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Synthesis and characterization of poly(terphenylenevinylene) derivatives containing alkoxy substituents and (or) phenyl pendant group

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Abstract

The blue electroluminescent polymers, poly(terphenylenevinylene) derivatives that have advantages of PPP and PPV, were prepared by Suzuki coupling reaction. The structure and properties of the polymers were analyzed by various spectroscopic methods. Poly(MHTPPV) and poly(TPPV) with phenyl pendant group in a vinyl bridge showed blue shifted absorption spectra, large band gap and enhanced thermal stability as compared with that of poly(MHTPV). The PL spectra of the films of the polymers showed maximum peaks at 450–460 nm, which are pure blue emissions. The blue electroluminescence ($\lambda_{max} = 450-460$ nm) was obtained with the turn on voltage of 8–10 V, when the simple light-emitting diodes of ITO/polymer/Al were fabricated. The excimer emission due to interchain interaction was reduced by the introduction of substituents into the vinyl bridge and (or) the main chain.

Keywords: Light emitting diode; Electroluminescence; Poly(terphenylenevinylene)

1. Introduction

Polymeric light emitting diodes have attracted tremendous attention in the past decade owing to their potential advantages such as outstanding mechanical and optical properties, low-cost manufacturing, and amenability to large area displays. Following the discovery of electroluminescence (EL) in poly(*p*-phenylenevinylene) (PPV) [1], various EL conjugated polymers have been synthesized and studied in detail [2–10]. The EL from these polymers can sweep the full range of the visible spectrum.

Amongst the variety of EL conjugated polymers, blue light emission is deemed desirable since it is generally more difficult to fabricate such LEDs from inorganic semiconductors. Furthermore, full color exhibition and white light devices need blue light. For blue emission, conjugated polymers need to have a large bandgap and defined optical properties. Earlier studies on blue LEDs were done mainly on polyalkylfluorene (PDAF) [10] and poly(*p*-phenylene)s (PPPs) [2]. Poly(*p*-phenylene) and its derivatives have good thermal and oxidative stability, however, exhibits low solubility and a high turn-on voltage. Low work function metals are required for efficient carrier injection into PPP derivatives. Furthermore, PPP and its derivatives are intrinsically violet blue emitters and present some difficulties in color tunability. Although PDAFs have been used to make efficient blue light emitting devices, they tend to form yellow- or green-emitting aggregates or excimers on heating during the device formation or operation. Thus, improvements in processability, mechanical properties and stability are desirable. Recently, research into new blue EL materials achieved by controlling the effective conjugation has been reported. For example, blue EL polymers have been synthesized through approaches such as capping a polymer backbone with non-conjugated units, separating the emitting units with non-conjugated spacers as in conjugated-nonconjugated block copolymers [11–15], inserting meta linkages in the main chain [16], or imposing steric distortions in the main chain [17–18]. Although there has been rapid progress, the fabrication of bright, efficient, electroluminescent, blue-emission devices still remains a big challenge [19].

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Recently, we reported the synthesis and properties of poly(biphenylenevinylene) (PBPV) derivatives with a controlled conjugation length of biphenylene vinylene unit, which is composed of alternating PPP and PPV units [20–21]. On the relating to the research, we reported the poly(terphenylenevinylene) (PTPV) derivatives as novel family of blue electroluminescent material [22–23].

In this article, we describe the synthesis and characterization of new blue-light-emitting, poly(terphenylenevinylene) derivatives, which are expected pure blue emission resulted from terphenylenevinylene backbone. And, on the basis of poly(terphenylenevinylene), our research also involved the effects of introduced substituents into the vinyl bridge and (or) main chain. Introducing substituents group to a vinyl bridge and (or) main chain, may expect to lead to enhanced solubility, oxidative and thermal stability, and reduced the formation of excimers owing to interchain interactions.

2. Experimental section

2.1. Materials

Tetrahydrofuran (THF) and diethylether were distilled from sodium benzophenone ketyl. Toluene was purified by distillation from CaH_2 and used immediately. Triphenylphosphine was purchased from Aldrich, recrystallized from degassed ethanol, and sublimed under vacuum prior to use. 1,4-Dibromobenzene, 4-bromobenzophenone, 4-bromobenzaldehyde, 4-bromobenzylbromide, trimethylborate, *n*-BuLi (2.5 M in heptane), 2-ethylhexylbromide, 4-methoxyphenol, and tetrakis(triphenylphosphine) palladium(0) were purchased from Aldrich. Other chemicals were used without further purification.

