Blue light-emitting Poly(*p*-phenylenevinylene) Derivative with Oxadiazole and Carbazole Pendant Groups

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ABSTRACT: A blue light-emitting statistical poly(*p*-phenylenevinylene) (PPV) copolymer with hole-transporting carbazole and electron-transporting oxadiazole pendant groups attached to the kinked *m*-terphenyl unit was prepared by Heck coupling between 1,4-divinylbenzene and dibromides. The latter were synthesized through pyrylium salts. The polymer had optical band gap of 2.89 eV and emission maximum at 446 nm in THF solution and 434 nm in thin film. It showed a pure blue emission with no aggregates or excimers formed even in solid state because of the long and bulky pendant groups. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3842–3849, 2006

Key words: poly(*p*-phenylenevinylene); 1,3,4-oxadiazole; carbazole; pyrylium salt; conjugated polymer; light emitting polymer; electron-affinity; hole-affinity; fluorescence; photophysics; synthesis

INTRODUCTION

Conjugated polymers have been extensively studied because of their potential applications.[1,2] Poly(*p*-phenylenevinylene) (PPV) is a green light emitting polymer, but the quantum efficiency of its light emitting diode (LED) is very low because of the imbalance of charge injection from both cathode and anode into the PPV.[3] Several approaches have been established to balance the electron and hole injections in PPV. These include the use of low work function metals as the cathode material, the fabrication of multi-layer LED, and the introduction of electron-withdrawing groups in PPV.[4,5] Electron-withdrawing groups in PPV can effectively enhance the electron affinity of PPV so as to balance the electron/hole injections into PPV.

The present investigation deals with the synthesis, characterization, and the optical properties of a novel PPV statistical copolymer that contains oxadiazol and carbazole moieties in the side groups. The purpose of this study is to incorporate electron donor and acceptor groups in the PPV chain to raise the HOMO level and reduce the LUMO level, respectively, and at the same time to maintain their emission color in the blue region. The introduction of oxadiazole and carbazole through a long alkylene spacer with PPV backbone provides a molecular dispersion of oxadiazole and carbazole in the material. The side chain oxadiazole and carbazole as well as the main chain PPV retain their own electron-transport,[6–12] hole-transport,[13] and emissive properties, respectively. The long alkylene spacers in the side groups enhance the solubility of the polymer. The PPV backbone carries substituted *m*-terphenyl segments. The introduction of a kinked structure along the polymer backbone has been established as a way to control the emitted light.[14–19]

The polymer was successfully prepared by a Heck coupling between 1,4-divinylbenzene, one dibromide with pendant oxadiazole groups and another dibromide with pendant carbazole groups. These dibromides were synthesized through pyrylium salts. This synthetic route has been widely used in our laboratory for the preparation of light emitting polymers.[20,21] The electron and hole affinity of the copolymer could be adjusted by changing the molar ratio of the two dibromides.

EXPERIMENTAL SECTION

Characterization methods

IR spectra were recorded on a Perkin–Elmer 16PC FTIR spectrometer with KBr pellets. ^{1}H NMR (400 MHz) spectra were obtained using a Brucker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. The PL and the PL excitation (PLE) spectra were obtained with a Perkin-Elmer LS45 luminescence spectrometer. The PL spectra were recorded with the corresponding excitation maximum as the excitation wavelength. The

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PLE spectra were recorded with the corresponding emission maximum as the emission wavelength. GPC analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters 2410) as detector using polysterene 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 N_2 atmosphere at a flow rate of 60 cm^3/min. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. 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. The excitation was performed at the corresponding excitation maximum and a solution in 1*N* H_2SO_4 of quinine sulfate, which has a Φ_f of 0.546 (λ_{ex} = 365 nm), was used as a standard.

Reagents and solvents

1,4-Divinylbenzene was synthesized according to a known method.[22] 4-Hydroxybenzoic acid and 4-hydroxybenzaldehyde were recrystallized from distilled water. Triethylamine was dried by distillation over KOH. *N*,*N*-Dimethylformamide (DMF) and 1,2-dichloroethane were dried by distillation over CaH_2. All other solvents and reagents were analytical-grade quality, obtained commercially, and used without further purification.

Preparation of monomers and polymers

4-hydroxybenzoic acid methyl ester **(1)**

Compound **1** was synthesized according to a reported method[23] that was modified as follows. A solution of 4-hydroxybenzoic acid (6.83 g, 48.90 mmol) in methanol (30 mL) containing a catalytic amount of concentrated sulfuric acid (four drops) was refluxed for 9 days. It was subsequently refrigerated for 24 h and the white precipitate was filtered, washed with water, and dried to afford **1**. It was recrystallized from methanol (2.31 g, yield 31%).

