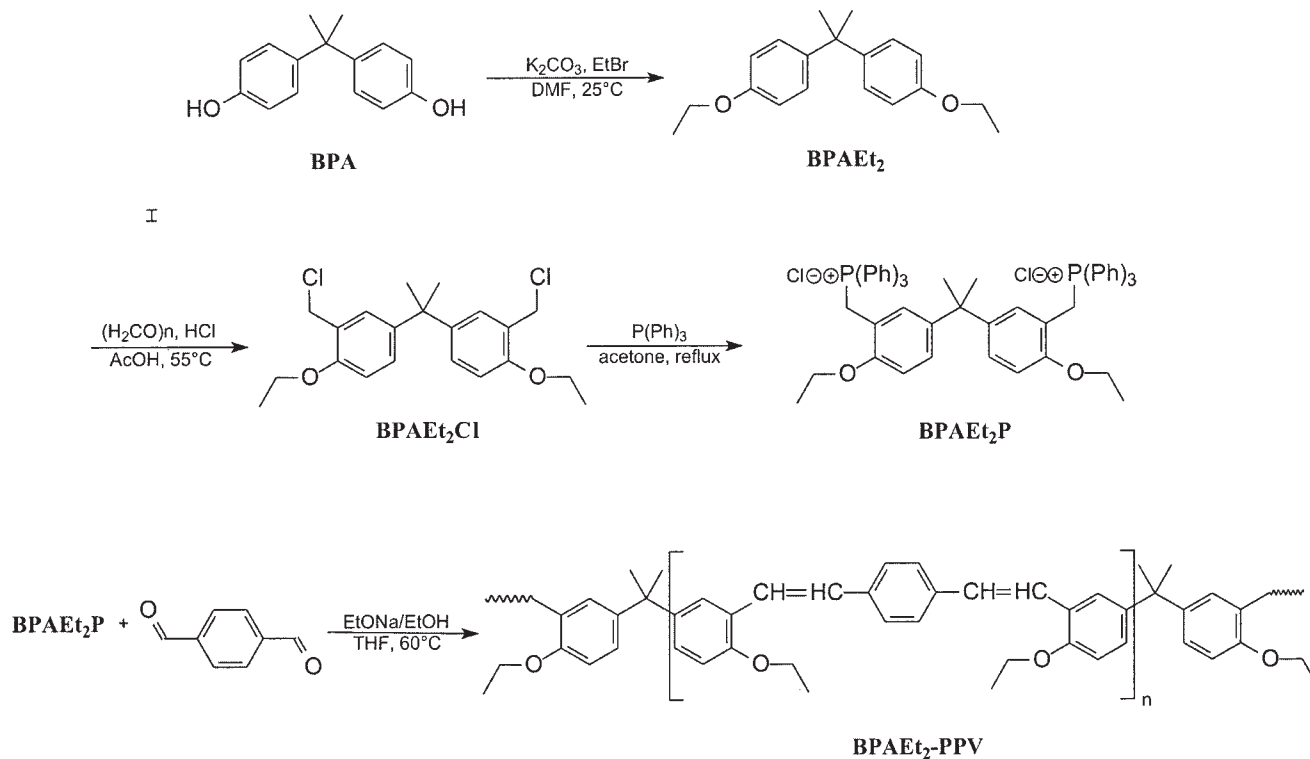
requirements for commercial use.⁵ Simple and stable blue-electroluminescent polymers are still lacking. Recently, interest has been focused on blue PLEDs for the realization of full-color LED displays^{6,7} and the main challenge is to develop bluelight-emitting diode materials capable of operating at low voltage, exhibiting good thermal and oxidative stability, and high photoluminescence (PL) efficiency with good processability and low price.

The first blue PLED was made using poly(9,9-dihexylfluorene).⁸ Other blue-emitting conjugated polymers have since been demonstrated, including 9,9-disubstituted polyfluorenes,⁹ polyphenylene derivatives,¹⁰ 3,4-disubstituted polythiophenes,¹¹ and poly(*m*-phenylenevinylene) derivatives.¹²

Poly(*p*-phenylenevinylene) (PPV)-type blue-emitting polymers can be obtained by a partial conversion of the precursor polymer in the sulfonium route to PPV, giving a high concentration of interruptions in the conjugated chain.^{13,14} In the same way, introducing comonomers with flexible linker groups into a step growth condensation route to PPV, can lead to blue-emitting copolymer.¹⁵ These methods, however, only allow limited control of the length and the distribution of conjugated segments. Hence, the emission occurs usually from the more highly conjugated segments, and the emission spectrum is therefore broadened and red-shifted. An alternative approach to achieve blue-

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Scheme 1 Synthetic route to BPAEt₂-PPV.

emitting PPV-type polymers alternating short, well-defined oligomeric PV units with nonconjugated spacer units in the polymer backbone. Such polymers usually exhibit good solubility, high PL quantum yields, and a narrower emission spectrum.

