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Synthesis of Soluble Phenyl-Substituted Poly(*p*-phenylenevinylenes) with a Low Content of Structural Defects

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ABSTRACT: The synthesis and characterization of two new soluble poly(*p*-phenylenevinylenes) (PPVs) are reported. The polymers are poly(2-(2′,5′-bis(octyloxy)benzene)-1,4-phenylenevinylene) (BOP-PPV) and poly(2-(2′,5′-bis(octyloxy)benzene)-5-methoxy-1,4-phenylenevinylene) (BOPM-PPV). Both polymers have been polymerized at high and low temperatures to study the formation of structural defects. It is shown that both methoxy groups as side chains and low polymerization temperatures decrease the content of defects in the final polymer. As a consequence, the polymers with lower concentration of defects exhibit higher electroluminescence yields in light-emitting diodes. In addition to this, the polymers with a low content of defects exhibited longer operational lifetimes in these devices. The highest photoluminescence quantum yield in the solid state and electroluminescence efficiency were found to be 72% and 1.74%, respectively.

Introduction

Organic polymers have traditionally been considered as insulators, and the electronic industry have taken advantage of this property in many applications. The concept of only being insulators changed in 1977, when Shirakawa et al. found that polyacetylene was capable to conduct electricity in the doped state.[1] Conjugated polymers was paid renewed research interest in 1990, when electroluminescence (EL) was found in poly(*p*-phenylenevinylene) (PPV).[2] Since then, extensive research has been focused on the development of polymers suitable for use as the active substances in light-emitting diodes (LEDs). Today, PPV and its derivatives are still one of the most promising class of conjugated polymers in LEDs. This is mainly due to their high luminescence efficiencies and readiness to polymerize to high molecular weight. The most frequently used polymerization method for soluble PPVs is dehydrohalogenation of 1,4-bis(halomethyl)benzenes, known as the Gilch route.[3] This procedure normally yields high molecular weight materials, number-average molecular weight on the order of 10^5, which gives the PPVs good film-forming properties.

It has been shown that phenyl-substituted PPVs have a higher resistance to photooxidation than other PPVs.[4] Recently, Becker et al. reported that longer lifetimes of LEDs, with phenyl-substituted PPVs as the active substances, could be reached by decreasing the formation of head-to-head (HH) and tail-to-tail (TT) couplings during polymerization (Scheme 1).[5] These structures were named tolane−bisbenzyl (TBB) defects. Becker et al. found that the introduction of a methoxy group (as for BOPM-PPV) decreased the amount of TBB content in the final polymer. It has also been shown that it is possible to decrease these structural elements by decreasing the polymerization temperature.[6]

In this paper, the synthesis and characterization of poly(2-(2′,5′-bis(octyloxy)benzene)-1,4-phenylenevinylene) (BOP-PPV) and poly(2-(2′,5′-bis(octyloxy)benzene)-5-methoxy-1,4-phenylenevinylene) (BOPM-PPV) are reported (Figure 1). The chemical structure of these polymers was designed to give high photoluminescence efficiencies (η_{PL}) in the solid state. It is known that excitons can diffuse to structural defects where nonradiative relaxation to the ground state can occur.[7,8] The two long alkyl chains in BOP-PPV and BOPM-PPV should prevent interchain exciton transfer to some extent and thereby decrease diffusion of excitons to defects. However, too large a separation of the polymer chains should be avoided since this can cause too low mobility of charges in LEDs.[9] To achieve better packing, and thereby higher mobility of charge carriers, straight alkyl chains instead of branched were used. This could be an advantage in LEDs but causes problems when it comes to solubility. To overcome the solubility problem, two long alkyl chains instead of one (which is more frequently used for phenyl-substituted PPVs and easier to synthesize) was the natural choice. Thereby, it was possible to obtain BOPM-PPV as a soluble homopolymer. Both polymers were made at high and low temperatures. A comparison of the effect, from both the polymerization temperature and the methoxy group, on formation of defects is reported.

Experimental Section

Measurements. NMR spectra were recorded on a Varian 400 MHz spectrometer with tetramethylsilane as internal reference. Mass spectra were recorded using a VG ZabSpec. Unless otherwise stated, electron impact was used as the ionization source. When fast atom bombardment (FAB) was used, the compound to be investigated was dissolved in

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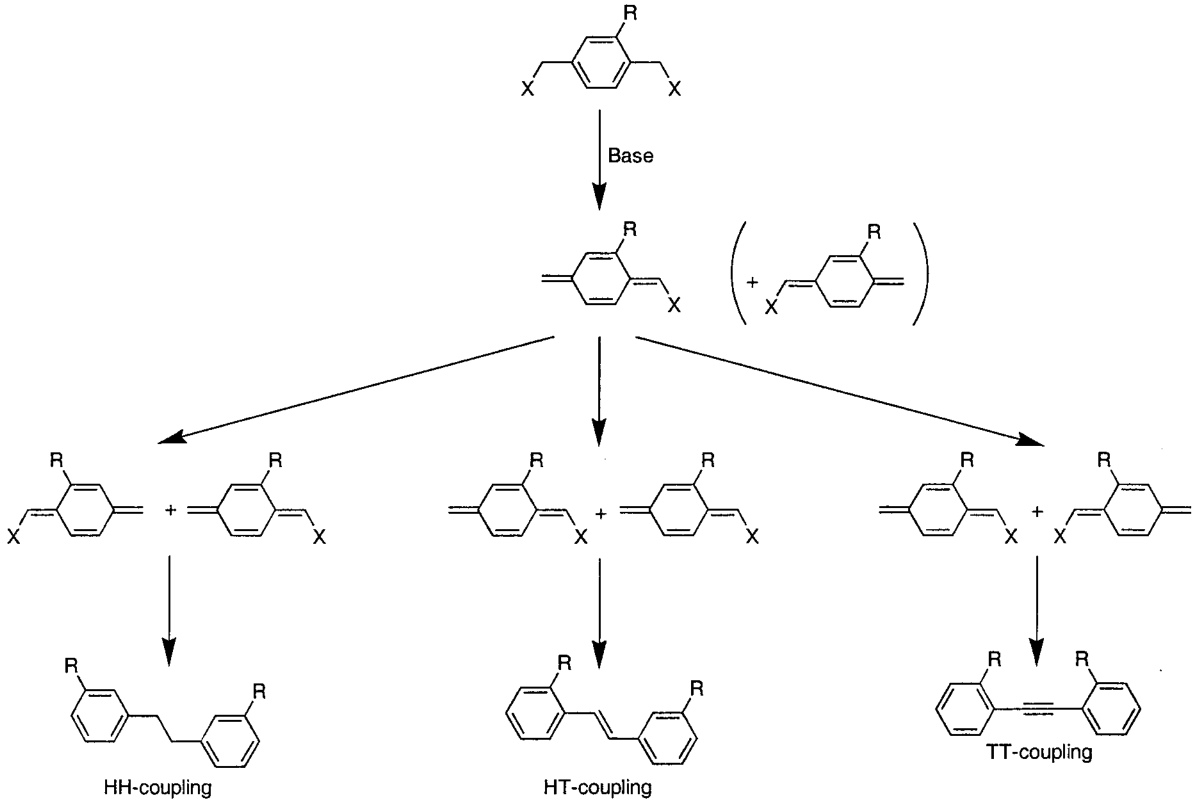
Scheme 1. Differences in the Polymerization Mechanism Leading to HH, HT, and TT Couplings



