

Novel Blue-Light-Emitting Polymers Based on a Diphenylanthracene Moiety

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ABSTRACT: New luminescent copolyethers with diphenylanthracene-emitting segments and electron-transporting benzoxazole phenyl were successfully synthesized by aromatic nucleophilic substitution. The polymers, characterized by NMR and IR spectroscopy, were obtained in high yields, showed good solubility in various organic solvents, and had high thermal stability with high glass-transition temperatures (125–129). The number-average molecular weights of the polymers were 10,000–20,000, and they had polydispersity indices of 1.2–1.4. The optical and electrochemical properties of the polymers were also investigated. The pure blue

emission for the polymers (maximum wavelength = 430–440 nm) was obtained with high photoluminescence quantum efficiency (76–78%) in a chloroform solution. The blue electroluminescence for the poly(TDPB) (maximum wavelength = 440 nm) was obtained with a turn-on voltage of 15–20 V when simple light-emitting diodes (indium tin oxide/polymer/Al) were fabricated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2151–2157, 2006

Key words: light-emitting diodes (LEDs); fluorescence; luminescence

INTRODUCTION

The discovery of electroluminescence (EL) polymers for light-emitting devices (LEDs) has stimulated tremendous research activity in the development of LEDs for display applications.^{1–4} The color that the polymers emit can be easily tailored by chemical modification of the polymer structures. However, efficient, highly bright, and stable blue-light-emitting materials are still under intensive research because blue light is necessary for full-color EL display applications. With blue-light-emitting polymers as primary materials, it is possible to generate other colors by a downhill energy-transfer process.⁵ Several classes of conjugated polymers have been demonstrated to emit blue light.^{6–10}

An effective approach to achieving wide energy band gaps for blue light is to control the conjugation length. One approach to achieving a blue emission is to insert a flexible, nonconjugated spacer into the backbone, which provides direct control of the conjugation length and improves the processability.^{11–17}

However, it usually reduces the glass-transition temperature (T_g), decreases the mobility of the charge carriers, and thus leads to a high threshold voltage, which generally causes damage to the device. An alternative approach is to incorporate a molecular linkage, an *m*-phenylene unit, or a nonconjugated, rigid spacer instead of a flexible spacer into the conjugated backbone, which not only fixes the effective conjugation length but also maintains the thermal stability.^{18–23} Recently, some groups have reported on poly(arylene ether)s containing charge-transporting units as blue-light-emitting materials and found that these polymers show both high thermal stability and good charge-transporting properties. However, most of the studies have been limited to designing bipolar polymers capable of transporting both electrons and holes.^{24,25}

In this article, we report a novel blue-light-emitting poly(aryl ether) containing benzoxazole phenyl and diphenylanthracene in the backbone. The design and synthesis of the polymer are based on the following considerations: (1) the ether linkage in the backbone provides a means of increasing the thermal stability and adjusting the length of conjugation; (2) the incorporation of the benzoxazolylphenyl moiety as an electron-transporting block into the polymer backbone provides the possibility of improving the electron-transporting ability of the resulting polymer because benzoxazole and oxadiazole derivatives have been widely incorporated into the polymer backbone and used as active materials or electron-transporting components in LEDs; and (3) the introduction of a benzo-

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xazolyphenyl moiety as a bulkier group is expected to realize efficient intramolecular energy transfer from benzoxazolyphenyl to diphenylanthracene and to reduce the self-quenching process of excitons caused by intermolecular interaction and thus enhance the photoluminescence (PL) efficiency.

EXPERIMENTAL

Materials

All reagent and solvents were purchased from Aldrich Chemical Co. and Fluka. Only analytical-grade chemicals were used. Quinine sulfate 7-hydrate was obtained from Kodak Eastman. Spectroscopic-grade CHCl_3 (Aldrich Chemical) was used for all absorption and emission experiments. American Chemical Society (ACS) reagent-grade CHCl_3 (Aldrich; 99.8%) was used for the preparation of the polymer films. All other compounds were used as received.

