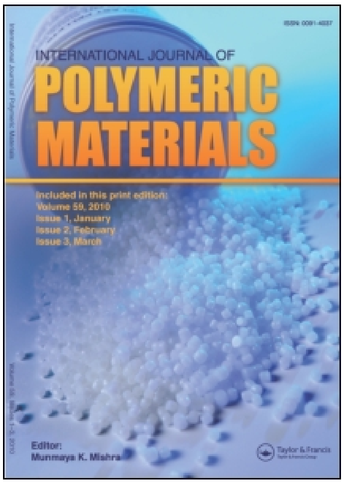
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Synthesis and Characterization of the Luminescent Poly[2-decyloxy-5-(2',5'-bis(decyloxy)phenyl)-1,4-phenylenevinylene]

Hung-Te Chang[a][b]; Hsun-Tsing Lee[c]; En-Chiuan Chang[a]; Mou-Yung Yeh[a]
[a] Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, R.O.C. [b] Department of Chemical Engineering, Wufeng Institute of Technology, Chia Yi, Taiwan, R.O.C. [c] Department of Chemical and Materials Engineering, Vanung University, Chung Li, Taiwan, R.O.C.

To cite this Article Chang, Hung-Te , Lee, Hsun-Tsing , Chang, En-Chiuan and Yeh, Mou-Yung(2007) 'Synthesis and Characterization of the Luminescent Poly[2-decyloxy-5-(2',5'-bis(decyloxy)phenyl)-1,4-phenylenevinylene]', International Journal of Polymeric Materials, 56: 5, 483 — 498

To link to this Article: DOI: 10.1080/00914030600945655

URL: http://dx.doi.org/10.1080/00914030600945655

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

International Journal of Polymeric Materials, 56:483–498, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600945655

Synthesis and Characterization of the Luminescent Poly[2-decyloxy-5-(2′,5′-bis(decyloxy)phenyl)-1,4-phenylenevinylene]

Hung-Te Chang
Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, R.O.C. and Department of Chemical Engineering, Wufeng Institute of Technology, Chia Yi, Taiwan, R.O.C.

Hsun-Tsing Lee
Department of Chemical and Materials Engineering, Vanung University, Chung Li, Taiwan, R.O.C.

En-Chiuan Chang
Mou-Yung Yeh
Department of Chemistry, National Cheng Kung University, Tainan, Taiwan, R.O.C.

Downloaded At: 17:20 30 January 2011

A new soluble luminescent poly[2-decyloxy-5-(2′,5′-bis(decyloxy)phenyl)-1,4-phenylenevinylene] (DBDP-PPV) is prepared by the dehydrohalogenation of 1,4-bis (bromomethyl)-2-decyloxy-5-(2′,5′-bis(decyloxy)phenyl) benzene (as monomer) in this study. The above monomer bearing decyloxy and 2′,5′-bis(decyloxy)phenyl substituents was prepared via such chemical reactions as alkylation, bromination, and Suzuki coupling reactions. The two asymmetric substituents on the phenylene ring make the DBDP-PPV soluble in organic solvents and eliminate the tolan-bis-benzyl (TBB) structure defects. The structure and properties of the DBDP-PPV are examined by ^{1}H-NMR, FT-IR, UV/Vis, TGA, photoluminescence (PL), and electroluminescence (EL) analyses. The DBDP-PPV film exhibits a PL peak at 519 nm. With the DBDP-PPV acting as a light-emitting polymer, a device is fabricated with a sequential lamination of ITO/PEDOT/DBDP-PPV/Ca/Ag. The EL spectrum of the device shows a maximum emission at 507 nm. The turn on voltage of the device is about 15.6 V. Its maximum brightness is 4.67 cd/m^2 at a voltage of 16.8 V.

Keywords: dehydrohalogenation, derivatives, electroluminescence, photoluminescence, poly(phenylenevinylene)

Received 24 July 2006; in final form 7 August 2006.

Address correspondence to Mou-Yung Yeh, Department of Chemistry, National Cheng Kung University, Tainan 70101, Taiwan, R.O.C. E-mail: htchung@mail.wfc.edu.tw

INTRODUCTION

Poly(*p*-phenylenevinylene) (PPV) was discovered as a light-emitting material for light-emitting diodes (LEDs) in 1990 [1]. Since then, there have been a lot of studies on the development of appropriate conjugated polymers for LEDs [2–9]. Of all conjugated polymers, PPV and its derivatives are still the most popular for the fabrication of LEDs today. This is because of their high luminescence efficiency in the LED application. PPV exhibits poor solubility in common organic solvents and limited processibility.

This is mainly due to the rigid main chain of repetitive phenylenevinylene units. There are two approaches to solve these difficulties. The first involves preparing a soluble precursor polymer and then casting it to obtain a film. For this approach, there are two generally used routs, that is the Wessling [10–11] and chlorine precursor routes (CPR) [12–13]. The second is through the incorporation of side chains to a polymer backbone. The incorporation of side chains is achieved by preparing a soluble polymer from a monomer having multiple substituents. For this second approach, the Gilch procedure [14] is the most frequently used polymerization method. The synthesis of poly(2-methoxy-5-dodecyloxy-1,4-phenylenevinylene) by the dehydrohalogenation of 1,4-bis (chloromethyl)-2-methoxy-5-dodecyloxy-benzene [15] is one example for the Gilch procedure. The Gilch procedure normally leads to PPV derivatives with high molecular weight and a good film-forming property.

Downloaded At: 17:20 30 January 2011

Recently, Becker et al. [16–17] discovered the presence of structure defects located in polymer main chains of the PPV derivatives prepared by the Gilch procedure. The structure defects are named tolan-bis-benzyl (TBB) defects. The increase in TBB content decreases the lifetime of the resultant LED device significantly [17]. However, Becker et al. [18] also found that the introduction of an alkoxy group with a strong electron-donating property decreases the TBB content in the polymer main chains of the PPV derivatives. This is due to the fact that the halomethyl group in the ortho position of the alkoxy group is more acidic than the other halomethyl group in the meta position. The difference in acidity or reactivity of these two halomethyl groups makes the polymerization reaction of the monomers proceed in a regular head-to-tail way [19].

In this article, the synthesis and characterization of poly[2-decyloxy-5-(2′,5′-bis-(decyloxy)phenyl)-1,4-phenylenevinylene] (DBDP-PPV) are reported. A decyloxy group and a 2′,5′-bis(decyloxy)phenyl group are respectively incorporated in the 2-position and 5-position of a phenylene ring. The incorporation of these two groups is expected to make the DBDP-PPV soluble in organic solvents and to suppress the presence of TBB defects in the polymer main chains. The electro-optical and thermal properties of the DBDP-PPV are also examined in this work.