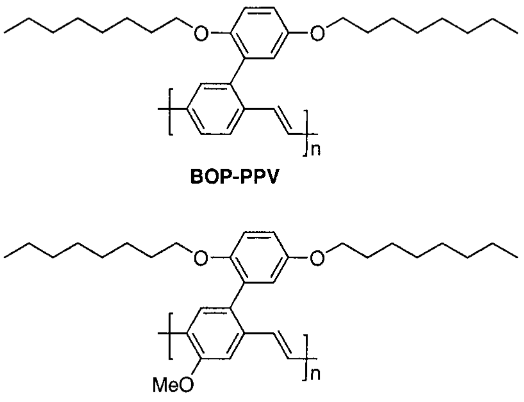


Figure 1. Chemical structures of the prepared polymers BOP-PPV and BOPM-PPV.

3-nitrobenzyl alcohol (NBA), and a beam of Cs ions was used to ionize the sample. Molecular weights of the polymers were determined by size-exclusion chromatography (SEC) by a Waters 712 WISP using SDVB columns at 25 °C. The calibration was made with a series of monodispersed polystyrene standards in $CHCl_3$. Detection was made by a Waters 410 differential refractometer and by a Waters 486 tunable absorbance detector. UV−vis spectra were recorded on a Lambda 9 spectrometer. The electrochemical spectroscopy measurements were made with a Autolab pgstat10. The photoluminescence (PL) spectra were measured by exciting the polymer samples with monochromatic light from a tungsten lamp, and the emission was measured with an Oriel Instaspec IV diode matrix spectrometer. Solutions used to detect UV−vis spectra and PL spectra were prepared from the polymer dissolved in $CHCl_3$. UV−vis spectra and PL spectra in the solid state were carried out on films spin-coated on quarts glass slides from $CHCl_3$ solution. An integrating sphere made by Labsphere was used to measure the PL efficiencies. These measurements were done as described in ref 10. Melting points were determined using a Mettler FP90 instrument with an Olympus BH-2 microscope. The diodes (ITO/PANI/polymer/Ba/Al) were made on glass substrates partly covered by an indium−tin oxide (ITO) layer. Polyaniline (PANI) (200 nm) was used as a buffer layer on top of the ITO. The polymers were spin-coated from 0.5% toluene solutions, which gave 70−75 nm thick polymer layers.

Materials. Unless otherwise stated, reagents were purchased from Aldrich and used without further purification. The *o*-xylene was anhydrous and packaged under nitrogen. 1,4-Bis(octyloxybenzene) was prepared according to literature procedures.[11] THF and diethyl ether were distilled over sodium and benzophenone.

4-Bromo-2,5-dimethylphenol (1). A solution of NBS (14.2 g, 80 mmol) in 50 mL of DMF was added dropwise to 2,5-dimethylphenol (10.0 g, 81.9 mmol) dissolved in 125 mL of DMF. The solution was stirred at room temperature overnight, and $Na_2S_2O_5$ (10%) was added to quench the reaction. Diethyl ether and 2 M HCl were added, and the two phases were separated. The water phase was extracted twice with diethyl ether. The resulting organic phases were combined and washed with 2 M HCl and water. The organic extracts were dried over Na_2SO_4 and evaporated to yield an oil that solidified upon standing. The crude product was recrystallized from hexane to yield 9.56 g (60%) of 4-bromo-2,5-dimethylphenol as needles; mp 86−87 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.18 (s, 3H), 2.30 (s, 3H), 4.60 (s, 1H), 6.66 (s, 1H), 7.26 (s, 1H). HRMS: Calcd for $C_8H_9{}^{79}BrO$: 199.984. Found: 199.981.

1-Bromo-4-methoxy-2,5-dimethylbenzene (2). To a stirred suspension of KOH powder (9.15 g, 163 mmol) in DMSO (60 mL) was added **1** (8.2 g, 40.8 mmol) and iodomethane (11.6 g, 81.7 mmol). After 1 h at room temperature, excess iodomethane was evaporated. Water and diethyl ether were added, and the two phases were separated. The water phase was extracted twice with diethyl ether. The combined organic phases were washed with 1 M NaOH and water. The organic extracts were dried over Na_2SO_4 and evaporated to yield 8.4 g (96%) of 1-bromo-4-methoxy-2,5-dimethylbenzene as an oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.17 (s, 3H), 2.35 (s, 3H), 3.79 (s, 3H), 6.68 (s, 1H), 7.26 (s, 1H). HRMS: Calcd for $C_9H_{11}{}^{79}BrO$: 213.999. Found: 213.994.

