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Synthesis, Photophysics, and Electroluminescence of Conjugated Poly(*p*-phenylenevinylene) Derivatives with 1,3,4-Oxadiazoles in the Backbone

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ABSTRACT: Starting from 4-bromobenzaldehyde or 1,4-benzenedicarboxaldehyde, two new poly(*p*-phenylenevinylene) derivatives **P1** and **P2** were synthesized by a five-step synthetic route. These fully conjugated polymers contain 1 or 2 oxadiazole rings and 3 or 4 vinylene bonds per repeat unit for **P1** and **P2**, respectively, and were amorphous and soluble in common organic solvents. The T_g values were 28 °C for **P1** and 57 °C for **P2**. The polymers emitted greenish-blue light in solution with photoluminescence (PL) emission maximum at 487–511 nm and yellowish-green light with PL emission maximum at 515–558 nm in thin films. Electroluminescence (EL) was achieved from single-layer LEDs of polymer **P1** with the configuration ITO/PEDOT/**P1**/Al with voltage-tunable EL colors from 558 nm (9 V) to 527 nm (16 V). The observed EL spectral blue shift with increasing voltage is a result of conformational changes of the polymer backbone with increase in temperature, as evidenced from the absorption and PL spectra changes upon annealing of **P1** thin films at different temperatures.

Introduction

Polymer light-emitting diodes (LEDs), based on conjugated polymers or polymers with conjugated segments or pendant groups, have recently attracted a lot of interest for their potential use in display technology.^{1–10} Poly(*p*-phenylenevinylene)s (PPVs) and stilbenoid oligomers are one of the most intensively investigated classes of emissive materials for fabrication of LEDs.^{1b} PPV-type materials are predominantly hole-conducting materials with high-lying LUMO levels. The unbalanced charge carrier transport properties and the relative high barrier for electron injection from electrode metals such as aluminum are disadvantages of these compounds.¹¹ Several strategies have been followed to improve the efficiency of LEDs with PPV as emitting layer. Additional layers of aryl-substituted 1,3,4-oxadiazole with high electron affinity between the luminescent material and the metal reduce the barrier for electron injection.¹² Other electron transport layers that have been used to improve EL emission efficiency of PPV-based LEDs include polyquinolines,^{6–8} polybenzobisazoles,⁹ and polypyridines.¹⁰ In addition, the substitution of PPV with electron acceptors like cyano groups enhances its electron affinity.¹³ Regarding the improvement of the electron affinity of the lumophore, stilbenoid chromophores with oxadiazoles as electron-withdrawing side chains or in the main chain are of current interest. Oxadiazole-based conjugated polymers have been shown

to be promising candidates for light-emitting devices^{14–17} due to their high electron affinity and hole-blocking ability as well as their thermal and hydrolytic stability and photostability.^{18–23}

The present paper describes the synthesis and characterization of two new PPV-type conjugated polymers with 1,3,4-oxadiazoles in the backbone. They were successfully synthesized from widely used and inexpensive starting materials by a five-step synthetic route, the last step of which was Heck coupling. The polymers are related, but their molecular structures are differentiated in order to provide a means for studying structure–property relationships. The electroluminescence and the associated photophysical properties of these polymers were also investigated.

Experimental Section

Characterization Methods. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ¹H NMR (400 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis absorption spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF or a Perkin-Elmer model Lambda 900 UV/vis/near-IR spectrophotometer. The PL spectra were obtained with a Perkin-Elmer LS45 luminescence spectrometer or Photon Technology International (PTI) Inc. model QM-2001-4 spectrofluorimeter. GPC analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters

2410) as detector using polystyrene as standard and THF as eluent. DSC and TGA were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA, and the weight loss comparisons were made between comparable specimens. The DSC thermograms were obtained at a heating rate of 10 °C/min in a N₂ atmosphere at a flow rate of 60 cm³/min. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N₂ or air at a flow rate of 60 cm³/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 10 °C/min in N₂ with a flow rate of 60 cm³/min. The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing powder of polymer for 3 min under 5–7 kpsi at ambient temperature. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

To measure the PL quantum yields (Φ_f), a degassed solution of polymer in THF was prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1, and the excitation was performed at the corresponding $\lambda_{\text{ex,max}}$. A solution of quinine sulfate in 1 N H₂SO₄, which has a Φ_f of 0.546 ($\lambda_{\text{ex}} = 365$ nm), was used as a standard. Cyclic voltammetry measurements of the polymers were done in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scan rate of 80 mV/s. Platinum wire electrodes were used as both counter and working electrodes, and silver/silver ion (Ag in 0.1 M AgNO₃ solution, from Bioanalytical Systems, Inc.) was used as a reference electrode. Using ferrocene as an internal standard, the potential values obtained were converted to vs SCE (saturated calomel electrode), and the corresponding highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the onset redox potentials.

Fabrication and Characterization of LEDs. The single-layer LEDs were fabricated as sandwich structures between aluminum (Al) cathodes and indium–tin oxide (ITO) anodes. ITO-coated glass substrates (Delta Technologies Ltd., Stillwater, MN) were cleaned sequentially in ultrasonic baths of detergent, 2-propanol/deionized water (1:1 volume) mixture, toluene, deionized water, and acetone. A 50 nm thick hole injection layer of poly(ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT) was spin-coated on top of ITO from a 0.7 wt % dispersion in water and dried at 150 °C for 1 h under vacuum. Thin films of polymer **P1** and its 6 wt % blends with 1,1-bis(di-4-tolylaminophenyl)cyclohexane (TAPC) were spin-coated from their chloroform solutions onto the PEDOT layer and dried at 50 °C in a vacuum overnight. The film thicknesses obtained were ca. 50 nm, which were measured by an Alpha-Step 500 surface profiler (KLA Tencor, Mountain View, CA). Finally, 100–130 nm Al electrodes were thermally evaporated through a shadow mask onto the polymer films using an AUTO 306 vacuum coater (BOC Edwards, Wilmington, MA), typical evaporations being carried out at base pressures lower than 2×10^{-6} Torr. The active area of each EL device was 0.2 cm². Electroluminescence (EL) spectra were obtained using a PTI QM-2001-4 spectrophotometer. Current–voltage characteristics of the LEDs were measured using a HP4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo). The luminance was simultaneously measured using a model 370 optometer (UDT Instruments, Baltimore, MD) equipped with a calibrated luminance sensor head (model 211). The device external quantum efficiencies were calculated using a standard expression involving the measured ratio of forward directed luminance and device current density, taking into account the EL spectral distribution and the photopic spectrum.²⁴ All the device fabrication and characterization steps were done under ambient laboratory conditions.

