Synthesis by Heck Coupling of Soluble, Blue-Light-Emitting Fully Conjugated Poly(*p*-phenylenevinylene)s with Highly Phenylated Side Groups

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ABSTRACT: Two new fully conjugated poly(*p*-phenylenevinylene)s (PPVs) were prepared by Heck coupling between *p*-divinylbenzene and two dibromides. The latter were synthesized by a six-step synthetic route using pyrylium salts. The polymers carried on the same phenyl ring two side oligophenyls per each repeat unit with various chemical structures. These polymers were amorphous and showed an excellent solubility being soluble in common organic solvents (THF, chloroform, methylene chloride, 1,2-dichloroethane). No weight loss was observed approximately up to 320−370 °C in N_2 or air, and the anaerobic char yield was around 80% at 800 °C. The T_g values ranged from 106 to 122 °C, and they could be controlled by the chemical structure of the side substituents. The polymers behaved as strongly blue-light-emitting materials in THF solution with PL maximum at 453 or 461 nm. These values are among the bluest emission peaks that have been reported for a fully conjugated PPV. The bulky side oligophenyls caused significant steric hindrance which interrupted the conjugation in the PPV backbone. At low temperature, the PL maximum in THF was red-shifted by 2−10 nm in comparison with the respective room temperature spectra. The red shift was greater for the polymer that carried longer side oligophenyls. The bulky side oligophenyls hindered chain interactions, and the polymer displayed little tendency for aggregate formation. The PL quantum yields in THF were 0.24−0.31.

Introduction

Poly(*p*-phenylenevinylene) (PPV) and its derivatives remain the most interesting and promising conjugated polymers for fabrication of light-emitting diodes (LEDs).[1] Since PPV is insoluble, to improve processability, flexible side chains such as alkoxy[2,3] have been introduced on the aromatic rings of the main chain. In addition, the structure of the PPV was modified to tune the wavelength of the emitted light. This has been achieved by controlling the conjugation length of the main chain to provide polymers emitting light from blue to orange yellow[2−5] and by introducing electron-withdrawing groups such as halogen,[6−9] nitro,[10,11] and cyano,[12,13] or electron-donating groups such as alkoxy groups[2−4] on the aromatic rings to give blue shift and red shift, respectively. Furthermore, electron-withdrawing groups such as cyano[14,15] have been introduced on the vinylene moiety to afford polymers that emitted visible light at longer wavelength and particularly red light. Block copolymers have been also synthesized for color tuning.[16]

Although a wide variety of PPV derivatives have been synthesized and used in LED applications, very few have shown high photoluminescence (PL) and electroluminescence (EL) efficiencies. This has been attributed to the fact that conjugated backbones tend to stack with each other due to interchain $\pi-\pi$ interactions which lead to a self-quenching process of excitons.[17,18] To overcome this problem, bulky aromatic substituents have been attached to the PPV backbone to prevent its close packing and therefore increase its PL efficiency.[19,20]

The present investigation deals with the synthesis and characterization of two new fully conjugated PPVs that carried on the same phenyl ring two highly phenylated side groups per each repeat unit. Specifically, these two side substituents contained different number of phenyl rings for each of the synthesized polymers in order to study the influence of their chemical structure on the polymer properties. To enhance the polymer solubility, a 2-ethylhexyl group was attached to the side oligophenyls. The polymers were synthesized by a convenient synthetic route through pyrylium salts. *p*-Xylene, a common and inexpensive compound, was used as starting material. This synthetic route can be applied for the preparation of other related polymers. The pyrylium salts have been used in our laboratory for the preparation of photonic polymers.[21−23]

The optical properties of these new polymers were of primary importance for our purpose, and they were studied in both solution and solid state. The polymers consisted of a PPV backbone that carried side oligophenyls. These polymers behaved as strongly blue-light-emitting materials. As was mentioned above, most of the synthesized fully conjugated PPVs emit green to red light, depending on their chemical structure. In the present case, an efficient and well-defined blue-light-emitting chromophore was obtained by the steric hindrance that was caused by the bulky side oligophenyls on the PPV backbone. In addition, the bulky side oligophenyls are expected to prevent close chain packing, thus increasing the polymer PL efficiency[19,20] and reducing the tendency for aggregate formation.

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 Bruker 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 detector using polysterene as standard and THF as 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 λ$_{ex,max}$, and a solution in 1 N H$_2$SO$_4$ of quinine sulfate, which has a Φ$_f$ of 0.546 (λ$_{ex}$ = 365 nm), was used.

Reagents and Solvents. *p*-Divinylbenzene was synthesized according to a reported method.[24] 4′-Phenylacetophenone and triethylphosphine were recrystallized from ethanol. 4-Methoxyphenylacetic acid sodium salt was prepared by reacting equimolar amounts of 4-methoxyphenylacetic acid with aqueous sodium hydroxide and subsequent fusing. Dimethylacetamide (DMAc) and 1,2-dichloroethane were dried by distillation over CaH$_2$. Triethylamine was dried by distillation over KOH. Acetophnone was distilled under vacuum. All other solvents and reagents were analytical-grade quality, purchased commercially, and used without further purification.

