

Synthesis and Photoluminescent Properties of Poly(arylene ether)s Containing Alternate Emitting and Electron-Transporting Moieties

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ABSTRACT: A new diphenylbutadiene-containing bisphenol was successfully synthesized from benzylideneaniline and 4-propenylanisole via an anil synthetic method. A series of copoly(arylene ether)s consisting of an alternate isolated blue chromophore (diphenylbutadiene) and an electron-transporting moiety (1,3,4-oxadiazole) was synthesized and characterized. High molecular weight copoly(arylene ether)s with an inherent viscosity of >0.5 dL/g were prepared by the nucleophilic displacement reaction of oxadiazole-activated bis-fluoro compounds with bisphenols. Introduction of ether linkages into the copolymers led to an enhanced solubility in organic solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone

(NMP). The resulting copolymers can be cast into tough and transparent films. The copolymers were amorphous in structure with high glass transition temperatures ranging from 182.29 to 194.50°C. They also exhibited good thermal stability with the maximum decomposition temperatures higher than 500°C in nitrogen. The absorption peaks of these copolymers in thin films varied from 375 to 391 nm, while the photoluminescent peaks varied from 410 to 433 nm. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1645–1651, 2003

Key words: light-emitting diodes (LED); polyaromatics; luminescence

INTRODUCTION

The first report on light emission from a poly(*p*-phenylenevinylene) (PPV) thin film¹ sandwiched between an anode and a cathode electrode was presented by Holmes and coworkers in 1990. The syntheses of electroluminescent polymers for organic light-emitting diodes (OLEDs) have been investigated extensively.² Conjugated polymers have been widely investigated as emissive layers in OLEDs because they exhibit unique processibility such as solution spin-coating, band-gap tunability, thermal stability, and mechanical flexibility and are less expensive. To facilitate solution spin-coating, to control the emissive color, and to improve the efficiency of emission, several conjugated polymers, such as PPV,³ poly(*p*-phenylene)s (PPPs),⁴ polyfluorenes (PFs),⁵ and polythiophenes (PTs),⁶ have been investigated. However, some problems still re-

main unresolved for polymer light-emitting diodes (LEDs) with respect to their luminescent efficiency and long-term stability. These shortcomings become the main hurdles for their commercialization and remain to be improved.

Many efforts have been devoted to enhance the electroluminescence (EL) efficiency. The emissive light of OLEDs arises from the recombination of electrons and holes, which are injected from the two opposite electrodes and become excitons in an emissive polymer layer. To achieve high EL efficiency, it is necessary to balance the rates of the injection of electrons and holes from the opposite electrodes into the polymer layer.⁷ In most PPVs and their derivatives, electron injection has been found to be more difficult than is holes injection. To overcome this problem, most conjugated polymers with their intrinsically low electron affinity require electron-injecting metal electrodes with a very low work function (such as Ca and Mg).⁸ Such metals, however, are very highly susceptible to atmospheric degradation, leading to poor stability of the devices. Accordingly, the use of polymers with high electron affinities is an alternative approach to increase the efficiency. Oxadiazole-containing conjugated polymers are considered as materials for the light-emitting devices⁹ due to their high electron af-

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finity and hole-blocking ability. For example, aromatic oxadiazole compounds such as 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) have been synthesized and used as electron-transporting materials in a multilayered LED device structure.¹⁰ Moreover, the fabrication of multilayered devices using the spin-coating methodology is tedious and tough work because it requires a careful selection of each layer material to prevent the solution of a subsequent layer to attack or to destroy the previous one. Therefore, the fabrication of a single-layer device with high efficiency and varying colors has recently attracted considerable attention.¹¹

This article involves the synthesis and characterization of a series of soluble and emissive poly(arylene ether)s with both an alternate isolated emitting chromophore and an electron-transporting 1,3,4-oxadiazole unit. The thermal and photoluminescent properties of these polymers were examined and are reported.

