Soluble and Strongly Photoluminescent Polyethers with Oligophenylene, *p*-Phenylenevinylene-, or *p*-Phenyleneethynylene-Based Chromophores

Ioakim K. Spiliopoulos* and John A. Mikroyannidis

Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece

ABSTRACT: New polyethers containing alternating rigid conjugated chromophores and nonconjugated aliphatic spacers were synthesized. The chromophores were of oligophenylene, *p*-phenylenevinylene, and *p*-phenyleneethynylene types. The polymers were amorphous and showed enhanced solubility in common organic solvents and T_g in the range 80−115 °C and satisfied thermal stability. The polymers showed blue fluorescence both in solution and in solid state. Their PL spectra displayed maxima at 390−453 and 407−464 nm in solution and in the solid state, respectively. The wavelengths of absorption and emission depended on the chemical structures of the chromophores. The PL quantum yields in solution were determined and ranged from 0.58 to 0.98.

Introduction

Conjugated polymers have attracted considerable attention in the past decade because of their potential utility in a wide variety of applications, such as light-emitting diodes,[1−4] photodiodes,[5] photovoltaic cells,[6] nonlinear optical materials,[7] and optically pumped lasers.[8] In particular, since the first report of light emitting diodes[9] based on poly(*p*-phenylenevinylene)s (**PPV**), numbers of polymers, mainly PPV, poly(*p*-phenylene)s (**PPP**), poly(thiophene)s, poly(*p*-phenylene ethynylene)s (**PPE**), and their derivatives, have been synthesized as candidates for polymeric light-emitting diodes.

Since conjugated polymers are insoluble materials, extensive research interest has been focused on preparing soluble polymers. The most popular way to achieve the above objective is the introduction of side aliphatic substituents along the rigid backbone. There are many examples of alkyl- or alkoxy-substituted PPV,[10−12] PPE,[13−15] and PPP.[16−18] Another method to obtain soluble polymers is the introduction of nonconjugated spacers in the main chain. The merits of such an approach are the improvement of processability of the polymers and the control of π conjugation length, resulting in polymers with well-defined lumophores. In the case of PPV, shortening of the effective conjugation length is essential in order to shift the emission spectrum from green to blue. In addition, the improvement of electroluminescence efficiencies due to the introduction of nonconjugated segments in the main chain have been reported.[19] Organosilicon moieties or linear aliphatic units have been used to obtain processable conjugated PPV[20−25] and PPP.[26,27] In contrast, there are a few examples of PPE containing nonconjugated spacers in the main chain.[28]

In the present work, we synthesized polyethers that contained alternating rigid conjugated and flexible nonconjugated blocks. The rigid blocks were of oligophenylene-, PPV-, or PPE-type. They were crucial to tailoring the band gap of the electronic transitions, which determines the wavelength of emitting light. The flexible spacers, which were of polyethylene type, con-

tributed to the enhanced solubility and processability of polymers.

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. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained using a Bruker spectrometer. The NMR spectra were recorded using DMSO-d_6 or CDCl$_3$ as solvent. 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 emission spectra were obtained with a Perkin-Elmer LS55B luminescence spectrometer. GPC analysis was conducted with an apparatus 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 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 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.

Reagents and Solvents. 4-Bromobenzaldehyde was recrystallized from methanol. Dimethylacetamide (DMAc), toluene, and 1,2-dichloroethane were dried by distillation over CaH$_2$. Acetophenone was purified by distillation under reduced pressure. Triethylamine was dried by distillation over KOH. 4-Methoxyphenylacetic acid sodium salt was prepared by reacting equimolar amounts of 4-methoxyphenylacetic acid with aqueous sodium hydroxide and subsequent fusing. Tri-*o*-tolylphosphine [P(*o*-tolyl)$_3$], Pd(OAc)$_2$, 1,6-dibromohexane, 1,10-dibromodecane, boron trifluoride etherate, acetic anhydride, and hydrobromic acid (47−49%) were used as supplied.

* Corresponding author. E-mail: mikroyan@chemistry.upatras.gr.

Preparation of Monomers. *p*-Divinylbenzene[29] and *p*-diethynylbenzene[30] were synthesized according to known methods. Compounds **1** and **2** were synthesized according to previously described methods.[31]

4,4′′′′-Dimethoxy-2′,6′,3′′′,5′′′-tetraphenyl-*p*-quinquephenyl (3). A flask was charged with a mixture of **2** (3.80 g, 5.32 mmol), 4-methoxyphenylacetic acid sodium salt (4.00 g, 21.28 mmol), and propionic anhydride (15 mL). The mixture was heated at the boiling temperature for 4 h. During this period the product precipitated from the reaction mixture. It was filtered off, washed with methanol, and dried to afford **3** as a whitish solid (3.58 g, 65%). It was recrystallized from *o*-dichlorobenzene. Mp: >300 °C.

IR (KBr, cm^{-1}): 1608, 1518, 1426 (aromatic); 1244 (C–O–C).

^{1}H NMR (DMSO-d_6), ppm: 7.92–7.49 (m, 8H, at positions 3, 5′,2′′,3′′,5′′,6′′,2′′′,6′′′); 7.26–7.13 (m, 20H, of the side phenyls); 6.74 (m, 4H, at positions 2, 6, 2′′′,6′′′); 6.58 (m, 4H, at positions 3, 5, 3′′′,5′′′); 3.72 (s, 3H, OCH$_3$).

4′,4′′′′-Dihydroxy-2′,6′,3′′′,5′′′-tetraphenyl-*p*-quinquephenyl (4). Compound **3** (1.00 g, 1.34 mmol) was dissolved by heating it in glacial acetic acid (50 mL). Hydrobromic acid 47–49% (3 mL) was added in portions to the refluxing solution over a period of 5 h. Refluxing was continued overnight. The solution was subsequently poured in water and the whitish precipitate was filtered, washed with water and then with methanol, and dried to afford **4** (0.93 g, 97%). It was recrystallized from *o*-dichlorobenzene. Mp: >300 °C.

