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Synthesis and electroluminescence properties of *ortho*-, *meta*- and *para*-linked polymers containing oxadiazole unit

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Abstract

A series of electroluminescent π-conjugated polymers containing an oxadiazole group in the backbone was prepared through Heck's coupling or Wittig's condensation reaction, poly[(2,5-bis(5-hexyloxyphenyl)-1,3,4-oxadiazole)-2,2-diylvinylene-*alt*-1,4-phenylenevinylene] (POOXPV), poly[(2,5-bis(2-hexyloxyphenyl)-1,3,4-oxadiazole)-5,5-diylvinylene-*alt*-1,4-phenylenevinylene] (PMOXPV) and poly[(2,5-diphenyl-1,3,4-oxadiazole)-2,4-diylvinylene-*alt*-1,4-(2,5-dihexyloxy)-phenylenevinylene] (PPOXPV). The three polymers were soluble in common organic solvents and showed good thermal stability. The maximum photoluminescence (PL) wavelengths of POOXPV, PMOXPV and PPOXPV appeared at 495, 470, and 510 nm, respectively. The electroluminescence (EL) spectra of POOXPV and PPOXPV showed maximum peaks at 500 and 510 nm, respectively, corresponding to greenish-blue light, with the single-layer light-emitting diodes of Al/polymer/ITO glass fabricated. In blending synthesized polymers with 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran (DCM), polymers are also believed to serve as an excellent polymer electron-transporting materials in our devices. © 2001 Published by Elsevier Science Ltd.

Keywords: Electroluminescent polymer; Oxadiazole unit

1. Introduction

Recently, π-conjugated electroluminescent polymers have attracted much attention as the best candidate for a flat panel display application after the discovery of light emission from poly(*p*-phenylenevinylene) (PPV) thin film [1] sandwiched between an anode and a cathode electrode. In order to facilitate the solution process, to control the color of emission and to enhance the efficiency of emission, many research groups have investigated and utilized the derivatives of PPV and many other conjugated polymers [2–4]. However, polymeric light-emitting diodes (LEDs) have some problems with their quantum efficiencies and lifetime, which are still not good enough for commercialization. But the ability to alter the $\pi-\pi^*$ energy gap through controlled changes in the molecular structure promises to provide various colors, and that is one of the strengths of polymeric LED materials compared to small molecules.

One major goal in the development of materials for polymeric LEDs is the improvement of quantum efficiency (%) of both photoluminescence (PL) and electroluminescence (EL). Much effort has been made to improve the quantum efficiency. In order to achieve high EL efficiency, it is necessary to balance the rate of injection of electrons and holes from opposite electrodes into the recombination zone [5]. In most PPV and its derivatives, electron injection has been found to be more difficult than hole injection. To achieve efficient electron injection, most conjugated polymers with their intrinsically low electron affinity require metallic electron injecting electrodes with very low work function, such as calcium [6,7]. However, since low work function metals easily react with atmospheric moisture and oxygen, special processing is required when they are used as electrode metal. The employment of polymers with high electron affinities is an alternative way and is considered to be highly desirable. Oxadiazole-based conjugated polymers have been shown to be promising candidates for light-emitting devices [8–11] due to their high electron affinity and hole blocking ability. In addition, poly(aromatic oxadiazole)s are well known for their thermal, hydrolytic and photo stability [12–17]. Aromatic oxadiazole compounds such as 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadizole (PBD)

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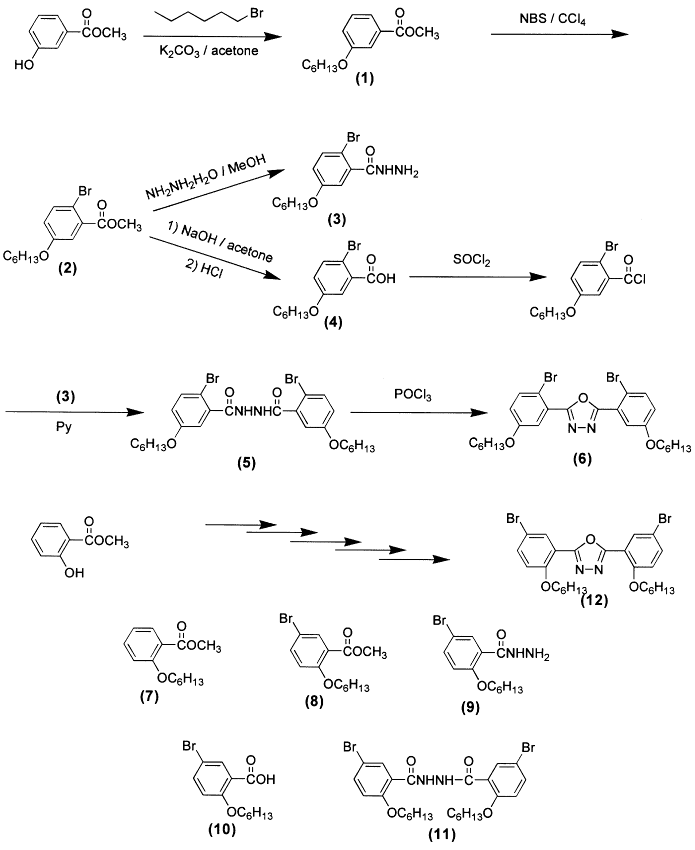


Scheme 1.

have been investigated as electron transporting materials in the multilayer LED device structure [18]. Another approach is by blending electron transporting molecules with luminescent polymers [19–21]. The efficiencies of these blend polymers are also improved owing to a decrease in the energy barrier between the electrodes and the luminescent polymers [22–24].