IR (KBr, cm^{-1}): 3308 (OH); 1682 (C=O); 1606, 1588, 1514, 1434 (aromatic); 1280, 1234, 1164 (C—O—C).

^{1}H NMR (DMSO-d_6, δ): 10.3 (s, 1H, OH); 7.84 (m, 2H, aromatic *ortho* to carbonyl); 6.88 (m, 2H, aromatic *ortho* to hydroxyl); 3.80 (s, 3H, CH_3).

4-acetoxybenzoic acid methyl ester **(2)**

Acetyl chloride (1.37 g, 14.60 mmol) was added dropwise at 0°C to a solution of **1** (2.22 g, 14.60 mmol) and triethylamine (2.22 g, 21.9 mmol) in acetone (20 mL) under N_2. The mixture was stirred at room temperature for 17 h in a stream of N_2. It was subsequently concentrated and water was added to the concentrate. The whitish precipitate was filtered, washed with water, and dried to afford **2**. It was recrystallized from methanol/water (4:1 v/v) (1.79 g, yield 63%).

IR (KBr, cm^{-1}): 1754, 1724 (C=O); 1600, 1506, 1436 (aromatic); 1284, 1216, 1192, 1110 (C—O—C).

^{1}H NMR (DMSO-d_6, δ): 7.95 (m, 2H, aromatic *ortho* to $COOCH_3$); 7.20 (m, 2H, aromatic *ortho* to $OCOCH_3$); 3.90 (s, 3H, $COOCH_3$); 2.10 (s, 3H, CH_3COO).

4-acetoxybenzoic acid hydrazide **(3)**

A mixture of **2** (13.08 g, 67.36 mmol), ethanol (30 mL), and hydrazine hydrate (10 mL) was refluxed for 20 h. It was subsequently concentrated and water was added to the concentrate. The white precipitate was filtered, washed with water, and dried to afford **3**. It was recrystallized from ethanol (7.62 g, yield 58%).

IR (KBr, cm^{-1}): 3318, 3196 (NH, NH_2); 1620 (C=O); 1590, 1510, 1466 (aromatic).

^{1}H NMR (DMSO-d_6, δ): 9.97 (broad, 1H, CONH); 7.97 (m, 2H, aromatic *ortho* to $CONHNH_2$); 7.26 (m, 2H, aromatic *ortho* to CH_3COO); 4.65 (broad, 2H, NH_2); 2.09 (s, 3H, CH_3COO).

Benzoic acid *n*-(4-acetoxybenzoyl)hydrazide **(4)**

A flask was charged with as solution of **3** (0.57 g, 2.93 mmol) in DMF (10 mL). Benzoyl chloride (0.41 g, 2.93 mmol), dissolved in DMF (5 mL), was added portionwise to the stirred solution at 0°C. Triethylamine (0.44 g, 4.35 mmol) was added to the stirred mixture at 0°C. The stirring of the mixture was continued at 70°C for 10 h under N_2. Then, it was concentrated under reduced pressure, and water was added to the concentrate. The whitish solid was filtered and recrystallized from ethanol/water (8:1 v/v) (0.29 g, yield 33%).

IR (KBr, cm^{-1}): 3264 (NH); 1672 (C=O); 1608, 1508, 1458 (aromatic).

^{1}H NMR (DMSO-d_6, δ): 10.50 (broad, 2H, CONH); 7.95 (m, 4H, aromatic *ortho* to carbonyl); 7.50–7.45 (m, 3H, aromatic *meta* and *para* to carbonyl); 7.25 (m, 2H, aromatic *ortho* to CH_3COO); 2.10 (s, 3H, CH_3COO).

4-(5-phenyl-1,3,4-oxadiazole-2-yl)phenol **(5)**

Compound **4** (0.26 g, 0.87 mmol) was dissolved via heating in $POCl_3$ (10 mL). The mixture was refluxed for 17 h. Then, 2 mL of aqueous hydrochloric acid 37% was added to the solution and it was refluxed for additional 2 h. The mixture was subsequently concentrated under reduced pressure, and water was added portionwise to the concentrate. The whitish precipitate was filtered, washed with water, and dried to afford **5**.

It was recrystallized from THF/*n*-hexane (0.19 g, yield 92%).

IR (KBr, cm^{-1}): 3384 (OH); 1610, 1552, 1496 (aromatic and oxadiazole ring); 1228 (C—OH).

