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Blue Electroluminescent Polymers: Control of Conjugation Length by Kink Linkages and Substituents in the Poly(*p*-phenylenevinylene)-Related Copolymers

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ABSTRACT: Poly[*o*(*m*,*p*)-phenylenevinylene-*alt*-2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene], *o*(*m*,*p*)-PMEH-PPV, and poly[*o*(*m*,*p*)-phenylenevinylene-*alt*-2,5-bis(trimethylsilyl)-*p*-phenylenevinylene], *o*(*m*,*p*)-PBTMS-PPV, of varying effective conjugation lengths were synthesized by the well-known Wittig condensation polymerization between the appropriate diphosphonium salts and the dialdehyde monomers such as terephthaldicarboxaldehyde, isophthalaldehyde, and phthalicdicarboxaldehyde. The conjugation lengths of the polymers were controlled by substituents and kink (ortho and meta) linkages. The resulting polymers were highly soluble in common organic solvents. The synthesized polymers showed UV−visible absorbance and photoluminescence (PL) in the ranges of 330−430 nm and 440−550 nm, respectively. The maximum emission peak of *p*-PMEH-PPV was blueshifted about 30 nm compared to that of MEH-PPV, which is due to an unsubstituted phenylene unit. In addition, *o*-PMEH-PPV and *m*-PMEH-PPV showed PL emission maximum peaks at 500 and 490 nm, respectively, because ortho and meta linkage of the *o*(*m*)-PMEH-PPV reduced π-conjugation lengths. The trimethylsilyl substituent has no electron-donating effect; therefore, the PL maximum of *p*-PBTMS-PPV was far more blueshifted (to 485 nm). Consequently, maximum PL wavelengths for *o*-PBTMS-PPV and *m*-PBTMS-PPV appeared around 470 and 440 nm, respectively. A single-layer light-emitting diode device was fabricated which has a simple ITO (indium−tin oxide)/polymer/Al configuration. The threshold bias of trimethylsilyl-substituted *o*(*m*,*p*)-PBTMS-PPV was in the range of 8−9 V. As in the photoluminescence spectra, the dramatic change of emission color was also shown in electroluminescence spectra of *p*-PMEH-PPV, *p*-PBTMS-PPV, and *o*-PBTMS-PPV when the operating voltage was about 8−9 V.

Introduction

Light-emitting diodes (LEDs) using luminescent-conjugated polymers as the emissive medium are currently under active development for display applications.[1−6] Electroluminescent (EL) polymeric materials offer a number of advantages, such as low operating voltages, completely visible colors, fast response times, high-quality displays, and ease device processability with semiconductor technologies, compared with inorganic EL materials.

Since the first report of the polymer light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,[1] a number of different polymers have been synthesized, and extended efforts have been made to obtain high-performance devices from polymeric materials. Multicolor display applications require at least three basic colors: red, green, and blue. Blue EL, which is difficult to achieve with inorganic semiconductors, has been sought in conjugated polymers having a high HOMO−LUMO energy gap, such as partially eliminated poly(*p*-phenylenevinylene) (PPV), poly(*p*-phenylene) (PPP), poly(alkylfluorene), and copolymers containing confined conjugated segments such as CN-MBC (conjugated−nonconjugated multiblock copolymer) type polymers.[7−12] However, they showed rather poor processability and mechanical properties and had high operating voltages in light-emitting diode devices. The search for a stable, highly efficient, and bright blue light-emitting polymer continues.

In this paper, we report on the syntheses and light-emitting properties of kinked poly(*p*-phenylenevinylene)-related copolymers. We attempted to gain control of conjugation lengths[13] and blue light emission by incorporating the *p*-, *m*-,[14,15] and *o*-phenylene unit in the polymer main chain and substituting side groups with slight electron-donating effect into the conjugated main chain. We obtained blueshifted emission by introducing para linkage of unsubstituted phenylene units in the polymer main chain, thus shortening the effective conjugation length of the polymer. Further blueshifted emissions have been obtained by incorporating *m*- and *o*-phenylene units, which also improved the processability of polymers.[15] Ortho-linked polymers have the same electronic structures as the para-linked polymers, but the bent (kinked) structures of ortho-linked polymers disrupt the conjugation in polymers in the same manner as cis linkages in poly(*p*-phenylenevinylene) (PPV) do.[16] Consequently, using these substituents and kink (ortho and meta) linkages, we obtained from yellow to blue emission color from our synthesized copolymers in the photoluminescence (PL) and electroluminescence (EL) spectra. The synthesized polymers showed good film-forming properties; that is, they were easily processable into the thin-film devices. Moreover, kinked polymers showed relatively low operating voltages in the EL devices compared to those of the various

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blue light-emitting polymers mentioned above.[17−19]

Most of all, we think the synthesis of a blue EL polymer containing an ortho-linked phenylene unit is first reported in this paper.

