ADVANCED FUNCTIONAL MATERIALS

Polymeric Alkoxy PBD [2-(4-Biphenylyl)-5-Phenyl-1,3,4-Oxadiazole] for Light-Emitting Diodes**

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The syntheses are reported of the title polymeric alkoxyPBD derivative **5** and the dipyridyl analogue **12** using Suzuki coupling reactions of 1,4-dialkoxybenzene-2,5-diboronic acid with 2,5-bis(4-bromophenyl)-1,3,5-oxadiazole, and its dipyridyl analogue, respectively. Thermal gravimetric analysis shows that polymers **5** and **12** are stable up to 370 °C and 334 °C, respectively. Films of polymer **5** spun from chloroform solution show an absorption at λ_{max} = 367 nm, and a weaker band at 312 nm, and strong blue photoluminescence at λ_{max} = 444 nm. The photoluminescence quantum yield (PLQY) was found to be 27 ± 3 %. For polymer **12**, the absorption spectra reveal bands of equal intensity at λ_{max} = 374 and 312 nm, with PL at λ_{max} = 475 nm. Device studies using polymer **12** were hampered by its instability under illumination and/or electrical excitation. Polymer **5** is stable under these conditions and acts as an efficient electron-transporting/hole-blocking layer. For devices of configuration ITO/PEDOT/MEH-PPV/polymer **5**/Al an external quantum efficiency of 0.26 % and brightness of 800 cd/m^2 was readily achieved: orange emission was observed, identical to the MEH-PPV electroluminescence.

1. Introduction

2-(4-Biphenylyl)-5-phenyl-1,3,4-oxadiazole (PBD) and its *tert*-butyl derivative (Bu-PBD) have been known as laser dyes for decades due to their high photoluminescence (PL) quantum efficiencies. During the past ten years, a new area of research also requiring highly fluorescent materials, namely polymer light-emitting diodes (LEDs),[1] has attracted extensive attention due to potential applications in display technologies.[2] An optimized LED requires efficient and balanced charge injection from both electrodes, comparable transporting properties of both holes and electrons, and a high quantum efficiency for the radiative decay process. Owing to their electron-deficient nature, molecular and polymeric derivatives of 1,3,4-oxadiazole have been explored in this context as electron-transporting materials in addition to their potential for light-emission.[3–5] Most importantly, Heeger et al. reported that by blending Bu-PBD with poly(*p*-phenylenevinylene) (PPV) or poly[2-methoxy-5-(2′-ethyl-hexoxy)-*p*-phenylene vinylene] (MEH–PPV) electroluminescence efficiencies could be doubled to 50 % of the corresponding photoluminescence.[6] We therefore anticipated that a polymer containing PBD as the repeating unit would exhibit interesting material and photophysical properties. We note that some diaryl-1,3,4-oxadiazole units have been incorporated into polymers either in the main chain or as pendants.[7] Among them, a methacrylate copolymer bearing pendant PBD substituents has been studied,[8] and recently PPV analogues bearing diaryl-1,3,4-oxadiazole[9] and bis(1,3,4-oxadiazole)[10] units normal to the main chain have been reported. We now report the synthesis and photophysical properties of alkoxy-solubilized poly(PBD) (**5**) and its application as an electron transport/hole blocking layer in LEDs. To the best of our knowledge, conjugated polymeric PBD has not been synthesized previously, so polymer **5** represents a new structural class of oxadiazole polymers. We also describe the pyridine analogue of poly(PBD), namely, polymer **12**. The reason for preparing **12** was that we have demonstrated that the introduction of pyridine units into poly(*p*-phenylene) type polymers improves electron-transporting properties of these materials.[11,12]

2. Results and Discussion

The synthesis of polymers **5** and **12**, shown in Schemes 1 and 2, respectively, proceeded via a copolymerization of bis(bromophenyl)oxadiazole (**4**) or its pyridine analogue (**10**) with diboronic acid (**3**)[13] via Suzuki coupling reactions. A model reaction for the polymerization leading to compound **11** was performed and the structures of both the polymers are well established by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, and by CHN analyses. The thermal properties of both polymers **5** and **12** were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA traces show that polymers **5** and **12** are stable up to 370 and 334 °C, respectively, to a weight loss of 5 %. Above these temperatures the polymers decomposed significantly to a residual mass of ca. 40 %. Measured by DSC, the

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[**] We thank the EPSRC for funding this work. We are very grateful to Covion for the supply of MEH–PPV and Bayer for the supply of PEDOT–PSS. IDWS is a Royal Society University Research Fellow.

