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Synthesis and properties of poly[2,6-(*p*-phenylvinyl)-4-(4'-octyloxybiphenyl-4-yl)quinoline]

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Summary

A novel polyquinoline (PQDBP8) containing the pendent 4'-octyloxybiphenyl group in the 4-position of the quinoline ring was prepared by the acid-catalyzed polymerization (Friedländer quinoline synthesis) of 1-(4-{2-[4-amino-3-(4'-octyloxybiphenyl-4-carbonyl)-phenyl]vinyl}phenyl)ethanone (**6**). PQDBP8 showed highly thermal stability (T_d = 384 °C, T_g = 183 °C). PQDBP8 showed blue fluorescence in dilute solution (λ_{max} = 449 nm) and green fluorescence in solid state (λ_{max} = 494, 540 nm) due to excimer formation. EL spectrum of PQDBP8 lies in the green region (λ_{max} = 572 nm) and PQDBP8/PVK blend film lies in the blue region (λ_{max} = 446 nm).

Introduction

Polyquinolines were developed during the 1970's by Stille and co-workers in response to increasing demand for polymeric materials with high thermal and oxidative stability (1,2). Recently, optical and electronic properties of polyquinolines such as electroluminescent (3), third order nonlinear optical (4), and photoconductive properties (5), have been studied extensively for their potential use in photonics and electronic applications. Generally high molecular weight polyquinolines can be obtained from the bis(aminoketone) monomers (AA type) and bis(ketomethylene) monomers (BB type) by Friedländer quinoline synthesis. Polyquinolines from the monomer containing both the ketomethylene moiety and the aminoketone group in one molecule (AB type) are also possible but are rare due to the difficulties of the synthesis. In this report, we synthesized a novel polyquinoline with the pendent 4'-octyloxybiphenyl group in the 4-position of the quinoline ring from an AB type monomer, as an extension of our polyquinoline study (5,6). PQDBP8 is expected to have good thermal and electrical properties due to its fully aromatic main-chain structure while maintaining good solubility in common organic solvents.

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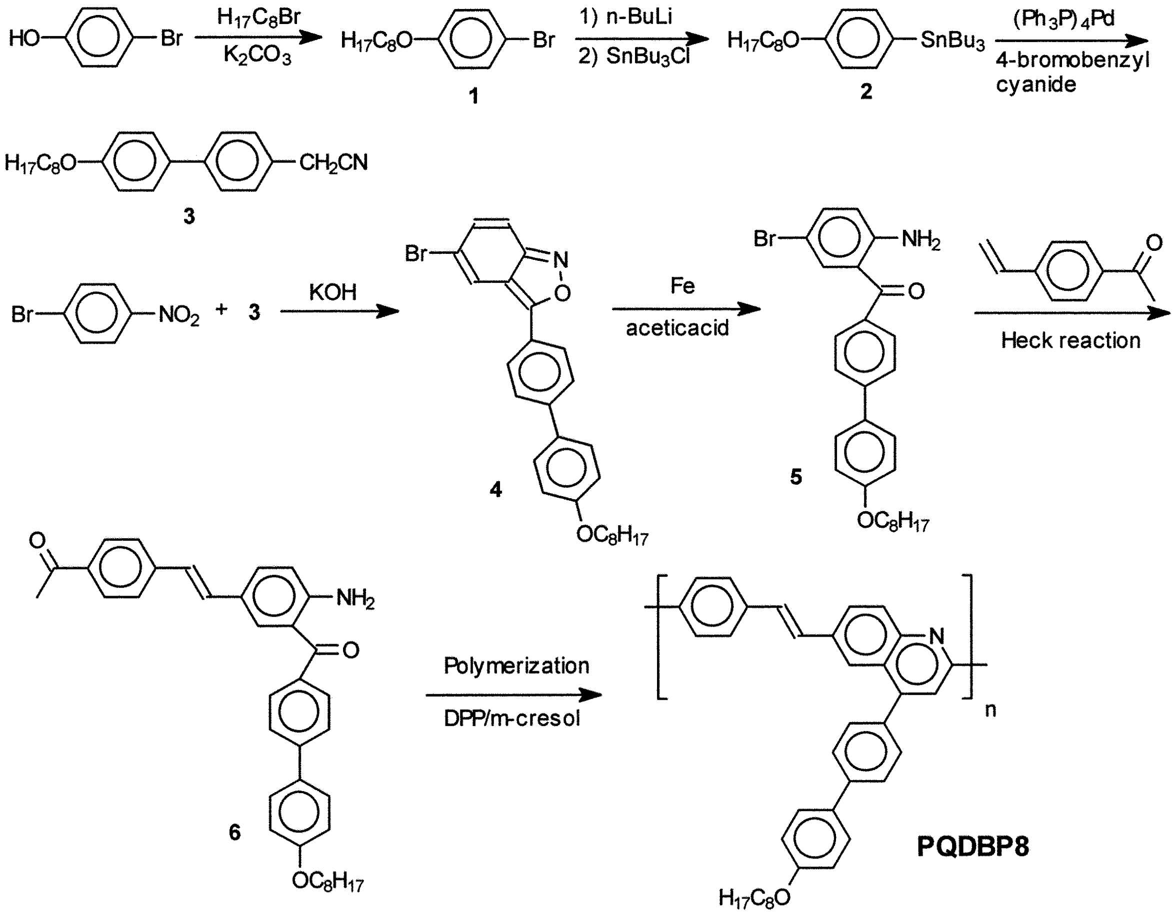