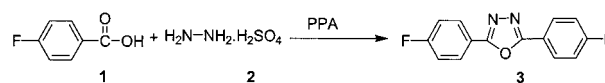
EXPERIMENTAL

Materials

All reagents and solvents were reagent grade and purified by the standard methods prior to use. 4-Fluorobenzoic acid was synthesized by the oxidation of 4-fluorotoluene with KMnO_4 . Benzylideneaniline **5** was prepared from aniline and 4-methoxybenzaldehyde according to the procedure reported in the literature.¹² Poly(phosphoric acid) (PPA), 4-propenylanisole **4**, sodium, aniline, triethylene glycol, *N,N'*-dimethylacetamide, *N,N*-dimethylformamide (DMF), toluene, anhydrous potassium carbonate, and 4,4'-isopropylidenediphenol (BPA) were obtained from commercial sources and used as received.

Instrumentation

The glass transition temperatures (T_g 's) were determined in a modulated TA DSC instrument (Model MDSC 2910) at a heating rate of 20°C/min under a nitrogen flow of 50 mL/min. The decomposition process of the polymers from 30 to 400°C was performed using a Seiko thermogravimetric analyzer (TGA/DTA; Model SSC-5200) under a protective helium atmosphere (100 mL/min) and a ramping rate of 20°Cmin⁻¹. NMR data were recorded at 400 MHz in a Bruker NMR instrument (Model DRX 400MHz) and were listed in parts per million (ppm) downfield from tetramethylsilane (TMS). Chloroform-*d*₁ (CDCl_3) was used as the solvent. Melting points were obtained on a melting-point apparatus. The inherent viscosity of the polymers was measured in an NMP solution at a concentration of 0.5 g/dL at 30°C using an Ubbelohde viscometer. The absorption and fluorescence spectra of the synthesized polymers in dilute chloroform so-



Scheme 1 Synthesis of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole **3**.

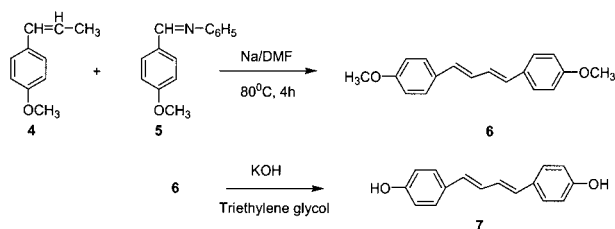
lutions, in solid powders, and in thick solid films (100 nm) on the quartz substrates were recorded by a Hitachi 330 UV-vis spectrophotometer and a Perkin-Elmer LS50 fluorescence spectrophotometer, respectively. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analyses were carried out on a Kratos KOMPACT MALDI-TOF-MS. The analyte consisted of 1:4:2 (wt) of the sample, lithium bromide, and the 1,8,9-trihydroxyanthracene (Dithranol) matrix. A sample with about 0.2 μL of this analyte was spotted on the sample slot and dried at a temperature of about 50°C. All spectra were recorded in the reflectron mode.

Preparation of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole **3**

The bis(fluoride) monomer **3** containing 1,3,4-oxadiazole was synthesized from 4-fluorobenzoic acid and hydrazine sulfate according to Scheme 1.¹¹ To a 250-mL round-bottom flask equipped with a temperature controller, a condenser, and an overhead mechanical stirrer was charged 4-fluorobenzoic acid **1** (4.2 g, 30 mmol), hydrazine sulfate **2** (2.0 g, 15 mmol), and PPA (40 g). The mixture was then heated to 80°C to dissolve the reactants, followed by further heating to 150°C, and kept at this temperature for 8 h. The resulting mixture was continually reacted at 200°C for 2 h to ensure the completion of the ring closure. The resulting mixture was finally precipitated out in 250 mL distilled water, filtered, and then dried in a vacuum oven. Upon recrystallizing from methanol, compound **3** was obtained in white crystals. Yield: 70%; mp: 204–205°C. ¹H-NMR (DMSO): δ (ppm) 7.40–7.50 (m, 4H), 8.10–8.20 (m, 4H). MALDI-TOF-MS: Found: 258.73; calcd for $\text{C}_{14}\text{H}_8\text{F}_2\text{N}_2\text{O}$: 258.22.