Bisphenol A (BPA) is an important industrial intermediate. This monomer is among the cheapest and the most used intermediates in macromolecular synthesis, especially in the elaboration of polycarbonates, epoxy resins, and polysulfones.^{16–18} However, it has never been exploited as the principal material for the synthesis of light-emitting polymers. In this contribution, we report the synthesis and characterization of the first PPV-type luminescent polymer incorporating the BPA aromatic ring into the chromophore unit.

EXPERIMENTAL

Materials and measurements

4,4'-Isopropylidenediphenol (BPA) was purchased from Acros (Morris Plains, NJ) and recrystallized twice from toluene. Anhydrous acetone, tetrahydrofuran (THF), and ethanol were freshly distilled before use. Other reagents and solvents were commercially available and used without further purification.

Melting points (mp) were determined on an Electrothermal Mode 9100 digital analyzer and were not corrected. ¹H NMR and ¹³C NMR spectral data were obtained on a Bruker AV 300 spectrometer. FTIR spec-

tra were acquired on a Perkin–Elmer BX FTIR system spectrometer by dispersing samples in KBr disks. The Raman spectrum was recorded on a DILORXY spectrometer employing a 633 nm laser beam. Steric exclusion chromatography was performed on a Waters Model 510 HPLC pump with a Waters 410 differential refractometer. The experiment was done using THF as solvent with standard polystyrene calibration. Thermogravimetric analysis (TGA) was carried out on a Setaram TG-DTA 92–10 thermal analyzer, under ambient atmospheric conditions at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed on a Setaram instrumentation-regulation DSC 131 system, under nitrogen atmosphere with a heating rate of 5°C/min. UV–Vis absorption spectra were recorded on a Cary 2300 spectrophotometer. Photoluminescence (PL) spectra were obtained on a Jobin Yvon TRIAX 190 spectrometer coupled to a nitrogen-cooled CCD camera. Samples were excited with a pulsed nitrogen laser line at 337 nm. For solid-state measurements, the films were deposited onto a quartz substrate from a chloroform solution. All measurements were performed at room temperature.

Synthesis of 2,2-bis(4-ethoxyphenyl)propane (BPAEt₂)

To a stirred mixture of BPA (10 mmol) and K₂CO₃ (40 mmol) in 20 mL of dimethylformamide, bromoethane