Scheme 1. Synthesis of **PQDBP8**.

Experimental

1-bromo-4-octyloxybenzene (**1**): A mixture of 34.6 g (0.2 mol) of 4-bromophenol, 34.6 mL (0.2 mol) of octylbromide, 27.64 g (0.2 mol) of potassium carbonate, and 100 mL of acetone was refluxed for 48 h. After cooling the mixture was poured into water and then extracted with ether. The extracts were washed with 10% sodium hydroxide, followed by water, and dried over $MgSO_4$. Removal of the solvent and distillation under reduced pressure yielded 49.76 g (87.2%) of colorless liquid: bp 132-134 °C (0.3 mm); ^{1}H NMR ($CDCl_3$) δ 7.32 (d, 2H), 6.76 (d, 2H), 3.88 (t, 2H), 1.77 (quint, 2H), 1.28-1.42 (10H), 0.89 (t, 3H). Anal. Calcd for $C_{14}H_{21}OBr$: C, 58.96; H, 7.42. Found: C, 58.71; H, 6.99.

(4-octyloxyphenyl)tributyltin (**2**): 1-bromo-4-octyloxybenzene (**1**) (28.52 g, 0.1 mol) was dissolved in 60 mL of dry THF and cooled to -78 °C. n-BuLi (62.5 ml, 1.6 M solution in hexane) was added under N_2 and stirred for 30 min. To this solution 27.12 g (0.1 mol) of tributyltinchloride in 60 mL of dry THF was added dropwise at -78 °C. The temperature was slowly raised overnight to room temperature. The reaction mixture was quenched with water and then extracted with ether. The organic extracts were dried over $MgSO_4$.

Removal of the solvent and distillation under reduced pressure yielded 43.4 g (87.6%) of colorless liquid: bp 180-182 °C (0.3 mm); ^{1}H NMR (CDCl3) δ 7.34 (d, 2H), 6.90 (d, 2H), 3.94 (t, 2H), 1.77 (quint, 2H), 0.86-1.58 (40H). Anal. Calcd for $C_{26}H_{48}OSn$: C, 63.04; H, 9.77. Found: C, 63.39; H, 8.92.

(4'-octyloxybiphenyl-4-yl)acetonitrile (**3**): A solution of 22.6 g (0.115 mol) of 4-bromobenzylcyanide, 2.69 g (2 mol%) of tetrakis(triphenylphosphine)palladium(0), and 100 mL of toluene was heated to reflux. To this solution 71.03 g (0.143 mol) of (4'-octyloxybiphenyl-4-yl)acetonotrile (**2**) in 100 mL of toluene was added dropwise. After refluxed for 48 h, the solution was hot filtered. The filterate was then allowed to cool to 0 °C and 25.66 g (69.2%) of white plate was obtained: mp 116-118 °C; IR (NaCl window) 2253 (CN) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.56 (d, 2H), 7.50 (d, 2H), 7.38 (d, 2H), 6.98 (d, 2H), 4.00 (t, 2H), 3.78 (s, 2H), 1.81 (quint, 2H), 1.29-1.50 (10H), 0.89 (t, 3H). Anal. Calcd for $C_{22}H_{27}NO$: C, 82.20; H, 8.47; N, 4.36. Found: C, 82.62; H, 7.91; N, 4.37.