2.2. Preparation of 1-methoxy-[4-(2′-ethylhexyl)oxy]benzene

One-neck flask equipped with a nitrogen inlet, Dean-stark trap and reflux condenser was charged with 4-methoxyphenol (22.4 g, 0.19 mol), potassium hydroxide (10.6 g, 0.19 mol) and benzene (200 ml). The reaction mixture was refluxed at 80 °C and was removed water for 24 h. Then, the mixture was cooled to room temperature and benzene solvent was evaporated. 2-Ethylhexylbromide (36.7 g, 0.19 mol), copper (0.3 g, 4.72 mmol) and NMP 100 ml were charged in the reaction mixtures. After the reaction mixture was refluxed at 160 °C for 48 h, the mixture was cooled to room temperature. The organic layer was extracted, washed with water, dried over $MgSO_4$ and filtered. The solution was evaporated and distilled under reduced pressure. (Yield = 95%, b.p. = 108 °C/1 mmHg). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ (ppm): aromatic (C–H), 6.9 (4H, s), $-OCH_2-$ and $-OCH_3$ 3.8 (5H, m), aliphatic (C–H) 1.8–0.9 (15H, m). FT-IR (NaCl, cm^{-1}): 3047 (aromatic C–H), 2846 (aliphatic CH_2), 1200 (C–O–C).

2.3. Preparation of 2,5-dibromo-1-methoxy-[4-(2′-ethylhexyl)oxy]benzene

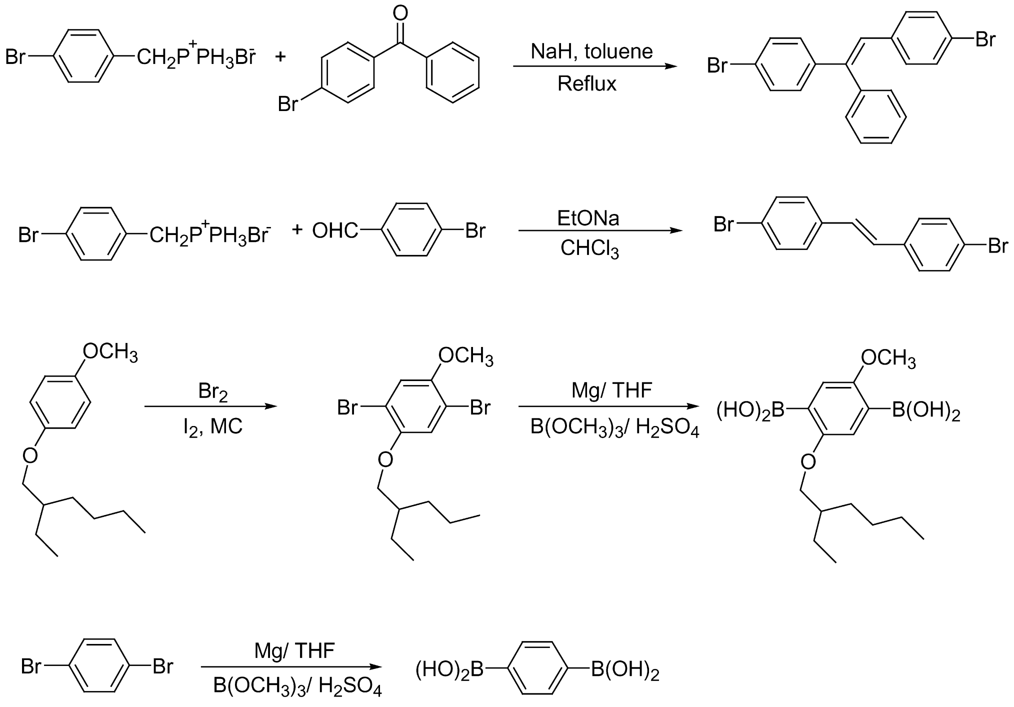
Bromine (64.9 g, 0.406 mol) was added dropwise over 30 min, to a stirred and ice-cooled solution of the 1-methoxy-[4-(2′-ethylhexyl)oxy]benzene (40.0 g, 0.169 mol) and iodine (0.3 g, 1.8 mmol) under rigorous exclusion of light at room temperature during 8 h. Twenty percent aqueous KOH solution (200 ml) was added and the mixture was stirred until the color disappeared. After the reaction mixture was extracted with dichloromethane, organic layer was washed with water, dried over $MgSO_4$ and filtered. The solution was evaporated and the crude product was distillated under reduced pressure. (Yield = 85%, b.p. = 134 °C/1 mmHg). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ (ppm): aromatic (C–H), δ 7.1 (2H, s), $-OCH_2-$ and $-OCH_3$ 3.8 (5H, m), aliphatic (C–H) 1.8–0.9 (15H, m). FT-IR (NaCl, cm^{-1}): 3047 (aromatic C–H), 2846 (aliphatic CH_2), 1200 (C–O–C), 1065 (aromatic C–Br).