2-Bromo-5-methoxyterephthalic Acid (3). $KMnO_4$ (13.0 g, 82 mmol) was added to **2** (8.0 g, 37.2 mmol) in water (125 mL) under stirring. After 1.5 h at reflux, another portion of $KMnO_4$ (13.0 g) was added, and the solution was refluxed for 16 h. Precipitated MnO_2 was filtered off. The desired product was precipitated by the addition of 2 M HCl to the filtrate. Filtration and drying afforded 3.8 g (37%) of 2-bromo-5-methoxyterephthalic acid as a colorless solid; mp 265 °C (dec). ^1H NMR (400 MHz, CD_3OD): δ (ppm) 3.92 (s, 3H), 7.48 (s, 1H), 7.99 (s, 1H). HRMS: Calcd for $C_9H_7{}^{79}BrO_5$: 273.948. Found: 273.935.

2-Bromo-5-methoxyterephthalic Acid Diethyl Ester (4). A stirred solution of **3** (1.6 g, 5.8 mmol) in ethanol (50 mL) and sulfuric acid (1 mL) was refluxed for 4 h. Excess ethanol was evaporated, and diethyl ether and Na_2CO_3 (10%) were added. The two phases were separated, and the organic phase was washed twice with Na_2CO_3 (10%) and water. Drying over Na_2SO_4 and evaporation yielded 1.29 g (67%) of 2-bromo-5-methoxyterephthalic acid diethyl ester as a solid; mp 55−57 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.38 (t, 3H), 1.42 (t, 3H), 3.92 (s, 3H), 4.37 (q, 2H), 4.43 (q, 2H), 7.34 (s, 1H), 8.00 (s, 1H). FABHRMS (NBA/Cs): Calcd for $(M+H)^+$ $C_{13}H_{14}{}^{79}BrO_5$: 331.018. Found: 330.978.

2-Bromo-1,4-bis(octyloxy)benzene (5). A solution of NBS (4.26 g, 23.7 mmol) in 50 mL of DMF was added dropwise to 1,4-bis(octyloxy)benzene (8.0 g, 23.9 mmol) dissolved in 75 mL of DMF. The solution was stirred at room temperature for 2 h, and $Na_2S_2O_5$ (10%), 2 M HCl, and pentane were added. The two phases were separated, and the water phase was extracted with pentane. The resulting organic phases were combined and washed with 2 M HCl and water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, pentane/dichloromethane (10/1) as eluent) to yield 5.8 g (59%) of 2-bromo-1,4-bis(octyloxy)benzene as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.85−0.92 (m, 6H), 1.23−1.58 (m, 20H), 1.70−1.84 (m, 4H), 3.88 (t, 2H), 3.95 (t, 2H), 6.78 (dd, 1H), 6.82 (d, 1H), 7.11 (d, 1H). HRMS: Calcd for $C_{22}H_{37}{}^{79}BrO_2$: 412.198. Found: 412.214.

1,4-Bis(octyloxy)benzene-2-boronic Acid (6). To a stirred solution of **5** (4.6 g, 11.1 mmol) in absolute diethyl ether (40 mL) under nitrogen was added *n*-BuLi (7.0 mL, 1.6 M in hexane, 11.2 mmol) at −78 °C. The solution was allowed to warm to room temperature for 30 min. The reaction mixture was then cooled to −78 °C, and tributyl borate (5.0 mL, 18.5 mmol) was added. The solution was allowed to warm to room temperature for 2 h before the reaction was quenched with the addition of 1 M HCl. The two phases were separated, and the water phase was extracted with two portions of diethyl ether. The combined organic extracts were washed successively with three portions of 1 M NaOH and water, dried over Na_2SO_4, and evaporated. The resulting colorless oil, which solidified upon standing, of crude 1,4-bis(octyloxy)benzene-2-boronic acid (4.0 g) was used without further purification.

2-Bromoterephthalic Acid Diethyl Ester (7). A stirred solution of 2-bromoterephthalic acid (10.0 g, 40.7 mmol) in ethanol (100 mL) and sulfuric acid (2 mL) was refluxed for 4 h. Excess ethanol was evaporated, and diethyl ether and Na_2CO_3 (10%) were added. The two phases were separated, and the organic phase was washed twice with Na_2CO_3 (10%) and water. Drying over Na_2SO_4 and evaporation yielded 8.0 g (67%) of 2-bromoterephthalic acid diethyl ester as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.38−1.45 (m, 6H), 4.37−4.46 (m, 4H), 7.79 (d, 1H), 8.01 (d, 1H), 8.31 (s, 1H). FABHRMS (NBA/Cs): Calcd for $(M+H)^+$ $C_{12}H_{14}{}^{79}BrO_4$: 301.008. Found: 300.975.

2-(2′,5′-Bis(octyloxy)benzene)terephthalic Acid Diethyl Ester (8a). To a stirred solution of **7** (0.725 g, 2.41 mmol) and $Pd(PPh_3)_4$ (100 mg, 86.5 μmol) under nitrogen in toluene (15 mL) was added excess **6** (2.0 g crude) and 1 M $NaHCO_3$ (10 mL). The reaction mixture was refluxed overnight. The two phases were separated, and the water phase was extracted with toluene. The catalyst was removed by filtering the organic solution through a short column of silica gel (product eluted with toluene). The solvent was evaporated to yield 1.30 g (97%) of 2-(2′,5′-bis(octyloxy)benzene)terephthalic acid diethyl ester as an oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84−0.92 (m, 6H), 1.06 (t, 3H), 1.14−1.57 (m, 22H), 1.40 (t, 3H), 1.71−1.79 (m, 2H), 3.71−3.78 (m, 2H), 3.94 (t, 2H), 4.11 (q, 2H), 4.39 (q, 2H), 6.79−6.88 (m, 3H), 7.92 (d, 1H), 8.00 (s, 1H), 8.04 (d, 1H). FABHRMS (NBA/Cs): Calcd for $C_{34}H_{50}O_6$: 554.361. Found: 554.351.