1616-301X/01/0102-0047 $ 17.50+.50/0

glass-transition temperature (T_g) of polymers **5** and **12** were 196 and 113 °C, respectively. A melting process was observed for **5** at 260 °C, while polymer **12** did not melt below 300 °C. Low-angle X-ray diffraction (XRD) experiments suggest that films of polymers **5** and **12** are amorphous.

The photophysical properties of both polymers **5** and **12** were studied. The absorption and PL spectra of a film of polymer **5** spun from chloroform solution are shown in Figure 1. The absorption shows a maximum at 367 nm and a second weaker but still well-defined band at 312 nm. The main absorption band is slightly blue-shifted with respect to polypyridine, but red-shifted with respect to the pyridine/phenylene copolymers that we have previously reported.[11] The additional absorption at 312 nm has however, no correspondence in the pyridine/phenylene containing copolymers[11] or in polypyridine. The film shows strong blue PL with a maximum at 444 nm, 0.586 eV lower in energy than the 367 nm absorption profile. PBD in solution absorbs at 300 nm and emits at 380 nm (in cyclohexane with 2 % chloroform).[14] The redder spectra in polymer **5** are due to the extended electron delocalization caused by polymerization, and the substituent effects of the alkoxy groups. The PL quantum yield (PLQY) of a spun film of polymer **5** was measured using an integrating sphere and was found to be 27 ± 3 %.

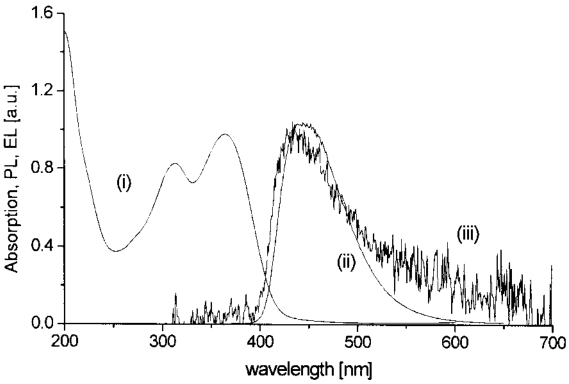
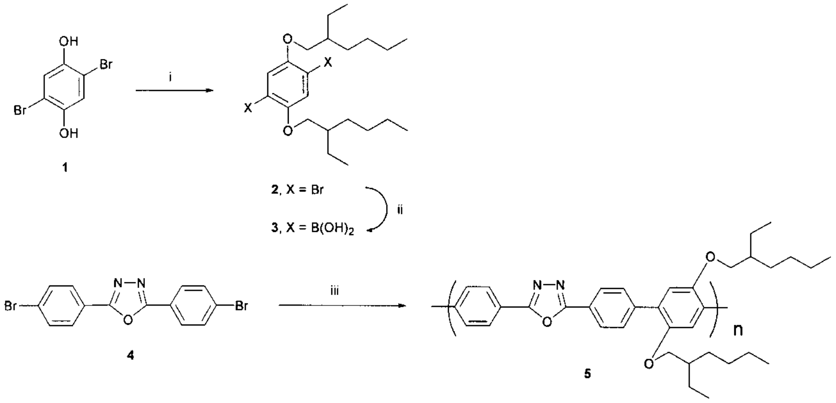
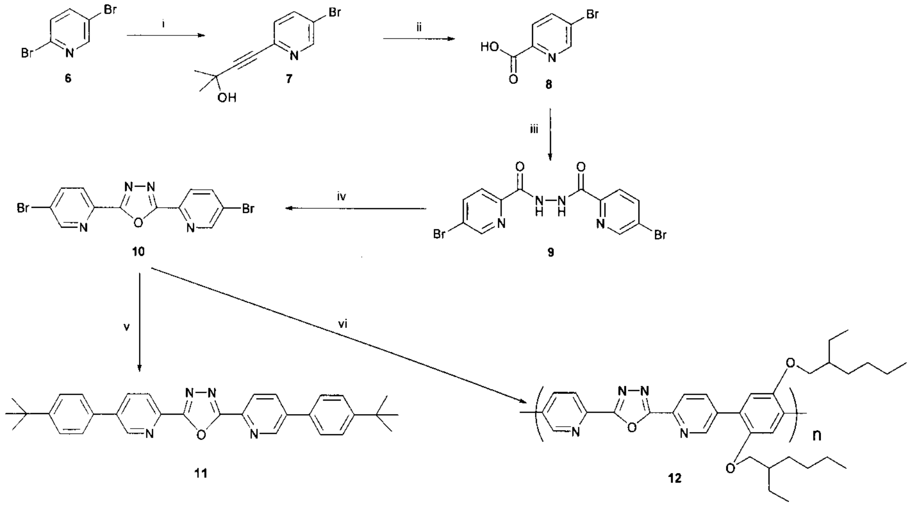