Preparation of 1,4-bis(4-methoxyphenyl)-1,3-butadiene **6**

1,3-Butadiene containing compound **6** was synthesized via an improved procedure of Paventi and Hay.¹² To a 100-mL three-neck round-bottom flask equipped with a magnetic stirrer, a reflux condenser, and a nitrogen inlet was charged 40 mL DMF. Metallic Na (1.0 g, 0.043 mol) was then added in several portions at room temperature under a slow stream of N_2 with stirring. The reaction temperature was thereafter increased to 110°C and maintained at this temperature until all the metallic sodium reacted with DMF to form



Scheme 2 Synthesis of 4,4'-(1,3-butadiene-1,4-diyl)bisphe- nol 7.

a yellow solution. The resulting mixture was then allowed to cool to an ambient temperature. To the above Na/DMF solution, another solution of benzylideneaniline 5 (4.2 g, 20 mmol) and 4-propenylanisole 4 (3.0 g, 20 mmol) in 15 mL DMF was introduced with stirring at 35°C. The reaction mixture was then heated to reflux 4 h under a nitrogen atmosphere. Upon cooling, the resulting mixture was poured into 200 mL distilled water. The product was filtered off and further washed alternatively with glacial acetic acid, ethanol, and water. Pure compound 6 was obtained in platelike white crystals with a very strong blue light fluorescence.

Yield: 70%; mp: 224–226 °C. $^1\text{H-NMR}$ (DMSO): δ (ppm) 3.80 (s, 6H), 6.50–7.00 (m, 4H), 7.15–7.50 (m, aromatic-8H). MALDI-TOF-MS: Found: 266.85; calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: 266.33.

Preparation of 4,4'-(1,3-butadiene-1,4-diyl)bisphe- nol 7 (Scheme 2)

The procedure to prepare bisphenol 7 was similar to that in the literature.¹¹ To a 100-mL three-neck round-

bottom flask with a mechanical stirrer, a condenser, and a nitrogen inlet was added 1,3-butadiene 6 (2.4 g, 9 mmol), KOH (14.0 g), and 40 mL triethylene glycol. The reaction mixture was heated to 200°C with stirring to dissolve the reactants and then reacted 12 h at this temperature to afford a yellow product. The resulting mixture was carefully poured into 200 mL water. The aqueous solution was neutralized with 6N HCl and then extracted with ethyl acetate. The organic layer was concentrated using a rotary vapor to give a crude product of 7. The crude product was dissolved in a dilute solution of sodium hydroxide and then filtered to remove undissolved impurities. Upon acidification of the filtrate to pH 6 with 6N HCl, white precipitates were formed and followed by extracting with ethyl acetate. After solvent removal and recrystallization from a methanol/toluene mixture, we obtained a slightly off-white, fluorescent crystalline powder that became pink upon exposure to ultraviolet light.

Yield: 46%; mp: 304–305°C. $^1\text{H-NMR}$ (DMSO): δ (ppm) 7.28 (d, 4H), 6.72 (d, 4H), 6.79 (d, 2H), 6.52 (d, 2H), 9.52 (s, 1H). MALDI-TOF-MS: found: 238.68; calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2$: 238.28.

General procedure for the synthesis of polymers 8

The preparation of polymers 8 is shown in Scheme 3 (Scheme 3) and the details are given as follows for a typical copolymer with 70 mol % BPA: To a 25-mL three-neck round-bottom flask equipped with a nitrogen inlet, a magnetic stirrer, a Dean-stark trap, and a condenser were charged BPA (0.1598 g, 0.7 mmol) and