2-(2′,5′-Bis(octyloxy)benzene)-1,4-bis(hydroxymethyl)benzene (9a). To a stirred solution of **8a** (1.21 g, 2.18 mmol) in absolute THF (20 mL) was added $LiAlH_4$ (0.5 g, 13.2 mmol) in portions. The solution was refluxed for 1 h before it was treated with water. The THF was evaporated, and diethyl ether and water were added. The two phases were separated, and the water phase was extracted twice with diethyl ether. The resulting organic phases were combined and washed with water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, the byproducts were eluted with dichloromethane and the product was eluted with ethyl acetate) to yield 0.98 g (96%) of 2-(2′,5′-bis(octyloxy)benzene)-1,4-bis(hydroxymethyl)benzene as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.83−0.90 (m, 6H), 1.10−1.54 (m, 21H), 1.72−1.80 (m, 3H), 3.69 (m, 1H), 3.89 (m, 1H), 3.90 (t, 2H), 4.39 (dd, 2H), 4.72 (s, 2H), 6.73 (d, 1H), 6.86 (dd, 1H), 6.92 (d, 1H), 7.21 (s, 1H), 7.39 (d, 1H), 7.52 (d, 1H). FABHRMS (NBA/Cs): Calcd for $C_{30}H_{46}O_4$: 470.340. Found: 470.314.

2-(2′,5′-Bis(octyloxy)benzene)-1,4-bis(bromomethyl)benzene (10a). To a solution of **9a** (0.90 g, 1.93 mmol) in absolute ether (15 mL) was added PBr_3 (0.80 g, 2.96 mmol). The solution was stirred at room temperature for 3 h, and $Na_2S_2O_5$ (10%) was added. The two phases were separated, and the water phase was extracted with diethyl ether. The organic phases were combined and washed with water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, dichloromethane as eluent) to yield 0.60 g (50%) of 2-(2′,5′-bis(octyloxy)benzene)-1,4-bis(bromomethyl)benzene as colorless crystals; mp 63.5−64.5 °C. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84−0.91 (m, 6H), 1.12−56 (m, 22 H), 1.72−1.80 (m, 2H), 3.76−3.84 (m, 2H), 3.94 (t, 2H), 4.39 (dd, 2H), 4.48 (s, 2H), 6.86 (d, 1H), 6.89 (s, 1H), 6.89 (d, 1H), 7.24 (d, 1H), 7.37 (dd, 1H), 7.50 (d, 1H). FABHRMS (NBA/Cs): Calcd for $C_{30}H_{44}{}^{79}Br_2O_2$: 594.171. Found: 594.194.

2-(2′,5′-Bis(octyloxy)benzene)-5-methoxyterephthalic Acid Diethyl Ester (8b). To a stirred solution of **4** (0.70 g, 2.11 mmol) and $Pd(PPh_3)_4$ (100 mg, 86.5 μmol) under nitrogen in toluene (20 mL) was added excess **6** (1.0 g crude) and 1 M $NaHCO_3$ (15 mL). The reaction mixture was refluxed overnight. The two phases were separated, and the water phase was extracted with toluene. The catalyst was removed by filtering the organic solution through a short column of silica gel (product eluted with diethyl ether). The solvent was evaporated to yield 1.11 g (90%) of 2-(2′,5′-bis(octyloxy)benzene)-5-methoxyterephthalic acid diethyl ester as an oil. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84−0.92 (m, 6H), 1.01 (t, 3H), 1.16−1.58 (m, 22H), 1.73−1.81 (m, 2H), 1.37 (t, 3H), 3.71−3.77 (m, 2H), 3.91−3.96 (m, 2H), 3.99 (s, 3H), 4.09 (q, 2H), 4.36 (q, 2H), 6.75−6.85 (m, 3H), 7.48 (s, 1H), 7.74 (s, 1H). FABHRMS (NBA/Cs): Calcd for $C_{35}H_{52}O_7$: 584.371. Found: 584.387.

2-(2′,5′-Bis(octyloxy)benzene)-5-methoxy-1,4-bis(hydroxymethyl)benzene (9b). To a stirred solution of **8b** (0.80 g, 1.37 mmol) in absolute THF (30 mL) was added $LiAlH_4$ (0.15 g, 3.95 mmol) in portions. The solution was kept at room temperature for 1 h before it was treated with water. The THF was evaporated, and diethyl ether and water were added. The two phases were separated, and the water phase was extracted twice with diethyl ether. The resulting organic phases were combined and washed with water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, the byproducts were eluted with dichloromethane/diethyl ether (10/1) and the product was eluted with diethyl ether) to yield 0.55 g (80%) of 2-(2′,5′-bis(octyloxy)benzene)-5-methoxy-1,4-bis(hydroxymethyl)benzene as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84−0.92 (m, 6H), 1.16−1.52 (m, 22H), 1.73−1.81 (m, 2H), 2.36 (dd, 1H), 2.86 (dd, 1H), 3.67 (m, 1H), 3.86 (m, 1H), 3.90 (t, 2H), 3.95 (s, 3H), 4.38 (dd, 2H), 4.70 (dd, 2H), 6.72 (d, 1H), 6.84 (dd, 1H), 6.93 (d, 1H), 7.07 (s, 1H), 7.13 (s, 1H). FAB-HRMS (NBA/Cs): Calcd for $C_{31}H_{48}O_5$: 500.350. Found: 500.341.

2-(2′,5′-Bis(octyloxy)benzene)-5-methoxy-1,4-bis(bromomethyl)benzene (10b). To a solution of **9b** (0.40 g, 0.80 mmol) in absolute ether (15 mL) was added PBr_3 (0.43 g, 1.6 mmol). The solution was stirred at room temperature for 4 h, and $Na_2S_2O_5$ (10%) was added. The two phases were separated, and the water phase was extracted with diethyl ether. The organic phases were combined and washed with water. The organic extracts were dried over Na_2SO_4, evaporated, and purified with column chromatography (silica gel, dichloromethane as eluent) to yield 139 mg (28%) of 2-(2′,5′-bis(octyloxy)benzene)-5-methoxy-1,4-bis(bromomethyl)benzene as colorless crystals; mp 72−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.84−0.92 (m, 6H), 1.16−1.52 (m, 22H), 1.73−1.81 (m, 2H), 3.80 (m, 2H), 3.93 (t, 2H), 3.95 (s, 3H), 4.39 (dd, 2H), 4.54 (d, 2H), 6.83−6.88 (m, 3H), 7.03 (s, 1H), 7.19 (s, 1H). FAB-HRMS (NBA/Cs): Calcd for $C_{31}H_{46}{}^{79}BrO_3$: 624.181. Found: 624.222.