2.4. Preparation of 1-methoxy-[4-(2′-ethylhexyl)oxy]benzene diboronic acid

2,5-Dibromo-1-methoxy-[4-(2′-ethylhexyl)oxy]benzene (40.0 g, 0.10 mol) was added drop-wise to magnesium powders (7.4 g, 0.30 mol) in boiling THF (250 ml). After the reaction mixture was refluxed for 2 h, the reaction mixture was cooled to − 70 °C using liquid nitrogen. Then, the undiluted trimethylborate (42.0 g, 0.40 mol) was added and stirred for 12 h at room temperature. After 2 M H_2SO_4 aqueous solution was added, the organic layer was extracted with ether, washed with water, dried over $MgSO_4$ and filtered. The solvent was evaporated and crude product was recrystallized in hexane to give product of white crystal. (Yield = 20%). ^{1}H-NMR ($CDCl_3$, 500 MHz) δ (ppm): aromatic (C–H), 7.1(2H, s), $-OCH_2-$ and $-OCH_3$ 3.8 (5H, m), aliphatic (C–H) 1.8–0.9 (15H, m). FT-IR (KBr, cm^{-1}): 3500–3150(O–H), 2846 (aliphatic CH_2), 1200 (C–O–C).

2.5. Synthesis of 4,4′-dibromostilbene

(2-Bromobenzyl)triphenylphosphonium bromide 20 g (39 mmol) and sodium hydride 2.5 g (102.9 mmol) dissolved in toluene (150 ml) under nitrogen. The solution was stirred for 3 h and then cooled to − 10 °C. 4-Bromobenzaldehyde 7.22 g (39 mmol) was added in the solution and refluxed for 24 h at 110 °C. After the reaction mixture was cooled to room temperature, the organic layer was extracted by methylene chloride. The product was obtained by chromatography with eluent of hexane. (Yield = 70%) ^{1}H-NMR (500 MHz, $CDCl_3$) (ppm): aromatic(C–H), δ 7.6 (4H, d), 7.5 (4H, d), 6.9 (2H, s), FT-IR (KBr) (cm^{-1}):3020 (aromatic and vinyl C–H), 1065 (aromatic C–Br).



Scheme 1. Synthetic routes of monomers.

2.6. Synthesis of poly(MHTPV)

The polymer was obtained from 0.578 g (1.786 mmol) of 1-methoxy(4-2′-ethylhexyl)oxy benzene diboronic acid and 0.6 g (1.786 mmol) of 4′,4″-dibromostillbene through typical Suzuki coupling reaction. The detailed procedures are described elsewhere [22]. (Yield = 60%) ^{1}H-NMR (500 MHz, $CDCl_3$) (ppm): aromatic (C–H), δ 7.6 −7.0 (11H, m), 6.9 (1H, s), 3.8 (5H, m), 1.6 (3H, m), 1.4–1.3 (6H, m), 0.8 (6H, m), FT-IR (KBr) (cm^{-1}): 3050, 3000 (aromatic and vinylic C–H), 2900 (aliphatic C–H), 1600 (C=C stretching) 1230 (C–O stretching), 960 (=C–H out of plane). Anal. Calcd for $C_{29}H_{32}O_2$: C, 84.46; H, 7.77; O, 7.77. Found: C, 84.34; H, 7.65; O, 8.01.

2.7. Synthesis of poly(TPPV)

The polymerization performed with benzene diboronic acid and [1,2-(4′,4″-dibromophenyl)-1-phenyl ethylene]. (Yield = 60%) ^{1}H-NMR (500 MHz, $CDCl_3$) (ppm): aromatic (C–H), δ 7.8 −7.0 (17H, m), 6.9 (1H, s) FT-IR (KBr) (cm^{-1}): 3000 (aromatic and vinylic C–H), 1600(C=C stretching), 960 (=C–H out of plane). Anal. Calcd for $C_{26}H_{18}$: C, 94.55; H, 5.45. Found: C, 94.42; H, 5.36.