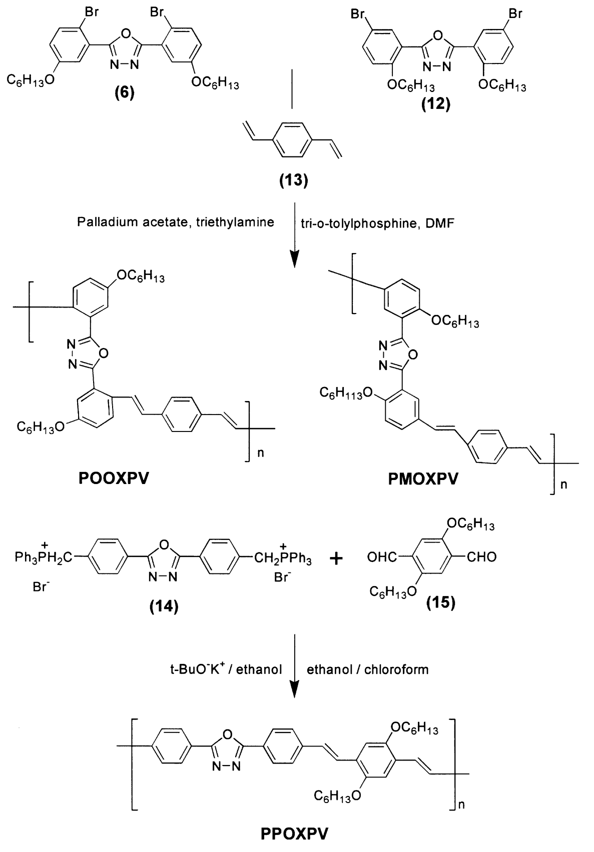
The present work involves the synthesis of a new series of soluble emissive alternating copolymers consisting of oxadiazole unit and phenylenevinylene (PV) moiety. The novel polymers are connected with *ortho*, *meta* and *para* linkages between the phenylenevinylene and the oxadiazole unit. Here, we describe the synthesis, characterization and light-emitting characteristics of poly[(2,5-bis(5-hexyloxyphenyl)-1,3,4-oxadiazole)-2,2-diylvinylene-*alt*-1,4-phenylenevinylene] (POOXPV), poly[(2,5-bis(2-hexyloxyphenyl)-1,3,4-oxadiazole)-5,5-diylvinylene-*alt*-1,4-phenylenevinylene] (PMOXPV) and poly[(2,5-diphenyl-1,3,4-oxadiazole)-2,4-diylvinylene-*alt*-1,4-(2,5-dihexyloxy)-phenylenevinylene] (PPOXPV). And to investigate the electron transporting properties, we blended synthesized polymers (as an electron transporting material) with poly(*N*-vinylcarbazole) (PVK) (as a hole transporting material) and 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran (DCM) (as an emissive material). The light-emitting properties of the blend polymers are described as well.

The synthetic details are given in Schemes 1 and 2 and in Section 2.

2. Experimental

2.1. Instruments

Chemical structures of the compounds were characterized by ^1H NMR spectra using a Bruker AM 200 spectrometer. Melting points were measured using an Electrothermal Model 1307 digital analyzer. FT-IR spectra were obtained with Bomen Michelson series FT-IR spectrometer. The elemental analyses were performed by the Seoul Branch Analytical Laboratory of the Korea Basic Science Institute. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymers were performed under nitrogen atmosphere at a heating rate of 10°C/min with a DuPont 9900 analyzer. The UV–visible spectra of the polymers were measured using a Shimadzu UV-3100 S. The PL spectra of the polymers were obtained using a Perkin–Elmer LS-50 luminescence spectrometer. The EL spectra were measured using a dual grating monochromator (Spex 270 M) with the photomultiplier tube (Hamamatsu R955) as a detector. The EL spectra were recorded at 3 nm resolution by computer through the photon counter (SR400)



Scheme 2.

averaging the signal from PMT while applying a direct current from a current/voltage source (Keithley 238). The current–voltage (*I*–*V*) and light brightness–voltage (*L*–*V*) characteristics were measured using a current/voltage source and a chromameter (Minolta cs-100). The injected current was measured by the voltage supply while applying forward bias. In addition, the emitted light was collected with a chromameter placed in front of the EL device and recorded by computer. The brightness of the EL device was measured using a Minolta CS-1000 spectroradiometer. All of the measurements mentioned above were performed in air and at room temperature.

2.2. Reagents

The PVK having a weight-average molecular weight of 69,000 g/mol, DCM, and rest of the reagents used were purchased from Aldrich Chemical Inc.

2.3. Synthesis of monomers

2.3.1. Methyl 3-hexyloxybenzoate (**1**)

First, 30 g of methyl 3-hydroxybenzoate (200.0 mmol) and 35 g of K_2CO_3 (1.2 eq.) were dissolved in acetone and 33.7 ml of *n*-bromohexane (1.2 eq.) was added. The solution was refluxed for 30 h while stirring. After the reaction had finished, water was poured into the reaction mixture and extracted with ethyl acetate, and then the solvent was evaporated using a rotary evaporator. The crude product was obtained as a liquid. The pure product was obtained by vacuum distillation at 142°C/3 mmHg. The product yield was 47.5 g (90%).

^1H NMR ($CDCl_3$, ppm) δ 7.6 (d, 1H), 7.5 (s, 1H), 7.3 (t, 1H), 7.0 (m, 1H), 4.0 (t, 2H), 3.9 (s, 3H), 1.7 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H). Elemental analysis ($C_{14}H_{20}O_3$): calc. C 71.16, H 8.53. Found C 71.14, H 8.45.

2.3.2. Methyl 2-bromo-5-hexyloxybenzoate (**2**)

To synthesize compound **2**, 29 g of methyl 3-hexyloxybenzoate (120.0 mmol), 32 g of *N*-bromosuccinimide (1.5 eq.) and a catalytic amount of benzoic peroxide (BPO) were dissolved in CCl_4. The reaction mixture was slowly refluxed up to 80°C for 3 h under nitrogen atmosphere. When the reaction was completed, succinimide appeared on the surface of the reaction mixture, and then this by-product was discarded through filtration. The filtrate was extracted with methylene chloride and water. The organic layer was collected and dried using $MgSO_4$ and the solvent was removed using a rotary evaporator. The crude product was purified by column chromatography (hexane/ethyl acetate = 20:1). The product was 35.0 g (92%).