Anal. Calcd for C$_{54}$H$_{38}$O$_2$: C, 90.22; H, 5.33. Found: C, 89.68; H, 5.28.

IR (KBr, cm^{-1}): 3346 (OH stretching); 1608, 1518, 1426 (aromatic); 1260, 1224, 1172 (C–OH stretching and OH deformation).

^{1}H NMR (DMSO-d_6), ppm: 7.78 (m, 4H, at positions 3′,5′,2′′,6′′); 7.45–6.78 (m, 4H, at positions 2′′,3′′,5′′,6′′ and 20H of side phenyls); 6.60–6.55 (m, 4H, at positions 2, 6, 2′′′,6′′′); 6.48 (m, 4H, at positions 3, 5, 3′′′,5′′′); 5.21 (s, 2H, OH).

4-(4-Bromophenyl)-2,6-diphenylpyrylium tetrafluoroborate (5). 4-Bromobenzaldehyde (3.50 g, 18.92 mmol) and acetophenone (4.55 g, 37.84 mmol) were dissolved in 1,2-dichlorobenzene (10 mL). Boron trifluoride etherate (5.94 mL, 47.30 mmol) was added to the solution. The solution was heated at 80 °C under N$_2$ for 3 h. It was subsequently concentrated under reduced pressure and the concentrate was triturated with ethanol. The precipitate was filtered, washed with ethanol, and dried to afford **5** as a yellow solid (5.75 g, 64%). It was recrystallized from acetic acid. Mp: 284–286 °C.

IR (KBr, cm^{-1}): 1622, 1582, 1492 (aromatic and pyrylium structure); 1072 (br, BF$_4^-$).

^{1}H NMR (DMSO-d_6), ppm: 8.21 (s, 2H, meta to O$^+$); 7.81–7.25 (m, 14H, other aromatic).

4-Methoxy-4′′-bromo-2′,6′-diphenyl-*p*-terphenyl (6). A mixture of **5** (2.64 g, 5.56 mmol), 4-methoxyphenylacetic acid sodium salt (2.09 g, 11.12 mmol) and acetic anhydride (4 mL) was stirred and refluxed for 3 h. It was subsequently cooled in refrigerator overnight and the precipitate was filtered, washed with methanol and dried to afford **6** as a white solid (1.85 g, 68%). It was recrystallized from acetonitrile. Mp: 174–176 °C.

IR (KBr, cm^{-1}): 1606, 1516, 1426 (aromatic); 1244 (C–O–C).

^{1}H NMR (CDCl$_3$), ppm: 7.54 (s, 2H, at positions 3′,5′); 7.49 (m, 4H, at positions 2′′,3′′,5′′,6′′); 7.14–7.04 (m, 10H, of side phenyls); 6.68, 6.66 (d, 2H, at positions 2, 6); 6.47, 6.45 (d, 2H, at positions 3, 5); 3.60 (s, 3H, OCH$_3$).

^{13}C NMR (CDCl$_3$), ppm: 157.50, 143.22, 142.32, 140.94, 139.81, 133.02, 132.35, 130.30, 129.12, 128.60, 128.53, 128.47, 128.13, 126.51, 121.84, 113.64, 59.84.

4-Hydroxy-4′′-bromo-2′,6′-diphenyl-*p*-terphenyl (7). Compound **6** (2.00 g, 4.07 mmol) was dissolved in glacial acetic acid (15 mL) by heating at boiling temperature. Hydrobromic acid 47–49% (3 mL) was added in portions over a period of 3 h. Refluxing was continued for 40 h. The solution was poured in ice–water and the white precipitate was filtered, washed with

water then with cold methanol and dried to afford **7** (1.75 g, 90%). It was recrystallized from ethanol 80%. Mp: 218–220 °C.

IR (KBr, cm^{-1}): 3562 (OH stretching); 1608, 1516, 1490, 1424 (aromatic); 1262 (C–OH stretching).

^{1}H NMR (CDCl$_3$), ppm: 7.54 (s, 2H, at positions 3′,5′); 7.49 (m, 4H, at positions 2′′,3′′,5′′,6′′); 7.12–7.05 (m, 10H, of side phenyls); 6.63, 6.61 (d, 2H, at positions 2, 6); 6.40, 6.37 (d, 2H, at positions 3, 5); 4.87 (s, 2H, OH).

^{13}C NMR (CDCl$_3$), ppm: 154.31, 143.21, 142.29, 134.04, 133.27, 133.19, 130.31, 129.34, 129.12, 128.53, 128.45, 127.95, 127.86, 126.64, 126.26, 114.82.

1,6-Bis(4-oxy-4′′-bromo-2′,6′-diphenyl-*p*-terphenylyl)-hexane (8a). A mixture of **7** (0.90 g, 1.89 mmol), 1,6-dibromohexane (0.23 g, 0.94 mmol), K$_2$CO$_3$ (0.32 g, 2.35 mmol), and DMF (7 mL) was refluxed under N$_2$ for 12 h. Then it was poured in water and the precipitate was filtered, washed with methanol and dried to afford **8a** as a white solid (0.90 g, 91%). It was recrystallized from acetonitrile. Mp: 125–127 °C.

Anal. Calcd for C$_{66}$H$_{52}$Br$_2$O$_2$: C, 76.45; H, 5.05. Found: C, 75.88; H, 5.09.

IR (KBr, cm^{-1}): 2934, 2861 (stretching of aliphatic C–H); 1606, 1514, 1492 (stretching of aromatic C–C); 1426 (stretching of aliphatic C–C); 1240 (C–O–C).

