Macromolecules **2001,** *34,* 5897−5901

Synthesis, Characterization, and Photophysical Studies of New Blue Light Emitting Segmented Copolymers

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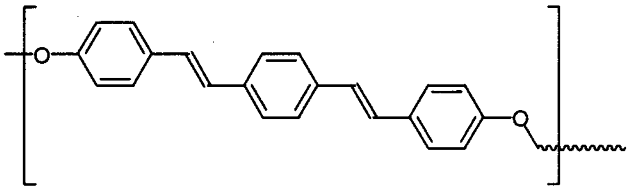
Received January 16, 2001; Revised Manuscript Received May 28, 2001

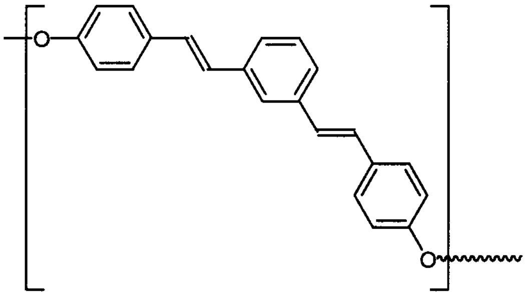
ABSTRACT: A series of new segmented copolymers containing *m*-phenylene in the chromophore unit have been synthesized by Wittig condensation. They are readily soluble in organic solvents and have high photoluminescence quantum yields in chloroform. Face-to-face π-stacking in the solid state is limited or prevented by molecular nonlinearity due to the *meta*-linkage and by the presence of a bulky *tert*-butyl group in the chromophores. Single-layer electroluminescence devices with an ITO/polymer/Ca−Al configuration emitted in the blue region (470−490 nm) for all of these systems.

Introduction

Light-emitting diodes (LED) using luminescent organic π-conjugated polymers as emissive layers have received attention in both academic research and industrial development.[1] The ready processability of organic polymers is one of their most attractive features, with potential for low-cost fabrication of large area displays. However, to optimize performance, the effect of polymer structure upon charge transport and emission properties must be better understood and controlled. In this context, synthesis of new luminescent polymers and studies of their photophysical properties are of fundamental interest.



para-linked, straight



meta-linked, bent

The first report of blue emission from a conjugated polymer LED was for poly(*p*-phenylene),[2] which is not soluble at higher molecular weights. Blue electroluminescence (EL) has also been demonstrated in PPV derivatives[3] among other structures.[4−8] This laboratory has reported on a class of alternating copolymers consisting of short *p*-phenylenevinylene-related moieties interspersed with flexible aliphatic spacers, which show blue emission.[9,10] Pang et al.[11] have described copolymeric arylenevinylene polymers containing alternating substituted *p*- and *m*-phenylenevinylene or phenyleneethynylene units. We now describe a related class of segmented blue emitting copolymers in which a *m*-phenylene unit is incorporated into the chromophore, instead of *p*-phenylene alone. The phenylenevinylene chromophore units remain covalently connected to conformationally flexible aliphatic segments. Phenylenevinylene is a strong fluorophore; hence, alternating block copolymers of phenylenevinylene are ideal photoluminescent material. This structural design reduces conjugation length relative to fully conjugated PPV variants, allowing shorter wavelength emission. Also, use of a *meta*-linked chromophore inhibits interchain interaction and excimer formation, which often limits emission efficiency through face-to-face quenching.[12−14] The *meta*-link is expected to constrain exciton mobility and thus to limit transport to quenching sites. The *m*-phenylene unit has seen some use in conjugated polymer architectures related to LED study[15] but has been more used to vary thermal stability, glass transition temperatures, and melting points for a variety of polymer systems.[16,17]

Experimental Section

All reagent chemicals were purchased from Aldrich Chemical Co. and were used as received unless otherwise stated. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analysis was carried out at the University of Massachusetts Microanalytical Laboratory.