Instrumentation

Melting points were determined on a Hoover capillary melting-point apparatus. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral data are expressed in parts per million with respect to an internal standard and were obtained in CHCl_3 or dimethyl sulfoxide on a Varian XL 300 NMR spectrometer. Thermogravimetric analysis (TGA) measurements were performed on a PerkinElmer Series 7 analysis system under N_2 at a heating rate of $10^\circ\text{C}/\text{min}$. Ultraviolet-visible (UV-vis) spectra and optical density measurements were obtained on an HP 8452A diode array spectrometer. The PL spectra were recorded with a Spex 312 scanning fluorometer. The excitation wavelength in all cases was 360 nm. The thickness was determined with a Sloan Dektak. The light intensities were measured with a silicon photodiode (model 1830-C, Newport Instruments). We determined the light output in nanowatts. The current-voltage and light-voltage curves were recorded automatically via the use of a custom LabView program written especially for this task.

Device fabrication

The substrate for device fabrication typically consisted of four indium tin oxide (ITO) lines. Lines (2 mm wide) of Al were deposited perpendicularly to the ITO lines via thermal evaporation at a pressure of 5×10^{-6} Torr. The aluminum was evaporated at a rate of 200 Å/s onto the films. The resultant thickness of the aluminum lines was typically between 1500 and 2000 Å. Each sample therefore had four ITO lines and four aluminum lines, the intersections of which gave 16 pixels or active devices that could be addressed individually by the connection of the appropriate leads to a power source.

Synthesis

Preparation of 9,10-dihydroxy-9,10-di(*p*-methoxyphenyl)anthracene

p-Methoxyphenyl magnesium bromide was obtained from *p*-methoxyphenyl bromide (92 g, 0.5 mol), and magnesium (12 g, 0.5 mol) was dropped into an ether solution of 9,10-anthraquinone (42 g, 0.2 mol) at -5 to 10°C . The Grignard reaction was carried out with mechanical stirring within 10 min to prevent a side reaction. After the reaction mixture was acidified with saturated aqueous ammonium chloride, the crude product was extracted with an ether solution. The ether solvent was evaporated, and the product was recrystallized with tetrahydrofuran and hexane as solvents. The product yield was 30 g (35%).

$^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ , ppm): 3.8 (6H, $-\text{OCH}_3$), 5.3 (2H, $-\text{OH}$), 7–8 (16H, ArH).

Preparation of 9,10-di(*p*-methoxyphenyl)anthracene

The obtained 9,10-dihydroxy-9,10-di(*p*-methoxyphenyl)anthracene (21 g, 0.05 mol) was dehydrated with potassium iodide (25 g, 0.15 mol) and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (78 g, 0.5 mol) in the solvent acetic acid (200 mL) for 4 h. After refluxing, the crude product was filtered and washed with water and ethyl ether. The product yield was 17.46 g (90%).

$^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ , ppm): 3.8 (6H, $-\text{OCH}_3$), 7–8 (16H, ArH).

Preparation of 9,10-di(*p*-hydroxyphenyl)anthracene

The ether cleavage reaction of 9,10-di(*p*-methoxyphenyl)anthracene (10 g, 0.025 mol) was carried out with excess HBr (48%) and in the solvent acetic acid at reflux for 24 h. The reaction mixture was cooled to recrystallize. The crude product was filtered and washed with water and acetic acid. The product yield was 9 g (90%).

