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Synthesis and properties of silyl-substituted PPV derivative through two different precursor polymers

Do-Hoon Hwang[1], In-Nam Kang[2], Jeong-Ik, Lee[2], Lee-Mi Do[1], Hye Yong Chu[1], Taehyoung Zyung[1], Hong-Ku Shim[2]

[1] Research Department, Electronics and Telecommunications Research Institute,
Yusong P.O. Box 106, Taejon 305-350, Korea

[2] Department of Chemistry, Korea Advanced Institute of Science and Technology,
Taejon 305-701, Korea

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Summary

We synthesized [poly(2,5-bis(trimethylsilyl)-1,4-phenylenevinylene)] (BTMS-PPV) via two different precursor polymers, i.e., a water-soluble sulfonium and an organic soluble thiophenoxy precursor polymers, and compared their properties with each other. The thiophenoxy precursor polymer shows a good thermal stability and it is eliminated from 320 °C. BTMS-PPV film through the thiophenoxy precursor route shows a blue-shifted UV-visible absorption and PL emission spectra compared with those from the water-soluble precursor route. A single layer EL device fabricated with BTMS-PPV from the thiophenoxy precursor polymer as an emitting layer shows the threshold voltage of 20 V and the emission maximum at about 545 nm. The external quantum efficiency of the device is greater than 6.0×10^{-4} % photons per electron in air and room temperature condition.

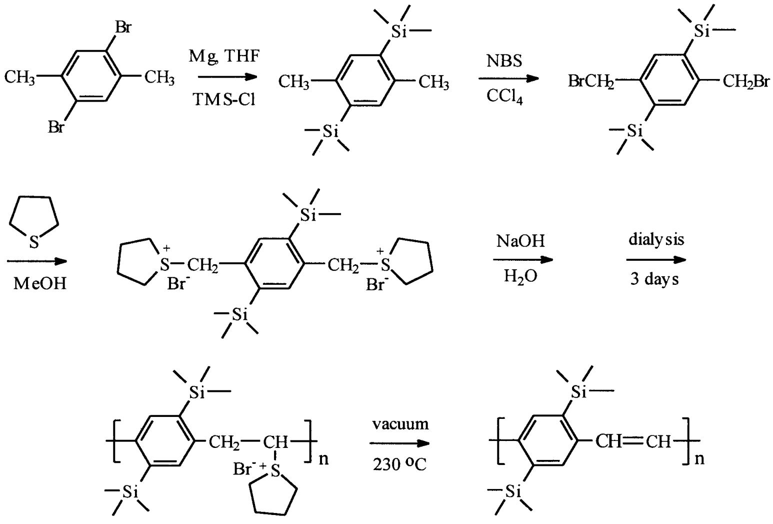
Introduction

Research on the organic conjugated polymers has emerged as one of the most exciting and interdisciplinary areas during a couple of decades because of the possible applications to the electronic and photonic devices.[1,2] Among them, interests in poly(1,4-phenylenevinylene) (PPV) and its derivatives have been spawned in recent years due to the fact that these polymers show a high electrical conductivity after doping,[3,4] optical nonlinearity,[5,6] and the electroluminescent (EL) properties.[7-10] Especially, the EL properties of these polymers have been extensively studied in these days for realization of a large area multi-color display. Substitution on the phenyl ring of PPV with different types of substituent shows the significant differences in electronic structures and morphologies of the corresponding polymers, and thus affects the electro-optical properties of the resulting polymers.[11,12] PPV and its derivatives have been synthesized through water-soluble[4,6,11], or organic-soluble precursor polymers.[13,14] Recently, we reported synthesis and light-emitting properties of silyl mono-substituted PPV derivatives such as poly(2-trimethylsilyl-1,4-phenylenevinylene)(TMS-PPV)[15] and poly(2-dimethyloctylsilyl-1,4-phenylenevinylene)(DMOS-PPV).[16,17] Silyl-substituted PPV derivatives show a good processibility and a high luminescence quantum efficiency.

Here we report the synthesis and the properties of silyl-disubstituted PPV derivative poly [2,5-bis(trimethylsilyl)-1,4-phenylenevinylene] (BTMS-PPV) through two different precursor polymers, i.e., a water-soluble sulfonium and a new thiophenoxy precursor polymer. The thiophenoxy precursor polymer shows an extremely good thermal stability. Properties of BTMS-PPV films made via two different routes are compared with each other. Synthetic routes for the BTMS-PPV are shown in synthetic scheme.

