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Synthesis, Optical Properties, and Electroluminescence of Conjugated Poly(*p*-phenylenevinylene) Derivatives Containing 1,3,4-Oxadiazole and Pyridine Rings in the Main Chain

JOHN A. MIKROYANNIDIS,¹ VASILIOS P. BARBERIS,¹ LIMING DING,² FRANK E. KARASZ²

¹Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece

²Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: Three new poly(*p*-phenylenevinylene) derivatives—PO, POD, and POP—with oxadiazole and pyridine rings along the main chain were synthesized via Heck coupling. The polymers were amorphous and dissolved readily in common organic solvents. They showed relatively low glass-transition temperatures (up to 42 °C) and satisfactory thermal stability. Solutions of the polymers emitted blue-greenish light with photoluminescence (PL) emission maxima around 460 nm and PL quantum yields of 0.28–0.49. Thin films of the polymers displayed PL emission maxima at 461–521 nm, and their tendency to form aggregates was significantly influenced by the chemical structure. Light-emitting diodes with polymers PO and POP, with an indium tin oxide/poly(ethylenedioxythiophene) (PEDOT)/polymer/Ca configuration, emitted yellow and green light, respectively, and this could be attributed to excimer emission. © 2004 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 42: 3212–3223, 2004

Keywords: conjugated polymers; electroluminescence; fluorescence; light-emitting polymers; 1,3,4-oxadiazole; poly(*p*-phenylenevinylene); photoluminescence; photophysics; pyridine; synthesis

INTRODUCTION

Polymer light-emitting diodes (LEDs)¹ have been studied extensively because they have remarkable advantages, such as thinness, flexibility, color versatility, and a 180° viewing angle, in comparison with inorganic LEDs. Poly(*p*-phenylenevinylene)s (PPVs) constitute one of the most intensively investigated classes of polymers for this purpose.² PPVs are predominantly hole-con-

ducting materials with high lowest unoccupied molecular orbital levels. The unbalanced charge-carrier-transport properties and the relatively high barrier for electron injection from electrode metals such as aluminum are disadvantages of these materials.³ For highly efficient LED devices, a balance in the injection of holes and electrons into the polymer emissive layer is necessary. Therefore, attention has been drawn to the development of polymers with improved electron-transport capability.^{3–6} Conjugated polymers with high electron affinities have lower barriers for electron injection from metal cathodes.^{7,8} Polymers containing electron-withdrawing units in the main chain or at side groups usually have

Correspondence to: J. A. Mikroyannidis (E-mail: mikroyan@chemistry.upatras.gr)

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high electron affinities. Copolymers containing 1,3,4-oxadiazole have been found to be very efficient electron-transporting and hole-blocking materials.^{4,6} Several oxadiazole-containing polymers have been synthesized as electron-transporting materials.⁹ Oxadiazole-containing light-emitting polymers have also been prepared in recent years.^{4,6,10–15} Similarly, as pyridine is a moderately electron-deficient π system, poly(pyridine)s have also acted as electron-injection/hole-blocking materials for organic LED fabrication.¹⁶ In another report, LEDs with poly(pyridylvinylene) as the emissive material and PPV as the hole-injection material were found to give improved external quantum efficiency.¹⁷

This article describes the synthesis and characterization of a new class of PPV-based conjugated polymers with 1,3,4-oxadiazole and pyridine rings in the backbone. They were successfully synthesized via Heck coupling and were expected to improve the electron-transport properties. This article is a continuation of our effort to prepare novel PPV-type polymers bearing oxadiazoles in the main chain or in the side groups.^{18,19}

EXPERIMENTAL

Characterization

IR spectra were recorded on a PerkinElmer 16PC Fourier transform infrared (FTIR) spectrometer with KBr pellets. ¹H NMR (400 MHz) spectra were obtained with a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. Ultraviolet–visible (UV–vis) spectra were recorded on a Beckman DU-640 spectrometer with spectrograde tetrahydrofuran (THF). The photoluminescence (PL) spectra were obtained with a PerkinElmer LS45 luminescence spectrometer. Gel permeation chromatography (GPC) analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters 2410) as a detector with polystyrene as a standard and THF as an eluent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA,

and weight-loss comparisons were made between comparable specimens. The DSC thermograms were obtained at a heating rate of 10 °C/min under an N₂ atmosphere at a flow rate of 60 cm³/min. Dynamic TGA measurements were made at a heating rate of 20 °C/min in an atmosphere of N₂ or air at a flow rate of 60 cm³/min. Thermomechanical analysis (TMA) was performed with a DuPont 943 TMA instrument with a loaded penetration probe at a scanning rate of 10 °C/min in N₂ with a flow rate of 60 cm³/min. The TMA experiments were conducted at least twice to ensure the accuracy of the results. The TMA specimens were pellets 8 mm in diameter and 2 mm thick that were prepared by the pressing of the polymer powder for 3 min under 5–7 kpsi at the ambient temperature. The glass-transition temperature (T_g) was assigned to the first inflection point in the TMA curve and was obtained from the onset temperature of this transition during the second heating. Elemental analyses were carried out with a Carlo Erba EA1108 analyzer.

For the measurement of the PL quantum yields (Φ_f), a degassed solution of the polymer in THF was prepared. The concentration was adjusted so that the absorbance of the solution was lower than 0.1. The excitation was performed at the corresponding PL excitation maximum ($\lambda_{ex,max}$), and a solution of quinine sulfate in 1 N H₂SO₄, which had a Φ_f value of 0.546 [excitation wavelength (λ_{ex}) = 365 nm], was used.

Reagents and Solvents

A Stille coupling reaction was used to prepare 1,4-didodecyloxy-2,5-divinylbenzene.²⁰ In particular, 1,4-bis(dodecyloxy)-2,5-dibromobenzene was reacted with tributylvinyltin in the presence of the catalyst PdCl₂(PPh₃)₂ and a few crystals of 2,6-di-*tert*-butylphenol with toluene as a solvent. Nicotinic acid was recrystallized from toluene. 4-Bromobenzoyl chloride was synthesized from the reaction of 4-bromobenzoic acid with thionyl chloride. 3-(4-Bromophenyl)acryloyl chloride was synthesized according to a reported method.¹⁸ Dimethylformamide (DMF) and triethylamine were dried by distillation over CaH₂ and KOH, respectively. All other solvents and reagents were analytical-grade, were purchased commercially, and were used without further purification.