Experimental Section

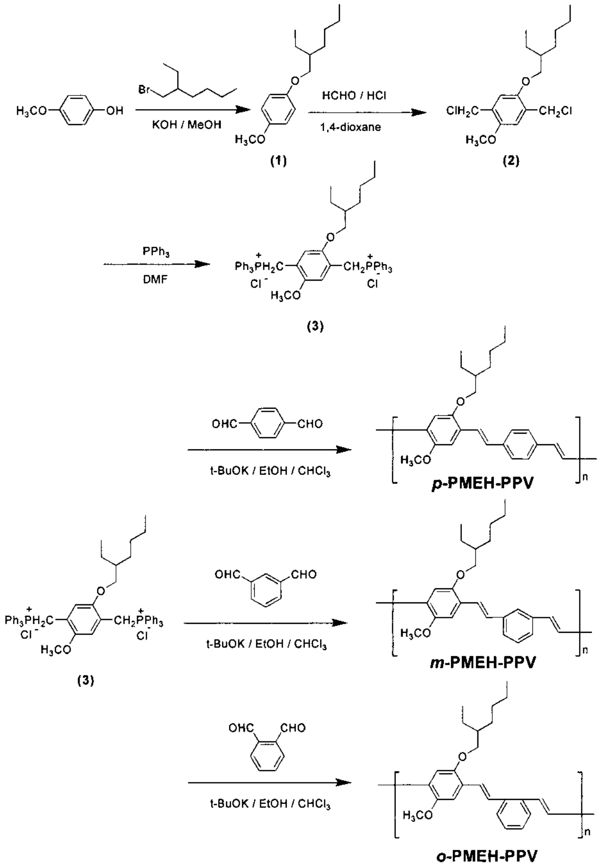
Materials. 2,5-Dibromo-*p*-xylene, trimethylsilyl chloride (TMS−Cl), *N*-bromosuccinimide (NBS), triphenylphosphine (PPh_3), 2-ethylhexylbromide, 4-methoxyphenol, potassium *t*-butoxide, terephthalicdicarboxaldehyde, isophthalaldehyde, and phthalicdicarboxaldehyde from Aldrich Chemical Co. were used without any further purification. Potassium carbonate, sodium hydroxide, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), 1,4-dioxane, 1,2-dichloroethane, acetic anhydride, benzene, hydrochloric acid, formaldehyde, ethanol, methanol, and chloroform from Junsei Chemical Co. were used without purification.

Instrumentation. Synthesized compounds were identified by ^1H NMR and ^{13}C NMR spectra that were collected on a Bruker AM 200 spectrometer. The UV−visible spectra of the *o*(*m*,*p*)-PMEH-PPV and *o*(*m*,*p*)-PBTMS-PPV were measured on a Shimadzu UV-3100S. The FT-IR spectra were measured by an EQUINOX 55 spectrometer. The thermogravimetric analyses (TGA) of polymers were performed under nitrogen atmosphere at a heating rate of 10 °C/min with Dupont 9900 analyzers. The photoluminescence spectra of the polymers were obtained by using Perkin-Elmer LS-50 luminescence spectrometer. The electroluminescence spectra were measured by using a dual-grating monochromator (Spex 270M) with a photomultiplier tube (Hamamatu R955) as a detector. The EL spectra were recorded at 2-nm resolution by a computer through the photon counter (SR400), averaging the signal from the PMT while applying direct current from the current−voltage source (Keithley 238). For the measurement of device properties, current−voltage ($I-V$) and light intensity−current ($L-I$) characteristics were measured by using a current−voltage source and an optical powermeter (Newport 835). The injected current was measured by the voltage supply while applying forward bias, and the emitted light was collected with a silicon photodetecter (Newport 818SL) placed in front of the device and recorded by a computer. At this time, the solid angle of light detection is very small; therefore, the great loss of the light detection is unavoidable. All of the measurements mentioned above were performed in air and at room temperature.

Syntheses of *o*(*m*,*p*)-PMEH-PPV. Monomer. *4-(2-Ethylhexyloxy)-1-methoxybenzene (**1**)* was synthesized by an adapted literature procedure.[19] **1** was prepared by reacting 20.0 g (1.6 mmol) of 4-methoxyphenol and 12.8 g (19 mmol) of potassium hydroxide in 150 mL of MeOH, and then 41 mL (21 mmol) of 2-ethylhexyl bromide was added to the solution and heated at 80 °C for 12 h. The resulting mixture was extracted with methylene chloride and 4-methoxyphenol was removed by column chromatography. Finally, the pure product was acquired by vacuum distillation. The product yield was 30.0 g (79%); ^1H NMR ($CDCl_3$, ppm) δ 6.8 (s, 4H), 3.8 (d, 2H), 3.7 (s, 3H), 1.6−1.2 (m, 9H), 0.9 (m, 6H). Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.22; H, 10.26. Found: C, 75.11; H, 10.23.

*1,4-Bis(chloromethyl)-5-(2-ethylhexyloxy)-2-methoxybenzene (**2**)* was synthesized by an adapted literature procedure.[19] **2** was prepared by reacting 30.0 g (130 mmol) of **1** with excess hydrochloric acid and formaldehyde in 1,4-dioxane. The reaction solution was heated at 90 °C for 72 h. The resulting mixture was extracted with ethyl acetate and water. The crude solid was dissolved in a small amount of hexane, and then, excess methanol was added. After filtration and vacuum-drying, a white solid was obtained. The product yield was 30.0 g (71%); mp 67−68 °C; ^1H NMR ($CDCl_3$, ppm) δ 6.8 (d, 2H), 4.5 (s, 4H), 3.8 (d, 2H), 3.7 (s, 3H), 1.6−1.3 (m, 9H), 0.9 (m, 6H). Anal. Calcd for $C_{17}H_{26}O_2Cl_2$: C, 61.26; H, 7.88. Found: C, 60.89; H, 7.57.