2.8. Synthesis of poly(MHTPPV)

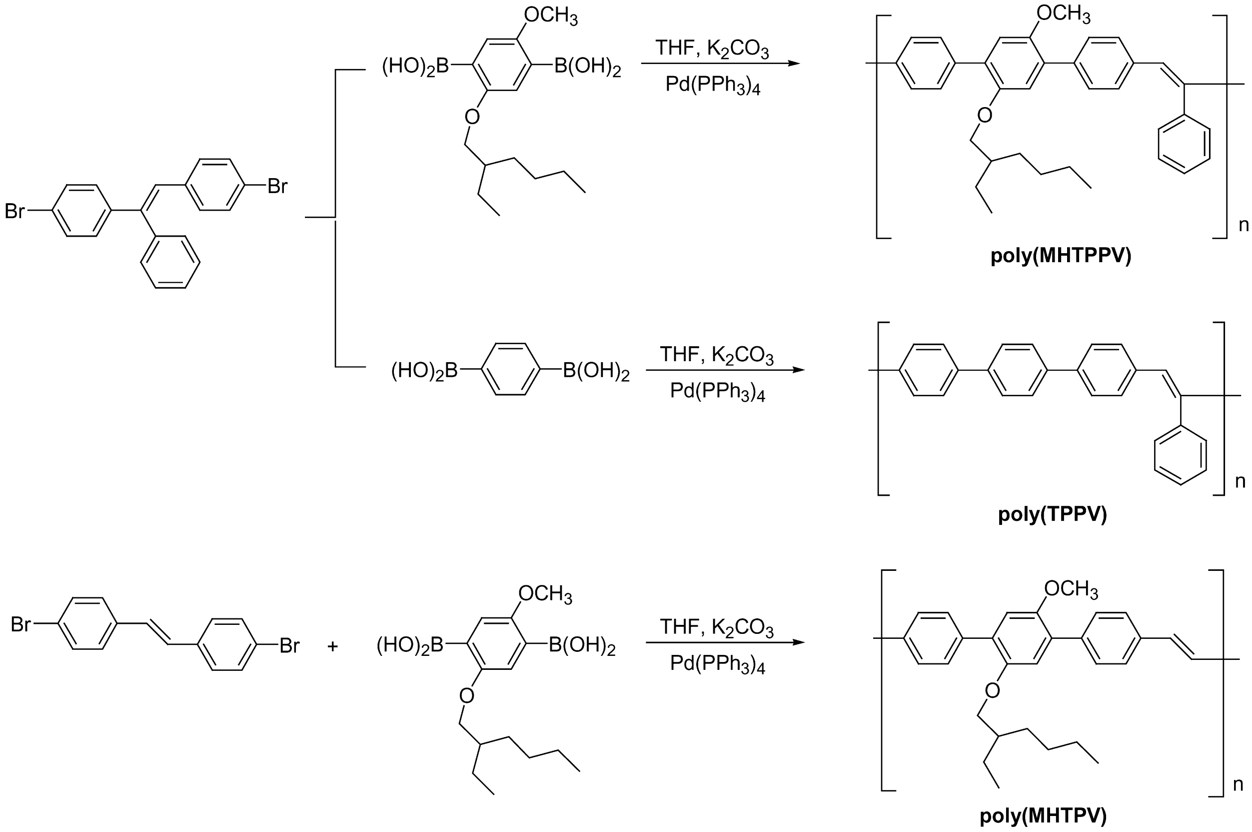
The polymerization was performed with 1-methoxy[4-2′-ethylhexyl]oxy] benzene diboronic acid and [1,2-(4′,4″-dibromophenyl)-1-pheny ethylene]. Yield = 60%. ^{1}H-NMR ($CDCl_3$): aromatic (C–H), δ 7.6 − 7.0 (15H, m), 6.8 (1H, s), 3.8 (5H, m), 1.7 (3H, m), 1.4–1.3 (6H, m), 0.9 (6H, m) FT-IR (KBr) (cm^{-1}): 3000 (aromatic and vinylic C–H), 2900 (aliphatic C–H), 1600 (C=C stretching), 1230 (C–O stretching), 960 (=C–H out of plane). Anal. Calcd for $C_{35}H_{34}O_2$: C, 86.42; H, 7.00; O, 6.58. Found: C, 86.31; H, 6.87; O, 6.82.

2.9. Measurements

A Genesis II FT-IR spectrometer was used to record IR spectra. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with the use of DRX 300 and 500 MHz NMR Bruker spectrometers, and chemical shifts are reported in ppm units with tetramethylsilane as internal standard. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA instrument 2050 thermogravimetric analyzer. The sample was heated using a 10 °C/min heating rate from 50 to 800 °C. Differential scanning calorimeter (DSC) was conducted under nitrogen on a TA instrument 2100 DSC. The sample was heated with 10 °C/min from 30 to 400 °C. UV–vis absorption spectra and photoluminescence (PL) spectra were measured by Perkin Elmer LAMBDA-900 UV/VIS/NIR spectrophotometer and LS-50B luminescence spectrophotometer, respectively. The device fabrication and instruments were performed as reported previously [22].

3. Results and discussions

The synthesis of the monomer and polymers are outlined in Scheme 1. The monomers were prepared by a Grignard



Scheme 2. Syntheses of poly(MHTPV), poly(TPPV), and poly(MHTPPV) [22,23].

reaction and Wittig reaction of (4-bromobenzyl)triphenylphosponium bromide with 4-bromobenzophenone and 4-bromobenzaldehyde, respectively. The polymerization was carried out using a typical Suzuki coupling reaction with good yield. After the polymerization, the end-capped reaction of the bromine end group and boronic acid end group, which both hamper the thermal stability and efficiency of PL, were accomplished by phenyl boronic acid and bromobenzene, respectively. The polymer structures shown were consistent with the elemental analyses and the spectroscopic data from ^{1}H-NMR and FT-IR (Scheme 2). Fig. 1 showed ^{1}H-NMR and IR spectra of poly(MHTPPV). In the ^{1}H-NMR spectrum, the vinylic proton peaks appeared at around 6.5–7.0 ppm with aromatic proton peaks. In the IR spectrum, a sharp absorption peak at 960 cm^{-1}, which corresponds to the out of plane bending mode of the trans-vinylene groups appeared, instead of disappearing of O–H stretching of boronic acid and aromatic C–Br stretching at 3500 and 1065 cm^{-1}, respectively. The obtained polymers were readily soluble in common organic solvents such as chloroform, dichloromethane, toluene and THF even though the polymers have a rigid terphenylenevinylene backbone. It may be resulted from introducing of the substituents into the vinyl bond and (or) main chain. The number and weight average molecular weights (M_n and M_w) and polydispersity index of polymers are listed in Table 1. The M_ns are 7300–8300, which are sufficiently high to be considered as a EL material.