^1H NMR ($CDCl_3$, ppm) δ 7.4 (d, 1H), 7.2 (s, 1H), 7.0 (d, 1H), 4.0 (s, 2H), 3.8 (t, 3H), 1.7 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H). Elemental analysis ($C_{14}H_{19}BrO_3$): calc. C 53.35, H 6.08. Found C 53.31, H 6.02.

2.3.3. 2-Bromo-5-hexyloxybenzoic hydrazide (**3**)

To obtain compound **3**, 29 g of methyl 2-bromo-5-hexyloxybenzoate (92.0 mmol) and an excess amount of hydrazide monohydrate were dissolved in methanol. The mixture was heated at 80°C for 30 h. After the reaction had been finished, solvent was removed using a rotary evaporator and then the reaction mixture was poured into cold water and precipitated. The precipitate was collected and dried in a vacuum oven. The pure white solid product was obtained. The yield was 26.7 g (92%).

M.p. 104.9–106.1°C. ^1H NMR ($CDCl_3$, ppm) δ 9.5 (s, 1H), 7.5 (d, 1H), 6.9 (d, 1H), 6.8 (s, 1H), 4.4 (s, 2H), 3.9 (t, 2H), 1.7 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H). Elemental analysis ($C_{13}H_{19}BrN_2O_2$): calc. C 49.54, H 6.08, N 8.89. Found C 49.54, H 6.03, N 8.98.

2.3.4. 2-Bromo-5-hexyloxybenzoic acid (**4**)

Compound **4** was prepared by reacting 20 g of methyl 2-bromo-5-hexyloxybenzoate (63.0 mmol) with 12.7 g of NaOH (5 eq.) in acetone at 60°C for 24 h. After the reaction was over, the solution was neutralized with dilute HCl and extracted with ethyl acetate. The crude solid product was recrystallized from methanol. The yellowish solid was obtained. The product yield was 17.2 g (92%).

M.p. 76.8–78.0°C. ^1H NMR ($CDCl_3$, ppm) δ 7.5 (d, 1H), 7.4 (s, 1H), 6.9 (d, 1H), 4.0 (t, 2H), 1.7 (m, 2H), 1.3 (m, 6H), 0.9 (m, 3H). Elemental analysis ($C_{13}H_{17}BrO_3$): calc. C 51.84, H 5.69. Found C 51.94, H, 5.64.

*2.3.5. Bis(2-bromo-5-hexyloxybenzoyl) hydrazine (**5**)*

First, 10 g of 2-bromo-5-hexyloxybenzoic acid (330.0 mmol) and 50 ml of thionyl chloride (20 eq.) were heated to 70°C for 4 h. After the reaction was completed, the excess thionyl chloride was removed by distillation. The obtained compound, 2-bromo-5-hexyloxybenzoyl chloride was dissolved in tetrahydrofuran and 10 ml of pyridine was added into the solution. Afterward, 10 g of 2-bromo-5-hexyloxybenzoic hydrazide (0.96 eq.) was slowly added in ice bath and the reaction proceeded at room temperature for 10 h. After the reaction was finished, the solution was extracted with ethyl acetate. The product was obtained by recrystallization with ether. The product yield was 13.5 g (71%).

M.p. 118.8–122.4°C. ^{1}H NMR ($CDCl_3$, ppm) δ 9.5 (s, 2H), 7.4 (m, 2H), 7.2 (s, 2H), 6.8 (d, 2H), 3.9 (t, 4H), 1.7 (m, 4H), 1.3 (m, 12H), 0.9 (m, 6H). Elemental analysis ($C_{26}H_{34}Br_2N_2O_4$): calc. C 52.19, H 5.73, N 4.68. Found C 52.15, H 5.68, N 4.78.

*2.3.6. Bis(2-bromo-5-hexyloxybenzyl)-1,3,4-oxadiazole (**6**)*

Compound **6** was prepared by reacting 9.2 g of bis(2-bromo-5-hexyloxybenzoyl) hydrazine (15.0 mmol) in 30 ml of $POCl_3$ (20 eq.) at 70°C for 30 h. After the reaction was completed, excess $POCl_3$ was removed by distillation. The reaction mixture was slowly added into water in ice bath and then the solution was extracted with ethyl acetate. The product was obtained by recrystallization from ether. The product yield was 7.3 g (82%).

M.p. 39.7–42.5°C. ^{1}H NMR ($CDCl_3$, ppm) δ 7.6 (d, 2H), 7.5 (s, 2H), 6.9 (d, 2H), 4.0 (t, 4H), 1.8 (m, 4H), 1.4 (m, 12H), 0.9 (m, 6H). Elemental analysis ($C_{26}H_{32}Br_2N_2O_3$): calc. C 53.81, H 5.56, N 4.83. Found C 53.76, H 5.51, N 4.82.

Bis(3-bromo-6-hexyloxybenzyl)-1,3,4-oxadiazole **12** was prepared by the same method (same scale) as bis(2-bromo-5-hexyloxybenzyl)-1,3,4-oxadiazole except for the starting materials (methyl 2-hydroxybenzoate).

*2.3.7. Methyl 2-hexyloxybenzoate (**7**)*

The product yield was 45.9 g (87%).

^{1}H NMR ($CDCl_3$, ppm) δ 7.7 (d, 1H), 7.4 (d, 1H), 6.8 (m, 2H), 4.0 (t, 2H), 3.8 (s, 3H), 1.8 (m, 2H), 1.4 (m, 6H), 0.9 (m, 3H). Elemental analysis ($C_{14}H_{20}O_3$): calc. C 71.16, H 8.53. Found C 71.16, H 8.50.