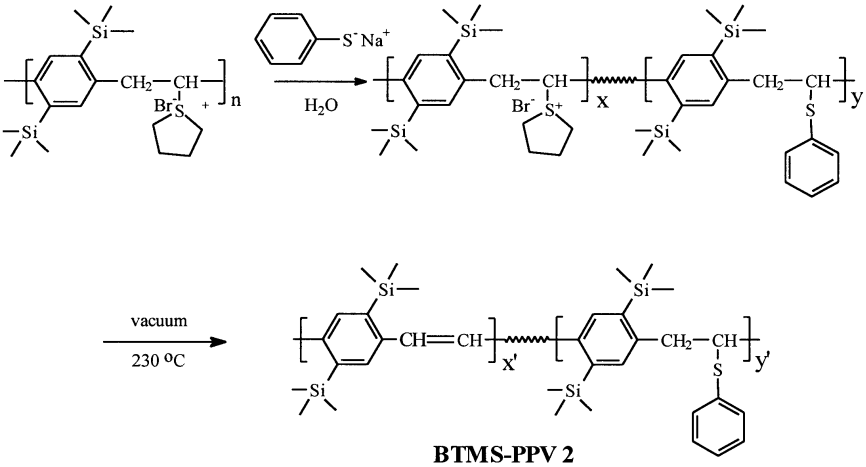
Synthetic Scheme

Scheme 1



BTMS-PPV 1

Scheme 2



BTMS-PPV 2

Experimental

Monomer synthesis

2,5-bis(trimethylsilyl)-p-xylene (1). To 20.0 g (75.8 mmol) of 2,5-dibromo-p-xylene diluted in anhydrous THF was added to 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 white soup-like Grignard reagent was formed, 30 mL of chlorotrimethylsilane was slowly added to this solution and the mixture was refluxed for 3 h. Reaction was quenched with dilute HCl solution. The reaction mixture was extracted three times with diethyl ether and distilled water, and the organic layer was separated and dried with magnesium sulfate, then solvent was removed by evaporation. 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 139.5, 139.1, 135.7, 22.6, -0.2. Elem anal. Calcd: C, 67.12: H, 10.46. Found: C, 66.88: H, 10.63.

2,5-bis(trimethylsilyl)-1,4-bis(bromomethyl) benzene (2). Compound **2** was prepared by reacting 5.0 g (20.0 mmol) of compound **1** with 7.1 g (40.0 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. Completion of the reaction was indicated by the appearance of succinimide on the surface of the solution. A yellow colored solution was obtained after filtration of succinimide. The solution was concentrated and poured into methanol. White pure solid **2** 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 142.1, 140.9, 137.4, 34.1, 0.3. Elem anal. Calcd: C, 41.18: H, 5.92. Found: C, 39.91: H, 5.73.

2,5-bis(trimethylsilyl)-1,4-phenylenedimethylene bis(tetrahydrothiophenium) bromide (3). The 4.0 g (9.8 mmol) of compound **2** and excess tetrahydrothiophene were stirred for 24 h at 50 °C in 20 mL of methanol. The salt monomer **3** was obtained by concentrating the reaction solution, precipitating in cold acetone, filtering and vacuum drying. The product yield was 4.9 g (85 %): mp 175-176 °C (decomposition). ^{1}H-NMR (D_2O) δ 7.60 (s, 2H), 4.70 (s, H_2O), 4.57 (s, 4H), 3.60-3.25 (m, 8H), 2.48-2.10 (m, 8H), 0.35 (s, 18H). (Figure 1 shows the ^{1}H-NMR spectrum of sulfonium salt monomer **3**) ^{13}C-NMR (D_2O) δ 156.5, 150.9, 146.8, 58.7, 55.2, 40.7, 11.8. Elem anal. Calcd: C, 45.20; H, 6.90. Found: C, 44.64; H, 6.87.