Preparation of the Monomers

5-Bromonicotinic Acid (1)

Compound **1** was prepared according to a reported method²¹ that was modified as follows. A flask was charged with a mixture of nicotinic acid (2.00 g, 16.2 mmol) and thionyl chloride (10 mL). A catalytic amount of DMF (two drops) was added, and the mixture was refluxed for 1 h. Then, bromine (4.07 g, 25.3 mmol) was added dropwise to the stirred mixture at 70 °C. The mixture was subsequently stirred and refluxed for 20 h. Volatile components were removed by concentration under reduced pressure. Water was added to the residue to hydrolyze the acid chloride, and the mixture was stirred for 1 h and then concentrated. The obtained solid was heated at about 110 °C *in vacuo* for 3 h to thermally decompose the hydrochloride salt. Then, it was recrystallized from boiling water to afford **1** (2.45 g, yield = 75%, mp = 180–182 °C).

IR (KBr, cm⁻¹): 3034, 1678, 1580, 1450, 1416, 1292, 1230, 1174, 1094, 1016, 904, 848, 768, 716, 688, 650, 552. ¹H NMR [dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), δ]: 9.05 (s, 1H, at position 2), 8.92 (s, 1H, at position 6), 8.39 (s, 1H, at position 4). ELEM. ANAL. Calcd. for C₆H₄BrNO₂: C, 35.67%; H, 1.99%; N, 6.93%. Found: C, 35.34%; H, 2.08%; N, 6.75%.

5-Bromonicotinoyl Chloride (2)

A mixture of **1** (0.84 g, 4.16 mmol), thionyl chloride (5 mL), and two drops of DMF was refluxed for 2 h. Then, it was concentrated under reduced pressure. The whitish residue was triturated with *n*-hexane and dried to afford **2** (0.80 g, yield = 87%, mp = 159–161 °C).

IR (KBr, cm⁻¹): 3102, 3050, 3026, 1724, 1628, 1588, 1526, 1410, 1378, 1236, 1206, 1156, 1104, 1022, 850, 790, 696, 658, 638. ¹H NMR (DMSO-*d*₆, δ): 9.10 (s, 1H, at position 2), 8.92 (s, 1H, at position 6), 8.50 (s, 1H, at position 4). ELEM. ANAL. Calcd. for C₆H₃BrClNO: C, 32.69%; H, 1.37%; N, 6.35%. Found: C, 32.50%; H, 1.28%; N, 6.52%.

5-Bromonicotinic Acid Hydrazide (3)

Anhydrous ethanol (ca. 10 mL) was added portionwise at 0 °C to a flask that was charged with **2** (4.80 g, 33.92 mmol). Triethylamine (4.46 g, 44.10 mmol) was subsequently added to the mixture at 0 °C. The mixture was stirred at room temperature for 3 h under N₂. Then, it was concentrated under reduced pressure to afford 5-bro-

monicotinic acid ethyl ester. The latter was not isolated and was converted into compound **3** as follows. Ethanol (20 mL) and hydrazine hydrate (5 mL) were added to the concentrate, and the mixture was refluxed for 5 h. It was subsequently concentrated under reduced pressure, and water was added to the concentrate. The silver precipitate was filtered and recrystallized twice from distilled water to afford **3** (1.44 g, yield = 20%, mp = 195–197 °C).

IR (KBr, cm⁻¹): 3288, 3206, 1656, 1630, 1538, 1416, 1334, 1306, 1202, 1162, 1014, 886, 746, 694, 654. ¹H NMR (DMSO-*d*₆, δ): 10.06, (broad, 1H, CONH), 8.94 (s, 1H, aromatic at position 2), 8.84 (s, 1H, aromatic at position 6), 8.37 (s, 1H, aromatic at position 4), 4.67 (broad, 2H, NH₂). ELEM. ANAL. Calcd. for C₆H₆BrN₃O: C, 33.36%; H, 2.80%; N, 19.45%. Found: C, 33.17%; H, 2.94%; N, 19.58%.

4-Bromobenzoic Acid N-(5-Bromopyridine-3-carbonyl)-hydrazide (4)

A flask was charged with a solution of **3** (0.67 g, 3.10 mmol) in DMF (10 mL). 4-Bromobenzoyl chloride (0.68 g, 3.10 mmol), dissolved in DMF (7 mL), was added portionwise to the stirred solution at 0 °C. Triethylamine (0.41 g, 4.03 mmol) was added to the stirred mixture at 0 °C. The stirring of the mixture was continued at 70 °C for 8 h under N₂. Then, it was concentrated under reduced pressure, and water was added to the concentrate. The whitish solid was filtered and recrystallized from ethanol to afford **4** (0.73 g, yield = 59%, mp = 263–265 °C).

IR (KBr, cm⁻¹): 3420, 3186, 3020, 1680, 1608, 1586, 1496, 1472, 1426, 1320, 1296, 1278, 1178, 1128, 1068, 1012, 850, 758. ¹H NMR (DMSO-*d*₆, δ): 10.85, 10.75 (broad, 2H, CONHNHCO), 9.03 (s, 1H, aromatic of pyridine at position 2), 8.95 (s, 1H, aromatic of pyridine at position 6), 8.47 (s, 1H, aromatic of pyridine at position 4), 7.86–7.84 (m, 2H, other aromatic ortho to carbonyl), 7.73–7.68 (m, 2H, aromatic ortho to Br). ELEM. ANAL. Calcd. for C₁₃H₉Br₂N₃O₂: C, 39.13%; H, 2.27%; N, 10.53%. Found: C, 38.92%; H, 2.34%; N, 10.45%.

3-Bromo-5-[5-(4-bromophenyl)-[1,3,4]oxadiazol-2-yl]-pyridine (5)

Compound **4** (0.20 g, 0.50 mmol) was dissolved via heating in POCl₃ (10 mL). The mixture was refluxed for 15 h and was subsequently concentrated under reduced pressure. Water was added to the concentrate, and a pale brown solid was

filtered, washed thoroughly with water, and dried to afford **5**. It was recrystallized from ethanol (0.13 g, yield = 68%, mp = 224–226 °C).