*2.3.8. Methyl 5-bromo-2-hexyloxybenzoate (**8**)*

The product yield was 32.3 g (85%).

^{1}H NMR ($CDCl_3$, ppm) δ 7.8 (s, 1H), 7.5 (d, 1H), 6.8 (d, 1H), 3.9 (t, 2H), 3.8 (s, 3H), 1.7 (m, 2H), 1.3 (m, 6H), 0.8 (m, 3H). Elemental analysis ($C_{14}H_{19}BrO_3$): calc. C 53.35, H 6.08. Found C 53.36, H 6.09.

*2.3.9. 5-Bromo-2-hexyloxybenzoic hydrazide (**9**)*

The product yield was 27 g (93%).

M.p. 83.4–85.5°C. ^{1}H NMR ($CDCl_3$, ppm) δ 8.9 (s, 1H), 8.2 (s, 1H), 7.4 (d, 1H), 6.8 (d, 1H), 4.0 (t, 2H), 3.9 (s, 2H), 1.8 (m, 2H), 1.3 (m, 6H), 0.8 (m, 3H). Elemental analysis ($C_{13}H_{19}BrN_2O_2$): calc. C 49.54, H 6.08, N 8.89. Found C 49.60, H 6.06, N, 8.92.

*2.3.10. 5-Bromo-2-hexyloxybenzoic acid (**10**)*

The product yield was 16.8 g (90%).

M.p. 70.6–72.3°C. ^{1}H NMR ($CDCl_3$, ppm) δ 8.2 (s, 1H), 7.6 (d, 1H), 6.9 (d, 1H), 4.2 (t, 2H), 1.8 (m, 2H), 1.3 (m, 6H), 0.8 (m, 3H). Elemental analysis ($C_{13}H_{17}BrO_3$): calc. C 51.84, H 5.69. Found C 51.83, H 5.66.

*2.3.11. Bis(5-bromo-2-hexyloxybenzoyl) hydrazine (**11**)*

The product yield was 14.3 g (75%).

M.p. 157.9–160.2°C. ^{1}H NMR ($CDCl_3$, ppm) δ 11.2 (s, 2H), 8.3 (s, 2H), 7.5 (d, 2H), 6.8 (d, 2H), 4.2 (t, 4H), 2.0 (m, 4H), 1.4 (m, 12H), 0.9 (m, 6H). Elemental analysis ($C_{26}H_{34}Br_2N_2O_4$): calc. C 52.19, H 5.73, N 4.68. Found C 52.25, H 5.70, N, 4.73.

*2.3.12. Bis(5-bromo-2-hexyloxybenzyl)-1,3,4-oxadiazole (**12**)*

The product yield was 7.0 g (80%).

M.p. 85.9–88.2°C. ^{1}H NMR ($CDCl_3$, ppm) δ 8.1 (s, 2H), 7.5 (d, 2H), 6.9 (d, 2H), 4.0 (t, 4H), 1.8 (m, 4H), 1.4 (m, 12H), 0.8 (m, 6H). Elemental analysis ($C_{26}H_{32}Br_2N_2O_3$): calc. C 53.81, H 5.56, N 4.83. Found C 53.80, H 5.58, N, 4.85.

*2.3.13. p-Divinylbenzene (**13**)*

The *p*-divinylbenzene was isolated from a mixture of *p*-divinylbenzene and *m*-divinylbenzene according to the procedure outlined in Ref. [25].

*2.3.14. 2,5-Bis(4-tolyene-triphenylphosphonium bromide)-1,3,4-oxadiazole (**14**)*

This monomer was synthesized by the previous work [11].

*2.3.15. 2,5-Bis(hexyloxy)terephthalaldehyde (**15**)*

This monomer was synthesized by the previous work [26].

2.4. Polymerization

A solution of 0.70 g of monomer **6** (1.2 mmol) (or monomer **12**) and 0.15 g of *p*-divinylbenzene (1.0 eq.) in 10 ml of *N,N*-dimethylformamide was prepared. Then 0.011 g of $Pd(OAc)_2$, 0.075 g of tri-*o*-tolylphosphine and 0.42 ml of triethylamine were added to the reaction mixture. The reaction proceeded at 100°C for 40 h under nitrogen atmosphere. After completion, the reaction mixture was poured into methanol. The crude product was obtained by filtration.

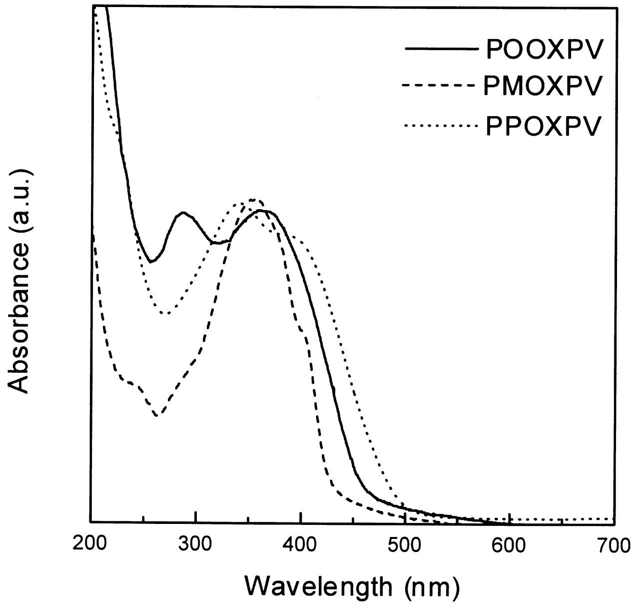


Fig. 1. UV–visible absorption spectra of POOXPV, PMOXPV and PPOXPV.