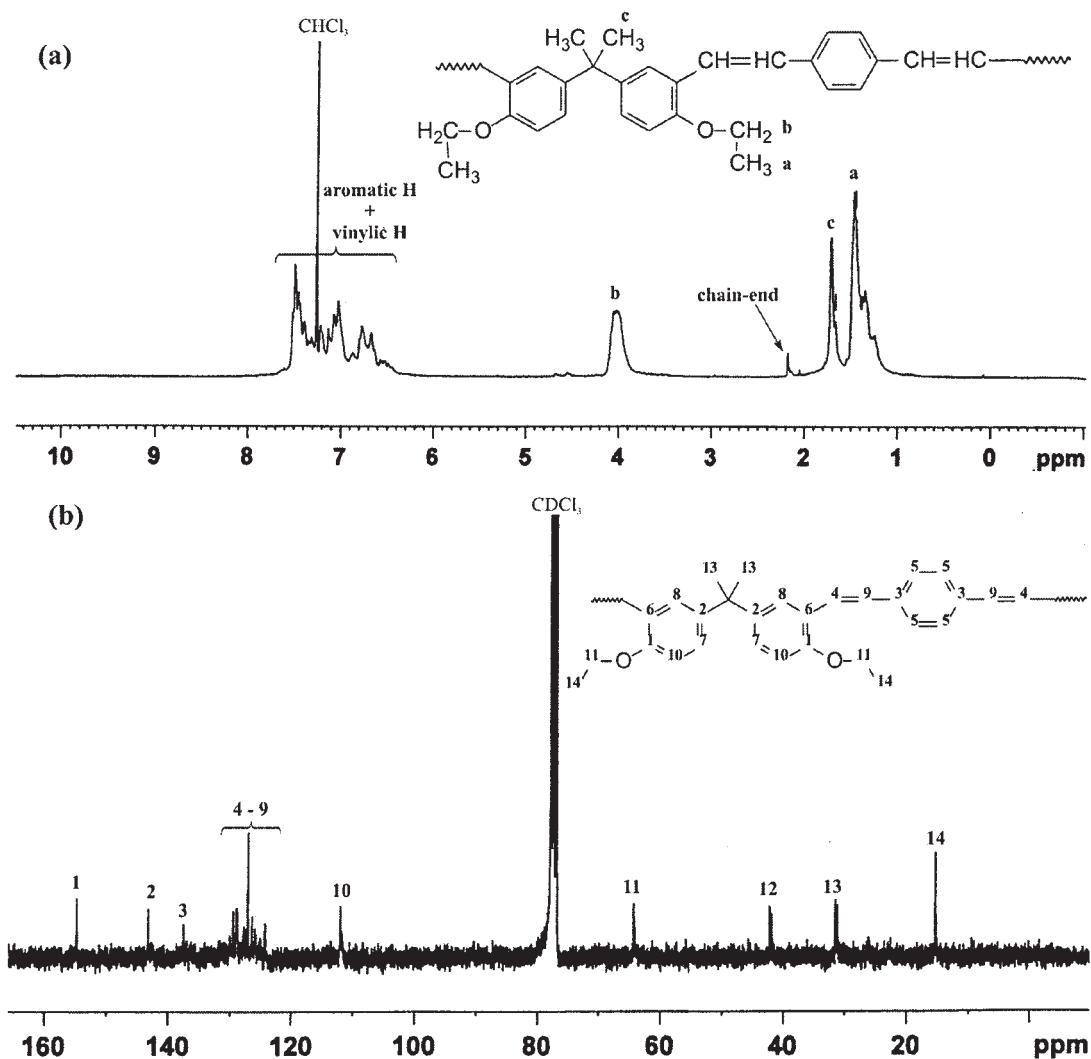


Figure 1 ^1H NMR (a) and ^{13}C NMR (b) spectra of $\text{BPAEt}_2\text{-PPV}$.

(30 mmol) was added dropwise. After stirring for 5 h at room temperature (25°C), the reaction mixture was poured into distilled water and extracted with diethyl ether. The extract was washed with distilled water, dried over anhydrous MgSO_4 , and then evaporated. The resultant crude product was purified by recrystallization from ethanol/water (3/1), to afford BPAEt_2 as needle-like white crystals.

Yield: 90%; mp: 48°C . ^1H NMR (300 MHz, CDCl_3 , δ): 7.13 (d, $J = 8.7$ Hz, 4H, Ar—H), 6.8 (d, $J = 8.7$ Hz, 4H, Ar—H), 4.00 (q, $J = 6.9$ Hz, 4H, —O— CH_2 —), 1.64 (s, 6H, $>\text{C}(\text{CH}_3)_2$), 1.40 (t, $J = 6.9$ Hz, 6H, — CH_3). ^{13}C NMR (75.5 MHz, CDCl_3 , δ): 156.76, 143.07, 127.75, 113.79, 63.35, 41.68, 31.12, 14.98. FTIR (cm^{-1}): 3064, 3047, 3035 (w, aromatic C—H stretching), 2975, 2935, 2877 (s, aliphatic C—H stretching), 1608, 1511 (s, C=C stretching), 1247 (s, C—O—C asymmetric stretching), 1049 (m, C—O—C symmetric stretching), 836 (s, aromatic C—H out-of-plane bending).

Synthesis of 2,2-bis(3-chloromethyl-4-ethoxyphenyl)propane (BPAEt_2Cl)

A mixture of BPAEt_2 (10 mmol), paraformaldehyde (2.5 g), and 37% aqueous HCl (8.5 mL) in acetic acid (30 mL) was heated at 55°C for 5 h. The resulting mixture was then poured into distilled water and extracted with diethyl ether. The organic layer was washed several times with distilled water and dried over anhydrous MgSO_4 . After solvent removal and two recrystallizations from hexane, BPAEt_2Cl was obtained as colorless crystals.

Yield: 75%; mp: 80°C . ^1H NMR (300 MHz, CDCl_3 , δ): 7.21 (d, $J = 2.7$ Hz, 2H, Ar—H), 7.10 (dd, $J_1 = 2.7$ Hz, $J_2 = 8.4$ Hz, 2H, Ar—H), 6.77 (d, $J = 8.4$ Hz, 2H, Ar—H), 4.63 (s, 4H, — CH_2 —Cl), 4.07 (q, $J = 6.9$ Hz, 4H, —O— CH_2 —), 1.64 (s, 6H, $>\text{C}(\text{CH}_3)_2$), 1.43 (t, $J = 6.9$ Hz, 6H, — CH_3). ^{13}C NMR (75.5 MHz, CDCl_3 , δ): 154.79, 142.70, 128.93, 128.41, 125.21, 111.33, 63.96, 42.18, 41.76, 31.08, 14.95. FTIR (cm^{-1}): 3041 (w, aro-

