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Communications to the Editor

A Soluble Blue-Light-Emitting Polymer

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Introduction. Burroughes et al.[1] first demonstrated the light-emitting property of poly(*p*-phenylenevinylene) (PPV) by fabricating a green-light-emitting diode (LED) using this polymer in the emitting layer. Since then a number of polymer LEDs have been reported, using different conjugated polymers[2-11] emitting in various portions of the visible spectrum. For several reasons, a polymer emitting blue light is particularly desirable.[9-11] To date only poly(alkylfluorene)[9] and poly(*p*-phenylene)[10] (PPP) have been reported to have such properties. It was conceivable that shortening the effective conjugation length of PPV would be one of the effective means of shifting the emission spectrum from green to blue because of the anticipated larger band gap. Burn et al.[5,6] have indeed shown that light from partially eliminated PPV was slightly blue-shifted relative to the emission of the "normal" material. However, because of the presumably random distribution of the conjugation lengths in these PPV derivatives, the emitted light was still essentially green. In this paper, we discuss the concept of designing PPV-based copolymers with a blue-light-emitting property based also on the knowledge that low molar mass conjugated organic molecules with photoluminescence maxima in the blue region often show parallel electroluminescence around the same wavelength[12,13] and that small molecules can be blended into an inert polymeric matrix to make a light-emitting layer in a LED device.[14] Thus, we specifically synthesized a copolymer containing alternating rigid and flexible blocks in which the former have a molecular structure analogous to the appropriate low molar mass conjugated molecules while the latter are blocks of polyethylene. The rigid blocks of specified and uniform conjugation lengths are crucial to the tailoring of the band gap of the electronic transition which determines the light-emitting spectrum. The flexible blocks, on the other hand, contribute to the solubility and film-forming properties of the polymer. The advantages of such a copolymer over a small molecule/inert polymeric matrix blend lie additionally in its homogeneity and the prevention of recrystallization or elution of the small molecules within the matrix.

The synthetic strategy (Figure 1) displays the chemical reaction scheme that was used to synthesize the copolymer and is based on these concepts.

The block copolymer was synthesized by using a Wittig reaction between the appropriate dialdehyde and 1,4-xylylenebis(triphenylphosphonium chloride) as shown. It forms homogeneous solutions in THF and chloroform from which transparent films can be cast. The films have good mechanical properties and are slightly yellow in thick section. It was found that this polymer indeed emits blue light, with a maximum peak in the electroluminescent spectrum at 465 nm.

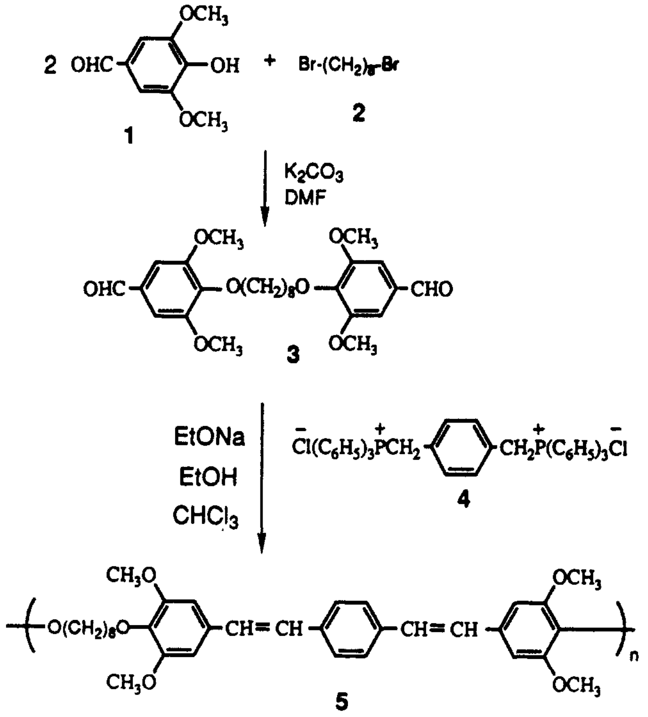

Figure 1. Reaction scheme for monomer and copolymer syntheses.

