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Control of Chromophore Length in Electroluminescent Polymers. Part II. Mainchain Polymers

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CONTROL OF CHROMOPHORE LENGTH IN ELECTROLUMINESCENT POLYMERS. PART II. MAINCHAIN POLYMERS

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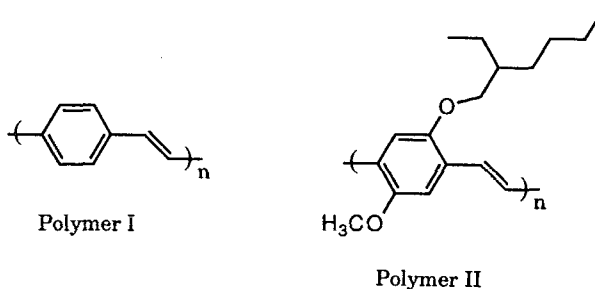
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ABSTRACT

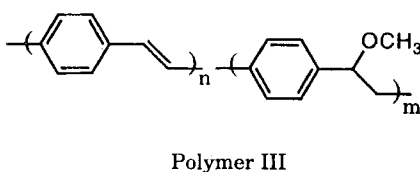
Electroluminescence emission has been demonstrated in mainchain polyesters and a structurally analogous polyamide. High molecular weight polyesters were synthesized by condensation of a dihydroxy functionalized, substituted, phenylene vinylene analogue, e.g., the lumophore, with a variety of dicarboxylic acid chlorides. The structure and hence the conjugation length of the emitting comonomer was predetermined prior to polymerization. Since the diacid moieties did not contribute to the conjugation length and hence the emission wavelength, the structure of the diacid was determined on the basis of its ease of synthesis, reactivity, and solubilizing ability in the final polymer. In each of the polyesters the electroluminescence wavelength of light-emitting diodes made from these polymers was similar to their photoluminescence emission spectrum in solution and the solid state at room temperature. The emission wavelengths ranged from blue to green. The polyamide exhibits a very broad band, nearly white electroluminescence. Diodes made from these polymers typically have external efficiencies $\leq 0.003\%$ with low turn-on voltages, e.g., 6–20 V.

INTRODUCTION

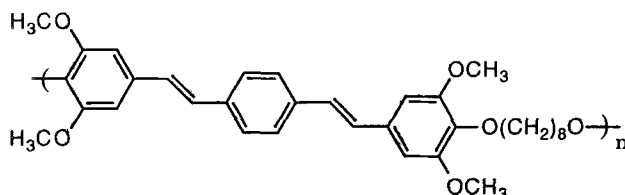
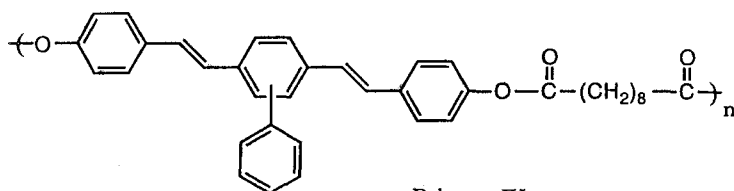
The first report of polymers exhibiting electroluminescence appeared in a patent application in 1989 followed by a publication in *Nature* in 1990 from a group of researchers from Cambridge University [1]. The polymer used in these studies was poly(*p*-phenylenevinylene) (**I**). Improved solubility and processing as well as wavelength shifts were realized by placing pendant groups on the backbone of the polymer, e.g., **II** [2].



The emission wavelength of mainchain polymers exhibiting electroluminescence may be affected by controlling the conjugation length of the emitting segments in the polymer backbone. There are two approaches by which this may be accomplished. The first of these requires the synthesis of polymers containing leaving groups which can be thermally eliminated after coating [3]. In this strategy the length of the chromophores is determined by the nature of the leaving groups and the extent of elimination, i.e., the reaction conditions. Chromophores produced in this way have a wide variety of lengths which cannot be precisely controlled and consequently produce broad spectral emission. An example of this modified poly(phenylenevinylene) is polymer **III**.



The second approach requires the synthesis of difunctional monomers which comprise conjugated segments; the conjugation length of the segments, and hence their emission wavelength, is predetermined and built into the monomer in the synthetic sequence. The difunctional monomer may then be polymerized with another difunctional monomer, the structure of which prevents or at least limits extension of the chromophore by limiting additional conjugation, i.e., the second monomer insulates the chromophores. There are at least two molecular architectures by which this may be accomplished: 1) the comonomer comprises a flexible spacer, e.g., one or more CH_2 groups (shown here as polymers **IV** [4] and **V** [5]); 2) the comonomer is a difunctional rigid spacer comprising a noncoplanar biphenyl.



This paper describes the synthesis, characterization, and electroluminescent behavior of three mainchain polyesters and a polyamide. Polyesters **VI** and **VII** are rigid/flexible-type polymers in that they contain an aliphatic diacid, and polyester **VIII** and polyamide **IX** comprise only rigid repeat units (Fig. 1). In the first two examples the chromophores are confined to the segment between the ester groups and are assembled before polymerization. In the latter two examples the preformed chromophores are extended slightly during the polymerization and are confined to the molecular segment of the repeat unit between the 1,1'-carbon atoms of the biphenyls [6]. All of the polyesters exhibit photo- and electroluminescent emission in the blue to green region of the spectrum. However, although the photoluminescence of the polyamide is blue-green in the solid state of room temperature, the electroluminescence is very broad band and visually appears blue-white.