^{1}H and ^{13}C NMR spectra were obtained using a Bruker DPX300 NMR spectrometer at 300 MHz. Gel permeation chromatography (GPC) was used to determine molecular weights of polymers with THF as an eluent and polystyrene as standard on a Waters GPC system equipped with a U6K injector and a model 410 differential refractometer. UV−vis absorption spectra were measured on an IBM 9420 spectrophotometer. Emission and excitation spectra were taken on a Perkin-Elmer LS 50B spectrometer with xenon lamp light source. Emission quantum yields in chloroform solvent were

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10.1021/ma010071y CCC: $20.00

determined at an excitation wavelength of 350 nm using external standard 9,10-diphenylanthracene in cyclohexane ($\phi_f = 0.90$) by a literature[18] procedure.

3,5-Bis(bromomethyl)-*tert*-butylbenzene (8). A solution of 5.0 g (30.81 mmol) of 5-*tert*-butyl-*m*-xylene, 13.7 g (77.0 mmol) of *N*-bromosuccinimide (NBS), and 0.1 g of 2,2′-azobis(isobutyronitrile) (AIBN) in 110 mL of carbon tetrachloride was refluxed for 8 h. After filtration of insoluble materials from the reaction mixture at room temperature, the filtrate was concentrated in vacuo to leave the white product, which on recrystallization from ethyl alcohol gave 3.6 g (46% yield) of **8** as colorless needles: mp 113−114 °C, lit.[19] mp 110−112 °C. ^{1}H NMR ($CDCl_3$, δ): 1.34 (s, 9H), 4.48 (s, 4H), 7.29 (d, $J = 2.2$ Hz, 1H), 7.38 (d, $J = 2.2$ Hz, 2H). Anal. Calcd for $C_{12}H_{16}Br_2$: C, 45.03; H, 5.04. Found: C, 44.87; H, 5.07.

3,5-Bis(triphenylphosphonium bromide)-*tert*-butylbenzene (7). A mixture of 5.0 g (15.6 mmol) of **8** and 8.50 g (32.4 mmol) of triphenylphosphine in 100 mL of anhydrous dimethylformamide was heated to 95−100 °C under nitrogen for 16 h. The white precipitate was filtered followed by washing with dimethylformamide and diethyl ether. After drying under vacuum, **7** was obtained as a white powder in 50% yield. ^{1}H NMR (CD_3OD, δ): 7.88 (m, 6H), 7.70 (m, 12H), 7.58 (m, 12H), 6.93 (s, 2H), 6.82 (s, 1H), 4.47 (d, $J = 21$ Hz, 4H), 0.85 (s, 9H). ^{13}C NMR (75.5 MHz, CD_3OD, δ): 162.72, 152.26, 136.43, 135.38, 135.31, 135.24, 131.55, 131.46, 131.37, 129.90, 119.70, 118.56, 36.1 (d, $J = 121$ Hz), 31.14, (31.65, 30.57, 29.93, weak peaks). Anal. Calcd for $C_{48}H_{46}Br_2P_2$: C, 68.28; H, 5.45; Br, 18.93; P, 7.34. Found: C, 67.92; H, 5.52; Br, 18.75; P, 7.18.

1,8-Bis(4-formyl-2,6-dimethylphenoxy)octane (4). A mixture of 3.10 g (20.6 mmol) of 3,5 dimethyl-4-hydroxybenzaldehyde, 2.81 g (10.3 mmol) of 1,8-dibromooctane, and 3.85 g (0.028 mol) of potassium carbonate in 30 mL of anhydrous dimethylformamide was heated to 60−65 °C for 16 h. The mixture was cooled to room temperature and poured into ice−water. The solid product was filtered, washed with water, and recrystallized twice from ethanol. The product was obtained as white crystals in 42% yield with mp 87−88 °C. ^{1}H NMR ($CDCl_3$, δ): 9.87 (s, 2H), 7.55 (s, 4H), 4.03 (t, $J = 4.4$ Hz, 4H), 2.36 (s, 12H), 1.84 (m, 4H), 1.41 (m, 8H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 192.06, 162.00, 132.46, 132.36, 131.09, 72.84, 30.78, 29.87, 26.44, 16.80. Anal. Calcd for $C_{26}H_{34}O_4$: C, 76.11; H, 8.29. Found: C, 75.89; H, 8.33.