Reagents and Solvents. The Stille coupling reaction was used to prepare 1,4-didodecyloxy-2,5-divinylbenzene.²⁵ In particular, the latter was prepared by reacting 1,4-bis(dodecyloxy)-2,5-dibromobenzene with tributylvinyltin in the presence of

the catalyst PdCl₂(PPh₃)₂, plus a few crystals of 2,6-di-*tert*-butylphenol using toluene as solvent.

4-Bromobenzaldehyde and 4-bromobenzoic hydrazide were recrystallized from methanol and ethanol, respectively. 1,4-Benzenedicarboxaldehyde and malonic acid were recrystallized from distilled water. Dimethylformamide (DMF) and dimethylacetamide (DMAc) were dried by distillation over CaH₂. Triethylamine was dried by distillation over KOH. All other solvents and reagents were analytical-grade quality, purchased commercially, and used without further purification.

Preparation of Monomers and Polymers. 4-Bromocinnamic Acid (1a). Compound **1a** was prepared by a reported method²⁶ that was modified as follows. A mixture of 4-bromobenzaldehyde (0.47 g, 2.54 mmol), malonic acid (0.40 g, 3.81 mmol), pyridine (15 mL), and piperidine (three drops) was refluxed for 20 h. It was subsequently concentrated under reduced pressure, and water was added to the concentrate. The pale brown precipitate was filtered, washed with water, and dried to afford **1a**. It was recrystallized from acetonitrile (0.36 g, yield 63%, mp 264–266 °C). IR (KBr, cm⁻¹): 3436, 1684, 1626, 1584, 1486, 1424, 1306, 1282, 1226, 1070, 1008, 980, 816, 706, 546, 486. ¹H NMR (DMSO-*d*₆, δ): 12.51 (broad, 1H, COOH); 7.66–7.59, 6.59 (m, 4H, aromatic and 2H, HC=CH).

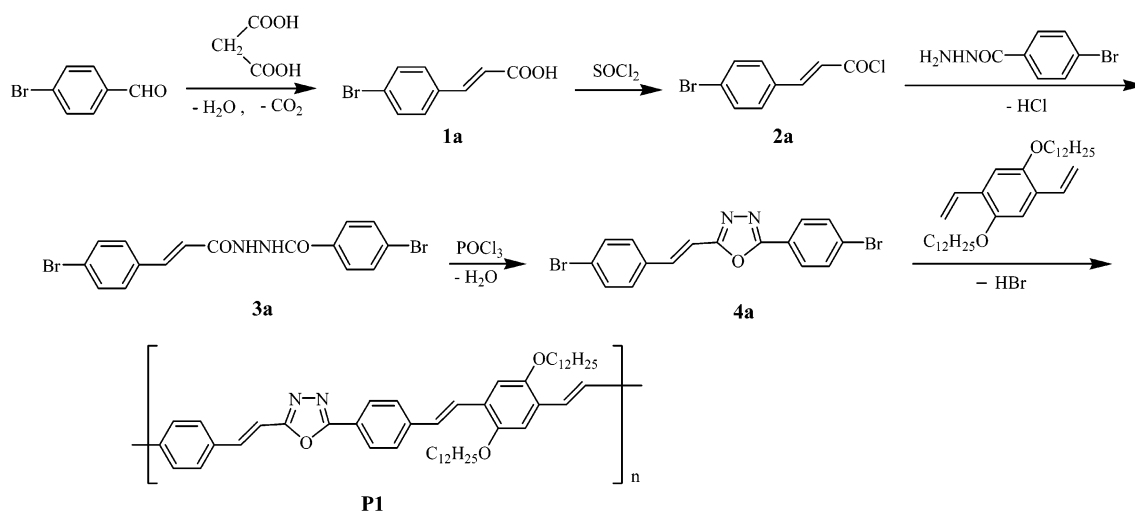
3,3'-(1,4-Phenylene)bis[2-propenoic acid] (1b). Compound **1b** was prepared by a reported method²⁷ that was modified as follows. A mixture of 1,4-benzenedicarboxaldehyde (3.51 g, 26.20 mmol), malonic acid (8.18 g, 78.60 mmol), pyridine (30 mL), and a catalytic amount of piperidine was stirred and heated at about 50 °C for approximately 0.5 h. Carbon dioxide was evolved, and a white solid precipitated. The mixture was subsequently heated at about 100 °C for 3 h. It was poured into water containing 5% (v/v) hydrochloric acid. The whitish solid was filtered, dried, and extracted with chloroform in a Soxhlet apparatus for 100 h to afford **1b**. It was recrystallized from DMF/CH₃CN [7.00 g, yield 70%, mp 345 °C dec (by DTA)]. IR (KBr, cm⁻¹): 3454, 1676, 1622, 1424, 1312, 1282, 1218, 1114, 980, 940, 878, 824, 680, 544, 506. ¹H NMR (DMSO-*d*₆, δ): 8.38–8.13 (m, 4H, aromatic); 7.17 (s, 2H, olefinic of position 1 of vinyl groups); 6.83 (s, 2H, olefinic of position 2 of vinyl groups). The carboxylic protons were unobserved.

4-Bromocinnamoyl Chloride (2a). Compound **2a** was prepared by a reported method²⁸ that was modified as follows. A flask equipped with a magnetic stirrer, condenser, and gas trap was charged with a mixture of **1a** (0.24 g, 1.06 mmol), thionyl chloride (5 mL), and a few drops of DMF. The mixture was stirred and refluxed for 5 h. Thionyl chloride was stripped off under vacuum, and the residue was triturated with petroleum ether. The white solid was filtered and dried to afford **2a**. It was recrystallized from diethyl ether/*n*-hexane (0.12 g, yield 47%, mp 104–106 °C). IR (KBr, cm⁻¹): 1748, 1725, 1622, 1606, 1588, 1562, 1488, 1402, 1324, 1292, 1262, 1184, 1114, 1070, 1026, 976, 810, 750, 638, 616, 484. ¹H NMR (CDCl₃, δ): 7.79–7.25, 6.66–6.62 (m, aromatic and HC=CH).