Fig. 1. Absorption (i), PL (ii), and electroluminescence (iii) spectra of films of polymer **5**.

Figure 2 shows the absorption and PL spectra of a film of polymer **12** spun from chloroform solution. The absorption of the film consists of two equally strong bands at 374 nm and 312 nm. The PL of the film has a maximum at 475 nm, which is significantly red-shifted as compared to the emission of the polymer **5**. Furthermore, the PL has a much more pronounced red tail than for polymer **5**. Our subsequent studies of this polymer were hampered by problems of stability under illumination and/or electrical excitation. The PLQY of polymer **12** was hard to estimate as the film degraded during the course of the experiment, but we estimate the PLQY to be approximately 6 % with substantial errors. A possible explanation for this degradation could be a cleavage of the polymer chain hence causing instability of the sample and resulting in the low PLQY. Initial studies showed an increased device efficiency compared to single layer MEH–PPV, but the instability of **12** in solution and as a thin film precluded further device studies.



Scheme 1. i) 2-Ethylhexyl bromide, DMF, K_2CO_3, 100 °C. ii) Dry THF, BuLi then triisopropyl borate. iii) DMF, $Pd(PPh_3)_4$, Na_2CO_3, 80 °C.



Scheme 2. i) 2-Methyl-3-butyn-2-ol, CuI, $Pd(PPh_3)_2Cl_2$, Et_3N, 20 °C. ii) $KMnO_4/H_2O$, 100 °C. iii) $SOCl_2$, ref. then $N_2H_4\cdot H_2O$/dry dioxane. iv) Polyphosphoric acid (PPA), 160 °C, hydrolysis. v) 4-*tert*-Butylbenzene boronic acid, DMF, $Pd(PPh_3)_4$, Na_2CO_3, 70 °C. vi) Compound **3**, DMF, $Pd(PPh_3)_4$, Na_2CO_3, 85 °C, 48 h then 100 °C, 12 h.

We have investigated polymer **5** as an electron-transporting polymer in bilayer LEDs. Devices were fabricated with MEH–PPV as the light-emitting layer on top of which a layer of the polymer **5** was spun. The electron-deficient nature of the oxadiazole ring makes it an ideal candidate for an electron-transporting/hole-blocking layer. In order to facilitate hole injection, indium tin oxide (ITO) was coated with a layer of poly(3,4-ethylene-

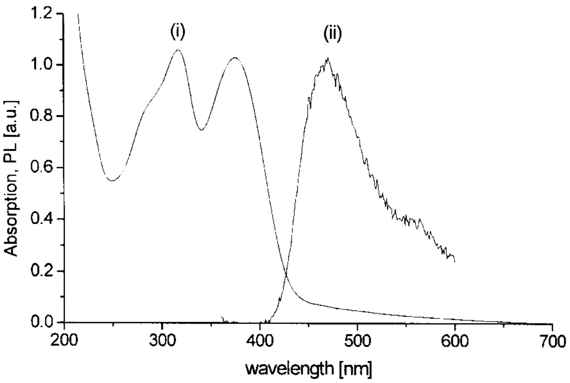


Fig. 2. Absorption (i) and PL (ii) spectra of films of polymer **12**.

