

Green electroluminescent diode from poly(2-trimethylsilyl-1,4-phenylene vinylene)

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Summary

Poly(2-trimethylsilyl-1,4-phenylenevinylene) (TMS-PPV) was synthesized through a organic-soluble precursor polymer, and its properties were characterized by UV-visible, FT-IR spectroscopy and thermal analysis. The EL devices were fabricated with TMS-PPV as an emitting layer, and ITO and aluminum as positive and negative electrodes, respectively. Threshold voltage of the device was about 15 V and the emission maximum was at about 540 nm with quantum efficiency of 3.5×10^{-4} % photons per electron in air and room temperature condition.

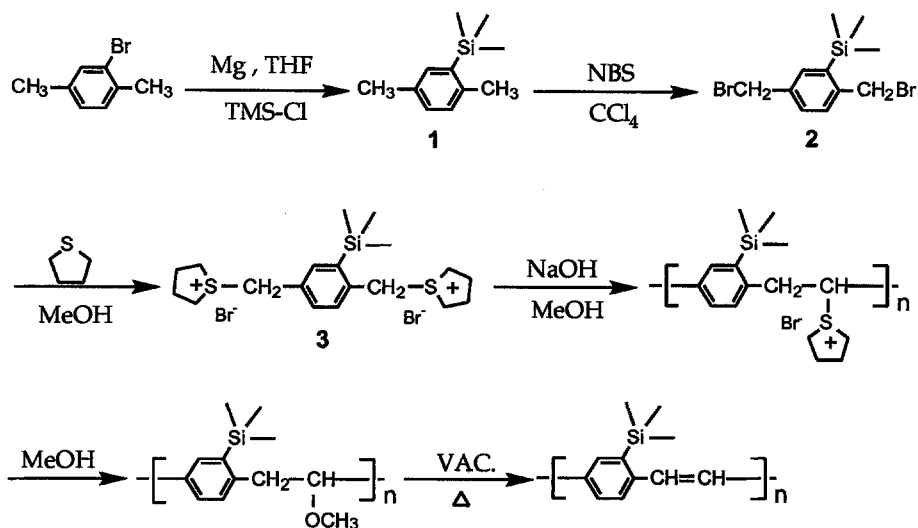
Introduction

The interests in light-emitting π -conjugated polymers have been increased in recent years since Burroughes et al. reported a green light-emitting diode (LED) using poly(p-phenylenevinylene) (PPV) as an emitting layer.¹ Organic polymer LEDs have many advantages in the development of a large-area visible light-emitting display, because of the good processibility, low operation voltage, fast response time and color tunability over full visible range.²⁻⁶ These features not only readily permit fabrication of EL devices but also offer the potential for practical application. Recently we reported the synthesis and multifunctional properties of silicon substituted soluble PPV derivative, poly(2-trimethylsilyl-1,4-phenylenevinylene) (TMS-PPV).⁷ The light-emitting properties of silicon substituted TMS-PPV is very interesting in many respects.

In this article, we report the detailed synthetic methods and characterization of TMS-PPV. EL devices were also fabricated and characterized with TMS-PPV as an emitting layer. The synthetic method of TMS-PPV is shown in following synthetic scheme.

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Synthetic Scheme



Monomer Synthesis

2-Trimethylsilyl-p-xylene (1). To 30 g of 2-bromo-p-xylene diluted in anhydrous THF was slowly added 6.8 g of clean magnesium turnings after initiation by 5 mol % of dibromoethane. When the magnesium was completely consumed, 40 mL of chlorotrimethylsilane was slowly added to this solution. The mixture was refluxed for 3 h, and the reaction was quenched with dilute HCl solution. The THF layer was separated, washed with water several times, and the solution was dried with magnesium sulfate, then THF was removed by distillation. After vacuum distillation, 24.5 g of a colorless liquid was obtained. The yield was 85 % : bp 52-54 °C at 0.8 Torr : ¹H-NMR (CDCl₃) δ 7.54 (s, 1H), 7.34 (s, 2H), 2.68 (s, 3H), 2.58 (s, 3H), 0.59 (s, 9H). ¹³C-NMR (CDCl₃) δ 140.30, 138.08, 135.00, 133.96, 129.84, 129.72, 22.44, 21.05, -0.12. Elem anal. Calcd: C, 74.06; H, 10.10. Found: C, 73.88; H, 10.13.

