Chem. Mater. **1995,** *7,* 1499–1503

Novel Blue Electroluminescent Polymers with Well-Defined Conjugation Length

Taehyoung Zyung,*[,†] Do-Hoon Hwang,[‡] In-Nam Kang,[‡] Hong-Ku Shim,[‡]
Wol-Yon Hwang,[†] and Jang-Joo Kim[†]

Research Department, Electronics and Telecommunications Research Institute, P.O. Box 106, Yusong, Taejon 305-600, Korea, and Department of Chemistry, Korea Advanced Institute of Science and Technology 373-1, Gusung-dong, Yusong-gu, Taejon 305-701, Korea

Received January 18, 1995[®]

Light emission from pale blue to greenish blue is successfully obtained from the diodes made of the trimethylsilyl-, monoalkoxy-, and dialkoxy-substituted polymers with well-defined conjugation length containing phenylenevinylene units. The conjugation length is adjusted by incorporating the nonconjugated spacer group in the backbone. The polymers are organic soluble and allow the fabrication of the light-emitting diode by spinning without further thermal processes. The fabricated devices show typical diode characteristics with operation voltages of 15–20 V, and the light is visible at the current density of about less than 0.5 mA/cm^2 for all three devices. The electroluminescence spectra are similar to the photoluminescence spectra and show the red shift as the electron-donation effects of the substituents become stronger. The bluest color of light emission corresponds to 470 nm for the polymer with trimethylsilyl substituent.

Introduction

Electroluminescent devices generating the light by applying the bias are very important for flat-panel displays and the light-emitting diodes. Demonstration of electroluminescence (EL) from organic molecules[1–3] has accelerated research on the light-emitting devices utilizing π-conjugated organic molecules and π-conjugated polymers. Many π-conjugated polymers have semiconducting properties and $\pi-\pi^*$ energy gap can be altered through controlled changes in the molecular structure. This is one of the important advantages over inorganic light-emitting diodes for various color generation. Another advantage is the processibility of light-emitting diodes, which are fabricated just by casting the luminescent polymer layer from solution. Poly(*p*-phenylenevinylene) (PPV) and its derivatives have shown good mechanical properties and various color generation,[4,5] and, recently, soluble PPV derivatives with relatively high luminescent efficiency made the fabrication process rather simple.[6]

Blue light generation is very desirable for application to the display and the light-emitting diodes. Inorganic semiconductors such as GaN and ZnSe have been used for blue light generation but are not effective for large-scale application. The feasibility and processibility of large-scale application using organic polymers spurred research into the use of π-conjugated polymers in blue light generation.[7–14] Blue EL from polyalkylfluorene[7] and poly(*p*-phenylene)[8] was observed, but they showed rather poor processibility and mechanical properties for the device. Therefore, many other materials have been utilized for blue EL generation, such as using nonconjugated polymers such as poly(vinylcarbazole)[9] and polycarbonate[10] and using a PPV derivative such as poly(*p*-phenylphenylene vinylene).[11]

For blue light emission, the bandgap of the semiconducting polymer must be wide. Shortening of conjugation length is an effective way for enlargement of the band gap.[15,16] The conjugation length of the conjugated polymer is effectively tailored by introducing the nonconjugated segments in the backbone.[13,14,17] The introduction of nonconjugated segments not only results in confinement of π-electrons in conjugated part but also improves the homogeneity of the film. However, from the view of chemical synthesis, it is hard to obtain the polymer with the short conjugation length of phenylenevinylene unit in a soluble form. The introduction

---

[†] Electronics and Telecommunications Research Institute.

[‡] Korea Advanced Institute of Science and Technology.

[®] Abstract published in *Advance ACS Abstracts,* June 15, 1995.

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 813.

(2) Adachi, C.; Tsutui, T.; Saito, S. *Appl. Phys. Lett.* **1990**, *56*, 799.

(3) Bolotin, B. M. *Organic Luminescent Materials*; VCH Verlaggesellshaft: Weinheim, Germany, 1988.

(4) 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.

(5) Zyung, T.; Hwang, D.-H.; Shim, H.-K.; Kim, J.-J.; Hwang, W.-Y. *Synth. Met.* **1995**, *71*, 2167.

