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Blue-Light-Emitting Poly(phenylenevinylene)s with Alkoxyphenyl Substituents: Synthesis and Optical Properties

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ABSTRACT: Two new poly(phenylenevinylene)s with alkoxyphenyl substituents were synthesized and characterized. The polymers were obtained in moderate molecular weights and were amorphous. They showed enhanced solubility in common organic solvents, T_g in the range 135–140 °C, and satisfactory thermal stability. The polymers displayed blue fluorescence both in solution and in the solid state, because side phenyls interrupted the effective conjugation length. Their PL spectra exhibited maxima around 420, 444, and 460 nm in solution and in solid state, respectively. The PL quantum yields in solution were determined and ranged up to 0.31. UV–vis, PLE, and PL studies in THF solution and in thin films revealed that the polymers showed a reduced tendency to form aggregates in solid state.

Introduction

Fully conjugated polymers belong to a class of materials with a large number of applications such as photo-diodes,¹ photovoltaic cells,² nonlinear optics,³ and laser devices.⁴ Their unique properties originate from delocalization of π -electrons. Since the discovery of light-emitting diodes⁵ based on poly(*p*-phenylenevinylene) (PPV), enormous research effort has been made in the field of conjugated polymers. Numbers of polymers have been synthesized as candidates for light-emitting diodes. The advantages of organic polymers over the inorganic molecules are their outstanding mechanical properties and, in particular, the unlimited accessible structures that allow one to tune the emitting light. Among the variety of conjugated polymers, PPV and its derivatives are the most popular.

The limited solubility of the conjugated polymers restricts their use. The most effective way to produce soluble polymers is the introduction of long aliphatic groups along the polymer backbone. Many PPVs with aliphatic substituents that showed enhanced solubility have been reported.^{7–16} In addition, they have been used as a tool for controlling the color of the emitting light. The steric interactions of side groups force the backbone to twist^{17,18} interrupting the effective conjugation length. As a result, a polymer with a well-defined chromophore could be prepared. In this way, the emission of PPV is shifted from green to blue.⁹ On the other hand, bulky aromatic substituents have been used to reduce the tendency of conjugated polymers to form aggregates.^{19–21} Conjugated polymers tend to stick cofacially due to interchain π -interaction. This leads to self-quenching process of excitons,²² reducing the efficiency of light-emitting diodes.

In this paper, we report the synthesis and characterization of new PPV derivatives bearing bulk alkoxyphenyl substituents. The introduction of pendant groups results in blue-light-emitting polymers with well-defined chromophore and reduced tendency to form aggregates.

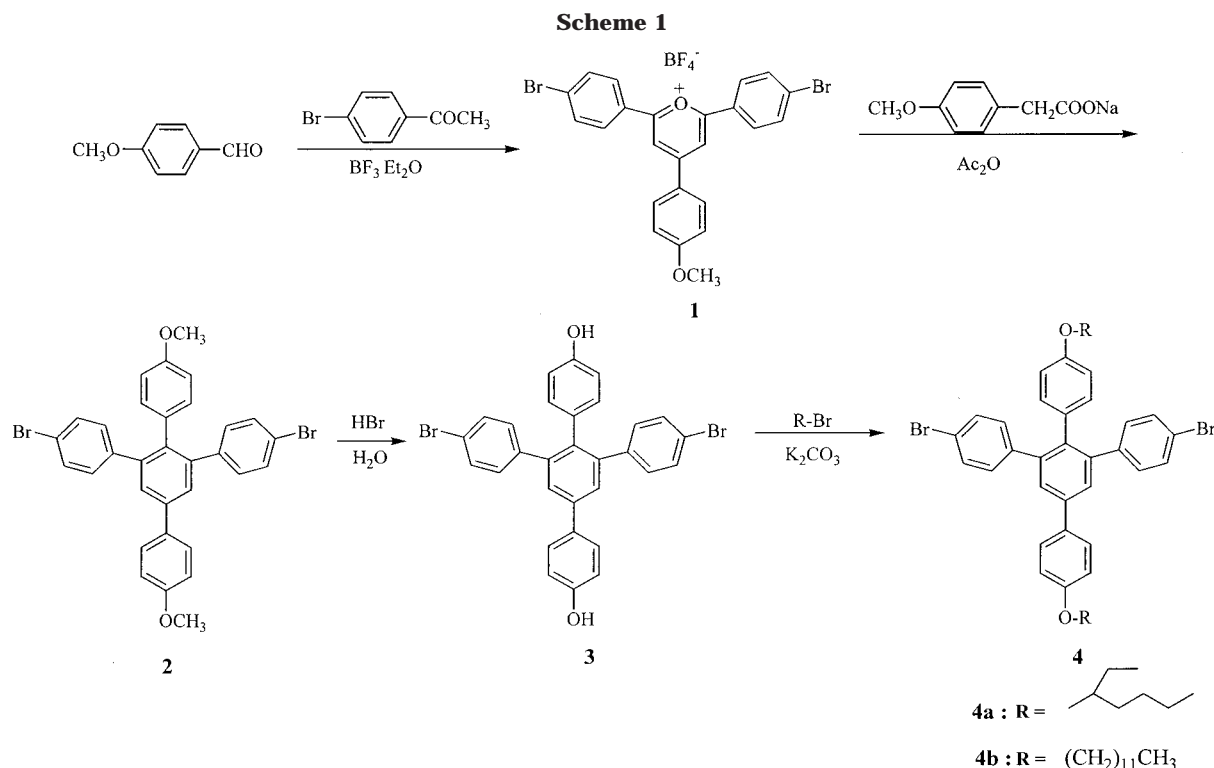
Experimental Section

Characterization Methods. Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were obtained using a Bruker spectrometer. The NMR spectra were recorded using DMSO-*d*₆ or CDCl₃ as solvent. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. GPC analysis was conducted with an apparatus Waters Breeze 1515 equipped with a 2410 differential refractometer as detector (Waters Associate) and Styragel HR columns using polystyrene as standard and THF as eluant. 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 N₂ atmosphere at a flow rate of 60 cm³/min. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N₂ or air at a flow rate of 60 cm³/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 N₂ with a flow rate of 60 cm³/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 Hewlett-Packard model 185 analyzer. The wide-angle X-ray diffraction patterns were obtained for powder specimens on a X-ray PW-1840 Philips diffractometer.

UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. The emission spectra were obtained with a Perkin-Elmer LS55B luminescence spectrometer. The PL quantum yields (Φ) of polymers were measured in diluted THF solution. The solutions were freshly prepared using anhydrous THF. The samples were deoxygenated by bubbling argon through the solutions. The concentrations of solution were adjusted so that their absorbance to be lower than 0.1. The exciting wavelength of samples was 374 nm. As the standard, quinine sulfate in 1 N H₂SO₄ was used, which has a Φ value of 0.546 with excitation at 350 nm.