1,8-Bis(4-formyl-2-ethoxyphenoxy)octane (5). Analogous to the procedure described above for **4**, 2.50 g (15.0 mmol) of 3-ethoxy-4-hydroxybenzaldehyde and 2.05 g (7.53 mmol) of 1,8-dibromooctane were allowed to react in ethanol with potassium carbonate (2.8 g, 0.020 mol), followed by recrystallization from ethanol to provide **5** in 51% yield as white crystals with mp 101−102 °C. ^{1}H NMR ($CDCl_3$, δ): 9.86 (s, 2H), 7.34 (m, 4H), 7.08 (d, $J = 2.4$ Hz, 2H), 4.02 (m, 8H), 1.89 (m, 4H), 1.44 (M, 14H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 191.38, 154.85, 149.52, 130.26, 127.01, 112.07, 111.17, 69.48, 64.91, 29.61, 29.27, 26.21, 15.06. Anal. Calcd for $C_{26}H_{34}O_6$: C, 70.60; H, 7.69. Found: C, 70.48; H, 7.75.

1,8-Bis(4-formylphenoxy)octane (6). This compound was synthesized by the literature procedure.[11] All physical and spectral properties were in accord with previously published values.

General Procedure for Polymerization. A freshly prepared solution of sodium ethoxide in anhydrous ethanol (3 M excess) was added dropwise to an equimolar mixture of dialdehyde and phosphonium salt in 3:1/v:v absolute ethanol and chloroform at room temperature under a nitrogen atmosphere. The mixture was stirred at room temperature for 16 h. The polymerization was quenched with 2% aqueous hydrochloric acid and stirred for 15 min. The resultant solid was dissolved in chloroform, the layers were separated, and the organic layer was isolated and then filtered. The solution was concentrated in vacuo and added dropwise to methanol at room temperature with stirring to precipitate the polymer. The polymer was then dried under vacuum and dissolved in anhydrous toluene containing a catalytic amount (5 mg per mol equiv of polymer) of iodine, and the mixture was refluxed overnight under nitrogen. After cooling, the toluene solvent was removed under reduced pressure, and the residue dissolved in chloroform followed by precipitation into methanol. The reprecipitation procedure was performed four times, and the final polymeric product was dried under vacuum at 40 °C.

Poly[1,8-octanedioxy-2,6-dimethyl-1,4-phenylene-1,2-ethenylene-5-*tert*-butyl-1,3-phenylene-1,2-ethenylene-3,5-dimethyl-1,4-phenylene] (1). The general procedure described above gave 38% yield of **1**. ^{1}H NMR ($CDCl_3$, δ): 7.54 (s, 1H), 7.47 (s, 1H), 7.38 (s, 2H), 7.21 (s, 4H), 7.04 (s, 4H), 3.78(m, 4H), 2.31 (s, 12H), 1.83 (m, 4H), 1.54 (m, 4H), 1.44 (m, 4H), 1.38 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 156.29, 138.0, 133.17, 131.55, 131.12, 128.65, 128.25, 127.38, 123.37, 121.56, 72.84, 35.13, 31.78, 30.87, 30.0, 26.59, 16.84. Anal. Calcd for $(C_{38}H_{48}O_2)_n$: C, 85.09; H, 8.95. Found: C, 84.38; H, 8.86.

Poly[1,8-octanedioxy-2-ethoxy-1,4-phenylene-1,2-ethenylene-5-*tert*-butyl-1,3-phenylene-1,2-ethenylene-5-ethoxy-1,4-phenylene] (2). The general procedure described above gave 41% yield of **2**. ^{1}H NMR ($CDCl_3$, δ): 7.48 (s, 1H), 7.38 (s, 2H), 7.08 (d, $J = 16$ Hz, 2H), 6.98 (d, $J = 16$ Hz, 2H), 6.94 (m, 6H), 4.14 (m, 4H), 4.03 (m, 4H), 1.85 (m, 4H), 1.48 (m, 14H), 1.38 (m, 9H), 1.25. ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 149.34, 137.97, 130.97, 128.84, 127.48, 123.22, 121.47, 120.42, 113.93, 111.78, 69.62, 65.10, 35.14, 31.79, 29.76, 29.63, 26.35, 15.38. Anal. Calcd for $(C_{38}H_{48}O_4)_n$: C, 80.29; H, 8.45. Found: C, 79.72; H, 8.33.