EXPERIMENTAL

General Procedures

Transparent indium/tin oxide (ITO) glass plates were used as the anode of the light-emitting diodes. Prior to the application of polymer, the ITO plates were washed with a detergent in an ultrasonifier for approximately 30 minutes. The plates were then rinsed with distilled water and dried by either heating in an oven at 110°C for 2 hours or in the vapors of refluxing isopropanol for 30 minutes. The cleaned plates were stored in a nitrogen-filled glove bag prior to use. Before attempting to spin on the polymer film, the plates were treated with purified xylene at 1500 rpm for 90 seconds which changed the surface energy and allowed the polymer solution to wet it. Thin films of polymer, in the range of 30–50 nm, were spin cast immediately onto the xylene-treated plates. The thickness of the film was controlled by means of the concentration of the polymer solution (typically 1% w/v) and the speed of the spinner (approximately 2000 rpm for 90 seconds). The coating was dried at 50°C for 15 minutes before vacuum depositing the cathode which consisted of approximately 200 nm of magnesium followed by 400 nm of aluminum.

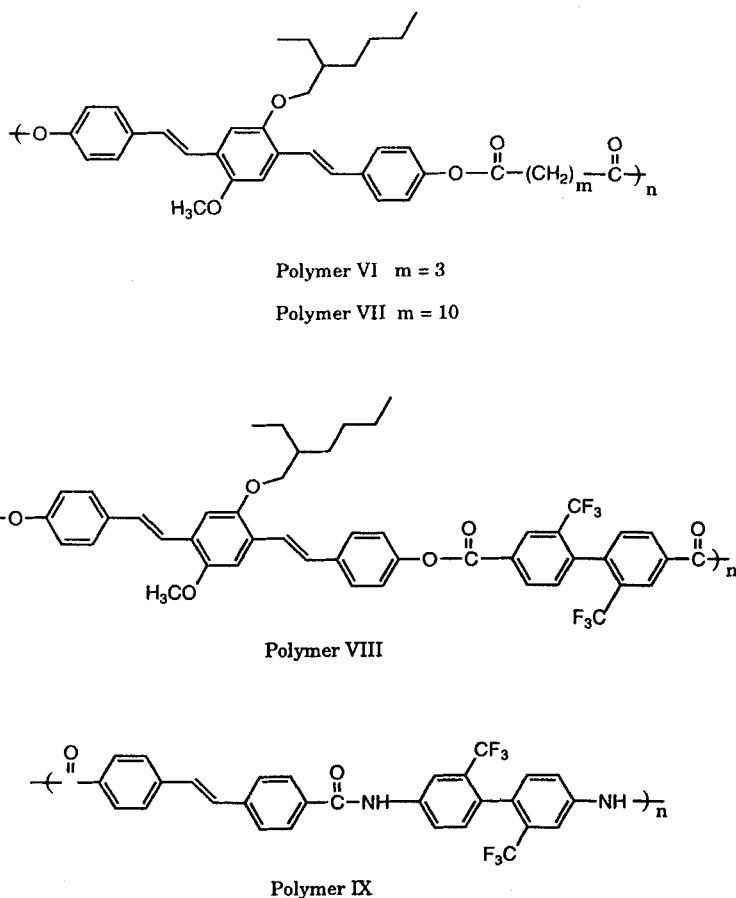


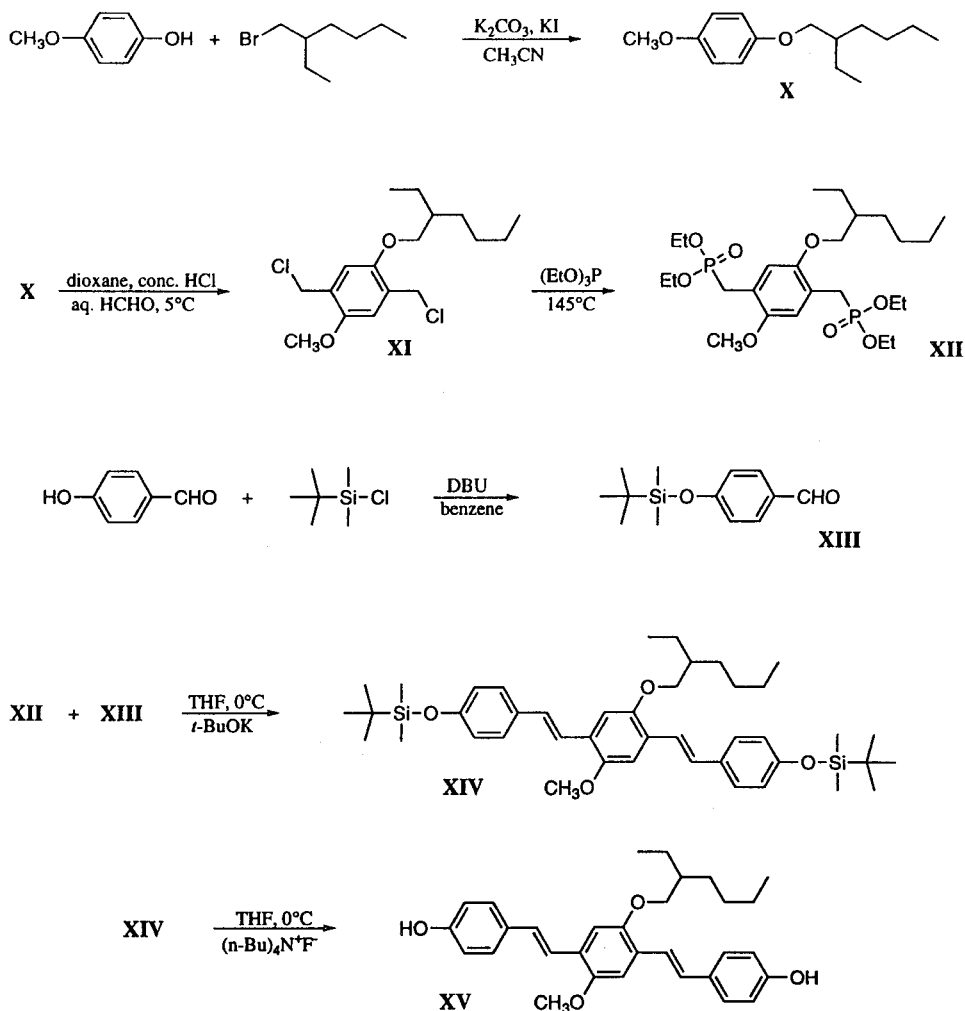
FIG. 1. The molecular structures of the polymers used in this study.