Reagents and Solvents. Dimethylacetamide (DMAc), toluene, and 1,2-dichloroethane were dried by distillation over CaH₂. Triethylamine was dried by distillation over KOH. 4-Methoxyphenylacetic acid sodium salt was prepared by reacting equimolar amounts of 4-methoxyphenylacetic acid

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with aqueous sodium hydroxide and subsequent fusing. 4-Methoxybenzaldehyde, 4-bromoacetophenone, tri-*o*-tolylphosphine [$\text{P}(\text{o-tolyl})_3$], $\text{Pd}(\text{OAc})_2$, 1-bromododecane, 1-bromo-2-ethylhexane, boron trifluoride etherate, acetic anhydride, and hydrobromic acid (47–49%) were used as supplied. *p*-Divinylbenzene²³ was synthesized according to known method.

Preparation of Monomers (Scheme 1). 4-(4-Methoxyphenyl)-2,6-di(4-bromophenyl)pyrylium tetrafluoroborate (1). Boron trifluoride etherate (5.84 mL, 46.51 mmol) was added to a solution of 4-methoxybenzaldehyde (2.53 g, 18.60 mmol) and 4-bromoacetophenone (7.40 g, 37.20 mmol) in 1,2-dichloroethane (8 mL). The mixture was heated at 80 °C, for 3 h under N_2 . The dark red solution was concentrated under reduced pressure, and the residue was triturated with ethyl acetate. The resulting solid was filtered, washed with ethyl acetate, and dried to afford **1** (7.27 g, 67%) as a yellow solid. It was recrystallized from acetic acid. Mp > 300 °C.

IR (KBr, cm^{-1}): 1628, 1586, 1510, 1488 (aromatic and pyrylium structure); 1246 (ether bond); 1074 (BF_4^-).

^1H NMR ($\text{DMSO}-d_6$), ppm: 8.14 (s, 2H, aromatic meta to O^+); 7.76–6.80 (m, 12H, other aromatic); 4.49 (s, 3H, OCH_3).

4,4'-Dibromo-2,5'-di(4-methoxyphenyl)-*m*-terphenyl (2). A mixture of **1** (2.50 g, 4.28 mmol), 4-methoxyphenylacetic acid sodium salt (1.61 g, 8.56 mmol), and acetic anhydride (3 mL) was refluxed for 3 h. Then it was cooled in a refrigerator overnight and compound **2** was crystallized. It was obtained as a white solid by filtration, washed with methanol and dried (1.49 g, 58%). It was recrystallized from acetonitrile. Mp: 118–120 °C.

IR (KBr, cm^{-1}): 2930, 2834 (C–H stretching of CH_3); 1610, 1516, 1486 (aromatic); 1246 (ether bond).

^1H NMR (CDCl_3), ppm: 8.34 (s, 2H, aromatic at positions 4',6' of *m*-terphenyl); 8.02, 7.99 (d, 4H, aromatic at positions 3,5,3'',5'' of *m*-terphenyl); 7.76, 7.74 (d, 4H, aromatic at positions 2,6,2'',6'' of *m*-terphenyl); 7.52–7.34 (m, 8H, aromatic of side phenyls); 4.62, 4.49 (d, 6H, OCH_3).

^{13}C NMR (CDCl_3), ppm: 159.98, 158.48, 141.86, 141.42, 141.33, 140.25, 137.34, 132.96, 131.92, 131.26, 129.08, 128.16, 120.00, 114.27, 113.61, 55.75, 55.43.

4,4'-Dibromo-2,5'-di(4-hydroxyphenyl)-*m*-terphenyl (3). Compound **2** (2.63 g, 4.38 mmol) was dissolved in glacial acetic acid by heating at boiling temperature. Hydrobromic acid 47–49% (3 mL) was added portionwise over a period of 3 h. The

solution was refluxed for additional 20 h and then cooled at room temperature. The white precipitate was filtered, washed with water and then with methanol, and dried to afford **3** (2.00 g, 80%). It was recrystallized from *o*-dichlorobenzene. Mp: 268–270 °C.

IR (KBr, cm^{-1}): 3540, 3413 (O–H stretching); 1610, 1589, 1518, 1486 (aromatic); 1266 (O–H deformation).

^1H NMR ($\text{DMSO}-d_6$), ppm: 9.62, 9.30 (d, 2H, OH); 7.64–7.54 (m, 6H, aromatic at positions 3,5,4',6',3'',5'' of *m*-terphenyl); 7.06 (d, 4H, aromatic at positions 2,6,2'',6'' of *m*-terphenyl); 6.87–6.47 (m, 8H, aromatic of side phenyls).

^{13}C NMR ($\text{DMSO}-d_6$), ppm: 158.29, 156.45, 141.88, 141.84, 140.12, 137.59, 133.09, 132.59, 131.37, 129.78, 129.64, 128.83, 127.87, 120.62, 116.68, 115.47.

4,4'-Dibromo-2,5'-di[4-(2-ethylhexyloxy)phenyl]-*m*-terphenyl (4a). A mixture of **3** (0.63 g, 1.10 mmol), 1-bromo-2-ethylhexane (0.47 g, 2.43 mmol), K_2CO_3 (0.46 g, 3.33 mmol), and DMF (10 mL) was heated at 100 °C overnight under N_2 . The mixture was subsequently poured into water, and the precipitate was filtered, washed with methanol, and dried to afford **4a** as a white solid (0.77 g, 88%). It was recrystallized from CH_3CN . Mp: 116–118 °C.

Anal. Calcd for $\text{C}_{46}\text{H}_{52}\text{O}_2\text{Br}_2$: C, 69.35; H, 6.58. Found: C, 68.81; H, 6.49.