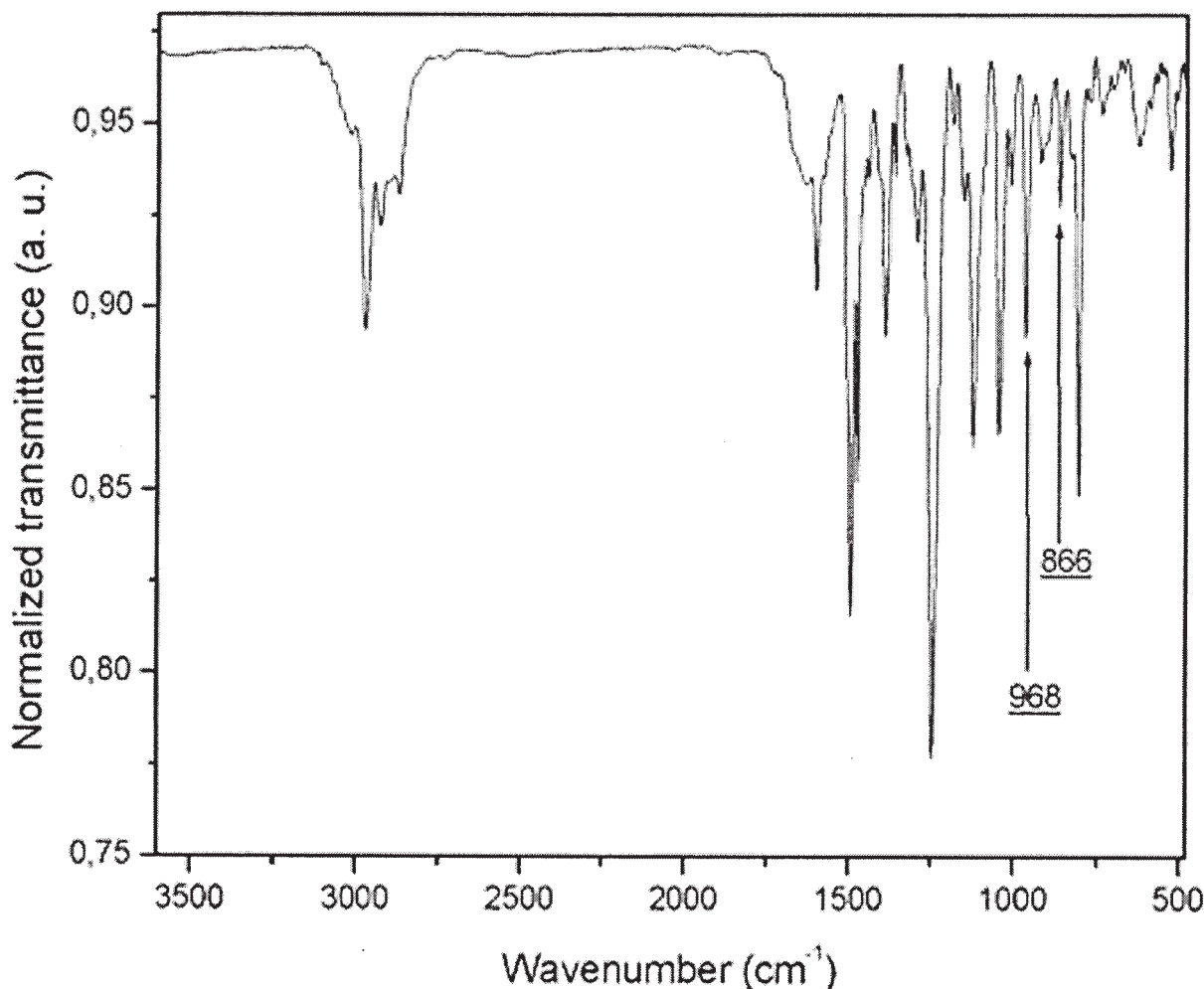


Figure 2 FTIR spectrum of BPAEt₂-PPV.

matic C—H stretching), 2981, 2921, 2875 (s, aliphatic C—H stretching), 1608, 1502 (s, C=C stretching), 1255 (m, C—O—C asymmetric stretching + CH₂—Cl out-of-plane bending) 1051 (s, C—O—C symmetric stretching), 815 (s, aromatic C—H out-of-plane bending), 603 (s, C—Cl stretching).

Synthesis of 2,2-bis(4-ethoxy-3-triphenylphosphoniomethylphenyl)propane dichloride (BPAEt₂P)

A solution of BPAEt₂Cl (10 mmol) and triphenylphosphine (22 mmol) in anhydrous acetone (50 mL) was stirred and heated at reflux for 4 h in an argon atmosphere. After cooling the reaction mixture, the resulting white precipitate was filtered off, washed with diethyl ether several times and dried under vacuum.

Yield: 90%; mp: 220°C. ¹H NMR (300 MHz, CDCl₃, δ): 7.80–7.45 (m, 30H, -P(Ph)₃), 7.14 (s, 2H, Ar—H), 7.02 (d, *J* = 8.7 Hz, 2H, Ar—H), 6.49 (d, *J* = 8.7 Hz, 2H, Ar—H), 5.18 (d, ²*J*_{H-P} = 14.1 Hz, 4H, —CH₂—P), 3.47 (q, *J* = 6.9 Hz, 4H, —O—CH₂—), 1.20 (s, 6H, >C(CH₃)₂), 0.99 (t, *J* = 6.9 Hz, 6H, —CH₃).

¹³C NMR (75.5 MHz, CDCl₃, δ): 154.60, 142.06, 134.93, 134.08 (d, *J* = 9.7 Hz), 131.43, 130.05 (d, *J* = 12.5 Hz), 118.03 (d, *J* = 85.5 Hz), 114.35 (d, *J* = 9.0 Hz), 110.70, 63.26, 40.99, 30.26, 24.77 (d, ¹*J*_{C-P} = 47.8 Hz, —CH₂—P), 14.55. FTIR (cm⁻¹): 3054 (w, aromatic C—H stretching), 2970, 2930, 2869 (m, aliphatic C—H stretching), 1618, 1504 (s, C=C stretching), 1259 (m, C—O—C asymmetric stretching), 1112 (s, P—C stretching), 1039 (s, C—O—C symmetric stretching), 839, 752, 692 (*m-s*, aromatic C—H out-of-plane bending), 512 (s, P—Cl stretching).