The electroluminescence properties of the diodes were measured by applying a controlled, variable voltage by means of a Hewlett-Packard 4145B semiconductor parameter analyzer and simultaneously measuring the current flowing through the polymer and the amount of light emitted by means of a photodetector (UDT Sensors, Model PIN 10 9245-1). The electroluminescence spectra were recorded using a JY CP2000 Spectrograph equipped with a Prism Research photodiode array.

Synthesis of the Diol Monomer (Scheme 1)

4-(2-Ethylhexyloxy)anisole (X)

To a solution of 4-methoxyphenol (15 g, 0.121 mol) in 200 mL of acetonitrile was added potassium carbonate (85 g, 5 equiv) and potassium iodide (10 g, 0.5 equiv). The mixture was stirred with a mechanical stirrer and heated to 70°C. 2-Ethylhexyl bromide (36 g, 0.186 mol) was added slowly dropwise; after addition



SCHEME 1. Synthetic route for the diol monomer.

was complete, the mixture was treated at reflux for 16 hours. Upon cooling, the mixture was filtered and washed twice with acetonitrile. The solvent was removed in vacuo, and the resulting liquid was redissolved in methylene chloride, filtered again, and the solvent was removed in vacuo. The product was distilled under reduced pressure (70°C at 0.3 mm), yielding 22.36 g (87%) of colorless liquid. FT-IR (NaCl) 2959, 2931, 2873, 2801, 1509, 1466, 1232, 1043, 824 cm^{-1} . UV (MeOH) $\lambda_{\text{max}} = 226$ nm ($\epsilon = 9.33 \times 10^3$). ^1H NMR (CDCl_3 , 300 MHz) δ : 6.88 (s, 4H), 3.85, 3.83 (d, $J = 6$ Hz, 2H), 3.80 (s, 3H), 1.76 (m, 1H), 1.65–1.23 (m, 8H), 0.99 (m, 6H). ^{13}C NMR (CDCl_3 , 300 MHz) δ : 153.68, 115.43, 114.95, 71.16, 55.66, 39.55, 30.62, 29.18, 23.93, 23.15, 14.15, 11.65.

2,5-Bis(chloromethyl)-4-(2-ethylhexyloxy)anisole (XI) [7]

To the solution of 4.9 g (20.7 mmol) of **X** in 100 mL of dioxane cooled to 5°C, 18 mL of concentrated HCl and 10 mL of 37% formaldehyde in water were added. Anhydrous HCl gas was bubbled for at least 60 minutes. The reaction was allowed to warm to room temperature and stirred for 2 hours. The solution was cooled to 5°C again, another 10 mL of formaldehyde was added, and HCl gas was bubbled for another 20 minutes. The reaction was stirred for at least 16 hours at room temperature and then refluxed for 3–4 hours. After cooling and removal of solvents, an off-white greasy solid remained. The crude product was dissolved in hexane, filtered, and precipitated by adding methanol and storing in the refrigerator. After filtering and washing with cold methanol, a white crystalline solid (5.0 g, 76%) was obtained. FT-IR (KBr) 2958, 2926, 2857, 1516, 1464, 1415, 1264, 1227, 1035, 733, 700, 612 cm⁻¹. UV (MeOH) $\lambda_{\max} = 212$ nm ($\epsilon = 2.82 \times 10^4$). ¹H NMR (CDCl₃, 300 MHz) δ : 6.92 (s, 1H), 6.91 (s, 1H), 4.63 (s, 4H), 3.88, 3.86 (δ , $J = 5$ Hz, 2H), 3.85 (s, 3H), 1.74 (m, 1H), 1.65–1.23 (m, 8H), 0.94 (m, 6H). ¹³C NMR (CDCl₃, 300 MHz) δ : 150.93, 150.85, 127.01, 126.80, 114.02, 113.36, 71.08, 56.30, 41.37, 39.58, 30.61, 29.10, 24.01, 23.05, 14.10, 11.23. MS, m/e 332.

2,5-Bis(diethoxyphosphonomethyl)-4-(2-ethylhexyloxy)anisole (XII) [8]

In a 100-mL three-neck flask fitted with an internal thermometer and short path distillation apparatus was added **XI** (4 g, 0.012 mol) to 30 mL of freshly distilled triethylphosphite. The reaction mixture was stirred and heated to 145°C for 2 hours (ethyl chloride was condensed into a collection flask). After cooling to 40°C, the flask containing ethyl chloride was removed. Excess triethylphosphite was then distilled under reduced pressure to leave behind a colorless oil. The oil was transferred to a single-neck flask and heated at 40–50°C in a vacuum oven overnight. Upon cooling, the oil solidified to a white greasy solid (6.2 g, 96%). FT-IR (NaCl) 2961, 2930, 2871, 1509, 1465, 1411, 1393, 1252, 1216, 1052, 1030, 961, 884 cm⁻¹. UV (MeOH) $\lambda_{\max} = 228$ nm ($\epsilon = 9.77 \times 10^3$). ¹H NMR (CDCl₃, 300 MHz) δ : 6.94, 6.93 (d, $J = 2$ Hz, 1H), 6.88, 6.87 (d, $J = 2$ Hz, 1H), 4.10–3.94 (m, 8H), 3.80 (s, 2H), 3.78 (s, 3H), 3.25, 3.23 (d, $J = 5$ Hz, 2H), 1.76–1.63 (m, 1H), 1.56–1.18 (m, 20H), 0.97–0.84 (6H). ¹³C NMR (CDCl₃, 300 MHz) δ : 150.87–150.74 (dd, $J = 3$ Hz), 150.67–150.54 (dd, $J = 3$ Hz), 119.31 (m), 114.82–114.73 (q, $J = 3$ Hz), 113.95–113.85 (q, $J = 3$ Hz), 71.4, 61.95–61.85 (dd, $J = 1$ Hz), 56.11, 39.64, 30.58, 29.10, 27.38–27.04 (d, $J = 25$ Hz), 23.89–23.03 (d, $J = 25$ Hz), 16.38–16.28 (dd, $J = 1$ Hz), 14.06, 11.14. MS, m/e 536.