Scheme 1. Synthetic Scheme of Poly[*o*(*m*,*p*)-phenylenevinylene-*alt*-2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene], *o*(*m*,*p*)-PMEH-PPV



*1-(2-Ethylhexyloxy)-4-methoxy-2,5-xylenebis(triphenylphosphonium chloride) (**3**)* was synthesized by an adapted literature procedure.[19] A solution of 5 g (15 mmol) of 1,4-bis(chloromethyl)-5-(2-ethylhexyloxy)-2-methoxybenzene and 8.7 g (33 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 11.2 g (87%); mp 218−219 °C; ^1H NMR ($CDCl_3$, ppm) 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 for $C_{53}H_{56}O_2Cl_2P_2$: C, 74.19; H, 6.53. Found: C, 70.32; H, 6.45.

Dialdehyde Monomer. Terephthaldicarboxaldehyde (para), isophthalaldehyde (meta), and phthalicdicarboxaldehyde (ortho) of Aldrich Chemical Co. were used without any further purification.

Polymerization of *o*(*m*,*p*)-PMEH-PPV. A solution of 1 g (1.2 mmol) of 1-(2-ethylhexyloxy)-4-methoxy-2,5-xylenebis-(triphenylphosphonium chloride) and 0.16 g (1.2 mmol) of each dialdehyde monomer (terephthaldicarboxaldehyde for *p*-PMEH-PPV, isophthalaldehyde for *m*-PMEH-PPV, and phthalicdicarboxaldehyde for *o*-PMEH-PPV) in 10 mL of chloroform was prepared. To 10 mL of ethanol, 0.67 g (6 mmol) of potassium *t*-butoxide was dissolved completely, and this base solution was carefully dropped into the solution of monomers. After 1−2 days, the polymer product was precipitated from methanol. The crude polymers were filtered and then purified by using a Soxhlet extractor in methanol for 3 days. The polymer yields were 0.30 g (30.0%) for *p*-PMEH-PPV, 0.25 g (25.0%) for *m*-PMEH-PPV, and 0.28 g (28.0%) for *o*-PMEH-PPV, respectively. Synthetic routes and polymer structures are shown in Scheme 1.

Syntheses of *o*(*m*,*p*)-PBTMS-PPV. Monomer. *2,5-Bis-(trimethylsilyl)-p-xylene (**4**)* was synthesized by an adapted literature procedure.[20] To 20.0 g (75.8 mmol) of 2,5-dibromo-*p*-xylene diluted in anhydrous THF was added 5.5 g (227.4 mmol) of clean magnesium turnings after initiation by 5 mol

% of dibromoethane, and then, this solution was refluxed for 3 h under nitrogen atmosphere. When a white, soupy Grignard reagent was formed, 30 mL of chlorotrimethylsilane was slowly added to this solution, and the mixture was refluxed for 3 h. The reaction was quenched with dilute HCl solution. The THF layer was separated and washed with water several times, the solution was dried with magnesium sulfate, and then, THF was removed by evaporation. A white, solid product was obtained by column chromatography using hexane as an eluent. The product yield was 14.1 g (74%); mp 56−57 °C; ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 2H), 2.43 (s,6H), 0.33 (s,18H); ^{13}C NMR ($CDCl_3$) δ 139.50, 139.14, 135.67, 22.55, −0.16. Anal. Calcd for $C_{14}H_{26}Si_2$: C, 67.12; H, 10.46. Found: C, 66.88; H, 10.63.

*2,5-Bis(trimethylsilyl)-1,4-bis(bromomethyl)benzene (**5**)* was synthesized by an adapted literature procedure.[20] **5** was prepared by reacting 5.0 g (20.0 mmol) of **4** with 7.1 g (40.4 mmol) of *N*-bromosuccinimide (NBS) in 40 mL of carbon tetrachloride. A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 90 °C for 3 h under nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution. A yellow solution was obtained after filtration of succinimide. The solution was concentrated and poured into methanol. The white pure solid was obtained by recrystallizing the resulting precipitate from methanol. The product yield was 5.1 g (62%); mp 96−97 °C; ^{1}H NMR ($CDCl_3$) δ 7.53 (s, 2H), 4.61 (s, 4H), 0.40 (s, 18H); ^{13}C NMR ($CDCl_3$) δ 142.12, 140.89, 137.40, 34.08, 0.28. Anal. Calcd for $C_{14}H_{24}Si_2Br_2$: C, 41.18; H, 5.92. Found: C, 39.91; H, 5.73.

*2,5-Bis(trimethylsilyl)-1,4-xylenebis(triphenylphosphonium bromide) (**6**)* was synthesized by an adapted literature procedure.[20] 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 was obtained as a white powder. The product yield was 6.1 g (89%); mp 299−300 °C; ^{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 for $C_{50}H_{54}Si_2Br_2P_2$: C, 64.35; H, 5.79. Found: C, 63.02; H, 6.04.

Dialdehyde Monomer. Terephthaldicarboxaldehyde (para), isophthalaldehyde (meta), and phthalicdicarboxaldehyde (ortho) from Aldrich Chemical Co. were used without any further purification, as was *o*(*m*,*p*)-PMEH-PPV.