3,3'-(1,4-Phenylene)bis[2-propenoyl chloride] (2b). Compound **2b** was synthesized according to the procedure described for **2a** as a pale yellow solid in 85% yield (2.23 g) by reacting **1a** (2.00 g, 9.20 mmol) with thionyl chloride (15 mL) in the presence of a few drops of DMF. The residue was triturated with diethyl ether, and the reaction product was recrystallized from dioxane (mp 171–172 °C, lit.²⁷ 171–172 °C). IR (KBr, cm⁻¹): 1678, 1622, 1512, 1424, 1312, 1282, 1220, 1112, 978, 940, 824, 678, 544, 506. ¹H NMR (acetone-*d*₆, δ): 7.60–7.35 (m, 4H, aromatic); 6.48 (s, 2H, olefinic of position 1 of vinyl groups); 6.32 (s, 2H, olefinic of position 2 of vinyl groups).

{2-[1-Oxo-3-(4-bromophenyl)-2-propenyl]hydrazide}-4-bromobenzoic Acid (3a). Compound **2a** (0.12 g, 0.47 mmol) dissolved in DMAc (3 mL) was added dropwise at 0 °C to a stirred mixture of 4-bromobenzoic hydrazide (0.10 g, 0.47 mmol), DMAc (5 mL), and triethylamine (0.05 g, 0.49 mmol). Stirring of the mixture was continued for 4 h at ambient temperature under N₂. The mixture was subsequently poured into water. The white precipitate was filtered, washed with water, and dried to afford **3a**. It was recrystallized from

Scheme 1



DMF/water (0.16 g, yield 80%, mp 189–191 °C). IR (KBr, cm^{-1}): 3192, 1638, 1596, 1562, 1492, 1468, 1372, 1224, 1180, 1154, 1072, 1010, 970, 900, 844, 818, 756, 710, 658, 620, 548, 516. ^1H NMR (DMSO- d_6 , δ): 10.66, 10.30 (m, 2H, CONH); 7.98–7.54, 6.80–6.76, 6.60–6.55 (m, 8H, aromatic and 2H, HC=CH).

{2,2'-[1,4-Phenylenbis(1-oxo-2-propene-3,1-diyl)]dihydrazide-*p*-bromobenzoic Acid (3b). Compound **3b** was synthesized according to the procedure described for **3a** as a white solid in 70% yield (0.39 g) by reacting **2b** (0.23 g, 0.90 mmol) with 4-bromobenzoic hydrazide (0.39 g, 1.80 mmol) in DMAc (6 mL) in the presence of triethylamine (0.19 g, 1.9 mmol). It was recrystallized from DMF (mp > 300 °C). IR (KBr, cm^{-1}): 3182, 1634, 1592, 1562, 1466, 1224, 1156, 1070, 1010, 964, 898, 836, 750, 710, 658, 546, 524. ^1H NMR (DMSO- d_6 , δ): 10.66, 10.31 (broad, 4H, CONH); 7.86–7.58 (m, 12H, aromatic, 2H, olefinic β to carbonyl); 6.83–6.79 (m, 2H, olefinic α to carbonyl).

[2-(4-Bromophenyl)-5-(4-bromostyryl)]-1,3,4-oxadiazole (4a). Compound **3a** (0.62 g, 1.46 mmol) was dissolved by heating in POCl_3 (25 mL). The mixture was refluxed for 17 h, and it was subsequently concentrated under reduced pressure. Water was added to the concentrate, and the whitish solid was filtered, washed thoroughly with water, and dried to afford **4a**. It was recrystallized from acetonitrile (0.36 g, yield 61%, mp 190–192 °C). IR (KBr, cm^{-1}): 1638, 1600, 1562, 1520, 1476, 1406, 1072, 1010, 976, 832, 814, 734, 720, 530, 508. ^1H NMR (DMSO- d_6 , δ): 8.05–7.17 (m, aromatic and HC=CH).

2,2'-(1,4-Phenylenedi-2,1-ethenediyl)bis[5-(4-bromophenyl)-1,3,4-oxadiazole] (4b). Compound **3b** (0.38 g, 0.62 mmol) was dissolved by heating in poly(phosphoric acid) (PPA) (20 g), and the solution was stirred and heated at 130 °C for 40 h. It was subsequently cooled and poured portionwise into ice–water. The pale yellow-brown precipitate was filtered, washed thoroughly with water, and dried to afford **4b**. It was recrystallized from DMF/water (0.18 g, yield 51%). IR (KBr, cm^{-1}): 1636, 1598, 1528, 1476, 1402, 1264, 1086, 1068, 964, 830, 810, 758, 730, 498. ^1H NMR (DMSO- d_6 , δ): 8.09–7.15 (aromatic, and HC=CH).

Polymer P1. A flask was charged with **4a** (0.1030 g, 0.254 mmol), 1,4-didodecyloxy-2,5-divinylbenzene (0.1263 g, 0.254 mmol), $\text{Pd}(\text{OAc})_2$ (0.0024 g, 0.011 mmol), and $\text{P}(o\text{-tolyl})_3$ (0.0177 g, 0.058 mmol). The flask was degassed and purged with N_2 . DMAc (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 precipitate was filtered, washed with methanol, and dried to afford **P1** (0.15 g, yield 80%). The number-average molecular weight (M_n) was 5600, and the polydispersity index was 1.9 (by GPC). IR (KBr, cm^{-1}): 2920, 2850, 1636, 1598, 1526, 1492, 1466, 1420, 1202, 1010, 962, 808, 852, 696.

For the ^1H NMR spectrum of **P1**, see Results and Discussion. Anal. Calcd for $(\text{C}_{50}\text{H}_{66}\text{N}_2\text{O}_3)_n$: C, 80.82; H, 8.95; N, 3.77. Found: C, 79.65; H, 9.12; N, 3.64.