EXPERIMENTAL

Materials

Benzoyl peroxide, 2,5-dimethylphenol, 1-bromodecane, N-bromosuccinimide (NBS), bromine, potassium hydroxide, potassium carbonate, tetrabutylammonium bromide (TBAB), anhydrous magnesium sulfate, sulfuric acid, carbon tetrachloride and acetic acid were purchased from Fluka Chemical (Ronkonkoma, NY). The n-butyl lithium (n-BuLi, 2.5 M in hexane) was purchased from Chemetall (Chang Bin Industrial park Hsien-si, Chang-Hua County, Taiwan, R.O.C.). Trimethyl borate, potassium tert-butoxide (t-BuOK), and iron (III) bromide were purchased from Sigma-Aldrich (Steinheim, Germany). Tetrakis(triphenylphosphine)palladium(0) and bromohydroquinone were purchased from ACROS (Geel, Belgium). All the aforementes reagents were synthetic grade and used as received. Tetrahydrofuran and 1,4-dioxane were synthetic grade and purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). They were dried over sodium and distilled prior to use.

Downloaded At: 17:20 30 January 2011

Instruments

Melting points of compounds at different synthesis stages were determined on a Buchi B-540 apparatus. The ^{1}H and ^{13}C-NMR spectra of the specimen solutions in $CDCl_3$ were measured by a Bruker Avance 300 spectrometer (300 MHz). FT-IR spectra were recorded by a Perkin Elmer Model Spectrum One spectrometer. The UV/Vis spectra of the samples in $CHCl_3$ were measured by a Shimadzu Model UV-160 spectrophotometer. The mass spectra were measured by a Bruker APEX II spectrometer. Elemental analyses were taken with a Heraeus CHN-O-Rapid Analyzer. The fluorescence spectra were recorded by a Hitachi F-4500 fluorescence spectrometer. The thickness of DBDP-PPV ultrathin film was measured by a Kosaka Laboratory ET-4000M photometer. The weight and number average molecular weights of DBDP-PPV were measured by a gel permeation chromatography (GPC) using an Analytical Scientific Instrument Model 500 system. Polystyrene standards were used for molecular weight calibration and tetrahydrofuran was used as carrier solvent. Thermal gravimetric analyses were performed on a Perkin Elmer Model TGA-7 thermogravimetric analyzer under a nitrogen stream and with a heating rate of 10°C/min.

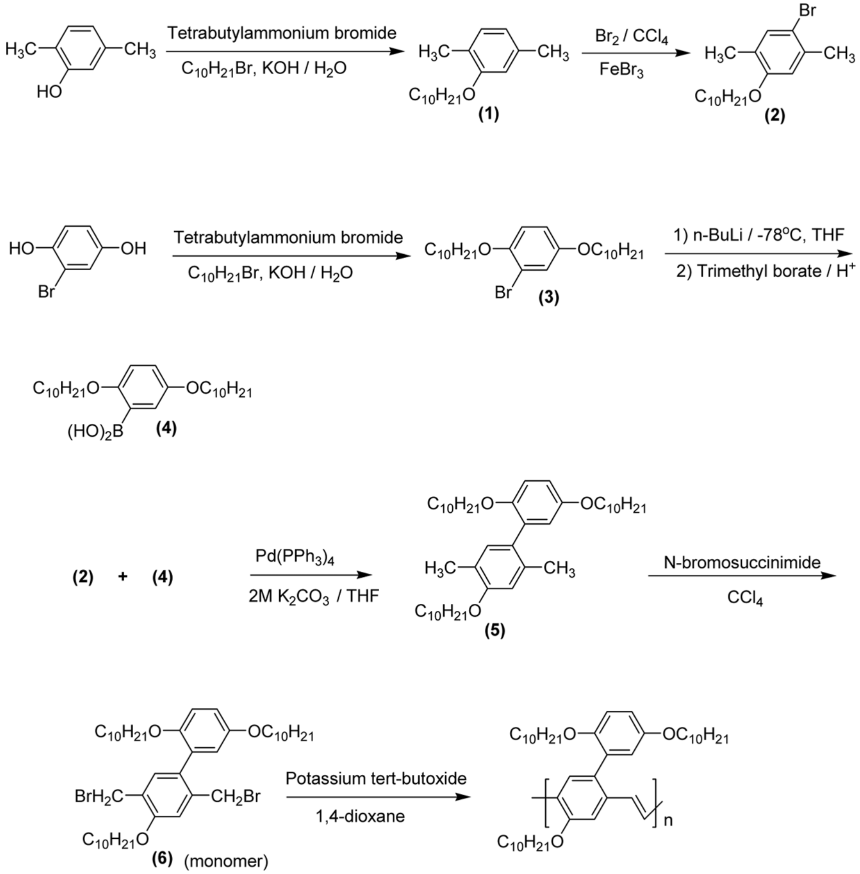
Synthesis Procedure

The synthesis route for the monomer and polymer is illustrated in Scheme 1. The monomer was prepared via such chemical reactions as alkylation, bromination, and Suzuki coupling reactions from the starting materials 2,5-dimethylphenol and bromohydroquinone. The DBDP-PPV was obtained by a method that is similar to the Gilch procedure.

Synthesis of 2-decyloxy-1,4-dimethylbenzene (1)

Compound (1) was prepared by the alkylation of 2,5-dimethylphenol with 1-bromodecane. A solution of 2,5-dimethylphenol (12.2 g, 100 mmol), potassium hydroxide (8.4 g, 150 mmol), and tetrabutylammonium

Downloaded At: 17:20 30 January 2011



SCHEME 1 Synthesis route for the monomer and polymer.

bromide (3.4 g, 105 mmol) in 50 ml H_2O was stirred at room temperature for 15 min. Then 1-bromodecane (22.1 g, 100 mmol) was added to the solution mixture. The reaction proceeded with stirring and heating for 22 h at reflux. After the reaction was completed, the reaction mixture was extracted with 30 ml diethyl ether. The organic diethyl ether layer was washed with aqueous sodium hydroxide solution (10%, 2 × 50 ml) and 100 ml H_2O successively. The resultant organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give the 2-decyloxy-1,4-dimethylbenzene **(1)** as pale brown oil (24.62 g) in 93% yield. ^1H NMR ($CDCl_3$): δ7.01 (d, J = 7.36 Hz, 1H, aromatic C−H), 6.69 (d, J = 7.72 Hz, 1H, aromatic C−H), 6.65 (s, 1H, aromatic C−H), 3.95 (t, J = 6.44 Hz, 2H, $-OCH_2$), 2.33 (s, 3H, aromatic CH_3), 2.20 (s, 3H, aromatic CH_3), 1.84–1.30 (m, 16H, aliphatic C−H), 0.91 (t, J = 6.52 Hz, 3H, aliphatic CH_3). FTIR (KBr pellet, cm^{-1}): 3072, 2924, 2856, 1615, 1586, 1509, 1463, 1415, 1378, 1265, 1158, 1131, 1040, 842, 802. FABMS$^+$: m/z; 262 (M + 1, 74), 121 (47), 105 (27).