Polymerization of *o*(*m*,*p*)-PBTMS-PPV. A solution of 1 g (1.1 mmol) of 2,5-bis(trimethylsilyl)-1,4-xylenebis(triphenylphosphonium bromide) and 0.13 g (1.1 mmol) of each dialdehyde monomer (terephthaldicarboxaldehyde for *p*-PBTMS-PPV, isophthalaldehyde for *m*-PBTMS-PPV, and phthalicdicarboxaldehyde for *o*-PBTMS-PPV) in 10 mL of chloroform was prepared. Into 10 mL of ethanol, 0.56 g (5 mmol) of potassium *t*-butoxide was dissolved, and this base solution was carefully dropped into the solution of monomers. After 1−2 days, the polymer product was precipitated from methanol. The crude polymers were filtered and then purified by using a Soxhlet extractor in methanol for 3 days. The polymer yields were 0.31 g (30.0%) for *p*-PBTMS-PPV, 0.23 g (23.0%) for *m*-PBTMS-PPV and 0.27 g (27.0%) for *o*-PBTMS-PPV, respectively. Synthetic routes and polymer structures are shown in Scheme 2.

Results and Discussion

The synthesized polymers were end-capped by triphenylphosphoniummethylbenzene chloride for removing the aldehyde end group of the synthesized polymers, because the carbonyl group is thought to be a quenching site in the electroluminescence mechanism.[16] Figure 1 shows the ^{1}H NMR spectra of *p*-PMEH-PPV. Around 10 ppm, the peak due to the aldehydic proton of the end group of *p*-PMEH-PPV disappeared after the end-capping reaction. Other synthesized polymers were end-capped in the same manner as *p*-PMEH-PPV. All of the synthesized polymers were highly soluble in common organic solvents such as tetrahydrofuran, chloroform, methylene chloride, 1,2-dichloroethane, DMF, and so on. They could spin-cast onto various substrates to give highly transparent homogeneous thin films without heat treatment. The polymerization results of ortho-, meta-, and para-linked polymers are summarized in Table 1. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymers, determined by gel permeation chromatography using polystyrene standards, were in the range of 2700−3900 and 3700−6100 with a polydispersity index of 1.25−2.05, respectively.

Scheme 2. Synthetic Scheme of Poly[*o*(*m*,*p*)-phenylenevinylene-*alt*-2,5-bis-(trimethylsilyl)-*p*-phenylenevinylene], *o*(*m*,*p*)-PBTMS-PPV

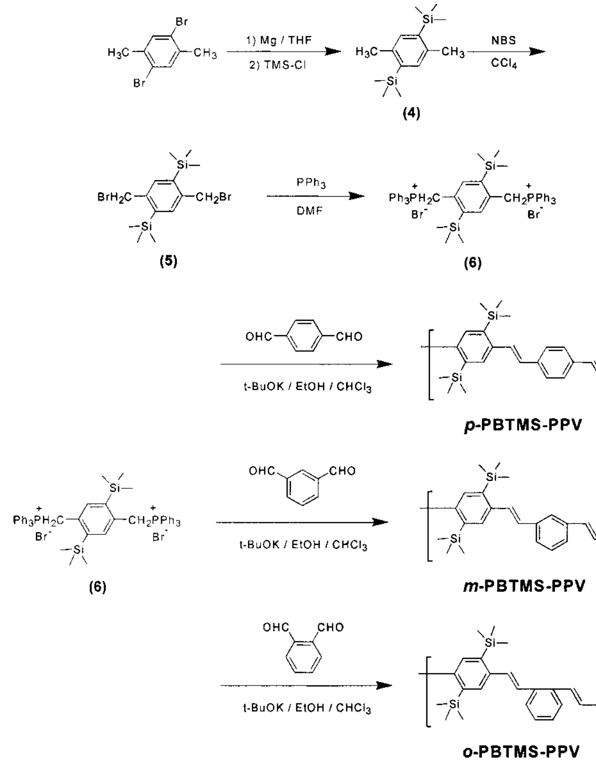


Figure 2 shows the typical FT-IR spectra of *p*-PBTMS-PPV. The comparison of the FT-IR spectrum of tereph-

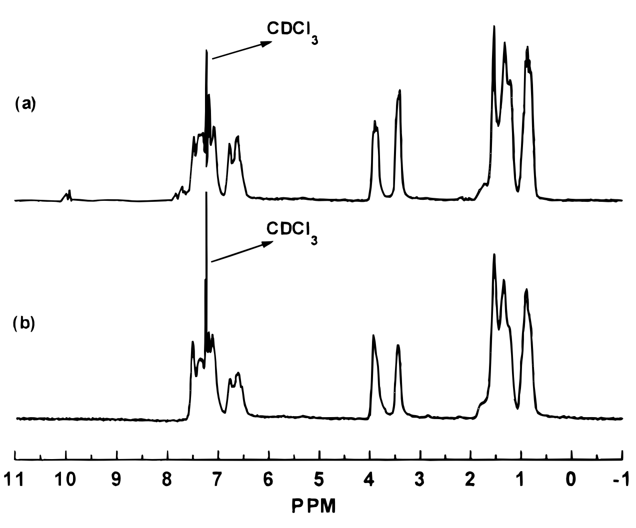


Figure 1. ^{1}H NMR spectra of the poly[*p*-phenylenevinylene-*alt*-2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene] (*p*-PMEH-PPV) in $CDCl_3$: (a) before and (b) after end-capping reaction.