Polymer Synthesis. Representative procedures for the preparation and isolation of polymers obtained at high and low polymerization temperatures follow.

Poly(2-(2′,5′-bis(octyloxy)benzene)-1,4-phenylenevinylene) (P1). A stirred solution of **10a** (150 mg, 0.251 mmol) in xylene (10 mL) under nitrogen was heated to reflux. Potassium *tert*-butoxide (0.75 mL, 1.0 M in THF, 0.75 mmol) was added under 2 min, and the reaction mixture was refluxed for 4 h. The polymer was precipitated by adding the xylene solution to methanol. The crude polymer was collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was again collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was filtered off, washed with methanol, and dissolved in chloroform with stirring at room temperature overnight. The resulting solution was filtered through a 325 mesh filter, and the polymer was precipitated by dropwise addition to methanol. The precipitated polymer was collected, washed with methanol, and dried under high vacuum to yield 58 mg (58%) of **P1**.

Poly(2-(2′,5′-bis(octyloxy)benzene)-5-methoxy-1,4-phenylenevinylene) (P5). A stirred solution of **10b** (125 mg, 0.199 mmol) in absolute THF (10 mL) under nitrogen was cooled to −35 °C. Potassium *tert*-butoxide at room temperature (3.2 mL, 1.0 M in THF, 3.20 mmol) was added under 2 min. After 4 h at −35 °C, the resulting polymer was precipitated in methanol. The crude polymer was collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was again collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was filtered off, washed with methanol, and dissolved in chloroform with stirring at room temperature overnight. The resulting solution was filtered through a 325 mesh filter, and the polymer was precipitated by dropwise addition to methanol. The precipitated polymer was collected, washed with methanol, and dried under high vacuum to yield 68 mg (73%) of **P5**.

P6. A solution of **P5** (50 mg) and potassium *tert*-butoxide (30 mg) in *o*-xylene (10 mL) was refluxed for 1 h. The polymer was precipitated in methanol and collected by filtration. The polymer was washed with methanol and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was again collected, washed with methanol, and stirred with a mixture of methanol and water (1/1) for 1 h. The polymer was filtered off, washed with methanol, and dissolved in chloroform with stirring at room temperature overnight. The resulting solution was filtered through a 325 mesh filter, and the polymer was precipitated by dropwise addition to methanol. The precipitated polymer was collected, washed with methanol, and dried under high vacuum to yield 45 mg (90%) of **P6**.

Results and Discussion

Synthesis and ^{1}H NMR Measurements. The polymers were prepared according to Scheme 2. The substituted terephthalic acid diethyl esters, **4** and **7**, were synthesized by Fisher esterification of the corresponding terephthalic acids. The disubstituted terephthalic acid **3** was prepared in a three-step reaction: bromination of 2,5-dimethylphenol with NBS, followed by methylation of the hydroxyl group, and oxidation at the benzylic positions gave **3** in 21% overall yield. Lithiation of **5** followed by addition of tributyl borate yielded the boronic acid **6**. The Suzuki coupling[12] of this boronic acid with **4** and **7** in toluene, in the presence of tetrakis(triphenylphosphine)palladium(0) as catalyst, gave **8b** and **8a**, respectively. Reduction of **8a** and **8b** with $LiAlH_4$ followed by bromine substitution of the resulting hydroxyl groups with phosphorus tribromide yielded the monomers **10a** and **10b**, respectively.

This route to phenyl-substituted 1,4-bis(bromomethyl)benzenes, first described by Becker et al.,[13] requires more steps than the more commonly used radical bromination reaction of phenyl-substituted *p*-xylenes.[4] Despite this, the easy product purification makes it advantageous. Whereas compound **9** does not move on silica gel with dichloromethane as eluent compound **8** and **10** goes with the front. It is also easy to separate **10a** and **10b** from the corresponding monobrominated materials, which is difficult with the radical bromination route. This makes it very easy to obtain pure monomers by column chromatography.

To investigate the amount of TBB defects produced, as a function of polymerization temperature, both monomers were polymerized in refluxing xylene (144 °C) and in THF at −35 °C. Previous studies have shown that some polymers obtained at low temperatures in THF are not fully dehydrobrominated.[6] To ensure complete dehydrobromination, BOP-PPV (**P2**) and BOPM-PPV (**P5**) polymerized at −35 °C were treated with potassium *tert*-butoxide in refluxing *o*-xylene for 1 h to give **P3** and **P6**, respectively. As shown in Table 1, the best yields were found for the low-temperature polymerizations. All polymers were soluble in $CHCl_3$ and xylene at room temperature. Both polymers obtained at lower polymerization temperature, especially BOPM-PPV, required more time to dissolve completely. Once these polymers were refluxed in xylene they were easier to dissolve. This is due to their lower molecular weight as shown in Table 1. The lower molecular weight of these polymers shows that chain scission of the polymer backbones occurs at elevated temperatures and explains why the molecular weights of **P1** and **P4** are relatively low. This observation also described in ref 8 can be used to decrease the molecular weight and introduce solubility to PPVs that form gels or microgels.

