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Synthesis by the Gilch Method of Blue-Light-Emitting Poly(*p*-phenylenevinylene) Derivatives Bearing Highly Phenylated Pendants

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Two novel poly(*p*-phenylenevinylene) (PPV) derivatives bearing highly phenylated side groups with different chemical structures were prepared by Gilch dehydrohalogenation polyaddition. The intermediate substituted 1,4-bis(bromomethyl)benzenes (monomers **6** and **11**) were synthesized by a convenient synthetic route utilizing pyrylium salts. The polymers were amorphous and showed limited solubility in THF, chloroform, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and 1,2-dichlorobenzene. They displayed relatively high T_g values (158−176 °C) and good thermal stability, being stable up to approximately 270−350 °C in N_2 or air and affording anaerobic char yields of 53−56% at 800 °C. The bulky side groups caused a significant steric effect on the PPV backbone and reduced the chromophore length. The solutions of polymers in THF emitted blue light with a maximum around 455 nm. This emission maximum is blue-shifted in comparison with that of other previously synthesized PPVs that emit green to red light. At low temperature, the photoluminescence (PL) spectra of polymers in THF became broader and were extended to longer wavelengths in comparison with the corresponding room-temperature spectra. The PL spectra of thin films of polymers were red-shifted with respect to those of solutions and showed a maximum at 476 nm.

Introduction

Poly(*p*-phenylenevinylene) (PPV) and its derivatives are still one of the most promising classes of conjugated polymers in light-emitting diodes (LEDs). This is mainly due to their high luminescence efficiencies and readiness to polymerize to high molecular weight. PPVs are either produced via a processable precursor polymer or, providing they have suitable solubilizing groups, directly from the respective monomers by dehydrohalogenation.[1] It is interesting to note that the precursor route has been less successful for the formation of PPV derivatives with electron-withdrawing groups attached directly to the phenyl group.[2,3] The most frequently used polymerization method for soluble PPVs is dehydrohalogenation of 1,4-bis(halomethyl)benzenes, known as the Gilch route.[4] This procedure normally yields high molecular weight materials, which gives the PPVs good forming properties.

Various techniques have been proposed to improve the efficiency of LEDs by modifying the chemical structure of the PPVs with bulky side groups or PPV-based alternating copolymers containing conjugated phenylenevinylene segments and nonconjugated spacers.[5−7]

These bulky side groups interrupt conjugation and interfere with the packing of the polymer chain, which results in the formation of amorphous PPVs. Recently, various bulky substituents such as alkoxy, alkylsilyl, phenyl, and fluorenyl groups have been substituted at the 2- or 2,5-positions of the PPV backbone to suppress the intermolecular interactions that lead to the formation of excimers.[8−12] These PPV derivatives showed not only, of course, good solubility in common solvents but also high PL efficiency, even in the solid state, and high LED performance. Another method to improve the efficiency of the devices is the blending system using hole-transporting materials to balance the injected charges.[13−15] However, the use of a polymer blending system in a polymer LED caused some phase separation during the long operation time of the device, which could be detrimental to the device's performance.

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The present investigation deals with the synthesis and characterization of two novel fully conjugated PPVs that carry at the 2-position a bulky highly phenylated side group. These PPVs were prepared via the Gilch method from substituted 1,4-bis(bromomethyl)benzenes. The latter were synthesized by a convenient synthetic route utilizing pyrylium salts. Recently, various photonic polymers have been synthesized in our laboratory through pyrylium salts.[16–18] The present PPVs contained a side substituent with four or five phenyl rings per each repeat unit. In addition, this side substituent carried three long and branched alkoxy groups to enhance the solubility of polymers. The preparation of these polymers is part of our effort for production of fully conjugated PPVs with bulky pendants that emit blue light. The bulky pendants interrupted the conjugation in the PPV backbone and reduced the chromophore length. Thus, these modified PPVs emitted blue light in contrast to the other PPVs that emit at longer wavelengths. Very recently, we have synthesized by Heck coupling and with use of pyrylium salts two soluble, blue-light-emitting fully conjugated PPVs that carry at the 2,5-positions of the PPV backbone two highly phenylated side groups.[19]

Experimental Section

Characterization Methods. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ^{1}H NMR (400 MHz) spectra were obtained using a Brucker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. The PL spectra were obtained with a Perkin-Elmer LS45 luminescence spectrometer. GPC analysis was conducted with a Waters Breeze 1515 series liquid chromatograph equipped with a differential refractometer (Waters 2410) as a detector using polysterene as a standard and THF as an eluent. DSC and TGA were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA and the weight loss comparisons were made between comparable specimens. The DSC thermograms were obtained at a heating rate of 10 °C/min in a N_2 atmosphere at a flow rate of 60 cm^3/min. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 10 °C/min in N_2 with a flow rate of 60 cm^3/min. The TMA experiments were conducted at least in duplicate to ensure the accuracy of the results. The TMA specimens were pellets of 8-mm diameter and 2-mm thickness prepared by pressing powder of polymer for 3 min under 5–7 kpsi at ambient temperature. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

To measure the PL quantum yields (Φ_f), a degassed solution of polymer in THF was prepared. The concentration was adjusted so that the absorbance of the solution would be lower than 0.1. The excitation was performed at the corresponding $\lambda_{ex,max}$ and a solution in 1 N H_2SO_4 of quinine sulfate, which has a Φ_f of 0.546 ($\lambda_{ex} = 365$ nm), was used.