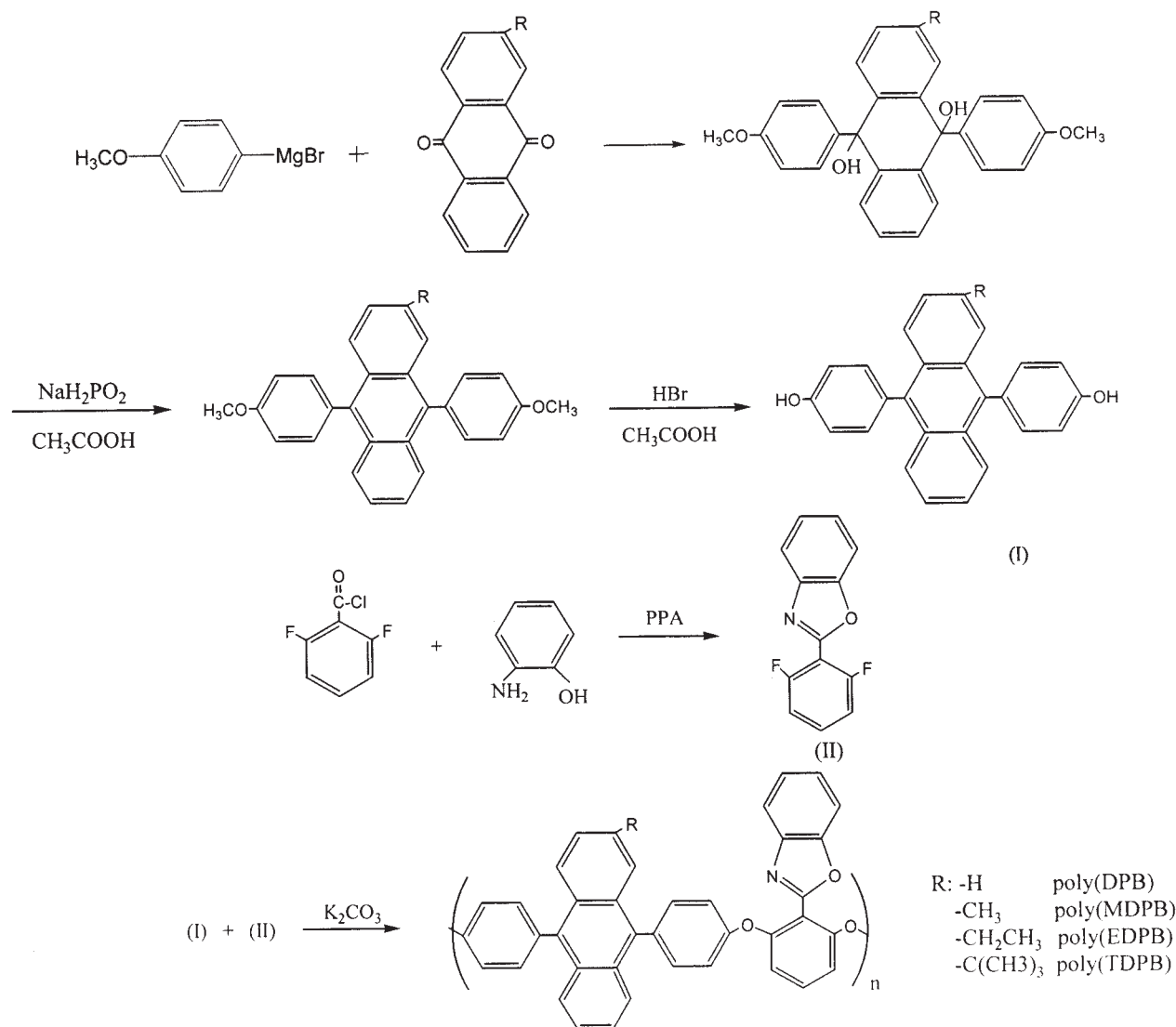
$^1\text{H-NMR}$ (200 MHz, acetone, δ , ppm): 2.9 (2H, $-\text{OH}$), 7–8 (16H, ArH).

Preparation of 9,10-di(*p*-hydroxyphenyl)anthracene derivatives

The synthesis of the derivatives was carried out with the same method used for 9,10-di(*p*-hydroxyphenyl)anthracene. The yields of the products were similar to that of 9,10-di(*p*-hydroxyphenyl)anthracene.

2-Methyl-9,10-di(p-hydroxyphenyl)anthracene $^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ , ppm): 2.1 (3H, $-\text{CH}_3$), 2.9 (2H, $-\text{OH}$), 7–8 (15H, ArH).