Preparation of Monomers and Polymers. 2,5-Dibromo-*p*-xylene (1). Compound **1** was synthesized according to a reported method.[25,26]

2,5-Dibromobenzene-1,4-dicarbaldehyde (2). Compound **2** was synthesized according to a reported method.[27,28]

4,4′-[1,4-(2,5-Dibromophenylene)]bis(2,6-diphenylpyrylium tetrafluoroborate) (3a). Boron trifluoride etherate (1.0 mL, 8.55 mmol) was added to a stirred mixture of **2** (0.50 g, 1.71 mmol), acetophenone (0.82 g, 6.84 mmol), and 1,2-dichloroethane (10 mL). The mixture was stirred and refluxed for 17 h. Then it was concentrated under reduced pressure, and ethanol (95%) was added to the concentrate. The yellow precipitate was filtered, washed with ethanol, and dried. It was recrystallized from chloroform/diethyl ether (0.80 g, yield 54%, mp 167−169 °C).

IR (KBr, cm^{-1}): 1622, 1599, 1492 (aromatic and pyrylium structure), 1083, 1056 (BF$_4^-$).

^{1}H NMR (CDCl$_3$, δ): 9.17 (m, 4H, aromatic meta to O$^+$); 7.67 (m, 8H, aromatic of side phenyls at ortho position); 7.46 (m, 8H, aromatic of side phenyls at meta position); 7.36 (m, 4H, aromatic of side phenyls at para position); 7.20 (m, 2H, aromatic ortho to Br).

^{13}C NMR (CDCl$_3$, δ): 170.01, 165.63, 135.83, 133.31, 130.18, 129.85, 128.91, 128.49, 128.07, 127.31, 125.23.

4,4′-[1,4-(2,5-Dibromophenylene)]bis[2,6-di(4-biphenylyl)pyrylium Tetrafluoroborate] (3b). Compound **3b** was prepared as a dark brown solid in 53% yield (1.94 g) by reacting **2** (0.90 g, 3.10 mmol) with 4′-phenylacetophenone (2.40 g, 12.4 mmol) and boron trifluoride etherate (1.9 mL, 15.5 mmol) in 1,2-dichloroethane (20 mL). The procedure described for **3a** was applied, and diethyl ether instead of ethanol was added to the concentrate. The reaction product was recrystallized from chloroform/diethyl ether (mp 157−159 °C).

IR (KBr, cm^{-1}): 1620, 1602, 1484 (aromatic and pyrylium structure), 1084, 1055 (BF$_4^-$).

^{1}H NMR (CDCl$_3$, δ): 9.18 (m, 4H, aromatic meta to O$^+$); 7.70−7.68 (m, 16H, aromatic of side biphenyls at positions 2′, 3′, 5′, 6′); 7.65 (m, 8H, aromatic of side biphenyls at positions

2, 6); 7.43 (m, 8H, aromatic of side biphenyls at positions 3, 5); 7.36 (m, 4H, aromatic of side biphenyls at position 4); 7.19 (m, 2H, aromatic ortho to Br).

^{13}C NMR (CDCl$_3$, δ): 170.89, 165.62, 138.66, 136.23, 129.87, 129.61, 129.35, 129.13, 129.03, 128.62, 127.70, 127.62, 127.55, 127.40.

4,4″″-Dimethoxy-2″,5″-dibromo-2′,6′,3″′,5″′-tetraphenyl-*p*-quinquephenyl (4a). A mixture of **3a** (0.79 g, 0.91 mmol), 4-methoxyphenylacetic acid sodium salt (0.34 g, 1.81 mmol), and acetic anhydride (3 mL) was stirred and refluxed for 4 h. It was subsequently cooled in a refrigerator overnight, and the brownish precipitate was filtered, washed with methanol, and dried to afford **4a**. It was purified by chromatography on a silica column using chloroform as eluent (0.42 g, yield 52%, mp 170−172 °C).

IR (KBr, cm^{-1}): 1598, 1512, 1492 (aromatic), 1246, 1178 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.64−7.23 (m, 30H, aromatic except those ortho to O), 6.97 (m, 4H, aromatic ortho to O), 3.83 (s, 6H, OCH$_3$).

4,4″″-Dimethoxy-2″,5″-dibromo-2′,6′,3″′,5″′-tetra(4-biphenylyl)-*p*-quinquephenyl (4b). Compound **4b** was synthesized as a pale brown solid in 62% yield (0.56 g) by reacting **3b** (0.88 g, 0.75 mmol) with 4-methoxyphenylacetic acid sodium salt (0.28 g, 1.50 mmol) and acetic anhydride (3 mL) according to the procedure described for **4a**. It was purified by chromatography on a silica column using chloroform as eluent (mp 185−187 °C).

IR (KBr, cm^{-1}): 1600, 1514, 1486 (aromatic), 1246, 1190 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.71−7.20 (m, 46H, aromatic except those ortho to O), 6.98 (m, 4H, aromatic ortho to O), 3.82 (s, 6H, OCH$_3$).