The crude product was dissolved in methylene chloride and precipitated in methanol for several times. After being filtered and vacuum-dried, the final polymer was obtained.

2.4.1. *Poly[(2,5-bis(5-hexyloxyphenyl)-1,3,4-oxadiazole)-2,2-diylvinylene-alt-1,4-phenylenevinylene]*

The product yield was 0.49 g (74%).

T_g 115°C. ^{1}H NMR ($CDCl_3$, ppm) δ 8.1–6.5 (br, 14H), 3.9 (br, 4H), 1.7–0.8 (br, 22H). Elemental analysis ($C_{36}H_{40}N_2O_3$): calc. C 78.80, H 7.35, N 5.11. Found C, 78.74, H 7.38, N 5.08.

2.4.2. *Poly[(2,5-bis(2-hexyloxyphenyl)-1,3,4-oxadiazole)-5,5-diylvinylene-alt-1,4-phenylenevinylene]*

The product yield was 0.47 g (71%).

T_g 106°C. ^{1}H NMR ($CDCl_3$, ppm) δ 8.1–6.9 (br, 14H), 4.1 (br, 4H), 1.8–0.8 (br, 22H). Elemental analysis ($C_{36}H_{40}N_2O_3$): calc. C 78.80, H 7.35, N 5.11. Found C 78.77, H 7.34, N 5.09.

2.4.3. *Poly[(2,5-diphenyl-1,3,4-oxadiazole)-2,4-diylvinylene-alt-1,4-(2,5-dihexyloxy)-phenylenevinylene]*

A solution of potassium *t*-butoxide (0.44 g, 3.97 mmol) in 15.0 ml of absolute ethanol was added to 15.0 ml of anhydrous chloroform/ethanol solution containing 0.53 g (0.4 eq.) of the dialdehyde monomer (**15**) and 1.47 g (0.4 eq.) of the salt monomer (**14**) at room temperature. The reaction mixture was stirred for 24 h at room temperature under nitrogen atmosphere. When the reaction was completed, the reaction mixture was extracted with excess methylene chloride and water. After having the solvent removed and being dried, the crude polymer product was obtained. The polymer was dissolved in methylene chloride and precipitated in methanol several times, and the final polymer was obtained. The product yield was 0.47 g (55%).

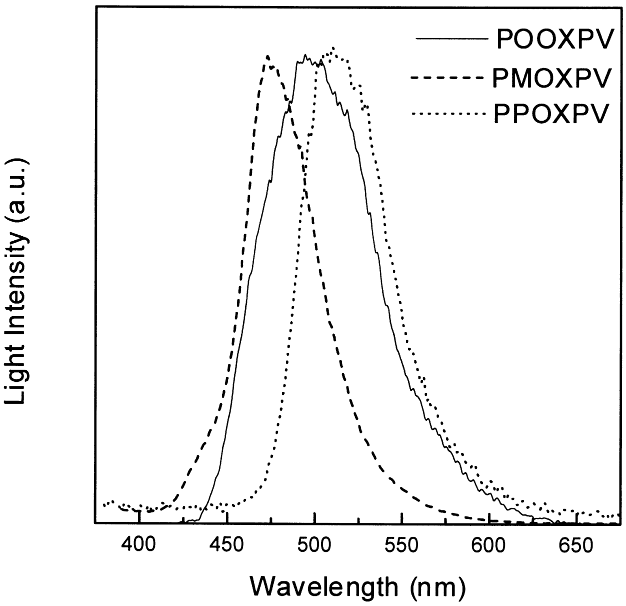


Fig. 2. PL spectra of POOXPV, PMOXPV and PPOXPV.

T_g 137°C. ^{1}H NMR ($CDCl_3$, ppm) δ 8.1–6.6 (br, 14H), 4.0 (br, 4H), 1.8–0.8 (br, 22H). Elemental analysis ($C_{36}H_{40}N_2O_3$): calc. C 78.80, H 7.35, N 5.11. Found C 78.92, H 7.34, N 5.07.

Thin films of three polymers could be obtained on ITO coated glasses with excellent reproducibility by spin cast from 1,2-dichloroethane solution. The EL device structures consist of aluminum as a cathode electrode and an ITO glass as an anode electrode with the light-emitting polymer sandwiched in between those electrodes. The film thickness measured using a Tencor Alpha-Step 500 profilter was about 100 nm. Electron-injecting aluminum contacts were formed by vacuum evaporation at pressures below 10^{-6} Torr, giving active areas of 0.2 cm^2.

3. Results and discussion

Although the synthetic routes of the polymers are a little bit complicated, we could obtain all of the intermediate compounds in high yields. These compounds were characterized by melting points, ^{1}H NMR, and elemental analyses. Compared with monomer **6**, the ^{1}H NMR spectrum of POOXPV exhibited the same peak positions except broad peaks. The same phenomenon was also observed with PMOXPV. Because newly formed vinylene hydrogen peaks in polymers overlap with the aromatic proton peaks at 6.5–8.1 ppm, the characteristic ^{1}H NMR peaks are not change after the polymerization. Additionally, the polymerization behavior of PPOXPV was monitored by FT-IR spectra in which the change in an aldehyde functional group of

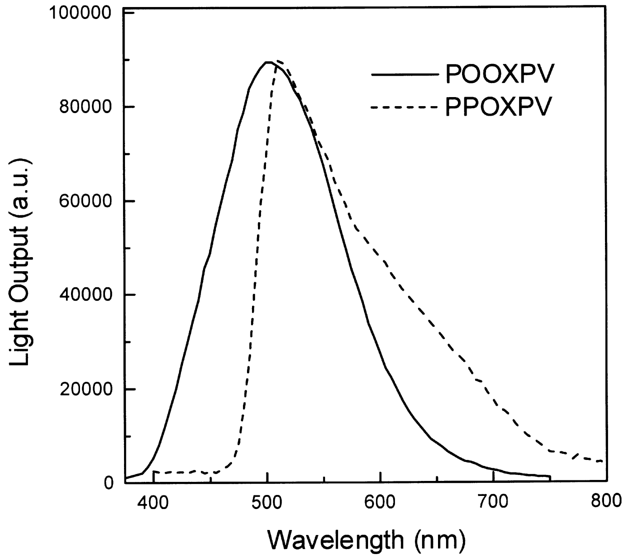


Fig. 3. Normalized EL spectra of POOXPV and PPOXPV at 15.0 V.

the monomer **15** can be investigated. (The monomer has an aldehyde functional group, but the polymer does not.) The FT-IR spectrum of PPOXPV exhibits neither the strong carbonyl peak at 1686 cm^{-1} nor the aldehydic hydrogen peak after polymerization.