2-Ethyl-9,10-di(p-hydroxyphenyl)anthracene $^1\text{H-NMR}$ (200 MHz, CDCl_3 , δ , ppm): 1.2 (3H, $-\text{CH}_3$), 2.1 (2H, $-\text{CH}_2-$), 2.9 (2H, $-\text{OH}$), 7–8 (15H, ArH).



Scheme 1 Synthetic scheme of the polymers.

2-*tert*-Butyl-9,10-di-(*p*-hydroxyphenyl)anthracene ¹H-NMR (200 MHz, CDCl₃, δ, ppm): 1.7 [9H, —C(CH₃)₃], 2.9 (2H, —OH), 7–8 (15H, ArH).

Preparation of 1-(2'-benzoxazole)-2,6-difluorobenzene

2,6-Difluorobenzoyl chloride (17.6 g, 0.1 mol) and 2-hydroxyaniline (10 g, 0.1 mol) in poly(phosphoric acid) (PPH) were refluxed for 5 h. The reaction mixture was cooled and digested in ice water. After the reaction mixture was extracted with ethyl ether, the ether was evaporated. The crude product was recrystallized in methanol. The product yield was 17 g (70%).

¹H-NMR (200 MHz, CDCl₃, δ, ppm): 7–8 (6H, ArH).

Polymerization

Polymerization of poly[9,10-diphenylanthracene-co-1'-(2''-benzoxazole)-2',6'-dioxypybenzene]. poly(*DPB),

poly[2-methyl-9,10-diphenylanthracene-co-1'-(2''-benzoxazole)-2'-b'-dioxypybenzene], poly(MDPB) poly[2-ethyl-9,10-diphenylanthracene-co-1'-(2''-benzoxazole)-2',6'-dioxypybenzene], poly(EDPB), poly[2-*tert*-butyl-9,10-diphenylanthracene-co-1'-(2''-benzoxazole)-2',6'-dioxypybenzene], poly(TDPB) 1-(2'-Benzoxazole)-2,6-difluorobenzene (0.231 g, 0.001 mol), corresponding 9,10-di-(*p*-hydroxyphenyl)anthracene derivatives (0.362 g, 0.001 mol), and K₂CO₃ (0.138 g, 0.001 mol) in a cosolvent (1:2 toluene/dioxane) were refluxed for 10 h. After the polymerization was completed, excess 1-(2'-benzoxazolyl)-2',6'-difluorobenzene was added for the end capping of hydroxy groups. After the end-capping reaction, the reaction temperature was reduced to room temperature, and water was added. The polymer was precipitated in methanol after the toluene solvent was evaporated and extracted with methylene dichloride. After the polymer was filtered, the polymer was dried in an oven.

TABLE I
Polymerization Results and Thermal Properties of Poly(DPB) Derivatives

Polymer	Yield (%)	M_n	M_w	PD	Decomposition temperature
Poly(DPB)	92	12,000	15,600	1.3	410
Poly(MDPB)	90	9,200	12,800	1.4	405
Poly(EDPB)	89	8,500	12,500	1.47	400
Poly(TDPB)	93	11,000	14,000	1.27	410

M_n = number-average molecular weight; M_w = weight-average molecular weight; PD = polydispersity.

RESULTS AND DISCUSSION

A synthetic scheme of the polymers is depicted in Scheme 1. The key monomer was synthesized from anthraquinone, which reacted with phenylmagnesium by the Grignard reaction to give 9,10-dihydroxy-9,10-di(*p*-methoxyphenyl)anthracene. After reduction with potassium iodide and sodium hypophosphite in acetic acid, 9,10-di(*p*-methoxyphenyl)anthracene was obtained and then demethylated with HBr in acetic acid to yield the monomers in a good yield. Another key monomer, 2,5-difluorobenzoxazole, was obtained from 2,5-difluorobenzoyl chloride and 2-hydroxyaniline in poly(phosphoric acid). The polymers were prepared by aromatic nucleophilic substitution in a high yield (>90%). The number-average molecular weight of the polymers was controlled by the ratio of the two bifunctional monomers. After the polymerization was completed, more excess benzoxazole was added for the end capping of the hydroxy group because it is known that a hydroxy group can quench PL of polymers.