5-bromo-3-(4'-octyloxybiphenyl-4-yl)benzo[c]isoxazole (**4**): To a stirred solution of 46 g (0.82 mol) of potassium hydroxide in 150 mL of methanol at ice bath temperature was added 14.14 g (44 mmol) of (4'-octyloxybiphenyl-4-yl)acetonitrile (**3**). To this slurry was added 8.08 g (40 mmol) of *p*-bromonitrobenzene in 100 mL of THF. The dark blue reaction mixture was stirred at 0 °C for 30 min and then heated to 65 °C for 48 h, and poured into 500 mL of water. The precipitate was isolated by suction filtration and then continuously extracted with methanol for 12 h. The light yellow solid was dried to afford 8.96 g (46.8%) of **4**: mp 173-175 °C; ^{1}H NMR ($CDCl_3$) δ 7.37-8.01 (m, 9H), 7.00 (d, 2H), 4.02 (t, 2H), 1.83 (quint, 2H), 1.30-1.55 (10H), 0.88 (t, 3H). Anal. Calcd for $C_{27}H_{28}NO_2Br$: C, 67.78; H, 5.90; N, 2.93. Found: C, 68.95; H, 5.30; N, 3.20.

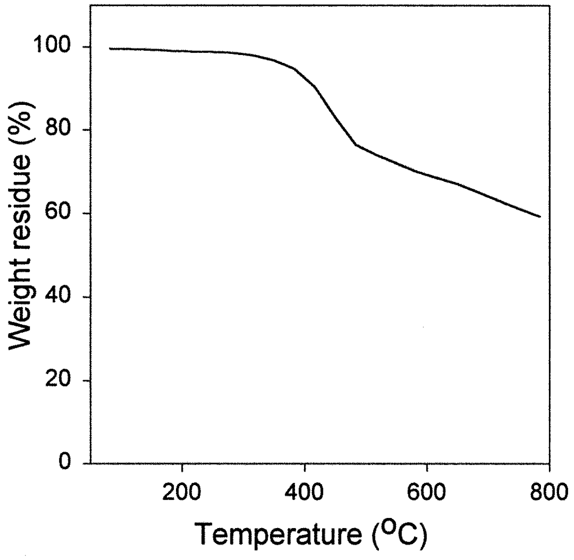
(2-amino-5-bromophenyl)-(4'-octyloxybiphenyl-4-yl)methanone (**5**): To a stirred suspension of 8.66 g (18 mmol) of 5-bromo-3-(4'-octyloxybiphenyl-4-yl)benzo[c]isoxazole (**4**) in 300 mL of glacial acetic acid at 95 °C was added 27 g (0.48 mol) of iron powder in eight equal portions for 1 h. When all iron had been added the reaction mixture was heated at 95 °C for 3 h, cooled, and poured into water. The precipitate was collected by suction filtration and filtered through silica gel methylene chloride as eluent. Removing of the solvent and recrystallization from MeOH/THF yielded 5.36 g (62%) of **5**: mp 164-167 °C; IR (NaCl window) 3356, 3466 (NH_2), 1632 (C=O, benzophenone) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35-7.72 (m, 8H), 7.00 (d, 2H), 6.67 (d, 1H), 6.02 (bs, 2H), 4.02 (t, 2H), 1.82 (quint, 2H), 1.30-1.50 (10H), 0.88 (t, 3H). Anal. Calcd for $C_{27}H_{30}NO_2Br$: C, 67.50; H, 6.29; N, 2.92. Found: C, 68.82; H, 5.83; N, 3.16.

1-(4-{2-[4-amino-3-(4'-octyloxybiphenyl-4-carbonyl)-phenyl]vinyl}phenyl)ethanone (**6**): A mixture of 1.20 g (2.5 mmol) of (2-amino-5-bromophenyl)-(4'-octyloxybiphenyl-4-yl)methanone (**5**), 0.457 g (3.13 mmol) of 4-vinylacetophenone, 0.0056 g (0.025 mmol) of palladium acetate, 0.0304 g (0.10 mmol) of tri-*o*-tolylphosphine, 2.6 mL of triethylamine, and 6.6 mL of DMF was heated at 90 °C overnight under N_2. The cooled reaction mixture was poured into water, collected by suction filtration, and recrystallized from ethanol to give 0.66 g (48.4%) of **6**: mp 202-204 °C; IR (NaCl window) 3360, 3466 (NH_2), 1680 (C=O, acetyl), 1635 (C=O, benzophenone), 962 (C=C, stilbene) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.78-7.91 (m, 17H), 6.22 (bs, 2H), 4.02 (t, 2H), 2.59 (s, 3H), 1.82 (quint, 2H), 1.30-1.50 (10H), 0.89 (t, 3H). Anal. Calcd for $C_{37}H_{39}NO_3$: C, 81.43; H, 7.20; N, 2.57. Found: C, 81.62; H, 6.94; N, 2.43.