^{1}H NMR (CDCl$_3$), ppm: 7.53 (s, 4H, at positions 3′,5′ of terphenyls); 7.48 (m, 8H, at positions 2′′,3′′,5′′,6′′ of terphenyls); 7.26–7.05 (m, 20H, of side phenyls); 6.63 (s, 4H, at positions 2, 6 of terphenyls); 6.43, 6.38 (d, 4H, at positions 3, 5 of terphenyls); 3.72 (m, 4H, O–CH$_2$–); 1.63–0.78 (m, 8H, –OCH$_2$-(CH_2)$_4$CH$_2$O–).

^{13}C NMR (CDCl$_3$), ppm: 157.73, 143.24, 142.38, 142.32, 139.84, 138.71, 133.19, 133.00, 132.29, 130.30, 129.10, 128.45, 128.10, 126.70, 122.14, 114.81, 68.05, 29.55, 26.44, 25.96.

1,10-Bis(4-oxy-4′′-bromo-2′,6′-diphenyl-*p*-terphenylyl)-decane (8b). Compound **8b** was prepared according to the procedure described for **8a** as a whitish solid in 89% yield by reacting **7** with 1,10-dibromodecane. It was recrystallized from acetone. Mp: 120–122 °C.

Anal. Calcd for C$_{70}$H$_{60}$Br$_2$O$_2$: C, 76.92; H, 5.53. Found: C, 76.48; H, 5.57.

IR (KBr, cm^{-1}): 2926, 2854 (stretching of aliphatic C–H); 1606, 1514 (stretching of aromatic C–C); 1426 (stretching of aliphatic C–C); 1242 (C–O–C).

^{1}H NMR (CDCl$_3$), ppm: 7.55 (s, 4H, at positions 3′,5′ of terphenyls); 7.50 (m, 8H, at positions 2′′,3′′,5′′,6′′ of terphenyls); 7.19–7.05 (m, 20H, of side phenyls); 6.67, 6.65 (d, 4H, at positions 2, 6 of terphenyls); 6.47, 6.44 (d, 4H, at positions 3, 5 of terphenyls); 3.81 (m, 4H, O–CH$_2$–); 1.65–0.98 (m, 16H, –OCH$_2$(CH_2)$_8$CH$_2$O–).

^{13}C NMR (CDCl$_3$), ppm: 157.76, 143.21, 142.37139.82, 138.94, 138.70, 132.98, 132.94, 130.30, 129.10, 128.46, 128.24, 128.10, 122.13, 113.86, 68.20, 29.85, 29.79, 29.66, 26.41.

Preparation of Polymers. Polymers PP6 and PP10. A flask was charged with a mixture of **4** (0.3100 g, 0.43 mmol), 1,6-dibromohexane (0.1053 g, 0.43 mmol), and K$_2$CO$_3$ (0.15 g, 1.08 mmol). The flask was degassed and purged with argon. DMF (6 mL) was added, and the mixture was refluxed for 12 h. It was subsequently poured into methanol, and the precipitate was filtered, washed with methanol and then with water, and dried to afford **PP6** (0.32 g, 94%).

Polymer **PP10** was similarly prepared from the polycondensation of **4** with 1,10-dibromodecane.

Polymers PV6 and PV10. A flask was charged with **8a** (0.7900 g, 0.72 mmol), *p*-divinylbenzene (0.0936 g, 0.72 mmol), Pd(OAc)$_2$ (0.0067 g, 0.03 mmol) and P(*o*-tolyl)$_3$ (0.0506 g, 0.17 mmol). The flask was degassed and purged with argon. DMAc (15 mL) and Et$_3$N (1 mL) were added under argon. The resulting solution was stirred and heated at 120 °C for 48 h. Then, it was poured into methanol, and the yellow precipitate was filtered, washed with methanol, and dried to afford **PV6** (0.70 g, 92%).
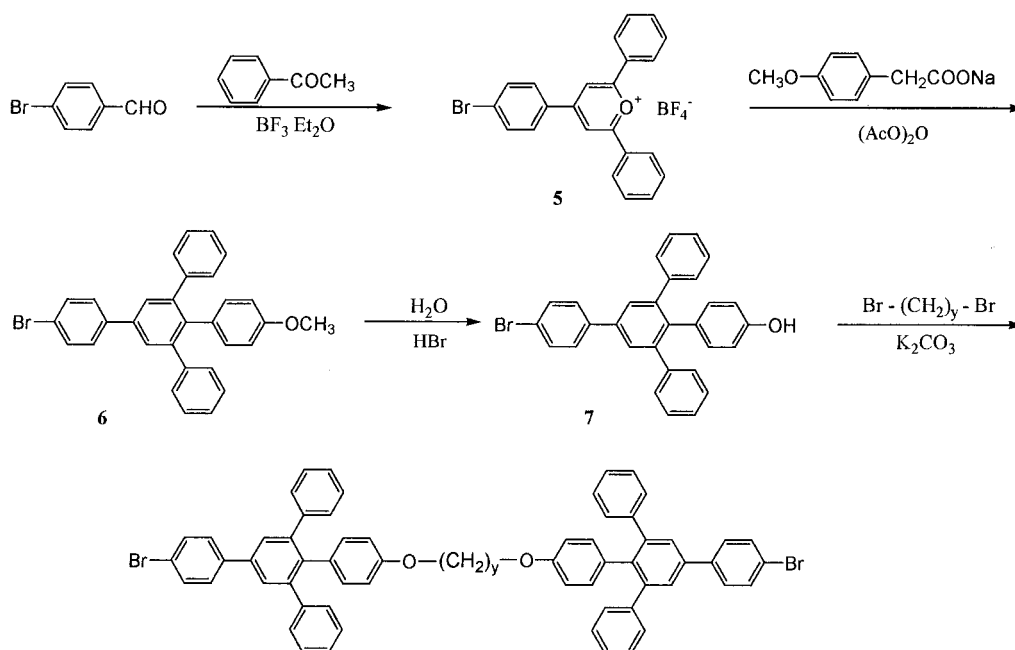
Polymer **PV10** was prepared from the reaction of *p*-divinylbenzene with **8b** according to the method described for PV6.