IR (KBr, cm^{-1}): 3024, 1602, 1476, 1444, 1406, 1272, 1082, 1012, 966, 898, 834, 740, 694. ^1H NMR ($\text{DMSO}-d_6$, δ): 9.28 (s, 1H, aromatic of pyridine at position 2), 8.96 (s, 1H, aromatic of pyridine at position 6), 8.77 (s, 1H, aromatic of pyridine at position 4), 7.85–7.83 (m, 2H, aromatic meta to Br), 7.70–7.68 (m, 2H, aromatic ortho to Br). ELEM. ANAL. Calcd. for $\text{C}_{13}\text{H}_7\text{Br}_2\text{N}_3\text{O}$: C, 48.98%; H, 1.85%; N, 11.03%. Found: C, 48.35%; H, 1.79%; N, 11.27%.

5-Bromonicotinic Acid N-[3-(4-Bromophenyl)-acryloyl]-hydrazide (**6**)

Compound **6** was prepared according to the procedure described for **4** as a whitish solid in a 72% yield (0.72 g) through the reaction of **3** (0.51 g, 2.36 mmol) with 3-(4-bromophenyl)-acryloyl chloride (0.57 g, 2.36 mmol) and triethylamine (0.31 g, 3.07 mmol) in DMF (7 mL). Compound **6** was recrystallized from dioxane (mp = 262–264 °C).

IR (KBr, cm^{-1}): 3172, 3008, 1642, 1606, 1488, 1430, 1284, 1226, 1176, 1072, 984, 818, 694, 494. ^1H NMR ($\text{DMSO}-d_6$, δ): 10.90, 10.41 (broad, 2H, CONHNHCO), 9.01 (s, 1H, aromatic of pyridine at position 2), 8.91 (s, 1H, aromatic of pyridine at position 6), 8.45 (s, 1H, aromatic of pyridine at position 4), 7.62–7.52, 6.78–6.53 (m, 4H, other aromatic, and 2H, olefinic). ELEM. ANAL. Calcd. for $\text{C}_{15}\text{H}_{11}\text{Br}_2\text{N}_3\text{O}_2$: C, 42.38%; H, 2.61%; N, 9.88%. Found: C, 42.04%; H, 2.57%; N, 9.93%.

3-Bromo-5-{5-[2-(4-bromophenyl)-vinyl]-[1,3,4]oxadiazol-2-yl}-pyridine (**7**)

Compound **7** was prepared according to the procedure described for **5** as a pale brown solid in a 95% yield (0.61 g) through the reaction of **6** (0.70 g, 1.64 mmol) with POCl_3 (10 mL). Compound **7** was recrystallized from dioxane (mp = 234–236 °C).

IR (KBr, cm^{-1}): 1686, 1628, 1586, 1520, 1488, 1402, 1272, 1074, 1010, 980, 816, 796, 694, 502. ^1H NMR ($\text{DMSO}-d_6$, δ): 9.00 (s, 1H, aromatic of pyridine at position 2), 8.92 (s, 1H, aromatic of pyridine at position 6), 8.46 (s, 1H, aromatic of pyridine at position 4), 7.87–7.46, 6.78–6.74 (m, 4H, other aromatic, and 2H, olefinic). ELEM. ANAL. Calcd. for $\text{C}_{15}\text{H}_9\text{Br}_2\text{N}_3\text{O}$: C, 44.26%; H, 2.23%; N, 10.32%. Found: C, 43.85%; H, 2.27%; N, 10.41%.

5-Bromonicotinic Acid N-(5-Bromopyridine-3-carbonyl)-hydrazide (**8**)

Compound **8** was prepared according to the procedure described for **4** as a white solid in a 35% yield (0.58 g) from the reaction of **2** (0.91 g, 4.13 mmol) with **3** (0.89 g, 4.13 mmol) and triethylamine (0.54 g, 5.37 mmol) in DMF (20 mL). The reaction mixture was concentrated under reduced pressure, and a dilute aqueous NaOH solution was added to the concentrate. The solid was filtered, washed with water, and recrystallized from DMF. It had a melting point that was greater than 300 °C.

IR (KBr, cm^{-1}): 3208, 3022, 1608, 1484, 1422, 1268, 1168, 1102, 1014, 900, 732, 692, 654, 612, 562. ^1H NMR ($\text{DMSO}-d_6$, δ): 10.82 (broad, 2H, CONHNHCO), 9.03 (s, 2H, at position 2), 8.94 (s, 2H, at position 6), 8.47 (s, 2H, at position 4). ELEM. ANAL. Calcd. for $\text{C}_{12}\text{H}_8\text{Br}_2\text{N}_4\text{O}_2$: C, 36.03%; H, 2.01%; N, 14.00%. Found: C, 35.88%; H, 2.12%; N, 14.36%.

2,5-Bis[3-bromopyridin-5-yl]-[1,3,4]oxadiazole (**9**)

Compound **9** was prepared according to the procedure described for **4** as a white solid in a 97% yield (0.35 g) through the reaction of **8** (0.41 g, 1.02 mmol) with POCl_3 (8 mL). It had a melting point that was greater than 300 °C.

IR (KBr, cm^{-1}): 3028, 1596, 1688, 1556, 1452, 1414, 1274, 1232, 1172, 1104, 998, 966, 936, 898, 786, 740, 696, 654. ^1H NMR ($\text{DMSO}-d_6$, δ): 9.03 (s, 2H, at position 2), 8.94 (s, 2H, at position 6), 8.48 (s, 2H, at position 4). ELEM. ANAL. Calcd. for $\text{C}_{12}\text{H}_6\text{Br}_2\text{N}_4\text{O}$: C, 37.73%; H, 1.58%; N, 14.66%. Found: C, 37.06%; H, 1.63%; N, 14.37%.

Preparation of the Polymers

Polymer PO

A flask was charged with **5** (0.1524 g, 0.400 mmol), 1,4-didodecyloxy-2,5-divinylbenzene (0.1992 g, 0.400 mmol), palladium(II) acetate [$\text{Pd}(\text{OAc})_2$] (0.0037 g, 0.016 mmol), and tri-*o*-tolylphosphine [$\text{P}(\text{o-tolyl})_3$] (0.0280 g, 0.092 mmol). The flask was degassed and purged with N_2 . DMF (5 mL) and triethylamine (2 mL) were added, and the mixture was stirred and heated at 110 °C for 24 h under N_2 . Then, it was filtered, and the filtrate was poured into methanol. The yellow-brown semisolid was isolated by decantation of the liquid, washed with methanol, and dried to afford PO (0.22 g, yield = 77%). The number-average

molecular weight (M_n) was 8400, and the polydispersity index was 2.1 (by GPC).