The ^{1}H NMR spectra of **P1** and **P3** are shown in Figure 2, and the ^{1}H NMR spectra of **P4** and **P6** are shown in Figure 3. The signals around 3.6−4.0 ppm arise from the methylenes next to oxygen in the side chains. **P4** and **P6** shows additional signals from the methoxy hydrogens around 3.9 ppm. These peaks are scaled to allow a direct comparison of the HH content between the polymers. Although not visible in ^{1}H NMR measurements, the TT coupling resulting in triple bonds should be produced in equal amounts. Becker et al. have assigned the CH_2CH_2 groups from HH couplings to peaks around 2.7−2.9 ppm.[14] The polymers investigated here show peaks in this region in various amounts. The

Scheme 2. Synthetic Route to BOP-PPV and BOPM-PPV

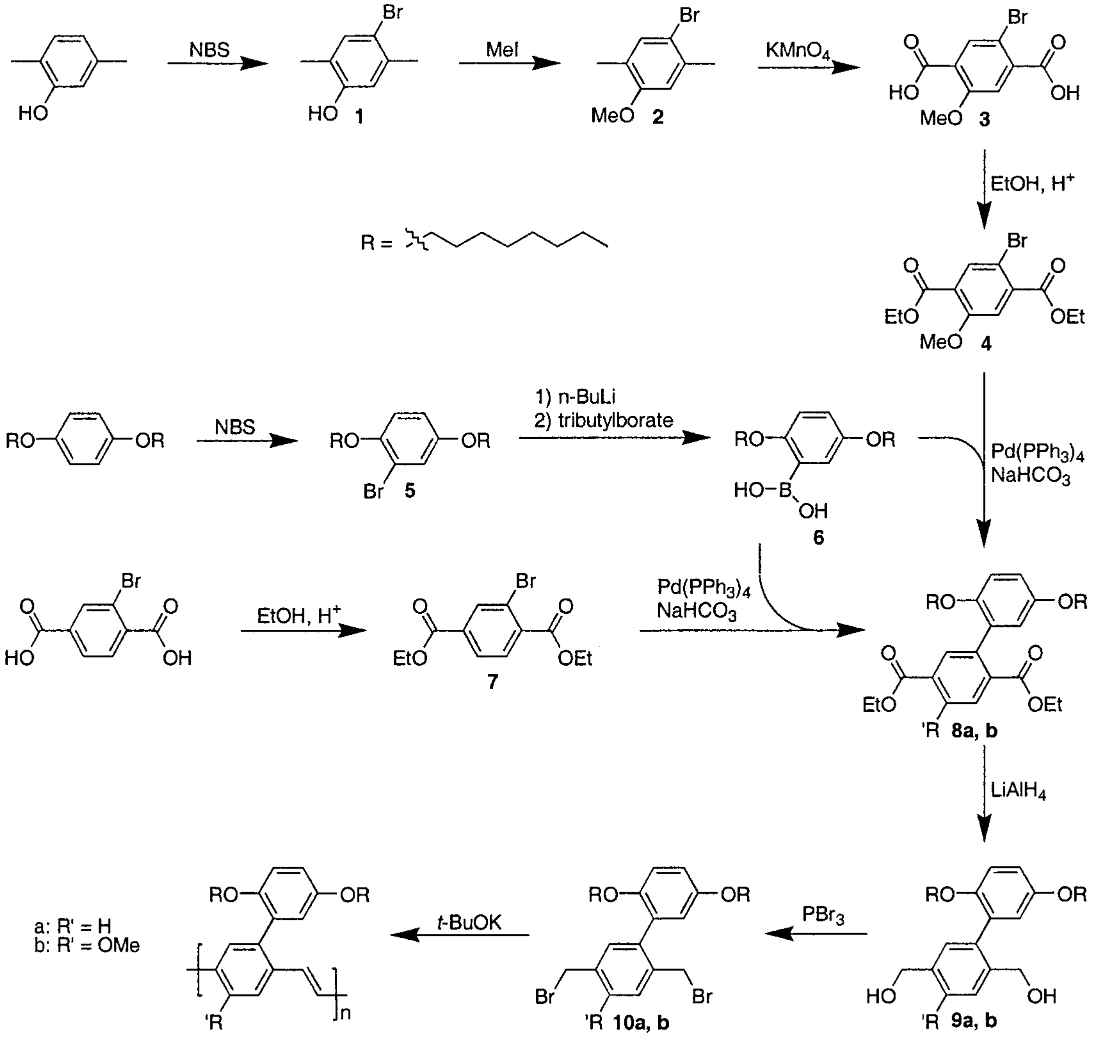


Table 1. Polymerization Parameters and Molecular Weights for P1–P6

entry	monomer	solvent	$M_n/M_w \times 10^{-3}$	poly-dispersity	yield (%)
P1	**10a**	xylene	41/191	4.7	53
P2	**10a**	THF	269/734	2.7	71
P3[a]		xylene	66/217	3.3	86
P4	**10b**	xylene	8/38	4.8	47
P5	**10b**	THF	76/584	7.7	73
P6[b]		xylene	30/298	9.9	90

[a] Polymer **3** was derived from **P2** after workup and treatment with excess *t*-BuOK in refluxing *o*-xylene. [b] Polymer **6** was derived from **P5** after workup and treatment with excess *t*-BuOK in refluxing *o*-xylene.

highest content was found for BOP-PPV polymerized at high temperature (5.8%) and the lowest for BOPM-PPV polymerized at low temperature (<1.0%) (Table 2). This is the first time a soluble PPV with such a low TBB content is reported. BOP-PPV polymerized at low temperature and BOPM-PPV polymerized at elevated temperature had HH contents in between these extremes, 3.5% and 2.0%, respectively. From these measurements, it is evident that a lower polymerization temperature gives a polymer with a lower content structural defects. The addition of methoxy groups to the polymer backbone also reduces the formation of defects. A more selective reaction, with a reduced rate of the reactions leading to TBB defects, is the most probable explanation for the effect of lowering the polymerization temperature. Not only these defects should be reduced by lowering the polymerization temperature. Most probably other defects acting as quenching sites for the excited states will be decreased as well, although they cannot be detected by NMR measurements. As described in ref 13, the electronic influence of the methoxy group will favor the formation of **Q1** over **Q2** (in contradiction to ref 13) (Scheme 3) by making the hydrogens on one of the bromomethyl groups less acidic. This electronic influence from the methoxy group, together with steric effects from the side chains, should have an effect on