4,4″″-Dihydroxy-2″,5″-dibromo-2′,6′,3″′,5″′-tetraphenyl-*p*-quinquephenyl (5a). A mixture of **4a** (0.33 g, 0.37 mmol) and pyridine hydrochloride (1.24 g) was refluxed for 12 h. Then, water was added to the reaction mixture, and the pale brown precipitate was filtered, washed with water, and dried to afford **5b**. It was recrystallized from dioxane/water (0.24 g, yield 75%, mp 208−210 °C).

IR (KBr, cm^{-1}): 3424 (OH stretching), 1600, 1530, 1482 (aromatic), 1244 (C−OH stretching).

^{1}H NMR (DMSO-d_6, δ): 9.28 (br, 2H, OH), 7.65−7.22 (m, 30H, aromatic except those ortho to O), 6.87 (m, 4H, aromatic ortho to O).

4,4″″-Dihydroxy-2″,5″-dibromo-2′,6′,3″′,5″′-tetra(4-biphenylyl)-*p*-quinquephenyl (5b). Compound **5b** was prepared as a brownish solid in 86% yield (0.36 g) by reacting **4b** (0.43 g, 0.36 mmol) with pyridine hydrochloride (2.1 g) according to the procedure described for **5a**. It was recrystallized from dioxane/water (mp 255−257 °C).

IR (KBr, cm^{-1}): 3434 (OH stretching); 1600, 1518, 1486 (aromatic), 1262 (C−OH stretching).

^{1}H NMR (DMSO-d_6, δ): 9.31 (br, 2H, OH), 7.70−7.18 (m, 46H, aromatic except those ortho to O), 6.89 (m, 4H, aromatic ortho to O).

4,4″′-Di[(2′-ethylhexyl)oxy]-2″,5″-dibromo-2′,6′,3″′,5″′-tetraphenyl-*p*-quinquephenyl (6a). A mixture of **5a** (0.21 g, 0.24 mmol), 2-ethylhexyl bromide (0.10 g, 0.52 mmol), K$_2$CO$_3$ (0.09 g, 0.62 mmol), and DMAc (6 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 pale brown precipitate was filtered, washed with methanol, and dried to afford **6a**. It was recrystallized from carbon tetrachloride/*n*-hexane (0.24 g, yield 75%, mp 195−197 °C).

IR (KBr, cm^{-1}): 2924, 2858 (C−H stretching of aliphatic segments), 1596, 1491, 1448 (aromatic), 1242, 1175 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.67−7.20 (m, 30H, aromatic except those ortho to O), 6.96 (m, 4H, aromatic ortho to O), 3.70 (d, 4H, OCH$_2$), 1.33, 0.91 (m, 30H, other aliphatic).

Anal. Calcd for C$_{70}$H$_{68}$Br$_2$O$_2$: C, 76.36; H, 6.22. Found: C, 75.89; H, 6.55.

4,4″′-Di[(2′-ethylhexyl)oxy]-2″,5″-dibromo-2′,6′,3″′,5″′-tetra(4-biphenylyl)-*p*-quinquephenyl (6b). Compound **6b**

was prepared as a pale brown solid in 98% yield (1.19 g) by reacting **5b** (1.02 g, 0.86 mmol) with 2-ethylhexyl bromide (0.37 g, 1.90 mmol) and K_2CO_3 (0.31 g, 02.25 mmol) in DMAc (10 mL) according to the procedure described for **6a**. It was recrystallized from carbon tetrachloride/*n*-hexane (mp 212–214 °C).

IR (KBr, cm^{-1}): 2926, 2857 (C–H stretching of aliphatic segments), 1600, 1518, 1486 (aromatic), 1265, 1177 (ether bond).

^{1}H NMR (CDCl$_3$, δ): 7.72–7.18 (m, 46H, aromatic except those ortho to O), 6.97 (m, 4H, aromatic ortho to O), 3.71 (d, 4H, OCH$_2$), 1.36, 0.89 (m, 30H, other aliphatic).

Anal. Calcd for $C_{94}H_{84}Br_2O_2$: C, 80.33; H, 6.02. Found: C, 79.85; H, 6.07.

Polymer Pa. A flask was charged with **6a** (0.1116 g, 0.101 mmol), *p*-divinylbenzene (0.0132 g, 0.101 mmol), Pd(OAc)$_2$ (0.0009 g, 0.004 mmol), and P(*o*-tolyl)$_3$ (0.0071 g, 0.023 mmol). The flask was degassed and purged with N$_2$. DMAc (4 mL) and Et$_3$N (2 mL) were added, and the mixture was stirred and heated at 110 °C for 48 h under N$_2$. Then, it was filtered, and the filtrate was poured into methanol. The yellow-brown precipitate was filtered, washed with methanol, and dried to afford **Pa** (0.10 g, yield 92%). The number-average molecular weight (M_n) was 15 000, and the polydispersity index was 1.5 (by GPC).

Anal. Calcd for $(C_{80}H_{76}O_2)_n$: C, 89.85; H, 7.16. Found: C, 89.12; H, 7.21.