Polymer P2. Polymer **P2** was prepared according to the procedure described for **P1** as a yellow-brown solid in 68% yield (0.17 g) from the reaction of **4b** (0.1580 g, 0.274 mmol) with 1,4-didodecyloxy-2,5-divinylbenzene (0.1365 g, 0.274 mmol), $\text{Pd}(\text{OAc})_2$ (0.0026 g, 0.12 mmol), $\text{P}(o\text{-tolyl})_3$ (0.0192 g, 0.063 mmol), DMAc (30 mL), and triethylamine (3 mL). The number-average molecular weight (M_n) was 4300, and the polydispersity index was 2.1 (by GPC). IR (KBr, cm^{-1}): 2922, 2850, 1633, 1604, 1548, 1530, 1493, 1464, 1417, 1202, 1071, 1032, 967, 672. ^1H NMR (CDCl_3 , δ): 8.12–6.90 (m, 14H, aromatic and 8H, HC=CH); 4.02 (m, 4H, OCH_2); 1.86, 1.26, 0.86 (m, 46H, other aliphatic). Anal. Calcd for $(\text{C}_{60}\text{H}_{72}\text{N}_4\text{O}_4)_n$: C, 78.91; H, 7.95; N, 6.13. Found: C, 78.03; H, 7.82; N, 6.20.

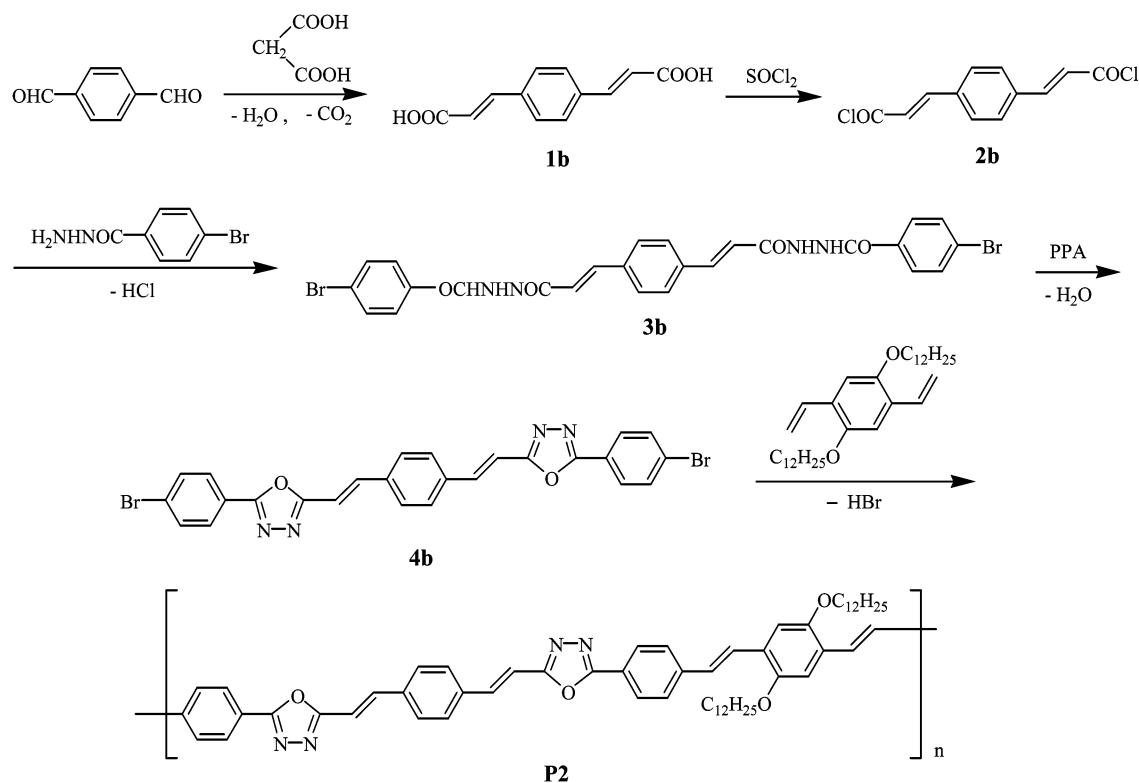
Results and Discussion

Synthesis and Characterization of Polymers. Schemes 1 and 2 outline the synthetic route to the synthesis of the monomers and polymers. In particular, 4-bromobenzaldehyde was condensed with malonic acid in pyridine in the presence of a catalytic amount of piperidine to afford 4-bromocinnamic acid (**1a**). 4-Bromocinnamoyl chloride (**2a**) was obtained from the reaction of **1a** with SOCl_2 utilizing DMF as catalyst. The condensation of **2a** with 4-bromobenzoic hydrazide afforded **3a**. Dehydrocyclization of **3a** using POCl_3 as both dehydrating agent and reaction solvent resulted in the oxadiazole derivative **4a**. Finally, the Heck coupling of **4a** with 1,4-didodecyloxy-2,5-divinylbenzene yielded polymer **P1**. An analogous reaction sequence of five steps was applied to prepare **P2** starting from 1,4-benzenedicarboxaldehyde. In this case, poly(phosphoric acid) (PPA) was used instead of POCl_3 for dehydrocyclization of **3b** due to its limited solubility.

The FT-IR and ^1H NMR spectra of the polymers were consistent with their chemical structures. In particular, the FT-IR spectrum of **P2** showed characteristic absorptions at 2922, 2850 (C–H stretching of aliphatic segments); 1604, 1494, 1464 (aromatic); 1633, 1548, 1530 (1,3,4-oxadiazole ring); 1202, 1071, 1032 (C–O–C stretching of ether bond and oxadiazole), and 967 cm^{-1} (HC=CH trans). The ^1H NMR spectrum of **P1** in CDCl_3 solution displayed peaks at 8.11–7.09, (m, 10H, aromatic, and 6H, HC=CH); 4.08 (m, 4H, OCH_2); 1.90, 1.26, 0.86 (m, 46H, other aliphatic).

Although the polymers contained phenylene or oxadiazole rings along the main chain and three or four

Scheme 2

Table 1. T_g Values and Thermal Stability of Polymers

polymer	T_g^a (°C)	in N_2			in air	
		T_1^b (°C)	T_{10}^b (°C)	Y_c^c (%)	T_1^b (°C)	T_{10}^b (°C)
P1	28	313	392	36	286	336
P2	57	340	411	42	325	404

^a T_g : glass transition temperature determined by the TMA method. ^b T_1 , T_{10} : temperatures at which weight loss of 1 and 10%, respectively, was observed by TGA. ^c Y_c : char yield at 800 °C by TGA.

vinylene bonds per repeat unit that led to a fully conjugated backbone, they showed excellent solubility because of the dodecyloxy side groups. Specifically, they dissolved at room temperature in THF as well as various chlorinated solvents such as chloroform, dichloromethane, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, chlorobenzene, and 1,2-dichlorobenzene. **P1** was more soluble in these solvents than **P2**. Transparent and self-standing films of the polymers can be cast using these solvents.