Experimental Section. Syntheses of Dialdehyde Monomer and Polymer. 1,2-Bis(4-formyl-2,6-dimethoxyphenoxy)octane (3): A solution of 3.64 g (0.02 mol) of 4-hydroxy-3,5-dimethoxybenzaldehyde and 2.72 g (0.01 mol) of 1,3-dibromooctane in 150 mL of DMF was stirred and heated to reflux. A total of 3.0 g (0.022 mol) of potassium carbonate was added in portions. The solution was stirred and refluxed overnight after the addition. The resulting mixture was poured into 2 L of distilled water. The precipitate was collected after standing 4 h, dried in air at ambient temperature, and recrystallized from ethanol. The yield of dialdehyde was 3.75 g (79%) with a mp 87-88 °C. ^{1}H NMR: δ 9.86 (s, 2 H, -CHO), 7.12 (s, 4 H, Ph), 4.06 (t, 4 H, $-OCH_2-$), 3.91 (s, 12 H, $-OCH_3$), 1.75, 1.46, 1.36 (m, 12 H, $-CH_2(CH_2)_6-$). Elem anal. Calcd: C, 65.81; H, 7.22. Found: C, 65,43; H, 7.20.

Poly[1,8-octanedioxy-2,6-dimethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-1,2-ethenylene-3,5-dimethoxy-1,4-phenylene] (5): To a stirred solution of 2.37 g (0.005 mol) of the dialdehyde (3) and 3.50 g (0.005 mol) of 1,4-xylylenebis(triphenylphosphonium chloride) (4) in 100 mL of anhydrous ethanol and molecular sieve-dried chloroform (3/1) was added dropwise at ambient temperature a solution of 0.28 g (0.012 mol) of sodium in 15 mL of anhydrous ethanol. The mixture was stirred for 4 h after the addition, and then 5 mL of 2% hydrochloric acid was added. The pastelike product was collected and thoroughly washed with ethanol/water (3/1) to remove the byproducts triphenylphosphine oxide and NaCl. It was subsequently isomerized into an all-trans configuration by refluxing for 4 h in toluene in the presence of a catalytic

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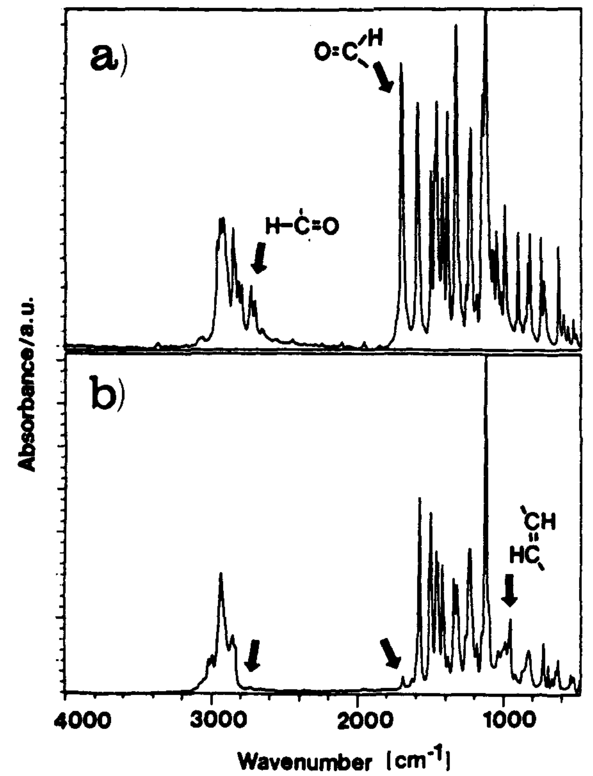
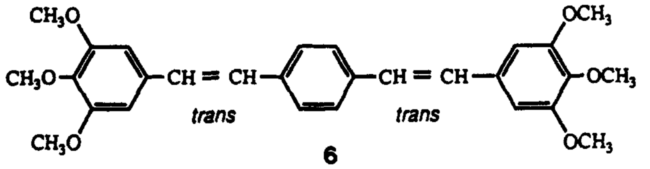


Figure 2. FTIR spectra of the dialdehyde monomer 3 (a) and of the copolymer 5 (b).

amount of iodine. After removal of the toluene, the product was dissolved in 10 mL of chloroform. The solution was slowly added to 200 mL of 90% ethanol to purify the copolymer by precipitation. The solid polymer product was dried in a vacuum oven at 40 °C at 0.2 mmHg for 1 week to give 2.45 g (90%) of copolymer 5. GPC measurement with polystyrene as the calibration standard shows a relative molecular weight of 34 000, dispersity 2.0. Elem anal. Calcd: C, 74.97; H, 7.40. Found: C, 74.00; H, 7.46.

A structurally analogous low molar mass molecule 6 was synthesized according to the procedure described elsewhere[15] and was used in a comparative study.



