Synthesis of a New Class of Processable Electroluminescent Poly(cyanoterephthalylidene) Derivative with a Tertiary Amine Linkage

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Received May 30, 1995
Revised Manuscript Received November 2, 1995

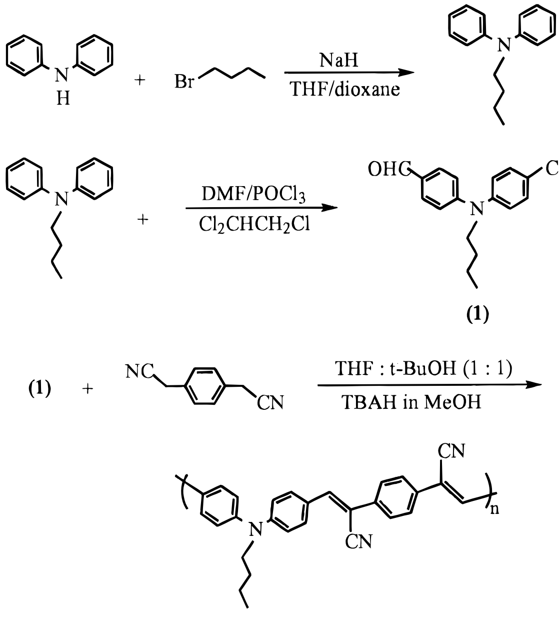
Introduction. Electroluminescent (EL) devices based on organic thin layers have attracted much attention because of their academic interest and potential applications as large-area light-emitting displays.[1−7] Since the first report of polymer light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) by Burroughes *et al.*,[4] a variety of conjugated polymers[5−11] have been reported to exhibit electroluminescence. Electroluminescence in conjugated polymers is well known to be generated by recombination of electrons injected into the conduction band and holes in the valence band to form singlet excitons.[12]For the conjugated polymers investigated so far, electron injection has proved to be more difficult than hole injection. Recently, Greenham *et al.* reported the fabrication of electroluminescent devices[7] using a novel family of soluble poly(cyanoterephthalylidene)s in which each arylene fragment carries solubilizing flexible alkoxyl groups. Because the incorporation of electron-withdrawing cyano groups into the vinylene moiety increased the electron affinity of those polymers, an air-stable metal electrode such as aluminum could be used for efficient electron injection.

Some researchers[13] reported processable and emission wavelength-controllable copolymers containing alternating π-conjugated rigid blocks and saturated aliphatic blocks. However, although the flexible aliphatic blocks contribute to the enhancement of solubility and film-forming properties of the polymer, they may act to hinder carrier injection and to reduce the mobility of the charged carriers. This kind of material requires high threshold voltages, which usually damage the organic materials.

In this paper, we report a new type of processable poly(cyanoterephthalylidene) derivative with tertiary amine linkages in the polymer main chain. This amine linkage with flexible *n*-butyl group limits the conjugation length of the π-conjugated system, which may determine the emission wavelength and may also have an influence on the threshold voltage. We discuss here the effect of the amine linkage on the device characteristics of the present polymers.

Scheme 1 shows the synthetic route used to produce the dialdehyde and the polymer **1**.

Scheme 1



Polymer 1

Experimental Section. Materials. Diphenylamine, 1-bromobutane, sodium hydride (95%), and phosphorus oxychloride were purchased from Aldrich Chemical Co. and used as received unless otherwise stated. Dimethylformamide (DMF) was purified by distillation over phosphorus pentoxide. All solvents used were purified by conventional methods. All other reagents were used as received.

Synthesis of *n*-Butyldiphenylamine. To sodium hydride (5.1 g, 0.20 mol) dispersed in 300 mL of THF and 1,4-dioxane (1:1) were added diphenylamine (30 g, 0.177 mol) and 1-bromobutane (34.3 g, 0.25 mol) in 50 mL of THF, portionwise. The reaction system was allowed to react for 12 h under reflux and then cooled to room temperature. After the removal of volatile materials under vacuum, chloroform (300 mL) and water (300 mL) were added to the residue. The chloroform layer was separated and washed with aqueous sodium carbonate (100 mL). The pure liquid product was isolated by column chromatography after drying and evaporating solvents [eluent, hexane:ethyl acetate (1:1)]. The yield of *n*-butyldiphenylamine was 93%. ^{1}H-NMR ($CDCl_3$): δ 7.36−7.04 (m, 10H, aromatic protons), 3.80 (t, 2H, NCH_2), 1.74 (m, 2H, NCH_2CH_2), 1.42 (m, 2H, CH_2CH_3), 1.02 (t, 3H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 148.1, 129.2, 120.9, 120.8 (aromatic carbons), 52.0 (NCH_2), 29.6, 20.3, 13.9 ($CH_2CH_2CH_3$). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.36; H, 8.46; N, 6.18.