Downloaded At: 17:20 30 January 2011

Synthesis of 1-bromo-4-decyloxy-2,5-dimethylbenzene (2)

Compound (2) was prepared by the bromination of 2-decyloxy-1,4-dimethylbenzene (1) with bromine. A solution of compound (1) (13.1 g, 50 mmol) and iron (III) bromide (1 g, 3 mmol) in 35 ml CCl_4 was stirred in an iced bath. Bromine (8 g, 50 mmol) was slowly added to the mixture solution through a condenser and stirred for 24 h. After the completion of reaction, the reaction mixture was washed with aqueous sodium hydroxide solution (10%, 2 × 50 ml) and 100 ml H_2O successively. Then the organic phase was dried over anhydrous magnesium sulfate and filtered. The solvent was distilled off under reduced pressure to give a pale yellow crude product. The crude product was washed with methyl alcohol, filtered, and dried under dynamic vacuum to give 1-bromo-4-decyloxy-2,5-dimethylbenzene (2) as a colorless solid (13.58 g) in 79% yield. Melting point: 52–53°C, ^1H NMR ($CDCl_3$): δ7.23 (s, 1H, aromatic C−H), 6.65 (s, 1H, aromatic C−H), 3.90 (t, J = 4.24 Hz, 2H, $-OCH_2$), 2.32 (s, 3H, aromatic CH_3), 2.13 (s, 3H, aromatic CH_3), 1.79–1.26 (m, 16H, aliphatic C−H), 0.86 (t, J = 6.6 Hz, 3H, aliphatic CH_3). FTIR (KBr pellet, cm^{-1}): 3072, 2924, 2847, 1631, 1606, 1567, 1496, 1462, 1383, 1363, 1163, 1034, 879, 835. FABMS$^+$: m/z; 341 (M + 1, 32), 200 (100), 184 (5), 154 (37). Elem. Anal. Calcd. for $C_{18}H_{29}BrO$: C, 63.34%; H, 8.56%. Found: C, 63.36%; H, 8.56%.

Synthesis of 2-bromo-1,4-bis(decyloxy)benzene (3)

Compound (3) was prepared by the alkylation of bromohydroquinone with 1-bromodecane. A solution of bromohydroquinone (7.56 g, 40 mmol), potassium hydroxide (5.64 g, 100 mmol), and tetrabutylammonium bromide (7.56 g, 23.4 mmol) in 35 ml H_2O was stirred at room temperature for 15 min. Then 1-bromodecane (22.1 g, 100 mmol) was added to the solution mixture. The reaction proceeded with stirring and heating for 24 h at reflux. After the reaction was completed, the reaction mixture was extracted with 30 ml diethyl ether. The organic diethyl ether layer was washed with aqueous sodium hydroxide solution (10%, 2 × 50 ml) and 100 ml H_2O successively. The resultant organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent of the organic phase was distilled off under reduced pressure with a rotary evaporator. Finally, the crude product was precipitated in methyl alcohol. After the precipitate was filtered and dried under dynamic vacuum, 2-bromo-1,4-bis(decyloxy)benzene (3) was obtained as a brown solid (15.23 g) in 81% yield. Melting point: 37.8–38.5°C, ^{1}H-NMR ($CDCl_3$): δ7.08 (s, 1H, aromatic C–H), 6.78 (d, J = 8.92 Hz, 1H, aromatic C–H), 6.76 (d, J = 6.16 Hz, 1H, aromatic C–H), 3.92 (t, J = 6.56 Hz, 2H, $-OCH_2$), 3.85 (t, J = 6.52 Hz, 2H, $-OCH_2$), 1.79–1.25 (m, 32H, aliphatic C–H), 0.86 (t, J = 6.40 Hz, 6H, aliphatic CH_3). FTIR (KBr pellet, cm^{-1}): 3012, 2924, 2854, 1600, 1574, 1494, 1469, 1272, 1208, 1044, 861. FABMS$^+$: m/z; 470 (M + 1, 44), 390 (22), 188 (100).

Downloaded At: 17:20 30 January 2011

Synthesis of 2,5-bis(decyloxy)phenyl Boronic Acid (4)

Compound (4) was prepared by the reaction of 2-bromo-1,4-bis(decyloxy)benzene (3) with trimethyl borate. 18 ml (45 mmol) n-BuLi (2.5 M in hexane) was added dropwise to a solution of 12.9 g (27.5 mmol) compound (3) in 60 ml of dry THF at −78°C. The mixture was stirred at −78°C, then warmed up to 0°C and cooled back to −78°C. To this mixture, 9.3 g (89 mmol) trimethyl borate were added in one shot and the resulting solution was warmed up to room temperature and stirred for 60 h further. The solution was then poured into a mixture of 600 g crushed ice and 600 g sulfuric acid (10%) under stirring. The resultant precipitate was filtered and washed, successively, with water and n-hexane several times. Finally, the 2,5-bis(decyloxy)phenyl boronic acid (4) was obtained as white solids (9 g) in 75% yield. Melting point: 86.1–87°C, ^{1}H-NMR (DMSO-d6): δ7.11 (s, 1H, aromatic C–H), 6.89 (s, 2H, aromatic C–H), 3.95 (t, J = 6.06 Hz, 2H, $-OCH_2$), 3.86 (t, J = 6.16 Hz, 2H, $-OCH_2$), 1.69–1.23 (m, 32H, aliphatic C–H), 0.84 (t, J = 4.78 Hz, 6H, aliphatic CH_3). FTIR (KBr pellet, cm^{-1}): 3499, 3364, 2941, 2919, 2850, 1585, 1495, 1470, 1420, 1331, 1221, 1146, 1048, 811.