Poly[1,8-octanedioxy-1,4-phenylene-1,2-ethenylene-5-*tert*-butyl-1,3-phenylene-1,2-ethenylene-1,4-phenylene] (3). The general procedure described above gave 34% yield of **3**. ^{1}H NMR ($CDCl_3$, δ): 7.48 (d, $J = 4.2$ Hz, 2H), 7.37 (s, 1H), 7.04 (d, $J = 16.0$ Hz, 2H), 6.98 (d, $J = 16.0$ Hz, 2H), 6.93 (m, 8H), 3.96 (m, 4H), 1.80 (m, 4H), 1.45 (m, 8H), 1.38 (s, 9H). ^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 159.25, 138.06, 132.42, 130.46, 128.56, 128.10, 127.32, 123.13, 121.52, 115.11, 68.42, 35.15, 31.82, 29.76, 29.69, 26.43. Anal. Calcd for $(C_{34}H_{40}O_2)_n$: C, 85.01; H, 8.33. Found: C, 84.12; H, 8.17.

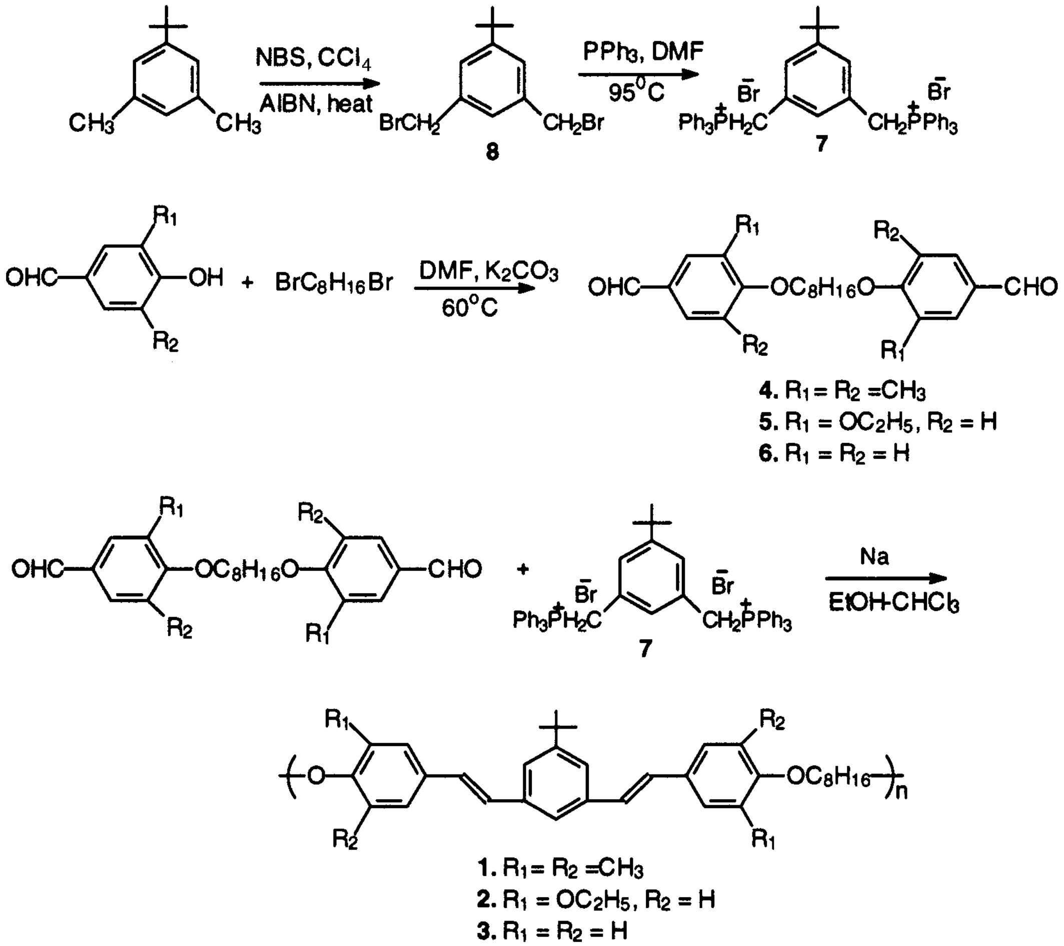
EL Device Fabrication. Single-layer LED devices were fabricated by spin-coating polymer solutions (200 mg/mL in chloroform, spin rate 3800 rpm) onto indium/tin oxide-coated glass substrates (DFC Corp.). Inert atmosphere conditions were maintained in a glovebox. Polymer film thickness was typically 90 nm, as determined by ellipsometry. A calcium cathode of about 400 nm thickness was vapor-deposited through a mask on top of the polymer films at 0.1 μTorr of pressure. A protective layer of aluminum was deposited on top of the calcium to increase stability of the cathode. Further details are given in previous publications from this group.[9,11]