Table 1. Polymerization Results of *o*(*m*,*p*)-PMEH-PPV and *o*(*m*,*p*)-PBTMS-PPV

polymers	yield (%)	M_n[a]	M_w[a]	PDI[a]
o-PMEH-PPV	28	2700	4100	1.52
m-PMEH-PPV	25	2700	3700	1.35
p-PMEH-PPV	30	3900	4900	1.25
o-PBTMS-PPV	30	2900	4100	1.44
m-PBTMS-PPV	23	2700	5400	1.98
p-PBTMS-PPV	27	3000	6100	2.05

[a] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

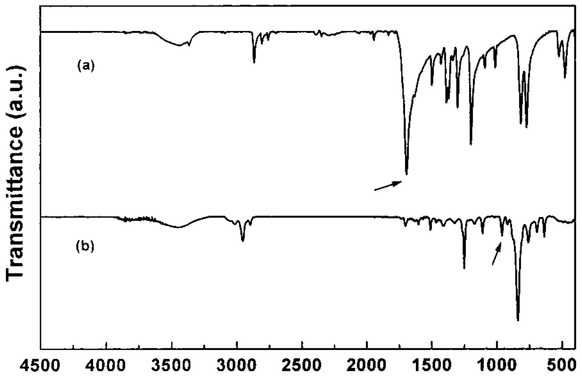


Figure 2. FT-IR spectra of (a) terephthaldicarboxaldehyde monomer and (b) *p*-PBTMS-PPV in KBr pellets.

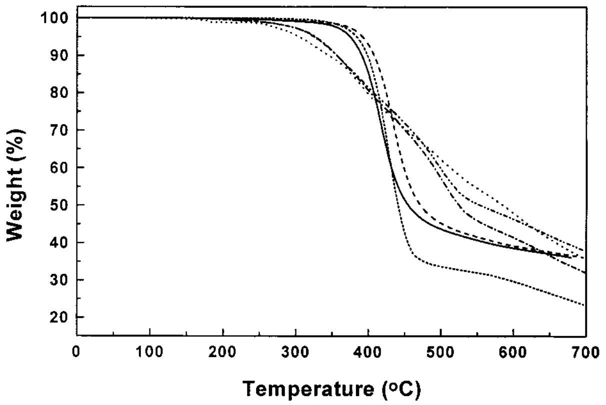


Figure 3. TGA thermograms of *o*-PMEH-PPV (—), *m*-PMEH-PPV (— —), *p*-PMEH-PPV(- - -), *o*-PBTMS-PPV (• — • — •), *m*-PBTMS-PPV (— • • —), and *p*-PBTMS-PPV (• • •).

thaldicarboxaldehyde monomer to that of the polymer showed a drastic decrease of the band at 1685 cm^{-1}, which is expected for the strong aldehyde carbonyl stretching band of the dialdehyde monomer. On the other hand, a weak and sharp absorption peak at 960 cm^{-1} corresponding to the out-of-plane bending mode of the *trans*-vinylene appeared.[19,21] This proves that the vinylene double bond formation and consequently the polymerization reaction have been successful. The thermal properties of the synthesized polymers were evaluated by means of TGA under nitrogen atmosphere. Figure 3 shows that all of the polymers exhibited good thermal stability up to 300 °C. PMEH-PPV polymers showed better thermal stability than that of the PBTMS-PPV series because of the high bond strengths of their side chains. The strength of the Si−C bond in PBTMS-PPV polymers is 451.5 kJ/mol which is lower than that of the C−O bond in PMEH-PPV polymers (1076.5 kJ/mol[22]). The lower decomposition temperatures of PBTMS-PPV polymers compared to those of PMEH-PPV polymers in the TGA thermograms (Figure 3) agree with the bond-strength data of the side chains of PMEH-PPV and PBTMS-PPV polymers.