(6) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

(7) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, Y. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.

(8) Grem, G.; Leditzky, G.; Ulrich, B.; Leising, G. *Synth. Met.* **1992**, *51*, 383.

(9) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1993**, *63*, 2627.

(10) Hosokawa, C.; Kawasaki, N.; Sakamoto, S.; Kusumoto, T. *Appl. Phys. Lett.* **1992**, *61*, 2503.

(11) Zhang, C.; von Seggern, H.; Pakbaz, K.; Kraabel, B.; Schmidt, H.-W.; Heeger, A. J. *Synth. Met.* **1994**, *62*, 35.

(12) Tachelet, W.; Jacobs, S.; Ndayikengurukiye, H.; Geise, H. J.; Gruner, J. *Appl. Phys. Lett.* **1994**, *64*, 2364.

(13) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules* **1993**, *26*, 1188.

(14) Sokolik, I.; Yang, Z.; Karasz, F. E.; Morton, D. C. *J. Appl. Phys.* **1993**, *74*, 3584.

(15) 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.

(16) Zyung, T.; Hwang, D.-H.; Kang, I.-N.; Shim, H.-K. SPIE '95, in press.

(17) Yang, Z.; Karasz, F. E.; Geise, H. J. *Macromolecules* **1993**, *26*, 6570.

(18) Hoger, S.; McNamara, J. J.; Schricker, S.; Wudl, F. *Chem. Mater.* **1994**, *6*, 171.

0897-4756/95/2807-1499$09.00/0

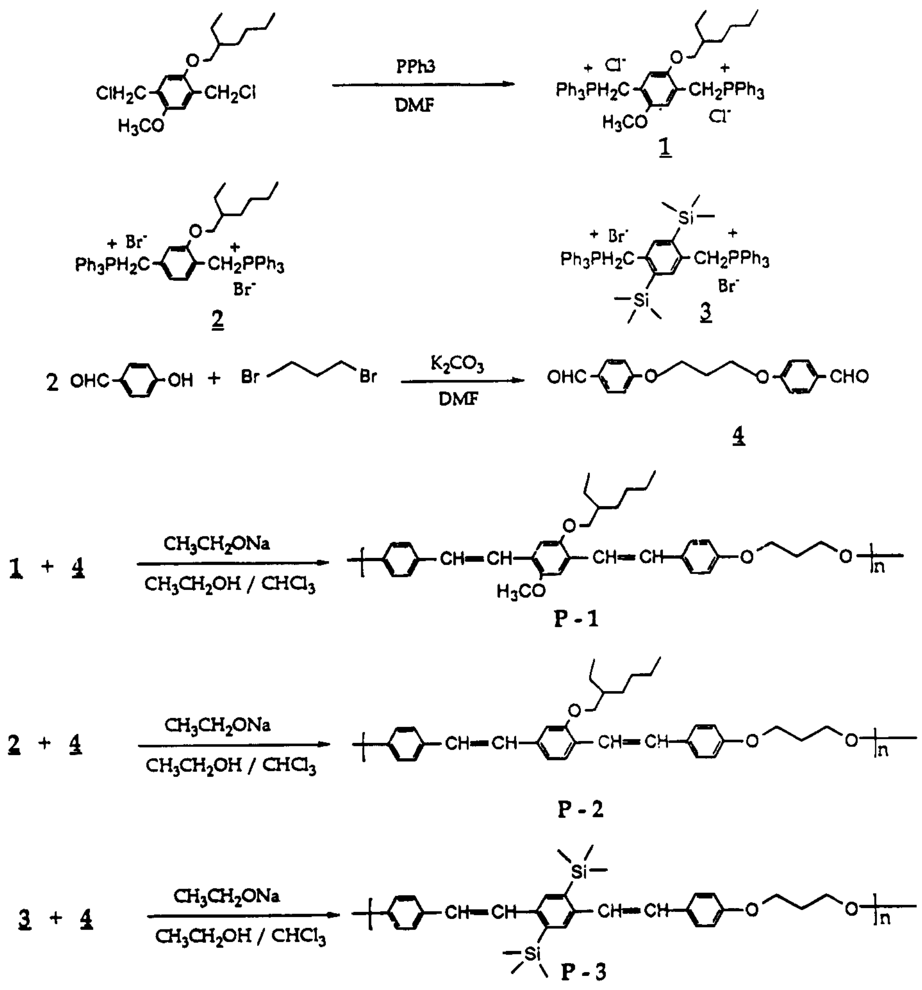

Figure 1. Chemical structures of the polymers synthesized in this study.