dioxythiophene)–poly(styrene sulfonic acid) PEDOT–PSS. Aluminum was used as the cathode. The current–field–light output characteristics of this device are shown in Figure 3. The external quantum efficiency was 0.26 % and brightnesses up to 800 cd/m^2 were readily achieved. For comparison we made a similar device without polymer **5**, i.e., with MEH–PPV as the only semiconducting polymer layer. We measured an external quantum efficiency of 0.01 %, and brightness in the region of 15 cd/m^2. Orange emission was seen from both device structures, the spectrum of which was identical to the MEH–PPV electroluminescence. These data clearly demonstrate the substantial improvement in device performance associated with polymer **5**. It was also possible to make blue LEDs with a single layer of polymer **5**, and a typical emission spectrum is shown in Figure 1. However, these had very low efficiency (2.6 × 10^{-3} %), presumably because of the difficulty of hole injection and transport into polymer **5**.

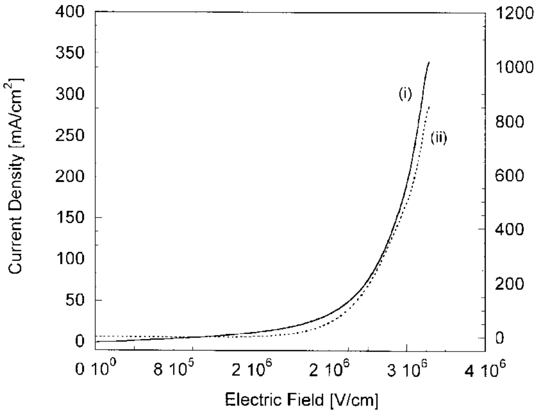


Fig. 3. Current density–field (i) and light-output–field (ii) of ITO/PEDOT/MEH–PPV/polymer **5**/Al device.

3. Conclusion

In conclusion we have synthesized conjugated polymeric PBD and demonstrated that it is an efficient electron transporting material for applications in polymer electronics. Replacing phenylene units with pyridylenes in the polymer does not improve the electron transporting properties.

4. Experimental

General: 2,5-Bis-(4-bromophenyl)-1,3,5-oxadiaxole was prepared as white crystals by dehydration of *N,N′*-bis-(4-bromobenzoic) hydrazide with $POCl_3$ under reflux, melting point (m.p.): 258.9–259.2 °C [15]. The latter compound was prepared from a reaction of 4-bromobenzoic hydrazide and 4-bromobenzoyl chloride in dry pyridine. 4-Bromobenzoic hydrazide and 4-bromobenzoyl chloride were purchased from Aldrich and were used without further purification. 2,5-Dibromohydroquinone was prepared from benzoquinone and hydrobromic acid using the procedure as reported [16]. $Pd(PPh_3)_4$ used as the catalyst in polymerizations was prepared as bright yellow crystals as reported [17], while $Pd(PPh_3)_2Cl_2$ was purchased from Avocado. All the palladium-catalyzed reactions were carried out under an argon atmosphere.

Melting points were determined in open-end capillaries using a Stuart Scientific melting point apparatus SMP3 at ramping rate of 5 °C/min without calibration. TGA and DSC were performed on a Perkin Elmer Pyric 1 TGA thermal analyzer, and all the experiments were carried out under nitrogen. The heating rate was 10 °C/min while the cooling prior to the subsequent heating scans for DSC was 50 °C/min. Elemental analyses were obtained on a Carlo–Erba Strumentazione instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Varian Unity 300 spectrometer at frequencies of 299.91 and 75.41 MHz, respectively. Mass spectra were obtained on a VG7070E instrument operating in electron impact mode at 70 eV. PL spectra were measured using a charge-coupled device (CCD) spectrograph. The excitation was provided by the 350 nm lines of a continuous-wave (CW) Ar-ion laser. Thin films of the polymers for optical studies were prepared by spin-coating onto spectrosil substrates. The PLQY was measured using an integrating sphere [18] with the 350 nm lines of a CW Ar-ion laser as excitation source. LEDs were fabricated by spin-coating the polymer layer(s) in air onto patterned ITO-coated glass (Merck, 20 $\Omega/\square$) which had previously been cleaned by ultrasound in acetone and isopropanol. PEDOT–PSS (EL grade, Bayer) was spun to 50 nm and subsequently dried in vacuum overnight at 50 °C. MEH–PPV and polymer **5** were spun from chlorobenzene and chloroform solutions, respectively. In spite of the potential problem of interdissolution of the two polymer layers, good quality films and devices were prepared. The thickness of the MEH–PPV layer was 90 nm and the film of polymer **5** was 20 nm thick. For single-layer polymer **5** devices a 50 nm layer was used. Aluminum cathodes were evaporated through a shadow mask under pressures of typically 10^{-6} mbar to define an active area of 2 mm^2. Current–voltage–light output characteristics were measured using a Keithley source-measure unit and multimeter, and the electroluminescence spectrum was measured with a CCD spectrograph.