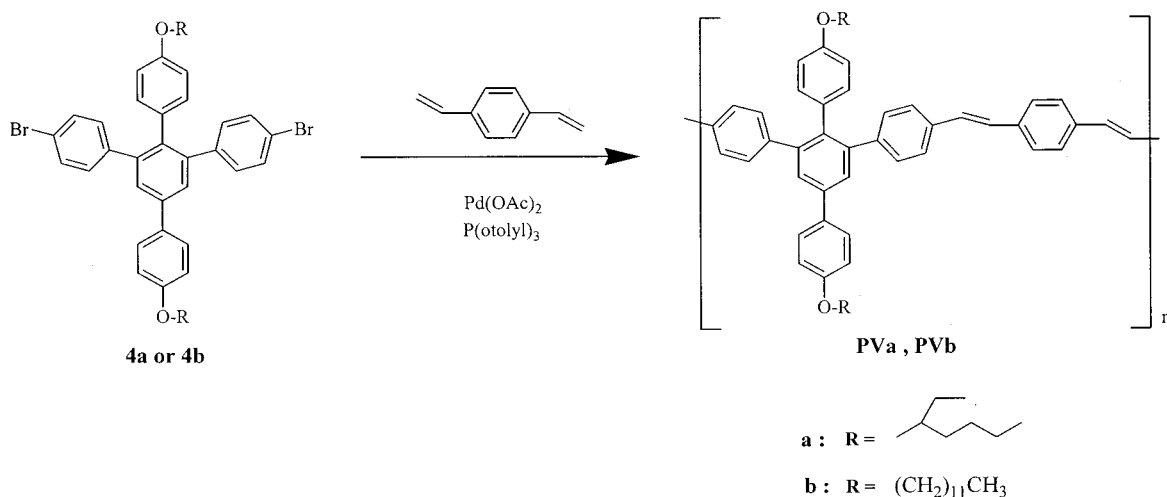
IR (KBr, cm^{-1}): 2956, 2924, 2856 (C–H stretching of the aliphatic segments); 1608, 1516, 1486 (aromatic); 1448 (C–C stretching of the aliphatic segments); 1244 (ether bond).

^1H NMR (CDCl_3), ppm: 7.49 (d, 2H, aromatic at positions 4',6' of *m*-terphenyl); 7.25, 7.23 (d, 4H, aromatic at positions 3,5,3'',5'' of *m*-terphenyl); 6.93, 6.91 (d, 4H, aromatic at positions 2,6,2'',6'' of *m*-terphenyl); 6.64–6.46 (m, 8H, aromatic of side phenyls); 4.08, 3.83 (d, 4H, OCH_2); 1.70–0.87 (m, 30H, other aliphatic).

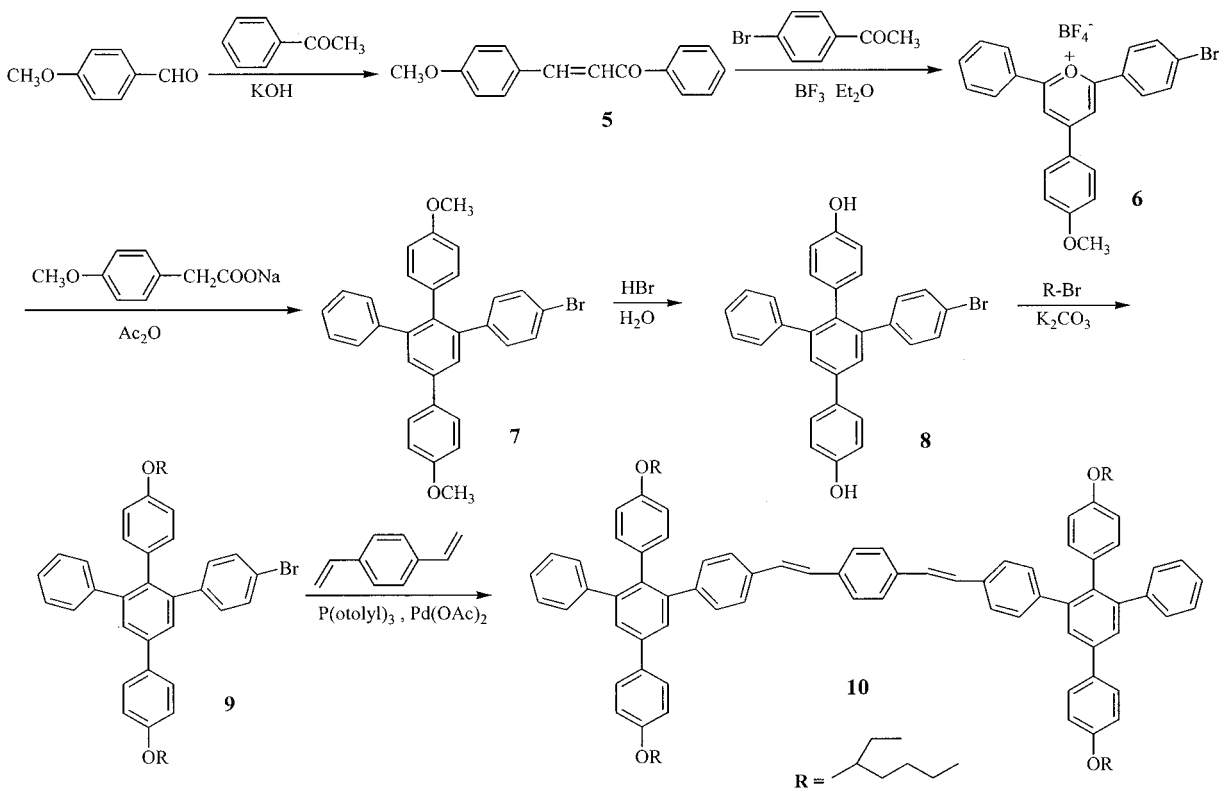
^{13}C NMR (CDCl_3), ppm: 159.94, 158.56, 141.91, 141.44, 140.26, 137.41, 134.08, 133.05, 132.92, 131.91, 128.45, 127.63, 120.96, 115.40, 114.22, 68.61, 68.36, 32.25, 30.03–29.70, 26.50–23.12, 14.32.

4,4'-Dibromo-2,5'-di(4-dodecyloxyphenyl)-*m*-terphenyl (4b). Compound **4d** was obtained as a white solid in 91% yield from the reaction of **3** with 1-bromododecane according to the procedure described for **4a**. It was recrystallized from dioxane/ethanol (1/2 v/v). Mp: 95–96 °C.

Scheme 2



Scheme 3



Anal. Calcd for $\text{C}_{54}\text{H}_{68}\text{O}_2\text{Br}_2$: C, 71.36; H, 7.54. Found: C, 70.94; H, 7.61.

IR (KBr, cm^{-1}): 2918, 2850 (C–H stretching of the aliphatic segments); 1608, 1518, 1486 (aromatic); 1452 (C–C stretching of the aliphatic segments); 1246 (ether bond).

^1H NMR (CDCl_3), ppm: 7.49 (d, 2H, aromatic at positions 4',6' of *m*-terphenyl); 7.22 (d, 4H, aromatic at positions 3,5,3'',5'' of *m*-terphenyl); 6.91 (d, 4H, aromatic at positions 2,6,2'',6'' of *m*-terphenyl); 6.63–6.48 (m, 8H, aromatic of side phenyls); 3.92, 3.77 (d, 4H, OCH_2); 1.73–0.81 (m, 46H, other aliphatic).