Downloaded At: 17:20 30 January 2011

Synthesis of 2-decyloxy-5-(2′,5′-bis(decyloxy)phenyl)-1,4-dimethylbenzene (5)

Compound (5) was prepared by the Suzuki coupling of 1-bromo-4-decyloxy-2,5-dimethylbenzene (2) with 2,5-bis(decyloxy)phenyl boronic acid (4). Suzuki coupling is the palladium-catalyzed cross coupling between organoboronic acids and halides. A mixture of compound (2) (4.09 g, 11.9 mmol), compound (4) (6.48 g, 14.9 mmol), 30 ml of 2M K_2CO_3 solution, 45 ml of THF, and Pd $(PPh_3)_4$(0.12 g) was stirred at room temperature under a nitrogen atmosphere for 10 min. After heating at reflux for 48 h, the reaction was terminated by adding 30 ml water. The resultant mixture was extracted with diethyl ether. The organic phase was dried with anhydrous magnesium sulfateand filtered through a filter paper. After the solvent of the organic phase was distilled off under reduced pressure in a rotary evaporator, yellowish viscose oil was obtained. The yield of the 2-decyloxy-5-(2′,5′-bis(decyloxy)phenyl)-1,4-dimethylbenzene (5) was 59% (4.6 g). ^{1}H-NMR ($CDCl_3$): δ6.94 (s, 1H, aromatic C−H), 6.86 (s, 1H, aromatic C−H), 6.81 (d, $J = 7.01$ Hz, 2H, aromatic C−H), 6.71 (s, 1H, aromatic C−H), 3.95 (m, 4H, $2 \times -OCH_2$), 3.78 (t, $J = 6.10$ Hz, 2H, $-OCH_2$), 2.21 (s, 3H, aromatic CH_3), 2.14 (s, 3H, aromatic CH_3), 1.83–1.19 (m, 48H, aliphatic C−H), 0.88–0.86 (m, 9H, aliphatic $3 \times CH_3$). FTIR (KBr pellet, cm^{-1}): 3025, 2922, 2854, 1613, 1513, 1469, 1384, 1243, 1113, 1031, 826. FABMS$^+$: m/z; 651 (M + 1, 30), 228 (32), 213(66), 165(48).

Synthesis of 1,4-bis(bromomethyl)-2-decyloxy-5-(2′,5′–bis(decyloxy)phenyl) benzene (6)

Compound (6) was prepared by the bromination of 2-decyloxy-5-(2′,5′-bis(decyloxy)phenyl)-1,4-dimethylbenzene (5) with N-bromosuccinimide. A solution of compound (5) (3.75 g, 5.7 mmol), benzoyl peroxide (0.15 g, 0.06 mmol) and N-bromosuccinimide (2.08 g, 11.68 mmol) in 200 ml CCl_4 was stirred at room temperature for 10 min. After heating at reflux for 36 h, the mixture was cooled to room temperature. The floating succinimide in the mixture was filtered away and the solvent was distilled off under reduced pressure in a rotary evaporator. After 30 ml ethyl alcohol was added to the residue, the desired product was precipitated. The precipitate was washed with ethyl alcohol, filtered and dried under dynamic vacuum to give 1,4-bis(bromomethyl)-2-decyloxy-5-(2′,5′-bis (decyloxy)phenyl)benzene (6) as a pale brown solid (2.54 g) in 54% yield. Melting point: 51.0–52.7°C, ^{1}H-NMR ($CDCl_3$): δ6.99 (s, 1H, aromatic C−H), 6.88 (s, 1H, aromatic C−H), 6.84 (d, $J = 6.93$ Hz, 2H, aromatic

C$-$H), 6.81 (s, 1H, aromatic C$-$H), 4.54 (d, J $=$ 5.39 Hz, 2H, $-CH_2Br$), 4.34 (d, J $=$ 9.34 Hz, 2H, $-CH_2Br$), 4.07 (t, J $=$ 6.21 Hz, 2H, $-OCH_2$), 3.93 (m, 4H, $2 \times -OCH_2$), 1.91–1.08 (m, 48H, aliphatic C$-$H), 0.89–0.85 (m, 9H, aliphatic $3 \times CH_3$). FTIR (KBr pellet, cm^{-1}): 3012, 2917, 2851, 1612, 1497, 1469, 1385, 1233, 1209, 1130, 1113, 1038, 862. $FABMS^+$: m/z; 809 (M $+$ 1,10), 649 (10), 226 (76), 198 (64).

Preparation of poly[2-decyloxy-5-(2′,5′-bis(decyloxy)phenyl)-1,4-phenylenevinylene] (DBDP-PPV)

A solution of compound (6) (0.40 g, 0.49 mmol) in 30 ml of dry 1,4-dioxane was stirred and heated at reflux under nitrogen atmosphere for 15 min. A fresh solution of potassium tert-butoxide (0.145 g, 2.6 equiv) in 1,4-dioxane (1.3 ml) was added drop by drop to the solution. The solution was then heated at 96°C for about 10 h and excess potassium tert-butoxide (0.112 g, 2.0 equiv) in 1,4-dioxane (1 ml) was syringed into the reaction mixture. After stirring for additional 12 h at 96°C, a viscose yellow/orange solution was obtained. This viscose solution was then cooled to 50°C and mixed with 0.19 ml solution of acetic acid in 1,4-dioxane where the equivalent of acetic acid was 1.5 times that of the base. After stirring for 20 min, the mixture was poured into 35 ml water with stirring and was further stirred for 10 min. Finally, the DBDP-PPV was precipitated from the mixture by adding 200 ml methyl alcohol. The DBDP-PPV was filtered, washed with some methyl alcohol, and dried under dynamic vacuum. The DBDP-PPV was obtained as an orange solid (0.28 g) in 88% yield. GPC (0.8 mg cm^{-3}, 22.6°C), weight-average molecular weight (Mw): 113,726 g/mole, number-average molecular weight (Mn): 17,208 g/mole, polydispersity (Mw/Mn) index: 6.6, and the degree of polymerization of DBDP-PPV: 26. ^1H-NMR ($CDCl_3$): δ7.0–6.6 (m, 10H, aromatic and vinyl C$-$H), 4.2–3.5 (m, 6H, $3 \times -OCH_2$), 1.9–0.7 (m, 57H, aliphatic C$-$H). FTIR (KBr pellet, cm^{-1}): 3034, 2924, 2856, 1599, 1472, 1389, 1217, 1033, 971, 854.