^{1}H NMR (DMSO-d_6, δ): 9.22 (s, 1H, OH); 8.11–7.50 (m, 7H, aromatic expect those *ortho* to hydroxyl); 7.10 (m, 2H, aromatic *ortho* to hydroxyl).

Anal. Calcd for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 69.84; H, 4.28; N, 11.68.

4-(6-bromohexyloxy)benzaldehyde **(6)**

A mixture of 4-hydroxybenzaldehyde (1.50 g, 12.28 mmol), 1,6-dibromohexane (17.98 g, 73.69 mmol), K_2CO_3 (1.70 g, 12.30 mmol), and acetone (30 mL) was refluxed for 2 days under N_2. It was subsequently rotary-evaporated to remove volatile components. The residue was distilled under reduced pressure) (~0.9 mmHg) to remove excess of 1,6-dibromohexane. Compound **6** was purified by chromatography on a silica column, using dichloromethane as eluent (R_f = 0.82, 2.20 g, yield 63%).

IR (film on sodium chloride plate, cm^{-1}): 2938, 2862 (aliphatic); 1690 (CHO); 1600, 1510, 1466 (aromatic); 1258, 1160 (C—O—C).

^{1}H NMR ($CDCl_3$, δ): 9.90 (s, 1H, CHO); 7.68 (m, 2H, aromatic *ortho* to CHO); 6.94 (m, 2H, aromatic *meta* to CHO); 3.95 (m, 2H, OCH_2); 3.30 (m, 2H, CH_2Br); 1.80, 1.70, 1.30 (m, 8H, other aliphatic).

{2-[4-formylphenyl-4-oxyhexyloxy-4-phenyl]-5-phenyl}-1,3,4-oxadiazole **(7)**

A mixture of **6** (2.20 g, 7.71 mmol), **5** (1.84 g, 7.71 mmol), K_2CO_3 (1.39 g, 7.71 mmol), and acetone (40 mL) was refluxed for 24 h under N_2. Then it was concentrated under reduced pressure to give a pale-brown semisolid. It was extracted with dichloromethane, washed with brine, dried (Na_2SO_4) and concentrated to afford **7**. It was purified by chromatography on a silica column, using dichloromethane as eluent (R_f = 0.35, 2.39 g, yield 70%).

IR (film on sodium chloride plate, cm^{-1}): 2942, 2862 (aliphatic); 1602, 1510, 1454 (aromatic and oxadiazole ring); 1258, 1170 (C—O—C).

^{1}H NMR ($CDCl_3$, δ): 9.86 (s, 1H, CHO); 8.11–8.10 (m, 4H, aromatic *ortho* to oxadiazole); 7.81 (m, 2H, aromatic *ortho* to CHO); 7.51–6.98 (m, 7H, other aromatic); 3.95 (m, 4H, OCH_2); 1.70, 1.30 (m, 8H, other aliphatic).

{2,6-bis(4-bromophenyl)-5-[phenyl-(1,3,4-oxadiazol-2-yl)-4-phenyl-4-oxyhexyloxy-4-phenyl]}pyrylium tetrafluoroborate **(8)**

A flask was charged with a mixture of **7** (2.37 g, 5.35 mmol), 4-bromoacetophenone (2.13 g, 10.70 mmol), 1,2-dichloroethane (30 mL), and boron trifluoride etherate (1.90 g, 13.38 mmol). The mixture was stirred and refluxed for 3 h under N_2. Then, it was concentrated under reduced pressure and ethanol 95% was added to the concentrate. After stirring for 1 h, the precipitate was filtered, washed with ethanol, and dried to afford **8** (2.64 g, yield 56%).

IR (KBr, cm^{-1}): 2928, 2856 (aliphatic); 1626, 1586, 1486 (aromatic, oxadiazole ring and pyrylium); 1264, 1170 (C—O—C); 1068 (BF_4^-).

^{1}H NMR (DMSO-d_6, δ): 9.18 (s, 2H, aromatic *ortho* to O^+); 8.52–7.50 (m, 17H, other aromatic except those *ortho* to alkoxy); 6.80 (m, 4H, aromatic *ortho* to alkoxy); 3.95 (m, 4H, OCH_2); 1.70, 1.30 (m, 8H, other aliphatic).