Synthesis of Dialdehyde 1. Dialdehyde **1** was synthesized by using the Vilsmeyer reaction. *N,N*-Dimethylformamide (140 g, 1.91 mol) cooled to 0 °C was treated dropwise with 136 g of phosphorus oxychloride (0.89 mol). The resulting orange solution was stirred at 0 °C for 1 h and at 25 °C for 1 h, and then *n*-butyldiphenylamine (20 g, 0.089 mol) in 40 mL of 1,1,2-trichloroethane was added slowly. The mixture was heated at 90 °C for 20 h, cooled, and poured onto 400 g of ice. A brown oil separated, which was taken up in dichloromethane. The extract was washed with saturated aqueous bicarbonate and then with water containing a little ammonium chloride, and the organic

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S0024-9297(95)00738-8 CCC: $12.00

layer was dried over anhydrous $MgSO_4$. The sovlent was removed under reduced pressure, and the crude viscous product was separated on a silica gel column, using hexane:ethyl acetate (1:1) as eluent. The yield of the dialdehyde was 47%. ^{1}H-NMR ($CDCl_3$): δ 9.84 (s, 2H, CHO), 7.77 (d, 4H, aromatic protons), 7.12 (d, 4H, aromatic protons), 3.80 (t, 2H, NCH_2), 1.66, 1.35, 0.91 ($CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 189.7 (CHO), 151.2, 130.8, 129.8, 119.9 (aromatic carbons), 51.5 (NCH_2), 28.8, 19.4, 13.1 ($CH_2CH_2CH_3$). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.80; H, 6.86; N, 4.93.

Polymerization. Under an argon atmosphere, to a stirred solution of equimolar quantities of dialdehyde **1** and 1,4-phenylenediacetonitrile in tetrahydrofuran and *tert*-butyl alcohol (1:1) was added dropwise 5 mol % of $(C_4H_9)_4NOH$ (TBAH, 1 M solution in methanol) at 45 °C for 20 min. The resulting pastelike polymeric product that precipitated from the solution during polymerization was collected and thoroughly washed with methanol to remove ionic species and unreacted compounds. The scarlet polymeric product was dried in a vacuum oven at 40 °C for 2 days. The polymer yield was 93%.

Characterization. ^{1}H- and ^{13}C-NMR spectra were recorded with the use of Bruker AM-200 and AM-300 spectrometers, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Infrared spectra were measured on a Bomem MB-100 Fourier transform spectrophotometer using KBr pellets. Elemental analysis was performed with a Perkin-Elmer 240 DS elemental analyzer. UV–visible absorption spectra were obtained in chloroform on a Shimadzu UV-3100 spectrophotometer. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high-pressure GPC assembly Model M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, refractive index detectors, solvent THF). Thermal analysis was carried out on a Dupont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10 °C/min. The photoluminescence spectra was recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. The polymer film was excited with several portions of visible light from the xenon lamp. For the measurement of EL, the polymer light emitting diode was constructed as follows: The glass substrate coated with transparent ITO electrode was cleaned by successive ultrasonic treatments in acetone and isopropyl alcohol, dried with nitrogen gas, and heated for further drying and larger conductivity of the transparent electrode. The polymer film was prepared by spin casting from 1,1,2-trichloroethane solution containing 3% polymer by weight. The resulting polymer film has a uniform surface with a thickness around 80 nm. Metal contacts (aluminum) were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below 4×10^{-6} Torr, yielding active areas of 0.2 cm^2. For the mesurements of device characteristics, current–voltage (I–V) characteristics were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818SL). All processing steps and measurements mentioned above were carried out in air and at room temperature.

Results and Discussion. The present polymer was synthesized using the well-known Knoevenagel condensation reaction in a way similar to that reported by the Cambridge group[7] to prepare cyano-substituted poly(phenylenevinylene)s. Careful control of polymerization conditions is required to obtain organosoluble polymer. The resulting polymer was highly soluble in common organic solvents such as THF, chloroform, methylene chloride, and 1,1,2-trichloroethane, but insoluble in hexane, ether, and highly polar alcoholic solvents such as methanol and ethanol. The molecular weight of polymer **1**, as determined by gel permeation chromatography using polystyrene standards, is $\bar{M}_n = 5800$, $\bar{M}_w = 17400$. The FT-IR spectrum of the polymer showed a drastic decrease in the intensity of the aldehyde carbonyl stretching band of the dialdehyde comonomer. Figure 1 shows the ^{1}H- (a) and ^{13}C-NMR (b) spectra of polymer **1** in which the assignment of the peaks is made. As the polymerization proceeded, the aldehyde proton peak of the monomer present at 9.84 ppm disappeared and a new sharp peak appeared at 7.48 ppm for the proton on the newly formed conjugated vinylic double bond (peak c). The assignment of the peaks as indicated in the spectra confirms the present polymer structure. The TGA thermogram of the polymer, run in an N_2 environment, showed the slow weight loss started at 290 °C, and 93% of total weight remained up to 450 °C.