of some substituents in the benzene ring is necessary to improve the solubility.[13,14]

In this paper, we report the blue electroluminescent diodes utilizing other PPV derivatives, of which the conjugation length is regulated by incorporating the nonconjugated spacer group in the conjugated backbone. The nonconjugated alkyl spacer group is designed to be as short as possible to keep the mechanical properties of PPV. Furthermore, the flexible long alkoxy side chains and trimethylsilyl groups were introduced to improve the solubility of the polymers. The improvement of the solubility enhances the processibility for the fabrication of a blue EL device. The trimethylsilyl substituent has almost the same electronic properties as hydrogen but helps the polymer to be organic soluble.[18] Alkoxy substituents acting as electron-donating groups are well-known. The blue light generation from the PPV derivative polymers with a small number of substituent on the benzene ring in a repeating unit is reported for the first time as far as the authors know.[12,14] The EL properties and the characteristics of the devices made of these three polymers are measured, and their results are discussed.

Experimental Section

The synthetic schemes and polymer structures are shown in Figure 1.

Synthesis of Monomers. [[(2-Ethylhexyl)oxy]-5-methoxy-1,4-xylylene]bis(triphenylphosphonium chloride) (1). A solution of 5.0 g (15.0 mmol) of [(2-ethylhexyl)oxy]-5-methoxy-1,4-bis(chloromethyl)benzene and 8.7 g (33.0 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 h. The resulting mixture was poured into diethyl ether. After filtration and vacuum drying, the monomer **1** was obtained as a white powder. The product yield was 11.2 g (87%): mp 201–202 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.87–7.54 (m, 30H), 6.75 (s, 1H), 6.53 (s, 1H), 5.06 (d, 2H), 4.95 (d, 2H), 2.94 (s, 2H), 2.79 (s, 3H), 1.30–0.95 (m, 9H), 0.84 (t, 3H), 0.71 (t, 3H). Anal. Calcd: C, 74.19; H, 6.53. Found: C, 70.32; H, 6.45.

[[(2-Ethylhexyl)oxy]-1,4-xylylene]bis(triphenylphosphonium bromide) (2). A solution of 5.0 g (13.0 mmol) of [(2-ethylhexyl)oxy]-1,4-bis(bromomethyl)benzene and 7.4 g (28.0 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 h. The resulting mixture was poured into diethyl ether. After filtration and vacuum drying, the monomer **2** was obtained as white powder. The product yield was 10.0 g (85%): mp 230–232 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.91–7.51 (m, 30H), 6.87 (d, 1H), 6.50 (d, 1H), 6.44 (s, 1H), 5.23 (d, 2H), 4.90 (d, 2H), 2.85 (s, 2H), 1.23–0.95 (m, 9H), 0.86 (t, 3H), 0.69 (t, 3H). Anal. Calcd: C, 68.11; H, 5.89. Found: C, 65.62; H, 5.78.

[2,5-Bis(trimethylsilyl)-1,4-xylylene]bis(triphenylphosphonium bromide) (3). A solution of 7.4 g (7.4 mmol) of 2,5-bis(trimethylsilyl)-1,4-bis(bromomethyl)benzene and 4.3 g (16.3 mmol) of triphenylphosphine in 30 mL of DMF was stirred and heated to reflux for 24 h. The resulting mixture was poured into diethyl ether. After filtration and vacuum drying, the monomer **3** was obtained as a white powder. The product yield was 6.1 g (89%): mp 299–300 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.94–7.55 (m 30H), 7.05 (s, 2H), 5.01 (d, 4H), −0.31 (s, 18H). Anal. Calcd: C, 64.35; H, 5.79. Found: C, 63.02; H, 6.04.