The weight-average molecular weights (M_w) of POOXPV, PMOXPV and PPOXPV, determined by gel permeation chromatography (GPC) based on polystyrene standards using THF as an eluent, were 9300, 10,400 and 7500, with polydispersity index of 1.5–2.0, respectively. All polymers were soluble in common organic solvents such as chloroform, THF and 1,2-dichloroethane. They showed good thermal stability in which the weight loss was less than 5% upon heating to above 330°C under nitrogen atmosphere.

The UV–visible absorption spectra of the polymer films are shown in Fig. 1. The UV–visible absorption edges are related to the effective π-conjugation length and the maximum light-emitting wavelength. The UV–visible absorption edge of the *para*-linked PPOXPV appears at the longest wavelength and that of the *meta*-linked PMOXPV is the shortest. This change of absorption edge indicates a reduction of the π-conjugation length in the kinked structure because the π-electron delocalization of the polymer with *ortho*-linked main chain is decreased by bent structure, and the π-conjugation by resonance in *meta* linkage does not exist between adjacent vinylenephenylene units compared to *para* linkage polymer [12,27–29].

Fig. 2 shows the film PL spectra of the polymers excited at 370 nm. The PL spectra of POOXPV and PPOXPV showed their maximum peaks at 495 nm and 510 nm, respectively, corresponding to a greenish-blue light emission, and that of PMOXPV gave a maximum peak at 470 nm corresponding to blue light emission.

Fig. 3 shows the EL spectra of POOXPV and PPOXPV. The EL spectra of POOXPV and PPOXPV showed maximum peaks at 500 and 510 nm, respectively, when investigated with the light-emitting device composed of Al/P/ITO (P = POOXPV or PPOXPV). The EL spectrum of PMOXPV is not presented in this paper due to its relatively low emission intensity and not enough stability to measure the spectrum at the measurable luminance. So we were unable to measure the light emission with our detecting system, but a low intense blue emissive light was observable with the naked eye. The PMOXPV has the relative

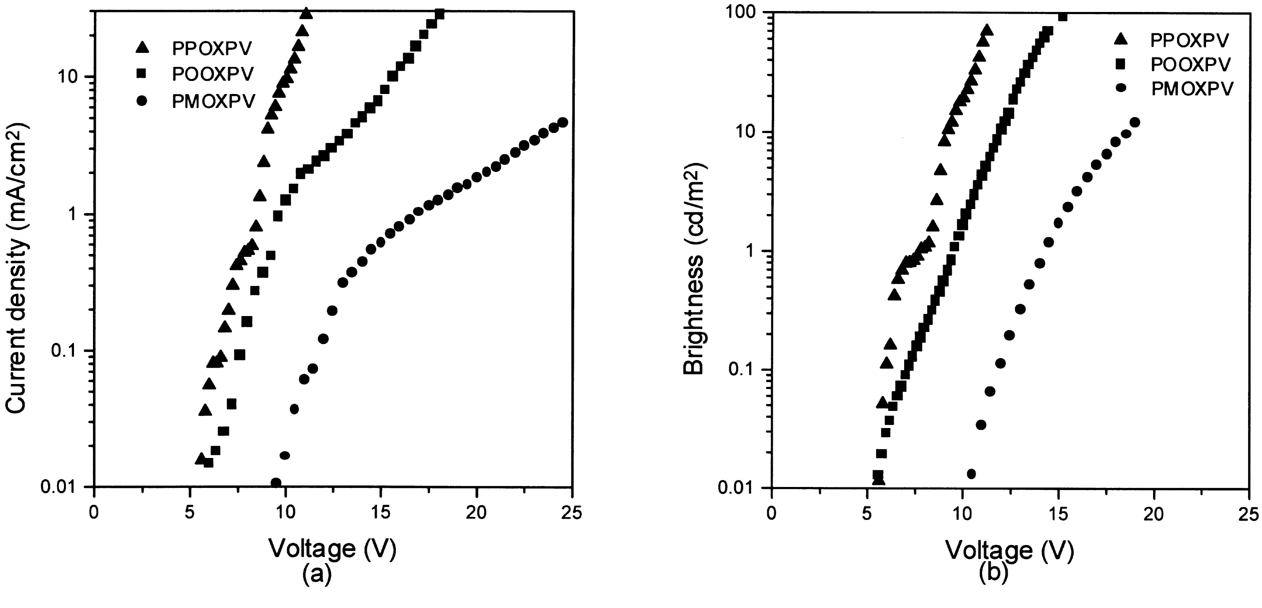


Fig. 4. EL characteristics of POOXPV (■), PMOXPV (●) and PPOXPV (▲) with an ITO/polymers/Al structure. (a) Current density vs. voltage and (b) Brightness vs. voltage.