2-Trimethylsilyl-1,4-bis(bromomethyl)benzene (2). Compound 2 was prepared by reacting 10 g of compound 1 with 21 g 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 5 h under a nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution. After evaporation of the solvent, a yellow oil was obtained. White pure product was obtained by silicagel column using hexane as an eluent. The product yield was 45 % (9 g) : mp 39-40 °C : ¹H-NMR (CDCl₃) δ 7.55 (s, 1H), 7.45 (s, 2H), 4.64 (s, 2H), 4.51 (s, 2H), 0.44 (s, 9H). ¹³C-NMR (CDCl₃) δ 143.29, 139.95, 136.92, 135.27, 131.44, 130.38, 33.66, 33.17, 0.30. Elem anal. Calcd: C, 39.28; H, 4.76. Found: C, 39.12; H, 4.52.

2-Trimethylsilyl-1,4-phenylenedimethylene bis(tetrahydrothiophenium) bromide (3). The 6 g of compound 2 and excess tetrahydrothiophene were reacted for 24 h at 50 °C in 30 mL of methanol. The monomer 3 was obtained by concentration of the reaction solution, precipitation in methylenechloride, filtration and vacuum drying. The product yield was 80 % (7.2 g) : mp 84-85 °C (dec) : $^1\text{H-NMR}$ (D_2O) δ 7.67 (s, 1H), 7.51 (s, 2H), 4.69 (H_2O , solvent), 4.52 (s, 2H), 4.47 (s, 2H), 3.48-3.34 (m, 8H), 2.26-2.09 (m, 8H), 0.31 (s, 9H). $^{13}\text{C-NMR}$ (D_2O) δ 155.94, 150.34, 147.72, 144.52, 144.18, 141.80, 58.70, 57.42, 55.38, 55.01, 40.80, 40.63, 12.03. Elem anal. Calcd: C, 44.51; H, 6.25. Found: C, 44.57; H, 6.13.

Polymerization

The monomer salt 3 (2 g, 3.9 mmol) was dissolved in 3.9 mL of methanol and then, the solution was cooled to 0 °C. The cold equimolar NaOH solution dissolved in 4 mL of methanol was added to the monomer solution. Soon, highly viscous gum was formed and this was completely dissolved with 20 mL of methanol and then, the precursor polymer solution was stirred at room temperature for 24 h. The viscosity of precursor polymer solution was gradually decreased, suggesting that the water-soluble precursor polymer was converting to the organic-soluble precursor polymer in methanol as shown in synthetic scheme. After stirring for several hours, the viscosity of the precursor polymer solution was disappeared, and the greenish colored organic-soluble precursor polymer was precipitated. This organic-soluble precursor polymer was soluble in dichloromethane, chloroform and other organic solvents. Pure organic-soluble precursor polymer (0.4 g) was obtained by reprecipitation of the polymer solution to hexane. GPC measurement of this polymer with polystyrene as the calibration standard showed a weight average molecular weight of 185,000 and polydispersity index of 2.0.

Characterization

Melting points were determined using a Electrothermal Model 1307 digital analyzer. $^1\text{H-NMR}$ spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were recorded on a Bomem Michelson series FT-IR spectrophotometer and UV-visible spectra were obtained with a Shimadzu UV-3100S. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min with DuPont 9900 analyzer. The photoluminescence (PL) spectra were recorded on a Perkin Elmer LS-50 fluorometer at room temperature utilizing a lock-in amplifier system with chopping frequency of 150 Hz and an Xenon lamp as an excitation light source. The excitation wavelength was 360 nm.