Polymers PE6 and PE10. A flask was charged with **8a** (0.5100 g, 0.492 mmol), *p*-diethynylbenzene (0.0620 g, 0.492

Scheme 1
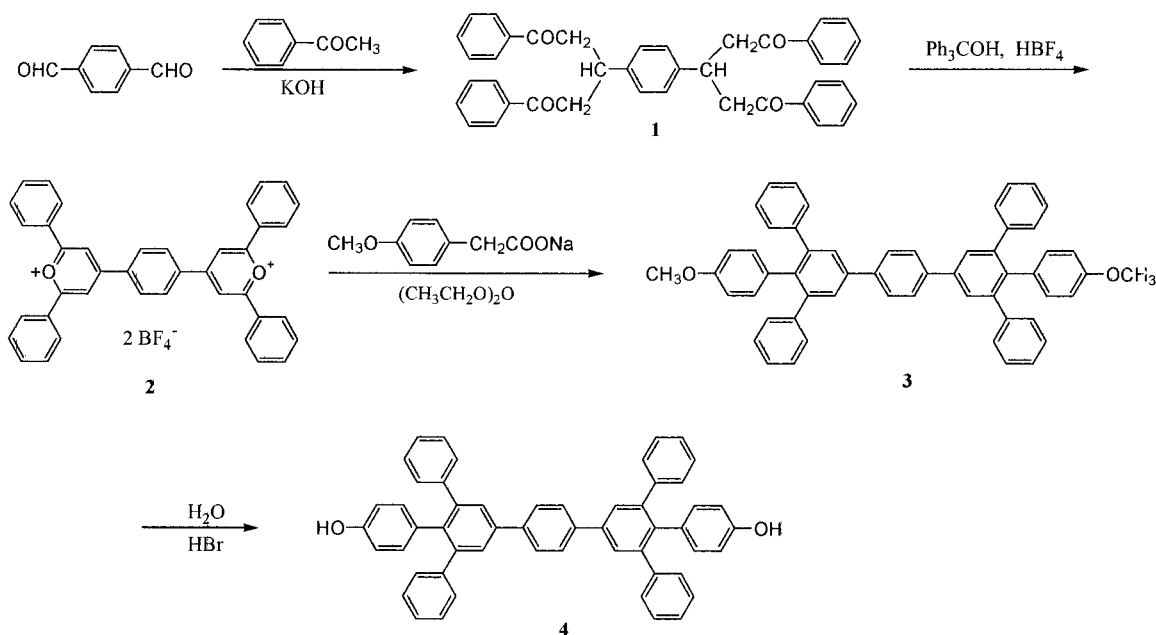
Scheme 2

8a : y=6; **8b** : y=10

mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.0207 g, 0.030 mmol), CuI (0.0208 g, 0.109 mmol), and PPh$_3$ (0.1050 g, 0.400 mmol). The flask was degassed and purged with argon. Toluene (15 mL) and Et$_3$N (2 mL) were added, and the obtained solution was heated at 70 °C for 48 h. After cooling to room temperature, the reaction mixture was filtered to remove the insoluble materials and the filtrate was poured into methanol. The yellow precipitate was filtered, washed with methanol, and dried to afford **PE6** (0.35 g, 71%).

**PE10** was synthesized by the same method from the reaction of **8b** with *p*-diethynylbenzene.

Results and Discussion

Scheme 1 outlines the synthesis of bisphenol **4**. The synthesis of tetraketone **1** and bispyrylium tetrafluoroborate **2** has been previously described. The conden-

sation of the latter with 4-methoxyphenylacetic acid sodium salt in the presence of propionic anhydride afforded compound **3**. The reaction of pyrylium salts with sodium salt of acetic acid or its derivatives has been well established and it has been used in our laboratory for the preparation of other desired monomers.[31,32] Compound **3** was hydrolyzed with aqueous hydrobromic acid solution to the corresponding bisphenol **4**.

The preparation of dibromo compounds **8a** and **8b** is shown in Scheme 2. 4-Bromobenzaldehyde reacted with acetophenone in the presence of boron trifluoride etherate to afford pyrylium salt **5**. The condensation of the latter with 4-methoxyphenylacetic sodium salt in the presence of acetic anhydride yielded methoxy compound **6**. Cleavage of methoxy groups with aqueous hydro-