*Polymer **5***: To the mixture of compounds **3** [13] (0.6333 g, 1.5 mmol) and **4** (0.5701 g, 1.5 mmol) was added freshly distilled dimethylformamide (DMF) (50 mL) and the mixture was purged with argon for 15 min. $Pd(PPh_3)_4$ (100 mg), and 1 M Na_2CO_3 solution (7.5 mL) was added sequentially. The flask was wrapped in Al foil and the mixture was stirred at 80 °C for 60 h under argon to obtain a light gray suspension. The mixture was cooled to room temperature, and water (200 mL) was added slowly with stirring. The light gray solid collected by suction filtration was washed with water and methanol. The solid was dissolved in chloroform (10 mL) then filtered through a Celite column. The filtrate was dropped into stirred methanol (250 mL) and the mixture was left standing overnight. Suction filtration followed by drying under high vacuum at 50 °C yielded polymer **5** as a light gray solid (0.65 g, 78 %). Anal. found (calcd. $C_{36}H_{44}N_2O_3$) C, 77.71 (78.23), H 7.95 (8.02), N 5.05 (5.07), Br 0 (0). ^{1}H NMR ($CDCl_3$) δ [ppm]: 0.80–0.90 (m, 6H), 1.20–1.40 (m, 8H), 1.67 (m, 1H), 3.91 (d, J = 4.8 Hz, 2H), 7.08 (s, 1H), 7.82 (d, J = 7.8 Hz, 2H), 8.25 (d, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ [ppm]: 11.15, 14.07, 23.03, 23.98, 29.02, 30.61, 39.58, 71.65, 115.44, 122.39, 126.49, 130.16, 130.25, 141.83, 150.45, 164.61. A gel permeation chromatography (GPC) measurement (THF eluent, polystyrene as standard) indicated M_w = 15 800 and polydispersity (PD) = 2.0.

*4-(2-Bromo-5-pyridyl)-2-methyl-3-butyn-2-ol **7***: To the solution of 2,5-dibromopyridine (9.48 g, 40 mmol) and 2-methyl-3-butyn-2-ol (3.36 g, 40 mmol) in dry THF (150 mL) was added CuI powder (220 mg). Triethylamine (20 mL, 143 mmol) was added using a syringe, and the solution was stirred at 20 °C for 10 min to obtain a clear yellow solution. $Pd(PPh_3)_2Cl_2$ (660 mg) was added in one portion and the mixture was stirred at 20 °C for 1 h, followed by gentle reflux for an additional 1 h. The mixture was cooled to 20 °C, and the solid formed during the reaction was removed by suction filtration. The solvent in the filtrate was removed by vacuum evaporation and the residue was chromatographed on silica eluted with dichloromethane–ether (2:1, v/v), followed by crystallization from acetonitrile to yield white plates of compound **6** (9.42 g, 98 %). m.p. = 94.8–96.2 °C. Anal. found (calcd. $C_{10}H_{10}BrNO$) C 50.06 (50.02), H 4.20 (4.20), N 5.91 (5.83). *m/z* (EI) = 224 (M^+–15, 100 %), 237 (1.29 %), 238 (1.73 %), 239 (M^+, ^{79}Br, 22.56 %), 240 (4.33 %), 241 (21.71 %), 242 (2.45 %). ^{1}H NMR ($CDCl_3$) δ [ppm]: 1.53 (s, 6H), 4.81 (s, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.64 (dd, J_{AB} = 8.4 Hz, J_{AC} = 2.4 Hz, 1H), 8.51 (d, J = 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ [ppm]: 30.84, 64.63, 79.84, 96.02, 119.66, 127.72, 138.72, 140.93, 150.44.