^{13}C NMR (CDCl_3), ppm: 159.89, 158.54, 141.92, 141.44, 140.26, 137.41, 134.08, 133.14, 132.83, 131.84, 128.45, 127.63, 120.96, 115.40, 114.22, 68.61, 68.36, 32.36, 30.34–29.70, 26.50, 23.18, 14.41.

Preparation of Polymers (Scheme 2). A flask was charged with **4a** (0.3398 g, 0.427 mmol), *p*-divinylbenzene (0.0555 g, 0.427 mmol), $\text{Pd}(\text{OAc})_2$ (4 mg, 0.018 mmol), and $\text{P}(\text{o-tolyl})_3$ (29.9 mg, 0.098 mmol). The flask was degassed and

purged with argon. DMAc (10 mL) and triethylamine (2 mL) were added, and the resulting solution was heated at 120 °C for 48 h. After cooling, the solution was poured into methanol, and the precipitate was filtered, washed with methanol, and dried. It was redissolved in THF and precipitated in methanol affording **PVa** as a yellow solid (0.32 g, 97%). M_n : 3100. PI: 2.81 (by GPC).

Anal. Calcd for $(\text{C}_{56}\text{H}_{60}\text{O}_2)_n$: C, 87.91; H, 7.90. Found: C, 86.84; H, 7.79.

Polymer **PVb** was obtained as a yellow solid in 95% yield from the reaction of **4b** with *p*-divinylbenzene. M_n : 3400; PI: 2.67 (by GPC).

Anal. Calcd for $(\text{C}_{64}\text{H}_{76}\text{O}_2)_n$: C, 87.62; H, 8.73. Found: C, 86.68; H, 8.81.

Preparation of Model Compound (Scheme 3). 4-Methoxybenzalacetophenone (5). To a stirred solution of 4-methoxybenzaldehyde (4.53 g, 33.29 mmol) and acetophenone (4.00 g, 33.29 mmol) in ethanol (20 mL) was added dropwise a

solution of KOH (1.66 g, 41.16 mmol) in water over a period of 30 min at room temperature. A white precipitate was formed, and stirring was continued overnight. The precipitate was filtered, washed with water and then with ethanol, and dried to afford **5** as a white solid (6.20 g, 78%). It was recrystallized from ethanol. Mp: 63–65 °C.

IR (KBr, cm^{-1}): 2918, 2842 (C–H stretching of CH_3); 1658 (C=O); 1600, 1576, 1512 (aromatic and double bond); 1264, 1212 (ether bond).

^1H NMR (CDCl_3), ppm: 7.98–6.94 (m, 9H aromatic and 2H double bond); 3.87 (s, 3H, OCH_3).

4-(4-Methoxyphenyl)-2-(4-bromophenyl)-6-phenylpyrylium tetrafluoroborate (6). Boron trifluoride etherate (2.64 mL, 21.01 mmol) was added to a solution of **5** (2.00 g, 8.40 mmol) and acetophenone (0.84 g, 4.20 mmol) in 1,2-dichloroethane (15 mL). The solution was heated at 80 °C for 3 h under N_2 . It was subsequently concentrated under reduced pressure, and the residue was triturated with dioxane. The resulting solid was filtered, washed with dioxane, and dried, yielding **6** as a yellow solid (1.42 g, 67%). It was recrystallized from acetic acid. Mp: 181–182 °C.

IR (KBr, cm^{-1}): 2919, 2854 (C–H stretching of CH_3); 1616, 1588, 1510, 1490 (aromatic and pyrylium structure); 1246 (ether bond); 1074 (BF_4^-).

^1H NMR ($\text{DMSO}-d_6$), ppm: 8.32 (s, 2H, aromatic meta to O^+); 7.90–7.40 (m, 4H, aromatic ortho and meta to Br); 7.21–6.88 (m, 9H, other aromatic); 4.38 (s, 3H, OCH_3).

4-Bromo-2',5'-di(4-methoxyphenyl)-*m*-terphenyl (7). Compound **7** was prepared in 62% yield by reacting **6** with 4-methoxyphenylacetic acid sodium salt according to the procedure described for **2**. It was recrystallized from CH_3CN . Mp: 170–172 °C.

IR (KBr, cm^{-1}): 3030 (C–H stretching of aromatic); 2930, 2832 (C–H stretching of CH_3); 1608, 1516 (aromatic); 1242 (ether bond).

^1H NMR (CDCl_3), ppm: 8.02 (s, 2H, aromatic at positions 4',6' of *m*-terphenyl); 7.85–7.42 (m, 9H, aromatic at positions 2, 3, 5, 6, 2'', 3'', 4'', 5'', 6'' of *m*-terphenyl); 7.25–7.08 (m, 8H, aromatic of side phenyls); 4.41, 4.34 (d, 6H, OCH_3).

4-Bromo-2',5'-di(4-hydroxyphenyl)-*m*-terphenyl (8). Compound **8** was prepared according to the procedure described for **3** as a white solid in 86% yield. It was recrystallized from *o*-dichlorobenzene. Mp: 165–167 °C.

IR (KBr, cm^{-1}): 3334 (O–H stretching); 1610, 1593, 1518 (aromatic); 1256 (O–H deformation).

^1H NMR ($\text{DMSO}-d_6$), ppm: 9.58, 9.31 (d, 2H, OH); 7.71–7.25 (m, 11H, aromatic of *m*-terphenyl); 6.91–6.53 (m, 8H, aromatic of side phenyls).

4-Bromo-2',5'-di[4-(2-ethylhexyloxy)phenyl]-*m*-terphenyl (9). Compound **9** was synthesized in 77% yield according to the method described for **4a**. It was recrystallized from CCl_4 . Mp: 122–124 °C.

IR (KBr, cm^{-1}): 2924, 2856 (C–H stretching of the aliphatic segments); 1608, 1516, 1488 (aromatic); 1454 (C–C stretching of the aliphatic segments); 1242 (ether bond).

^1H NMR (CDCl_3), ppm: 7.48–6.96 (m, 11H, aromatic of *m*-terphenyl); 6.62–6.51 (d, 8H, aromatic of side phenyls); 3.95, 7.84 (d, 4H, OCH_2); 1.75–0.80 (m, 30H, other aliphatic).

1,4-Bis[4-[2,5-di(4-(2-ethylhexyloxy)phenyl)-3-phenyl]phenylstyryl]benzene (10). Model compound **10** was prepared as a yellowish solid in 90% yield by reacting *p*-divinylbenzene with double molar amount of **9** according to the method described for polymer **PVa**. It was recrystallized from ethyl acetate. Mp: 165–167 °C.