Reagents and Solvents. 2,5-Dimethylphenol and 4-methoxyacetophenone were recrystallized from EtOH/diethyl ether

and diethyl ether/petroleum ether, respectively. 4-Methoxyphenylacetic acid sodium salt was prepared by the reaction of equimolar amounts of 4-methoxyphenylacetic acid with aqueous sodium hydroxide and subsequent fusing. Dimethylacetamide (DMAc), 1,2-dichloroethane, and tetrahydrofuran (THF) were dried by distillation over CaH_2. *N*-Bromosuccinimide (NBS) was rapidly recrystallized from boiling distilled water. All other solvents and reagents were analytical-grade quality, purchased commercially, and used without further purification.

Preparation of Monomers and Polymers. *4-(2,5-Dimethylphenoxy)benzaldehyde (**1**).* A flask was charged with a mixture of 2,5-dimethylphenol (1.48 g, 11.75 mmol), 4-fluorobenzaldehyde (1.75 g, 14.10 mmol), K_2CO_3 (3.25 g, 23.5 mmol), and DMAc (10 mL). The mixture was stirred and refluxed overnight under N_2. It was subsequently concentrated under reduced pressure and water was added to the concentrate. The precipitate was extracted with chloroform. The organic layer was washed with water, dried (MgSO$_4$), and concentrated to afford **1** as a brownish liquid (2.54 g, yield 96%).

IR (KBr, cm^{-1}): 2924, 2858 (C–H stretching of methyl groups); 1694 (C=O); 1600, 1580, 1502 (aromatic); 1254, 1228, 1156 (ether bond).
^{1}H NMR (CDCl$_3$, δ): 10.02 (s, 1H, CHO); 7.60–6.55 (m, 7H, aromatic); 2.25–2.18 (m, 6H, CH$_3$).

*4-[4-(2,5-Dimethylphenoxy)phenyl]-2,6-di(4-methoxyphenyl)-pyrylium tetrafluoroborate (**2**).* Boron trifluoride etherate (3.5 mL, 28.10 mmol) was added to a stirred mixture of **1** (2.54 g, 11.24 mmol), 4-methoxyacetophenone (3.37 g, 22.48 mmol), and 1,2-dichloroethane (20 mL). The mixture was stirred and refluxed for 4 h under N_2. It was subsequently concentrated under reduced pressure, and ethanol 95% was added to the concentrate. The precipitate was isolated by filtration and stirred into water for 3 h. Then, it was filtered and dried to afford **2** as an indian red solid. It was recrystallized from chloroform/diethyl ether (3.31 g, yield 51%, mp 80–82 °C).

IR (KBr, cm^{-1}): 2922, 2835 (C–H stretching of methyl and methoxy groups); 1620, 1600, 1506, 1462, 1440 (pyrylium and aromatic structure); 1258, 1174 (ether bond); 1028 (BF$_4^-$).
^{1}H NMR (CDCl$_3$, δ): 8.16–7.95 (m, 2H, aromatic *meta* to O$^+$); 7.52–6.57 (m, 15H, other aromatic); 3.80 (m, 6H, OCH$_3$); 2.31–2.18 (m, 6H, CH$_3$).

*4-Methoxy-2′,6′-di(4-methoxyphenyl)-4′′-(2,5-dimethylphenoxy)-p-terphenyl (**3**).* A mixture of **2** (1.98 g, 3.43 mmol), 4-methoxyphenylacetic acid sodium salt (1.29 g, 6.87 mmol), and acetic anhydride (5 mL) was stirred and refluxed for 4 h. It was subsequently cooled in a refrigerator overnight and the precipitate was filtered, washed with methanol, and dried to afford **3** as a pale brown solid. It was recrystallized from carbon tetrachloride/*n*-hexane (0.25 g, yield 13%, mp 103–105 °C).

IR (KBr, cm^{-1}): 2930, 2836 (C–H stretching of methyl and methoxy groups); 1600, 1576, 1506, 1458 (aromatic); 1252, 1220, 1170 (ether bond).
^{1}H NMR (CDCl$_3$, δ): 7.57–7.04 (m, 12H, aromatic except those *ortho* to O); 6.97–6.92 (m, 9H, aromatic *ortho* to O); 3.82 (m, 9H, OCH$_3$); 2.30–2.17 (m, 6H, CH$_3$).

*4-Hydroxy-2′,6′-di(4-hydroxyphenyl)-4′′-(2,5-dimethylphenoxy)-p-terphenyl (**4**).* Compound **3** (0.94 g, 1.63 mmol) was dissolved in glacial acetic acid (20 mL) upon heating. Aqueous hydrobromic acid 47% (5 mL) was added in portions over a period of 20 h. Refluxing was continued for an additional 4 h. The mixture was subsequently concentrated under reduced pressure and water was added to the concentrate. The brown precipitate was filtered, washed with water, and dried to afford **4**. It was recrystallized from EtOH/water (0.83 g, yield 92%, mp 115–117 °C).

IR (KBr, cm^{-1}): 3370 (OH stretching); 2922, 2834 (C–H stretching of methyl groups); 1600, 1502, 1456 (aromatic); 1254, 1220, 1168 (ether bond and C–OH stretching).
^{1}H NMR (DMSO-d_6, δ): 9.30 (br, 3H, OH); 7.58–7.05 (m, 12H, aromatic except those *ortho* to O); 6.93–6.88 (m, 9H, aromatic *ortho* to O); 2.28–2.19 (m, 6H, CH$_3$).