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5-Bromopyridine-2-carboxylic Acid **8**: Compound **7** (6.83 g, 28.45 mmol) was suspended in water (250 mL) and the mixture was heated to ca. 90 °C. $KMnO_4$ powder (15 g) was added in small portions with vigorous stirring until the purple color persisted. The mixture was then heated and stirred for an additional 1 h at 100 °C, followed by a suction filtration to remove the resulting MnO_2 solids. The colorless filtrate was concentrated by vacuum evaporation to ca. 50 mL, then acidified with 48 % hydrobromic acid to ≈ pH 4. The white solid was collected and washed with a large volume of water, then crystallized from ethanol–H_2O to yield compound **8** as white needles (4.53 g, 76 %), m.p. ≥ 350 °C. Anal. found (calcd. $C_6H_4BrNO_2$) C 35.60 (35.67), H 2.22 (2.00), N 6.72 (6.93). m/z (EI) = 157 (M^+–44, 100 %), 201 (M^+, ^{79}Br, 13.63 %), 202 (1.16 %), 203 (13.41 %), 204 (1.13 %). ^1H NMR (dimethyl sulfoxide-d_6, DMSO-d_6) δ [ppm]: 7.99 (dd, J_{AB} = 8.7 Hz, J_{AD} = 0.6 Hz, 1H), 8.25 (dd, J_{AB} = 8.4 Hz, J_{AC} = 2.4 Hz, 1H), 8.85 (dd, J_{AC} = 2.4 Hz, J_{AD} = 0.6 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ [ppm]: 124.18, 126.40, 140.10, 147.10, 150.36, 165.56.

N,N′-Bis(5-bromopyridine-2-carbonyl) hydrazine **9**: Compound **8** (1.01 g, 5 mmol) was dissolved in thionyl chloride (10 mL) and the mixture refluxed for 12 h to obtain a clear yellow solution. The excess thionyl chloride was removed by distillation. Dry dichloromethane (5 mL) was added to the residue, then removed by distillation. The procedure was repeated three times then the product was dried under vacuum to obtain a white solid of the acid chloride of compound **8**. Dry 1,4-dioxane (20 mL) was added to dissolve the solid, followed by the addition of hydrazine monohydrate (0.125 g, 2.5 mmol) quickly with vigorous stirring at 20 °C. The mixture was ultrasonicated for 10 min then warmed to 50 °C for 0.5 h. Water (50 mL) was added. The white crystalline solid obtained by suction filtration was washed with water and ethanol. Recrystallization from DMF–water mixture yielded compound **9** as white needles (0.66 g, 66 %). Anal. found (calcd. $C_{12}H_8Br_2N_4O_2$) C 35.78 (36.03), H 2.32 (2.02), N 13.60 (14.01). m/z (EI) = 91 (100 %), 398 (M^+, ^{79}Br, 25.02 %), 399 (3.55 %), 400 (45.58 %), 401 (8.26 %), 402 (23.75 %), 403 (3.20 %). ^1H NMR (DMSO-d_6) δ [ppm]: 7.98 (d, J = 8.4 Hz, 1 H), 8.28 (dd, J_{AB} = 8.4 Hz, J_{AC} = 2.1 Hz, 1H), 8.83 (d, J = 2.4 Hz, 1H), 10.74 (s, 1H). ^{13}C NMR (DMSO-d_6) δ [ppm]: 123.90, 124.27, 140.55, 147.91, 149.47, 162.36.