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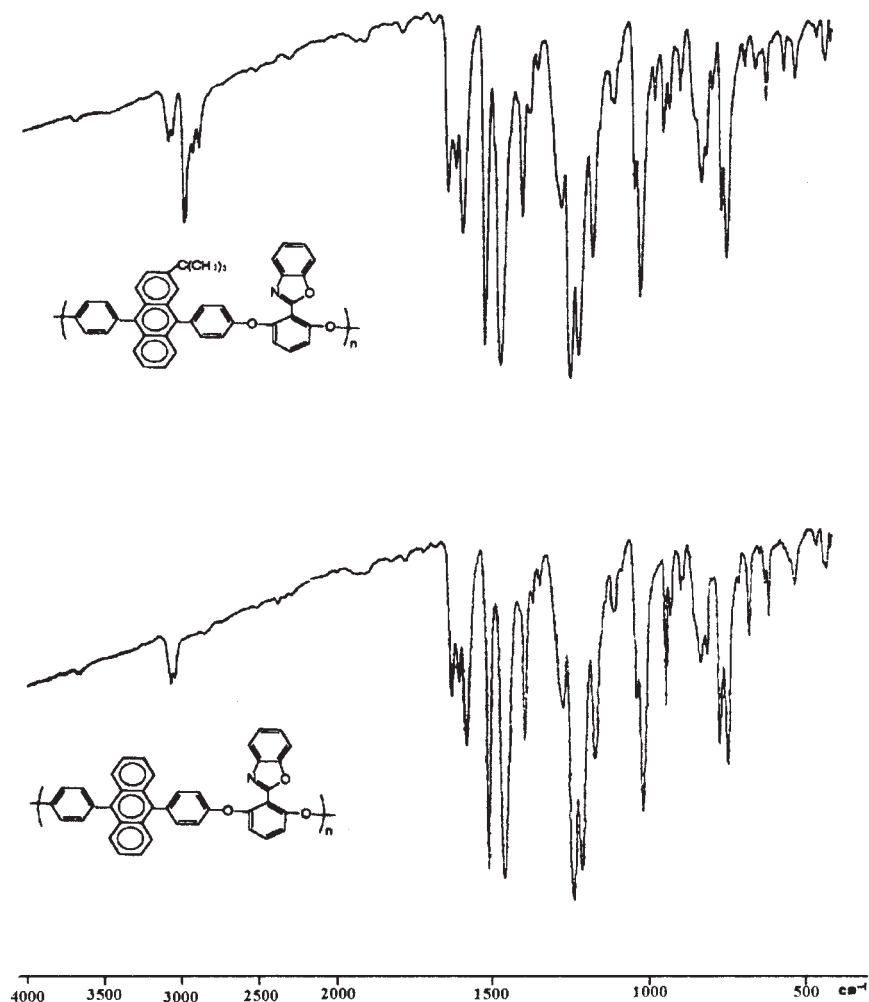


Figure 1 IR spectroscopy of poly(DPB) and poly(TDPB).