EL Device Fabrication and Measurement of Electroluminescence

For electroluminescence (EL) experiment, the organic-soluble precursor polymer was dissolved in dichloroethane, and coated on the glass substrate with ITO electrode which is cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol. The precursor polymer coated on the substrate was eliminated at 240 °C for 3 h under reduced pressure, then thick aluminum was vacuum deposited on the top of the polymer layer at the pressure below

4×10^{-6} Torr. The aluminum electrode has the diameter of 5 mm. Spectroscopic measurement uses a dual grating monochromator (Spex 270M) with the photomultiplier tube (Hamamatsu R955) as a detector. EL spectra were recorded by computer while applying direct current from the current/voltage source (Keithly 248). For the measurement of device characteristics, current-voltage (I-V) and light intensity-current (L-I) characteristics were measured using the current/voltage source and optical powermeter (Newport 818SL). All the measurements mentioned above were performed in air and at room temperature.

Results and Discussion

Figure 1 shows the FT-IR spectra of the organic-soluble precursor polymer (a) and thermally eliminated TMS-PPV (b). The characteristic absorption peak of the water-soluble precursor polymer at $3100\text{--}3300\text{ cm}^{-1}$ which is due to the absorbed water, is not observed in the spectrum (a). The absorption peak at 960 cm^{-1} is highly increased after thermal elimination, which corresponds to the out-of-plane bending mode of trans vinylene groups, suggesting that the generated double bonds in the main chain are mainly trans configuration.

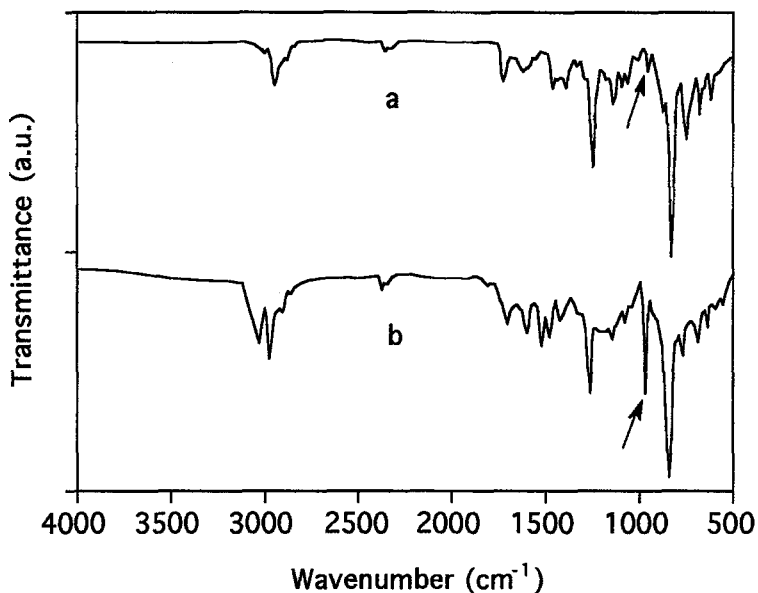


Figure 1. FT-IR spectra of (a) organic-soluble precursor polymer and (b) TMS-PPV eliminated at $240\text{ }^{\circ}\text{C}$ for 2 h.

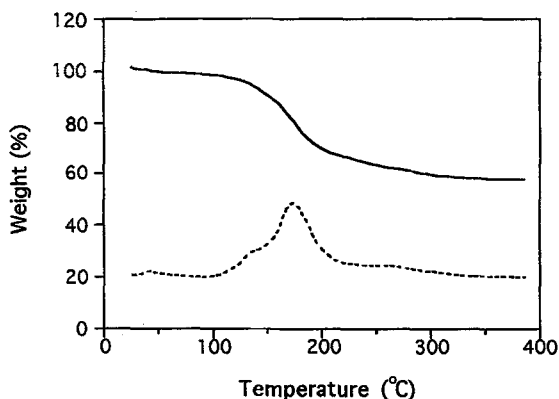


Figure 2. TGA thermogram of precursor polymer of TMS-PPV

A weak but sharp absorption peak of the same position in the spectrum of organic-soluble precursor polymer is due to the premature elimination during polymerization and film casting.