Scheme 3

PP6 y = 6

PP10 y = 10

Scheme 4

PV6 y = 6

PV10 y = 10

PE6 y = 6

PE10 y = 10
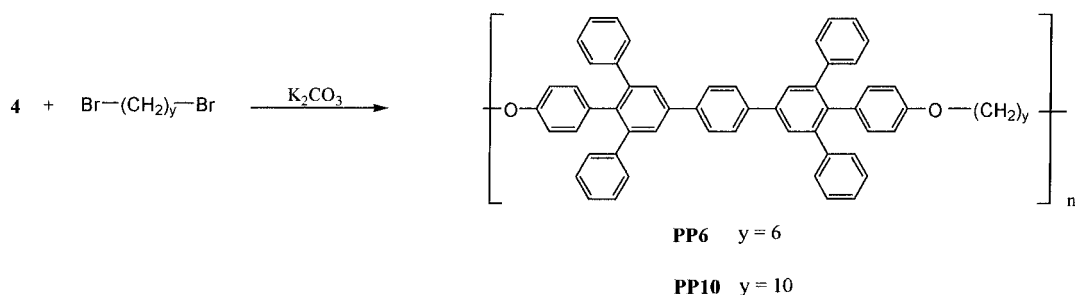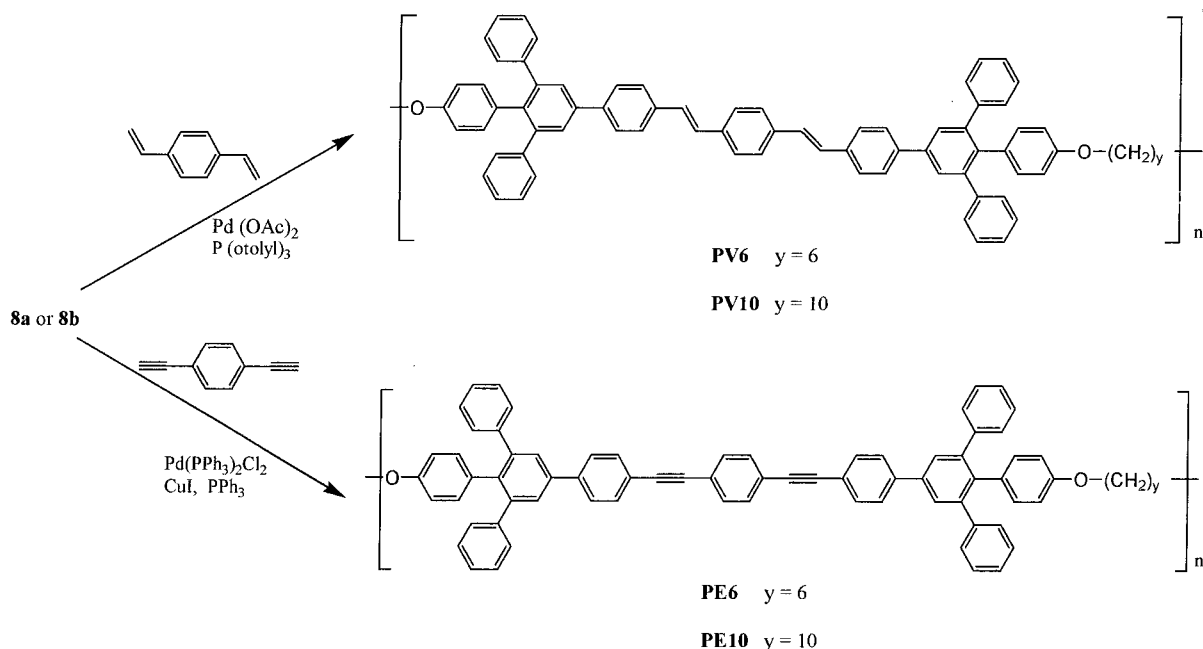
bromic acid solution afforded phenol **7**. The Williamson reaction of the obtained phenol with α,ω-dibromohexane or decane yielded dibromo compounds **8**. All monomers were characterized by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

Bisphenol **4** and dibromo compounds **8** were used as starting materials for the preparation of aromatic–aliphatic polyethers. More particularly, bisphenol **4** reacted with 1,6-dibromohexane or 1,10-dibromodecane to afford polymers **PP6** or **PP10** (Scheme 3). In addition, the Heck coupling of dibromo compounds **8** with *p*-divinylbenzene or *p*-diethynylbenzene is shown in Scheme 4. Dibromides **8a** and **8b** reacted with *p*-divinylbenzene to afford polyethers **PE6** and **PE10**. The reaction yields and GPC data of all polymers are listed in Table 1. The molecular weights of polymers **PV** and **PE** were rather low (2400–5900), but they are comparable to those of other PPV and PPE derived by the same method. It is known that the reaction of vinyls or alkynes with aryl bromides is less effective than that with aryl iodides.

Structural characterization of polymers was accomplished by FT-IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and elemental analysis as well as with wide-angle X-ray diffraction. Figure 1 displays the FT-IR spectrum of polymer **PP6**. It showed characteristic absorption of the ether bond at 1242 cm^{-1} (C–O–C stretching) and of the aliphatic chain at 2926, 2854 (C–H stretching), and 1426 cm^{-1} (C–C stretching). Besides absorption bands

Table 1. Preparation Yields, GPC Data and Elemental Analyses of Polymers

polymer	yield (%)	GPC data		empirical formula	elemental anal. (%)		
		M_n	DI			C	H
PP6	94	2800	2.8	$(C_{60}H_{48}O_2)_n$	calcd	89.97	6.04
					found	88.67	6.11
PP10	97	3600	2.3	$(C_{64}H_{56}O_2)_n$	calcd	89.68	6.59
					found	88.71	6.49
PV6	92	2900	2.7	$(C_{76}H_{60}O_2)_n$	calcd	90.80	6.02
					found	89.73	6.10
PV10	93	2400	3.2	$(C_{80}H_{68}O_2)_n$	calcd	90.53	6.46
					found	89.16	6.53
PE6	71	3300	2.5	$(C_{76}H_{56}O_2)_n$	calcd	91.17	5.64
					found	90.04	5.52
PE10	89	5900	2.1	$(C_{80}H_{64}O_2)_n$	calcd	90.87	6.10
					found	89.93	6.05