4-(*t*-Butyldimethylsiloxy)benzaldehyde (XIII)

To a solution of DBU (1,8-diazobicyclo[5.4.0]undec-7-ene, 4.3 mL, 0.0288 mol) and 4-hydroxybenzaldehyde (3.0 g, 0.0245 mol) in 50 mL of benzene was added *tert*-butyl-dimethylsilyl chloride (4.11 g, 0.027 mol) at room temperature [9]. A precipitate formed immediately and the reaction was stirred for about 4 hours. The solution was filtered through a sintered glass funnel and washed twice with 0.1 N HCl, 3 times with saturated aqueous sodium bicarbonate, and 3 times with

saturated aqueous sodium chloride. The organic layer was then dried over anhydrous sodium sulfate, and the solvent was removed under reduced pressure. The crude material was purified by flask-to-flask distillation under full vacuum to yield 5.39 g (93%) of a colorless liquid. FT-IR (NaCl) 2956, 2933, 2859, 1699, 1598, 1508, 1275, 1157, 909, 842 cm^{-1} . UV (MeOH) $\lambda_{\text{max}} = 270 \text{ nm}$ ($\epsilon = 1.55 \times 10^4$). ^1H NMR (CDCl_3 , 300 MHz) δ : 9.68 (s, 1H), 7.57 (d, $J = 9 \text{ Hz}$, 2H), 6.72 (d, $J = 9 \text{ Hz}$, 2H), 0.74 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (CDCl_3 , 300 MHz) δ : 190.87, 161.48, 131.90, 130.38, 120.46, 25.54, 18.24, -4.37 . MS, m/e 2.37.

2,5-Bis[4-(*t*-butyldimethylsilyloxy)styryl]-4-(2-ethylhexyloxy)anisole (XIV)

To a solution of **XII** (1.11 g, 2.10 mmol) in 20 mL of dry THF cooled to 0°C was added 1 M potassium *tert*-butoxide in THF by syringe (4.3 mL, 4.41 mmol). The aldehyde **XIII** (1.0 g, 4.2 mmol) was added dropwise by syringe to the red-colored solution. The solution was then allowed to warm to room temperature during which time the color changed from red to fluorescent yellow. After stirring for 3 hours, THF was removed under reduced pressure, and the resulting oil was taken up in methylene chloride and washed three times with saturated NaCl solution. The organic layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. The crude product was purified by flash chromatography with silica gel, eluting with 3/1 (v/v) hexanes/methylene chloride. In addition, mixed fractions were further purified on prep TLC plates. The combined yield was 0.88 g (60%). FT-IR (KBr) 2957, 2924, 1600, 1519, 1260, 912 cm^{-1} . UV (CH_2Cl_2) $\lambda_{\text{max}} = 392 \text{ nm}$ ($\epsilon = 4.07 \times 10^4$). ^1H NMR (CDCl_3 , 300 MHz) δ : 7.42 (m, 5H), 7.34 (d, $J = 8 \text{ Hz}$, 1H), 7.10 (m, 4H), 6.84 (dd, $J = 13 \text{ Hz}$, 4H), 3.94 (d, $J = 5 \text{ Hz}$, 2H), 3.88 (s, 3H), 1.83 (ddd, $J = 6 \text{ Hz}$, 1H), 1.58 (m, 4H), 1.20 (br s, 4H), 1.0 (s, 18H), 0.98 (t, $J = 6 \text{ Hz}$, 3H), 0.93 (t, $J = 6 \text{ Hz}$, 3H), 0.21 (s, 12H). ^{13}C NMR (CDCl_3 , 300 MHz) δ : 155.35, 155.33, 151.18, 131.46, 131.39, 128.40, 128.19, 127.77, 127.62, 126.82, 126.60, 121.61, 121.47, 120.38, 120.34, 119.72, 110.18, 108.93, 71.81, 56.37, 39.84, 31.01, 29.34, 25.76, 24.30, 23.19, 18.3, 14.2, 11.41, -4.32 . MS, m/e 702.

2,5-Bis(4-hydroxystyryl)-4-(2-ethylhexyloxy)anisole (XV)

To a stirred solution of **XIV** (1.12 g, 1.59 mmol) in THF at 0°C was added tetra-*n*-butylammonium fluoride (1.0 M in THF, 4.7 mL, 4.7 mmol) slowly dropwise by syringe [10]. The solution was allowed to warm to room temperature and stirred for 30 minutes. Reaction was complete as demonstrated by TLC (methylene chloride). The THF was removed under reduced pressure, and the resulting yellow oil was washed with dilute aqueous HCl and saturated aqueous NaCl solutions. The organic layer was dried over anhydrous sodium sulfate, filtered, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography with silica gel, eluting with sequentially added solutions of methylene chloride, 0.5% methanol in methylene chloride, and 1.0% methanol in methylene chloride. The light yellow powder (0.57 g, 75.5%), once isolated, is only slightly soluble in methylene chloride. FT-IR (KBr) 3400, 2930, 1615, 1535, 1210, 1000 cm^{-1} . UV (CH_2Cl_2) $\lambda_{\text{max}} = 392 \text{ nm}$ ($\epsilon = 4.27 \times 10^4$). ^1H NMR (CDCl_3 , 300 MHz) δ : 7.38 (m, 6H), 7.05 (m, 4H), 6.8 (m, 4H), 5.08 (br s, 2H), 3.90 (d, $J = 6 \text{ Hz}$, 2H), 3.86 (s, 3H), 1.73 (ddd, $J = 6 \text{ Hz}$, 1H), 1.64 (br s, 2H), 1.48 (m, 3H), 1.40

(m, 3H), 0.92 (t, $J = 7$ Hz, 3H), 0.88 (t, $J = 7$ Hz, 3H). ^{13}C NMR (CDCl_3 , 300 MHz) δ : 155.07, 151.23, 151.15, 131.07, 130.97, 128.23, 127.99, 127.85, 126.72, 126.51, 121.46, 121.25, 115.63, 115.58, 110.13, 108.98, 71.82, 56.13, 39.78, 30.95, 29.28, 23.13, 14.15, 11.34. MS, m/e 472.