Results and Discussion

The structures and synthetic routes to polymers **1**−**3** are depicted in Scheme 1. Monomers **4**−**6** were synthesized by condensation of 4-hydroxybenzaldehyde derivatives with 1,8-dibromooctane. Monomer **7** was synthesized in two steps from 5-*tert*-butyl-*m*-xylene in 42% yield by benzylic bromination followed by conversion to the triphenylphosphonium salt. Polymerization was carried out by Wittig condensation at room temperature using sodium ethoxide in 3:1/v:v ethanol/chloroform as solvent. The polarity of the solvent was controlled by the mixture ratio to provide reasonable reaction rates. The polymers were isolated by filtration and were purified by precipitation from chloroform into methanol. This initial product, which has a mixture of *cis*- and *trans*-olefin geometries, was then isomerized to the *trans* configuration by boiling in toluene in the presence of catalytic amounts of iodine. The isomerized polymers were further purified by multiple precipitations into methanol. After drying in vacuo at 40 °C, the polymers were typically obtained in 35−40% yields as fibrous buff-colored solids.

The structures of polymers **1**−**3** were confirmed by NMR, FTIR, and elemental analysis. The ^{1}H NMR

Scheme 1



signals in the olefinic regions showed coupling constants of ~16 Hz at about δ7 ppm, typical for *trans*-stilbene moieties. Postisomerization ^{1}H NMR spectra showed no detectable peaks attributable to the *cis* isomer in the δ 6.5–7.0 ppm region. The polymers readily dissolved in polar solvents such as THF, chloroform, and other halogenated solvents. GPC gave number-average molecular weights for **1**–**3** in the range 15–20 000 with a moderate polydispersity of 2.5–2.8. Typical degrees of polymerization were 30–40.

The UV–vis absorption spectra for the polymers **1**–**3** in chloroform (10 μM) are shown in Figure 1, and related data are presented in Table 1. The width of the peaks is associated with the presence of unresolved vibronic structure and other inhomogeneous broadening. The large molar absorption coefficients show the dominance of strongly allowed π–π* transitions from the phenylenevinylene segments. Because of the electron-donating effect of alkoxy groups in **2**, its absorption maximum is somewhat displaced to a lower energy relative to **1**. However, the transition probability (represented by the extinction coefficient) for **2** is also lowered by comparison to **1** and **3**. The lowest energy absorption peaks of these *m*-phenylenevinylene containing polymers are significantly blue-shifted by comparison to the analogous copolymers containing *p*-phenylenevinylene moieties.[19] This agrees with the expectation that the *meta*-linkage will interrupt the main chromophore chain conjugation.

Upon excitation at 320 nm, the emission spectra for **1**–**3** in chloroform (10 μM) appear as relatively broad bands (Figure 1). The maximum of the alkoxy-substituted **2** is slightly red-shifted by comparison to unsubstituted **3** (Table 1), parallel to the UV–vis spectral results. The small red shifts observed for both UV–vis and emission spectra of **2** relative to those of **1** and **3** contrast with the behavior of fully conjugated PPV, in which the introduction of alkoxy groups results in a much larger red shift in both absorption and emission spectra.[20] Polymers **1** and **2** have significant emission shoulders and **2** exhibits a long tail on the high-wavelength side. Also, the emission quantum yields of **1**–**3** in CHCl$_3$ show significant substitutent effects (Table 1). Nonradiative deactivation of singlet excitons is presumably promoted by the presence of the alkoxy