{4,4′′-dibromo-5′-[phenyl-(1,3,4-oxadiazol-2-yl)-4-phenyl-4-oxyhexyloxy-4-phenyl]}-1,1′,3′, 1′′-terphenyl **(9)**

A mixture of **8** (2.53 g, 2.84 mmol), CH_3COONa (0.47 g, 5.73 mmol), and acetic anhydride (7 mL) was stirred and refluxed for 6 h under N_2. Then, it was concentrated under reduced pressure and water was added to the concentrate to precipitate viscous oil. Upon stirring the mixture at ambient temperature for 2 days, the viscous oil was converted to a brown solid that was filtered, washed with water, and dried to afford **9** (1.90 g, 84%).

IR (KBr, cm^{-1}): 2932, 2858 (aliphatic); 1604, 1488, 1434 (aromatic and oxadiazole); 1274, 1250, 1070 (C—O—C).

^{1}H NMR (DMSO-d_6, δ): 8.12–8.10 (m, 4H, aromatic *ortho* to oxadiazole); 7.73–7.50 (m, 16H, other aromatic except those *ortho* to alkoxy); 6.90 (m, 4H, aromatic *ortho* to alkoxy); 3.94 (m, 4H, OCH_2); 1.69, 1.29 (m, 8H, other aliphatic).

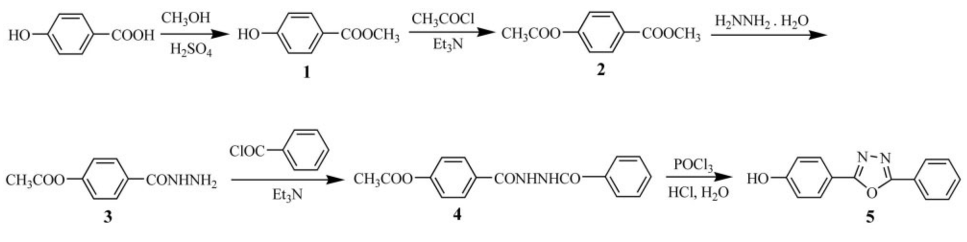
Anal. Calcd for $C_{44}H_{36}Br_2N_2O_3$: C, 66.01; H, 4.53; N, 3.50. Found: C, 65.72; H, 4.48; N, 3.57.

4-[6-carbazol-9-yl)hexyloxy]benzaldehyde **(10)**

A mixture of **6** (1.24 g, 4.35 mmol), carbazole (0.73 g, 4.35 mmol), K_2CO_3 (0.84 g, 5.02 mmol), and acetone (40 mL) was stirred and refluxed for 3 days under N_2. Then, it was concentrated to give viscous oil. It was extracted with dichloromethane, washed with water, dried (Na_2SO_4), and concentrated to afford **10**. It was purified by chromatography on a silica column, using dichloromethane as eluent (R_f = 0.81, 1.20 g, yield 74%).

IR (film on sodium chloride plate, cm^{-1}): 2938, 2860 (aliphatic); 1708 (CHO); 1602, 1510, 1452 (aromatic and carbazole segment); 1254, 1166 (C—O—C).

^{1}H NMR ($CDCl_3$, δ): 9.85 (s, 1H, CHO); 8.02–7.21 (m, 8H, aromatic of carbazole segment and 2H, aromatic *ortho* to CHO); 6.98 (m, 2H, aromatic *ortho* to alkoxy);



Scheme 1

3.95 (m, 2H, OCH_2); 3.74 (m, 2H, CH_2N); 1.77, 1.70, 1.30 (m, 8H, other aliphatic).

{2,6-Bis(4-bromophenyl)-4-[6-(carbazol-9-yl)hexyloxy-4-phenyl]}pyrylium tetrafluoroborate **(11)**

A flask was charged with a mixture of **10** (1.25 g, 3.36 mmol), 4-bromoacetophenone (1.34 g, 6.73 mmol), 1,2-dichloroethane (25 mL), and boron trifluoride etherate (1.19 g, 8.38 mmol). The mixture was stirred and refluxed for 3 h under N_2. It was subsequently concentrated under reduced pressure and ethanol 95% was added to the concentrate. After stirring for 1 h, the dark blue precipitate was filtered, washed with ethanol, and dried to afford **11** (1.75 g, yield 64%).

IR (KBr, cm^{-1}): 2926, 2856 (aliphatic); 1654, 1584, 1484 (aromatic, carbazole segment and pyrylium); 1248, 1172 (C—O—C); 1076 (BF_4^-).