Figure 2 shows the TGA thermogram of the organic-soluble precursor polymer film. In this thermogram, the elimination reaction is almost occurred before 200 °C, and then slowly shows a small weight loss up to 400 °C. It has been reported that organic-soluble precursor polymer is not completely eliminated by thermal treatment and needed suitable acid catalyst to eliminate completely.^{2,8} Based on this thermogram, the organic-soluble precursor polymer was eliminated at 240 °C for 2 h under reduced pressure without acid catalyst in order to obtain partially conjugated structures.

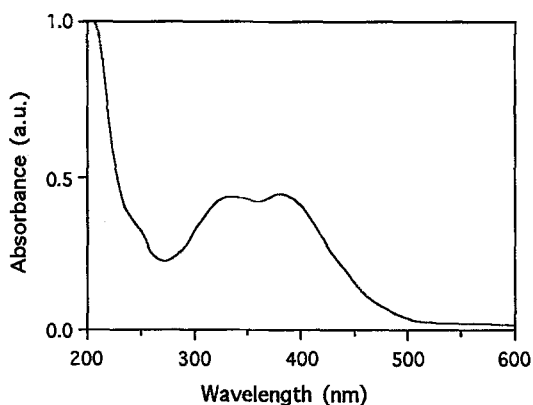


Figure 3. UV-visible spectrum of TMS-PPV

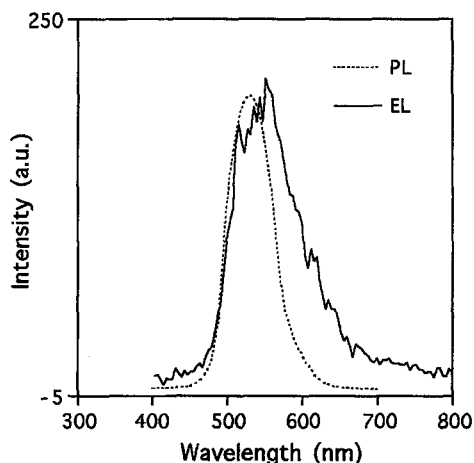


Figure 4. PL and EL spectra of TMS-PPV

Figure 3 shows the UV-visible spectrum of TMS-PPV film. The absorption maximum and the edge are 380 nm and 480 nm, respectively. These are more blue-shifted ones than those of the completely eliminated TMS-PPV (420 nm/510 nm).⁷ Blue-shifted absorption indicates that the methoxy substituted organic-soluble precursor polymer could not be completely eliminated by thermal elimination.⁸⁻¹⁰ So we suppose that a small amount of methoxy substituted non-conjugated parts still remain in conjugated polymer chains and make the conjugation length of the polymer to be short.

Figure 4 shows the photoluminescence (PL) and the electroluminescence (EL) spectra of TMS-PPV film. TMS-PPV shows its PL emission maximum at about 530 nm. The EL spectrum is very close to that of PL indicating the origin of the emission is the same for both cases. The emission maximum of EL spectrum is located at about 540 nm which corresponds to the green light emission.

Figure 5 (a) shows the current-voltage characteristics measured from a typical Al/TMS-PPV/ITO device. The forward current increases with increasing forward bias voltage and the curve shows typical diode characteristics. Here, the forward bias current is obtained when the ITO electrode is positively biased and the metal electrode negatively. Figure 5 (b) shows the voltage dependence of emission intensity from the device. Light emission becomes visible at a bias of just about 15 V.