Thermal characterizations of the polymers were accomplished by DSC and TGA. The DSC thermograms obtained from the second heating of the polymers (Fig. 2). The poly(MHTPV), poly(MHTPPV) and poly(TPPV) show a narrow endotherm at 135, 140 and 146 °C, respectively and no additional melting transition. The glass transition increased in the following order; poly(MHTPV) containing methoxy and ethylhexyloxy substituents at the main chain < poly(MHTPPV) containing methoxy and ethylhexyloxy substituents at the main chain and phenyl substituent at the vinyl bond < poly(TPPV) containing phenyl substituent at the vinyl bond. These observations indicated that phenyl substituent at the vinyl bridge has the effect of restricted chain rotations more than methoxy and ethylhexyloxy substituents at the phenyl ring. The TGA thermograms in a

Table 1
The number and weight average molecular weights (M_n and M_w), polydispersity index (PDI)

Polymer	(M_n)	(M_w)	PI
Poly(MHTPV)	7800	14,000	1.8
Poly(TPPV)	8300	13,500	1.6
Poly(MHTPPV)	7300	15,300	2.1

Molecular weight was determined by GPC in THF based on polystyrene standards.

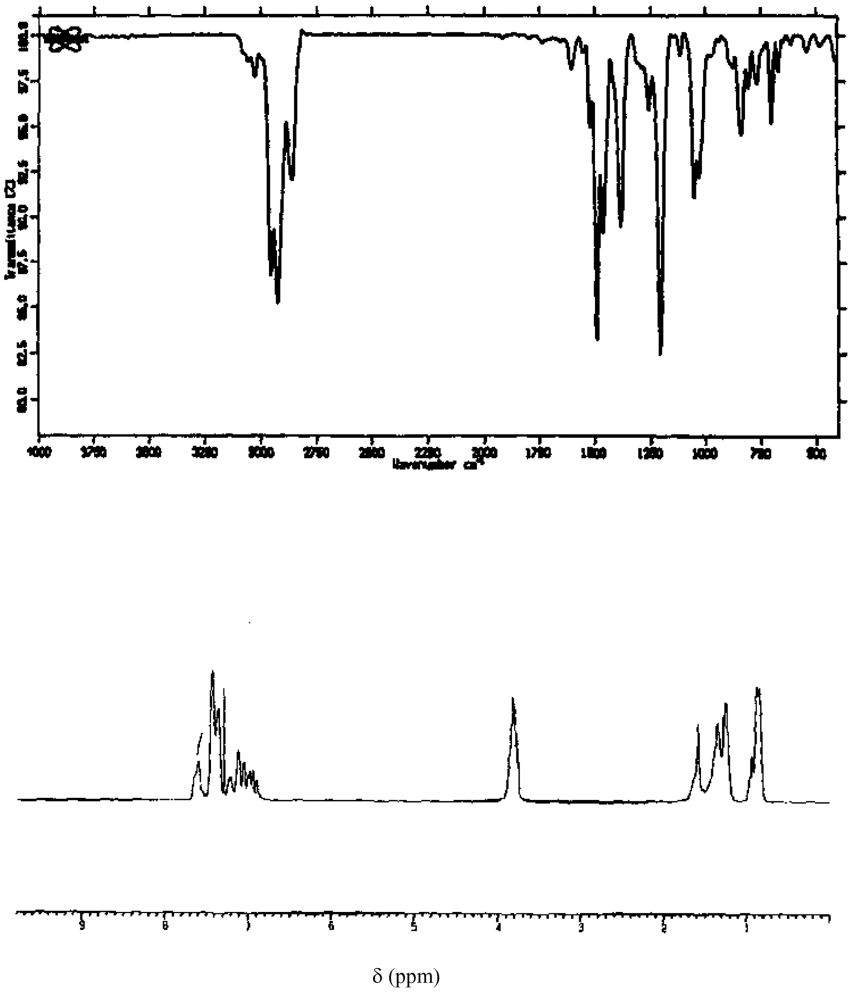


Fig. 1. IR and ^{1}H-NMR spectra of poly(MHTPPV).

nitrogen atmosphere showed that poly(TPPV) has good thermal stability and no weight loss up to 420 °C (Fig. 3). The weight loss of poly(TPPV) is 5% on heating to 430 °C. Poly(MHTPV) and poly(MHTPPV) have similar thermal stability and show no weight loss up to 350 °C. The weight loss of poly(MHTPV) and poly(MHTPPV) are 5% on heating 410 and 420 °C, respectively. The results can be explained by the aliphatic substituents at the main chain that deteriorates thermal stability.