Synthesis of poly[2,2-bis(4-ethoxyphenyl)propane-*alt*-1,4-divinylbenzene] (BPAEt₂-PPV)

To an equimolar mixture of BPAEt₂P (1 mmol) and terephthalaldehyde (1 mmol) in 30 mL of anhydrous THF was added dropwise 5 mL of 1.6M sodium ethoxide solution (freshly prepared by dissolving cleaned sodium metal in “superdry” ethanol) at 60°C under an argon atmosphere. The mixture was stirred for 24 h. The resulting polymer was precipitated in methanol and collected by filtration. Further

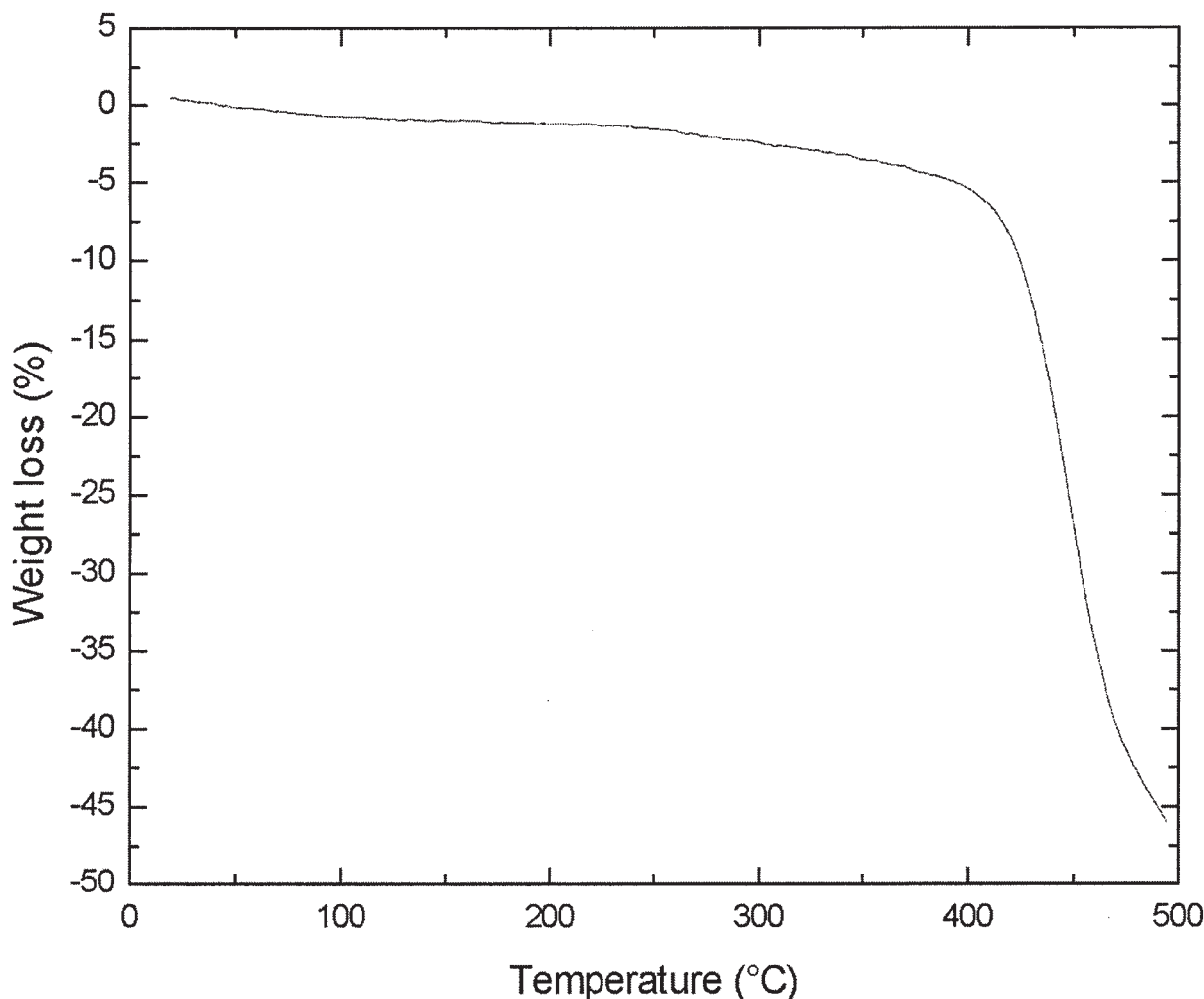


Figure 3 TGA thermogram of BPAEt₂-PPV.

purification was carried out by dissolving the polymer in chloroform, filtration, and precipitation in methanol. After drying under vacuum, a brown powder was obtained in 60% yield.