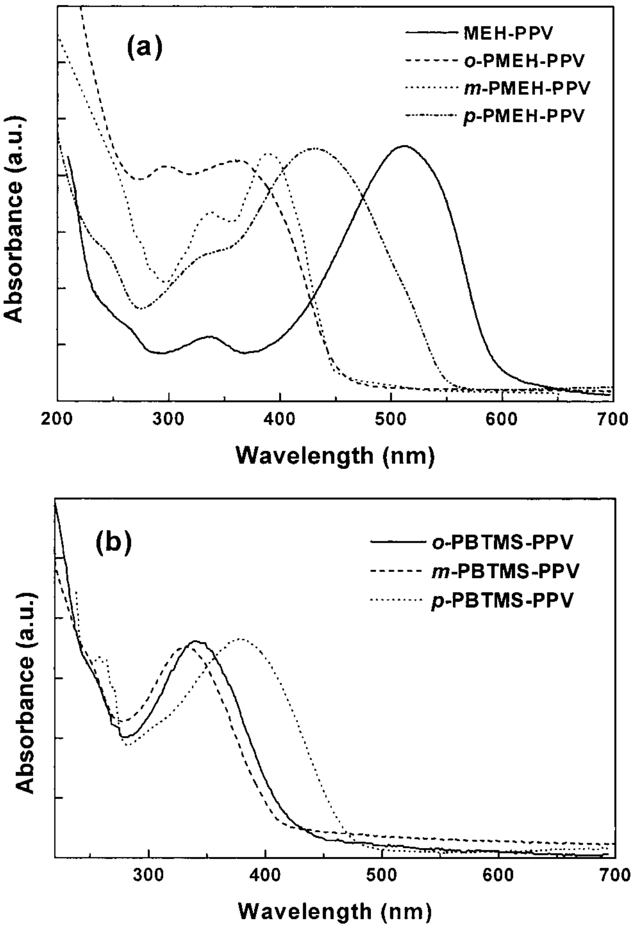


Figure 4. UV−visible spectra of (a) *o*-PMEH-PPV, *m*-PMEH-PPV, and *p*-PMEH-PPV and (b) *o*-PBTMS-PPV, *m*-PBTMS-PPV, and *p*-PBTMS-PPV thin films coated on a quartz plate.

Optical and Photoluminescence Properties. Figure 4a,b shows the UV absorption spectra of *o*(*m*,*p*)-PMEH-PPV and *o*(*m*,*p*)-PBTMS-PPV in a thin film onto a quartz plate. As shown in the absorption spectra, the well-known polymer MEH-PPV[23] showed the maximum absorption wavelength (λ_{max}) at 510 nm. But the synthesized *p*-PMEH-PPV showed a 430 nm absorption maximum due to the unsubstituted phenylene unit in the alternating copolymer system. For *o*-PMEH-PPV and *m*-PMEH-PPV, the maximum absorption wavelengths appeared at 360 and 390 nm, respectively. The absorption maximum bands of the *o*(*m*)-PMEH-PPV were more blueshifted compared to those of *p*-PMEH-PPV. This means that the π-electron delocalization of the polymer main chain was interrupted by ortho and meta linkage, yielding a reduction of the π-conjugation length.[24] Son et al.[16] reported that cis linkages in the PPV main chain interrupt the conjugation. Trans and cis linkages have almost the same electronic structures, but the cis linkage is bent (kinked) type structure. This deviation from the linearity of cis linkage can interrupt linear coplanarity for conjugation, which results in a diminished conjugation length compared to that of trans. In our system, we used meta and ortho linkages for reducing the conjugation. Meta system was reported elsewhere.[15,24] The *o*-phenylene system has a far more bent (kinked) structure than that of the para system. Consequently, the π-electron delocalization of the polymer main chain was interrupted by ortho linkage,

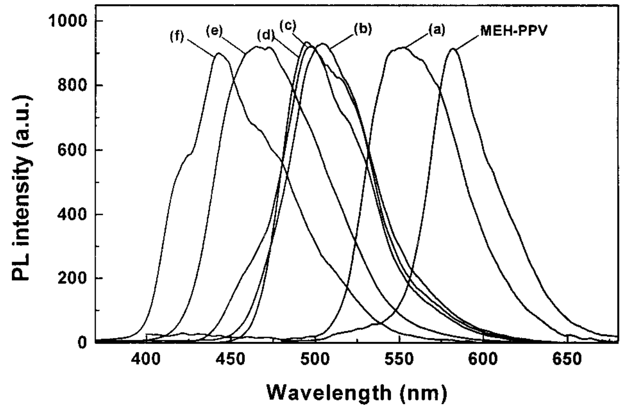


Figure 5. Photoluminescence spectra of (a) *p*-PMEH-PPV, (b) *o*-PMEH-PPV, (c) *m*-PMEH-PPV, (d) *p*-PBTMS-PPV, (e) *o*-PBTMS-PPV, and (f) *m*-PBTMS-PPV thin films coated on a quartz plate.

yielding a decrease of π-conjugation length. The trimethylsilyl-substituted alternating copolymers, *o*(*m*,*p*)-PBTMS-PPV, showed similar absorption profiles. Because the trimethylsilyl substituent has little electron-donating property[25] compared to that of the alkoxy substituents of *o*(*m*,*p*)-PMEH-PPV, the *p*-PBTMS-PPV polymer showed a maximum absorption at 380 nm, which is blue shifted about 50 nm compared to that of *p*-PMEH-PPV. The maximum absorption wavelengths of *o*-PBTMS-PPV and *m*-PBTMS-PPV are 340 and 330 nm, respectively. Like *o*(*m*)-PMEH-PPV, the maximum absorption wavelengths of *o*(*m*)-PBTMS-PPV were blueshifted for the same reason as that of *p*-PBTMS-PPV.

The photoluminescence spectra showed drastic changes of emission color because of substituents and kink (ortho and meta) effects (Figure 5). These PL spectra were recorded with an excitation wavelength corresponding to the absorption maximum wavelength of the polymer. The photoluminescence spectra of MEH-PPV showed that the emission maximum is 580 nm.[19] The emission of *p*-PMEH-PPV was blueshifted about 30 nm because of the unsubstituted phenyl unit in the alternating copolymer system. As a result of the larger decrease of the alkoxy (ether) substituent in *p*-PMEH-PPV than that of MEH-PPV, the electron density of the conjugated main chain in *p*-PMEH-PPV diminished. Consequently, *p*-PMEH-PPV, whose emission is blueshifted compared with that of MEH-PPV, has a larger band gap than does MEH-PPV. For the case of *o*-PMEH-PPV and *m*-PMEH-PPV, the emission peaks were more blueshifted compared to that of *p*-PMEH-PPV, showed at around 500 and 490 nm, respectively, due to the same reason as that of optical absorption spectra.