Synthesis of the Polyesters

Copolymer of 2,5-Bis(4-hydroxystyryl)-4-(2-ethylhexyloxy)anisole and Dodecanedioyl dichloride (VII)

In a two-neck flask, **XV** (0.3 g, 0.63 mmol) and triethylamine (0.439 mL, 3.15 mmol) in methylene chloride were allowed to stir until all materials were dissolved. The bright yellow solution was cooled to 0°C , and dodecanedioyl dichloride (0.157 mL, 0.63 mmol) was added very slowly by syringe. The resulting yellow solution with a blue-green tinge was allowed to warm to room temperature. The solution was stirred overnight during which time it appeared to thicken. The solution was washed once with saturated aqueous sodium chloride, three times with dilute aqueous HCl, and three times with saturated aqueous sodium chloride. The polymer was precipitated into rapidly stirring methanol, filtered, and dried. After a second precipitation into methanol, 0.29 g (66%) of yellow polymer was obtained. $M_n(\text{GPC}) = 35,782$; $M_w(\text{GPC}) = 116,207$; $M_w/M_n = 3.2$ in THF. FT-IR (KBr) 3450, 2920, 1758, 1632, 1505, 1200 cm^{-1} . UV (CH_2Cl_2) $\lambda_{\text{max}} = 392$ nm ($\epsilon = 3.72 \times 10^4$). ^1H NMR (CDCl_3 , 300 MHz) δ : 7.46 (t, $J = 7$ Hz, 4H), 7.41 (d, $J = 5$ Hz, 1H), 7.35 (d, $J = 5$ Hz, 1H), 7.02 (m, 8H), 3.92 (d, $J = 7$ Hz, 2H), 3.85 (s, 3H), 2.53 (t, $J = 7$ Hz, 2H), 2.51 (t, $J = 7$ Hz, 2H), 1.76 (m, 6H), 1.56 (m, 4H), 1.38 (m, 15H), 0.95 (t, $J = 7$ Hz, 3H), 0.88 (t, $J = 7$ Hz, 3H). $\eta_{\text{inh}} = 1.45$ dL/g at 30°C in CHCl_3 .

Copolymer of 2,5-Bis(4-hydroxystyryl)-4-(2-ethylhexyloxy)anisole and Glutaryl Dichloride (VI)

This polymer was synthesized by the same procedure as that used for polymer **VII**; in this case glutaryl dichloride was substituted for dodecanedioyl dichloride. The yield of polymer was 75%. $M_n(\text{GPC}) = 49,787$; $M_w(\text{GPC}) = 129,224$; $M_w/M_n = 2.6$ in THF. FT-IR (KBr) 3540, 2930, 1760, 1509, 1207, 1124 cm^{-1} . UV (THF) $\lambda_{\text{max}} = 394$ nm ($\epsilon = 4.37 \times 10^4$). ^1H NMR (CDCl_3 , 300 MHz) δ : 7.47 (m, 3H), 7.40 (d, $J = 6$ Hz, 1H), 7.34 (d, $J = 5$ Hz, 1H), 7.08 (m, 9H), 3.90 (d, $J = 7$ Hz, 2H), 3.86 (s, 3H), 2.73 (m, 4H), 2.18 (m, 2H), 1.78 (ddd, $J = 6$ Hz, 1H), 1.55 (m, 6H), 1.33 (m, 2H), 0.90 (t, $J = 7$ Hz, 3H), 0.88 (t, $J = 7$ Hz, 3H). $\eta_{\text{inh}} = 1.34$ dL/g at 30°C in CHCl_3 .

Copolymer of 2,5-Bis(4-hydroxystyryl)-4-(2-ethylhexyloxy)anisole and 2,2'-Bis(trifluoromethyl)-4,4'-biphenyldicarbonyl Chloride [11] (VIII)

This polymer was synthesized using the same procedure given for polymers **VI** and **VII**; in this example 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarbonyl chloride was substituted for dodecanedioyl dichloride and gave a 99% yield of polymer. $M_n(\text{GPC}) = 39,984$; $M_w(\text{GPC}) = 213,105$; $M_w/M_n = 5.25$ in THF. FT-IR (KBr) 3450, 1750, 1648, 1525, 1345 cm^{-1} . UV (THF) $\lambda_{\text{max}} = 396$ nm ($\epsilon = 4.79 \times 10^4$). ^1H NMR (THF- d_8 , 300 MHz) δ : 8.37 (m, 3H), 8.22 (m, 2H), 7.56–7.24 (m, 8H),

7.10 (m, 7H), 3.86 (m, 3H), 3.70 (br s, 2H), 1.64–1.32 (m, 3H), 1.17 (br s, 2H), 0.79 (t, $J = 7$ Hz, 3H), 0.72 (t, $J = 7$ Hz, 3H). $\eta_{\text{inh}} = 3.80$ dL/g at 30°C in THF.

Synthesis of the Polyamide

Poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene-*trans-p,p'*-stilbenedicarboxamide] (IX)

The procedure for the preparation of the polyamide used in this work was described previously [11]. The sample used in the present experiments had $\eta_{\text{inh}} = 7.5$ dL/g in 5% LiCl/DMAc at 30°C; $M_n \sim 22,000$ (TMU). Solutions of the polymer in TMU were spin cast onto ITO-coated glass plates followed by deposition of a Mg/Al cathode.

RESULTS AND DISCUSSION

Synthesis and General Properties

The synthesis of monomer **XV** requires a six-step reaction sequence. The yields in individual steps ranged from a low of 60% for phosphonate Wittig-type coupling of 2 moles of aldehyde **XIII** with a mole of diphosphonate ester **XII** to a high of 96% for the synthesis of **XII**.