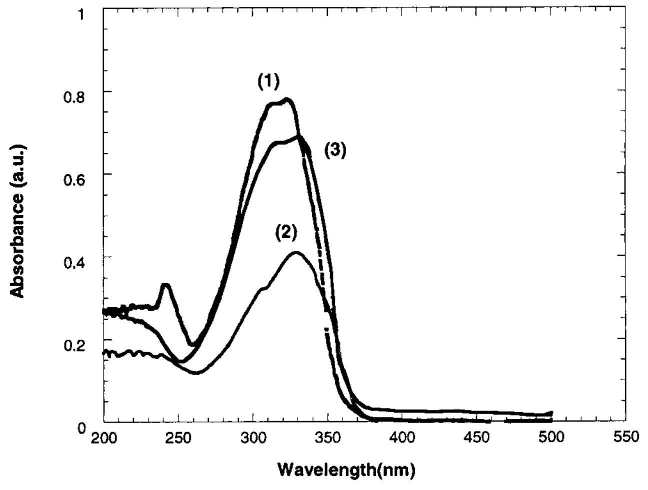


Figure 1. Absorption spectra of polymers **1**–**3** in chloroform (10 μM) at room temperature.

Table 1. Photophysical Properties of 1–3 in Chloroform (10^{-5} M)

polymers	λ_{max}(ab), nm	$\epsilon_{max} \times 10^4$, M^{-1} cm^{-1}	band gap, eV[a]	λ_{max} (em), nm[b]	λ_{max} (ex), nm[c]	ϕ_f[d]
1	321	3.20	3.42	401 406, 432 (sh)	321	0.31
2	328	1.75	3.39	402	336	0.34
3	330	2.06	3.53	385 396 (sh)	333	0.47

[a] Optical band gaps are taken as $E_{(0-0)}$. [b] Excited at 320 nm. [c] Monitoring at emission maxima. [d] 9,10-Diphenylanthracene as standard.

Table 2. Optical Properties of Polymers 1–3 in Thin Films

polymers	λ_{max} (PL),[a] nm	λ_{max} (EL), nm	Stokes[b]
1	399	479	74
2	416	471	87
3	406	487	85

[a] Excited at 320 nm. [b] Difference between absorption and emission maxima in solid state.

groups in **2** due to spin–orbit coupling,[21] consistent with its reduced quantum yield relative to that of **1**.

Excitation spectra are typically identical to the corresponding solution-state absorption spectra. However, the excitation spectra of **1**–**3** in chloroform, monitored at their respective emission maxima, differ somewhat from the solution-state absorption spectra. The most prominent peaks in the excitation spectra are red-shifted (Table 1) relative to the lowest energy absorption peaks. A similar effect has been seen in other conjugated polymer systems and suggests that PL emission is dominated by the states that are near the edge of the band gap.[22]

The solution optical band gaps (assumed to be approximately given by the 0–0 electronic energy band[23]) are also reported in Table 1. $E_{(0-0)}$ was assumed to be the crossing point of the excitation and emission spectra. The gap is decreased by the presence of electron-donating substituents as expected, especially by the alkoxy groups. Since $E_{(0-0)}$ is governed by effective conjugation length, these results indicate that the alkoxy groups on the terminal rings of the chromophore effectively increase conjugation. The analogous methyl substituents on the terminal phenyl rings, however, slightly decrease the optical band gap in the present systems.

The emission maxima of thin films of **1**–**3** excited at 320 nm are listed in Table 2. All the films display maxima essentially identical to those found in solution (Figure 2). Often, π–π interactions or aggregation of π-conjugated polymer chains in the solid state lead to a red shift in the emission spectrum relative to the solution phase.[24] Quantum mechanical analyses have demonstrated the orbital interactions that cause this effect.[25] Our results are consistent with an absence of organized solid-state π–π stacking or aggregation in **1**–**3**, presumably due to the bent *meta*-linkage and bulky *tert*-butyl group in the chromophore.