correlated with aromatic rings were observed at 3028 cm^{-1} (C–H stretching) and 1608, 1516 cm^{-1} (C–C stretching). Figures 2 and 3 show the ^{1}H and ^{13}C NMR spectra of polyether **PV10** in CDCl$_3$ solution. The ^{1}H NMR spectrum displayed multiplets at 3.81 and 1.65–1.20 ppm assigned to the aliphatic chain. Aromatic and olefinic protons were overlapped and appeared in the region of 7.66–6.45 ppm. Olefinic protons were observed at 7.11 ppm thus supporting the formation of trans double bond. This feature was in agreement with the IR spectrum of **PV10**, which showed absorption at 966 cm^{-1} due to the C–H out-of-plane bending mode of the 1,2-disubstituted trans vinylene unit. In the ^{13}C NMR spectrum of **PV10**, the olefinic carbons appeared at 129
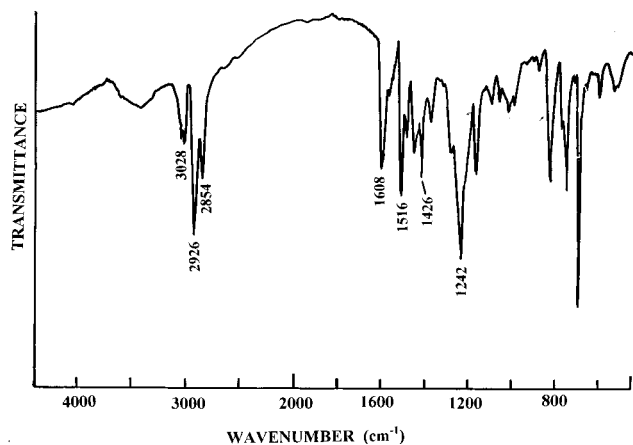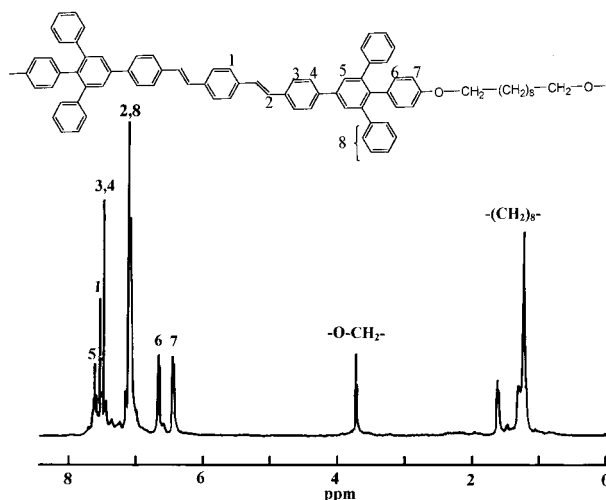
Figure 1. FT-IR spectrum of polymer **PP6**.

Figure 2. ¹H NMR spectrum of polymer **PV10** in CDCl₃ solution.

ppm, indicating the presence of a trans double bond. The ¹³C NMR spectrum of **PE10** in CDCl₃ (Figure 4) displayed a peak at about 90 ppm associated with the carbons of triple bond. Although the spectroscopic analysis confirmed the structures of the synthesized polymers, elemental analyses exhibited an aberration between the calculated and experimental values (Table 1). This is obviously due to the low molecular weights of the polymers.

The introduction of aliphatic spacers into the main chain aimed to reduce the stiffness and enhance the solubility of polymers. The synthesized polyethers were readily soluble at room temperature in common organic solvents such as chloroform, tetrahydrofuran, dichloromethane, 1,2-dichloroethane, and chlorobenzene. Solutions of the polymers could be spin cast forming transparent and pinhole-free thin films. The polymers exhibited comparable solubilities regardless of the length of aliphatic spacer or the chemical structure of the rigid block.

The crystallinity of the as prepared polymers was estimated by WAXD. All polymers displayed amorphous or microcrystalline natures that reflect their enhanced solubility.

Thermal characterization of polymers was accomplished by DSC, TMA and TGA. The glass transition temperatures (T_g) of polymers were determined by means of TMA utilizing a penetration probe. The T_g was

Figure 3. ¹³C NMR spectrum of polymer **PV10** in CDCl₃ solution.

Figure 4. ¹³C NMR spectrum of polymer **PE10** in CDCl₃ solution.

assigned by the first inflection point in TMA curve, and it was obtained from the onset temperature of this transition. The T_gs of polymers ranged from 80 to 115 °C, and they are listed in Table 2. Since the polymers
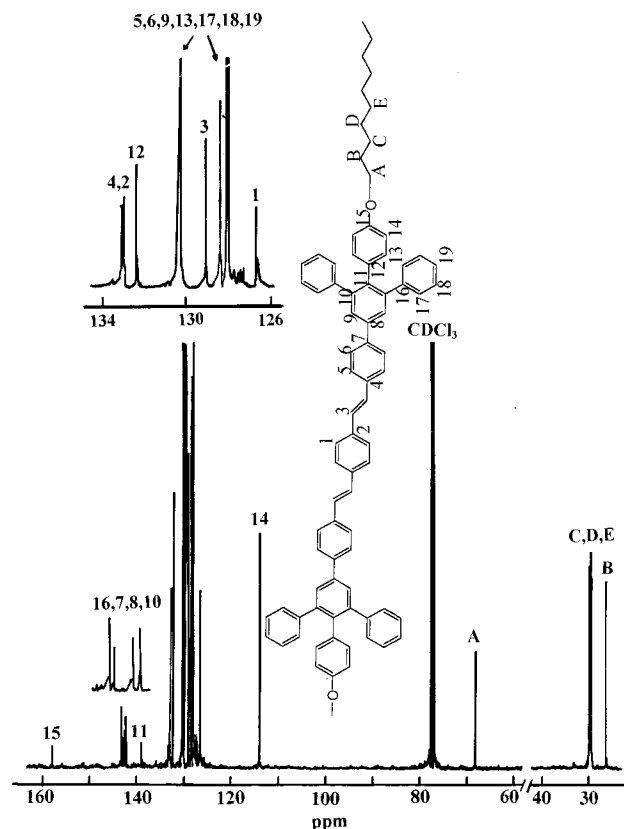
Table 2. TMA and TGA Data of Polymers

| | TMA | TGA | | | | |
| | | in N_2 | | | in air | |
polymer	$T_g{}^a$ (°C)	$T_1{}^b$ (°C)	$T_{10}{}^b$ (°C)	$Y_c{}^c$ (%)	T_1 (°C)	T_{10} (°C)
PP6	87	285	387	55	280	368
PP10	80	280	396	58	270	374
PV6	100	300	432	53	290	390
PV10	87	290	425	50	280	378
PE6	115	310	440	70	300	403
PE10	92	300	420	65	290	435

^{a} T_g: Glass transition temperature. ^{b} T_1, T_{10}: Temperatures at which weight loss of 1 and 10%, respectively, was observed. ^{c} Y_c: Char yield at 800 °C.