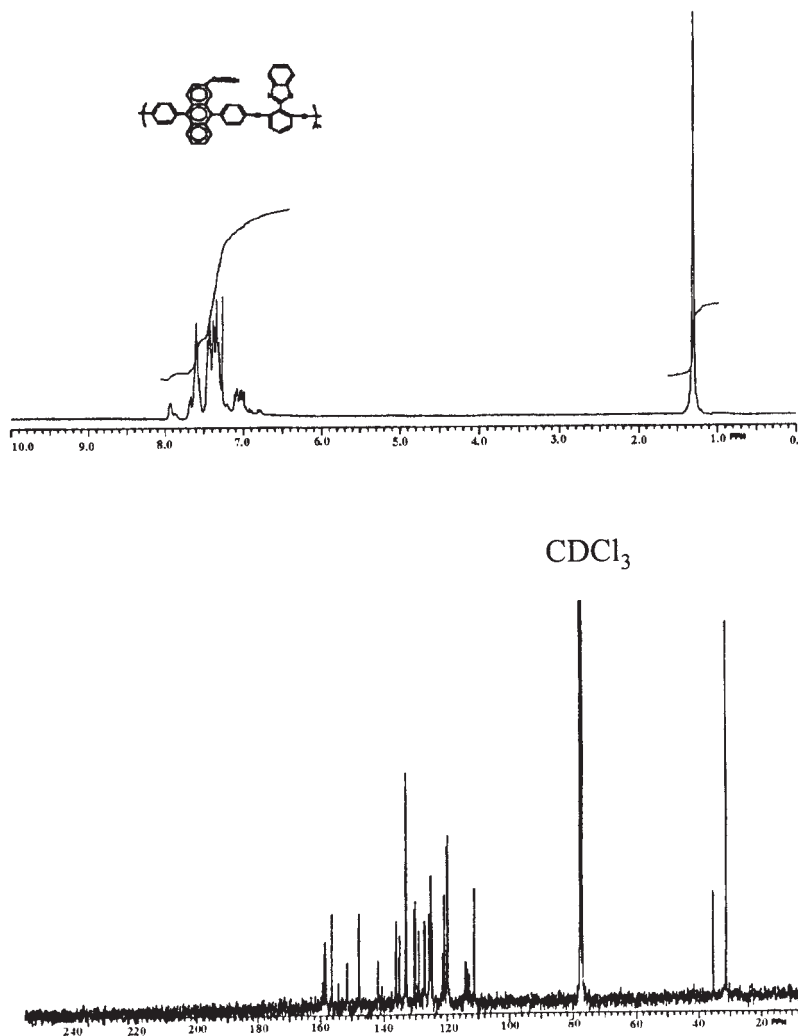


Figure 2 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopy of poly(TDPB).

Gel permeation chromatography measurements of these polymers with polystyrene as the calibration standard showed a weight between 10,000 and 20,000 and a polydispersity index of 1.5–2.0. TGA was carried out for the bulk-state polymer at a rate of $10^\circ\text{C}/\text{min}$ in nitrogen gas. TGA thermograms of the polymers showed that all the polymers had good thermal stability up to 400°C . The T_g 's of the polymers by means of differential scanning calorimetry at a rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere appeared at $125\text{--}129^\circ\text{C}$. The good thermal stability promised that the polymers could endure the high temperatures in the process of fabrication and operation. The detailed molecular weights, polydispersity indices, and decomposition temperatures determined from TGA thermograms are listed in Table I. The elemental analysis results of the polymers agreed with their chemical structures. The IR spectra showed strong absorption peaks at $1050\text{--}1150\text{ cm}^{-1}$ due to C—O—C stretching and a peak at 1607 cm^{-1} due to C=N stretching in the benzoxazole. The absence of the absorption peaks around 3500 cm^{-1} indicated that the polymerization was com-

pleted and the terminal hydroxy group was terminated (Fig. 1). Figure 2 shows the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of poly(TDPB). The assignments of the peaks, as indicated in the spectra by comparison with literature values, confirmed the molecular structure.

The UV-vis absorption spectra of the obtained polymer in a CHCl_3 solution had similar maxima at 270, 365, 378, and 399 nm, regardless of the substituents; these are characteristic absorptions of diphenylanthracene. Upon UV excitation, solutions of the polymer exhibited very intense fluorescence with a maximum at $430\text{--}440\text{ nm}$ (Table II). The fact that the emission band was much narrower than the absorption bands and showed well-resolved vibronic bands was consistent with the emission from localized excited states, most likely after a migration of the excitons along the polymer main chain to segments that represented low energy states. The PL quantum yield of the polymers in CHCl_3 solutions was measured to be approximately $0.72 \pm 10\%$ upon excitation at 365 nm. The high quantum efficiency may have resulted from intramolecular energy transfer from a benzoxazole unit with a wide