Polymer Pb. Following the procedure described for **Pa**, polymer **Pb** was prepared as a yellow-brown solid in 53% yield (0.36 g) by reacting **6b** (0.6996 g, 0.498 mmol) with *p*-divinylbenzene (0.0648 g, 0.498 mmo), Pd(OAc)$_2$ (0.0046 g, 0.020 mmol), P(*o*-tolyl)$_3$ (0.0348 g, 0.114 mmol), DMAc (5 mL), and Et$_3$N (2 mL). The number-average molecular weight (M_n) was 18 000, and the polydispersity index was 1.7 (by GPC).

Anal. Calcd for $(C_{104}H_{92}O_2)_n$: C, 90.92; H, 6.75. Found: C, 90.18; H, 6.68.

Results and Discussion

Synthesis and Characterization of Polymers. Polymers **Pa** and **Pb** were synthesized by seven steps according to Scheme 1. In particular, *p*-xylene was brominated in the presence of FeCl$_3$ to 2,5-dibromo-*p*-xylene.[25,26] This was oxidized by means of CrO$_3$/H$_2$SO$_4$ to 2,5-dibromo-1,4-benzenedicarbaldehyde.[27,28] The latter reacted with acetophenone or 4′-phenylacetophenone in the presence of BF$_3$·Et$_2$O to yield pyrylium salts **3**.[29,30] These reacted subsequently with 4-methoxyphenylacetic acid sodium salt in acetic anhydride to afford the substituted *p*-quinquephenyls **4**.[31] The methoxy groups of the latter were cleaved by pyridine hydrochloride to bisphenols **5**.[32] These reacted with 2-ethylhexyl bromide in the presence of K$_2$CO$_3$ to yield the alkoxy derivatives **6**. Finally, the Heck coupling[33] of the latter with *p*-divinylbenzene afforded polymers **P**.

The polymerization was carried out in DMAc as solvent and polymers **Pa** and **Pb** were obtained in 92 and 53% yields, respectively, by precipitation from the reaction solution into methanol. The number-average molecular weight (M_n) for **Pa** and **Pb** was rather low (15 000 and 18 000) with a polydispersity index of 1.5 and 1.7, respectively. It is well established that GPC, with polystyrene as calibration standard, misrepresents the M_n values of rigid or semirigid polymers.[34] Usually, the polymers that have been prepared by the Heck coupling possess a relatively low degree of polymerization.

The IR and NMR spectra of polymers are consistent with the chemical structures. The FT-IR spectrum of the typical polymer **Pb** showed characteristic absorption bands at 2950 and 2925 (C–H stretching of the aliphatic segments), 1599, 1511, 1484 (aromatic), 1242, 1204,

1192 (ether bond), and 963 cm^{-1} (HC=CH trans). It should be noted that the parent dibromide **6b** did not show any absorption around 963 cm^{-1}. This proves the formation of vinylene double bond, and consequently the polymerization reactions were successful.

The ^{1}H NMR spectra of polymers showed rather broad signals typical of polymeric materials. The various aromatic protons were overlapped thus contributing to the broadening of the spectra. As the polymerization proceeded, the terminal vinyl peaks of the *p*-divinylbenzene present at 5.2, 5.7, and 6.7 δ disappeared, and a newly vinylene proton peak of the polymer overlapped with the aromatic protons. Specifically, the ^{1}H NMR spectrum of **Pb** in CDCl$_3$ displayed peaks at 7.73–7.18 (m, 50H, aromatic except those ortho to O), 7.12 (m, 4H, HC=CH), 6.95 (m, 4H, aromatic ortho to O), 3.72 (d, 4H, OCH$_2$), 1.26, and 0.87 (m, 30H, other aliphatic). The ^{1}H NMR spectrum of **Pa** did not differ remarkably from that of **Pb**, but the ratio of the peaks assigned to the aromatic vinylene and aliphatic protons was 1.12/1.00. The absence of peaks around 6.5 δ indicated that no *cis*-vinylene bonds were present. This feature conforms with the IR data which supported that all vinylene bonds were in the trans conformation. Evidence for the structure of the polymers was also obtained from their ^{13}C NMR spectra.

The polymers were readily soluble at room temperature in common organic solvents such as tetrahydrofuran, chloroform, methylene chloride, 1,2-dichloroethane, and polar aprotic solvents. Polymer **Pb** bearing 4-biphenylyl groups was more soluble in these solvents than **Pa** because larger quantities of the former dissolved in the same solvent volume. Despite their relatively low molecular weight, the polymers could be spin-cast without any difficulty, giving transparent and homogeneous thin films.

The crystallinity of the polymers was estimated by wide-angle X-ray diffractograms for powder specimens at room temperature. The polymers displayed amorphous X-ray diffraction patterns. This is reasonable due to the stiffness of the conjugated backbone and the bulky side groups that increased significantly the disorder in chains. The amorphous nature of the polymers reflects to their enhanced solubility.