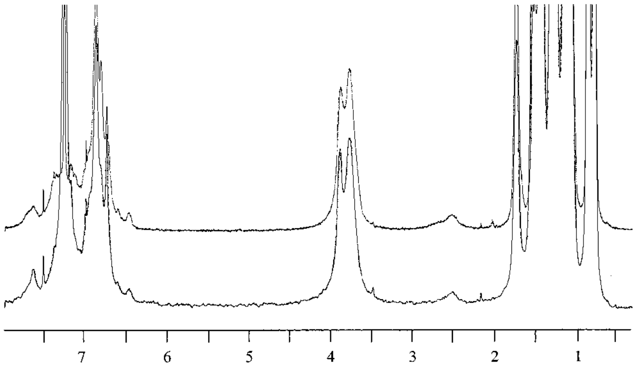


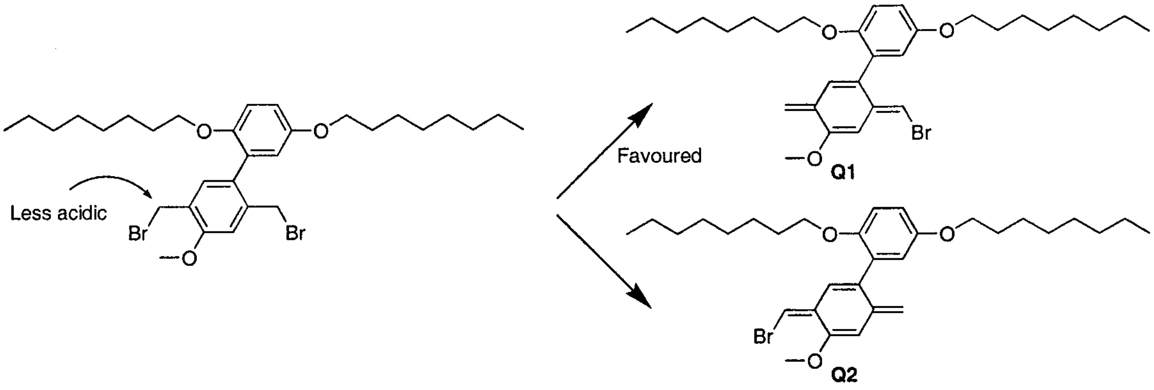
Figure 2. ^{1}H NMR of **P1** (top) and **P3** (bottom). Peaks around 3.7 ppm have the same integrated area.

Table 2. Content of TBB Defects and PL, EL, and Absorption Data for P1−P6

entry	TBB content (%)	abs_{max} (nm) $CHCl_3$	PL_{max} (nm) $CHCl_3$	η_{PL} (%) $CHCl_3$	abs_{max} (nm) film	PL_{max} (nm) film	η_{PL} (%) film	η_{EL} (%)	$t_{1/2}$[a] (h)
P1	5.8	430	485, 517	88	430	496, 530	58	1.23	0.85
P2	3.5	436	485, 518	89	436	499, 535	72		
P3	3.5	436	485, 518	88	436	498, 535	60	1.34	1.48
P4	2.0	451	514, 550	75	462	553	41	0.45	1.75
P5	<1.0	460	515, 553	79	465	553	51		
P6	<1.0	460	515, 555	79	463	529, 561	40	1.74	9.0

[a] Half-lifetime of operating diodes at accelerated conditions (80 °C).

Scheme 3. Influence of a Methoxy Group on Formation of Quinoid Structures



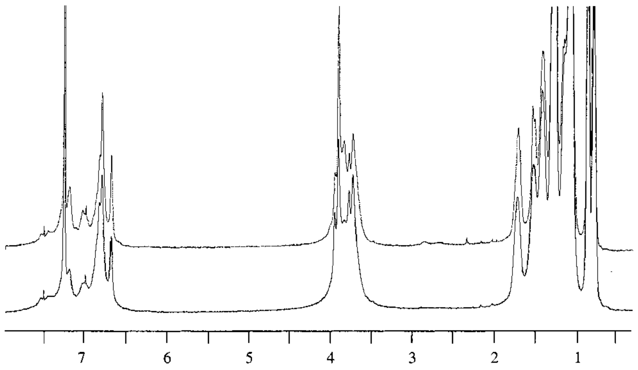


Figure 3. ^1H NMR of **P4** (top) and **P6** (bottom). Peaks around 3.8 ppm have the same integrated area.

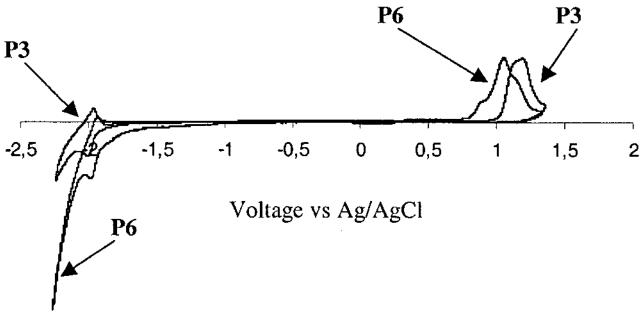


Figure 4. Electrochemical spectroscopy of **P3** and **P6**.

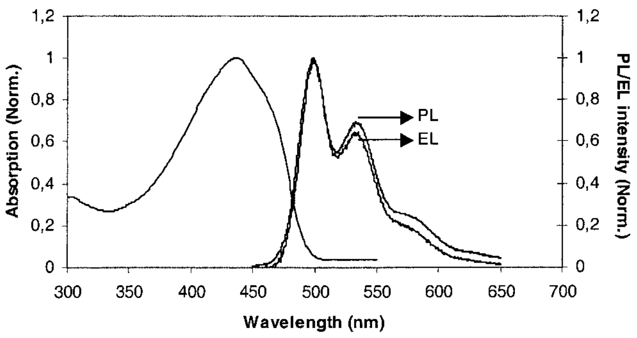


Figure 5. Absorption, PL, and EL spectra of **P3** (solid state).

the formed quinoid structure **Q1**, and the preferred polymerization path will be the desired HT coupling. A more careful study of the NMR spectra reveals that noncharacterized peaks around 6.5 and 7.5 ppm follows the trend seen for the peaks around 2.7 ppm. These peaks might correspond to the aromatic protons in the vicinity of TBB defects.