^1H NMR (DMSO-d_6, δ): 9.19 (s, 2H, aromatic *ortho* to O^+); 8.51–7.21 (m, 18H, other aromatic except those *ortho* to alkoxy); 6.78 (m, 2H, aromatic *ortho* to alkoxy); 3.94 (m, 2H, OCH_2); 3.75 (m, 2H, CH_2N); 1.76, 1.71, 1.29 (m, 8H, other aliphatic).

{4,4′′-dibromo-5′-[6-(carbazol-9-yl)hexyloxy-4-phenyl]}-1,1′,3′,1′′-terphenyl **(12)**

A mixture of **11** (1.75 g, 2.16 mmol), CH_3COONa (0.36 g, 4.39 mmol), and acetic anhydride (5 mL) was stirred and refluxed for 6 h under N_2. Then it was concentrated under reduced pressure and water was added to the concentrate. The mixture was stirred at room temperature for 8 h. The brown precipitate was filtered, washed with water, and dried to afford **12** (1.50 g, yield 97%).

IR (KBr, cm^{-1}): 2930, 2858 (aliphatic); 1604, 1508, 1484 (aromatic and carbazole segment); 1242, 1072 (C—O—C).

^1H NMR (DMSO-d_6, δ): 8.02–7.20 (m, 21H, aromatic except those *ortho* to alkoxy); 6.91 (m, 2H, aromatic *ortho* to alkoxy); 3.95 (m, 2H, OCH_2); 3.74 (m, 2H, CH_2N); 1.77, 1.70, 1.30 (m, 8H, other aliphatic).

Anal. Calcd for $C_{42}H_{35}Br_2NO$: C, 69.15; H, 4.83; N, 1.92. Found: C, 68.73; H, 4.76; N, 1.98.

Polymer **P**

A flask was charged with 1,4-divinylbenzene (0.1074 g, 0.825 mmol), compound **9** (0.4623 g, 0.577 mmol), compound **12** (0.1805 g, 0.247 mmol), $Pd(OAc)_2$ (0.0077 g, 0.034 mmol), and P(*o*-tolyl)$_3$ (0.0578 g, 0.257 mmol). The flask was evacuated and purged with argon. Then, DMF (10 mL) and triethylamine (2 mL) were added and the mixture was heated at 120°C for 40 h. Subsequently, it was poured in methanol and the precipitate was filtered off, washed with methanol and dried. Polymer **P** was purified by dissolving in THF and was precipitated in methanol. It was obtained as a yellow-brown solid in 89% yield (0.55 g).

Anal. Calcd for $(C_{53.4}H_{43.7}N_{1.7}O_{2.4})_n$: C, 85.82; H, 5.85; N, 3.19. Found: C, 85.13; H, 5.97; N, 3.11.

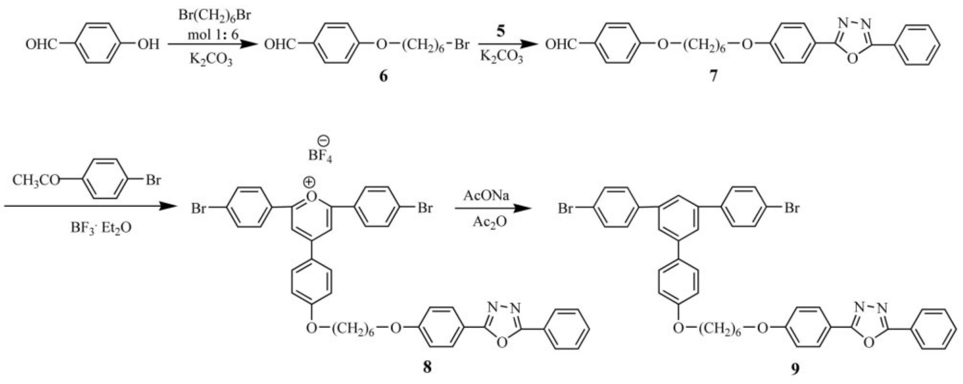
For characterization of **P** see Results and Discussion section.

RESULTS AND DISCUSSION

Synthesis and characterization

Scheme 1 outlines the synthesis of compound **5.** This synthetic route is slightly different from the one that has been reported.[24] Specifically, in the present case, 4-hydroxybenzoic acid, the starting material, reacted with acetylchloride to afford the corresponding acetoxy derivative. Following the construction of the oxadiazole ring, the acetoxy group was hydrolyzed by acid catalyzed hydrolysis. This hydrolysis took place in the step of cyclodehydration of hydrizide **4** in $POCl_3$ by means of the hydrochloric acid, which is formed during the cyclodehydration or is added further. In the literature method,[24] 4-methoxybenzoic acid was used as starting material and the methoxy group was hydrolyzed by concentrated aqueous HI.