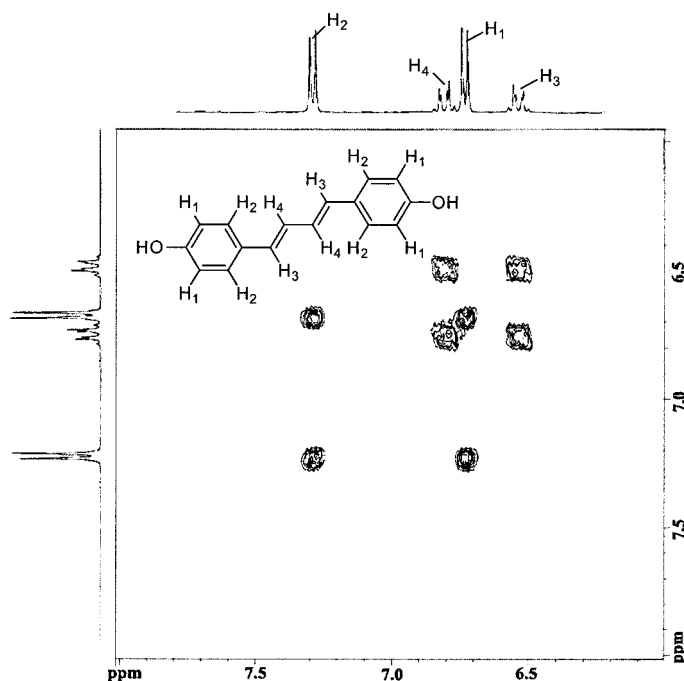
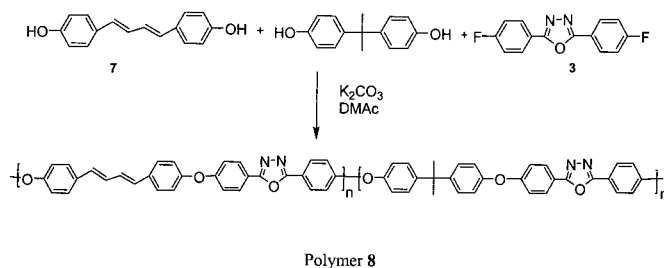


Figure 1 H–H cosy spectrum of 4,4'-(1,3-butadiene-1,4-diyl)bisphe- nol 7.



Scheme 3 Synthesis of polymers 8.

biphenol 7 (0.0715 g, 0.3 mmol). Then, 5 mL of DMAc, 5 mL of toluene, and potassium carbonate (0.1935 g, 1.4 mmol) were introduced to the reaction flask. The reaction mixture was heated to 150°C and maintained at this temperature for 2–3 h to azeotrope off the resulting water with toluene under a nitrogen atmosphere. The remaining toluene was then completely removed at this temperature. Upon cooling, 0.2583 g (1 mmol) of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole 3 was added. The mixture was heated again to 165°C and refluxed until the mixture became very viscous. After cooling, the viscous solution was diluted with 3 mL DMAc and poured into 200 mL of methanol. To purify the polymers 3, the collected precipitates were continuously washed with distilled water and extracted with chloroform by a Soxhlet extractor. The resulting solution was concentrated, followed by precipitating in methanol to afford the final product. The purified polymer in a white fluffy fibril was dried at 100°C under a vacuum for 24 h.

RESULTS AND DISCUSSION

Synthesis of 1,4-bis(4-methoxyphenyl)-1,3-butadiene 6

As shown in Scheme 2, 1,4-bis(4-methoxyphenyl)-1,3-butadiene 6 was synthesized by employing a Schiff base reaction of *trans*-anethole 4 and Schiff base 5 in a strong base solution of a Na/DMF mixture. Compound 5 was synthesized from anisaldehyde and an-

iline in the lab. This is a very clean reaction with high yield. Because of the prolonged refluxing time at high temperature, the reaction system should be carefully protected in a nitrogen atmosphere to avoid the oxidation of the resulting conjugated double–double bond. This became particularly important for the products that require electronic-grade purity. After collecting the synthesized compound 6 via filtration and washing, the crude 6 was recrystallized three times to ensure electronic-grade purity.