1,3-Bis(4-formylphenoxy)propane (4). A solution of 10.0 g (81.9 mmol) of 4-hydroxybenzaldehyde, 8.3 g (41 mmol) of 1,3-dibromopropane, and 6.2 g (45.1 mmol) of potassium carbonate in 100 mL of DMF was stirred and refluxed for 24 h. The resulting mixture was poured into cold water. The precipitate was collected and dried in vacuum desiccator. Pure white solid product was obtained by recrystallizing the precipitate from ethanol. The product yield was 8.8 g (76%): mp 129–130 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.79 (d, 4H), 6.83 (d, 4H), 4.22 (t, 4H), 2.30 (q, 2H). ^{13}C NMR ($CDCl_3$) δ 190.7, 163.7, 131.9, 130.0, 114.6, 64.4, 28.8. Anal. Calcd: C, 71.82; H, 5.67. Found: C, 70.43; H, 5.60.

Polymerization. A solution of 0.3 g of sodium ethoxide in 10 mL of anhydrous ethanol was added to a stirred solution of 0.5 g (1.6 mmol) of the dialdehyde monomer **4** and 1.4 g (1.6 mmol) of [(2-ethylhexyl)oxy]-5-methoxy-1,4-xylylenebis(triphenylphosphonium chloride) (monomer **1**) in 10 mL of ethanol and 10 mL of chloroform at room temperature. Soon, a yellow-green precipitate was formed and the mixture was stirred for 10 h after the addition. The reaction mixture was extracted with dichloromethane and water. After drying and removing the solvent, crude polymer product was obtained. Then the product was redissolved in dichloromethane and precipitated in methanol. After filtration and vacuum drying, yellow-green poly[1,3-propanedioxy-1,4-phenylene-1,2-ethenylene(2-ethylhexyl)oxy-5-methoxy-1,4-phenylene)-1,2-ethenylene-1,4-phenylene] (**P-1**) was obtained. Poly[1,3-propanedioxy-1,4-phenylene-1,2-ethenylene((2-ethylhexyl)oxy-1,4-phenylene)-1,2-ethenylene-1,4-phenylene] (**P-2**) and poly[1,3-propanedioxy-1,4-phenylene-1,2-ethenylene(2,5-bis(trimethylsilyl)-1,4-phenylene)-1,2-ethenylene-1,4-phenylene] (**P-3**) were synthesized by a synthetic method similar to that for **P-1**.

Device Fabrication. For the measurement of EL properties, the polymer light-emitting devices are constructed as follows: The glass substrates coated with an ITO electrode were cleaned by successive ultrasonic treatment for an hour in acetone and isopropyl alcohol. The substrates were dried with nitrogen gas and heated at 100 °C for further drying and enhancing the conductivity of ITO electrode. The polymer film thicknesses of about 130–150 nm were obtained by spin coating the filtered polymer solutions on the substrates at a rate of 4000 rpm for 15 s and drying in a vacuum oven for several hours. Aluminum was vapor deposited for the top electrode at a pressure below 4×10^{-6} Torr, yielding an active size of a 5 mm diameter. There are no carrier-transport layers between EL layer and electrodes at this time.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were recorded on Bomem Michelson series FT-IR spectrophotometer (MB-100). UV–vis spectra were obtained with a Shimazu UV-3100S. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min with DuPont 9900 analyzer. Elemental analyses were performed with Perkin-Elmer Elements Analyzer (Model 240C).

The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with chopping frequency of 150 Hz, and the polymer film is excited with ultraviolet light at 330 nm from the xenon lamp. EL spectra measurements use a dual-grating monochromator (Spex 270M) with the photomultiplier tube (Hamamatzu R955) as a detector. EL spectra were recorded at 2 nm resolution by computer through the photon counter (SR 400) averaging the signal from PMT 10 times while applying direct current from the current/voltage source (Keithley 238).

For the measurement of device properties, current–voltage (I–V) characteristics and light intensity–current (L–I) characteristics were measured using the current/voltage source and the optical powermeter (Newport 835). The injected current was measured by the voltage supply (Keithley 238) while applying the bias and recorded by computer. At the same time, the emitted light was collected with Si photodetector (Newport 818SL) placed in front of the device and recorded by the computer. At this time, the solid angle of light detection is very small; therefore, the great loss of the light detection is unavoidable. All the measurements mentioned above were performed in air and at room temperature.