2,5-Bis(5-bromo-2-pyridyl)-1,3,4-oxadiazole **10**: Compound **9** (0.90 g, 2.25 mmol) was mixed with polyphosphoric acid (ca. 10 mL) and P_2O_5 (1 g) and the mixture was stirred for 6 h at 160 °C. Water (80 mL) was added to the cooled mixture followed by standing overnight. An off-white solid was collected by suction filtration of the mixture and washed sequentially with a large volume of water, 1 % Na_2CO_3, and methanol. The solid was crystallized from DMF to yield compound **10** as white plates (0.73 g, 85 %). m.p. 309.8–311.0 °C. Anal. found (calcd. $C_{12}H_6Br_2N_4O$) C 37.82 (37.73), H 1.56 (1.58), N 14.68 (14.67). m/z (EI) = 156 (100 %), 380 (M^+, ^{79}Br, 22.66 %), 381 (3.38 %), 382 (44.04 %), 383 (6.42 %), 384 (22.49 %), 385 (3.26 %). ^1H NMR (DMSO-d_6) δ [ppm]: 8.21 (d, J = 8.1 Hz, 1H), 8.34 (d, J = 8.4 Hz, 1H), 8.95 (s, 1H).

2,5-Bis[5-(4-tert-butylphenyl)-2-pyridyl]-1,3,4-oxadiazole **11**: To the suspension of compound **10** (191 mg, 0.5 mmol) and 4-*tert*-butylbenzeneboronic acid (267 mg, 1.5 mmol) in freshly distilled DMF (15 mL) was added $Pd(PPh_3)_4$ (40 mg). The mixture was stirred at 20 °C for 2 min then 1 M Na_2CO_3 (2 mL) was added. The color of the suspension changed quickly from deep yellow to light yellow. After 70 h of stirring at 70 °C, the yellow mixture was cooled to 20 °C and methanol (50 mL) was added. An off-white solid was obtained by suction filtration and washed successively with methanol, water, and methanol. The solid was dissolved in chloroform, filtered through a short column (ca. 10 cm) of silica (eluted with chloroform–ethyl acetate), then recrystallized from ethyl acetate to afford white crystals of compound **11** (216 mg, 88 %). m.p. 325.8 °C. Anal. found (calcd. $C_{32}H_{32}N_4O$) C 77.74 (78.66), H 6.49 (6.60), N 11.64 (11.47). m/z (EI) = 488 (M^+, 100 %), 473 (M^+–15, 84.69 %). ^1H NMR ($CDCl_3$, 200 MHz) δ [ppm]: 1.38 (s, 9H), 7.59 (q, J = 8.2 Hz, 4H), 8.09 (dd, J_{AB} = 8.2 Hz, J_{AC} = 2.0 Hz, 1H), 8.39 (d, J = 8.4 Hz, 1H), 9.06 (s, 1H). ^{13}C NMR ($CDCl_3$) δ [ppm]: 31.29, 34.77, 123.32, 126.35, 126.98, 133.69, 134.99, 138.74, 141.55, 148.87, 152.34, 164.57.

Polymer **12**: By analogy with the preparation of polymer **5**, polymer **12** was synthesized from diboronic acid **3** (0.4222 g, 1 mmol) and compound **10** (0.3820 g, 1 mmol) in freshly distilled DMF (50 mL), in the presence of $Pd(PPh_3)_4$ (72 mg) and 1 M Na_2CO_3 (3 mL), after vigorous stirring at 85 °C for 48 h and 100 °C for 12 h. The yield of **12** after purification was 0.52 g (94 %). Anal. found (calcd. $C_{34}H_{42}N_4O_3$) C 72.50 (73.62), H 7.31 (7.63), N 9.71 (10.10), Br 1.49 (0) (%). ^1H NMR ($CDCl_3$, 200 MHz) δ [ppm]: 0.87 (t, J_{AB} = 5.2 Hz, 6H), 1.26–1.43 (m, 8H), 1.69 (m, br, 1H), 3.93 (d, J_{AB} = 4.0 Hz, 2H), 7.09 (s, 1H), 8.17 (d, J_{AB} = 8.2 Hz, 1H), 8.43 (d, J_{AB} = 8.0 Hz, 1H), 9.06 (s, 1H). ^{13}C NMR ($CDCl_3$, 50.29 MHz) δ [ppm]: 11.05, 13.98, 22.93, 23.97, 28.97, 30.56, 39.46, 71.84, 115.09, 122.53, 127.47, 136.32, 137.79, 141.60, 150.77, 150.87, 164.66. GPC using polystyrene as standard indicated that M_n = 16 000, M_w = 26 600, M_z = 51 200, and PD = 1.66.

Received: October 30, 2000

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