Cleavage of methyl ethers

The methyl group is a very stable protecting group, and, therefore, it is difficult to remove before its use. Numerous methods have been adopted to deprotect the methoxyl group, and typical reagents used include trimethylsilyl iodide (TMSI) in CH₂Cl₂,¹⁴ BBr₃ in CH₂Cl₂,¹⁵ and EtSNa in DMF.¹⁶ However, LiI in collidine¹⁷ appears to be a far superior reagent compared to the previous ones. Nevertheless, this reaction generally takes a long period of several days to complete the cleavage of all the O—Me bonds. In this work, we performed the cleavage using potassium hydroxide, which can dissolve in triethylene glycol. The reaction was conducted at 200°C for 12 h. To prevent the product from being oxidized, the demethylation reaction is run under ultrahigh purity nitrogen and shielded from light using aluminum foil. Upon deprotection, bisphenol 7 is quite unstable and can be easily

TABLE I
Properties of Polymers 8

Polymers 8	Yield (%)	η_{inh}^a (dL/g)	T_g (°C)	TGA ^b $T_{-5\%}$ (°C)	TGA ^c T_{max} (°C)
Polymer 8(0)	96.5	0.99	182.29	486.0	538.8
Polymer 8(10)	86.2	1.21	187.59	451.1	514.8
Polymer 8(20)	71.4	0.87	190.89	447.1	511.4
Polymer 8(30)	61.6	0.54	191.20	277.9	511.7
Polymer 8(40)	18.8	0.53	192.30	274.1	511.0
Polymer 8(50)	10	^d	194.50	268.9	511.2

^a Inherent viscosities measured in NMP (0.5 g/dL) at 30 ± 1°C using an Ubbelohde viscometer.

^b Five percent weight-loss temperature under a nitrogen flow of 150 mL/min.

^c Maximum weight-loss temperature under a nitrogen flow of 150 mL/min.

^d Inherent viscosities not obtained because its low solubility in NMP at 30°C.

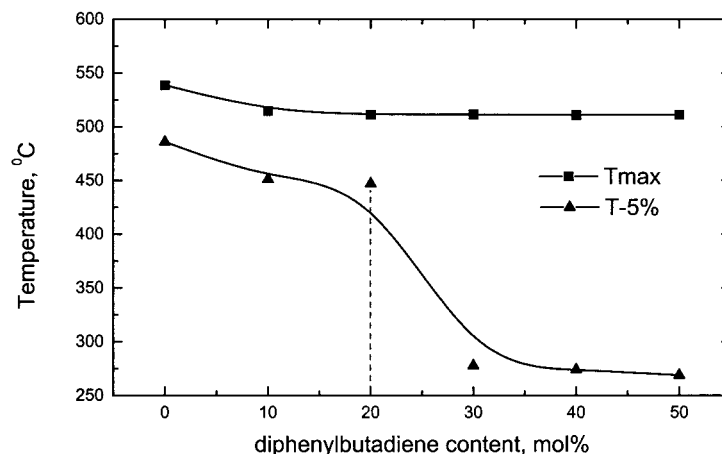


Figure 2 Five percent weight-loss temperature of the polymers versus a varying diphenylbutadiene content.

oxidized due to the presence of butadiene moieties. In general, the appearance of the resulting **7** changes progressively from light yellow to greenish gray in a short period, even though it was protected from light. In this sense, fresh or newly synthesized bisphenol **7** is generally used for the following syntheses of polymers. An H—H cosy NMR spectrum of fresh bisphenol **7** is given in Figure 1 that clearly indicates the molecular structure.

An alternate approach to stabilize bisphenol **7** is to react isocyanates with **7** to give *N*-carbamates that can be easily purified via recrystallization. This reaction is a simple addition reaction without any by-product formation with a high yield.¹⁸ The resulting phenolic urethanes (*N*-carbamate) can decompose at temperatures as low as 150°C. Purer polymers can be obtained via this method.