Polymerization

Synthesis of the polymer BTMS-PPV1 through the water-soluble precursor route. The salt monomer **3** (1.0 g, 1.7 mmol) was dissolved in 100 mL of deionized water and then cooled down to 0 °C. Equimolar cold 1.0 N NaOH solution was added to the salt monomer solution. Soon, homogeneous and highly viscous precursor polymer solution was formed. After stirred for 1 h at 0 °C, the reaction was quenched by neutralization with 0.5 N aqueous HCl solution. The neutralized polyelectrolyte precursor solution was dialyzed with deionized water for 4 days to remove the unreacted monomers and low molecular weight oligomers using a dialysis tube with molecular weight cutoff at 12,000. The films coated from the aqueous precursor polymer solution were subjected to thermal elimination in vacuum (10^{-3} Torr) at 230 °C for 10 h to be converted the final polyconjugated polymer films.

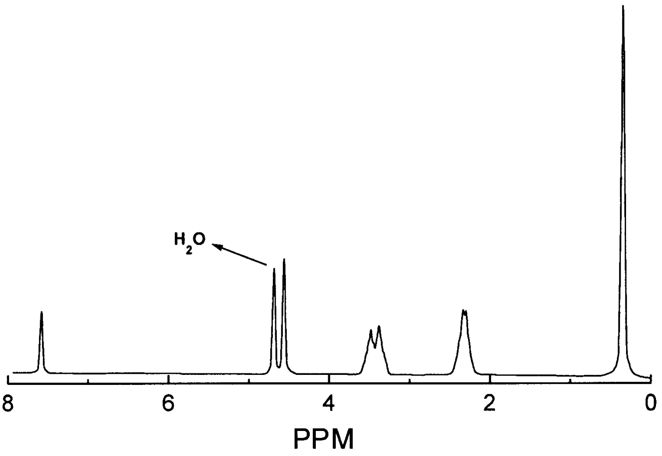


Figure 1. ^{1}H-NMR spectrum of sulfonium salt monomer **3**

Synthesis of the polymer BTMS-PPV2 through the thiophenoxy precursor route. Thiophenol (0.37 g, 3.4 mmol) was dissolved in 20 mL of dry THF, and 0.12 g (5.1 mmol) of sodium hydride was added into this solution. Soon hydrogen gas was evolved violently and white salt precipitate was formed. The reaction was quenched by adding 10 mL of deionized water into the reaction mixture. This sodium thiophenoxide solution was slowly added into the dialyzed water-soluble precursor polymer at 0 °C. Pale green colored thiophenoxy precursor polymer was precipitated in the reaction mixture. The precipitate was filtered, washed with methanol and dried under vacuum for 10 h at room temperature. The synthesized thiophenoxy precursor polymer is soluble in common organic solvent such as chloroform, dichloroethane, THF etc. GPC measurement of this polymer with polystyrene as the calibration standard showed the average molecular weight (M_w) of 1,000,000 and polydispersity index of 2.5. The thiophenoxy precursor polymer film was eliminated at 230 °C for 10 h to obtain BTMS-PPV2.

Characterization

Melting point was determined using an Electrothermal Model 1307 digital analyzer. ^{1}H-NMR and ^{13}C-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. Photoluminescence spectra were obtained by exciting the polymer film with 350 nm from Zenon lamp.

EL device fabrication and measurement of electroluminescence

ITO coated glass substrates were cleaned by successive ultrasonic treatments for an hour in acetone and isopropyl alcohol. The substrates were dried with nitrogen gas and heated at 100 °C for further.