Fabrication of the LED Device

A glass substrate with a 170 nm thin film of indium-tin oxide (ITO) on one side was successively washed with water, acetone, and isopropyl alcohol under ultrasonic wave. The surface electrical resistance of the ITO film is 7 Ohm/cm^2. The poly(3,4-ethylenedioxythiophene) (PEDOT) doped by aqueous polystyrenesulfonate solution was spin-coated on the ITO film to act as a hole-injection layer with a thickness of 50 nm. A thin DBDP-PPV film (98 nm) was then spin-coated on the PEDOT layer with a spin rate of 400 rpm and duration of 15 s. Prior to the spin coating, the 1.14 wt% DBDP-PPV solution in *p*-xylene was

Downloaded At: 17:20 30 January 2011

filtered through a 0.45 μm pore size filter. For the fabrication of a cathode, a layer of calcium (10 nm) was deposited on the DBDP-PPV layer under a high vacuum of 5×10^{-6} torr. Finally, a protection layer of silver (100 nm) was deposited on calcium layer under vacuum. All measurements of the device characteristics were conducted in air at room temperature. The active area of the device is about 0.24 cm^2.

RESULTS AND DISCUSSION

Structure of the DBDP-PPV

The ^{1}H-NMR spectrum of the DBDP-PPV solution in $CDCl_3$ is shown in Figure 1. The peak of $CDCl_3$ is at 7.26 ppm. It shows that the two proton peaks of 1,4-bisbromomethyl groups of the monomer (compound (6)) at 4.54 and 4.34 ppm have disappeared and a new broad peak has appeared in the range of 7.0–6.6 ppm. The new bimodal peak results from the protons of aromatic rings and the conjugated vinylene double bonds. It also shows the oxymethylene and alkyl proton peaks in the range of 4.2–3.5 and 1.9–0.7 ppm, respectively.

The formation of TBB defects in PPV derivatives prepared by the Gilch procedure can be ascribed to a side reaction, that is the head to head (or tail to tail) coupling during the polymerization process [16]. The ^{1}H-NMR signals of $CH_2{-}CH_2$ groups resulting from the head to head coupling should appear at around 2.7–2.9 ppm [16]. However,

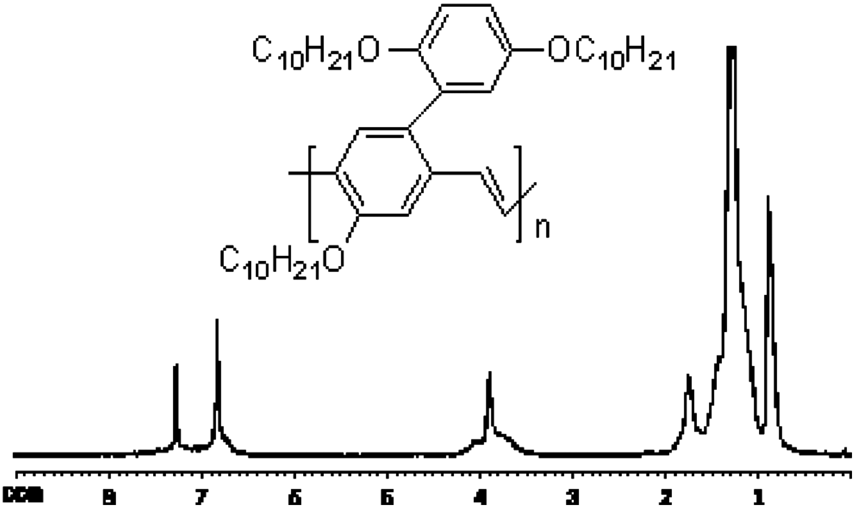


FIGURE 1 ^{1}H-NMR spectrum of the DBDP-PPV in $CDCl_3$.

Downloaded At: 17:20 30 January 2011

there are no such signals around 2.7–2.9 ppm in Figure 1. This indicates that the polymerization process for the DBDP-PPV in this study proceeded mainly in a regular head-to-tail way. There are two reasons for this regular head-to-tail coupling. One is the steric hindrance effect of 5-(2′,5′-bis(decyloxy)phenyl substituent on the phenylene ring of compound (6). The other reason is that the bromomethyl group in the ortho position relative to 2-decyloxy substituent on the phenylene ring of compound (6) is more acidic than the other bromomethyl group in the meta position. The difference in acidity or reactivity of these two bromomethyl groups can be attributed to the strong electron-donating property of the 2-decyloxy substituent of compound (6).

Figure 2 shows FT-IR spectrum of the DBDP-PPV. The absorption peak at 3034 cm^{-1} is due to the C–H stretching of aromatic ring. The peaks at 2924 and 2856 cm^{-1} are due to the C–H stretching of alkyl side chains and one at 1599 cm^{-1} is due to the aromatic ring stretching. The absorption peaks at 1472 and 1389 cm^{-1} are due to $-CH_2-$ segmental bending of the alkyl side chains and one at 1217 cm^{-1} is due to the C–H in plane bending of aromatic ring. The peak at 1033 cm^{-1} is due to the symmetric C–O–C bond stretching and one

Downloaded At: 17:20 30 January 2011

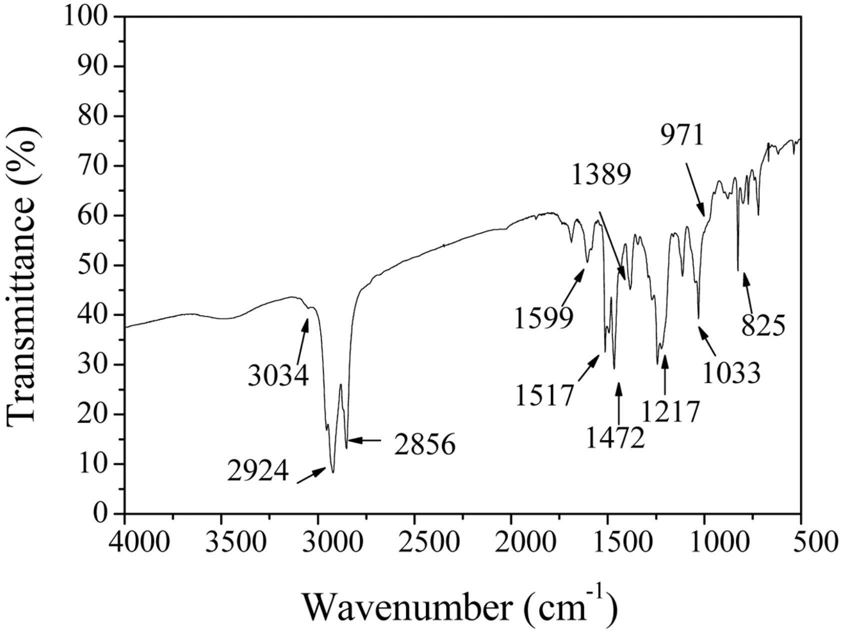


FIGURE 2 FT-IR spectrum of the DBDP-PPV film on KBr.