The PL spectra of *o*(*m*,*p*)-PBTMS-PPV polymer thin film coated on a quartz plate were also shown in Figure 5. The emission of the *p*-PBTMS-PPV was found at 485 nm. This result indicates that the trimethylsilyl substituent has a smaller electron-donating effect[25] than that of the alkoxy substituents. With an excitation wavelength of 340 nm, the PL spectra of *o*-PBTMS-PPV and *m*-PBTMS-PPV gave the peaks in the blue emissive region at 470 and 440 nm, respectively. The PL emission of conjugated polymers is evolved from the UV−visible absorption edge of conjugated polymers. For *m*-PBTMS-PPV and *o*-PBTMS-PPV, the UV−visible absorption λ_{max}, absorption edge, and PL emission maxima had the same trend, that is, *m*-PBTMS-PPV showed absorption and emission which were blueshifted compared to those of *o*-PBTMS-PPV. The UV−visible absorption spectra of *m*-PMEH-PPV and *o*-PMEH-PPV showed that the UV−visible absorption λ_{max} of *o*-PMEH-PPV is 30 nm lower than that of *m*-PMEH-PPV. However, *o*-PMEH-PPV a had slightly higher UV−visible absorption edge than did *m*-PMEH-PPV. The photoluminescence spectra of *o*-PMEH-PPV and *m*-PMEH-PPV showed the same results as the difference in the UV−visible absorption edge of *o*-PMEH-PPV and *m*-PMEH-PPV. The emission peak of *m*-PMEH-PPV is 10 nm lower than that of *o*-PMEH-PPV. Consequently, we found the meta linkage in PMEH-PPV and PBTMS-PPV polymers reduced conjugation slightly more than the ortho linkage in corresponding polymers by speculating the UV−visible absorption edge and PL emission maxima. Although the meta is less bent than the ortho linkage, these results come from the different electronic structure of a meta system[25] compared with those of ortho and para systems. The relative PL intensities of the PMEH-PPV and PBTMS-PPV series were measured, and the order of PL intensity has been observed to be para- < ortho- < meta-linked polymers. The enhanced PL efficiencies of *m*- and *o*-phenylene-containing polymers compared to those of para-linked polymers are due to the hindrance in the packing of the polymer chains. These results mean that ortho and meta linkage in the alternating copolymer system interrupt the conjugation and interfere with the packing of the polymer chains, which results in the formation of amorphous polymers for an increased luminescence.[16] Consequently, we synthesized blue light-emitting conjugated polymers by introducing the kink linkages and nonelectron-donating substituent without any conjugation blocking segment such as oxygen or alkyl spacers. All of the optical absorption and photoluminescence results of the synthesized alternating copolymers are summarized in Table 2.

Table 2. UV−visible and Photoluminescence Properties of *o*(*m*,*p*)-PMEH-PPV and *o*(*m*,*p*)-PBTMS-PPV

polymers	UV−vis λ_{max} (nm)[a]	PL λ_{max} (nm)[a]
o-PMEH-PPV	360	500
m-PMEH-PPV	390	490
p-PMEH-PPV	430	550
o-PBTMS-PPV	340	470
m-PBTMS-PPV	330	440
p-PBTMS-PPV	380	485

[a] The values listed were measured in the thin-film state on the quartz plate.

Electroluminescence Properties and Current−Voltage−Luminance (I−V−L) Characteristics. A single-layer light-emitting diode was fabricated by using ITO as the anode and Al as the cathode, respectively. The *o*(*m*,*p*)-PMEH-PPV and *o*(*m*,*p*)-PBTMS-PPV polymers described above were deposited onto indium−tin oxide-covered glass substrates by spin-casting the soluble polymers in cyclohexanone. The spin-casting technique yielded uniform films with thicknesses of about 50−60 nm. The Al electrode (cathode) was then evaporated onto this in vacuo with thickness of about 120 nm.

Figures 6 and 7 showed the current−voltage (*I*−*V*) and the luminance−voltage (*L*−*V*) characteristics of the single-layer light-emitting diode of ITO/*o*(*m*,*p*)-PBTMS-PPV/Al. The forward bias current was obtained when the ITO electrode was positively biased and the Al electrode was negatively biased. The current increased with increasing forward bias voltage, which indicated typical rectifying characteristics. The threshold voltages of PBTMS-PPV polymers were in the range 8−9 V,

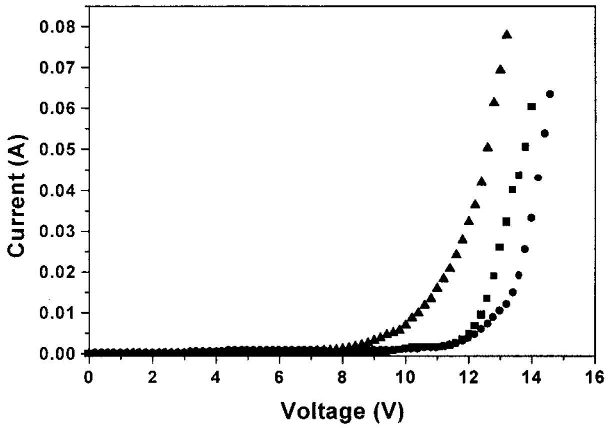


Figure 6. Current−voltage ($I-V$) characteristics of the single-layer light-emitting diode of ITO/*o*-PBTMS-PPV/Al (■), ITO/*m*-PBTMS-PPV/Al (●), and ITO/*p*-PBTMS-PPV/Al (▲).