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Characterization of the Dialdehyde and Polymer. The ^1H NMR and ^{13}C NMR spectra (see below) were obtained on Varian XL-300 and XL-200 spectrometers, respectively. The samples were dissolved in $CDCl_3$; chemical shifts shown are referred to TMS. GPC measurements were performed on a Waters Model 500 with a Waters 416 differential refractometer and a Waters data module 730, using THF as solvent. Polystyrene standards (Polymer Laboratories Ltd., U.K.) were used for calibration. DSC measurement was performed on a Perkin-Elmer DSC-7. Elemental analyses were carried out by the Microanalysis Laboratory of the University of Massachusetts, Amherst, MA. The UV spectra were recorded on an IBM 9420 UV–vis spectrophotometer. Photoluminescence (PL) and electroluminescence (EL) spectra were obtained using a Perkin-Elmer MPF-66 fluorescence spectrophotometer.

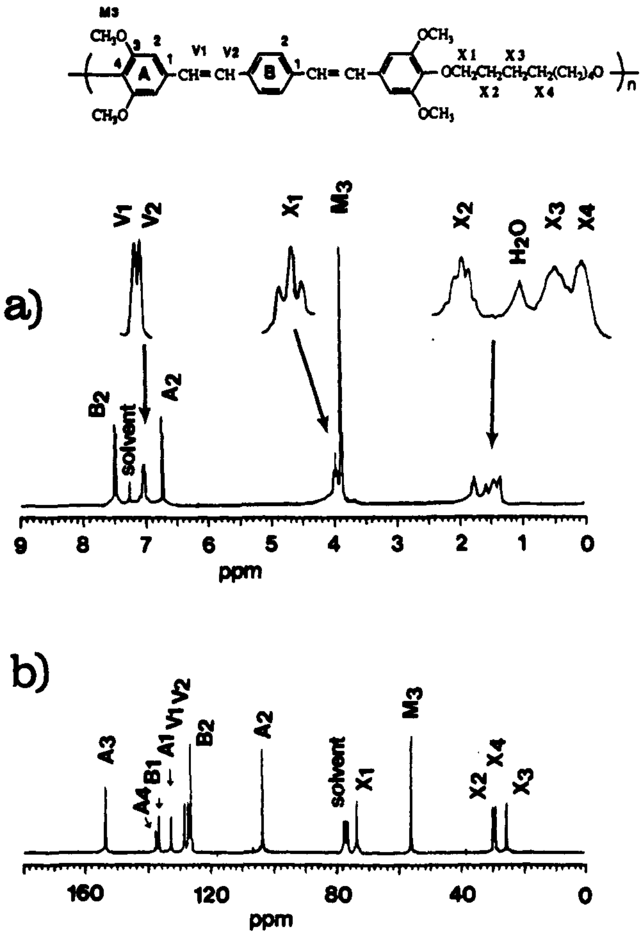

Figure 3. (a) ^1H NMR and (b) ^{13}C NMR spectra of copolymer 5.

Fabrication of the LED Device. A solution of the copolymer 5 in $CHCl_3$ was filtered and spin-coated on a precleaned glass substrate covered with an ITO conducting layer. Typical thicknesses of the copolymer films were 30–80 nm. The film was dried in vacuum, and aluminum electrodes were evaporated onto it in a vacuum of ca. 10^{-5}–10^{-6} Torr. Wires were attached to the respective electrodes with a conductive epoxy adhesive.

Results and Discussion. Figure 2 shows the FTIR spectra of copolymer 5 and of the dialdehyde monomer 3. In spectrum a, absorption at 1701 and 2730 cm^{-1} clearly indicates the existence of the aldehyde group, whereas in b, their intensities are drastically decreased and at the same time a new maximum at 959 cm^{-1} appears which implies the formation of *trans*-vinylene. Figure 3 shows the ^1H NMR and ^{13}C NMR spectra of the copolymer. The assignments of the peaks[16] as indicated in the spectra by comparison with literature values confirm the molecular structure. A DSC trace of the copolymer displays what appears to be a glass transition at 341 K (T_g can be increased when the alkane block is shortened);[16] no melting or other thermal event in the measured temperature range 303–490 K was seen. No liquid crystalline behavior was observed. The results are consistent with the assumption of an amorphous homogeneous copolymer.

The UV spectrum of the copolymer in Figure 4 shows the same maximum absorption wavelength and is similar to that of the low molar mass molecule 6 structurally analogous to the rigid block of 5. It should be noted again that highly transparent pinhole-free, homogeneous, thin films could be formed, by spin-coating, from a $CHCl_3$ solution of 5.