TABLE II
Optical Properties of Poly(DPB) Derivatives

Polymer	UV (λ_{\max}) ^a	PL λ_{\max}^a	PL QY ^c	UV λ_{\max}^b	PL λ_{\max}^b
Poly(DPB)	263, 360, 379, 399	429, 440	0.73	271, 362, 376, 400	445
Poly(MDPB)	261, 358, 376, 397	425, 436	0.72	271, 364, 382, 404	440
Poly(EDPB)	263, 358, 376, 397	425, 438	0.72	271, 358, 382, 402	445
Poly(TDPB)	263, 360, 377, 403	440	0.76	267, 362, 378, 400	440

^a The spectra were obtained in CHCl_3 .

^b The spectra were obtained from spin-coated films.

^c QY = quantum yield.

band gap to a diphenylanthracene unit with a small band gap. For the measurement of the intramolecular energy transfer, the PL spectrum was measured in a dilute solution ($<10^{-5}$ M). When the poly(TDPB) was excited at either 270 or 365 nm, the same PL spectrum, with a maximum wavelength (λ_{\max}) of 440 nm, was observed (Fig. 3). A homogeneous and pinhole-free thin film was obtained via spin casting from a CHCl_3 solution. The solid-state PL spectra of the polymers had a maximum peak of 440–450 nm corresponding to pure blue light. The solid PL showed a 10–15-nm-redshifted emission in comparison with those of a solution. The band gaps between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), taken from the onset of the absorption spectra, were 2.92–2.95 eV for the polymers. A wide band gap of polymers is desirable for their use as charge-injection materials for blue-light-emitting materials.

To study the ionization energy and the optical energy gap, the electrochemical analysis was carried out with cyclic voltammetry (CV). CV of polymer-coated

ITO and Al plates was measured in a three-electrode compartment cell with a Pt wire counter electrode and a Ag/AgNO₃ (0.1M) reference at a scanning rate of 50 mV/s. The electrolyte was a 0.1M Bu₄NClO₄ solution in anhydrous acetonitrile, and the cell was purged with nitrogen. The onset of reduction (E_{red}) and oxidation (E_{ox}) peak potentials for poly(TDPB) were measured to be -1.25 and 1.57 V, respectively. Regardless of the substituents, the polymers showed similar onsets of E_{red} and E_{ox} . According to the reported empirical equation by de Leeuw et al.,²⁶ energy level of LUMO ($E_{\text{LUMO}} = E_{\text{onset(red)}} + 4.4$ eV) and energy level of HOMO ($E_{\text{HOMO}} = E_{\text{onset(ox)}} + 4.4$ eV, where $E_{\text{onset(ox)}}$ and $E_{\text{onset(red)}}$ are the onset potentials for the oxidation and reduction processes of a polymer versus a saturated calomel electrode, respectively). The LUMO and HOMO energy levels of the polymer were estimated to be 3.15 and 5.97 eV, respectively. The results showed that the LUMO energy levels of the polymers were almost the same as those of some poly(aromatic oxadiazole)s.²⁷ The fact implies that the polymers may have electron-injection properties typical of oxadia-