*4-[(2′-Ethylhexyl)oxy]-2′,6′-di[4-(2′-ethylhexyl)oxy]phenyl-4′′-(2,5-dimethylphenoxy)-p-terphenyl (**5**).* A mixture of **4** (0.81 g,

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1.47 mmol), 2-ethylhexylbromide (0.94 g, 4.85 mmol), K_2CO_3 (0.81 g, 5.88 mmol), and DMAc (8 mL) was stirred and refluxed for 24 h under N_2. Then, it was concentrated under reduced pressure, and methanol was added to the concentrate. The precipitate was filtered, washed with methanol, and dried to afford **5**. It was recrystallized from carbon tetrachloride/*n*-hexane (1.05 g, yield 80%, mp 73–75 °C).

IR (KBr, cm^{-1}): 2956, 2926, 2858 (C–H stretching of aliphatic segments); 1604, 1576, 1504, 1460 (aromatic); 1252, 1168 (ether bond).

^{1}H NMR (DMSO-d_6, δ): 7.60–7.00 (m, 12H, aromatic except those *ortho* to O); 6.97–6.92 (m, 9H, aromatic *ortho* to O); 2.27–2.18 (m, 6H, CH_3); 3.47, 1.35, 0.89 (m, 51H, aliphatic segments).

*4-[(2′-Ethylhexyl)oxy]-2′,6′-di[4-(2′-ethylhexyl)oxy]phenyl-4″-[2,5-bis(bromomethyl)phenoxy]-p-terphenyl (**6**).* To a solution of **5** (0.42 g, 0.47 mmol) in carbon tetrachloride (20 mL) were added NBS (0.17 g, 0.99 mmol) and azobis(isobutyronitrile) as an initiator. The reaction mixture was heated to reflux for 4 h under N_2. The completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution. The latter was filtered and the filtrate was concentrated. Ethanol was added to the concentrate and the yellow-brown precipitate was filtered, washed with ethanol, and dried to afford **6**. It was recrystallized from carbon tetrachloride/*n*-hexane (0.28 g, yield 57%, mp 96–98 °C).

IR (KBr, cm^{-1}): 2956, 2926, 2860 (C–H stretching of aliphatic segments); 1602, 1504, 1460 (aromatic); 1252, 1170 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.62–7.36 (m, 12H, aromatic except those *ortho* to O); 6.98–6.92 (m, 9H, aromatic *ortho* to O); 4.47 (m, 4H, CH_2Br); 3.46, 1.34, 0.90 (m, 51H, aliphatic segments).

Anal. Calcd for $C_{62}H_{76}Br_2O_4$: C, 71.26; H, 7.33. Found: C, 70.87; H, 7.35.

*Polymer **P1**.* Compound **6** (0.34 g, 0.32 mmol) was dissolved in anhydrous THF (8 mL). To this stirred solution was added dropwise 1.3 mL of 1.0 M solution of potassium *tert*-butoxide (1.3 mmol) in anhydrous THF at room temperature. The mixture was stirred at ambient temperature for 8 h under N_2. The viscous mixture was then poured into 50 mL of stirred methanol. The resulting orange-yellow precipitate was collected by filtration and washed with methanol. The solid powder was extracted with chloroform overnight. After removal of the solvent, the final polymer was dried under vacuum to afford polymer **P1** (0.12 g, yield 42%). The number-average molecular weight was 28 000, and the polydispersity index was 3.0 (by GPC).

IR (KBr, cm^{-1}): 2956, 2926, 2857 (C–H stretching of aliphatic segments); 1602, 1504, 1460 (aromatic); 1246, 1170 (ether bond); 963 (HC=CH trans).

^{1}H NMR (DMSO-d_6, δ): 7.63–7.05 (m, 12H, aromatic except those *ortho* to O and 2H, HC=CH); 6.97–6.93 (m, 9H, aromatic *ortho* to O); 3.50, 1.35, 0.87 (m, 51H, aliphatic segments).

Anal. Calcd for $(C_{62}H_{74}O_4)_n$: C, 84.31; H, 8.44. Found: C, 83.76; H, 8.48.

*2,6-Bis(4-methoxyphenyl)-4-(2,5-dimethylphenyl)pyrylium tetrafluoroborate (**7**).* Boron trifluoride etherate (6.5 mL, 51.75 mmol) was added to a stirred mixture of 2,5-dimethylbenzaldehyde (2.81 g, 20.70 mmol), 4-methoxyacetophenone (6.23 g, 41.4 mmol), and 1,2-dichloroethane (20 mL). The mixture was stirred and refluxed for 17 h under N_2. It was subsequently concentrated under reduced pressure, and ethanol 95% was added to the concentrate. The brown precipitate was isolated by filtration and stirred into water for 3 h. Then, it was filtered, dried, and extracted with boiling ether for 1 h (2.60 g, yield 26%, mp 236–238 °C).

IR (KBr, cm^{-1}): 2950, 2832 (C–H stretching of methyl and methoxy groups); 1619, 1600, 1514, 1476, 1459 (pyrylium and aromatic structure); 1260, 1216, 1180 (ether bond); 1060 (BF_4^-).

^{1}H NMR (CDCl$_3$, δ): 8.18–7.96 (m, 2H, aromatic *meta* to O$^+$); 7.54–7.10 (m, 7H, aromatic except those *ortho* to O); 6.97 (m, 4H, aromatic *ortho* to O); 3.83 (m, 6H, OCH$_3$); 2.38–2.30 (m, 6H, CH_3).

*4-Methoxy-2′,6′-di(4-methoxyphenyl)-3″,6″-dimethyl-p-ter-phenyl (**8**).* A mixture of **7** (1.08 g, 2.23 mmol), 4-methoxyphenylacetic acid sodium salt (0.84 g, 4.46 mmol), and acetic anhydride (4 mL) was stirred and refluxed for 4 h. Compound **8** was obtained as a whitish solid according to the procedure described for **3**. It was recrystallized from carbon tetrachloride/*n*-hexane (0.22 g, yield 20%, mp 178–180 °C).