Downloaded At: 17:20 30 January 2011

at 971 cm^{-1} is due to the C−H out-of-plane bending of trans-vinylene unit. The peak at 824 cm^{-1} is due to the C−H out-of-plane bending of aromatic ring. The results of Figure 2 also confirm the formation of DBDP-PPV.

Optical Properties of the DBDP-PPV

Figure 3 shows UV/Vis spectra of the DBDP-PPV film (a) and solution in $CHCl_3$ (b). Both DBDP-PPV film and solution show two absorption peaks at 300 and 460 nm. For the assignment of these two peaks, the UV/Vis spectrum of the DBDP-PPV is compared with that of the poly(2,5-didecyloxy-*p*–phenylenevinylene) (decyloxy-PPV) film reported in literature [20]. The decyloxy-PPV and DBDP-PPV have a similar structure except that the former is without the 2′,5′-bis(decyloxy)phenyl substituent. The UV/Vis spectrum of the decyloxy-PPV exhibits only one absorption peak at 470 nm. This peak is due to the $\pi \rightarrow \pi^*$ transition of PPV conjugated segments. The absorption peak of decyloxy-PPV is in close vicinity to that of the DBDP-PPV at

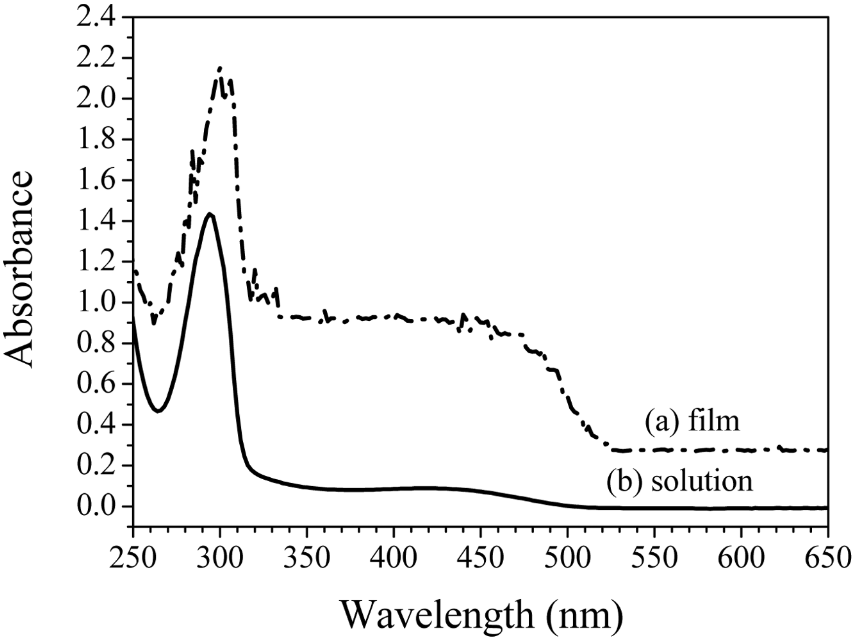


FIGURE 3 UV/Vis spectra of the DBDP-PPV film (a) and solution in $CHCl_3$ (b).

460 nm. This leads to the conclusion that the $\pi \rightarrow \pi^*$ transition of PPV conjugated segments causes the absorption peak of DBDP-PPV at 460 nm. Consequently, the other absorption peak of DBDP-PPV at 300 nm is due to the $\pi \rightarrow \pi^*$ transition of 2′,5′-bis(decyloxy)phenyl substituent.

The optical energy (E, in eV) is described by the following equations:

$$\mathrm{E} = \mathrm{h} \times \mathrm{c}/\lambda \tag{1}$$

$$1\,\mathrm{eV} = 1.602 \times 10^{-19}\ \mathrm{Joule}$$

where h is the Planck constant (6.63×10^{-34} Joule-s), c (3×10^8 m/s) is the light velocity, and λ is the wavelength of absorption threshold. Using the value of absorption threshold λ (520 nm, (Figure 3(a)), it is deduced that the energy band gap of DBDP-PPV film is 2.38 eV.

Figure 4 shows the photoluminescence (PL) spectra (excited wavelength, 390 nm) of the DBDP-PPV film and solutions. The PL emission peaks of DBDP-PPV in THF at the concentrations of 0.14 wt% and 0.28 wt% are 489 and 495 nm, respectively. On the other hand, the

Downloaded At: 17:20 30 January 2011

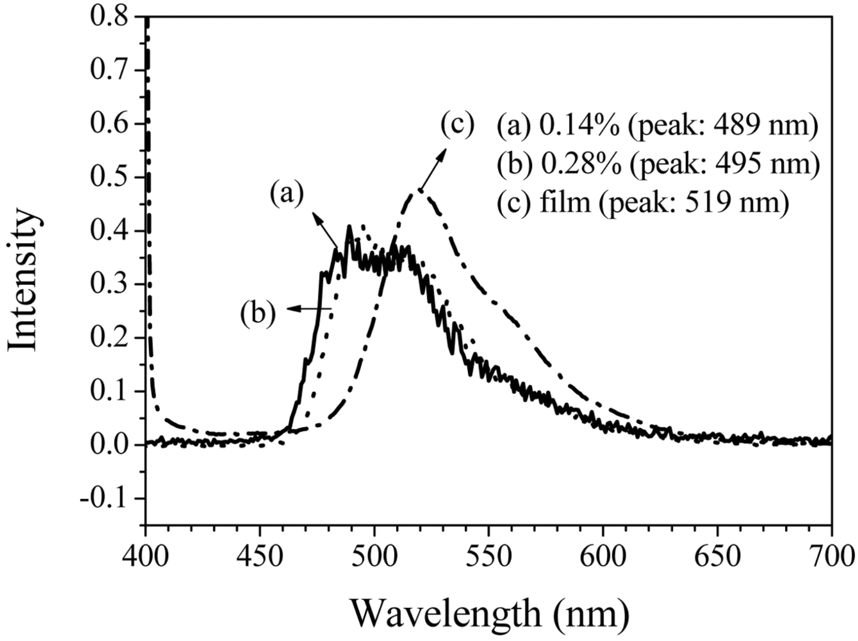


FIGURE 4 PL spectra of the DBDP-PPV solution in THF ((a) 0.14 wt%, (b) 0.28 wt%), and (c) DBDP-PPV film.