Fig. 4 shows the optical absorption and PL spectra of a dilute solution of the polymers in chloroform. The maximum absorption of polymers showed 350–375 nm. The maximum absorption peaks of the polymer are 70–90 nm blue shifted as compared with that of PPV [24], 10–20 nm blue shifted as compared with that of PBPV [20–21] and 10–20 nm red shifted as compared with that of PPP [25]. These shifts may originate from the terphenylene vinylene units composed of PPP and PPV units. The maximum absorption peaks of polymers are increased as following order: poly(TPPV) < poly(MHTPPV) < poly(MHTPV). The result can be explained that the phenyl substituent at vinyl bridge inhibit the main chain coplanarity and lead to blue-shifting of maximum absorption peak, however, the methoxy and ethylhexyloxy substituents at main chain are electron donating groups and lead to red-shifting of the maximum absorption peak. The band-gap energy of the new polymers estimated from extrapolation of the low energy absorption spectra was about 2.85, 2.96, and 2.99 eV for poly(MHTPV), poly(MHTPPV) and poly(TPPV), respectively.

The polymer emitted strong blue fluorescence under

Table 2
Electrochemical properties of poly(terphenylenevinylene) derivatives

Polymer	$E_{\text{onset}}^{\text{ox}}$ (V)[a]	$E_{\text{onset}}^{\text{red}}$ (V)[a]	HOMO[b] (eV)	LUMO[c] (eV)	E_g^{el} (eV)[d]	E_g^{opt} (eV)[e]
Poly(MHTPV)	0.89	− 1.95	5.69	2.85	2.84	2.85
Poly(TPPV)	1.03	− 1.95	5.83	2.85	2.98	2.99
Poly(MHTPPV)	0.93	− 2.03	5.73	2.77	2.96	2.96

[a] Potential values are vs Fc/Fc$^+$.
[b] Determined from the onset oxidation potential.
[c] Determined from the onset reduction potential.
[d] Electrochemical band gap estimated using $E_g^{\text{el}} = E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$.
[e] Optical band gap, calculated from the absorption edge of the UV–vis spectrum.

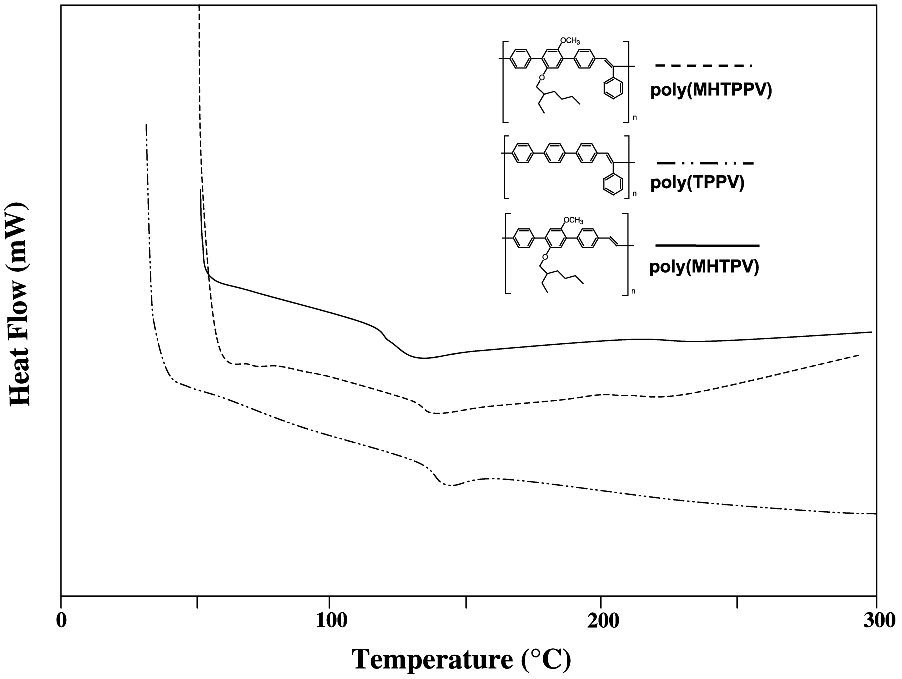


Fig. 2. DSC thermograms for poly(terphenylenevinylene) derivatives with a heating rate of 10 °C/min^{-1} in nitrogen.

ultraviolet irradiation in a chloroform solution and in the film. The PL spectra were recorded with an excitation wavelength corresponding to the absorption maximum wavelength of the polymers.