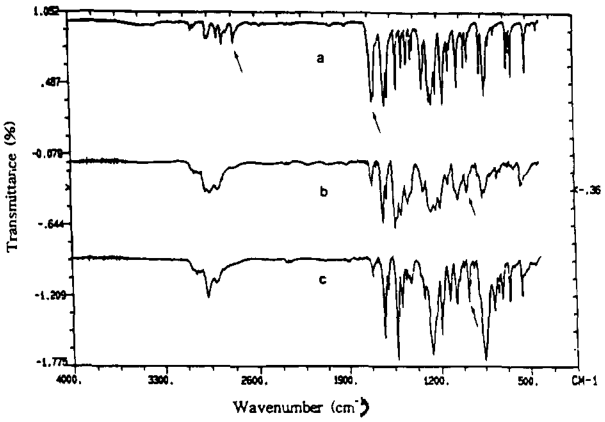

Figure 2. FT-IR spectra of the monomer **4** (a) and the polymers **P-1** (b) and **P-3** (c).

Table 1. Molecular Weight, Polydispersity Indexes, Decomposition Temperatures, and Summary of the UV–Vis and PL Spectra of the Synthesized Polymers

polymer	M_N	M_w	P.D.	T_d (°C)	λ_{max} (UV) (nm)	λ_{edge} (UV) (nm)	λ_{max} (PL) (nm)
P-1	7600	22000	2.9	240	398	451	498
P-2	2700	11000	4.1	210	365	433	477, 500
P-3	2100	7200	3.5	200	349	420	467, 490

Results and Discussion

All the synthesized polymers were soluble in organic solvents such as chloroform, dichloromethane, tetrahydrofuran, etc. Good-quality polymer thin films can be obtained by just spin coating the filtered polymer solutions without any further thermal processes.

GPC measurements of these polymers with polystyrene as the calibration standard show the weight average molecular weight between 10 000 and 20 000 with the polydispersity indexes of 2–4. TGA thermograms of the polymers show that all of the polymers have good thermal stability up to 200 °C, but a small amount of weight loss starts between 200 and 250 °C. The detailed molecular weights, polydispersity indexes, and decomposition temperatures determined from TGA thermograms are listed in Table 1.

Figure 2 shows the FT-IR spectra of the dialdehyde monomer **4** and the polymer films of **P-1** and **P-3**. In Figure 2a, the dialdehyde monomer **4** shows the strong absorption peak of the aldehyde carbonyl group at 1692 cm^{-1} and also the characteristic absorption peak of aldehydic hydrogen at 2760 cm^{-1}. However, in Figure 2b,c, these absorption peaks drastically decreased after polymerization. On the contrary, a weak but sharp absorption peak at 960 cm^{-1} which corresponds to an out-of-plane blending mode of the *trans*-vinylene groups, suggesting that the generated double bonds are mainly in the trans configuration.

Numerical values obtained from the optical absorption spectra of the polymers **P-1**, **P-2**, and **P-3** in film state are summarized in Table 1. The onset of the π–π^* transition of **P-3** is about 420 nm, and this is blue shifted from that of the ordinary PPV by 80 nm. The shorter conjugation length causes blue shift. The onset of the π–π^* transition of **P-1** and **P-2** shifts to 450 and 430 nm, respectively. These red shifts of **P-1** and **P-2** polymers from **P-3** can be attributed to the increment of the number of electron-donating alkoxy groups incorporated in the phenylenevinylene unit.