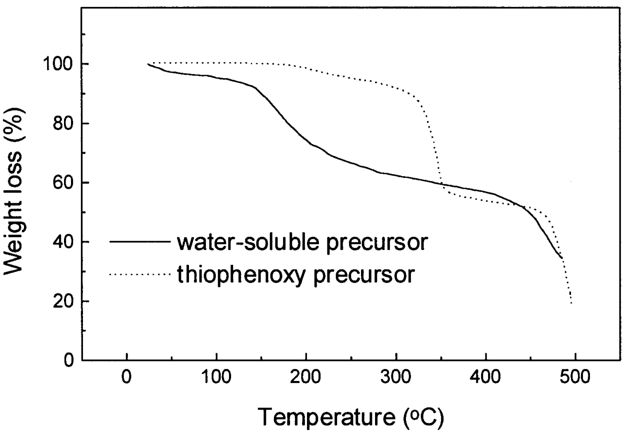


Figure 2. TGA thermogram of water-soluble and thiophenoxy precursor polymer

The polymer film with 100 nm thickness was obtained by spin coating the filtered polymer solutions on the substrates and drying in vacuum oven for 2 h at 100 °C. The spin coated precursor polymer film was thermally treated for elimination reaction at 230 °C for 10 h. Aluminum was vapor deposited for the top electrode at the pressure below 1 x 10^{-6} Torr, yielding active area of 3.14 mm^2. EL spectra were measured using a monochromator (Jobin-Yvon HR320) with the photomultiplier tube (Hammamatsu R928). Current-voltage (I-V) and light intensity-current (L-I) characteristics were measured using the current/voltage source (Kethley 238) and the calibrated silicon photodetector (Newport 818SL). The emitted light was collected with the photodetector placed in front of the device. All the measurements were performed in air at room temperature.

Results and Discussion

Figure 2 shows TGA thermograms of the water-soluble and the thiophenoxy precursor polymer films. The water-soluble precursor polymer film is slowly eliminated from 140 °C and the elimination reaction is completed at about 200 °C. Interestingly, the thiophenoxy precursor polymer film shows very good thermal stability up to higher than 300 °C. The thiophenoxy precursor polymer film is abruptly eliminated from 320 °C and decomposes at about 460 °C. This is the highest elimination temperature among the reported PPV precursor polymers such as the water-soluble sulfonium[4,6,11], the methoxy[14] or halogen[13] substituted organic-soluble precursor polymers.

The elimination reaction was performed at 230 °C for 10 h for both the water-soluble and the thiophenoxy precursor polymer films. In this elimination condition, the water-soluble precursor polymer would convert to fully conjugated form, but the thiophenoxy precursor polymer would not be fully eliminated, so it may form a partially conjugated system.

UV-visible spectra confirm the above assumption. UV-visible spectra of BTMS-PPV1 and BTMS-PPV2 films are shown in Figure 3. BTMS-PPV1 film shows an absorption maximum and an edge at about 390 nm and 500 nm, respectively. BTMS-

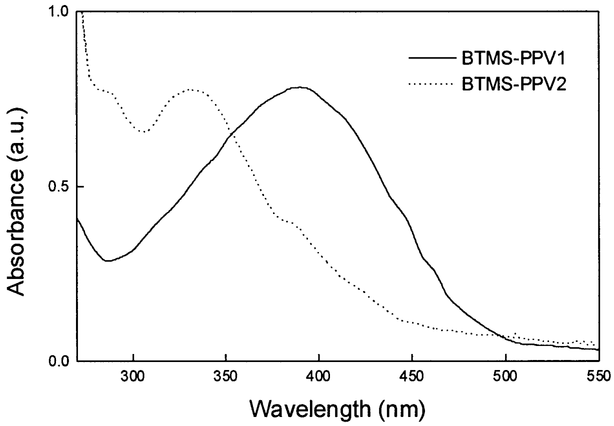


Figure 3. UV-visible spectra of (a) BTMS-PPV 1 and (b) BTMS-PPV 2 film

PPV2 film shows a blue-shifted absorption spectrum compared with BTMS-PPV1. It shows the absorption maximum and the edge at about 330 nm and 450 nm, respectively. We suppose that this blue shift of BTMS-PPV2 film in UV-visible spectrum is due to the uneliminated thiophenoxy segments in polymer chains, which break the conjugation of BTMS-PPV. BTMS-PPV2 film also shows a shoulder peak in UV absorption spectrum at about 390 nm.

Figure 4 shows the PL emission spectra of BTMS-PPV1 and BTMS-PPV2 film. BTMS-PPV2 film also shows a blue shifted PL emission spectrum compared with that of BTMS-PPV1.

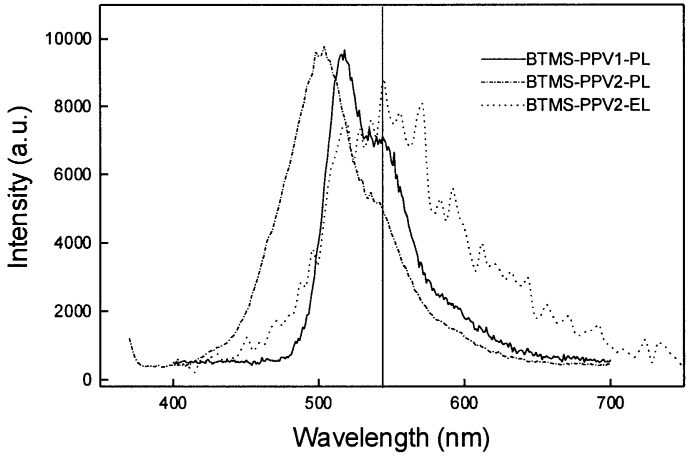


Figure 4. PL spectra of BTMS-PPV1 and BTMS-PPV2, and EL spectrum of ITO/BTMS-PPV2/Al device.