Synthesis of polymers **8**

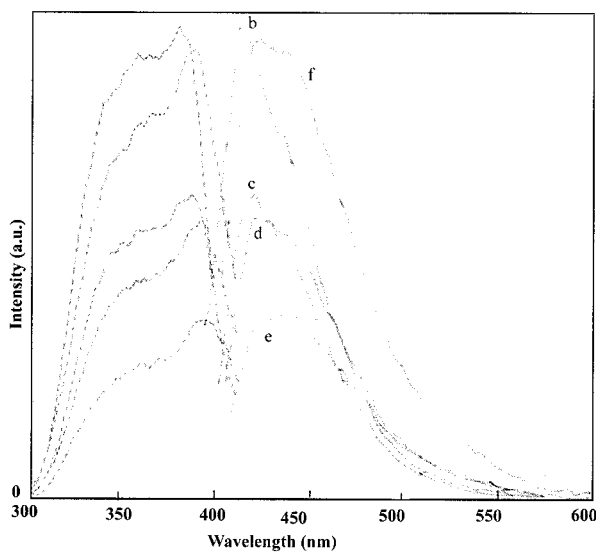
The synthesis of polymers **8** is depicted in Scheme 3. The polymers with various compositions are denoted as polymer **8**(xx%). The xx% indicates the content of bisphenol **7** within the polymers. 1,3,4-Oxadiazole derivatives, which are commonly used as an electron-transporting layer in an OLED, contain electro-with-

drawing groups so that they can activate the nucleophilic displacement reaction. The polycondensation of bisphenol **7**, BPA with 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole, was carried out using the standard polymerization methods for the synthesis of poly(arylene ether)s. The reaction was conducted at a temperature below 175°C to avoid the decomposition of BPA in the presence of the base medium. The reaction periods increased from 4 to 12 h with an increasing molar bisphenol **7** content since the solubilities of the corresponding polymers produced in DMAc tended to decrease with increase of the biphenol **7** content. When the biphenol **7** molar content was greater than 40%, the produced polymers precipitated out directly from the polymerization solution because of their poor solubility. In this respect, we cannot afford a polymer with a biphenol **7** molar content higher than 60% owing to its insolubility in DMAc. From Table I, it can be seen that the synthesized polymers exhibit high inherent viscosities (IVs). The molecular weight and yield increase with an increasing BPA content. Polymer **8** with a molar diphenylbutadiene content greater than 40% was obtained in a very low yield due to the introduction of the rigid diphenylbutadiene moiety in the backbone. The purified polymers are soluble in

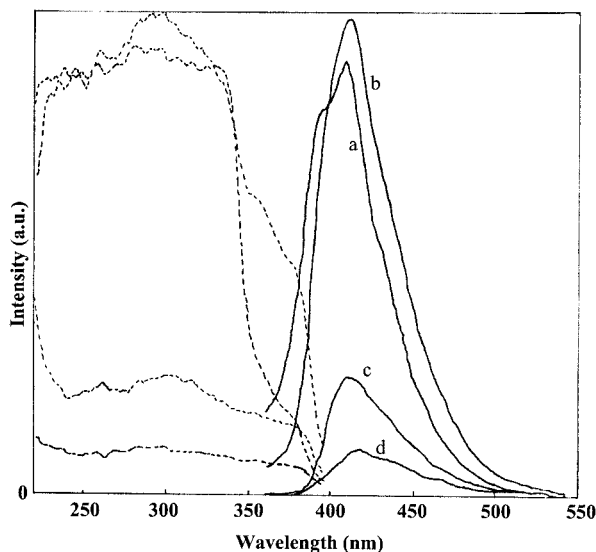
TABLE II
Maximum Absorption and Photoluminescent Wavelengths of the Polymers **8**

Polymers 8	Absorption peak in CHCl ₃ (nm)	PL emission peak in CHCl ₃ (nm)	Absorption peak in film (nm)	PL emission peak in film (nm)	Stokes shift ^a
Polymer 8 (0)	368	409	375	410	35
Polymer 8 (10)	371	411	379	413	34
Polymer 8 (20)	376	417	385	419	34
Polymer 8 (30)	380	417	390	419	29
Polymer 8 (40)	379	427	390	433	42
Polymer 8 (50)	381	427	391	433	44

^a Stokes shift (in nm) = PL (film) – absorption (film).