All three polyesters were obtained in good yields and high molecular weights by reacting the diol **XV** with diacid chlorides in methylene chloride using a large excess of triethylamine as the base. The polymers exhibit good solubility in common, low boiling solvents such as CHCl_3 and/or THF. For polymers **VI** and **VII** the solubility is enhanced by the incorporation of the 2-ethylhexyl group on the chromophore in analogy to the result shown by Braun and Heeger in poly(phenylene vinylene) [2]. The solubility of polymer **VIII**, which is wholly aromatic, is further enhanced by the presence of the noncoplanar biphenyl diacid moiety. However, the polyamide relies on the noncoplanar biphenyl moiety for solubility exclusively since it does not contain the 2-ethylhexyl group.

Since the three polyesters absorb in the 392–396 nm region of the spectrum, it must be concluded that neither the aromatic nor the aliphatic spacers are necessary for controlling the absorption wavelength of the chromophore, i.e., the ester functionality effectively confines the conjugation to the phenylene core itself. Conversely, the amide functionality will extend conjugation between phenyl rings due to the partial double bond character of the C–N bond, and in polyamide **IX** the noncoplanar biphenyl plays a crucial role in limiting the chromophore. Hence, this polymer is colorless and has a λ_{max} at 350 nm (in 5% LiCl/dimethylacetamide) [6].

Emission spectra of solutions and films of the polyesters **VI** and **VII** are nearly identical to one another; the blue fluorescence of the latter is shown in Fig. 2. Polyester **VIII** containing a slightly longer chromophore emits blue-green light (Fig. 3). The polyamide also exhibits a blue-green fluorescence.

It is well known that the electronic and steric nature of the substituents on the 2,2'-positions of biphenylene-containing polymers play a crucial role in determining absorption wavelength and solubility. Furthermore, since the polymers presented in this paper are amorphous and since liquid- or gas-phase dihedral angle values for

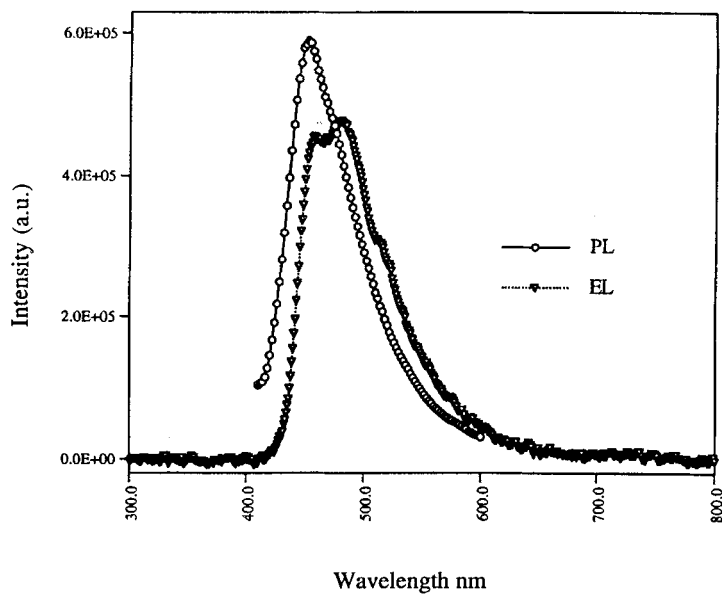


FIG. 2. Photoluminescence and electroluminescence spectra of polymer VII.

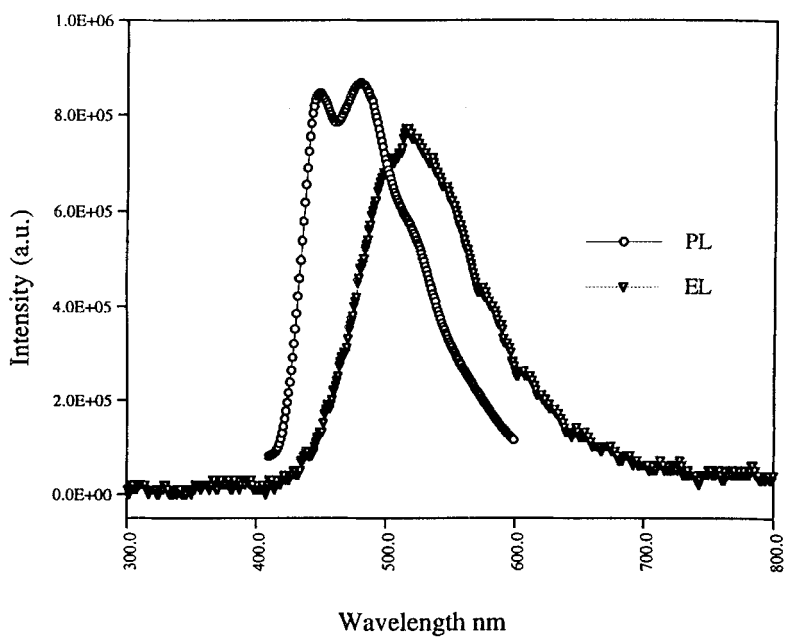


FIG. 3. Photoluminescence and electroluminescence spectra of polymer VIII.

most of the substituted biphenyl moieties utilized are nonexistent, we employed molecular modeling to obtain information on the bond order of the 1,1'-bond of biphenyls with a variety of substituents at the *ortho* positions (see Appendix). From this information we are able to predict the dihedral angle between the phenyl rings and on this basis avoid groups that impart too small an angle to effectively prevent conjugation. From Fig. 4 it can be seen that the difference in bond length for the various atoms and groups range from 1.487 Å (increased double bond character, bond order = 1.500) to 1.521 Å (bond order = 1.000); the corresponding dihedral angles are in the range of 42 to 115°. In regard to the bond angles, the calculated values, which assume isolated molecules and as such are "gas-phase" values which are reasonable approximations for amorphous polymers, show trends that would be expected based on steric interactions. There are, however, three notable exceptions, namely, methoxy, trifluoromethyl, and nitro, which may be attributable to the fact that the calculation method employed considers electronic as well as steric effects. We discuss this in some detail in the Appendix.