IR (KBr, cm^{-1}): 2924, 2860, 1682, 1586, 1480, 1424, 1400, 1320, 1298, 1070, 1012, 846, 758, 696, 546. ^1H NMR (CDCl_3 , δ): 9.26 (s, 1H, aromatic of pyridine at position 2), 8.86 (s, 1H, aromatic of pyridine at position 6), 8.57 (s, 1H, aromatic of pyridine at position 4), 7.71–7.05 (m, 6H, other aromatic, and 4H, $\text{HC}=\text{CH}$), 3.95 (m, 4H, OCH_2), 1.78, 1.42, 1.26, 0.87 (m, 46H, other aliphatic). ELEM. ANAL. Calcd. for $(\text{C}_{47}\text{H}_{63}\text{N}_3\text{O}_3)_n$: C, 78.69%; H, 8.84%; N, 5.85%. Found: C, 78.24%; H, 8.97%; N, 5.78%.

Polymer POD

Polymer POD was prepared according to the procedure described for PO as a yellow-brown solid in a 64% yield (0.45 g) through the reaction of **7** (0.3779 g, 0.966 mmol) with 1,4-didodecyloxy-2,5-divinylbenzene (0.4812 g, 0.966 mmol), $\text{Pd}(\text{OAc})_2$ (0.0090 g, 0.040 mmol), $\text{P}(o\text{-tolyl})_3$ (0.0676 g, 0.222 mmol), DMF (5 mL), and triethylamine (2 mL). M_n was 7600, and the polydispersity index was 1.9.

IR (KBr, cm^{-1}): 2920, 2850, 1624, 1496, 1464, 1422, 1386, 1212, 1070, 1012, 964.

For the ^1H NMR spectrum of POD, see the Results and Discussion section.

^{13}C NMR (CDCl_3 , δ): 165.17, 161.24, 153.92, 151.23, 150.06, 146.20, 139.25, 136.79, 133.76, 132.78, 131.59, 129.52, 129.42, 128.40, 127.14, 125.05, 121.52, 118.28, 114.99, 112.22, 110.65, 32.32, 30.05, 29.99, 29.85, 29.75, 29.69, 29.51, 23.09, 15.12. ELEM. ANAL. Calcd. for $(\text{C}_{49}\text{H}_{65}\text{N}_3\text{O}_3)_n$: C, 79.10%; H, 8.80%; N, 5.65%. Found: C, 78.83%; H, 8.86%; N, 5.47%.

Polymer POP

Polymer POP was prepared according to the procedure described for PO as a yellow-brown semi-solid in a 71% yield (0.20 g) through the reaction of **9** (0.1438 g, 0.406 mmol) with 1,4-didodecyloxy-2,5-divinylbenzene (0.2023 g, 0.406 mmol), $\text{Pd}(\text{OAc})_2$ (0.0038 g, 0.017 mmol), $\text{P}(o\text{-tolyl})_3$ (0.0283 g, 0.093 mmol), DMF (5 mL), and triethylamine (2 mL). M_n was 9800, and the polydispersity index was 2.3 (by GPC).

IR (KBr, cm^{-1}): 2924, 2854, 1676, 1602, 1500, 1466, 1422, 1388, 1206, 1038, 966, 704. ^1H NMR (CDCl_3 , δ): 9.22 (s, 2H, aromatic of pyridine at position 2), 8.94 (s, 2H, aromatic of pyridine at position 6), 8.47 (s, 2H, aromatic of pyridine at position 4), 7.62–6.82 (m, 2H, other aromatic, and

4H, $\text{HC}=\text{CH}$), 3.95 (m, 4H, OCH_2), 1.77, 1.46, 1.27, 0.88 (m, 46H, other aliphatic). ELEM. ANAL. Calcd. for $(\text{C}_{46}\text{H}_{62}\text{N}_4\text{O}_3)_n$: C, 76.84%; H, 8.69%; N, 7.79%. Found: C, 76.47%; H, 8.82%; N, 7.63%.

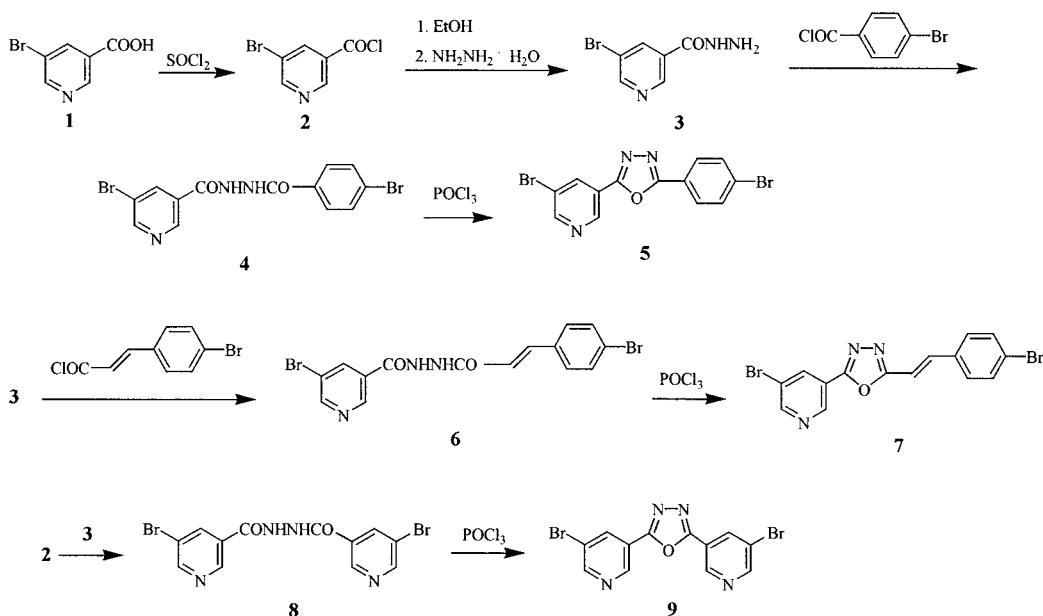
LED Fabrication and Measurements

Poly(ethylenedioxythiophene/poly(styrene sulfonate) (PEDOT/PSS) (Bayer Co.) was spin-cast directly onto indium tin oxide (ITO) glass as the anode. The polymer solutions (10 mg/mL in chloroform) were filtered through 0.2- μm Millex-FGS filters (Millipore Co.) and were spin-cast onto dried PEDOT/ITO substrates under a nitrogen atmosphere. Calcium electrodes 400 nm thick were evaporated onto the polymer films at about 10^{-7} Torr, and they were followed by a protective coating of aluminum. The electroluminescent properties of the devices sealed in argon were characterized with a system constructed at the University of Massachusetts and described elsewhere.²²