Schemes 2 and 3 show the synthesis of dibromides **9** and **12**, respectively. The key step for this synthesis is the preparation of the intermediate pyrylium salts **8** and **11** from the reaction of a substituted benzaldehyde with 4-bromoacetophenone in the presence of BF_3 Et_2O.[25–28] These pyrylium salts reacted, subsequently, with acetic anhydride/sodium acetate, leading to the substituted dibromo-*m*-terphenyls. It is well established that 2,4,6-triarylpyrylium salts react with



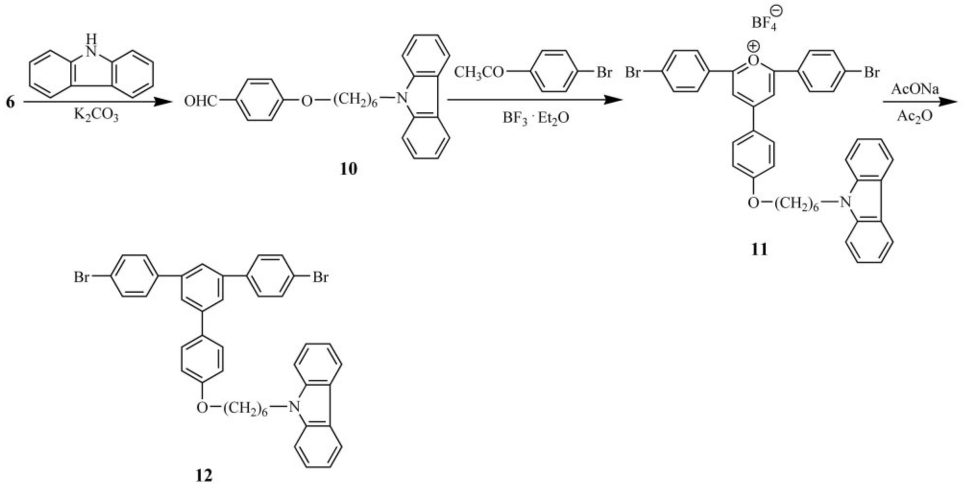
Scheme 2

excess carboxylic acid anhydrides in the presence of a condensing agent like sodium acetate, affording 1,3,5-triarylbenzene.[29]

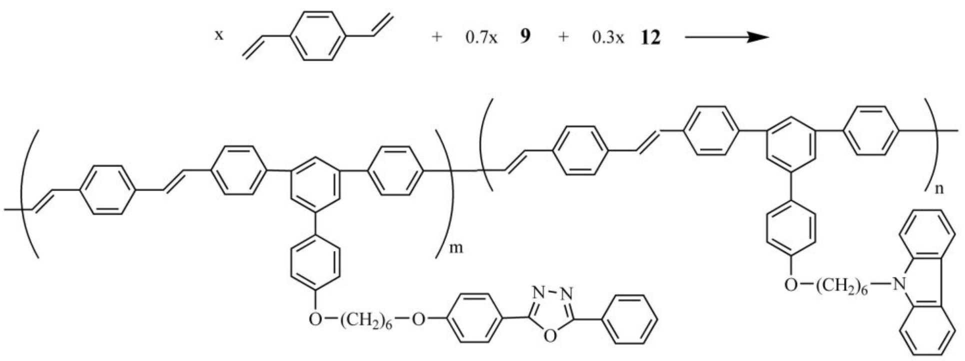
Polymer **P** was prepared by palladium catalyzed Heck coupling[30] of 1,4-divinylbenzene with dibromides **9** and **12** (Scheme 4). The comonomer feed ratio of **9/12** was 70:30. Since PPV derivatives are predominantly hole-conducting materials,[31] dibromide **9** with the electron-transporting oxadiazole segments was introduced to the feed in higher molar ratio than dibromide **12** with the hole-transporting carbazole segments.

The polymer was soluble in common organic solvents such as THF, chloroform, 1,2-dichloroethane, and dichloromethane. Smooth and optically clear films can be prepared by spin coating. The enhanced solubility of the polymer was ascribed to the long alkylene spacers and the kinked structure of *m*-terphenyl. The number-average molecular weight (M_n) of polymer was determined by GPC against polystyrene standards to be 7200 with a polydispersity of 1.80.