Downloaded At: 17:20 30 January 2011

emission peak of the DBDP-PPV film is at 519 nm. The wavelength of the emission peak increases as the concentration of the DBDP-PPV goes up. The PL emission has a red shift of about 30 nm from a dilute solution state (0.14 wt%) to a film state. The shift is probably due to the more aggregated conformation of the polymer main chains in a film state than in a solution state. The more aggregated conformation makes the energy band gap for the $\pi \rightarrow \pi^*$ transition of the conjugated segments smaller. Thus the energy transfer process takes place more easily in a film state than in a solution state [20].

Thermal Stability of the DBDP-PPV

Figure 5 shows the result of TGA measurement of the DBDP-PPV. There is no appreciable weight loss below 200°C. The weight loss begins to increase pronouncedly at 210°C, at which the decomposition of the alkoxy substituents starts to take place. The weight loss reaches 5% as the temperature increases to 254°C. The weight loss above 275°C is due to the decomposition of the rigid conjugated main chains

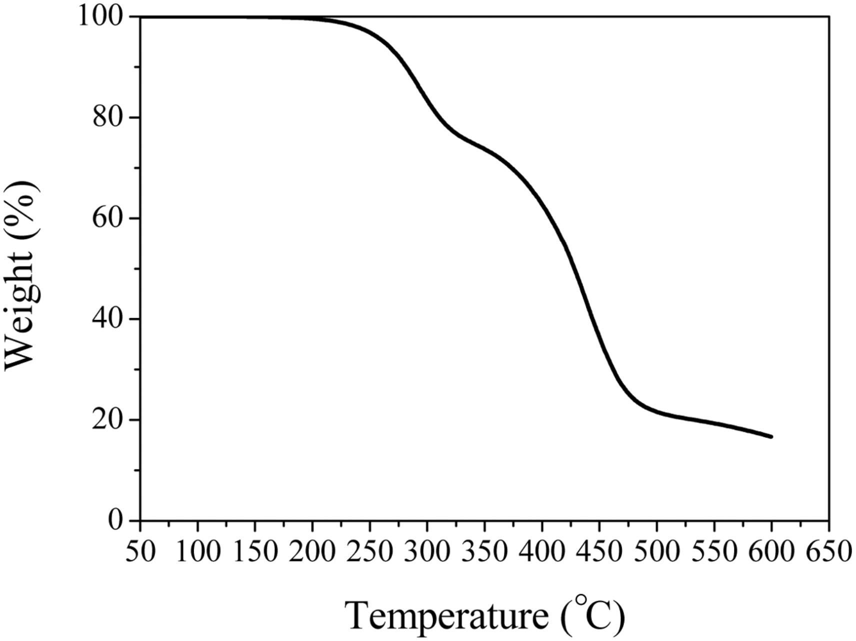


FIGURE 5 TGA thermogram of the DBDP-PPV under a nitrogen stream.

as is observed with polyaniline [21]. The high thermal resistance property of the DBDP-PPV is significant to its application in LED device.

Performance in LED Application

Figure 6 shows the PL and electroluminescence (EL) spectra of the DBDP-PPV film. The EL spectrum of the ITO/PEDOT/DBDP-PPV/Ca/Ag device shows a maximum emission band at around 507 nm, which corresponds to a bluish-green light. On the other hand, the PL spectrum of the DBDP-PPV film shows an emission maximum at 519 nm. Generally, PL and EL spectra of the polymer with conjugated segments are nearly the same. However, a small shift of about 12 nm has developed for PL and EL spectra of the DBDP-PPV in this study. A possible interpretation of the shift is that the vibronic peak intensity is transferred to lower energy in PL compared to EL [22].

Figure 7 shows the luminescence efficiency-voltage-brightness characteristics of the device. The turn-on voltage of the device is about 15.6 V. The maximum brightness and luminance efficiency of the device are 4.67 cd/m^2 and 0.0053 cd/A, respectively, both at a voltage

Downloaded At: 17:20 30 January 2011

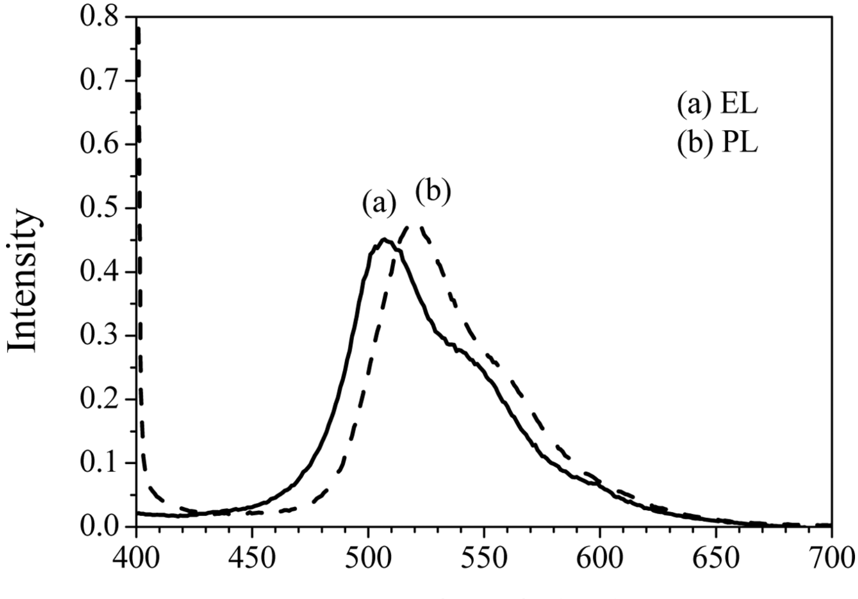


FIGURE 6 PL (a) and EL (b) spectra of the DBDP-PPV film.