Table 3. Absorption and PL Data of Polymers

polymer	$\lambda_{a,max}$ in soln^a (nm)	$E_g{}^b$ (eV)	$\lambda_{f,max}$ in soln^c (nm)	$\lambda_{f,max}$ in thin film^c (nm)	Φ_f in soln^d
PP6	247, 306	3.47	396 (305)	407 (305)	0.98
PP10	254, 304	3.50	390 (305)	408 (305)	0.85
PV6	258, 289, 367	2.89	428, 453 (367)	461 (367)	0.70
PV10	254, 287, 367	2.89	426, 450 (367)	464 (367)	0.91
PE6	256, 286, 361	2.94	413 (361)	423 (361)	0.58
PE10	256, 294, 349	2.98	413 (349)	422 (349)	0.90

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

contained long aliphatic moieties into their backbone, they displayed relatively low T_gs. Upon comparing **PP**, **PV**, and **PE** polymers, it is seen that those with shorter aliphatic spacers showed higher T_gs than the corresponding with longer aliphatic spacers. The DSC thermograms of polymers did not show distinct endotherms associated with melting thus confirming their amorphous character. In addition, they did not display T_g transitions even after repeated runs. No liquid crystalline behavior was observed probably due to the long length of rigid groups and the presence of the side phenyls which prevented a packing with supramolecular order. The absence of liquid crystallinity was also confirmed by polarized microscopy. The results were consisted with the WAXD data that indicated amorphous polymers.

The thermal stability of polymers was estimated by TGA. The temperatures at which weight losses of 1 and 10% were observed in both N_2 and air as well as the anaerobic char yields (Y_c) at 800 °C are summarized in Table 2. The polymers were stable up to 270−310 °C, in N_2 or air, and afforded Y_c of 50−70%. Polymers prepared from 1,6-dibromohexane were more thermally stable than the corresponding prepared from 1,10-dibromodecane. The polymers can be used as light-emitting layer in EL devices, since their sufficient thermal stability prevents their thermal decomposition from heat produced during the operation of the device.

The photophysical properties of polymers were investigated by UV−vis and photoluminescence spectroscopy. The UV−vis maxima and the optical energy gaps (E_g) for all polymers are listed in Table 3. The E_g values were determined from the onset wavelength of the UV−vis spectra. The UV−vis spectra of polymers in THF solution are shown in Figure 5. It seems that **PP6** and **PP10** exhibited two maxima around 254 and 304 nm. It is interesting that the E_g values (3.47 eV and 3.50 eV) of these polymers were higher than the corresponding
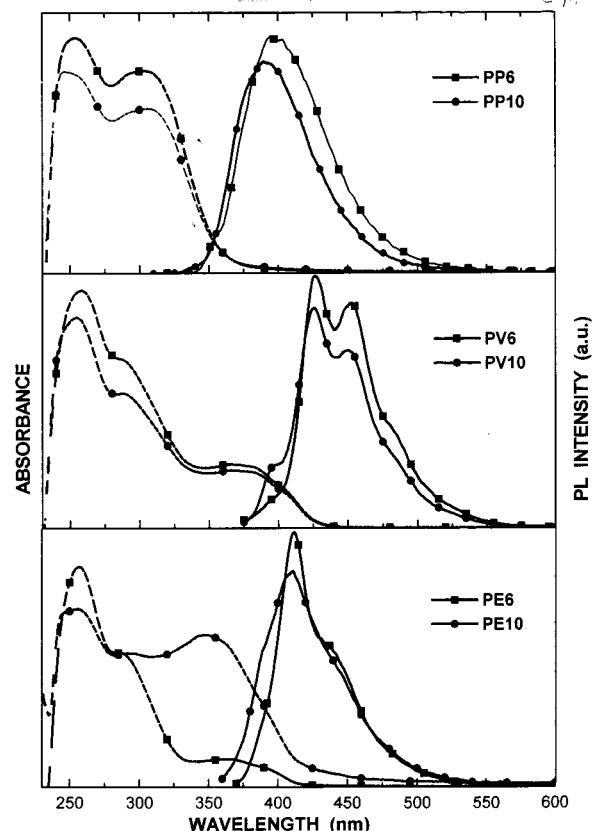

Figure 5. UV−vis (dashed lines) and PL (solid lines) spectra of all polymers in THF solution. The intensities were arbitrarily chosen in order to optimally fit the curves.

values reported for unsubstituted PPP (<3.0 eV),[33] but they were in the region for substituted PPP (>3.3 eV). Upon incorporation of the vinylene or the ethynylene units into the rigid segment, absorptions at longer wavelengths were observed due to increase of the chromophore length. Polymers **PV6** and **PV10** showed three maxima at about 256, 288, and 367 nm. The short wavelength absorptions at 256 and 288 nm could be assigned to the aromatic groups, while the long wavelength absorption at 367 nm was attributed to the electron transition π-π^* along the conjugated rigid block. Polyethers **PE6** and **PE10** showed long wavelength absorptions at 349 and 361 nm, respectively.