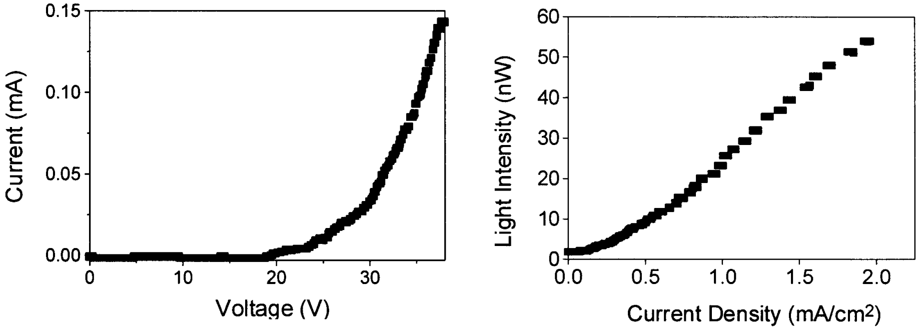


Figure 5. I-V (left) and L-I (right) curves of ITO/BTMS-PPV2/Al device

BTMS-PPV1 shows a peak emission at about 518 run and BTMS-PPV2 at about 505 nm. In both spectra, emission shoulders are observed at the same wavelength of 545 nm.

It was hard to make a high quality BTMS-PPV1 film, so only a single layer device with BTMS-PPV2 was fabricated for EL measurement. The EL emission spectrum from the ITO/BTMS-PPV2/A1 device is shown in Figure 4. The EL peak is red-shifted compared with the PL peak of BTMS-PPV2. The EL peak is at about 545 nm, which is coincident with the shoulder peaks in PL spectra of both BTMS-PPV1 and BTMS-PPV2 film. The difference between PL and EL from BTMS-PPV2 is not fully understood, but it is likely that the different emission centers dominate in the PL and EL process. Photogenerated emission does not rely on the carrier mobility so that the excitations generated in the less mobile portions of the film can contribute to the emission. In fact, such regions of the film may dominate the PL because the nonradiative recombination is enhanced in highly mobile regions. For EL, the oppositely charged carriers must move sufficiently close to each other to recombine radiatively, therefore the EL spectra might be more characterized with the higher mobile regions of the film. Since the longer conjugated segments should have high mobility, they would produce the red-shifted EL behavior.

Figure 5 (a) shows the current-voltage characteristics measured from the ITO/BTMS-PPV2/A1 device. The forward current increases with increasing forward bias voltage and the curve shows a typical diode characteristics. The light emission from the device becomes observable at a bias voltage of about 20 V. The dependence of the emission intensity on the current exhibits an approximately linear increase with the injected current. The measured quantum efficiency of the diode is 6.0 x 10^{-4} % in air and at room temperature condition. In the same measurement condition, PPV and MEH-PPV showed the quantum efficiencies of 4.0 x 10^{-5} and 6.4 x 10^{-5} % photons/electron respectively, when aluminum and ITO were employed as negative and positive electrodes.[15]

Conclusively, BTMS-PPV has been synthesized through the water-soluble sulfonium and the thiophenoxy precursor polymer routes. The thiophenoxy precursor polymer shows the extremely good thermal stability compared with other reported PPV precursor polymers. The BTMS-PPV2 shows the blue-shifted UV-visible and the PL emission spectra than the BTMS-PPV1 due to shorter conjugation length. The single layer EL device using BTMS-PPV2 (ITO/BTMS-PPV2/A1) has been fabricated and the green light emission from the device becomes observable at a bias voltage of 20 V. The measured external quantum efficiency of the device is 6.0 x 10^{-4} %. The thiophenoxy precursor polymer route is a useful way for PPV synthesis and may be a good candidate for LED application.

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