IR (KBr, cm^{-1}): 3026 (C–H stretching of aromatic); 2956, 2926, 2870 (C–H stretching of the aliphatic segments); 1608, 1516 (aromatic); 1454, 1434 (C–C stretching of the aliphatic segments); 1242 (ether bond); 964 (HC=CH *trans*).

^1H NMR (CDCl_3), ppm: 7.61–7.48 (m, 38H aromatic and 4H olefinic); 3.95–3.76 (d, 8H, OCH_2); 1.78–0.76 (m, 60H, other aliphatic).

Results and Discussion

Preparation of Monomers and Polymers. Scheme 1 outlines the method applied for the preparation of

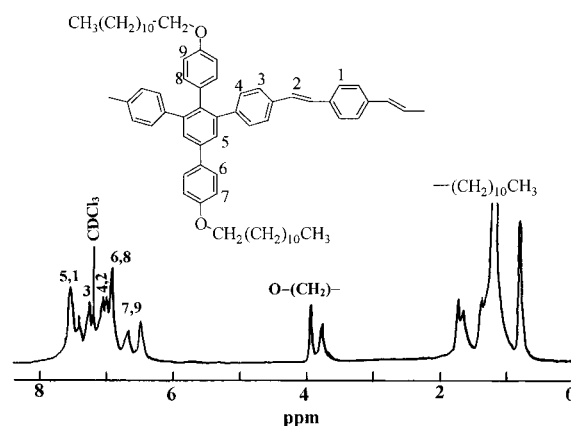


Figure 1. ^1H NMR spectrum of **PVb** in CDCl_3 solution.

monomers. This method has been developed in our laboratory and has been used for the preparation of other photonic polymers.^{24,25} The key step is the synthesis of the pyrylium salt and its reaction with substituted acetic acid anhydride. More particularly, the reaction of 4-methoxybenzaldehyde with 4-bromoacetophenone in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ yielded pyrylium salt **1**. The latter was condensed with 4-methoxyphenylacetic acid anhydride, generated in situ from 4-methoxyphenylacetic acid sodium salt and acetic anhydride, to afford compound **2**. The methoxy groups of **2** were hydrolyzed by means of hydrobromic acid to the corresponding bisphenol **3**. Dialkoxy-substituted dibromides **4** were synthesized by the Williamson reaction of **3** with bromoalkanes.

Compounds **4** were used as starting materials for the preparation of the polymers (Scheme 2). The Heck reaction of **4** with *p*-divinylbenzene yielded polymers **PVa** and **PVb**. The polymers were obtained in high yields (95–97%) and the molecular weights (M_n) ranged from 3100 to 3400. It is known that in the most cases the molecular weights of the polymers obtained via Heck coupling are relatively low.

Scheme 3 depicts the synthetic route applied for the preparation of model compound **10**. The method for the synthesis of monobromo compound **9** was similar to that used for monomers **4**. The only difference was the two-step synthesis of pyrylium salt **6**. Specifically, the latter was prepared by the condensation of 4-methoxybenzaldehyde with acetophenone to yield **5**, which subsequently afforded **6** by reacting with 4-bromoacetophenone in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Compound **10** was prepared by the Heck reaction of *p*-divinylbenzene with a double molar amount of **9**.

Characterization of Polymers. The structural characterization of polymers was accomplished by elemental analysis and FT-IR, ^1H NMR, and ^{13}C NMR spectroscopy as well as X-ray. Figure 1 shows the ^1H NMR spectra of polymer **PVb** and the assignments of peaks. The spectrum was in agreement with the proposed structure. It showed multiplets at the regions of 3.94–3.77 and 1.74–0.80 ppm assigned to the aliphatic protons. Aromatic and olefinic protons were overlapped and appeared in the region of 7.55–6.49 ppm. The olefinic protons resonated at 7.00 ppm, thus supporting the formation of a *trans* olefinic bond. This observation is consistent to the FT-IR spectrum of polymer, which presented an absorption at 964 cm^{-1} characteristic of 1,2-disubstituted *trans*-vinylene unit.

The introduction of side aliphatic groups along the polymers backbone aimed to produce soluble polymers.

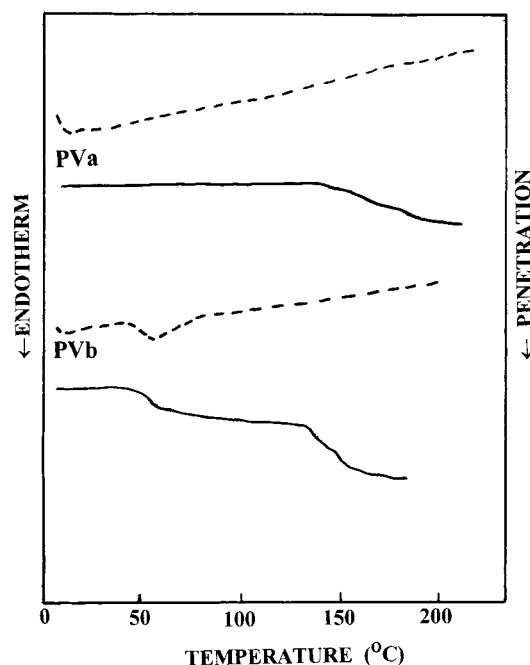


Figure 2. DSC (dashed lines) and TMA (solid lines) thermograms of polymers.

The synthesized polymers were soluble at room temperature in common solvents such as THF, CHCl_3 , 1,2-dichloroethane, and chlorobenzene. They presented comparable solubilities regardless of the length of the side aliphatic chain. The enhanced solubility of polymers was in line with their amorphous nature as detected by WAXD. This feature could be attributed to the noncoplanar structure of the dibromides moieties as discussed below.

Thermal characterization of polymers was accomplished by DSC, TMA, and TGA. DSC thermograms (Figure 2) of polymer **PVb**, bearing dodecyloxy side groups, showed a weak endotherm in the region around 55 °C attributable to the melting of side aliphatic groups. This feature has also been observed for other alkyl-⁹ and alkoxy-substituted²⁶ PPV. Polymer **PVa** with 2-ethylhexyloxy groups lacks endotherm associated with melting of side groups. The DSC curves of polymers did not exhibit melting or other transition even after repeated scans. The absence of melting as well as of thermotropic behavior was also verified by polarized microscopy. The T_g transitions of polymers were determined by the TMA method using a penetration probe (Figure 2). **PVb** showed T_g at 135 °C. In addition, it exhibited a relaxation at the region of 50–55 °C which is attributed to the melting of aliphatic groups. This relaxation was also detected at the same region by DSC. **PVa** exhibited T_g at 140 °C.