The DSC traces of polymers did not display any transition associated with T_g or melting even during repeated scans. The absence of melting confirms the amorphous character of polymers. The T_g's were determined by the TMA method utilizing 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 **Pa** exhibited lower T_g (106 °C) than **Pb** (122 °C). The attachment of the 4-biphenylyl groups increased not only the free volume of **Pb** but also its rigidity. These values of T_g are comparable with those of other PPVs with bulky pendants such as dihexylfluorenyl-substituted PPV derivatives (113–148 °C)[35] or triphenylamine-substituted PPV (140 °C)[36] but lower than that of PPV derivatives with cyanophenyl pendant (180–192 °C).[37] The T_g values of the present polymers are around 40–60 °C higher than that of the soluble poly[2-methoxy-5-(2′-ethylhexyloxy-1,4-phenylenevinylene] (MEH–PPV) (~65 °C).[38] The presence of the side oligophenyls suppressed the flexibility of the polymers and increased their T_g's. This is an advantage because it has been reported that the lifetime of EL
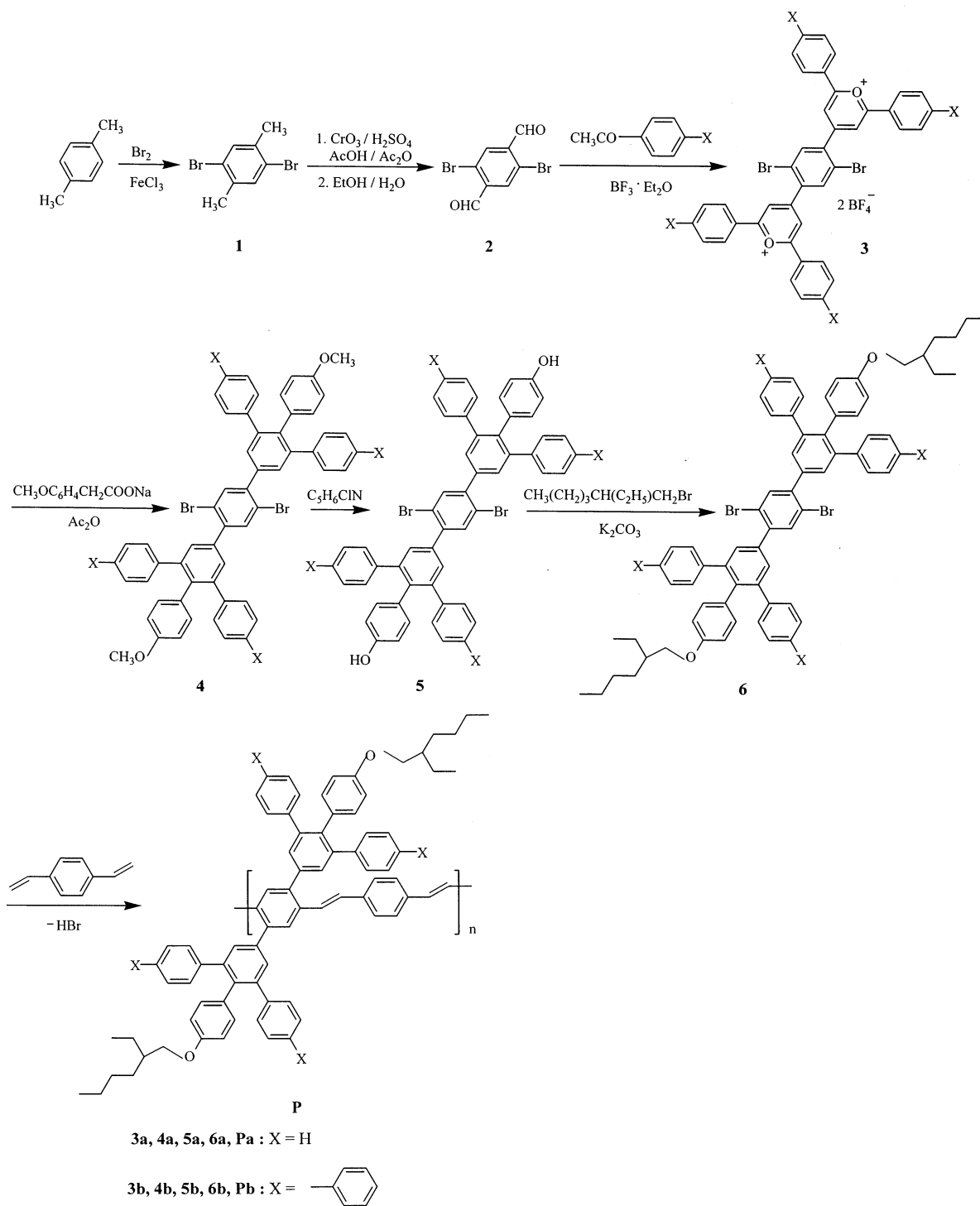
Scheme 1

3a, 4a, 5a, 6a, Pa : X = H

3b, 4b, 5b, 6b, Pb : X = —⟨phenyl⟩

Table 1. TMA and TGA Data of Polymers

	TMA	TGA				
		in N_2			in air	
polymer	$T_g{}^a$	$T_1{}^b$	$T_{10}{}^b$	$Y_c{}^c$	$T_1{}^b$	$T_{10}{}^b$
Pa	106	367	474	76	363	469
Pb	122	328	437	78	323	418