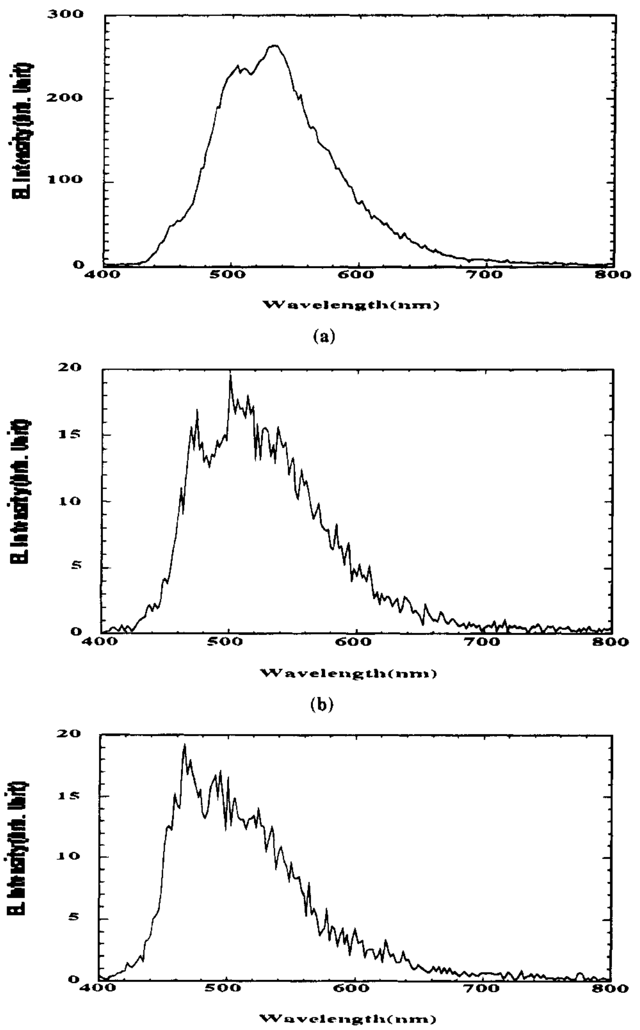

Figure 3. Electroluminescence spectra for **P-1** (a), **P-2** (b), and **P-3** (c) polymers.

The observed emission maxima from the photoluminescence (PL) spectra of the polymer films are also listed in Table 1. All of the polymers show their emission in blue or blue-green region, but the changes of the emission maxima of the polymers are not so large as the absorption maxima in the absorption spectra. Red shifts of the emission maxima from the absorption maxima for all the polymers mean the optical transitions between the subbands inside the $\pi-\pi^*$ optical gap.

The room-temperature EL spectra of three thin polymer films in a device configuration are shown in Figure 3. The EL light from all three polymers shows a Stokes' shift from the absorption peak. Both PL and EL spectra of all the polymers show two peaks, and the peaks are red shifted from the position of trimethylsilyl-substituted polymer with the increasing electron donation effect of the substituent. The EL color is changed from pale blue to greenish blue as determined by naked eye. Three EL spectra are similar to the respective photoluminescence spectra (one example is shown in Figure 4 with absorption spectrum for the polymer **P-3**) indicating that the same excitations are involved in both cases.

In the case of photoluminescence, the photoexcitation of the electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) is known to generate a singlet exciton, which in turn decays radiatively with emission of light.[19] The same species are formed in the case of EL, that is, the singlet excitons are formed in the polymer films by recombining the positive and negative polarons generated from the injected holes and electrons into the HOMO and the LUMO, respectively. The radiative decay from these singlet excitons is responsible for the EL.[19]

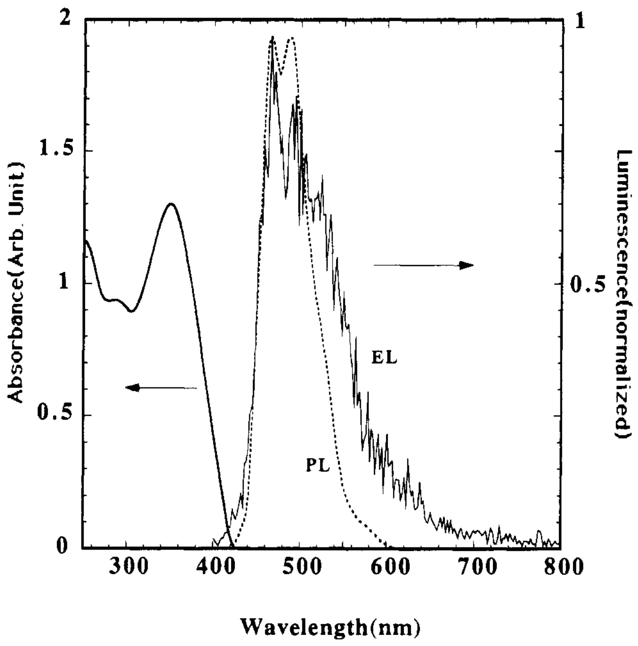

Figure 4. Absorption (thick solid line), electroluminescence (thin solid line), and photoluminescence (dashed line) spectra for the **P-3** polymer.