IR (KBr, cm^{-1}): 2950, 2834 (C–H stretching of methyl and methoxy groups); 1610, 1510, 1454 (aromatic); 1290, 1244, 1176 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.36–7.02 (m, 11H, aromatic except those *ortho* to O); 6.78 (m, 6H, aromatic *ortho* to O); 3.76–3.73 (m, 9H, OCH$_3$); 2.39–2.36 (m, 6H, CH_3).

*4-Hydroxy-2′,6′-di(4-hydroxyphenyl)-3″,6″-dimethyl-p-ter-phenyl (**9**).* Compound **9** was prepared as a brownish solid according to the procedure described for **4**. It was recrystallized from EtOH/water (yield 90%, mp 185–187 °C).

IR (KBr, cm^{-1}): 3366 (OH stretching); 2924, 2833 (C–H stretching of methyl groups); 1610, 1512, 1440 (aromatic); 1255, 1232, 1172 (ether bond and C–OH stretching).

^{1}H NMR (DMSO-d_6, δ): 9.32 (br, 3H, OH); 7.38–7.03 (m, 11H, aromatic except those *ortho* to O); 6.87 (m, 6H, aromatic *ortho* to O); 2.40–2.34 (m, 6H, CH_3).

*4-[(2′-Ethylhexyl)oxy]-2′,6′-di[4-(2′-ethylhexyl)oxy]phenyl-3″,6″-dimethyl-p-terphenyl (**10**).* Compound **6** was prepared as a brown solid according to the procedure described for **5**. It was recrystallized from THF/*n*-hexane (yield 81%, mp 86–88 °C).

IR (KBr, cm^{-1}): 2958, 2926, 2860 (C–H stretching of aliphatic segments); 1608, 1510, 1458 (aromatic); 1242, 1176 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.48–7.05 (m, 11H, aromatic except those *ortho* to O); 6.98 (m, 6H, aromatic *ortho* to O); 2.41–2.36 (m, 6H, CH_3); 3.46, 1.32, 0.90 (m, 51H, aliphatic segments).

*4-[(2′-Ethylhexyl)oxy]-2′,6′-di[4-(2′-ethylhexyl)oxy]phenyl-3″,6″-bisbromomethyl-p-terphenyl (**11**).* Following the synthetic procedure described for **6**, compound **11** was prepared as a brownish solid. It was purified by chromatography on a silica column using ethyl acetate as eluent (yield 45%, mp 122–124 °C).

Anal. Calcd for $C_{56}H_{72}Br_2O_3$: C, 70.58; H, 7.62. Found: C, 70.16; H, 7.59.

IR (KBr, cm^{-1}): 2958, 2926, 2858 (C–H stretching of aliphatic segments); 1608, 1510, 1460 (aromatic); 1244, 1176 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.52–7.06 (m, 11H, aromatic except those *ortho* to O); 6.97 (m, 6H, aromatic *ortho* to O); 4.45 (m, 4H, CH_2Br); 3.48, 1.35, 0.90 (m, 51H, aliphatic segments).

*Polymer **P2**.* Polymer **P2** was prepared as an orange-yellow powder in 48% yield according to the procedure described for polymer **P1**. The number-average molecular weight was 24 000, and the polydispersity index was 2.7 (by GPC).

The IR spectral data of **P2** are given in the Results and Discussion section. For ^{1}H NMR spectrum of **P2** see Figure 1.

Anal. Calcd for $(C_{56}H_{70}O_3)_n$: C, 85.01; H, 8.92. Found: C, 84.92; H, 8.87.

Results and Discussion

Synthesis and Characterization of Polymers. As shown in Schemes 1 and 2 the intermediate substituted 1,4-bis(bromomethyl)benzenes **6** and **11** were prepared through pyrylium salts. The key step of the synthetic route was the preparation of the pyrylium salts by reacting an aromatic aldehyde with 4-methoxyacetophenone in the presence of boron trifluoride etherate.[20,21] They reacted subsequently with 4-methoxyphenylacetic