Fabrication and characterization of diode

A single-layer device was prepared via spin coating (2000 rpm) on ITO (20 Ω /square) from a 10% polymer/CHCl₃ solution. The film obtained was then annealed at 40°C for 2 h. The pretreatment of ITO included routine sonication first in acetone and then in isopropyl alcohol. The thin aluminum layer was deposited as the cathode by thermal evaporation at less than 10⁻⁵ Torr. The current-voltage (I-V) characteristic was recorded with a Keithley 236 source meter. The fabrication and characterization of the device were performed in air at room temperature.

RESULTS AND DISCUSSION

Synthesis and characterization of BPAEt₂-PPV

The synthetic route to the polymer, denoted BPAEt₂-PPV, is shown in Scheme 1.

The synthetic pathway of BPAEt₂-PPV is quite simple, with a good yield in every step and using relatively cheap starting materials. The polymer was found to have good solubility in common organic solvents such as THF, CH₂Cl₂, and CHCl₃.

The polymer structure was established by ¹H NMR, ¹³C NMR (Fig. 1), FTIR (Fig. 2), and Raman spectroscopic analysis.

The ¹H NMR spectrum showed a broad peak between 7.70 and 6.20 ppm assigned to phenylene and vinylic protons. The —CH₂O— group and the two methyl groups appear respectively, in the ranges 4.20–3.80 ppm and 1.80–1.00 ppm. Absence of the aldehyde terminal groups was supported by the absence of the corresponding peak from the ¹H NMR spectrum (~ 10 ppm). On the other hand, the appearance of a weak signal at 2.18 ppm suggests a toluene end-group (Ar—CH₃). In fact, regarding the quantum efficiency, this feature is very significant knowing that carbonyl is a fluorescence-quencher group.¹⁹

The valence band of aromatic and vinylic C—H appears at 3020 cm⁻¹, and the valence bands of the aliphatic C—H groups are seen between 3000 and