No phase transitions of the polymers were recorded by DSC, even after repeated scans, thus supporting their amorphous character. The T_g s of the polymers were determined by thermomechanical analysis (TMA) when a penetration probe was used (Table 1). The T_g was obtained from the onset temperature of the dropping step that was recorded during the second heating. The lower T_g value of **P1** (28 °C) than that of **P2** (57 °C) is ascribed to a higher composition of the side alkoxy groups in its backbone. In addition, for this reason **P1** was thermally less stable than **P2** and afforded lower anaerobic char yield (Y_c) at 800 °C (Table 1). No weight loss was observed up to approximately 290–340 °C in N_2 or air, and the Y_c was about 40%.

Optical Properties of Polymers. The UV–vis absorption, PL excitation (PLE), and PL emission spectra of polymers **P1** and **P2** were recorded both in solution and in thin film (Figures 1–4), and the spec-

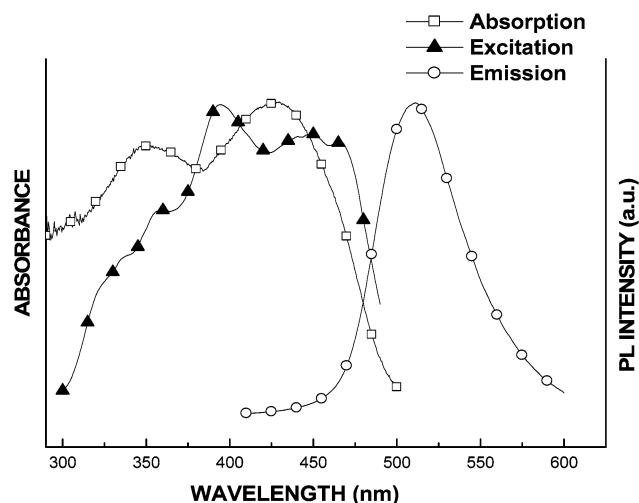


Figure 1. Absorption and PL excitation spectra as well as PL spectrum of polymer **P1** in THF solution.

troscopic data are collected in Table 2. Both polymers contain distyrylbenzene moieties along the main chain that are connected with phenylene and/or oxadiazole rings. **P1** has a repeat unit with one oxadiazole ring, whereas **P2** possesses a longer repeat unit with two oxadiazole rings. Therefore, the two polymers are related but have distinct differences in the molecular structures that can lead to differing optical properties.

The UV–vis absorption spectrum of **P1** in THF (Figure 1) showed two peaks with maxima ($\lambda_{a,\max}$) at 348 and 428 nm that can be assigned to the phenylene or oxadiazole rings and the $\pi-\pi^*$ transition along the conjugated backbone, respectively. In contrast, the absorption spectrum of **P2** in THF (Figure 2) showed only one peak with $\lambda_{a,\max}$ at 360 nm. The PLE spectra of the polymers in THF overlapped significantly with

Table 2. Optical Properties of Polymers

polymer	$\lambda_{a,max}^a$ in soln (nm)	$\lambda_{ex,max}^b$ in soln (nm)	$\lambda_{f,max}^c$ in soln (nm)	Φ_f^d in soln	$\lambda_{a,max}^a$ in thin film (nm)	E_g^e (eV)	$\lambda_{ex,max}^b$ in thin film (nm)	$\lambda_{f,max}^c$ in thin film (nm)
P1	348, 428 ^f	394	511	0.34	349, 428 ^f	2.38	470	558
P2	360	395	487	0.22	366	2.49	472	515

^a $\lambda_{a,max}$: the absorption maxima from the UV-vis spectra in THF solution or in thin film. ^b $\lambda_{ex,max}$: the PL excitation maxima in THF solution or in thin film. ^c $\lambda_{f,max}$: the PL maxima in THF solution or in thin film. ^d Φ_f : PL quantum yield. ^e E_g : the optical energy gap calculated from the UV-vis spectra in thin film. ^f Italic numerical values denote absolute maxima.

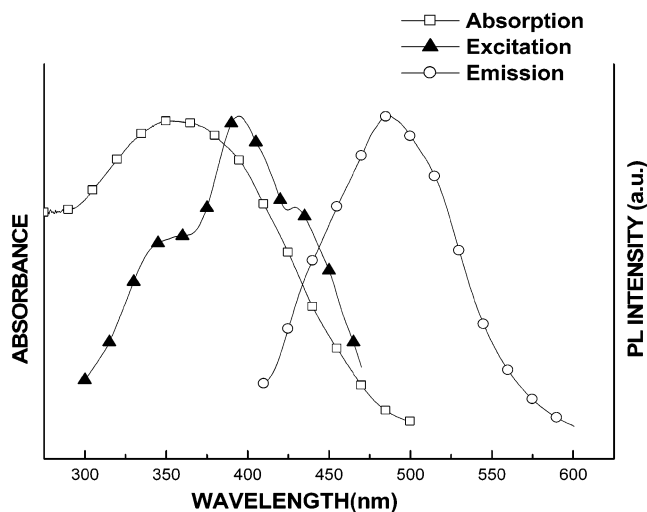


Figure 2. Absorption and PL excitation spectra as well as PL spectrum of polymer **P2** in THF solution.

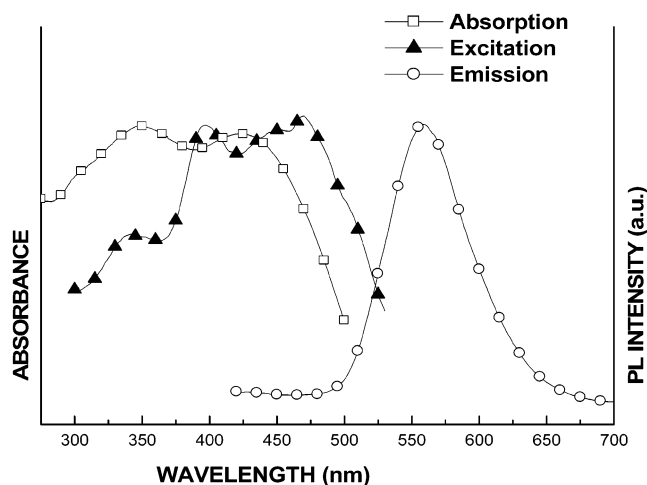


Figure 3. Absorption and PL excitation spectra as well as PL spectrum of polymer **P1** in thin film.

the corresponding absorption spectra and displayed identical absolute maximum ($\lambda_{ex,max}$) at 395 nm.