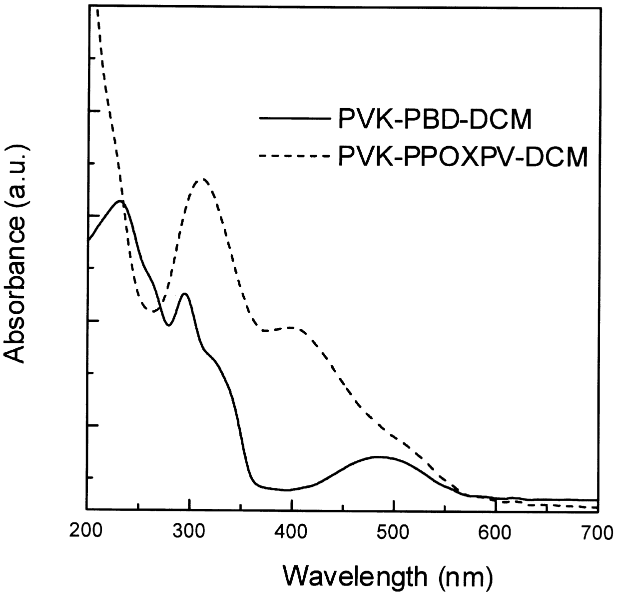


Fig. 5. UV–visible absorption spectra of blend polymers.

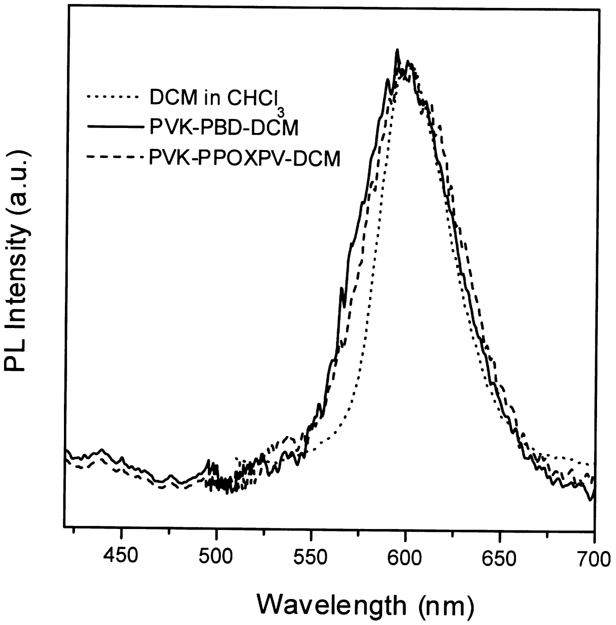


Fig. 6. PL spectra of blend polymers.

poor conductivity and high operating voltage. Therefore the *meta*-linked polymer device was quickly degraded at high operating voltage.

Fig. 4 shows the characteristics of the current and emission-light intensity against applied voltage. The turn-on voltages of POOXPV, PMOXPV and PPOXPV were observed to be at 5.5, 9.5, and 6.0 V, respectively (all polymer films have almost the same thickness, around 100 nm). The devices fabricated with POOXPV or PMOXPV showed higher turn-on voltages than PPOXPV because of the shorter conjugation length and less effective π-electron delocalization through the kinked polymer main-chain.

In order to observe electron transporting ability, Mori synthesized a polyester containing oxadiazole units in a main chain and fabricated a LED device by mixing electron-transport (synthesized polymer), hole-transport (PVK) and low molecular emissive materials together in a single solvent, and studied its characteristics by comparison with PBD [30]. So, we also fabricated an LED device by blending the synthesized polymers (electron transporting material), PVK (hole transporting material) and DCM (emissive material). DCM is a very efficient arylidene laser dye and was first used as a highly fluorescent dopant in organic electroluminescent device by Tang [31]. The DCM gave red-light emission from the single-layer device with PBD (as electron-transporting additive)-doped PVK [32]. We fabricated LED devices having PVK-PBD-DCM and PVK-synthesized polymer-DCM blends. The blending ratios were 15/5/1 by weight percent. The UV–visible absorption spectra of PVK-PBD-DCM and PVK-PPOXPV-DCM are shown in Fig. 5. The representative π–π^* absorption transition peaks of PVK, PBD, PPOXPV and DCM appear between 230 and 500 nm. The short wavelength absorption regions are due to PVK, PBD and PPOXPV, and the long wavelength absorption regions are by DCM. These are typical characteristics of the PVK-PBD(PPOXPV)-DCM blend absorption spectra, and showed no interaction between the three different materials in the ground state.

The film PL spectra of the blend polymers and the solution PL of DCM in chloroform (at 10^{-6} mol% concentration) are shown in Fig. 6. The blend polymers were excited at 370 nm. Regardless of the blend systems, the blend polymers exhibited very strong emissions around 595 nm, corresponding to DCM, and the emissions of PVK, PBD and PPOXPV were not found. From these results, we can guess that the energy transfer occurred in PPOXPV or PBD to DCM.

In device fabricated with PVK-DCM, DCM emits orange-red light at high voltage, but the emission efficiency is very low. However, by adding PBD or PPOXPV to PVK-DCM, we can obtain the EL characteristics. Fig. 7 shows the normalized EL spectra of the blend polymers. The maximum EL emission was at 600 nm, corresponding to the DCM emissive wavelength due to the energy transfer from PBD or PPOXPV to DCM, just like the PL spectra.