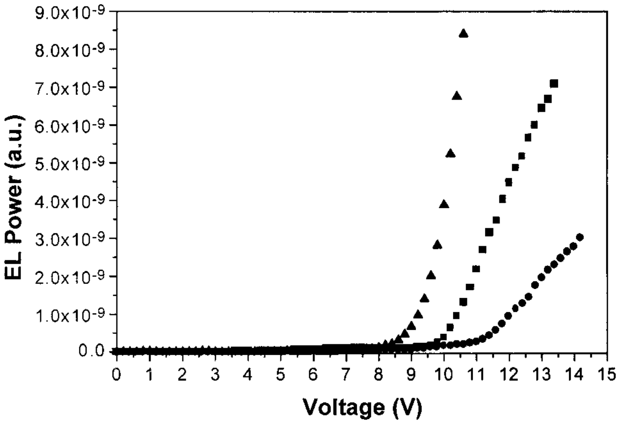


Figure 7. Luminance−voltage ($L-V$) characteristics of the single-layer light-emitting diode of ITO/*o*-PBTMS-PPV/Al (■), ITO/*m*-PBTMS-PPV/Al (●), and ITO/*p*-PBTMS-PPV/Al (▲).

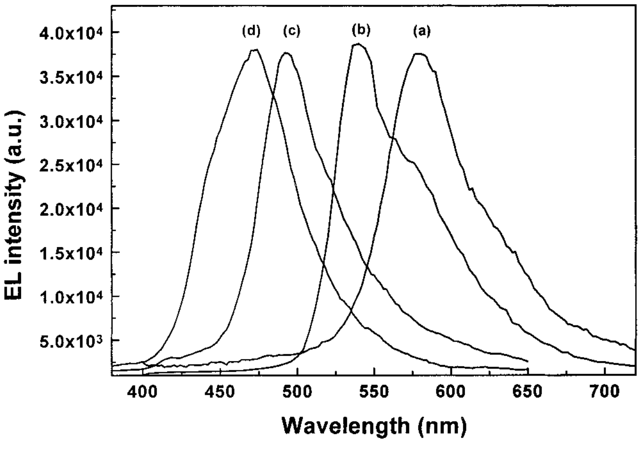


Figure 8. Electroluminescence (EL) spectra of the single-layer light-emitting diodes of (a) MEH-PPV, (b) *p*-PMEH-PPV, (c) *p*-PBTMS-PPV, and (d) *o*-PBTMS-PPV, which have ITO/polymer/Al configuration.

which was very low compared with that of other PPV-based blue light-emitting block copolymers. *p*-PBTMS-PPV exhibited the highest EL power at lower operating voltages because of the effective π-conjugation due to the para-linked linear main chain (Figure 7).

The electroluminescence spectra of MEH-PPV, *p*-PMEH-PPV, *p*-PBTMS-PPV, and *o*-PBTMS-PPV polymer films are shown in Figure 8. The *p*-PMEH-PPV polymer film showed maximum EL emission at 540 nm, which was similar to that of the PL spectrum of *p*-PMEH-PPV, corresponding to the greenish-yellow region. The electroluminescence spectra of *o*-PBTMS-PPV and *p*-PBTMS-PPV exhibited similar EL emissive bands at 470 and 490 nm, respectively. This result showed a pure blue emission in the case of *o*-PBTMS-PPV due to the reduced π-conjugation length by the nonlinear ortho linkage and trimethylsilyl substituent, even though it is very difficult to get a pure blue emission from the fully conjugated PPV derivatives.

Conclusions

We synthesized ortho-, meta-, and para-linked phenylene units contained PPV derivatives, *o*(*m*,*p*)-PMEH-PPV and *o*(*m*,*p*)-PBTMS-PPV, through the well-known Wittig condensation polymerization. The π-conjugation lengths of synthesized polymers were regulated by kink (ortho and meta) linkages and substituents effects. The synthesized polymers were completely soluble in common organic solvents. They could spin-cast onto various substrates to give highly transparent homogeneous thin film without heat treatment. In the UV−visible and photoluminescence spectra, the maximum absorption and PL emission spectra were dramatically blueshifted because of the ortho and meta linkages or the trimethylsilyl substituent. Consequently, *o*-PBTMS-PPV and *m*-PBTMS-PPV showed blue emission at 470 and 440 nm, respectively, without any nonconjugated segments. Single-layer light-emitting diodes of ITO/*p*-PMEH-PPV or *o*(*m*,*p*)-PBTMS-PPV/Al were fabricated. The electroluminescence spectra of *o*-PBTMS-PPV and *p*-PBTMS-PPV gave the highest peaks in the EL emissive band at 470 and 490 nm, respectively, which were pure blue and greenish blue, when an operating voltage of 8−9 V was applied.

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