The thermal stability of polymers was estimated by TGA. The temperatures at which 1% and 10% weight losses were observed in N_2 and air as well as the anaerobic char yields (Y_c) at 800 °C are listed in Table 1. It is seen that the polymers despite the presence of the aliphatic units showed sufficient thermal stability.

Optical Properties. The optical properties of the polymers were examined by UV-vis and photoluminescence spectroscopy. The absorption, photoluminescence excitation (PLE) and PL maxima as well as the quantum yields of polymers in THF solutions and in thin films are summarized in Table 2.

Table 1. TGA Data of Polymers

polymer	in N_2			in air	
	T_1^a (°C)	T_{10}^a (°C)	Y_c^b (%)	T_1 (°C)	T_{10} (°C)
PVa	320	480	47	285	440
PVb	320	470	61	280	450

^a T_1 , T_{10} : Temperatures at which weight losses of 1 and 10%, respectively, were observed. ^b Y_c : Char yield at 800 °C.

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

	polymer	
	PVa	PVb
$\lambda_{a, \text{max}}$ in solution ^a (nm)	374	374
E_g^b (eV)	3.0	3.0
$\lambda_{\text{ex, max}}$ in solution ^c (nm)	386	386
$\lambda_{\text{f, max}}$ in solution ^d (nm)	420, 444 (374)	423, 444 (374)
$\lambda_{a, \text{max}}$ in thin film ^a (nm)	380	380
$\lambda_{\text{ex, max}}$ in thin film ^c (nm)	396	396
$\lambda_{\text{f, max}}$ in thin film ^d (nm)	460 (380)	460 (380)
Φ_f in solution ^e	0.30	0.31

^a $\lambda_{a, \text{max}}$: The absorption maximum from the UV-vis spectra in THF solution or in thin film. ^b E_g : The optical energy gaps calculated from the UV-vis spectra in THF solution. ^c $\lambda_{\text{ex, max}}$: The PL excitation maxima in THF solution or in thin film. ^d $\lambda_{\text{f, max}}$: The PL maxima in THF solution or in thin film. Numbers in parentheses indicate the excitation wavelength. ^e Φ_f : PL quantum yield.

The UV-vis spectra of polymers in dilute THF solution (Figure 3a) showed a single featureless peak centered at 374 nm due to the π - π^* electron transition. No absorption detected above 420 nm. The optical energy gap (E_g) of **PVa** and **PVb**, calculated from the onset of their absorption curves, was 3.0 eV.

The polymers showed blue photoluminescence in THF solution (Figure 3b). Both polymers exhibited well-resolved vibrational peaks at about 420 and 444 nm. The photoluminescence excitation spectra monitored at both peaks, except a difference in the intensity, were identical, supporting the point that these PL peaks originated from the same electronic state. The PL spectra found to be nearly independent of the concentration. Figure 4 presents the PL spectra of **PVa** at concentrations of 10^{-3} and 10^{-4} %. It is seen that both solutions provided identical spectra with maxima at 422 and 446 nm. Although the concentration of solution differed by 10 orders of magnitude, no red shift was detected even at the long wavelengths region. This observation suggests that the emission stemmed from a single chain.

The absorption and emission spectra were strongly blue shifted relative to known PPV polymers. In particular, the PL spectra of **PVa** and **PVb** were more than 40 nm hypsochromically shifted relative to alkoxy-substituted PPV.²⁶ As a result, the synthesized polymers emit in the blue region, while the emission of PPV takes place in the yellow-green region. This behavior arose from the interruption of the conjugation due to the insertion of phenyl substituent at 2' position of *m*-terphenyl. The steric interaction of this bulk substituent with two ortho phenyls of the main chain increases the torsion angle. The optimized geometry of dibromides **4**, calculated by CS Chem. 3D Std modeling program, revealed that the rings of *m*-terphenyl are not coplanar with large twist angles. These are large enough to cause an efficient interruption of conjugation length. Figure 4 shows the PL spectra of polymers **PVa** and model compound **10**. Their spectra were almost identical, implying that the two molecules possess the same efficient conjugation length. In addition, it suggests that

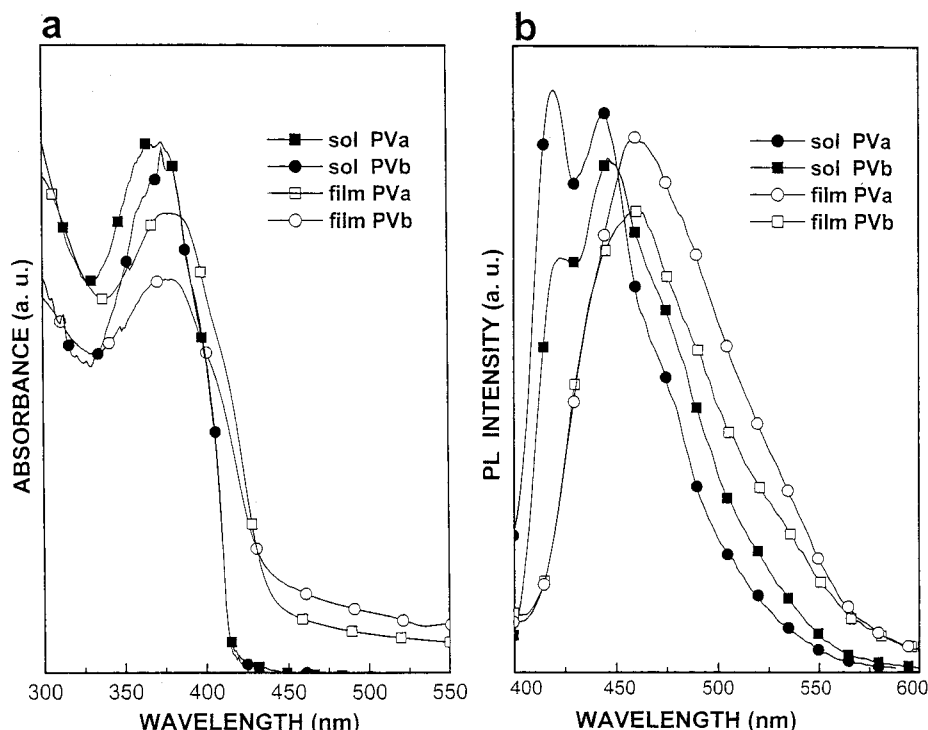


Figure 3. (a) UV-vis and (b) PL spectra of polymers in THF solution and in film. The intensities were arbitrarily chosen in order to optimally fit the curves.