The electrochemical behaviors of the obtained polymers were investigated by cyclic voltammetry and the data are tabulated in Table 2. Upon the cathodic sweep, the poly(MHTPV), poly(MHTPPV) and poly(TPPV) exhibited with a formal reduction potential ($E^{o\prime}$) at -1.95, -2.03 and -1.95 vs Fc/Fc + (FOC) couple, respectively. Based on the onset potentials for the oxidation and reduction, the HOMO and LUMO energy levels of the new polymers were estimated regarding the energy level of FOC reference (4.8 eV below the vacuum level) [26]. The energy band gap

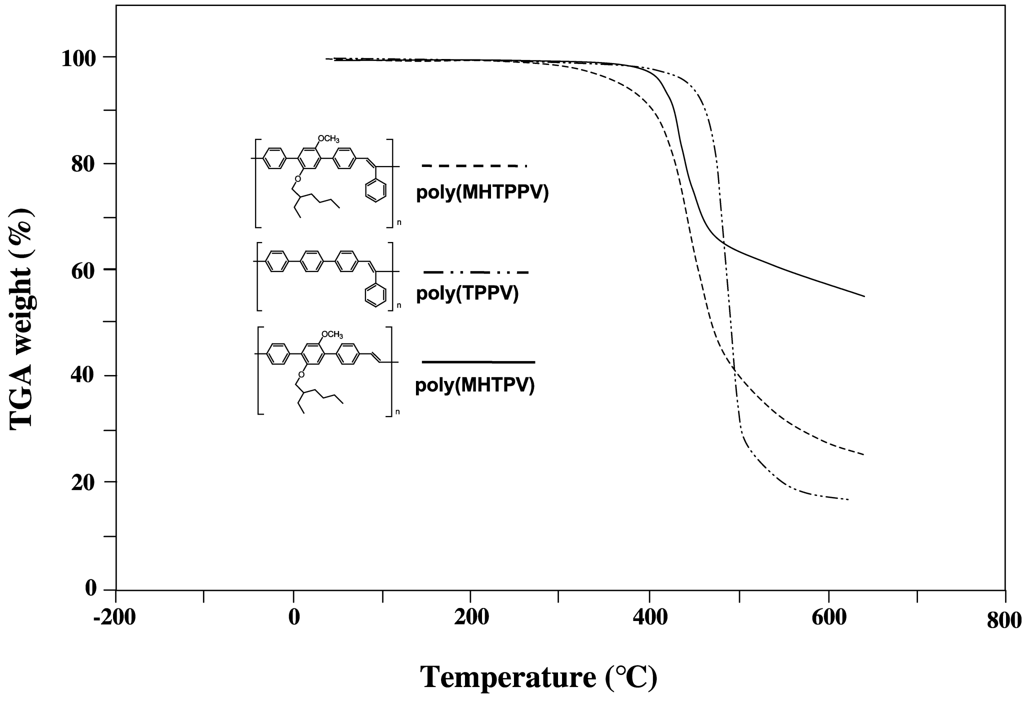


Fig. 3. TGA thermograms for poly(terphenylenevinylene) derivatives in a nitrogen atmosphere.

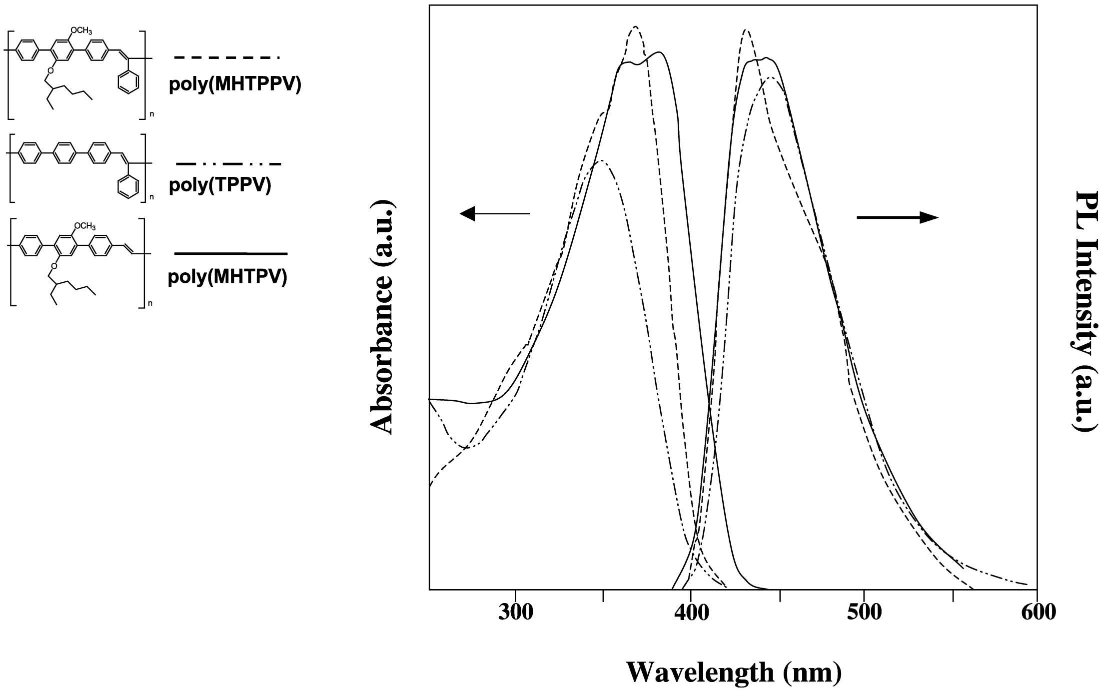


Fig. 4. UV–vis absorption and photoluminescence spectra in $CHCl_3$ of poly(terphenylenevinylene) derivatives.

of polymers was consistent with the results of the optical absorption threshold, and the polymers having phenyl substituent at the vinyl bond showed a bigger band gap.