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Scheme 1
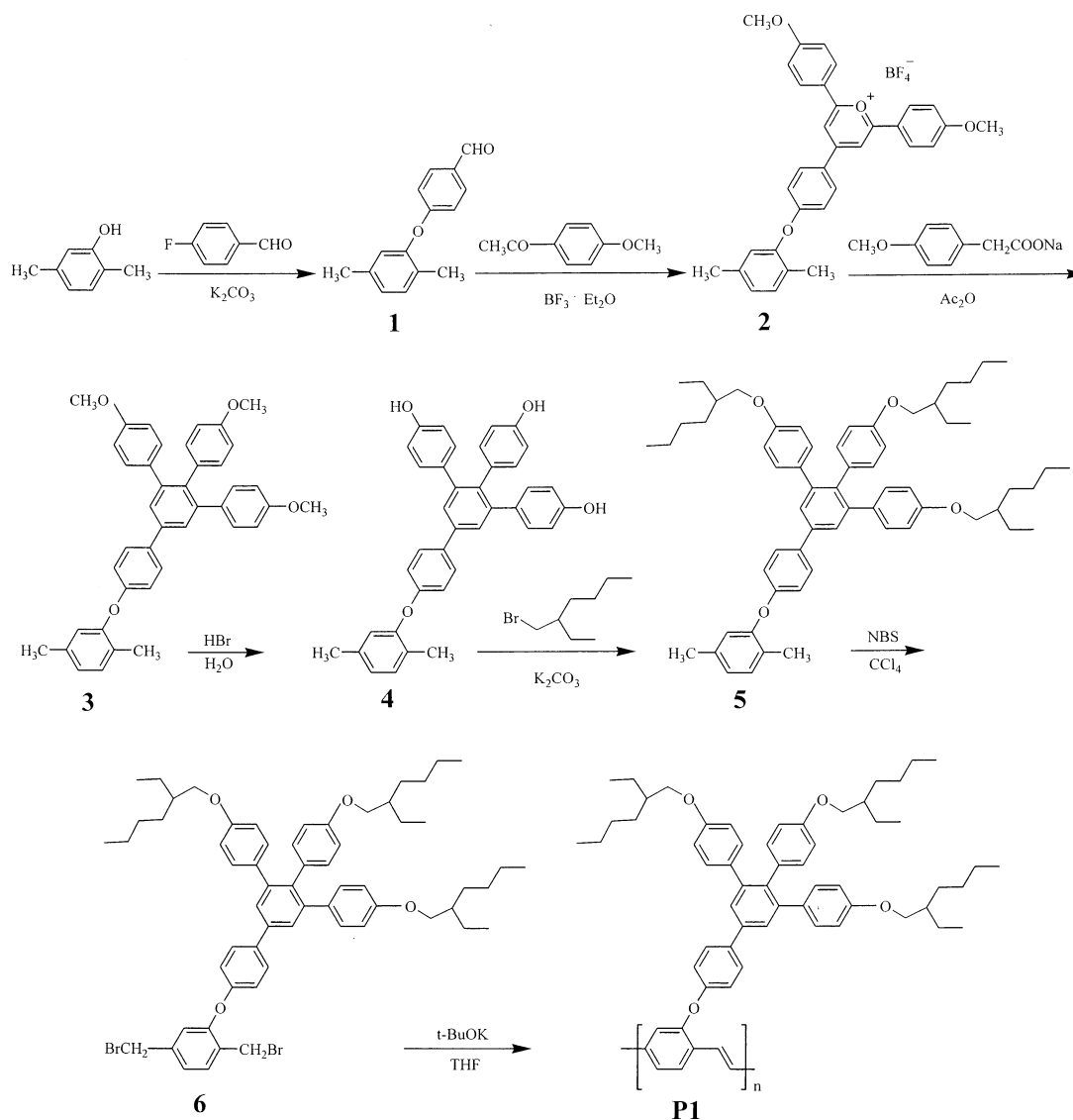
anhydride, generated in situ from 4-methoxyphenylace-tic acid sodium salt and acetic anhydride, to yield aromatic compounds with multiple phenyl rings.[22] The methoxy groups of the latter were hydrolyzed by means of aqueous hydrobromic acid to the corresponding phenols.[23] These reacted with a branched aliphatic bromide in the presence of potassium carbonate to afford the alkoxy derivatives. The bromination of the substituted *p*-xylenes to the corresponding 1,4-bis(bromomethyl)-benzenes was carried out with *N*-bromosuccinimide in carbon tetrachloride using azobis(isobutyronitrile) as a radical initiator.[24]

Monomers **6** and **11** were easily polymerized to the corresponding **P1** and **P2** polymers with potassium *tert*-butoxide (4.0 equiv) in THF at room temperature according to the standard Gilch method (Schemes 1 and 2). This method requires the use of excess strong alkali to ensure the formation of the fully eliminated structure.

Therefore, the base acts not only as a condensing agent but also as a dehydrobrominating agent. The reaction solution became progressively viscous as well as perfectly homogeneous without any precipitates. The polymers were isolated in 42−48% yields by pouring the mixture into a nonsolvent (methanol). GPC analysis with polystyrene as the standard for calibration revealed that the number-average molecular weight (M_n) of the polymers were 24 000−28 000 with a polydispersity index of 2.7−3.0. Although the molecular weights are generally overestimated by the calibration of polystyrene standards[25] owing to the stiffness of the conjugated polymers, such as PPV derivatives, the results indicated that the polymers had relatively high molecular weight.

The structure of the polymers was identified by FT-IR and[1]H NMR spectroscopy. The FT-IR spectrum of polymer **P2** was compared with that of the substituted 1,4-bis(bromomethyl)benzene **11**. In particular, **P2** showed characteristic absorption bands at 2958, 2928, 2870 (C−H stretching of aliphatic segments); 1608,