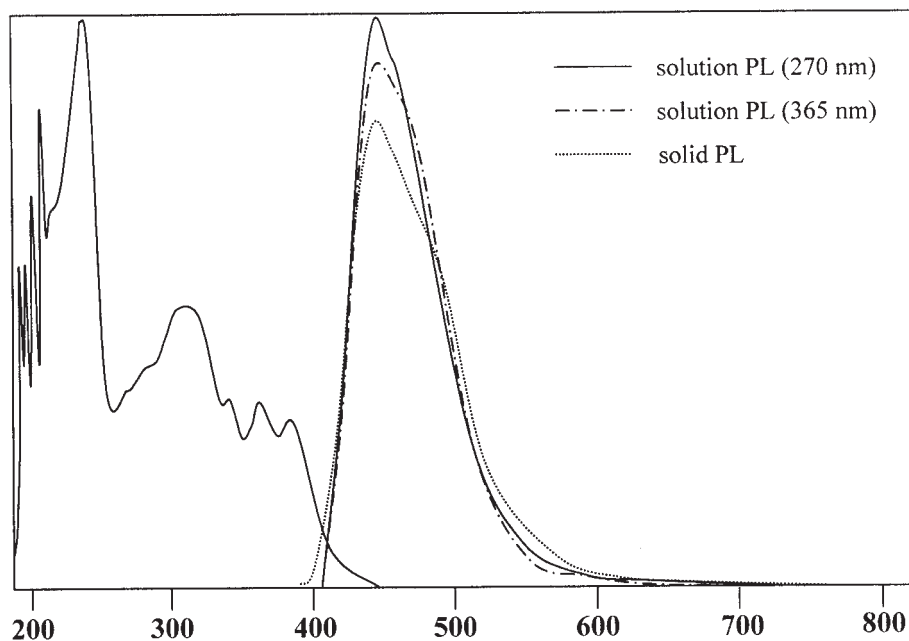


Figure 3 UV-vis and PL spectra of poly(TDPB) in CHCl_3 .

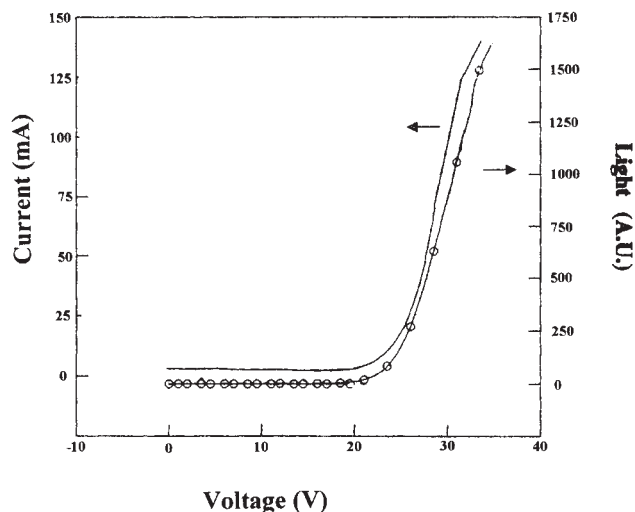


Figure 4 Light-voltage and current-voltage plots of an ITO/poly(TDPB)/Al device.

zole-containing electron-transporting materials when they are used as emitters in polymeric polymer light emitting diodes (PLEDs).

The ITO/polymer/Al single-layer light-emitting diode was fabricated. The polymer was deposited onto an ITO-coated glass substrate via the spin casting of the polymer solution in chlorobenzene. A uniform polymer film was obtained with a thickness of about 130 nm. Aluminum was thermally evaporated onto the polymer film as a top electrode. Under a forward bias, the single-layer diode began to emit visible pure blue light around 15–20 V. The current-voltage curve of the ITO/polymer/Al device, displayed in Figure 4, shows typical diode characteristics. The EL spectrum was similar to the PL spectrum of the polymer. It indicated that the same excited states were involved in the two processes. The preliminary results showed that the polymers could be potential materials for polymer LEDs. Because the polymers showed that hole injection was difficult, the performance and characterization of the fabricated polymeric LEDs were measured under ambient conditions, and higher performance polymeric LEDs made out of these new polymers could be expected under optimized device fabrication conditions. In addition, the polymers could be used as hole-blocking and electron-transporting materials because of their low HOMO level and facility of electron injection due to the low LUMO level.

CONCLUSIONS

We synthesized new blue-light-emitting polyethers containing diphenylanthracene derivatives and ben-

zoxazolylphenyl in the polymer main chain by aromatic nucleophilic substitution. These polymers showed good solubility, good thermal stability, and high PL quantum efficiency. The incorporation of benzoxazole units lowered the LUMO level and could make electron injection to the polymers from the anode easy. Pure blue emissions were obtained from a single-layer LED fabricated from the polymers.

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