Electroluminescence

In this study, single-layered devices for electroluminescence measurements were prepared by spin casting from a chloroform solution of the appropriate polymer onto ITO-coated glass. Pinhole-free transparent films were obtained with thicknesses ranging from 30 to 60 nm. After spin casting, the films were dried in a N₂ purged oven for 2 hours before the Al cathode was vacuum deposited. The Al electrode was deposited at 10⁻⁵-10⁻⁶ torr at a thickness of 400 nm. All devices were tested under ambient conditions at room temperature; no precautionary measures were taken to exclude water or oxygen from the samples after the devices were fully fabricated. Light emission occurred when a ramped voltage was applied to the

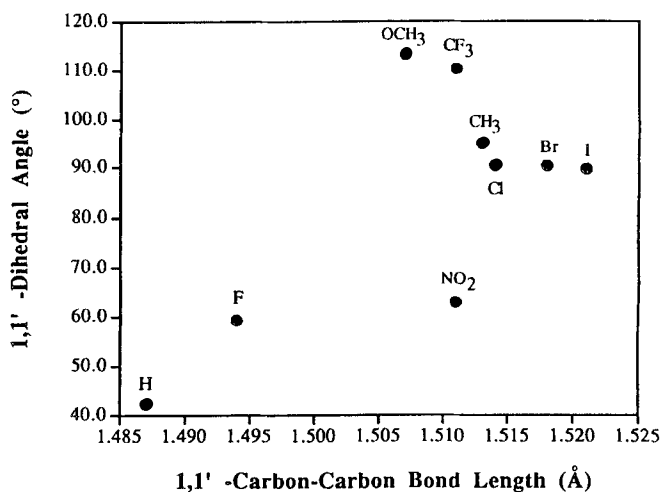


FIG. 4. Gas-phase phenyl-phenyl dihedral angle in 2,2'-disubstituted biphenyl.

device such that the ITO electrode was the anode and the Al electrode was the cathode, i.e., a forward bias. The light emitted was visible in a darkened room.

Figure 2 shows the photo- and electroluminescence emission of polymer **VII**. As expected, the emission wavelengths are very similar with the latter being slightly red shifted. Light emitted from this device was blue; a maximum intensity of 6.2 cd/m^2 was obtained. For polymer **VIII**, EL emission is shifted significantly toward longer wavelength relative to PL emission (Fig. 3). Light emitted from this device appeared green and achieved a maximum intensity of 6.0 cd/m^2 . These spectral differences are usually attributed to heating effects which are an inherent part of electroluminescence. However, the reason for polymer **VIII** EL emission being more sensitive to heating than polymer **VII** is not understood at this time.

A typical light-current-voltage curve (LIV) for polymer **VIII** is shown in Fig. 5. The current-voltage relationship demonstrates typical rectifying behavior for an LED. A turn-on voltage of 15 V was realized, and a maximum of 45 mA, corresponding to a current density of 360 mA/cm^2 , could be pushed through the device as a bias of $\sim 30 \text{ V}$. The light intensity-current (L-I) curve shows a linear relationship at low current, to $\sim 6 \text{ mA}$. Above 6 mA there is a discontinuity in the L-I curve over a 6–10 mA region leading to a second, less efficient region of the L-I curve. The external efficiency of the lower and upper portions of the curve were 0.0035 and 0.0015%, respectively. The discontinuity in the L-I curve could be due to a number of different phenomena which may be taking place during device operation. The most plausible explanation seems to be saturation of the majority charge carriers as the voltage increases above some critical value. Charges injected above the saturation point would migrate through the EL layer and be quenched at the opposite electrode without formation of a singlet exciton—the species responsible for light emission in LEDs. This explanation is supported by the fact that subsequent operation of the same device demonstrates similar behavior. Operation at higher voltage leads to severe degradation in device performance with the formation of clearly visible dark spots on the device during operation. One plausible explana-

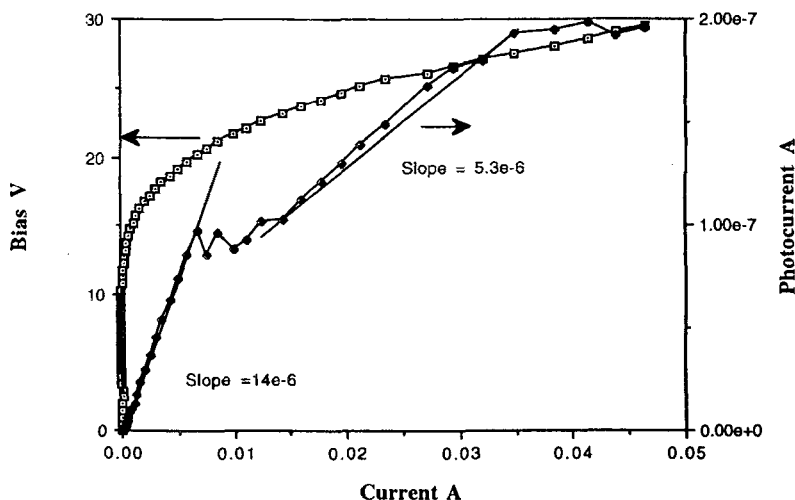


FIG. 5. An LIV curve for polymer **VIII**.