RESULTS AND DISCUSSION

Synthesis and Characterization

The basic strategies employed for the synthesis of the polymers are based on the Heck reaction²³ between a dibromide and dialkoxydivinylbenzene. The synthetic routes to the three dibromides **5**, **7**, and **9**, which were used as reagents in the Heck reaction, are illustrated in Scheme 1. More specifically, **1** was prepared through the refluxing of a solution of bromine (1.5 mol) and nicotiny chloride hydrochloride (1 mol) in excess thionyl chloride for a long time and the subsequent hydrolysis of the acid chloride and thermal decomposition of the hydrochloride salt.²¹ Compound **1** reacted with thionyl chloride to yield **2**. The latter afforded the corresponding ethyl ester and subsequently acid hydrazide **3** through reactions with anhydrous ethanol and hydrazine hydrate, respectively. Then, compound **3** reacted with 4-bromobenzoyl chloride to yield bishydrazide **4**. Finally, **4** was dehydrated by means of POCl_3 to afford dibromide **5**. In the latter reaction, POCl_3 served both as a reagent and a reaction solvent. The dehydration reaction was complete because the FTIR spectrum of **5** lacked the strong absorption of **4** associated with the hydrazide carbonyl. An analogous synthetic route was applied to the synthesis of dibromides **7** and **9**.



Scheme 1

Polymers PO, POD, and POP (Chart 1) were prepared from the reaction of 1,4-didodecyloxy-2,5-divinylbenzene with dibromides **5**, **7**, and **9**, respectively, via Heck coupling. They were obtained in 64–77% yields, M_n ranged from 7600 to 9800, and the polydispersity index was 1.9–2.3.

The structures of the polymers were confirmed by elemental analyses as well as FTIR, ^1H NMR, and ^{13}C NMR spectroscopy. Figure 1 shows typi-

cal FTIR and ^1H NMR spectra of POD. The FTIR spectrum of POD showed absorptions at 2920 and 2850 (C—H stretching of aliphatic segments),

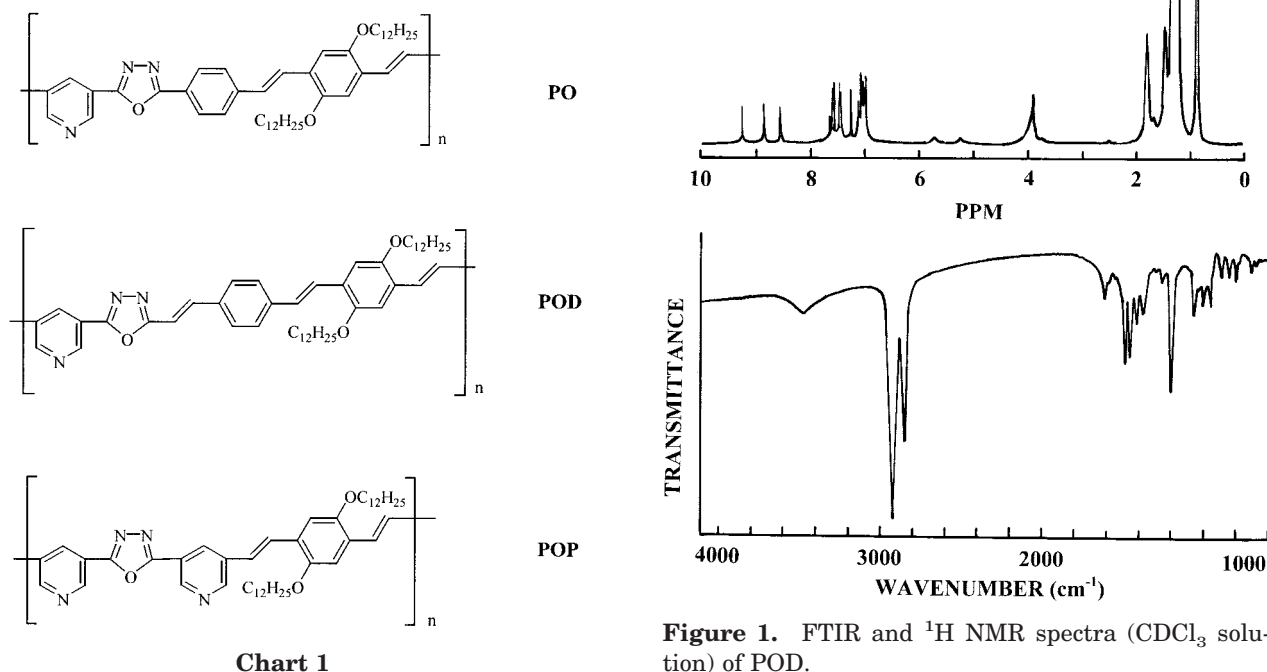


Figure 1. FTIR and ^1H NMR spectra (CDCl_3 solution) of POD.

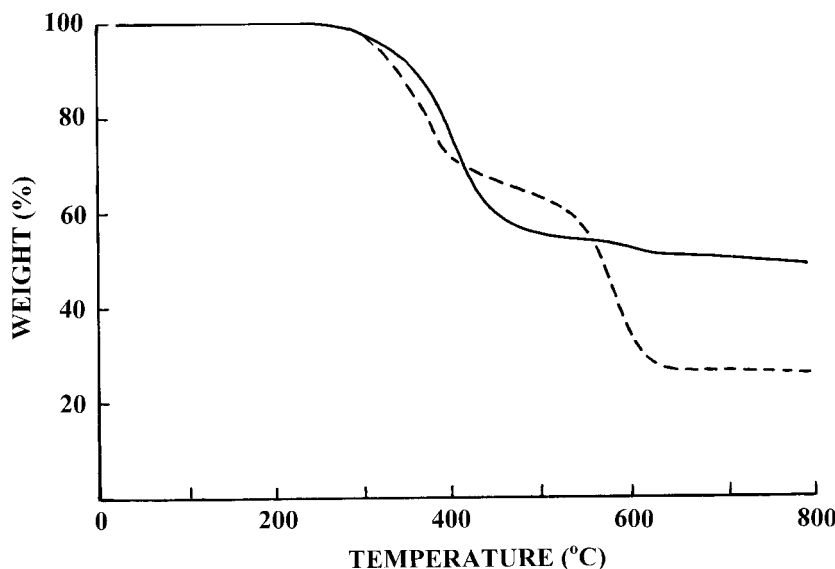


Figure 2. TGA traces of POD in (—) N₂ and (---) air.