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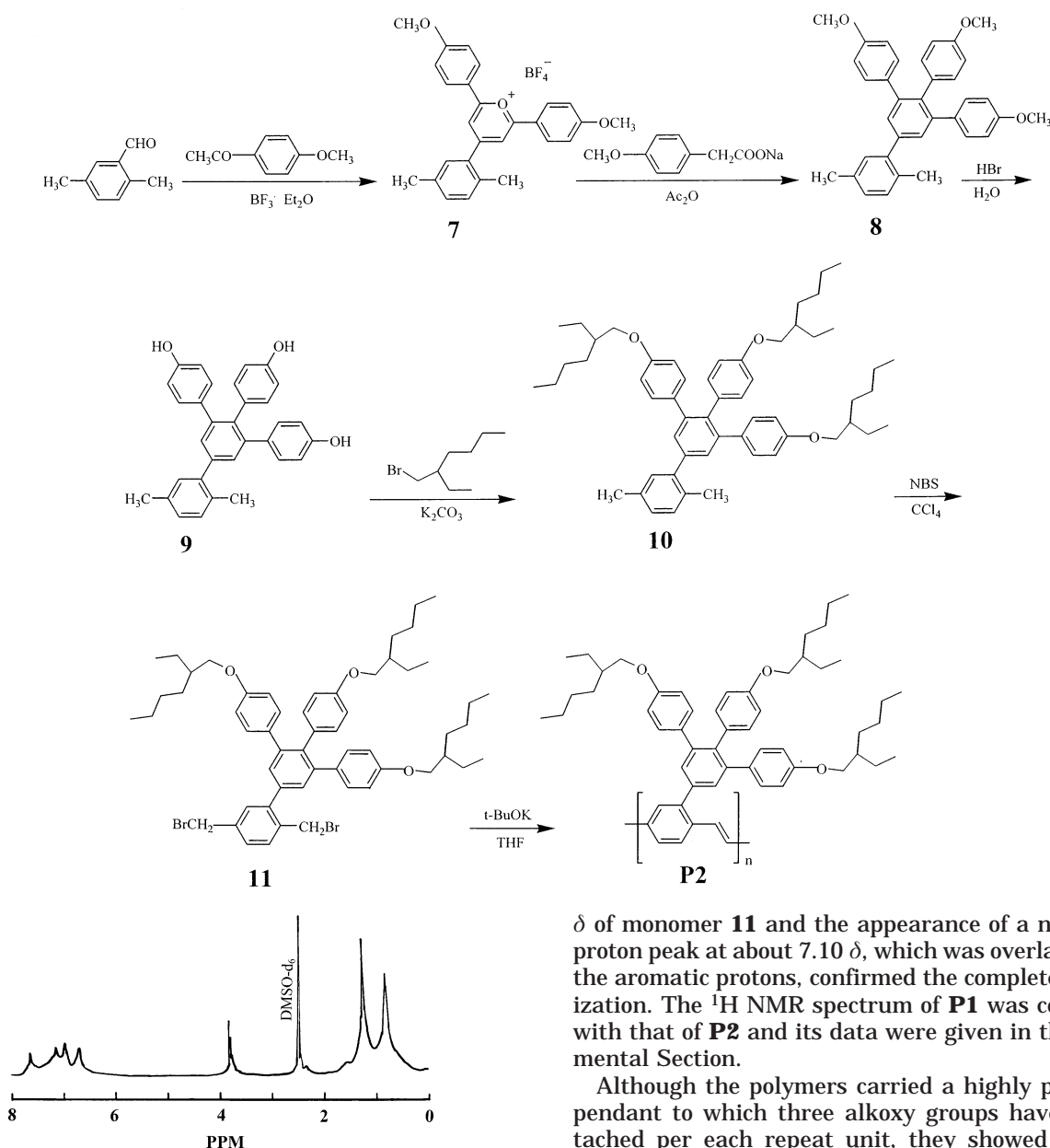(25) Kreyenschmidt, M.; Uckert, F.; Müllen, K. *Macromolecules* **1995**, *28*, 4577.

Scheme 2

Figure 1. ^{1}H NMR spectrum of polymer **P2** in DMSO-d_6 solution.

1510, 1456 (aromatic); 1242, 1176 (ether bond) and 962 cm^{-1} (HC=CH trans). The spectrum of **11** was very similar but did not display any absorption at about 962 cm^{-1} that was assigned to the out-of-plane deformation of the trans vinylene moiety. This suggested that the vinylene group formed through the Gilch route was in trans configuration. When **P2** was subjected to annealing at 200 °C for 6 h under reduced pressure (ca. 12 mmHg), the relative intensity of the band at 962 cm^{-1} was not significantly increased. The result indicated that no additional double bonds were formed when the polymer was thermally treated.

The ^{1}H NMR spectrum of **P2** in DMSO-d_6 solution (Figure 1) displayed peaks at 7.68−6.99 (m, 11H, aromatic except those *ortho* to O and 2H, HC=CH), 6.71 (m, 6H, aromatic *ortho* to O), 3.77 (d, 6H, OCH$_2$), 1.27 and 0.86 (m, 45H, other aliphatic). The disappearance of the characteristic benzylic proton peak around 4.45

δ of monomer **11** and the appearance of a new vinylic proton peak at about 7.10 δ, which was overlapped with the aromatic protons, confirmed the complete polymerization. The ^{1}H NMR spectrum of **P1** was comparable with that of **P2** and its data were given in the Experimental Section.

Although the polymers carried a highly phenylated pendant to which three alkoxy groups have been attached per each repeat unit, they showed a limited solubility in common organic solvents such as THF, chloroform, 1,2-dichloroethane, 1,1,2,2-tetrachloroethane, and 1,2-dichlorobenzene. Polymer **P1** was less soluble than **P2** obviously due to the introduction of the diphenyl ether moiety. It should be noted that the parent dibromides **6** and **11** were readily soluble in common organic solvents.

The WAX-ray diffractograms for powder specimens of polymers revealed their amorphous character. Such a behavior was expected because the polymers possessed a stiff conjugated backbone as well as bulky and noncoplanar highly phenylated side groups that hindered the chain packing. Despite their amorphous nature, the polymers displayed a limited solubility in common organic solvents, as was mentioned above, attributable to the PPV backbone.