^{a} T_g = glass transition temperature (in °C). ^{b} T_1 and T_{10} = temperatures (in °C) at which weight loss of 1 and 10%, respectively, was observed. ^{c} Y_c = char yield (in %) at 800 °C.

devices is directly related to the T_g values and thermal stability of the polymers used.[39,40]

Since the polymers were composed mainly of aromatic structure, they showed an outstanding thermal stability that was ascertained by TGA in N_2 and air. Figure 1 presents typical TGA traces of **Pa**. Certain TGA data for both polymers are summarized in Table 1. The polymers were stable up to approximately 320−370 °C in N_2 and air and afforded anaerobic char yield of around 80% at 800 °C. This value of char yield is remarkably high and can be compared with that of heat-resistant polymers. However, both polymers were roughly decomposed beyond 500 °C in air. **Pa** was slightly more thermostable than **Pb**.

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] in solution at RT (nm)	$\lambda_{f,max}$[c] in solution at ca. −50 °C (nm)	Φ_f[d] in solution	$\lambda_{ex,max}$[b] in thin film (nm)	$\lambda_{f,max}$[c] in thin film (nm)
Pa	271	340, *391*[e]	453	435, *455*	0.24	400	*442*, 512
Pb	283	340, *391*	461	471	0.31	400	*482*, 512

[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] Φ_f = PL quantum yields. [e] Italic numerical values denote absolute maxima.
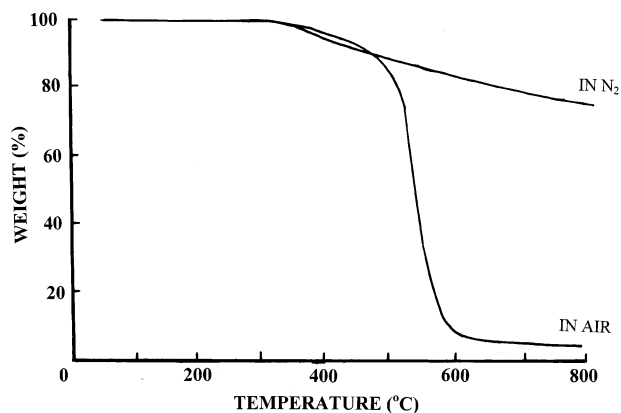

Figure 1. TGA traces in N_2 and air of polymer **Pa**. Conditions: gas flow, 60 cm³/min; heating rate, 20 °C/min.

Optical Properties of Polymers. The polymers presented interesting optical properties because their backbone consisted of fully conjugated PPV that carried highly phenylated side groups.

The UV−vis and the PL excitation (PLE) as well as the photoluminence (PL) spectroscopic data of polymers both in THF solution and in thin films are listed in Table 2 and presented in Figures 2, 3, and 5. The UV−vis spectra of polymers **Pa** and **Pb** showed maximum ($\lambda_{a,max}$) at 271 and 283 nm, respectively, assigned to the phenyl rings. Both spectra were broad especially at the longer wavelength region owing to the $\pi−\pi^*$ transitions of the side oligophenyls and the conjugated PPV backbone. Because of this broadening, the absorption edge and consequently the optical band gap energy could not be precisely calculated.

The PLE spectra of polymers in THF displayed maximum ($\lambda_{ex,max}$) at 391 nm and a shoulder around 340 nm, thus supporting two exiting sites. Since the parent dibromides **6** exhibited $\lambda_{ex,max}$ near 340 nm, the exciting sites at 340 and 391 nm correspond to the emission bands at shorter and longer wavelengths that resulted from the oligophenyl and the conjugated backbone, respectively. The PLE maximum was significantly red-shifted in comparison with the absorption maximum. However, the broad right side of the UV−vis curve, which is associated with the $\pi−\pi^*$ transitions of the side oligophenyls and the conjugated PPV backbone, overlaps with the PLE curve.

The solutions of polymers **Pa** and **Pb** in THF showed intense blue fluorescence with maximum ($\lambda_{f,max}$) at 453 and 461 nm, respectively, by exciting at the corresponding $\lambda_{ex,max}$ (Figures 2 and 3). It is well established that the fully conjugated PPVs display $\lambda_{f,max}$ between 490 and 510 nm that is located in the green emission. Although the present polymers contained a PPV backbone, they emitted at shorter wavelength than PPVs. It should be noted that the parent dibromides **6** exhibited $\lambda_{f,max}$ near 395 nm that arose from the substituted *p*-quinquephenyl. Thus, the polymers emitted at a $\lambda_{f,max}$ which is longer than that of the substituted *p*-quinquephenyl and
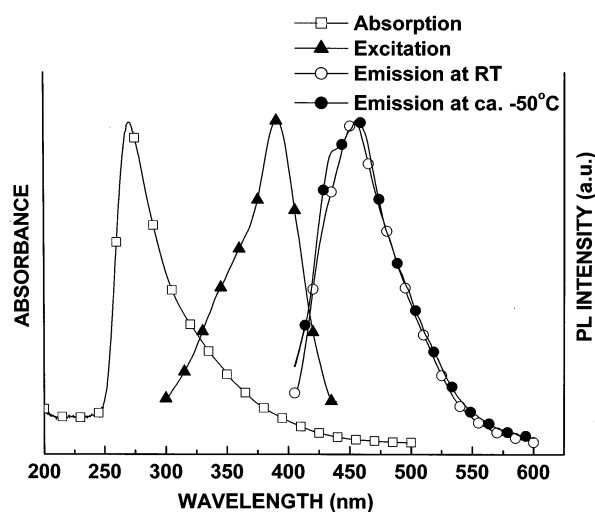