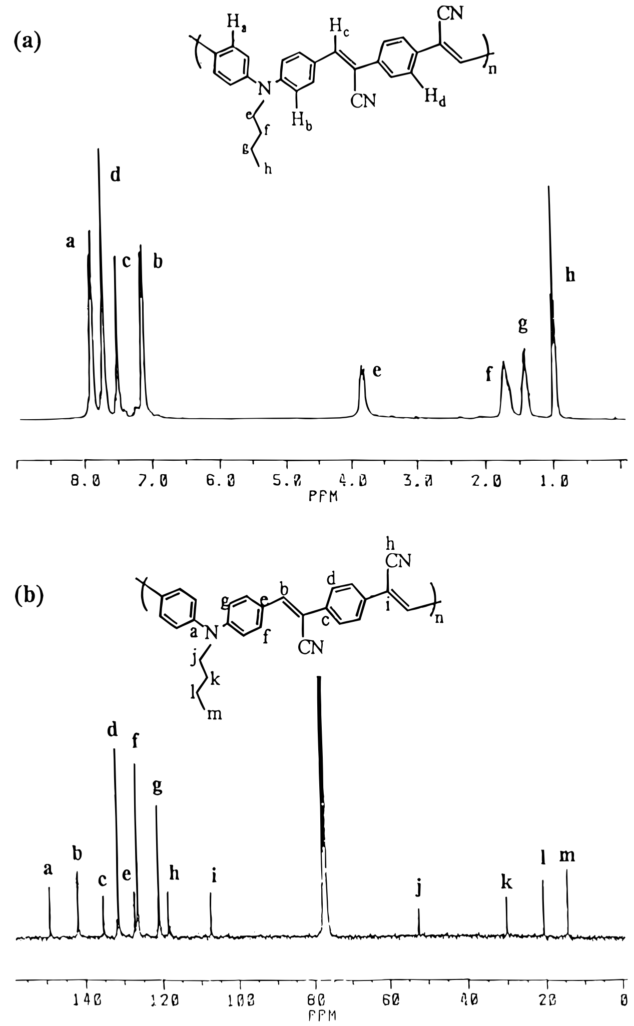


Figure 1. ^{1}H (a) and ^{13}C-NMR (b) spectra of polymer **1** in $CDCl_3$.

Figure 2 shows the absorption spectrum of diluted polymer solution (a) and the photoluminescence spectrum (b) of polymer **1** thin film coated on quartz. All processing steps for EL characteristic measurements were carried out in air and at room temperature. As shown in the absorption spectrum, the present polymer

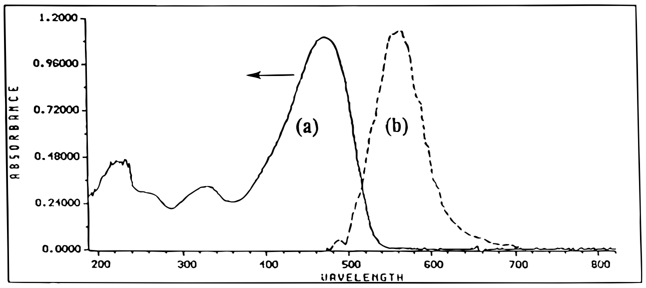
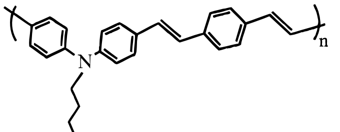


Figure 2. UV–visible spectrum (a) of polymer **1** in CHCl$_3$ solution and the PL spectrum (b) of the polymer **1** thin film.

has a strong absorption band at around 480 nm, which is attributed to the $\pi-\pi^*$ transition of the conjugated segments. In the case of polymer **2** without cyano functional groups given below, which was prepared by a typical Wittig reaction,[14,15] the maximum absorption band was considerably blue-shifted ($\lambda_{\max} = 410$ nm).[16]



Polymer 2

As indicated by the bathochromic shift of the absorption maxima bands resulting from the $\pi-\pi^*$ transition of the conjugated polymer backbone, the incorporation of the electron-withdrawing cyano group into the vinylene moiety forces the π-conjugated segment to be more planar and longer via resonance interaction between the electron-withdrawing cyano group and the nonbonding electrons on the nitrogen atom as the electron-donating group. As a result of this interaction, the nonbonding electrons become part of the π-conjugated system on the polymer main chain. The PL spectrum was independent of the wavelength of excitation.