Thermal and thermomechanical characterization of polymers was accomplished by DSC, TMA and TGA. The DSC traces of polymers showed during the first heating a broad endotherm around 100 °C assigned to the evaporation of specimen moisture. In contrast, they

Table 1. T_g Values and Thermal Stability of Polymers

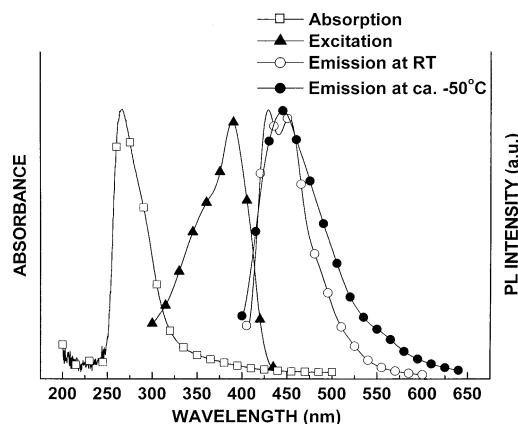| polymer	$T_g{}^a$ (°C)	in N$_2$			in air	
		$T_1{}^b$ (°C)	$T_{10}{}^b$ (°C)	$Y_c{}^c$ (%)	$T_1{}^b$ (°C)	$T_{10}{}^b$ (°C)
P1	158	336	415	53	267	347
P2	176	351	456	56	310	437

^{a} T_g: glass transition temperature determined by the TMA method. ^{b} T_1, T_{10}: temperatures at which weight loss of 1 and 10%, respectively, was observed by TGA. ^{c} Y_c: char yield at 800 °C by TGA.
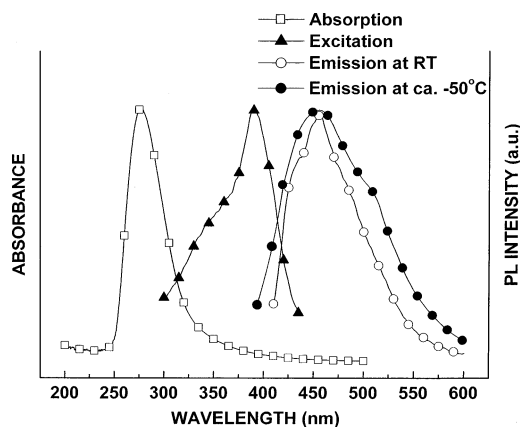
Figure 2. Absorption and PL excitation spectra as well as PL spectra at room temperature and at low temperature (ca. −50 °C) of polymer **P1** in THF solution.

did not exhibit any transition during the second heating. The absence of melting endotherm confirmed the amorphous character of polymers. Note that the T_g's of the related PPVs, that have been prepared in our laboratory by Heck coupling,[19] could also not be detected by DSC. The T_g transitions of the present polymers were clearly recorded by the TMA method using a loaded penetration probe (Table 1). The T_g is assigned by the first inflection point in the TMA curve and it was obtained from the onset temperature of this transition during the second heating. Polymer **P1** showed lower T_g (158 °C) than **P2** (176 °C), owing to the flexible diphenyl ether bond that decreased the rigidity of the side chain. In addition, polymer **P1** carried longer side groups than **P2,** which increased the free volume of this polymer. Generally, the relatively high T_g values of the present polymers in comparison with those of other PPVs constituted an additional advantage since the lifetime of EL devices is directly analogous to the T_g's and thermal stability of the polymers utilized.[26,27]

Certain TGA data for both polymers are listed in Table 1. The polymers showed a relatively high initial decomposition temperature being stable up to approximately 270−350 °C in N$_2$ and air. However, their anaerobic char yield (Y_c) at 800 °C was slightly low (53−56%) due to the presence of the three long alkoxy groups per each repeat unit. Polymer **P2** was more thermally stable than **P1** and it can be seen from Table 1 that all its TGA data were higher than those of **P1**.

Optical Properties of Polymers. Figures 2−4 depict the UV−vis and the PL excitation (PLE) spectra as well as the PL spectra of polymers both in THF

(26) Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* **1997**, *70*, 1929.
(27) Fink, R.; Heischkel, Y.; Thelakkat, M.; Schmidt, H. *Chem. Mater.* **1998**, *10*, 3620.

Figure 3. Absorption and PL excitation spectra as well as PL spectra at room temperature and at low temperature (ca. −50 °C) of polymer **P2** in THF solution.
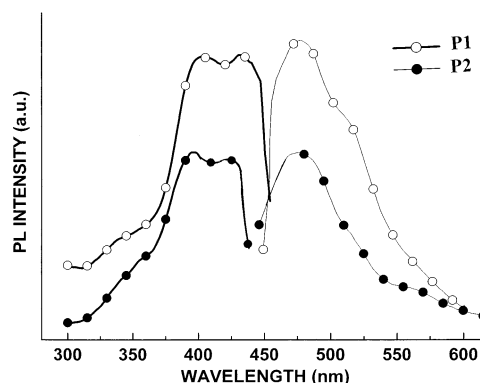
Figure 4. PL excitation spectra (bold line) and PL spectra (thin line) in thin films of polymers **P1** and **P2**.

solution and in thin films. Table 2 summarizes the spectroscopic data obtained from these Figures.

The UV−vis spectra of **P1** and **P2** in THF showed maximum ($\lambda_{a,max}$) at 277 and 267 nm, respectively, originating from the aromatic side chain. It is well-established that in PPVs the $\pi−\pi^*$ absorption of the conjugated polymer main chain appears at longer wavelength. In the present case, the absorption position of the backbone $\pi−\pi^*$ transition was blue-shifted. This was attributed to the bulky side substituents which disrupted the coplanarity of the π-conjugated backbone and caused a partial destruction of the π-delocalization along the backbone.[28] It seems from Figures 2 and 3 that the UV−vis curves of both polymers were rather broad at the longer wavelength side due to the $\pi−\pi^*$ transitions of the conjugated backbone. However, the absorption of this transition was not clear since a shoulder did not appear at the right side of the UV−vis curve, as usually occurs in other related polymers. Note that the UV−vis spectra of the intermediate bis(bromomethyl) monomers **6** and **11** showed comparable $\lambda_{a,max}$ but lacked the broadening at the right side of the curve.