The blue electroluminescent ($\lambda_{max} = 450-460$ nm) was obtained with the turn on voltage of 8–10 V, when the simple light emitting diodes of ITO/polymer/Al were fabricated (Fig. 5). The electroluminescent spectra were similar to the PL spectra of polymers except a small shoulder appeared around 530 nm (Fig. 6). This small shoulder may result from interchain excimer emission. The intensity of the shoulder is decreased in following order: poly(MHTPV) < poly(TPPV) < poly(MHTPPV). From the result, the steric effect of phenyl substituent at the vinyl bridge interrupt the formation of excimers owing to

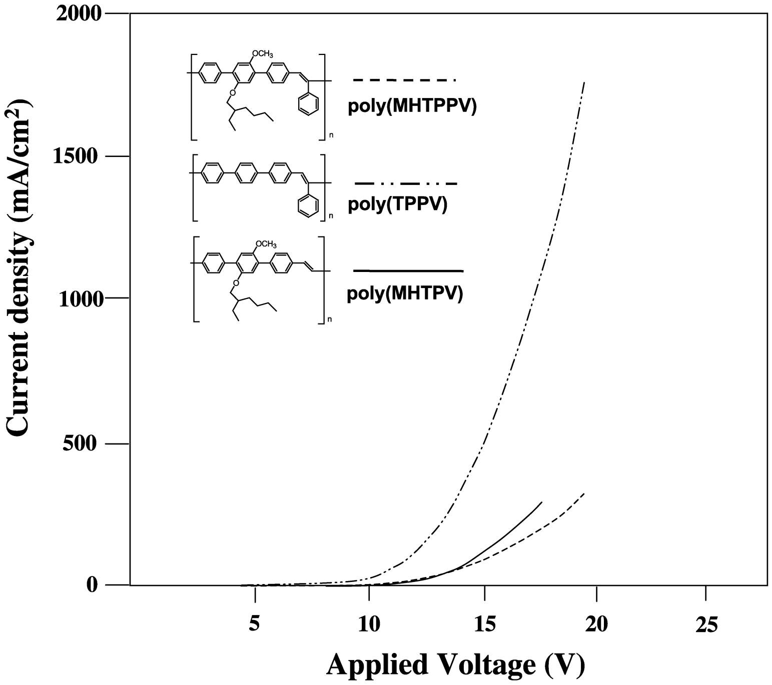


Fig. 5. The characteristics of the current vs voltage of the ITO/polymer/Al devices.

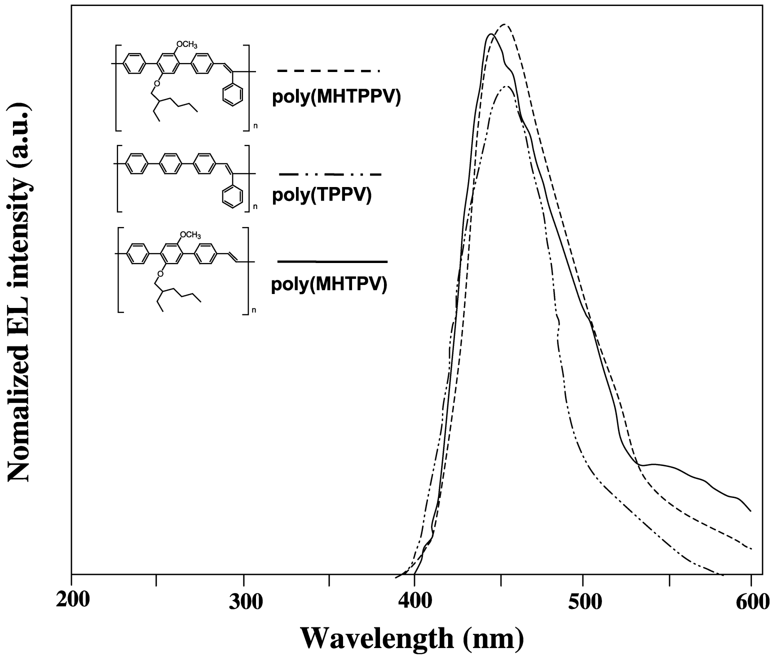


Fig. 6. Electroluminescence spectra of ITO/polymer/Al structured devices.

interchain interactions, and π-staking between the conjugated segments.

4. Conclusion

The new blue-light-emitting conjugated polymers, poly (terphenylenevinylene) derivatives, having advantages of both PPP and PPV, have been synthesized and characterized. The synthesized polymers have good solubility and thermal stability. The introduction of the phenyl pendant group into the vinyl bond led to steric hindrance, which shortens the effective conjugation length, interrupts interchain interactions, widens the band gap and increases thermal stability.

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