The emission spectra obtained for the polymers remain unchanged upon excitation at different frequencies within their absorption envelopes. Again, the probable reason is the design of polymers **1**–**3**. The bulky *tert*-butyl group in **1**–**3** renders π–π stacking and van der Waals interactions in the polymer backbones (intra- and interchain) less effective. Therefore, excimer emission is less likely, due to lack of favorable interchromophore interactions.[12,26]

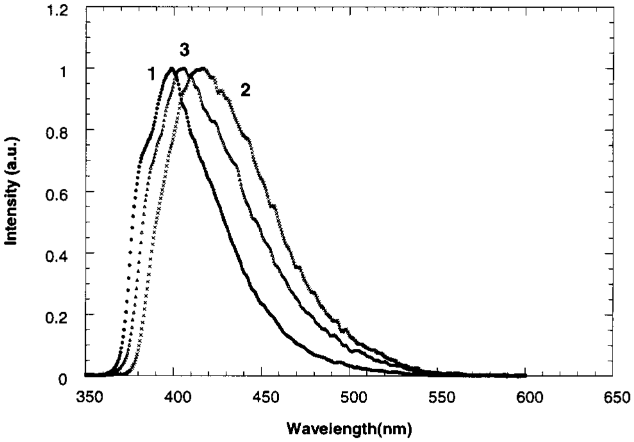


Figure 2. Emission spectra of polymers **1**–**3** in thin films at room temperature (ordinate in arbitrary units scaled to similar peak heights; excitation at 320 nm).

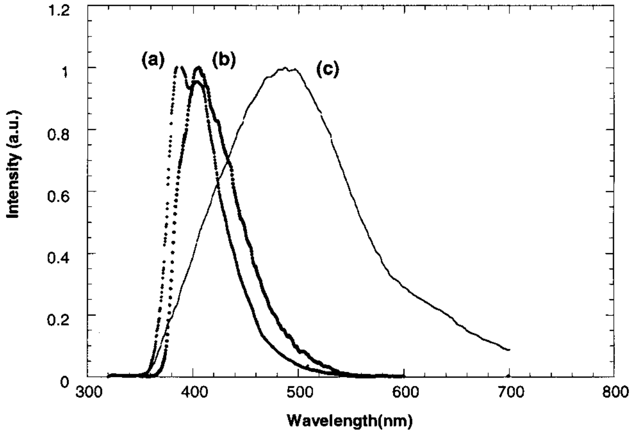


Figure 3. Polymer **3**: photoluminescence in chloroform solution excited at 320 nm (a), photoluminescence in solid film (b), and electroluminescence in an ITO/**3**/Ca–Al device (c). Ordinate scale is in arbitrary units scaled to allow comparison of peak shapes and maxima.

Single-layer LED (ITO/polymer/Ca–Al) devices were fabricated according to previously[9,11] described standard procedures in our laboratory. EL spectra were obtained at 20 V using a pulse voltage source. The maxima of the respective EL spectra are given in Table 2. Although the maxima are located in the blue region of the visible spectra, the peaks are broader and red-shifted up to 83 nm compared to the corresponding PL spectra of the films (Figure 3). We are presently investigating the cause of this unusual disparity between PL and EL emission maxima in these systems. Similar behavior has been reported, for example, recently in a triarylamine-based polymer[27] and a binaphthalene-containing conjugated polymer.[28] For the latter systems, the EL emission maximum was red-shifted by about 157 and 146 nm, respectively, compared to the PL maximum. It is typically argued that the EL and PL spectra of organic polymer films originate from the same excited state.[29] However, the latter results are inconsistent with this commonly used hypothesis. While the possibility exists in some cases that LED fabrication and testing may lead to structural changes in the emitting chromophores, there is also the possibility that different photophysical mechanisms lead to the emission peak maxima for the PL and EL.[30] It is important to note that the emission spectra of polymer films are not necessarily inherent to individual polymer chains but instead reflect the nature of excited states in the bulk. Morphological factors and structural defects will have considerable influence in some systems.

Conclusions

We have described general synthetic methods to synthesize *meta*-linked phenylenevinylene segmented copolymers with moderately high molecular weights. Absorption and emission measurements clearly indicate that the expected interruption of π-conjugation along the backbone of the chromophore due to the *meta*-connection. In addition, the use of *meta*-linkages and bulky alkyl substitution effective limits the typical red shifts seen in comparisons of solid film to solution phase luminescence, presumably by limiting solid-state packing and aggregation between chromophores. By limiting such aggregation and packing effects, it is easier to limit variation in solid-state luminescence behavior caused by processing effects. These findings should assist in the design of new chromophoric and hole-injection materials for light emitting devices.

Acknowledgment. The authors gratefully acknowledge funding from the Air Force Office of Scientific Research.

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MA010071Y