The polymers emitted greenish-blue light in solution with PL maxima ($\lambda_{f,max}$) at 511 nm for **P1** and 487 nm for **P2** (Figures 1 and 2). Thus, the emission maximum of **P1** is red-shifted by 24 nm compared to that of **P2**, suggesting increased electron delocalization along the **P1** backbone. This could be due to the higher composition of the electron-donating dodecyloxy groups per repeat unit of **P1** and/or a possible disruption of the conjugation along the backbone caused by the two oxadiazole rings in **P2**. Thus, increase in the oxadiazole composition in the polymer backbone of **P2** did not extend the effective chromophore. This PL emission of both the polymers is blue-shifted in comparison to poly-(2,5-dialkoxy-1,4-phenylenevinylene)s (513 nm).²⁹ The PL quantum yields (Φ_f) of the polymers in THF solution

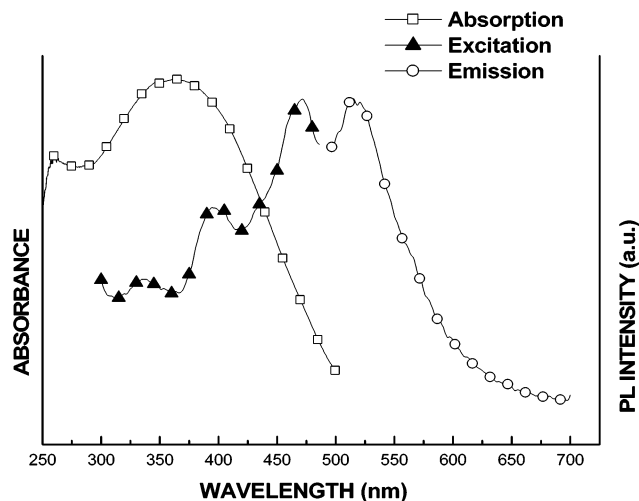


Figure 4. Absorption and PL excitation spectra as well as PL spectrum of polymer **P2** in thin film.

(Table 2) were determined³⁰ using quinine sulfate as a standard. **P1** with a shorter repeat unit was more fluorescent than **P2** with a higher Φ_f value of 0.34 vs 0.22 for **P2**.

The absorption spectra of the polymer thin films (Figures 3 and 4) spin-coated on quartz substrate were almost identical with those in solution. This suggests that the molecular arrangement of polymer chains is same both in solution and in thin film, and consequently the polymers lack order even in the solid state. The optical band gaps (E_g) of the polymers determined from the absorption edge were 2.38 and 2.49 eV for **P1** and **P2**, respectively. The value of 2.38 eV for **P1** is lower than those that have been reported for other related PPV polymers bearing oxadiazole rings along the main chain (2.44–2.53 eV).^{14,15} The polymers emitted yellowish-green light in thin film with PL maxima at 558 nm for **P1** (Figure 3) and 515 nm for **P2** (Figure 4). However, the PL emission of **P2** thin film was very weak compared to that of **P1**.

Electrochemical Properties. Parts a and b of Figure 5 show the cyclic voltammograms of polymers **P1** and **P2**, respectively. Figure 5a shows a reversible reduction with an onset potential at ca. -1.8 V vs SCE (saturated calomel electrode) for **P1**, whereas the oxidation is irreversible with an onset at ca. 0.65 V vs SCE. This suggests that the presence of one oxadiazole ring per repeat unit in the main chain has made the polymer more suitable for n-doping than p-doping. On the basis of the onset redox potentials, the electron affinity (LUMO level) and ionization potential (HOMO level) of **P1** are estimated to be 2.60 and 5.05 eV, respectively, by using a value of -4.4 eV as the SCE energy level relative to vacuum.³¹ The corresponding electrochemical band gap is 2.45 eV, which matches fairly well with the optical band gap of 2.38 eV. Figure 5b shows an irreversible oxidation for **P2** with an onset potential of

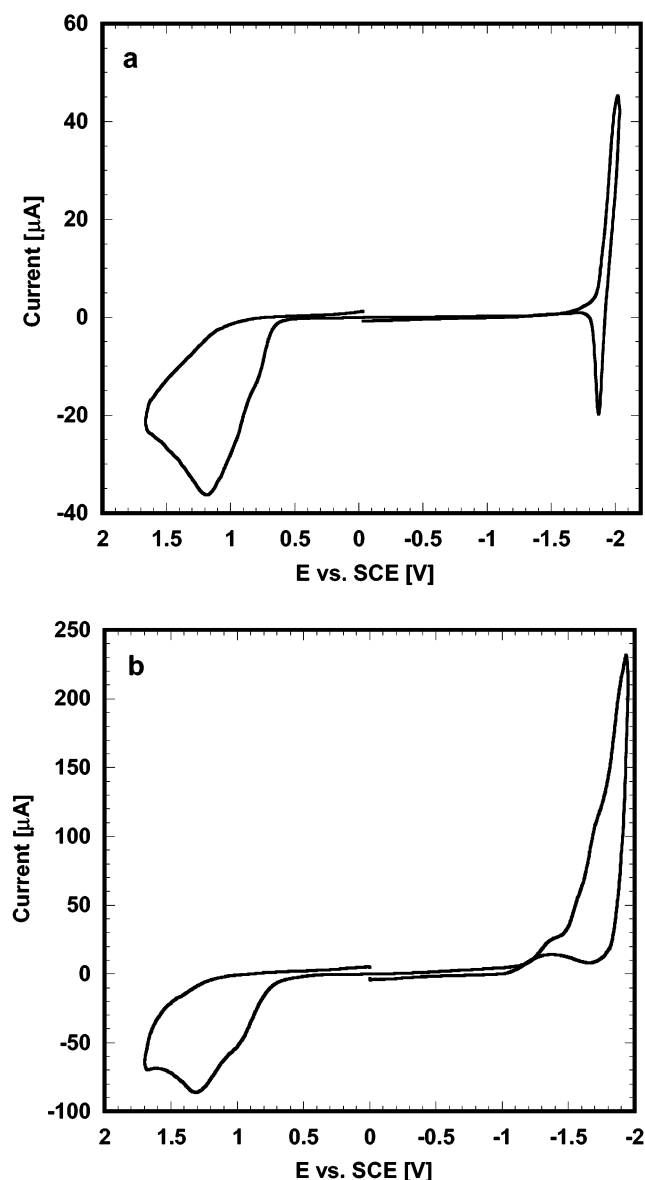


Figure 5. Cyclic voltammograms of (a) **P1** and (b) **P2** in 0.1 M TBAPF₆ in acetonitrile at 80 mV/s scan rate.