1624, 1496, and 1464 (aromatic and oxadiazole), 1212, 1070, and 1012 (C—O—C stretching of ether bond and oxadiazole), and 964 cm⁻¹ (HC=CH). The ¹H NMR spectrum of this polymer in a CDCl₃ solution displayed peaks at 9.25 (s, 1H, aromatic of pyridine at position 2), 8.85 (s, 1H, aromatic of pyridine at position 6), 8.55 (s, 1H, aromatic of pyridine at position 4), 7.65–6.94 (m, 6H, other aromatic, and 6H, HC=CH), 4.00–3.89 (m, 4H, OCH₂), and 1.79, 1.47, 1.27, and 0.88 δ (m, 46H, other aliphatic). All the polymers were readily soluble at room temperature in common organic solvents such as THF, chloroform, dichloromethane, 1,1,2,2-tetrachloroethane, chlorobenzene, and *o*-dichlorobenzene.

The DSC traces of the polymers did not show any transition even after repeated scans; this indicated their amorphous nature. We attempted to determine the *T_g* values of the polymers by TMA with a penetration probe. The *T_g* values of PO and POP were lower than 25 °C, but they could not be precisely determined with the instrument used. The TMA traces of POD showed a reproducible dropping step, from which *T_g* was determined to be 42 °C. POD contained three vinylene bonds along the main chain per repeat unit, whereas the other two polymers contained two vinylene bonds. Because the polymers had comparable chemical structures, the existence of the additional vinylene bond in POD was likely responsible for its higher *T_g* value. Certain other related polymers synthesized in our laboratory¹⁸ showed *T_g*'s of 28–57 °C. *T_g* of POD was comparable to that of

poly(2,5-didodecyloxy-1,4-phenylenevinylene)²⁴ but lower than that of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene].²⁵ The two dodecyloxy side groups per repeat unit of these polymers gave rise to low *T_g*'s. The relatively low *T_g*'s of the polymers constitute a drawback for many applications, such as emissive materials in LEDs.²⁶

Figure 2 presents typical TGA traces of POD in N₂ and air. No weight loss was observed up to approximately 260 °C, and the anaerobic char yield was approximately 50% at 800 °C. It seems that the thermal degradation of this polymer took place in two distinguishable steps under air, the first of which was assigned to the thermally sensitive alkoxy side groups.

Optical Properties

The spectroscopic properties of the polymers were measured both in dilute THF solutions and in thin films, which were obtained via spin casting from THF solutions. Figures 3 and 4 present the UV-vis absorption, photoluminescence excitation (PLE), and PL emission spectra of polymers in solutions and thin films, and all the spectroscopic properties are summarized in Table 1.

The optical properties of the polymers were comparable because their chemical structures were only slightly differentiated. The absorption spectra in THF (Fig. 3) showed a shoulder around 370 nm attributable to the π–π* transition along the conjugated backbone. In addition, they dis-