Polymerization: A solution containing 0.55 g (1 mmol) of **6**, 5 ml of *m*-cresol and 5 g of diphenylphosphate was heated to 140-142 °C for 72 h under N_2. After cooling the polymer was precipitated by pouring the reaction mixture into 500 mL of ethanol containing 50 mL of triethylamine. The polymer was continuously extracted in Soxhlet apparatus with ethanol. After drying 0.40 g (72.7%) of poly[2,6-(*p*-phenylvinyl)-4-(4'-octyloxybiphenyl-4-yl)quinoline] was obtained. Anal. Calcd for $(C_{37}H_{35}NO)n$: C, 84.0; H, 6.88; N, 2.57. Found: C, 87.18; H, 6.93; N, 2.75.

Characterization: IR spectra were recorded from NaCl window on a Midac FT-IR spectrophotometer and a Varian 200 (200MHz) were used for NMR measurements. GPC analysis of the polymer was performed on a Waters HPLC component system equipped with five ultra-μ -styragel columns (10^5, 10^4, 10^3, 500Å) using THF as solvent. DSC analysis was performed on a Perkin Elmer DSC7 at a heating rate of 10 °C/min and TGA analysis was conducted with a Du Pont 2950 at a heating rate of 20 °C/min under nitrogen gas flow. UV-vis spectrum was recorded with a HP 8452A Diode Array spectrophotometer. Photoluminescence (PL) spectra and electroluminescence (EL) spectra were obtained using ISS K2 multifrequency phase fluormeter equipped with 300W-xenon arc lamp.

LED device fabrication: 20 mg of PQDBP8 was dissolved in 1 mL of cyclohexanone to make 2.0 wt% solution which was filtered through a pore size of 0.2 μ m. The LED structure consists of an aluminum contact on the surface of PQDBP8 which was spin cast on plasma treated ITO glass. Aluminum was deposited onto the surface of the spin-cast film by vacuum evaporation at pressure below 10^{-6} torr, yielding an active layer with a area of 0.18 cm^2. All processing steps were carried out in air. In case of PQDBP8/PVK blend film, 5 mg of PQDBP8 and 20 mg of PVK were dissolved in 1 mL of cyclohexanone to make 2.5 wt% solution.



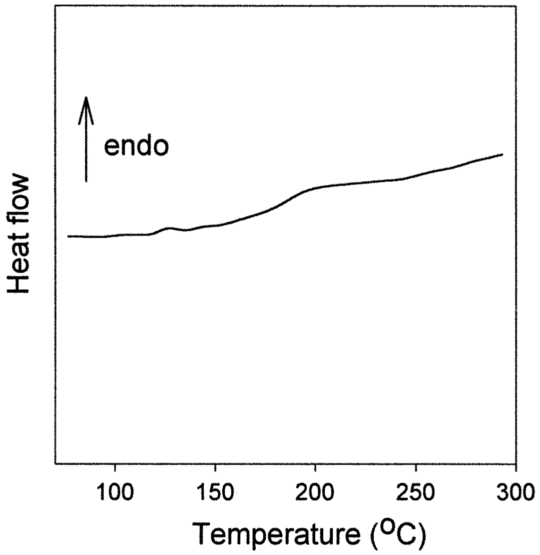


Fig. 1. TGA thermogram of PQDBP8

Fig. 2. DSC thermogram of PQDBP8

Results and Discussion

The synthesis of the monomer and polymer is outlined in Scheme 1. Acetonitrile compound **3** was obtained by the palladium catalyzed coupling reaction (7) of **2** and 4-bromobenzylcyanide. The product was easily isolated and purified in good yields. No separation by chromatography was required. Compound **3** was condensed with 4-bromonitrobenzene to produced benzisoxazole intermediate **4**, which was hydrogenated to the *o*-benzoylamine compound **5** (8). Compound **5** was then coupled with 4-vinylacetophenone (9) by Heck reaction (10) to give target monomer. The new polymer PQDBP8 was synthesized by Friedländer polyquinoline synthesis with good yield. The disappearance of a doublet absorption band of amine, carbonyl strechings of acetyl and benzophenone unit of IR spectrum and the disappearance of broad singlet peak around 6.22 ppm(-NH_2) and singlet peak at 2.59 ppm(-$COCH_3$) in NMR spectrum confirmed the complete cyclization. The molecular weight of PQDBP8 is M_w= 1.46x10^4, M_n = 5.3x10^3. PQDBP8 was soluble in common organic solvents such as THF and cyclohexanone.