Figure 2. Absorption and PL excitation spectra as well as PL spectra at room temperature and at low temperature (ca. −50 °C) of polymer **Pa** in THF solution.
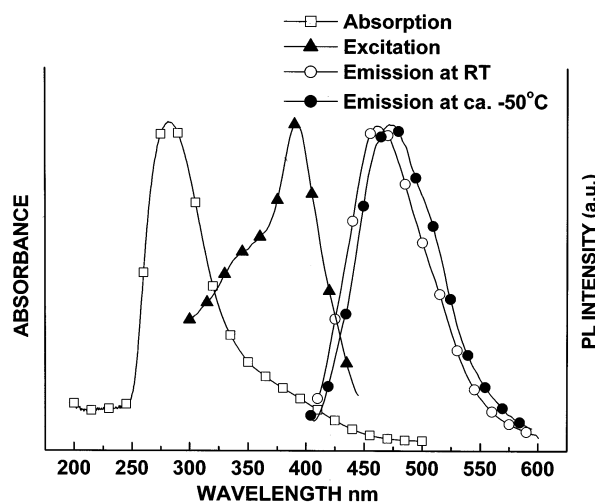

Figure 3. Absorption and PL excitation spectra as well as PL spectra at room temperature and at low temperature (ca. −50 °C) of polymer **Pb** in THF solution.

shorter than that of PPVs. This interesting emission behavior of polymers was attributed to the bulky side oligophenyls which caused a significant steric hindrance on the PPV backbone. In particular, it is well established that in a nonsubstituted PPV the dihedral angle (the angle between the plane of the phenyl ring and that of the vinylene segment) was found to be 8° and 9° for 13 and 20 °C, respectively, which permits the conjugation through it.[41,42] In the present case, the bulky side oligophenyls, due to their steric hindrance, increased this dihedral angle and interrupted the conjugation. Thus, a well-defined chromophore was obtained that emitted pure blue light. An analogous behavior has been observed in polyphenylenes.[43] So far, the PL emission peaks of 488 and 490 nm have been presented by Hsieh

Figure 5. PL excitation spectra (bold line) and PL spectra (thin line) in thin films of polymers **Pa** and **Pb**.
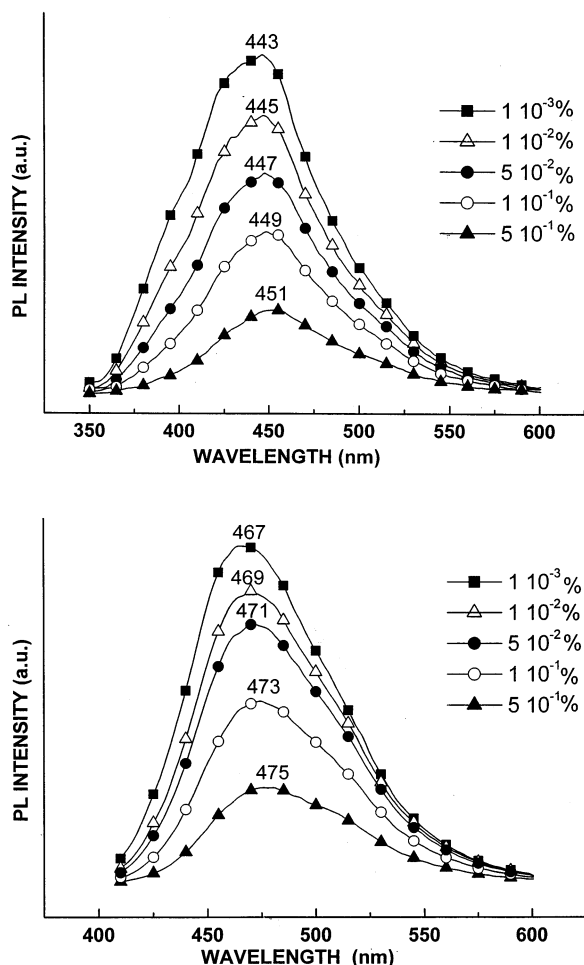
Figure 4. PL spectra of polymer **Pa** (top) and **Pb** (bottom) at various concentrations in THF solutions with excitation at the corresponding $\lambda_{ex,max}$.

et al.[19] as well as Peng et al.[20] as the bluest emission peaks that have been reported for a fully conjugated PPV with 2,3-diphenyl[19] or 2-biphenylyl[20] substituents. Consequently, the values of 453 and 461 nm for the PL maximum of the present polymers are further blue-shifted in comparison to the above values and are located in the middle of the blue light region. To the best of our knowledge, these values of $\lambda_{f,max}$ in solution of the present polymers are among the bluest emission peaks that have been reported for a fully conjugated PPV. The fabrication of polymer blue-light-emitting devices, which cannot be easily prepared from inorganic materials, as well as of multiccolor electroluminescent devices is still of interest.