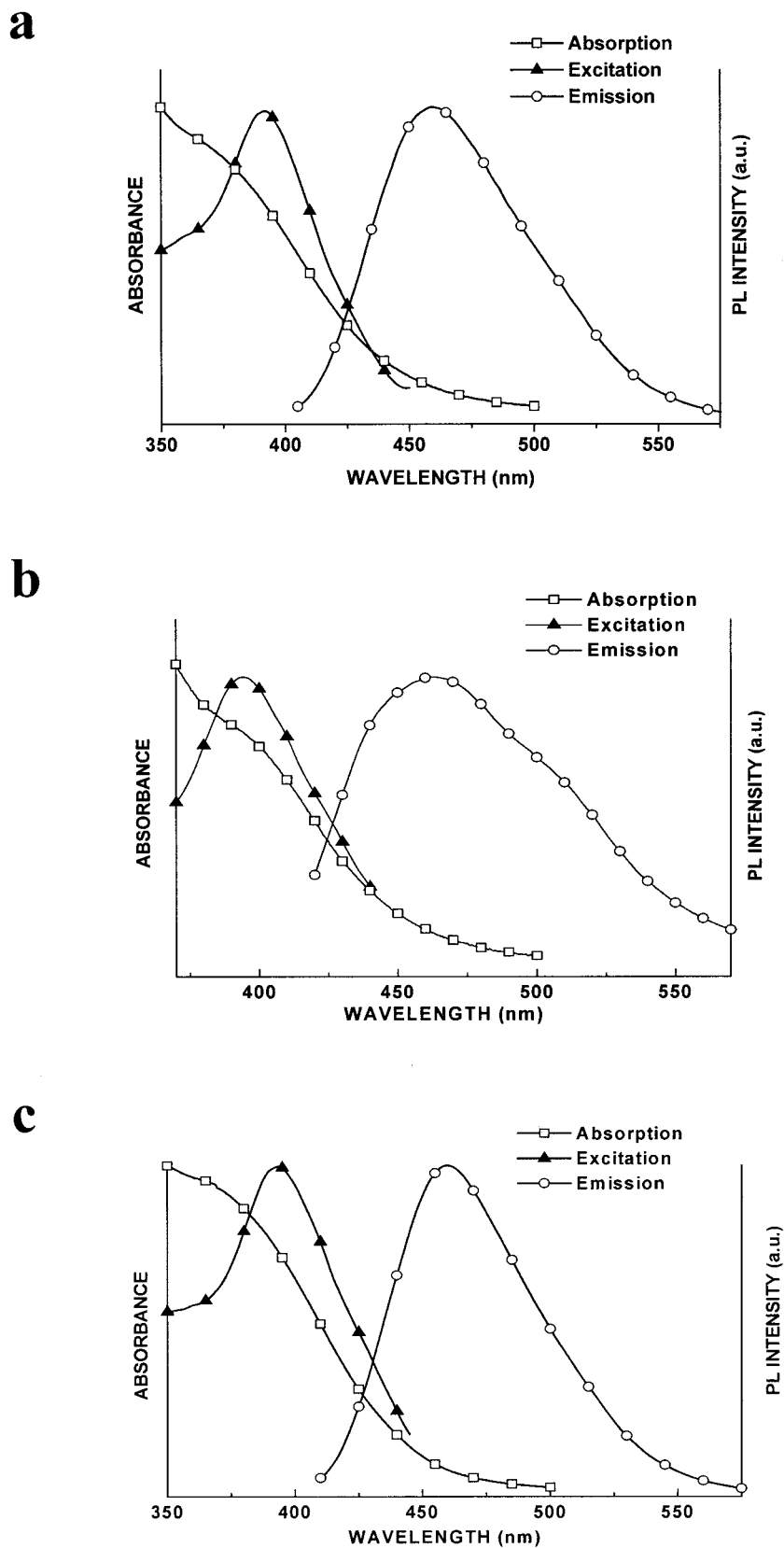


Figure 3. UV-vis absorption, PLE, and PL spectra (THF solution) of (a) PO, (b) POD, and (c) POP.

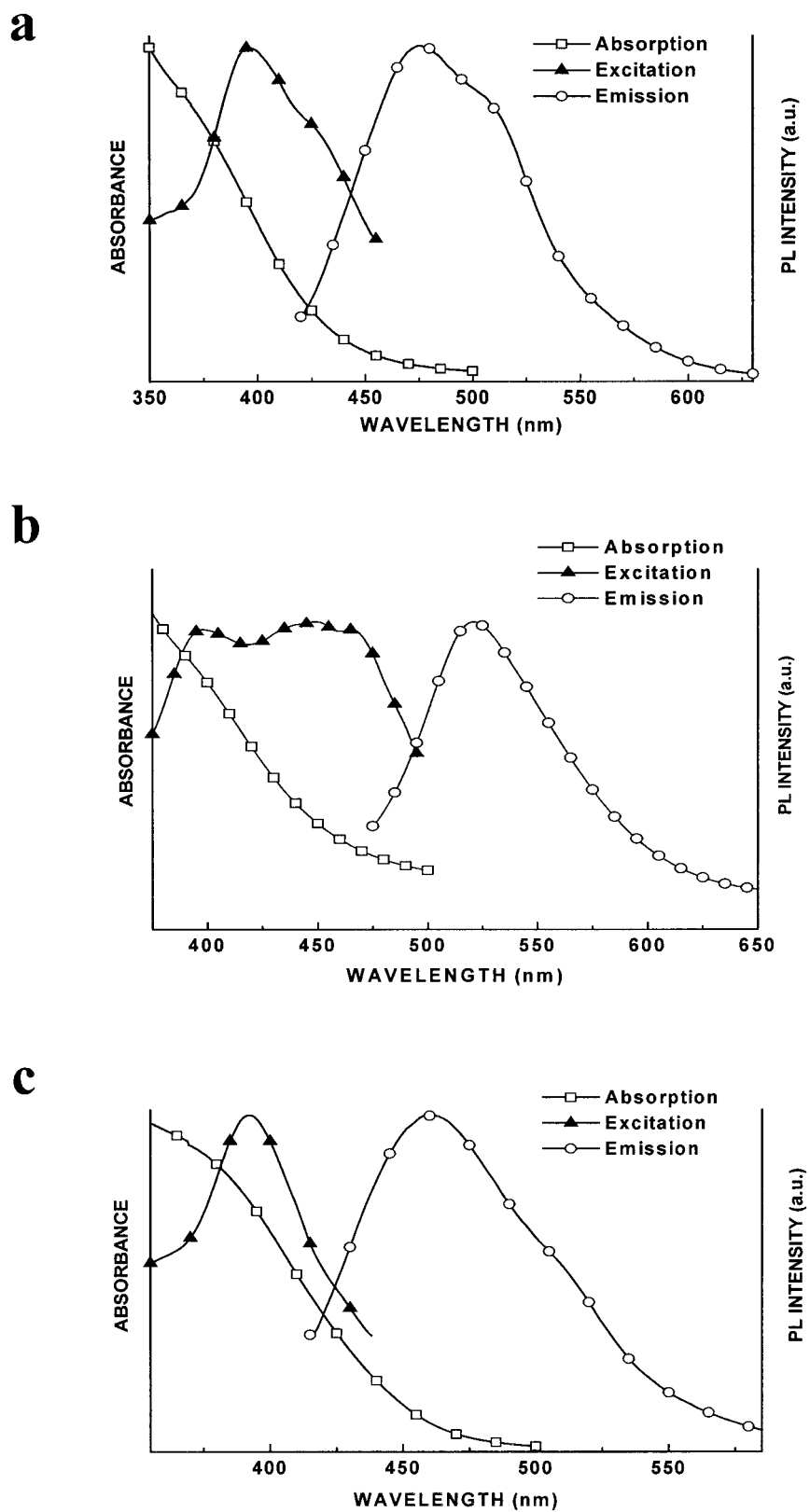


Figure 4. UV-vis absorption, PLE, and PL spectra (thin film) of (a) PO, (b) POD, and (c) POP.

Table 1. Optical Properties of the Polymers

Polymer	$\lambda_{a,max}$ in a THF Solution (nm)	$\lambda_{ex,max}$ in a THF Solution (nm)	$\lambda_{f,max}$ in a THF Solution (nm)	ϕ_f in Solution	$\lambda_{a,max}$ in a Thin Film (nm) ^a	E_g (eV) ^b	$\lambda_{ex,max}$ in a Thin Film (nm)	$\lambda_{f,max}$ in a Thin Film (nm)
PO	242, 290, 375	392	459	0.28		2.83	396	475
POD	234, 321, 390	394	463	0.49		2.70	398, 448	521
POP	242, 279, 370	394	460	0.38		2.75	392	461

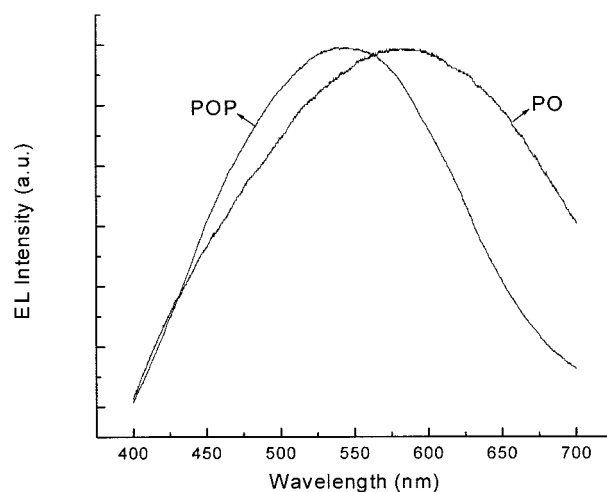
^a The italicized numbers denote absolute maxima. The PLE spectra were recorded with the corresponding $\lambda_{f,max}$ value as the emission wavelength. The PL spectra were recorded with the corresponding $\lambda_{ex,max}$ value as the excitation wavelength.