Current–voltage ($I-V$) characteristics of the polymers were measured using a device configuration of aluminum/polymer/ITO. The forward bias current is obtained when the ITO electrode is positively biased and the aluminum electrode is negative. The current increases with increasing forward bias voltages and the reverse bias current remains small, which is a typical rectifying diode characteristic. The threshold voltage of polymer **1** is about 4.5 V, which is considerably lower compared with the PPV-based block copolymer[13,17] and side-chain polymer,[18] although the conjugation length of this polymer was limited by the tertiary amine group. Polymer **2** without cyano groups also exhibited similar $I-V$ curves with a threshold voltage of about 3.5 V (thickness: 70 nm). It is apparent that the introduction of electron-withdrawing cyano groups has little effect on lowering the threshold voltage for the present polymer systems. Instead, incorporation of an amine linkage leads to a lower threshold voltage. This phenomenon is probably due to a characteristic of the amine linkage. The nonbonding electrons on the nitrogen atom partially join the π-conjugated system.

The EL spectra of polymers **1** and **2** are very similar to the PL spectra exhibiting maximum emission bands at around 560 and 530 nm, respectively, which indicates that the origin of the light emission in both cases is the same (see Figure 3). The radiative recombination in the photoluminescence is known to be due to the formation of the singlet exciton.[12] Figure 4 compares the dependence of the EL intensities of the polymer diodes on the injection current. The emission intensity of polymer **1** was slightly higher than that of polymer **2** without the cyano group. As is typical of polymer LED devices, the emission intensities of the devices linearly increased with increasing injected current, tending to a slight saturation at high injected current. This linear dependence of the EL intensity on the current clearly indicates that the emission is due to the recombination of the charge carriers injected from the electrodes into the bulk of the polymer film to form the singlet exciton responsible for the emission. Moreover, slight saturation of emission intensity is a common phenomenon of conventional EL diodes[19] such as GaAs and GaInP LEDs and may be explained by the increase in nonradiative recombination.[19] Current densities used in this study were up to 100 mA/cm^2.

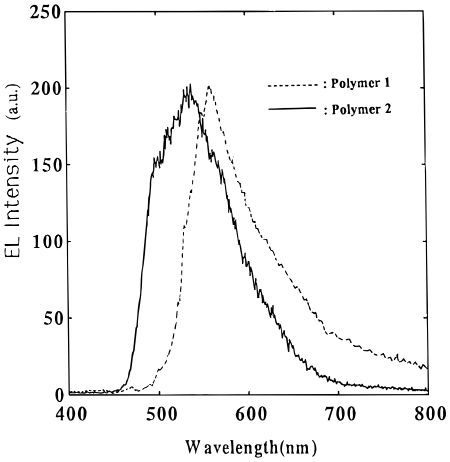


Figure 3. Electroluminescence spectra of the polymer **1** and polymer **2** light-emitting device.

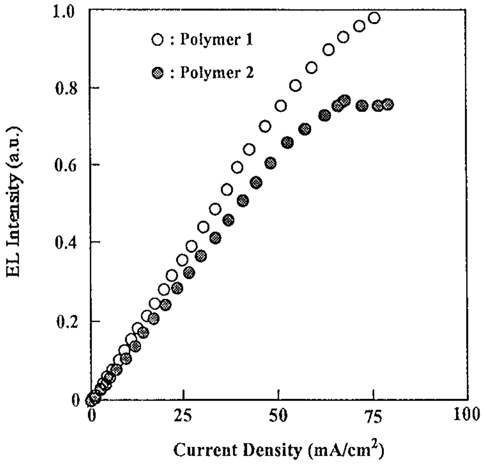


Figure 4. Dependence of EL intensity on injection current of polymer **1** and polymer **2**.

Studies on new polymers having different substituents and other single atoms such as oxygen and sulfur linkages instead of a nitrogen atom are in progress.

Conclusions. A new class of EL polymers with uniform conjugation length regulated by tertiary amine linkages has been synthesized by the Knoevenagel or Wittig condensation reaction. These polymers showed a relatively low threshold voltage compared with a block copolymer having similar conjugated units. The synthetic strategy for the present polymers with a nitrogen atom linkage instead of a nonconjugated segment provides a relatively simple route for the synthesis of a new series of polymers, with low threshold voltages, exhibiting a range of emission spectra.

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MA950738E