Figure 5 shows the respective solid-state photoluminescence (PL) and the electroluminescence (EL) spectra for 5 and its absorption spectrum. The PL spectrum was

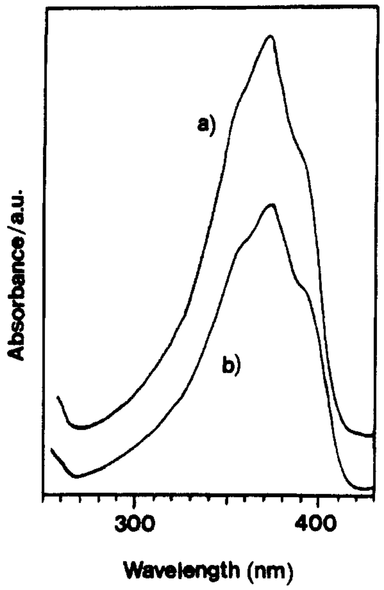

Figure 4. UV spectra of the model compound **6** (a) and of the copolymer **5** (b) in a $CHCl_3$ solution. The spectra are offset for clarity.

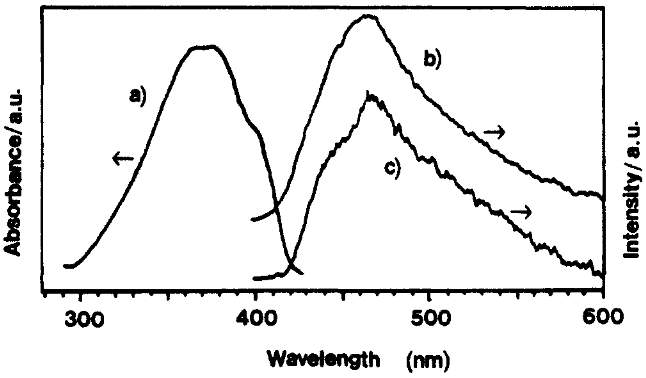

Figure 5. (a) UV absorption spectrum, (b) photoluminescence spectrum (measured at room temperature with an excitation wavelength of 370 nm), and (c) electroluminescence spectrum (measured at 77 K) of the copolymer **5**. Spectra b and c are offset for clarity.

independent of the wavelength of the excitation. The EL spectrum was measured at 77 K by applying a dc voltage to the LED with positive polarity at the ITO electrode, using an electrical field strength exceeding 1 MV/cm. In an inert atmosphere EL could also be seen up to room temperature, although, if the field is applied in air at room temperature, EL ceases in a few minutes. The intensity of the EL maximum observed was roughly proportional to the current. Current densities used were up to 0.1 A/cm^2. The EL and PL spectra were similar (Figure 5), a result indicating the common mechanistic origin of the photon emission. Details of the luminescence measurements are reported elsewhere.[17]

Copolymer **5** has obvious advantages over a low molar mass molecule/polymer matrix composite in an LED device. It has an intrinsic solubility that greatly facilitates fabrication of the device and enhances the film quality of the emitting layer. The uniform conjugation length of **5** determines the spectral purity of the light emitted by the LED device, which in this case is in the blue region. In conventional precursor-originating PPV, it is very difficult to control the effective conjugation length, which is often determined by a random distribution of chemical and morphological defects in the chain.

Conclusions. A new macromolecule has been designed and synthesized by combining uniform conjugated units of specified length with intervening flexible-chain aliphatic oligomeric segments. The basic design concepts can be extended to produce useful soluble materials emitting in other regions of the spectrum and possessing optimized mechanical, optical, and electrical properties.

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References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(2) Nakano, T.; Doi, S.; Noguchi, T.; Ohnishi, T.; Iyechika, Y. Eur. Pat. Appl. EP 443861, Aug 28, 1991; *Chem. Abstr.* **1992**, *116*, P71721k.
(3) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.
(4) Braun, D.; Heeger, A. J.; Kroemer, H. *J. Electron. Mater.* **1991**, *20*, 945.
(5) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H. *J. Chem. Soc., Chem. Commun.* **1992**, 32.
(6) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.
(7) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.
(8) Braun, D.; Gustafsson, G.; McBranch, D.; Heeger, A. J. *J. Appl. Phys.* **1992**, *72*, 564.
(9) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.
(10) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.
(11) Bradley, D. D. C. *Chem. Br.* **1991**, *27*, 719.
(12) Adachi, C.; Tsutsui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799.
(13) Pope, M.; Swenberg, C. E. *Electronic Processes in Organic Crystals*; Oxford University Press: Oxford, U.K., 1982.
(14) Kido, J.; Kohda, M.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1992**, *61*, 761.
(15) Verbruggen, M.; Yang, Z.; Lenstra, A. T. H.; Geise, H. J. *Acta Crystallogr.* **1988**, *C44*, 2120.
(16) Yang, Z.; Karasz, F. E., to be published.
(17) Sokolik, I.; Yang, Z.; Hu, B.; Karasz, F. E.; Morton, D. C., to be published.