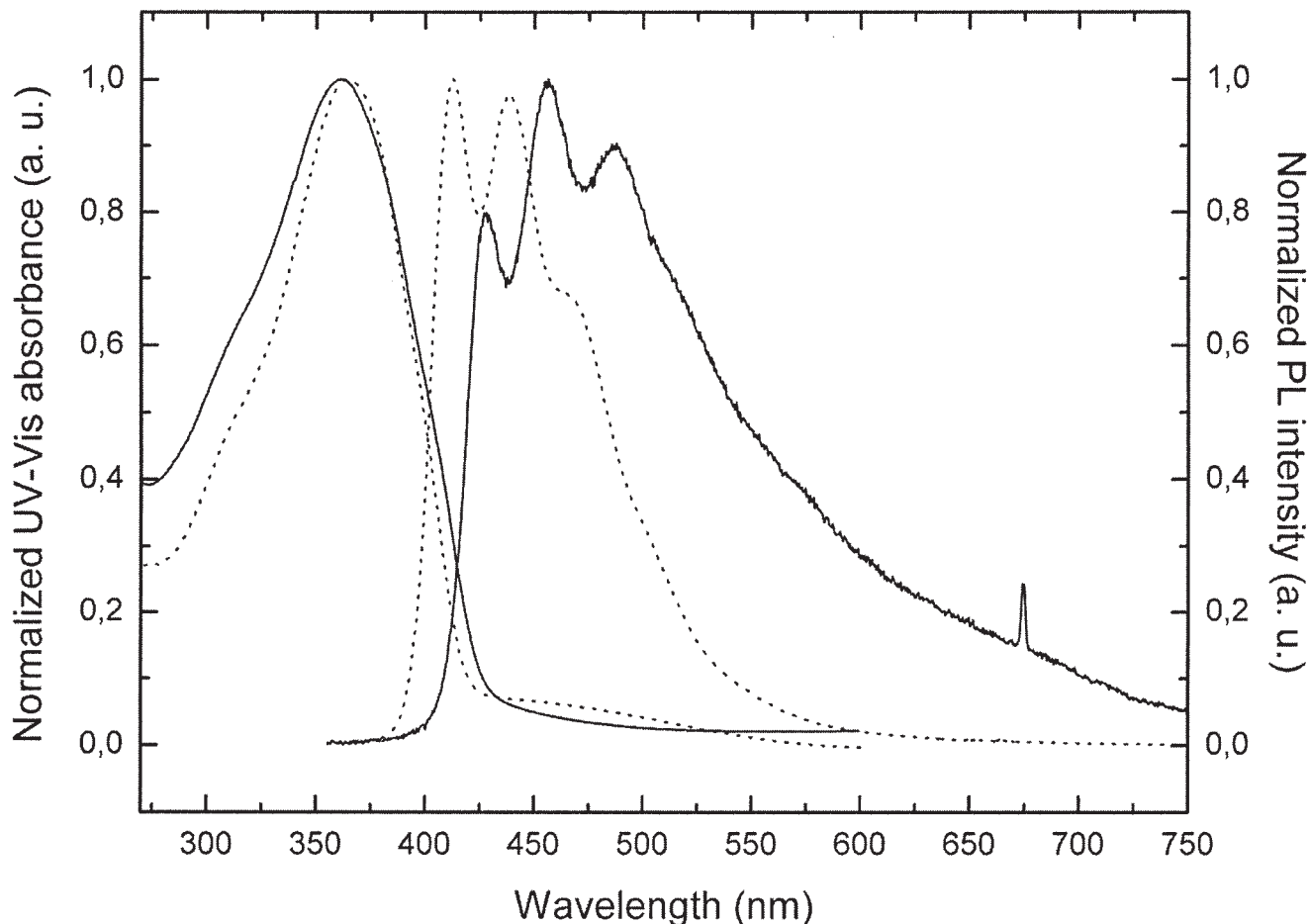


Figure 4 UV-Vis absorption and PL spectra of **BPAEt₂-PPV** in chloroform (dotted line) and in the solid state (solid line).

2800 cm^{-1} . The aromatic ring and vinylic $\text{C}=\text{C}$ stretching vibrations and deformation vibrations of the aliphatic chains appear between 1700 and 1350 cm^{-1} . The strong band at 1246 cm^{-1} is attributed to the asymmetric $\text{C}-\text{O}-\text{C}$ vibration. The band at 1043 cm^{-1} is attributed to the symmetric $\text{C}-\text{O}-\text{C}$ vibration. The out-of-plane vibration of the aromatic hydrogen shows a strong absorption at 806 cm^{-1} . The spectrum showed the presence of both *cis* (866 cm^{-1}) and *trans* (968 cm^{-1}) vinylic absorptions.²⁰ This is confirmed in the Raman spectrum by two bands at 1291 cm^{-1} (for *cis* $\text{HC}=\text{CH}$ stretching) and 1314 cm^{-1} (for *trans* $\text{HC}=\text{CH}$ stretching).²¹

By comparing the ¹H NMR signal integration for toluene terminal groups and $-\text{OCH}_2-$ units, the number-average degree of polymerization (DP_n) was estimated to be ~ 10 . SEC analysis showed a number-average molecular weight (M_n) of 3200 ($DP_n = 7$) and a polydispersity index (PDI) of 1.53. However, the results obtained by NMR are more exact. Indeed, this method is an absolute method contrary to the SEC, which is related to the hydrodynamic volume of the polymer and whose results depend on the nature of polymer used as reference.

Thermal properties of luminescent polymer are one of the most important properties for both processing and PLED applications.²² The thermal stability of **BPAEt₂-PPV** was investigated by TGA and DSC. The TGA thermogram (Fig. 3) shows that the weight loss of polymer is 5% on heating at 400°C under ambient atmospheric conditions, and no distinct weight loss was observed at lower temperature. The DSC result indicates that the polymer displays a T_g at $\sim 107^\circ\text{C}$ and a melting peak at 133°C. A relatively low T_g (73°C) has been reported for a polymer containing almost the same conjugated segment of **BPAEt₂-PPV** and a longer flexible spacer segment.²³ So, the polymer **BPAEt₂-PPV** is thermooxidatively quite stable and has a relatively high T_g , which may be favorable for long-life operation when used in light-emitting devices.²⁴

Optical properties

The UV-Vis absorption and PL spectra of a dilute chloroform solution and of a thin film of **BPAEt₂-PPV** spin coated on a silica plate are depicted in Figure 4.