In addition, the PL spectra of polymers in THF were recorded at low temperature (ca. −50 °C) to investigate the temperature effect on the emission curve (Figures 2 and 3). The $\lambda_{f,max}$ of **Pa** and **Pb** was red-shifted by 2 and 10 nm, respectively, at low temperature. Moreover, **Pa** showed a new shoulder at 435 nm. At low temperature, the rotation between the adjacent phenyls is reduced, and the conjugation can be extended.[44] Since **Pb** carried longer side oligophenyl chains than **Pa**, the effect of the low temperature was greater for the former polymer, and therefore it displayed a higher red shift of the emission maximum. The PPV backbone of polymers was more consolidated than the side oligophenyl chains due to the olefinic bonds, and consequently its rotation was not considerably affected by the low temperature.
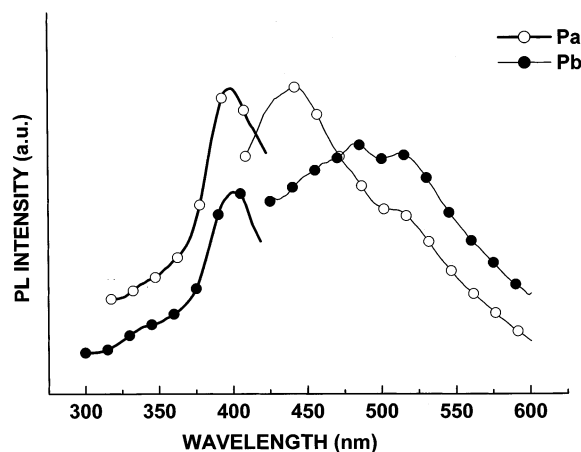
The influence of the polymer concentration in THF solution on the characteristics of the emission curve was also investigated. Figure 4 depicts the PL spectra of polymers with a wide concentration range in THF. It seems that, with increasing the polymer concentration, the profile of the PL spectrum remained unchanged, but the curve became less intense and the $\lambda_{f,max}$ was slightly red-shifted (8 nm). These results indicated that for both polymers the existence of chain associations was not important due to the bulky and highly phenylated side groups that prevented chain interactions.

To evaluate the emission efficiency of polymers, the PL quantum yields (Φ_f) in THF solution were determined[45] relative to quinine sulfate (Table 2). The latter presents a Φ_f of 0.546 by exciting at 365 nm. **Pb** showed higher Φ_f value (0.31) than **Pa** (0.24). It has been reported that the introduction of appropriate substituents to the PPV backbone to prevent its close packing could increase the PL and EL efficiency. Indeed, Hsieh et al.[19] as well as Peng et al.[20] have determined very high PL efficiencies (>50%) in both solution and thin film for PPV polymers that contained 2,3-diphenyl[19] or 2-biphenylyl[20] substituents. Although the Φ_f values of the present polymers were lower than those of the literature, the results showed that the Φ_f was increased with increasing the size of the PPV substituents.

The films of the polymers that were prepared by spin-casting displayed $\lambda_{ex,max}$ at 400 nm, which was red-shifted by 9 nm in comparison with the solutions (Figure 5). Their PL spectra were rather broad with $\lambda_{f,max}$ at 442 and 482 nm for **Pa** and **Pb**, respectively, and with a common shoulder at 512 nm. These results indicated that the polymers had a little tendency to form aggregates in solid state.

Conclusions

Starting from *p*-xylene and using pyrylium salts, two dibromides **6a** and **6b** were synthesized and polymerized by Heck coupling with *p*-divinylbenzene to afford the respective polymers **Pa** and **Pb**. Their main chain consisted of PPV and carried on the same phenyl ring two side oligophenyls per each repeat unit. The polymers were amorphous and dissolved readily at ambient temperature in common organic solvents such as THF, chloroform, methylene chloride, and 1,2-dichloroethane. They were stable up to approximately 320−370 °C in N₂ or air and afforded anaerobic char yields of about 80% at 800 °C. Their T_g values were relatively high

(106−122 °C). The solutions of polymers in THF emitted intense and pure blue light with maximum at 453 or 461 nm. These PL maxima are among the bluest emission peaks that have been reported for a fully conjugated PPV. Steric hindrance introduced by the bulky side oligophenyls interrupted the conjugation in the PPV backbone. At low temperature, **Pb** with longer side oligophenyls showed in THF higher red shift (10 nm) in comparison with the room temperature spectrum than **Pa** (2 nm) because the rotation between the adjacent phenyls was reduced. The PL quantum yields in THF were 0.24−0.31. The bulky side oligophenyls hindered the formation of aggregates in both solution and solid state.

Supporting Information Available: FT-IR spectrum of polymer **Pb** (Figure S1), ^{1}H NMR spectrum of polymer **Pb** in CDCl$_3$ solution (Figure S2), ^{13}C NMR spectrum of polymer **Pb** in CDCl$_3$ solution (Figure S3), and X-ray diffraction patterns of polymers **Pa** and **Pb** (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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