Fig. 8 shows the electrical characteristics of the blend polymers. Forward bias current was obtained when the ITO was used as a positive electrode and Al electrode as the ground. The forward current increased with increasing forward bias voltage for all devices. As shown in Fig. 8(a), PPOXPV blend system showed lower turn-on voltage compared to PBD blend system due to the π-conjugated polymer structure of PPOXPV. Fig. 8(b) shows that both blend systems exhibited almost the same brightness, which were greatly enhanced values compared to the blend systems without PBD or PPOXPV. Therefore we found

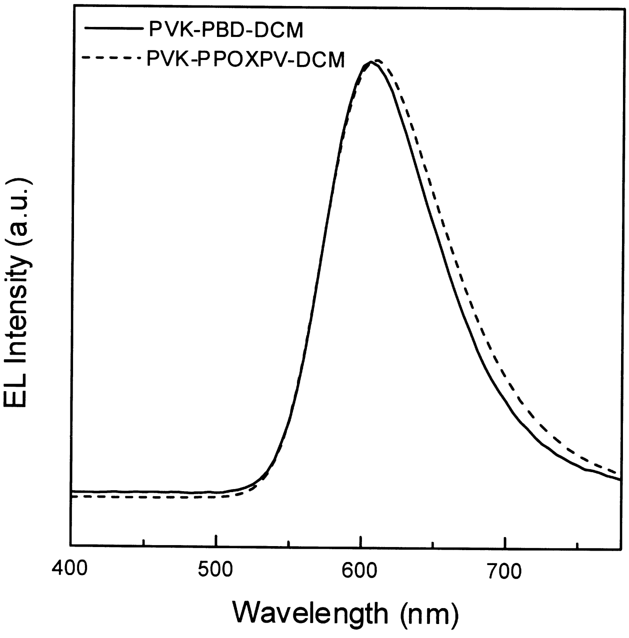


Fig. 7. Normalized EL spectra of blend polymers at 15.0 V.

that PPOXPV polymer can function as an electron transport material in the same manner as PBD, a low-molecular electron-transporting compound. Moreover, A PVK-PPOXPV-DCM system did not indicate a phase separation and recrystalization according to blend ratios compared to a PVK-PBD-DCM system. The optical and electrical properties of POOXPV and PMOXPV blending systems also showed the same results as those of PPOXPV. Quantum efficiency (%) [33] and turn-on voltages of the blend polymer devices are listed in Table 1 (We calculated EL quantum efficiencies at 60 cd/m^2). The devices showed almost the same quantum efficiencies.

Table 1
Comparison of quantum efficiency and turn-on voltage between Al/PVK-PBD-DCM/ITO and Al/PVK-synthesized polymer-DCM/ITO

Configuration of EL device (anode/EL polymer/cathode)	Quantum efficiency (%)	Maximum brightness (cd/m^2)	Turn-on voltage (V)
ITO/PVK-PBD-DCM/Al	0.1	250	*5.0*
ITO/PVK-POOXPV-DCM/Al	0.1	240	*2.5*
ITO/PVK-PMOXPV-DCM/Al	0.09	200	*6.5*
ITO/PVK-PPOXPV-DCM/Al	0.1	260	*2.0*

4. Conclusions

We synthesized *ortho*, *meta* and *para* linked polymers composed of an oxadiazole unit and phenylenevinylene moiety. The synthesized polymers were soluble in common organic solvents and showed good thermal stability. The POOXPV and PPOXPV polymers showed the maximum EL emission wavelengths at 500 and 510 nm, respectively, corresponding to greenish-blue light. Fabricated Al/P/ITO (P = POOXPV, PMOXPV, or PPOXPV) single layer devices had the turn on voltages at 5.5, 9.5, 6.0 V, respectively. Moreover, we found that synthesized polymers can serve as an excellent polymer electron transporting material from the results of blend device study with DCM.

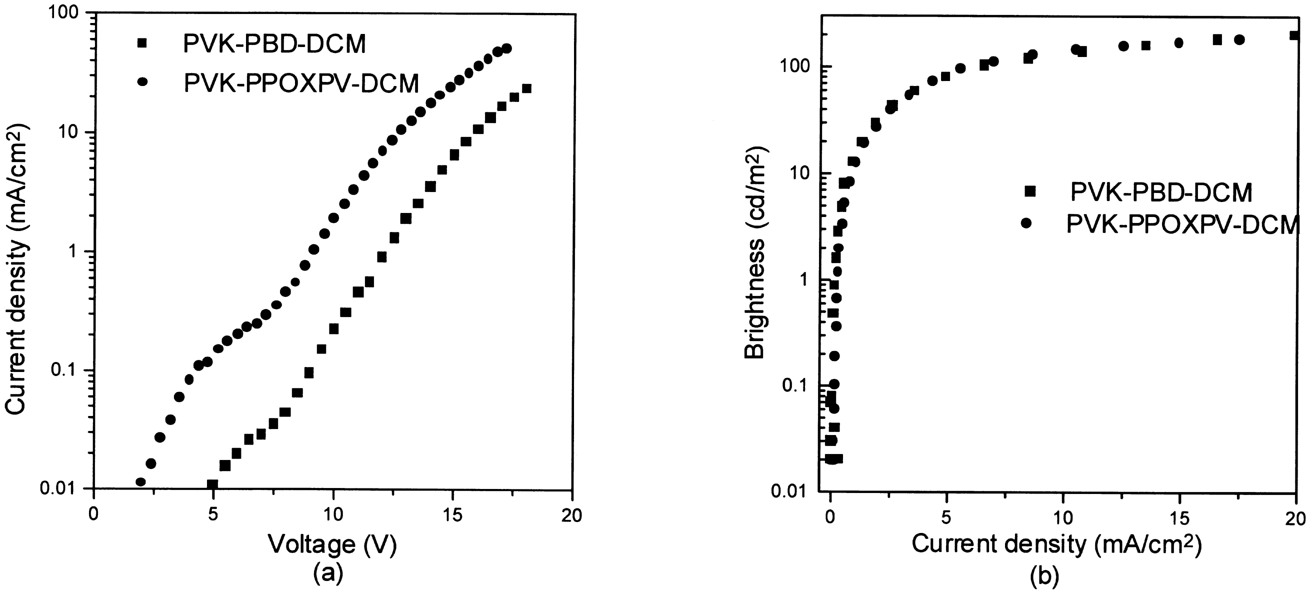


Fig. 8. EL characteristics of blend polymers with an ITO/polymers/Al structure. (a) Voltage vs. current density and (b) Current density vs. brightness.

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