Figure 1 and 2 present the TGA and DSC thermogram of PQDBP8. PQDBP8 showed highly thermal stability with initial decomposition temperature of 384 °C and retained 58% of its mass up to 800 °C and had T_g of 183 °C.

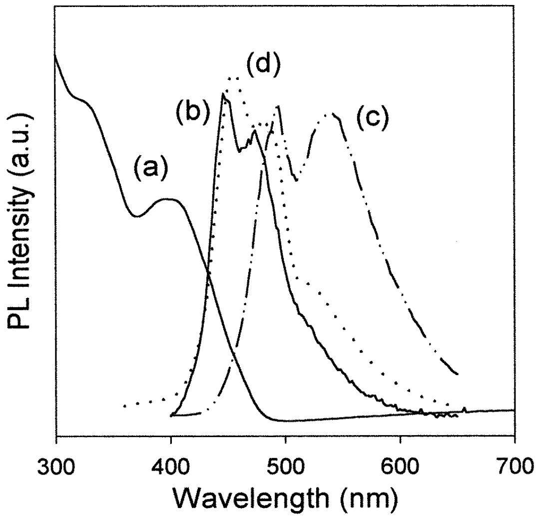


Fig. 3. (a) UV absorption spectrum, (b) PL spectrum of solution (10^{-5}M), (c) PL spectrum of film of PQDBP8 and (d) PL spectrum of PQDBP8/PVK blend film.

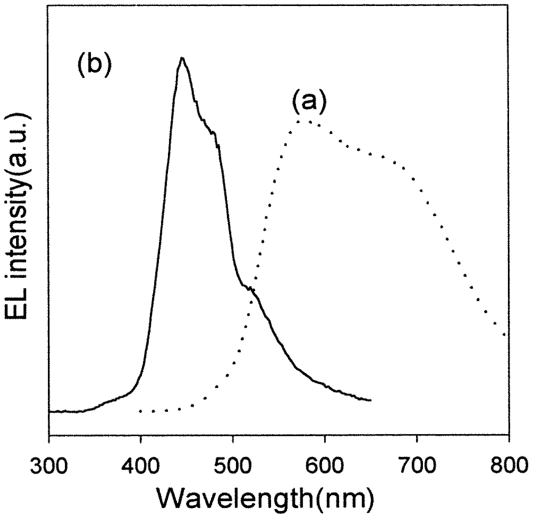


Fig. 4. (a) EL spectrum of PQDBP8 and (b) EL spectrum of PQDBP8/ PVK blend film

Figure 3 shows the absorption and emission spectra of PQDBP8. The UV-visible absorption peak of PQDBP8 was 398 nm, which is attributed to the π-π^* transition. The PL spectra of PQDBP8 showed emission maximum of 449 nm and minor peak at 474 nm for dilute solution (in THF, 10^{-5} M) when excited at 365 nm. For thin film, PQDBP8 had two peaks at 494 nm and 540 nm and showed green emission. This broad peak around 540 nm is likely duo to interchain excimer emission (11-13). We supposed that in spite of the pendent group, the chain stacking was not suppressed sufficiently duo to the rigid-rod main-chain structure. To study the excimer formation of PQDBP8 in solid state, PQDBP8 was blended with PVK (14, 15). Broad peak around 540 nm disappeared in PQDBP8/PVK blend film (20/80 by weight, excited at 340 nm), which is originated from the dilution effect of PVK. The dilute solution emission spectrum can be attributed to the singlet excited states of single chain but thin film emission of the conjugated polymer is originated from mainly singlet excimers. Figure 4 presents electroluminescence (EL) spectrum of PQDBP8 and PQDBP8/PVK blend film. The emission maximum for PQDBP8 occurred around 572 nm with shoulder around 650 nm in the green region and PQDBP8/PVK blend film showed blue emission with emission maximum around 446 nm with minor shoulder around 480 and 520 nm.

In summary, a novel AB type polyquinoline, poly[2,6-(*p*-phenylvinyl)-4-(4'-octyloxybiphenyl-4-yl)quinoline] (PQDBP8) was synthesized successfully by Friedländer polyquinoline synthesis and its thermal and luminescent properties were investigated. PQDBP8 was thermally stable with T_d of 384 °C and T_g of 183 °C. PQDBP8 showed blue emission in dilute solution and green electroluminescence in thin film state and PQDBP8/PVK blend film (20/80 by weight) showed blue elctroluminescence due to dilution effect.

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