Electrochemical Spectroscopy. The cyclic voltammograms of **P3** and **P6** are shown in Figure 4. The electrochemical spectroscopy measurements were made in a single-compartment electrochemical cell, with 0.1 M tetrabutylammonium perchlorate in acetonitrile, purged with nitrogen. The cell had a Pt counter electrode and a Ag/AgCl reference electrode. The polymers were adsorbed on a Pt wire from chloroform solution. The sweep rate was 100 mV/s, and the polymers were both reduced and oxidized (in that order). We were able to detect reduction of the polymers around −1.9 to −2.0 V, without any distinct differences between the two polymers. However, from the voltammograms it is evident that the oxidation potentials between the polymers differ slightly. The oxidation potential maxima for **P3** and **P6** are 1.19 and 1.07 V, respectively. In addition to this, the oxidation potential onset of **P6** is lower than for **P3**, which certainly makes it easier to inject holes from the anode. The oxidation potential curve is also more fine structured for **P6**.

Absorption, Photoluminescence, and Electroluminescence Properties. The absorption and photoluminescence (PL) spectra in the solid state and electroluminescence (EL) spectra of **P3** and **P6** are shown in Figure 5 and Figure 6, respectively. The absorption and PL maxima for all polymers are shown in Table 2. The absorption maxima in solution for the polymers polymerized at high temperatures are somewhat blue-shifted compared to the polymers obtained at lower temperatures. It seems like a lower polymerization temperature gives polymers with a higher degree of

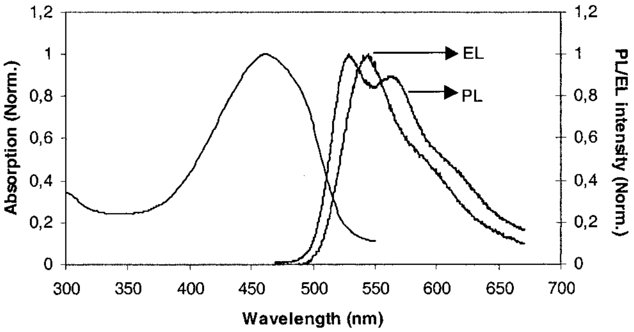


Figure 6. Absorption, PL, and EL spectra of **P6** (solid state).

regioregularity and, thereby, a longer effective conjugation with red-shifted absorption. The PL spectra in film are red-shifted compared to those in solution. This is caused by interchain interactions in films. All PL spectra of the BOP-PPVs (**P1**−**P3**) show two distinct maxima in both solution and film, which implies relatively ordered local structures. The same is observed for all BOPM-PPVs (**P4**−**P6**) in solution. In films though, only one of these polymers shows two maxima (**P6**) whereas **P4** and **P5** only have one peak, but still vibronic fine structures. The emissions of these two polymers are also somewhat red-shifted compared to **P6**. The reason to this behavior is unclear but could be due to a larger degree of close packing of these polymers during spin-coating, which should red-shift the emission.

From Table 2, it is seen that all polymers exhibit very high photoluminescence quantum yields (η_{PL}) in solution. The η_{PL} of the BOP-PPVs (88−89%) were found to be slightly higher than the η_{PL} of the BOPM-PPVs (75−79%). The η_{PL} in film showed the same trend between the polymers. In the solid state, the polymers obtained at lower polymerization temperatures without additional base treatment (**P2** and **P5**) showed the highest η_{PL}, 72% and 51%, respectively. The η_{PL} of **P2** is the highest value for PPVs, measured with an integrating sphere, reported in the literature. Additional base treatment of **P2** at elevated temperature reduced the η_{PL} from 72% to 60%. The same treatment of **P5** reduced the η_{PL} from 51% to 40%. As described in ref 6, polymerization of PPVs at −35 °C leaves some bromine in the final polymers, which can be removed by base treatment at elevated temperatures. The residual bromine gives saturated structures along the polymer backbone, which hinders transport of excited states to nonradiative quenching sites. This explains why the η_{PL} of **P2** and **P5** are higher than for the corresponding polymers with additional base treatment.

The external quantum efficiencies of light-emitting diodes (η_{EL}) of **P1**, **P3**, **P4**, and **P6** are shown in Table 2. From these measurements it is clear that a decreased TBB content is correlated to the η_{EL}. A decreased TBB content for BOP-PPV from 5.8% to 3.5% increases the η_{EL} from 1.23% to 1.34%. This trend is more clear for BOPM-PPV where a decreased TBB content from 2.0% to <1.0% increased the η_{EL} from 0.45% to 1.74%. Recently, it was reported that the lifetime of LEDs, with phenyl-substituted PPVs as the active material, was increased with a lower content of TBB defects. It was shown that a decreased TBB content from 6% to 3% resulted in a lifetime that was 30 times longer.[5,13] This observation is in line of what we see in our diodes. Since a lower polymerization temperature gives a decreased content of TBB defects, a direct comparison of exactly the same polymer with different TBB content is made in this study. The stability measurements of the diodes were made under accelerated conditions at 80 °C. The half-lifetimes of the diodes at these conditions are shown in Table 2. From these values it is clear that a lower TBB content will give polymers that last longer in diodes, although they did not last as long as those described in ref 12. The explanation to this behavior has been given by Becker et al.[13]

Conclusions

This study has shown that it is possible to prepare soluble phenyl-substituted PPVs with a low content of structural defects. The formation of defects can be decreased by either of two ways or by a combination of them; it has been shown that a lower polymerization temperature and/or addition of electron-releasing groups to each repeating unit will lower the concentration of unwanted structural elements in the final polymer. A decreased content of defects yielded polymers that exhibited higher luminescence quantum yields and longer operational lifetimes in diodes.

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