ca. 0.75 eV vs SCE. The estimated HOMO level is 5.15 eV, which is higher than that of **P1**, probably due to the presence of an additional oxadiazole ring in the main chain. A clear reduction wave could not be observed for **P2**, making the estimation of the LUMO level very approximate.

Electroluminescence Properties. The current density–voltage–luminance characteristics of **P1** LED of the type ITO/PEDOT/**P1**/Al are shown in Figure 6a. The turn-on voltage of the diode is ca. 9 V with a maximum brightness of 23 cd/m² and maximum external quantum efficiency of 0.002% at 16 V. The corresponding EL spectra shown in Figure 6b reveal a voltage-tunable EL colors. At the turn-on voltage of 9 V, the EL maximum is at 558 nm (yellow), which is the same as the homopolymer PL maximum. However, the EL spectra gradually blue-shifted with increase in applied bias, showing EL maxima at 545 nm at 13.5 V, 540 nm at 15 V, and finally 527 nm at 16 V. This trend was repeatable in all the fabricated devices and was consistent for a single active pixel or freshly turned-on pixels at each individual applied bias. Moreover, the shift was ir-

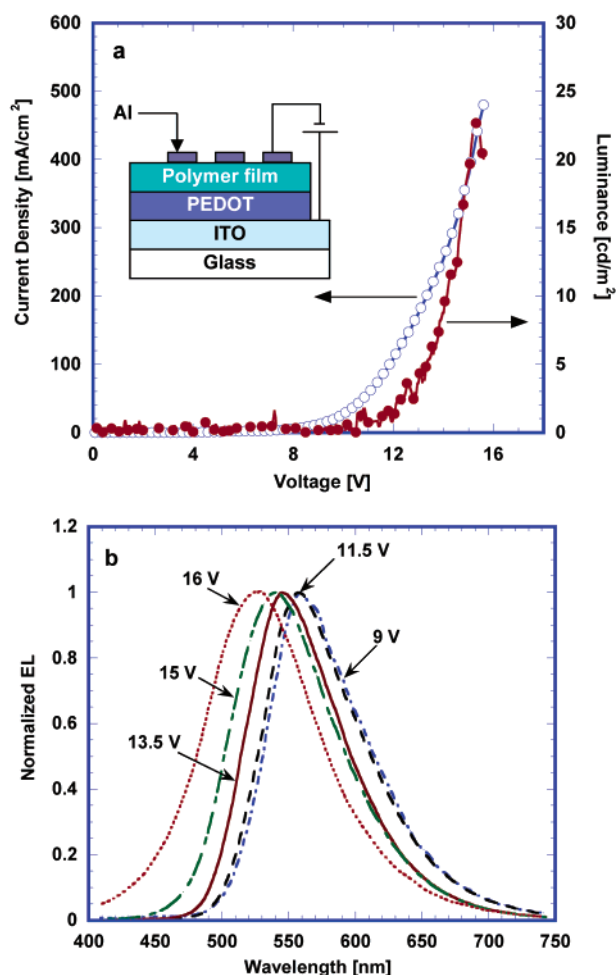


Figure 6. (a) Current density–voltage–luminance characteristics of LED from polymer **P1** and (b) EL spectra of corresponding device. The inset shows the device schematic.

reversible in that, for a device working at 16 V (527 nm), decreasing the applied bias back down to 9 V did not shift the EL maximum to 558 nm. This suggests that the application of higher electric fields and the consequent greater local heating in the polymer film leads to changes in the conformation of the polymer backbone. The plausible reasons for the origin of this shift in EL spectra are discussed later.

To improve the device performance and efficiency, a blend of **P1** was made with a hole transport molecule, 6 wt % 1,1-bis(di-4 -tolylaminophenyl)cyclohexane (TAPC), to enhance the hole transport through the device. The current density–voltage–luminance characteristics of the corresponding LED are shown in Figure 7a. The turn-on voltage of the diode is ca. 10 V. A maximum brightness of 70 cd/m² and a maximum external quantum efficiency of 0.01% at 17.5 V were seen. This represents factors of 3–5 enhancement in performance compared to the **P1** LED. The modest EL device efficiencies could be further improved by optimizing the blend composition. A voltage-tunable EL color is again seen in the corresponding EL spectra shown in Figure 7b. At the lower voltage of 11 V, the EL maximum is at 556 nm, and then the EL spectra gradually blue shift with increase in applied bias, showing EL maxima at 542 nm at 15 V and finally 513 nm at 17.5 V. As with the neat **P1** device, this trend was repeatable and irreversible for a given active pixel.