The forward bias current is obtained when the transparent electrode is positively biased and the metal electrode grounded. Figure 5 shows the current density vs voltage characteristics measured from a metal/polymer/transparent electrode device for all the polymers. The forward current increases in all cases with increasing forward bias voltage, and the reverse bias current remains small; the rectification ratios are approximately 10^3.

Polymers **P-1**, **P-2**, and **P-3** show high threshold voltages of about 15–20 V in comparison with about 8 V of a monoalkoxy-substituted PPV derivative (poly(2-methoxy-1,4-phenylenevinylene) (PMPV) derivative)[5] but lower current densities. The PMPV derivative contains also the conjugated and the nonconjugated segments, but the length of each segment is much longer than the polymers used here and the alkoxy substituent is also attached to the benzene ring. The current densities at which the emission light becomes visible turned out to be less than 0.5 mA/cm^2 in comparison with 250 mA/cm^2 of the PMPV derivative. This indicates that the barriers for the carrier injection from the electrode into the polymers are much higher, and the quantum efficiency may be higher than those of the PMPV derivative. This indicates that the barriers for the carrier injection from the electrode into the polymers are much higher, and the quantum efficiency may be higher than those of the PMPV derivative. The shortening of the conjugation length results in a larger

---

(19) Holmes, A. B.; Bradley, D. D. C.; Brown, A. R.; Burn, P. L.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Gymer, R. W.; Halliday, D. A.; Jackson, R. W.; Kraft, A.; Martens, J. H. F.; Pichler, K.; Samuel, I. D. W. *Synth. Met.* **1993**, *55–57*, 4031.

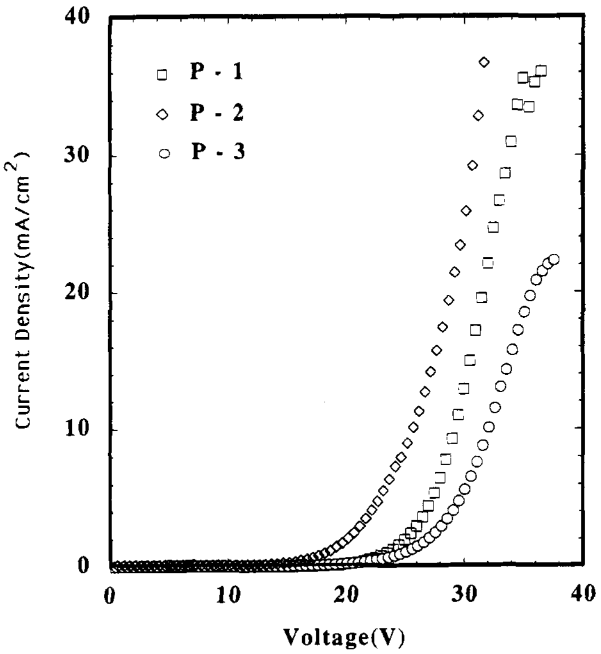

Figure 5. Current vs applied voltage characteristics of **P-1** (square), **P-2** (diamond), and **P-3** (circle) polymer light-emitting devices.