(a)



(b)

Figure 3 (—) Photoluminescence and (---) UV absorption spectra of polymers **8** (a) in solid powder and (b) in thin film at room temperature. DPB content for polymers **8**: (a) 0%; (b) 10%; (c) 20%; (d) 30%; (e) 40%; (f) 50%.

common solvents such as NMP, DMAc, and hot CHCl_3 .

Thermal property of polymers **8**

The thermal property plays an important role for the stability of polymers used for the OLED applications. As can be seen in Table I, polymers **8** exhibit high T_g 's ranging from 182 to 195°C due to the incorporation of

the diphenylbutadiene moiety. Furthermore, the thermogravimetric data in the same table also reveals that the synthesized polymers **8** are thermooxidatively stable, and all maximum weight loss temperatures are higher than 510°C. As depicted in Figure 2, the 5% weight-loss temperature decreases dramatically in the case where the molar diphenylbutadiene content is higher than 20%, while the maximum weight-loss temperature decreases slightly with an increasing molar diphenylbutadiene content. This presumably resulted from the thermal instability of butadiene moieties that can generate free radicals and undergo a free-radical reaction at temperatures higher than 180°C. The weight loss may have resulted from the cleavage of butadiene moieties. Despite this, these polymers possess good thermal properties and show promising high thermal stability during their service in OLEDs.

Absorption and photoluminescent properties of polymers **8**

From the structural point of view, the backbone of the polymers synthesized here shows a well-conjugated structure because the butadiene groups are linked to the *para*-position of the phenylene rings. The absorption and fluorescence spectra of these polymers with varying butadiene content in solid thin film are shown in Figure 2. As expected, it can be seen from Table II that the absorption and photoemitting wavelengths of the polymers depend on the content of the butadiene moiety in the polymers. Both the absorption wavelengths and photoemitting wavelengths gradually shift the peak wavelengths to longer wavelengths with an increasing butadiene moiety content. This tendency to increase diminishes when the butadiene content reaches 40%. Moreover, all the synthesized polymers exhibit a photoemitting light in a blue color. In addition to the peak wavelengths, other critical PL parameters of the synthesized polymers are also listed in the same table. The absorption and photoemitting wavelengths of the polymers in chloroform show maximum peaks ranging from 368 to 381 nm, and the photoluminescent spectra show maximum peaks ranging from 409 to 427 nm. The diphenylbutadiene emission chromophore emits blue light, as expected. In comparing the absorption spectra of these polymers in solution, a small red shift of 6–11 nm in the peak wavelength is observed for the thin films (Table II). Such small shifts in the spectra suggest that there is no major change in the molecular configuration of these polymers when they are dissolved in solution or in thin film. Moreover, the polymers possess good film-forming properties that have resulted from the BPA moieties in the backbone. The copolymerization makes the polymer chain more flexible, thereby reducing the crystallization and improving the thermal sta-

bility. The absorption and fluorescence spectra of the synthesized polymers in solid powders and in thick solid films (100 nm) on the quartz substrates are shown in Figure 3(a,b), respectively. It is noted that the same emitting spectrum can be obtained in spite of the different emitting wavelengths adopted for these polymers.

CONCLUSIONS

A new diphenylbutadiene-containing bisphenol can be synthesized from benzylideneaniline and 4-propenylanisole via an anil synthetic method. High molecular weight copoly(arylene ether)s consisting of an alternate isolated blue chromophore and an electron-transporting structure were synthesized from oxadiazole-activated bis-fluorocompounds and bisphenols. The resulting copolymers can be cast into tough and transparent films. The copolymers are amorphous in structure with high glass transition temperatures ranging from 182.29 to 194.50°C. They also exhibit good thermal stability with the maximum decomposition temperatures greater than 510°C in nitrogen. The maximum absorption peak of these copolymers in thin films ranges from 375 to 391 nm, while the corresponding photoluminescent peaks vary from 410 to 433 nm. The emissive chromophore emits blue light, as expected. These copolymers show promise for use as materials for LEDs.

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