The polymers showed violet-blue to blue photoluminescence. The PL spectra of polymers in THF solution are presented in Figure 5. Polymers **PP6** and **PP10** showed PL maxima at 390 and 396 nm, respectively, with excitation at 305 nm. The emission took place at similar wavelengths with other polyphenylenes containing aliphatic spacers,[27,34] and it was blue shifted relative to PPP.[35] As expected, PL spectra of polymers **PV6** and **PV10** were red shifted, in comparison to **PP6** and **PP10** and presented well-resolved vibrational peaks at about 428 and 450 nm. An analogous behavior has been reported for PPV with interrupted conjugation.[12] The present polymers displayed pure blue light emission. Polymers **PE6** and **PE10** showed blue light emission but their PL maxima were about 15 nm blue shifted relative to **PV** polymers, affording single peak at 413 nm. It is known that the alkoxy-substituted PPE[36] emits at shorter wavelengths (450−480 nm) than the analogous PPV (>500 nm).[37] With respect to these values, **PV** and **PE** polymers showed PL maxima strongly blue shifted. The PL spectra of **PE6** and **PE10** showed
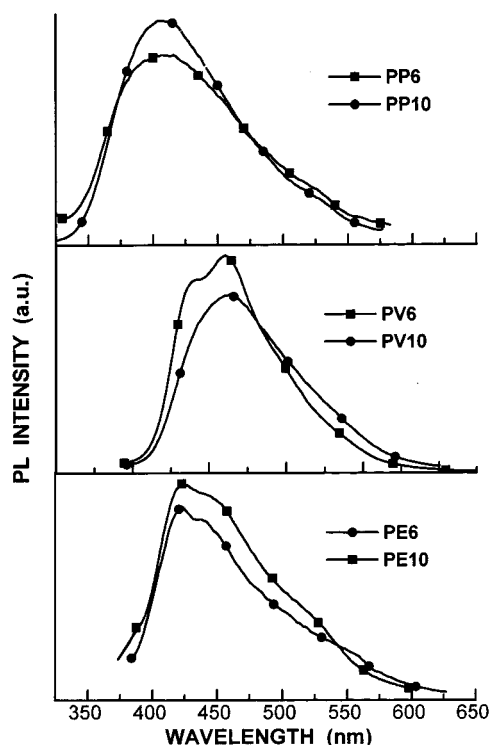
Figure 6. PL spectra of all polymers in thin films. The intensities were arbitrarily chosen in order to optimally fit the curves.

Figure 7. Emission as well as ASE spectra for different pump pulse energies of a **PE10**/PMMA film, detected at 90° angle to the excitation beam.

identical PL maxima although their UV−vis maxima appeared at different wavelengths. This means that the aliphatic spacers of these polymers affected the UV−vis absorption and emission in a different way. In addition, the PL spectra were narrower than those of UV−vis with well-resolved vibronic bands. These features have been previously described for substituted PPE and they have been attributed to the emission from localized excited states after migration of the latter to the segments that represent low energy states.[38] The observed blue shifted emission of the present polymers in comparison to PPP, PPV, and PPE suggests an efficient interruption of conjugation by the aliphatic units.

The photoluminescence quantum yields (Φ) of polymers in THF solutions were measured relative to quinine sulfate ($\Phi = 0.546$)[39] and they are listed in Table 3. The synthesized polymers showed high Φ values ranged from 0.58 to 0.98. These values were unusually high compared with those of other PPP, PPV, and PPE. Such a behavior could be attributed to the insertion of a nonconjugated spacer between the lumophores, which possibly traps the excitons.[19]

The photoluminescence behavior of polymers was also investigated in solid state. Figure 6 depicts the PL spectra of thin films of polymers obtained by spin coating on quartz plates from THF solutions. The PL maxima are summarized in Table 3. The solid-state PL spectra were broader and red shifted toward lower energies in comparison with the spectra obtained from solutions. Specifically, the PL maxima of the films were about 10 nm red shifted compared to those of solution owing to aggregation effects.[40] This means that the emission of polyethers **PV** and **PE** remained in blue region, as in solution, but the emission of **PP** polymers shifted from violet-blue in solution to blue in film. The PL maxima of **PV** polymers conform to literature data
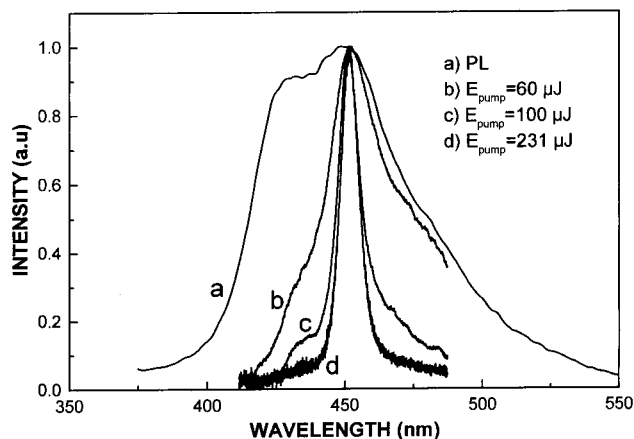
for other phenylenevinylene polymers with aliphatic spacers.[37]

Preliminary experiments for polymer **PV6** and **PV10** indicate that they can be used as efficient blue laser materials in solution and in film. These polymers show enhanced spectral narrowing (SN) when excited by a N_2 laser. SN was observed in THF solutions as well as in film "diluted" with PMMA. The narrow emission was detected at a direction perpendicular to the excitation direction and was attributed to amplified spontaneous emission (ASE). Figure 7 presents the emission spectra of a **PV10**/PMMA film with a ration of 0.4/100 for different excitation energies. The film was prepared by casting from a viscous solution of these polymers in THF onto a clean glass slide. At low energies the spectrum was wide, typical of spontaneous emission. As the laser pulse energy reaches the threshold energy for stimulated emission, a directional emitted light followed by SN was observed. The first indication of SN was detected at 60 μJ. Above this value a well-resolved narrow spectrum is dominant with a full width at half-maximum of about 7 nm. The ASE peak is close to the PL peak where the gain is higher. These results are an indication that **PV10** is intrinsically a good laser material in solid state. These results will be presented in a forthcoming publication.[41]

Conclusions

A series of aliphatic−aromatic polyethers were prepared via Williamson reaction and Heck coupling. They possessed chromophores of oligophenylene, phenylenevinylene or phenyleneethynylene type. The presence of aliphatic spacers in the main chain results in polymers with enhanced solubility and reduced T_g, but with satisfied thermal stability. The nonconjugated aliphatic units among chromophores interrupted efficiently the conjugation providing polymers with well-defined chromophores. The tuning factor of the emissive wavelength was the type of chromophore. Polymers containing oligophenylene units as chromophore displayed violet-blue emission in solution whereas the introduction of vinylene or ethynylene units shifted the emission in blue area. In the solid-state, all polymers displayed pure blue emission regardless of the chromophore type. The polymers showed high quantum yields up to 0.98.

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