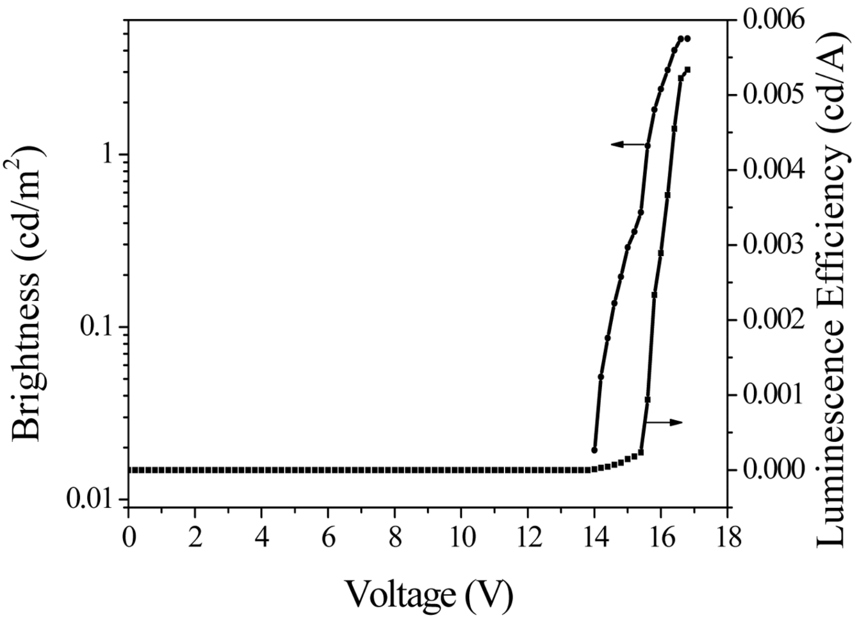


FIGURE 7 Luminescence efficiency-voltage-brightness curves of the ITO/PEDOT/DBDP-PPV/Ca/Ag device.

Downloaded At: 17:20 30 January 2011

of 16.8 V. The authors hope that a higher EL performance of the device could be obtained by optimizing the device structure in their future work.

CONCLUSIONS

This study shows that it is possible to prepare a new soluble luminescent DBDP-PPV without TBB defects by a method that is similar to the Gilch procedure. The monomer (compound (6)) was synthesized via such chemical reactions as alkylation, bromination, and Suzuki coupling reactions from the starting materials 2,5-dimethylphenol and bromohydroquinone. The incorporation of a decyloxy substituent in the 2-position of the phenylene ring makes the DBDP-PPV soluble in organic solvents and suppresses the occurrence of TBB defects during the polymerization process. The energy band gap of DBDP-PPV film is 2.38 eV. The PL emission of DBDP-PPV has a red shift of about 30 nm from a dilute solution state (0.14 wt%) to a film state. The shift is probably due to the more aggregated conformation of the polymer main chains in a solid state than in a solution state. With the

DBDP-PPV acting as a light emitting material, the EL spectrum of the device shows an emission peak at 507 nm. The maximum brightness of the device is 4.67 cd/m^2 at a voltage of 16.8 V.

REFERENCES

[1] Burroughes, J. H., Bradley, D. D. C., Brown, A. R., Marlks, R. N., Mackay, K., Friend, R. H., Burn, P. L., and Holmes, A. B., *Nature* **347**, 539 (1990).

[2] Yu, G., *Synth. Met.* **80**, 143 (1996).

[3] Andersson, M. R., Johansson, D. M., Theander, M., and Inganas, O., *Synth. Met.* **119**, 63 (2001).

[4] Carter, J. C., Grizzi, I., Heeks, S. K., Lacey, D. J., Latham, S. G., May, P. G., Delospaños, O. R., Pichler, K., Towns, C. R., and Wittmann, H. F., *Appl. Phys. Lett.* **71**, 34 (1997).

[5] Greenham, N. C., Moratti, S. C., Bradley, D. D. C., Friend, R. H., and Holmes, A. B., *Nature* **365**, 628 (1993).

[6] Yang, Y., Pei, Q., and Heeger, A. T., *J. App. Phys.* **79** (2), 934 (1996).

[7] Fang, H., Wang, S., Xiao, S., Li, Y., Liu, Y., Fan, L., Shi, Z., Du, C., and Zhu, D., *Synth. Met.* **128**, 253 (2002).

[8] Kobayashi, S. and Haga, Y., *Synth. Met.* **87**, 31 (1997).

[9] Harrison, N. T., Baigent, D. R., Samnel, I. D. W., and Friend, R. H., *The Am. Phys. Soc.* **53**, 15815 (1996).

[10] Wessling, R. A. and Ziemmerman, R. G., U.S. Patent, 3,706,677 (1972).

[11] Lenz, R. W., Chien, C. H., Stenger-Smith, J., and Karasz, F., *J. Polym. Sci. Part A: Polym. Chem.* **26**, 3241 (1988).

[12] Swatos, W. J. and Gordon III, B., *Polym. Prepr.* **31** (1), 505 (1990).

[13] Hsieh, B. R., Autonladis, H., Bland, D. C., and Feld, W. A., *Adv. Mater.* **7**, 36 (1995).

[14] Gilch, H. G. and Wheelwright, W. L., *J. Polym. Sci. Part A-1: Polym. Chem.* **4**, 1337 (1966).

[15] Sarneck, G. J., Burn, P. L., Kraft, A., Friend, R. H., and Holmes, A. B., *Synth. Met.* **55–57**, 914 (1993).

[16] Becker, H., Spreitzer, H., Ibron, K., and Kreuder, W., *Macromolecules* **32**, 4925 (1999).

[17] Becker, H., Spreitzer, H., Kreuder, W., Kluge, E., Schenk, H., Parker, I., and Cao, Y., *Adv. Mater.* **12**, 42 (2000).

[18] Becker, H., Spreitzer, H., Kreuder, W., Kluge, E., Vestweber, H., Schenk, H., and Treacher, K., *Synth. Met.* **122**, 105 (2001).

[19] Ruiz, J. P., Dharia, J. R., Reynold, J. R., and Buckley, L. J., *Macromolecules* **25**, 849 (1992).

[20] Doi, S., Kuwabara, M., Noguchi, T., and Ohnishi, T., *Synth. Met.* **55–57**, 4174 (1993).

[21] Chen, S. A. and Lee, H. T., *Macromolecules* **26**, 3254 (1993).

[22] Berggren, M., Gustafsson, G., Inganas, O., Anderson, M. R., Wennerstron, O., and Hjertberg, T., *Adv. Mater.* **6**, 448 (1994).

Downloaded At: 17:20 30 January 2011