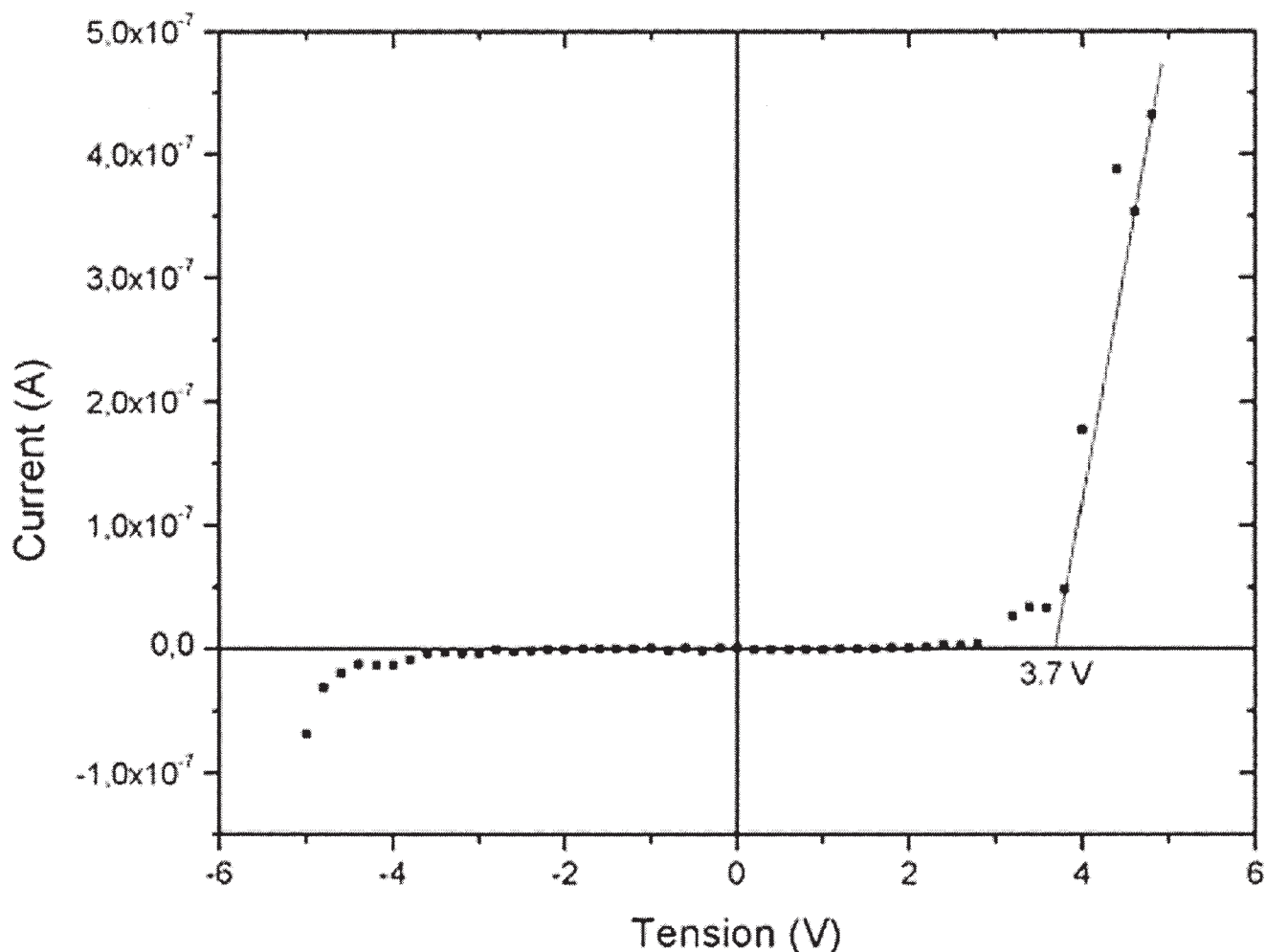


Figure 5 Current-voltage curve of ITO/ BPAEt₂-PPV/Al diode.

As the sp^3 site arising from the BPA (Scheme 1) disrupts the conjugation, the copolymer can be seen as a chain of loosely coupled PV oligomers, similar enough to the compound $n = 3$.²⁵ Indeed in solution, this oligomer and our copolymer present quite comparable spectral features: a broad absorption band and a structured PL emission.

The copolymer shows an absorption maximum at 364 nm (3.4 eV) and emits blue light with peak maxima at 412 nm (3.0 eV) and 439 nm with a shoulder at ~ 470 nm. Noteworthy, the emission peak is especially narrow with a full width at half-maximum of ~ 85 nm, which is in agreement with the confined emitting chromophore structure. More precisely, by comparison with the $n = 3$ oligomer solution, the copolymer spectra, for absorption as well for emission, exhibit an overall blue shift by 0.2 eV due to the electronic effect of the ethoxy groups.

In the solid state, the absorption spectrum of the copolymer reveals nearly the same maximum and shape as in solution. In contrast, the emission spectrum is slightly broadened and red-shifted (~ 17 nm

i.e., 0.1 eV) with three emission maxima at 428, 456, and 488 nm. The third peak corresponds to an enhancement of the shoulder shown in the solution emission. From the onset of film absorption (427 nm), the optical band-gap is calculated to be 2.9 eV.

Electrical properties

A single-layer device with the configuration ITO/BPAEt₂-PPV/Al has been fabricated to investigate the I-V characteristic of the polymer. As shown in Figure 5, the I-V curve indicates typical diode behavior with a relatively low turn-on voltage of 3.7 V.

No electroluminescence could be recorded for this simple device. The reason is probably the confinement that increases the exciton binding energy and the electrical bandgap, and thus the energy barriers at electrodes. Furthermore for a single-layer diode, it is difficult to get a balanced injection of holes and electrons. Thus, the turn-on voltage indicates the threshold of unipolar injection. Work is in progress to build multilayer devices.

CONCLUSIONS

A new copolymer (**BPAEt₂-PPV**), consisting of alternating O-diethylated BPA and divinylbenzene units, has been synthesized and characterized. The well-defined degree of conjugation in the oligomeric PV segment results in a chromophore that exhibits blue PL (428, 456, and 488 nm). The polymer is intrinsically soluble and has a number-average molecular weight of 3200 with a PDI of 1.53. **BPAEt₂-PPV** is thermally stable up to 400°C under ambient atmospheric conditions and displays a T_g of 107°C. The band-gap energy of the polymer is about 2.9 eV. The I–V characteristic of the device with an ITO/**BPAEt₂-PPV**/Al configuration demonstrates typical diode behavior and a relatively low turn-on voltage of 3.7 V. In further work, this new photoluminescent polymer will be characterized in different light-emitting-device configurations.

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