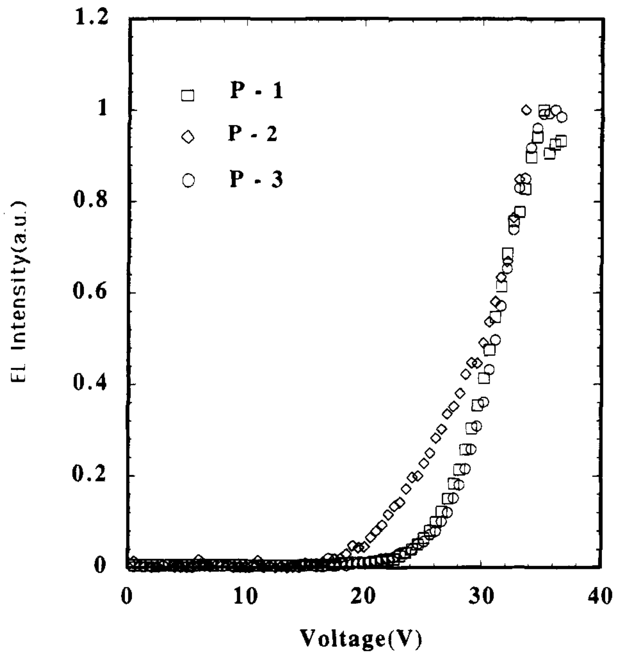

Figure 6. EL intensity vs applied voltage following through three light emitting devices. **P-1** (square), **P-2** (diamond), and **P-3** (circle).

bandgap so that the barrier height for the carrier injection may be higher. The small increase in the barrier heights can produce higher threshold voltages and less major carrier injection in these three polymers. Figure 6 shows the voltage dependence of electroluminescence from the devices. The emitted light becomes detectable at almost same bias as those obtained from the $I-V$ characteristics measurements.

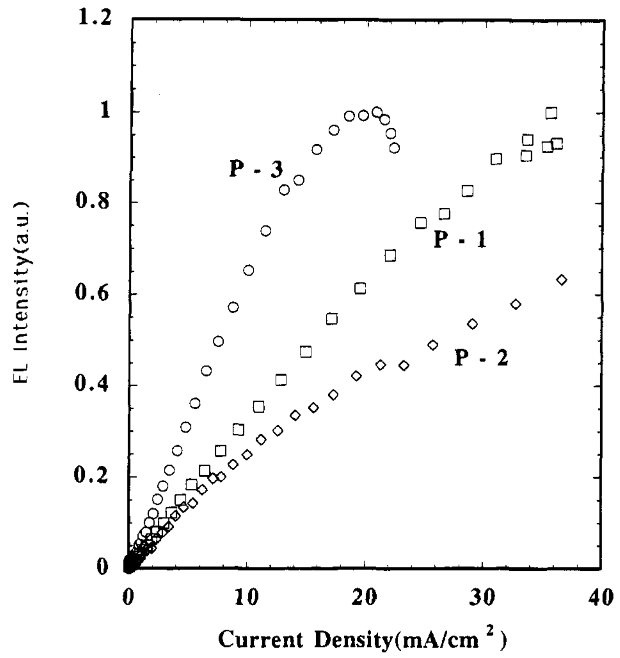

Figure 7. Current dependence of the EL intensities for **P-1** (square), **P-2** (diamond), and **P-3** (circle) polymer light-emitting devices.

The dependence of the emission intensity on the injected current is shown in Figure 7. As is the typical polymer LED devices, the emission intensity exhibits an approximately linear increase with injection current. This linear dependence of the EL intensity on the current is attributed to linear response of the recombination of the charge carriers injected from the electrodes into the bulk of the polymer film.[20] It is hard to know accurate external quantum efficiency, defined as photons generated per electrons injected, of the device since the collection of emission light is not perfect. However, we can estimated from the $L-I$ characteristic curves that the quantum efficiencies are at least on the order of the 10^{-4} photons/electron.

Conclusions

Blue electroluminescent devices have been successfully fabricated using PPV derivative polymers with well-defined conjugation length backbone. The trimethylsilyl, monoalkoxy, and dialkoxy substituents are attached on the central benzene ring in the conjugated segment. The trimethylsilyl-substituted polymer improves the solubility and shows bright blue EL. The more alkoxy groups attached to the benzene ring, the more red shift the EL peak is observed, due to electron-donating effect. The EL spectra are similar to the PL spectra, indicating the origin of the light emission in both cases is the same. The devices show the typical diode characteristics with high threshold voltage but low current density compared to PMPV derivative. A small increase in the barrier height and non-Ohmic contact between the polymer and the electrode for the injection of major carrier may result in the high threshold voltage. The efficiencies are still low, which may be improved by packaging the device under oxygen-free environment and using the low work function metal electrode as a cathode.

Acknowledgment. The authors would like to thank Dr. B.-S. Yoo for helpful discussions.

CM950033R

---

[20] Kao, K. C.; Hwang, H. *Electrical Transport in Solids*; Pergamon: Oxford, UK, 1981; p 541.