The dependence of the emission intensity on the injected current and current density is shown in Figure 6 (a) and (b), respectively. As is the typical polymer LED device, the emission intensity exhibits an approximately linear increase with injected current, but at the higher current or current density, the EL intensities are rapidly increased.

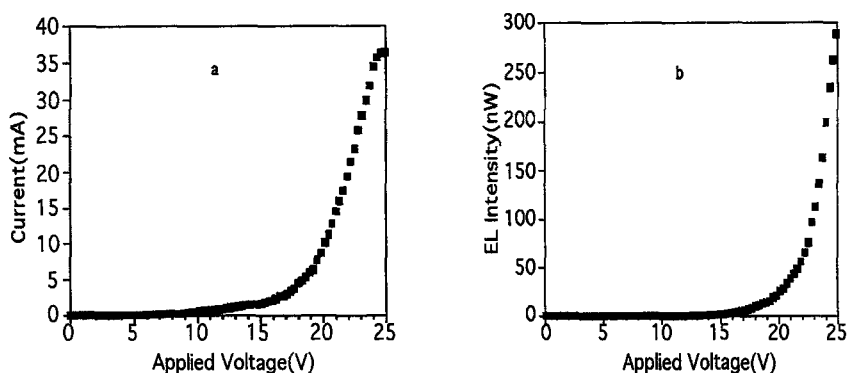


Figure 5. Voltage-current (a) and voltage-EL intensity characteristics (b) of TMS-PPV

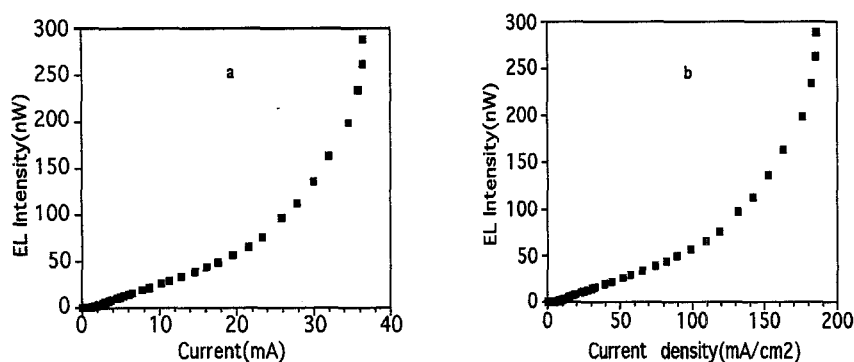


Figure 6. Current-EL intensity (a) and current density-EL intensity characteristics (b) of TMS-PPV

The measured quantum efficiency of the diode is $3.5 \times 10^{-4} \%$ at current density of 178 mA/cm^2 , in air and at room temperature condition. In the same measurement condition, PPV and MEH-PPV showed the efficiencies of $4.0 \times 10^{-5} \%$ and $6.4 \times 10^{-5} \%$ photons/electron, respectively when aluminum and ITO were employed as negative and positive electrodes.¹² TMS-PPV shows about 10 times higher efficiency compared with PPV. This improved efficiency is attributed to the relatively short conjugation length than the fully conjugated PPV and MEH-PPV. Bradley et al. reported the correlation between conjugation length and nonradiative decay rate in PPV.⁹ The nonradiative decay rate increases with increasing polymer chain conjugation, and Burn et al. also reported enhancement of the efficiencies by controlling the amount of

nonconjugated segments in electroluminescent copolymers.^{2,8,10} The nonconjugated methoxy groups induce local variation in the π - π^* electronic energy gap at both the molecular and supramolecular level. Variations at the molecular level can act to trap excitons, hindering their migration to quenching sites, and so these materials give strongly enhanced quantum yields for electroluminescence.

The TMS-PPV film which has a good processibility from the soluble-precursor polymer and high quantum efficiency may be a good candidate for application to the polymer LEDs.

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