^b $\lambda_{a,max}$ could not be determined because of the broadening of the absorption curve. The optical energy gap calculated from UV-vis spectra in a thin film.

played maxima [i.e., absorption maxima from UV-vis spectra ($\lambda_{a,max}$)] near 240 and 290 nm (not shown) that were assigned to the phenylene and oxadiazole rings. The PLE spectra overlapped the absorption spectra and exhibited a maximum ($\lambda_{ex,max}$) near 394 nm. The solutions of the polymers emitted intense blue light with a PL maximum ($\lambda_{f,max}$) at about 460 nm. POD showed slightly higher electron delocalization along the polymer backbone than the other polymers because its $\lambda_{f,max}$ value was redshifted by 3–4 nm on account of the presence of the additional vinylene bond in the main chain. Furthermore, the PL curve of POD was broader and displayed a small shoulder at approximately 510 nm because of chain interactions even in dilute solutions. This PL emission of the polymers was blueshifted in comparison with poly(2,5-dialkoxy-1,4-phenylenevinylene)s (513 nm).²⁴ The PL efficiency of the polymers in THF was estimated through a determination²⁷ of their Φ_f values with respect to quinine sulfate (Table 1). Φ_f ranged from 0.28 to 0.49, and POD showed higher PL efficiency than the other two polymers.

The absorption spectra of the polymer thin films (Fig. 4) were rather broad, and so their $\lambda_{a,max}$ values could not be precisely determined. However, their optical energy band gap was calculated from the absorption edge in the thin films to be 2.70–2.83 eV (Table 1). The PLE spectra showed absolute $\lambda_{ex,max}$ values comparable to those in solution. Moreover, POD displayed another PLE peak at 448 nm that was significantly redshifted with respect to the solution value because of the formation of aggregates. The strong tendency of this polymer to form aggregates in the solid state was also established from its PL spectrum. In particular, the polymer thin films emitted blue, green, and blue light with $\lambda_{f,max}$ values

of 475, 521, and 461 nm for PO, POD, and POP, respectively. Hence, POP did not form aggregates in the solid state because its $\lambda_{f,max}$ value was almost the same in solutions and thin films. This feature is very attractive for the performance of LED devices. In contrast, PO and POD exhibited a tendency for aggregate formation, which was greater for the latter polymer, because their $\lambda_{f,max}$ values were redshifted by 16 and 58 nm, respectively, with respect to the solution values. This behavior could be assigned to the longer repeat unit of POD, which increased the distance between the adjacent alkoxy side groups and consequently the chain interactions. Generally, the PL emissions of these polymers in solutions and thin films were blueshifted in comparison with those of the other related polymers, PPV derivatives bearing oxadiazoles in the main chain.¹⁸ This behavior was ascribed to the presence of the 3,5-

**Figure 5.** EL spectra of ITO/PEDOT/PO/Ca and ITO/PEDOT/POP/Ca devices.

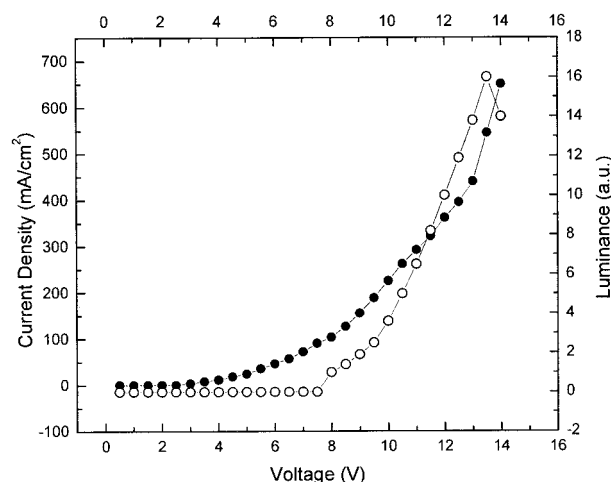


Figure 6. Relationship of (●) the current density, the voltage, and (○) the luminance for an ITO/PEDOT/POP/Ca device.

disubstituted pyridine in the backbone of these polymers, which reduced electron delocalization along the backbone.

To investigate the EL properties of these samples, we made double-layer LEDs with an ITO/PEDOT/polymer/Ca configuration. The POD device gave off a green emission at 5 V, but unfortunately the EL spectrum could not be obtained because of the weakness of the emission. PO and POP devices started emitting yellow and green light, respectively, at 8 V. The peak wavelengths for their EL spectra were 582 and 544 nm, respectively (Fig. 5). The longer phenylenevinylene conjugated block that appeared in the PO chain allowed the polymer to have a lower band gap and redshifted emission. Compared with the film PL spectra, the EL spectra showed remarkable redshifts, indicating possible excimer emissions from the devices. Figure 6 shows the current density–voltage–luminance characteristics for an ITO/PEDOT/POP/Ca device. Because of the low molecular weights, uniform spin-coating films of high quality for these samples were very difficult to obtain. The film morphological defects might act as exciton quenching centers, leading to very low quantum efficiency. Increasing the molecular weights of these samples and further improving the film-forming properties could be useful for improving the device performance.

CONCLUSIONS

Starting with readily available and inexpensive starting materials and following a convenient

synthetic route, we synthesized three new PPV-type polymers by Heck coupling. They showed excellent solubility in common organic solvents, were amorphous, and had relatively low T_g 's. The polymers behaved as blue or green luminescent materials with PL emission maxima near 460 nm in solutions and 461–521 in thin films. The Φ_f values were 0.28–0.49 in solution. The chain interactions of the polymers in the solid state were considerably affected by their chemical structure. One of the synthesized polymers, which contained one oxadiazole and two pyridine rings per repeat unit, had identical PL emission maxima in solutions and thin films and did not form aggregates.

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