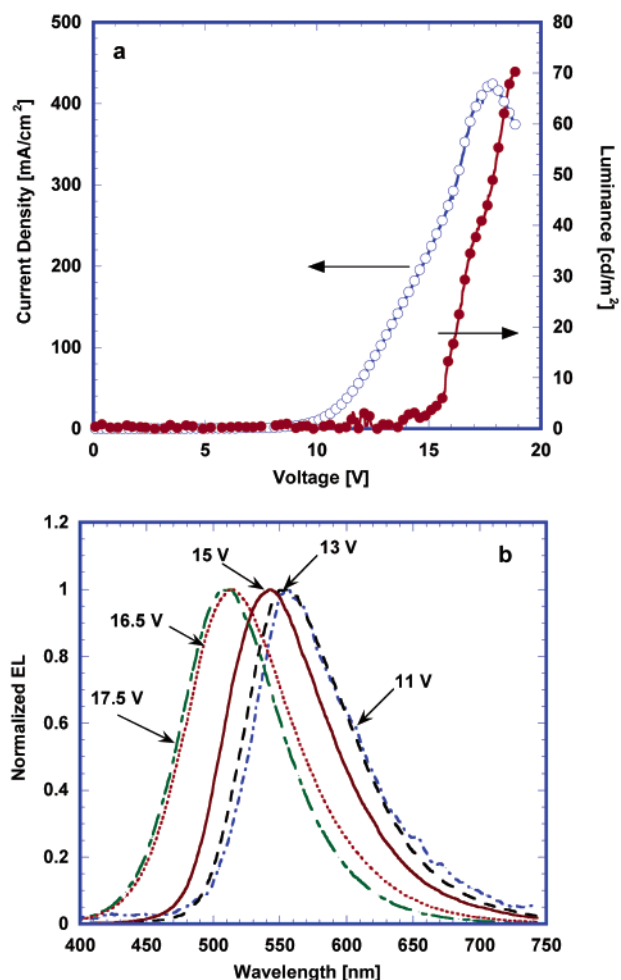


Figure 7. (a) Current density–voltage–luminance characteristics of LED from 6 wt % blend of TAPC with polymer **P1** and (b) EL spectra of the corresponding device.

In the case of polymer **P2**, the devices did not show measurable EL properties as the PL emission was very weak compared to that of **P1**.

Origin of Voltage-Tunable EL Spectra. To investigate the reason for the observed blue shift in the EL spectra of homopolymer **P1** (Figure 6b) with increasing bias, we examined the photophysics of **P1** thin films annealed at different temperatures. After the initial drying of the films at 40 °C in a vacuum overnight, they were then annealed at temperatures of 150, 175, and 200 °C for 1 h under vacuum and cooled back down to room temperature. The optical absorption and PL emission spectra of the annealed films are shown in parts a and b of Figure 8, respectively. In the normalized absorption spectra shown in Figure 8a, two peaks are seen for the film dried at 40 °C—one at 353 nm and the other at 434 nm. The peak at 353 nm can be assigned to the oxadiazole or phenyl rings, and the one at 434 nm to the π – π^* transition of the conjugated PPV backbone. For the films annealed at 150, 175, and 200 °C, the π – π^* transition peak gradually blue shifts to 427, 412, and 401 nm, respectively (indicated by the arrow), whereas the peak at 353 nm is unchanged. Correspondingly, a slight increase in the absorption band edge is also observed. This indicates that there is a conformational change along the backbone with temperature leading to subtle changes in the electronic band structure of **P1**.

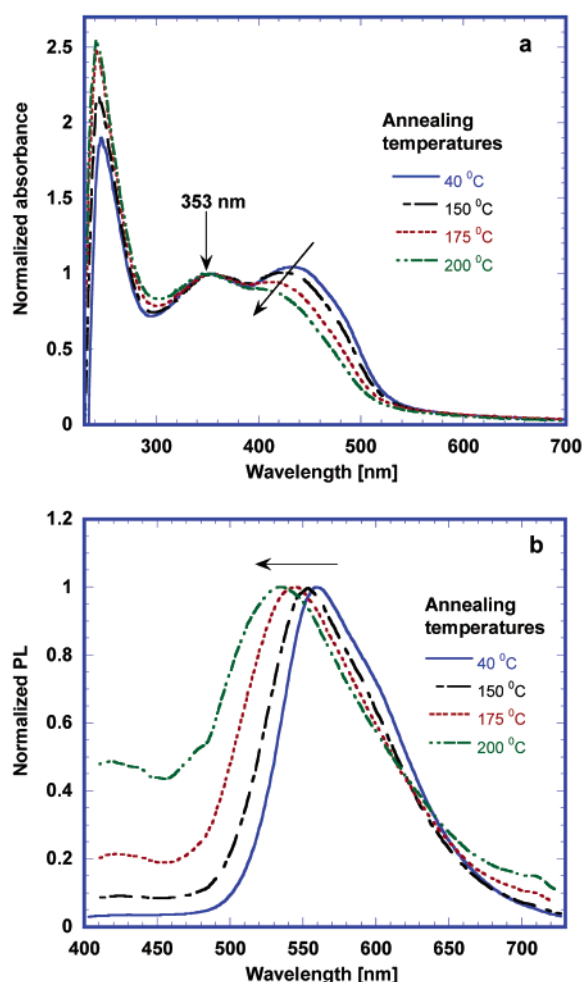


Figure 8. (a) Optical absorption spectra and (b) PL emission spectra (370 nm excitation) of thin film of homopolymer **P1** annealed at different temperatures in a vacuum for 1 h.

The normalized PL emission spectra of the annealed **P1** films are shown in Figure 8b. With excitation at 370 nm, we see a distinct blue shift in the PL maxima with increasing annealing temperatures. For the films annealed at 40, 150, 175, and 200 °C, the PL maxima are seen at 558, 553, 545, and 533 nm, respectively. This suggests that the emission originates from varying conformations of the polymer backbone. It should also be noted that the T_g of **P1** is low (28 °C) due to the long dodecyloxy side groups. Hence, the polymer lends itself to facile rearrangements, of the *cis*–*trans* type for instance, along the backbone with increasing temperature. A similar thermochromic effect has been previously reported for cyano-substituted poly(2,5-dialkoxy-*p*-phenylenevinylene)s having hexyloxy, octyloxy, and decyloxy side groups.³² Comparison of the PL spectra in Figure 8b to the EL spectra of **P1** LEDs in Figures 6b and 7b suggests that the same conformational changes occur in the presence of local heat developed under the application of electric field in the homopolymer LED, leading to the observed blue shift in the EL maxima with increasing bias. The observed coupling of thermochromism with electroluminescence of **P1** is an interesting new phenomenon not previously seen in conjugated polymers, and thus it warrants a future detailed study.

Conclusions

Two new PPV-type conjugated polymers **P1** and **P2** with different chemical structures were synthesized by Heck coupling. Upon comparing these polymers, **P1** was found to be more soluble in common organic solvents, less thermally stable with a lower T_g and more fluorescent material with lower optical band gap than **P2**. The PL emission maxima of the polymers were at 487–511 nm in solution and 515–558 nm in thin films. EL was achieved from single layer LEDs of **P1** with a voltage-tunable EL color from 558 nm (9 V) to 527 nm (16 V). The observed blue shift in the EL spectra with increasing bias is a result of changes in structural conformations of the polymer backbone, leading to subtle variations in the electronic band structure.

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