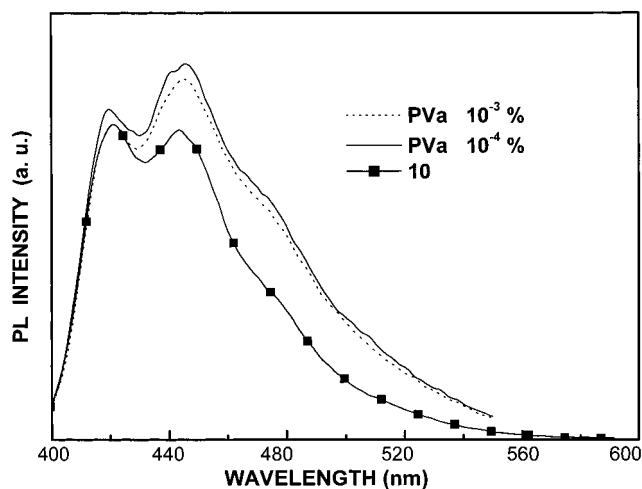


Figure 4. PL spectra of **PVa** at concentrations 10^{-3} and 10^{-4} % in THF as well as of model compound **10**. The intensities were arbitrarily chosen in order to optimally fit the curves.

there is no conjugation between the adjacent repeating units of the polymer. This observation strongly supports the assumption that the bulk substituents limited the conjugation length.

The photoluminescence quantum yields (Φ) of polymers in THF were measured relative to quinine sulfate.²⁷ Polymers **PVa** and **PVb** exhibited Φ values of 0.30 and 0.31, respectively. The rather low Φ values could be attributed to nonradiative decay. Polymers **PVa** and **PVb** showed much higher absorbance relative to excitation intensity in their PLE spectra (presented below), which indicates higher probability for non-radiative decay.²⁸ In addition, the Φ of model compound **10** in THF solution was 0.33, which is comparable, within experimental error, to those of polymers. This indicates that the relative low molecular weights of polymers did not affect significantly the Φ values and

generally their optical properties. Analogous behavior has been observed for other PPV polymers prepared by Heck coupling of aryl dibromides.⁹

The UV-vis and PL spectra of polymers were also recorded in dilute chlorobenzene (CB) solution. These spectra were identical in both THF and CB. For MEH-PPV it has been postulated that it forms coils that are more tightly in THF while in CB tends to "unfold", hence the red shift of its absorbance and emission in CB.²⁹ This is due to the fact that THF dissolved preferentially the side aliphatic chains and CB the main rigid chain. Polymers **PVa** and **PVb** should form random coils of the same amount of expansion in both solvents, judging from UV-vis and PL spectra. Probably, the twisted structure of dibromide segments led to a loose packing of chain, allowing the accessibility of solvents which dissolve both main chain and aliphatic side groups.

Optical properties of polymers were also examined in the solid state. Thin films of polymers were prepared by spin casting on quartz plates from their THF solutions. The UV-vis spectra of films are presented in Figure 3a. It is seen that the UV-vis maxima of polymers were about 6 nm red shifted relative to those of solutions. In addition, the absorption edge was red shifted toward the low energies region. The PL spectra of films are shown in Figure 3b. The emission of films centered at 460 nm and originated from species which existed in ground state as demonstrated by finite absorption in this spectral region. The emission of films was red shifted by 16 nm relative to solutions, became structureless and extended into long wavelengths.

The red shift of emission of films could be attributed to excimer clusters or aggregates. If excimers were responsible one would expect that UV-vis and PLE spectra of film would be identical to those of solution. In contrast PL spectra are expected to be strongly Stokes shifted. This is because the excimer exists only in excited state. As aggregates exist in both ground and

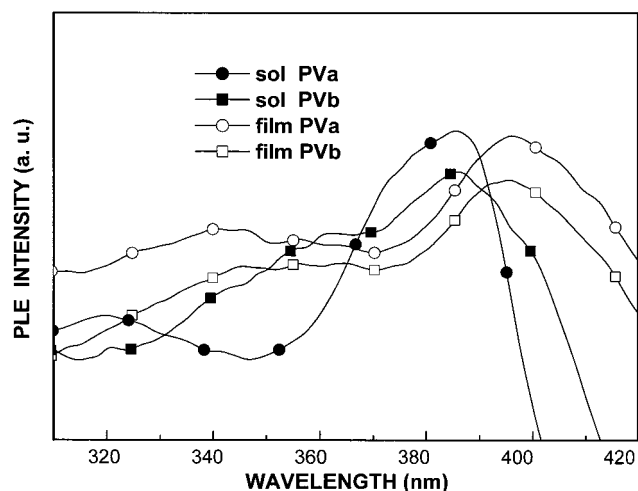


Figure 5. PLE spectra of polymers in THF solution and in film. The intensities were arbitrarily chosen in order to optimally fit the curves.

excited state, discrepancies between film and solution are detected for UV-vis, PLE and PL spectra. A first indication that excimer formation should be excluded is arisen from Figure 4, which demonstrated that the emission was nearly independent of concentration. This suggests no excimer formation, since excimers formed spontaneously in solution. In contrast, in the solutions of pyrene, which forms excimer, as the concentration increases the emission of pyrene is replaced by featureless excimer emission.³⁰

Evidences for aggregates formation arise from Figure 3. The UV-vis maxima of films were red shifted relative to solutions and extended in long wavelengths showing directly accessible states in films. This is consistent to the formation of aggregates rather than of excimers, since the latter cannot be directly excited.³¹ This observation is more pronounced in PLE spectra of polymers. Figure 5 presents the PLE spectra of both polymers in solution and in solid state. The excitation spectra of films are bathochromically shifted relative to those of solutions by 10 nm. This again suggests that in films exist species directly accessible spectroscopically. The red shift of UV-vis and PLE spectra of films relative to those of solutions could be attributed to the delocalization of ground state over several polymer chains. On the other hand, the red shift of the films' PL suggests that delocalization also occurs in the excited state. This strongly indicates the formation of aggregates that exist in both ground and excited state. These features are in contrast to those reported for CN-substituted PPV.³² The authors, on the basis of the fact that emission of film was red shifted while absorption remained unchanged, suggested that excimers, which show delocalization only in the excited state, were responsible for the bathochromical shift of emission of film.