The chemical structure of the polymer was verified by FTIR and ^{1}H NMR spectroscopy (Fig. 1). The FTIR spectrum of **P** showed characteristic absorption bands at 2926, 2861 (C—H stretching of aliphatic moieties); 1660, 1598, and 1498 (aromatic and oxadiazole); 1244, 1170 (C—O—C stretching of the ether bond and oxadiazole); 1466 (carbazole moieties), and 964 cm^{-1} (*trans* olefinic bond). The ^{1}H NMR spectrum of **P** in CDCl$_3$ displayed multiple peaks at 8.10–6.90 (aromatic and olefinic protons), 3.95 (OCH$_2$), 3.85 (NCH$_2$) and 1.80–1.30 ppm (other aliphatic). The molar ratio **9/12** of the two comonomers in the copolymer can be estimated from the integrals of the peaks at 3.95 and 3.85 ppm assigned to the OCH$_2$ and NCH$_2$ groups, respectively. In particular, the integrals ratio OCH$_2$/NCH$_2$ was 6.2 from which a molar ratio 72/28 of the two comonomers was calculated, which roughly conforms to that in the reaction feed. Although it is difficult to distinguish the aromatic from the olefinic protons, the ^{1}H NMR spectrum indicated the formation of *trans* double bonds during polymerization because it lacked a peak of *cis*-olefinic protons at about 6.50 ppm. This was further substantiated by the absorption at 964 cm^{-1} and the absence of a band near 690 cm^{-1}



Scheme 3



P

Scheme 4

associated with the *cis*-olefinic bond in the IR spectrum. The DSC thermogram did not exhibit any transition even after repeated scans, thus confirming the amorphous nature of polymer. The long and bulky side groups increased the disorder in chain packing and contributed to the amorphous character of **P.** The polymer was stable up to about 300°C and showed a satisfactory thermal stability for fabrication of LEDs.

Optical properties

Figures 2 and 3 depict the UV–vis absorption, PLE, and PL emission spectra of polymer **P** in dilute ($10^{-5}M$) THF solution and in thin film, respectively. The latter was obtained on a quartz substrate by spincasting from THF solution. The absorption spectra of **P** both in THF and thin film showed a broad absorption corresponding to the π–π^* transition of the backbone, which was extended from 325 to 425 nm with maximum at 365 nm. This absorption is comparable with other related PPVs that contained kinked structure of *m*-terphenyl or 2,6-diphenylpyridine along the backbone.[19] However, this absorption is strongly blue shifted when compared with PPVs, which have been prepared from 1,4-divinylbenzene and 1,4-diiodo-2,5-dialkoxybenzene (459 nm),[32] because the latter lacked a kinked structure and had the electron-donating alkoxy groups. The optical band gap (E_g) of **P** calculated from the onset of the absorption spectrum in thin film was 2.89 eV. This value of E_g is higher than those of PPV derivatives with *m*-terphenyl or 2,6-diphenylpyridine kinked segments[19] (2.61–2.66 eV) or oxadiazoles[6] (2.44–2.46 eV) along the main chain but slightly lower than those of PPVs with oxadiazoles[33] (2.10–2.13 eV) in side chains.

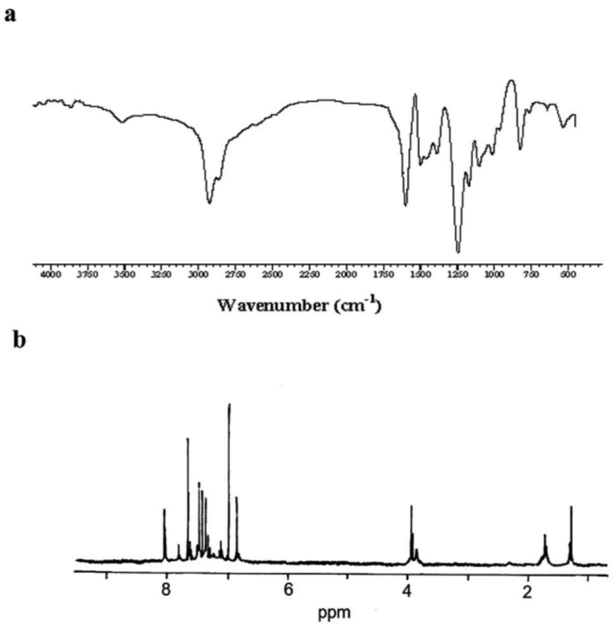


Figure 1 (a) FTIR spectrum and (b) ^1H NMR spectrum in $CDCl_3$ solution of polymer **P**.