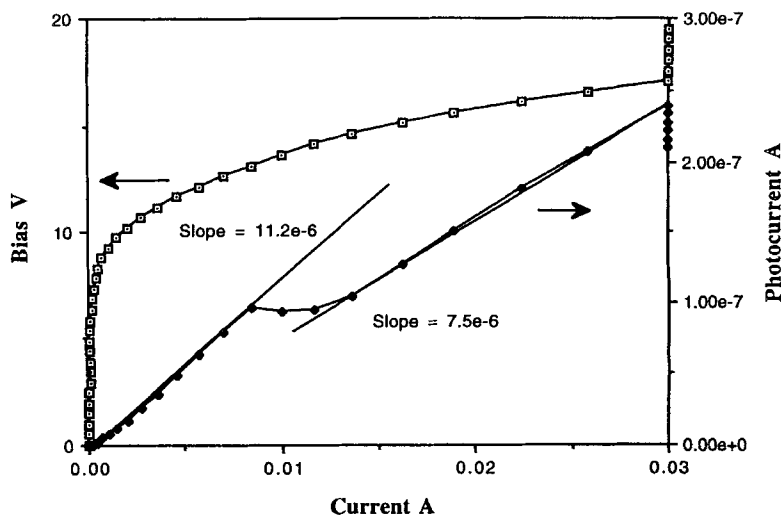


FIG. 6. An LIV curve for polymer VII.

tion for this is oxidation of the polymer or the electrode during device operation. Another explanation is delamination of either electrode from the EL layer.

Polymer VII exhibited similar LIV behavior (Fig. 6). The voltage-current curve was characteristic of a rectifying diode; the L-I curve showed a discontinuity at low current, similar but not identical to that exhibited by polymer VIII, with an external efficiency at low and high currents of 0.003 and 0.0017%, respectively.

Although the efficiencies of the devices presented are rather modest, it should be noted that these systems have not been optimized. No effort has yet been made to incorporate charge confinement layers or use lower work-function metals such as Mg or Ca. The utilization of any or all of these modifications should improve the device performance.

CONCLUSION

Better control of the emission wavelength of polymeric light-emitting diodes may be attained by synthesizing the chromophore prior to polymerization. In condensation polymers this also requires that the chromophore contain at least two polymerizable functionalities such as $-\text{OH}$ or $-\text{NH}_2$ groups, etc. The polymers chosen for this study are soluble in solvents that are amenable to solution casting. Good solubility is due to several factors such as the nature of the substituents on the rigid segment, the ratio of flexible chain length to rigid segment length, the type of linking group generated during polymerization, and for those polymers which comprise biphenyl moieties, the electronic and steric nature of the substituents on the biphenyl repeat unit.

The polyesters exhibit an electroluminescence emission wavelength similar to the photoluminescence wavelength of the polymers in the solid state. The EL emission wavelength of the polyamide is much broader than its PL wavelength. The

electroluminescence efficiency of these polymers, when used in single layer LEDs, is very similar to that of other mainchain polymers such as the poly(phenylenevinyl-enes) and the polythiophenes.

APPENDIX

The 1,1'-carbon-carbon bond distances and the phenyl-phenyl dihedral angles for a series of 2,2'-disubstituted biphenyls, where the substituents were H, F, Cl, Br, I, OCH₃, CF₃, and NO₂, were calculated using quenched molecular dynamics. Potential energy minimizations were carried out with the MM2 force field, inclusive of additional contributions due to 1) nonbonded attractive electrostatic interactions from charge-dipole interactions and 2) delocalization effects on bond orders from the extended pi system. This implementation is commercially available from Cambridge Scientific Computing, Inc. It uses a quadratic van der Waals falloff rather than Allinger's exponential falloff when two atoms are close to the small contact distance. Otherwise the sixth power dispersive attraction can dominate the exponential repulsion term during molecular dynamics since high energy conformations are sampled. Additionally, longer range cutoffs are used for charge-charge, charge-dipole, and dipole-dipole interactions than for van der Waals dispersive interactions. Pi systems are defined for the biphenyl structures, and Praiser-Parr-Popple pi orbital SCF computations are employed. The pi-SCF computations yield bond orders which are used to modify bond lengths and stretching force constants for each sigma bond in the pi system. The modified values are used in the mechanics portion of the computation to further refine the structure of the low energy conformation. Donor-acceptor substitution effects on the above biphenyl structures were also investigated using the 4-amino-4'-nitro analogs. Quenched molecular dynamics calculations were carried out by sampling higher energy conformations from dynamics followed by potential energy minimization with molecular mechanics.

The most significant change in bond order occurs between -F and -Cl substituents which corresponds to a 31° dihedral angle increase, indicating that the phenyl rings are orthogonal in the latter. This suggests that a -Cl, -Br, -I, -CH₃, -CF₃, and -OCH₃ substituents may be used for the purpose of limiting conjugation.

The dihedral angle caused by the presence of the methoxy group is 20° larger than that of the methyl group. To rationalize this finding, three factors must be considered. First, the methoxy group sweeps out a much larger trajectory than a methyl group due to rotation around the phenyl-oxygen bond and to the fact that it is one bond removed from the phenyl. Second, donation of electron density by the methoxy group into the phenyl ring increases the electron density in the 1,1'-carbon-carbon bond. Third, dispersive interactions, including hydrogen bonding, between the methoxy oxygen and phenyl hydrogens on the neighboring phenyl are increased.

The length of the 1,1'-C-C bond is decreased for the trifluoromethyl substituents relative to that for the methyl group, i.e., increased bond order, and the dihedral angle is twisted 15° further from orthogonality. This result may be attributed to a hydrogen-bonding-type interaction between one fluorine of each trifluoro-

methyl group and an *ortho* hydrogen on the same phenyl as well as an interaction between one of the other two fluorines of each group and an *ortho* hydrogen on the opposing phenyl.

The large 1,1'-C—C bond length and small dihedral angle caused by the nitro group, in spite of the fact that the nitro group occupies a volume larger than Br, may be rationalized in the following manner. The nitro group is planar to the phenyl ring to which it is bonded; this results in a significant increase in conjugation between the phenyl rings. In addition, large attractive charge-dipole and dipole-dipole electrostatic contributions between nitro groups results in a decrease in potential energy as these groups approach each other. These two effects cause the 1,1'-bond to shorten and, somewhat surprisingly, the dihedral angle to decrease relative to groups of equivalent size.

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