A technique that enables to detect the formation of aggregates is the monitoring of PL at different excitations energies. The site selective fluorescence method has been used to prove the existence of aggregations in ladder poly(*p*-phenylene)s³³ and in poly(*p*-pyridyl vinylene).³⁴ The PL spectra of **PVa** and **PVb** in films were recorded with excitation at the maximum of absorption (high energy radiation) and at long wavelength (low energy radiation) where the absorption of films is minimal. Although the emission maxima of both

films were different under high or low energy excitation, there were no clear evidences of site selective effects. In the case of **PVb**, the PL maximum was 460 nm under excitation at 380 nm, while excitation at 420 nm provided a broad spectrum centered at 466 nm. However, the emission edges of both spectra were almost the same. These findings showed that the differences of the spectra were minimal and hardly supported multiple emitting sites in film. These minimal differences, which are within experimental error, as well as the small shifts of UV-vis and PL spectra of films relative to solutions (about 6 and 16 nm, respectively) possibly imply a reduced tendency of polymers to form aggregates. The bulk side phenyls, which prevent a dense chain packing, are responsible for this behavior. It is known that planarity of conjugated moieties controls the π - π interaction which are responsible for the red shift of the films' emission.³⁵

Conclusions

New PPV derivatives carrying bulk side phenyls have been synthesized via Heck coupling. Long alkoxy substituents were used in order to produce soluble materials in common organic solvents. The presence of bulky pendant phenyls results in amorphous materials which showed neither melting nor thermotropic behavior. In addition steric interaction of side phenyl with phenyl rings of the main chain caused an efficient interruption of the conjugation length which led to strong blue shift of the emission. The polymers showed blue photoluminescence in both solution and film. Solutions of polymers exhibited rather low quantum efficiencies attributable to non radiative decay. The red shifts of UV-vis, PLE, and PL spectra of films relative to those of solutions suggest the formation of new species in films that absorb and emit at longer wavelengths. These species are found to be aggregates.

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References and Notes

- (1) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.
- (2) Yu, G.; Heeger, A. J. *J. Appl. Phys.* **1995**, *78*, 4510.
- (3) Brown, R.; Pomp, A.; Hart, C. M.; Deleeuw, D. M. *Science* **1995**, *270*, 974.
- (4) Tessler, N.; Denton, G. J.; Friend, R. H. *Nature* **1996**, *382*, 695.
- (5) Burroughes, J. H.; Bradley, D. D. C.; Brown, R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
- (6) For a review, see: Kraft, A.; Grimsdale, X.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.
- (7) Jang, M. S.; Song, S. Y.; Lee, J.-I.; Shim, H.-K.; Zyung, T. *Macromol. Chem. Phys.* **1999**, *200*, 1101.
- (8) Chen, Z.-K.; Meng, H.; Lai, Y.-H.; Huang, W. *Macromolecules* **1999**, *32*, 4351.
- (9) Hilberer, A.; Brouwer, H.-J.; Van der Scheer, B. J.; Wildeman, J.; Hadzioannou, G. *Macromolecules* **1995**, *28*, 4525.
- (10) Cho, H. N.; Kim, J. K.; Kim, D. Y.; Kim, C. Y.; Song, N. W.; Kim, D. *Macromolecules* **1999**, *32*, 1476.
- (11) Morati, S. C.; Cervini, R.; Holmes, A. B.; Baigent, D. R.; Friend, R. H.; Greenham, N. C.; Gruner, J.; Hamer, P. J. *Synth. Met.* **1995**, *71*, 2117.
- (12) Johansson, D. M.; Theander, M.; Inganas, O.; Andersson, M. R. *Synth. Met.* **2000**, *113*, 293.
- (13) Park, L. S.; Han, Y. S.; Hwang, J. S.; Kim, S. D. *J. Polym. Sci., Part A: Polym. Sci.* **2000**, *38*, 3173.
- (14) Gurge, R. M.; Sarker, A. M.; Lathi, P. M.; Hu, B.; Karasz, F. E.; *Macromolecules* **1996**, *29*, 4287.

- (15) Liao, L.; Pang, Y.; Ding, L.; Karasz, F. E. *Macromolecules* **2001**, *34*, 6756.
- (16) Gurge, R. M.; Sarker, A. M.; Lathi, P. M.; Hu, B.; Karasz, F. E. *Macromolecules* **1997**, *30*, 8286.
- (17) Gill, R. E.; Malliaras, G. G.; Wildeman, G.; Hadziioannou, G. *Adv. Mater.* **1994**, *6*, 132.
- (18) Yu, B.; Holdcroft, S. *Macromolecules* **1993**, *26*, 4457.
- (19) Peng, Z.; Zhang, J.; Yu, B. *Macromolecules* **1999**, *32*, 5162.
- (20) Hsieh, B. R.; Yu, Y.; Forsythe, E. W.; Schaaf, M.; Feld, W. W. *J. Am. Chem. Soc.* **1998**, *120*, 231.
- (21) Setayesh, S.; Grimdale, A. C.; Weil, T.; Enkelmann, V.; Mullen, K.; Meghdali, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946.
- (22) Rothberg, L. J.; Yan, M.; Kwock, E. W.; Miller, T. M.; Galvin, M. E.; Son, S.; Papadimitrakopoulos, F. *IEEE Trans. Electron Devices* **1997**, *44*, 1258.
- (23) Storey, B. T. *J. Polym. Sci., Part A* **1965**, *3*, 265.
- (24) Spiliopoulos, I. K.; Mikroyannidis, J. A. *Macromolecules* **2001**, *34*, 5711.
- (25) Mikroyannidis, J. A. *Macromol. Chem. Phys.* **2001**, *202*, 2367.
- (26) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.
- (27) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.
- (28) Gettinger, C. L.; Heeger, A. J.; Drake, J. M.; Pine, D. G. *J. Chem. Phys.* **1994**, *101*, 1673.
- (29) Nguyen, T. Q.; Doan, V.; Schwartz, B. J. *J. Chem. Phys.* **1999**, *110*, 4068.
- (30) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.
- (31) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals*; Oxford University Press: New York, 1982.
- (32) Samuel, I. D. W.; Rumbles, G.; Collison, C. J.; Moratti, S. C.; Holmes, A. B. *Chem. Phys.* **1998**, *227*, 75.
- (33) Lemmer, U.; Heun, S.; Mahrt, R. F.; Scherf, U.; Hopmeier, M.; Siegner, U.; Gobel, E. O.; Mullen, K.; Bassler, H. *Chem. Phys. Lett.* **1995**, *240*, 373.
- (34) Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafson, T. L.; Fu, D. K.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1996**, *54*, 9180.
- (35) Zheng, M.; Sarker, A. M.; Gurel, E. E.; Lathi, P. M.; Karasz, F. E.; *Macromolecules* **2000**, *33*, 7426.

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