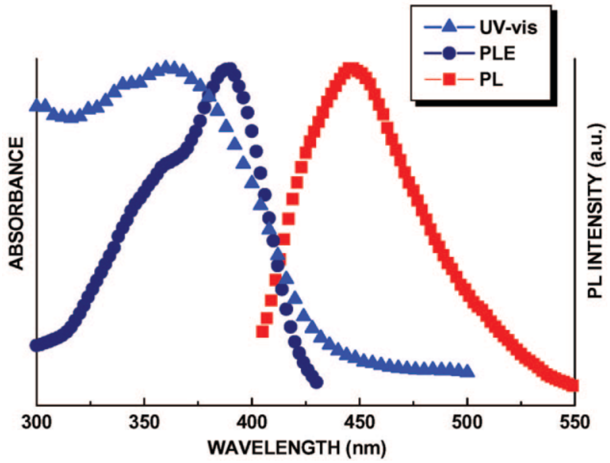


Figure 2 UV–vis, PLE, and PL spectra of polymer **P** in THF solution. The PL spectrum was recorded at the excitation wavelength of 390 nm. The PLE spectrum was recorded at the emission wavelength of 446 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

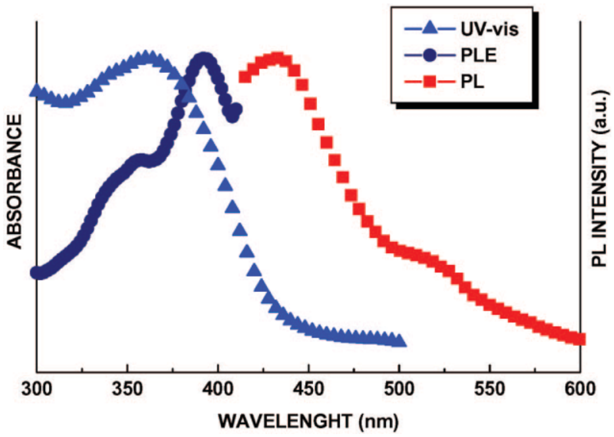


Figure 3 UV–vis, PLE, and PL spectra of polymer **P** in thin film. The PL spectrum was recorded at the excitation wavelength of 392 nm. The PLE spectrum was recorded at the emission wavelength of 434 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The PLE spectra of **P** in THF and thin film were significantly overlapped with the absorption spectra with a shoulder around 360 nm and maximum at 390 nm. The shoulder near 360 nm of the PLE spectrum corresponds to the absorption maximum. However, the PLE maximum was red shifted relative to the absorption maximum probably because the PLE spectrum was much higher affected by the aggregated states or the chromophores with long conjugation length than the absorption spectrum.[11]

Polymer **P** behaved as a blue emitting material with emission maximum at 446 nm for THF solution and 434 nm for thin film. The wide emission curves are located approximately at 400–550 nm indicating that conjugation is extended to the whole polymer. The PL quantum yield (Φ_f) of the polymer in THF solution was 0.21 relative to quinine sulfate.[34] This value of Φ_f is lower than that of our related PPVs (0.40–0.61) with kinked moieties along the main chain.[19] Polymer **P** emitted blue light while the alkoxy substituted PPVs[32] emitted green-yellow light (520–551 nm). This behavior was assigned to the electron-donating alkoxy groups of these PPVs. In addition, the *m*-terphenyl kinked structure along the polymer backbone of **P** caused a partial interruption of the conjugation.

In the majority of conjugated polymers, the emission maximum in solid state is red shifted relative to that in solution because of the formation of aggregates/excimers. An opposite effect was observed in the present case. The long and bulky side groups along with the kinked structure of *m*-terphenyl limited the chain interactions and hampered the formation of aggregates/excimers. However, the PL spectrum of **P** in thin film showed a shoulder at the longer wavelength region (~520 nm). The emission of **P** is blue shifted in solution and especially in thin film by 20 and 110 nm, respectively, when compared with the related PPV with *m*-terphenyl moieties along the main chain.[19] This feature could be attributed to the longer side groups of **P** that depressed the inter- and intrachain interactions.

CONCLUSIONS

A blue emitter statistical PPV copolymer with bipolar pendant groups and *m*-terphenyl moieties along the main chain was synthesized by Heck polymerization. The introduction of the electron-rich carbazole and the electron-deficient oxadiazole groups could increase both hole and electron affinities. The polymer was soluble in common organic solvents and emitted pure blue light with emission maximum at 446 nm in THF solution and 434 nm in thin film. The long and bulky pendant groups depressed the chain interactions and hindered the formation of aggregates/excimers even in solid state.

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