The UV−vis spectra of polymers were not strongly dependent on thermal history. In particular, they remained almost unchanged following annealing at 200 °C for 6 h under vacuum. As was mentioned above,

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Table 2. UV−Vis, PLE, and PL Data of Polymers

polymer	$\lambda_{a,max}$[a] in solution (nm)	$\lambda_{ex,max}$[b] in solution (nm)	$\lambda_{f,max}$[c,d] in solution at RT (nm)	$\lambda_{f,max}$[c,d] in solution at ca. −50 °C (nm)	Φ_f[e] in solution	$\lambda_{ex,max}$[b] in thin film (nm)	$\lambda_{f,max}$[c] in thin film (nm)
P1	277	390	455	<u>455</u>, 514	0.12	402, 431	476
P2	267	388	428, <u>452</u>	453	0.10	397, 425	476

[a] $\lambda_{a,max}$: the absorption maxima from the UV−vis spectra in THF solution. [b] $\lambda_{ex,max}$: the PL excitation maxima in THF solution or in thin film. [c] $\lambda_{f,max}$: the PL maxima in THF solution or in thin film. [d] Underlined numerical values denote absolute maxima. [e] Φ_f: PL quantum yields.

neither the FT-IR spectra of polymers changed considerably after this annealing.

The PLE spectra of polymers in THF displayed maximum ($\lambda_{ex,max}$) near 390 nm and a shoulder at about 340 nm, assigned to the conjugated backbone and the aromatic side chain, respectively. This was substantiated from the fact that the intermediate bis(bromomethyl) monomers **6** and **11** showed in THF $\lambda_{ex,max}$ approximately at 340 nm. The $\lambda_{ex,max}$ was red-shifted in comparison with the $\lambda_{a,max}$. However, the broad right side of the absorption curve, which is associated with the $\pi-\pi^*$ transition of the polymer backbone, overlaps with the PLE curve. The PLE spectra of polymers were recorded for emitting wavelengths of maximum fluorescence intensities.

The PL spectra of polymers in THF exhibited maximum ($\lambda_{f,max}$) around 455 nm, which is located in the blue-light region, upon excitation at the corresponding $\lambda_{ex,max}$. The wavelength ranges of the emitted light by the two polymers were comparable with **P1** emitting light in the slightly longer wavelength. The PL spectrum of **P2** was composed of well-resolved vibronic bands which appeared at 428 and 452 nm. It is well-known that the fully conjugated PPVs show $\lambda_{f,max}$ in a longer wavelength range and emit green to red light. In the present case, the bulky side chains caused significant steric effects on the backbone and reduced the effective conjugation length, as was mentioned above. Thus, these polymers emitted blue light, even though they carried a PPV main chain. This behavior conforms with our previous data obtained from related PPVs that have been derived by Heck coupling.[19] Hsieh et al.[10] as well as Peng et al.[12] have synthesized fully conjugated PPVs with 2,3-diphenyl or 2-biphenylyl side substituents that emerged emission peaks at 488 and 490 nm, respectively.

The PL spectra of polymers in THF obtained at low temperature (ca. −50 °C) are compared with those obtained at room temperature in Figures 2 and 3. It seems that the former were broader and extended mainly to the longer wavelength region. Furthermore, **P1** displayed at low temperature a new shoulder at about 514 nm. This behavior observed at low temperature was ascribed to the reduction of the rotation between the adjacent phenyls that increased the conjugation length.[29]

The polymers exhibited relatively low emission efficiency in THF solution since their PL quantum yields,

which were determined[30] relative to quinine sulfate, were 0.10−0.12 (Table 2). It has been reported that PPVs bearing bulky side substituents prevented close chain packing and increased the PL and EL efficiency.[10,12] The reasons for the relatively low PL efficiency of the present polymers cannot be detected.

Finally, the optical properties of thin films of polymers that were prepared by spin-casting were investigated (Figure 4). Their PLE spectra were broad with two peaks around 400 and 430 nm. The PL spectra of films exhibited $\lambda_{f,max}$ at 476 nm for both polymers. This maximum was red-shifted by approximately 20 nm in comparison with that of solutions, due to the formation of aggregates.

Conclusions

Two new substituted 1,4-bis(bromomethyl)benzenes **6** and **11** were synthesized through pyrylium salts and were polymerized by the Gilch method to afford the PPV derivatives **P1** and **P2**, respectively. They contain a highly phenylated pendant at the 2-position to which three alkoxy groups were attached. The polymers were amorphous and showed a limited solubility in common organic solvents. Their initial decomposition temperature in N_2 and air was relatively high (270−350 °C) but the anaerobic char yield at 800 °C was slightly low (53−56%). The chemical structure of the pendant influenced the T_g values of polymers which ranged from 158 to 176 °C. The polymers behaved as blue-light emitting materials in THF solution with a PL maximum near 455 nm. This value is one of the bluest emission peaks that have been reported for a fully conjugated PPV. The PL spectra of polymers in THF were red-shifted when they were obtained at low temperature. The PL quantum yields in THF were rather low (0.10−0.12). Thin films of polymers emitted at 476 nm, indicating the formation of aggregates.

Supporting Information Available: FT-IR spectrum of polymer **P2** and monomer **11** (Figure S1). TGA traces in N_2 and air of polymer **P2** (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 6756.

(30) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991. There are not any toxicity data for the synthesized compounds. Therefore, due to the fact that toxicity is not known, these compounds should be treated as toxic.