Synthesis and Characterization of Poly(*p*-phenylenevinylene) Derivatives Containing Alkylphenylsilyl Pendant Group

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Abstract

A new class of soluble PPV derivatives containing dimethyldodecylsilylphenyl unit as a pendant was synthesized by Gilch polymerization method. The resulting electroluminescent (EL) polymers showed good solubility, good film-forming ability onto the ITO substrate, and exhibited an amorphous morphology due to dimethyldodecylsilylphenyl branched group linked to the polymer backbone. The weight average molecular weights and polydispersities of the present EL polymers were in the range of 8.0-80.0 x 10^4 and 2.67-7.80, respectively. The resulting EL polymers revealed a high thermal stability of up to 355-410°C. Their glass transition temperatures were in the range of 104-251°C. The emission colors could be tuned from green to orange-red colors by changing the MEH-PPV contents in copolymer systems. The turn-on voltages of the EL polymers were in the range of 1.8–4.0 V.

1. Introduction

Organic light-emitting display (OLED) have attracted much attention because of their wide viewing angle, fast switching time compared to conventional flat panel liquid crystal displays (LCDs), and their potential application for large-area flat panel display that can be driven at low voltage [1]. Since Tang and VanSlyke have demonstrated a high efficiency LED consisting of light-emitting layers and carrier transport layers [2], various kinds of electroluminescent polymers as well as organic fluorescent dyes have been developed in order to obtain high efficiency, long lifetime, and even white-color emission materials for LCD backlight [3]. Among the conjugated polymers, poly(*p*-phenylene vinylene) (PPV) and its derivatives are known as the most promising materials for the application of polymer LEDs. These materials have been synthesized by precursor routes or Gilch method leading to soluble and high molecular weight polymers. Recently, there has been increasing interest in the silyl-substituted luminescent polymers, in which silyl moieties are introduced either as side chains or as a segment integrated into the polymer backbones [4]. A systematic study on the synthesis of polymers combining silyl side chains and substitution on the chemical, physical, and optoelectronic properties of the polymers is interesting to materials scientists and synthetic organic chemists. The attractive properties of silyl-substituted PPVs are their extremely high PL quantum efficiency, good solubility, and uniform film morphology in the film state. Therefore, it is meaningful to design and synthesis of silyl-substituted PPVs with the aim of keeping or even further enhancing the PL efficiency and the processability by a highly branched side groups associated with the larger atom size of Si and the longer bond length of C-Si. Recently, we have synthesized a novel EL polymers, such as alkoxyphenyloxy substituted PPVs and blending systems with oxadiazole containing electron transport polymer, to improve the device performance. In the present article, we report a new series of color tunable PPV derivatives containing dimethyldodecylsilyl phenyl side group by Gilch polymerization for high molecular weight and good thermal stability. In order to improve the EL efficiency, the bulky dimethyl dodecylsilyl group was introduced into the *ortho*-

position of phenyl substitutent, which increases intramolecular steric hindrance between dimethyloctyl silylphenyl group and vinylic proton to afford amorphous morphology and good solubility behaviors.

2. Experimental

Synthesis of 1-bromo-2-(dimethyldodecylsilyl) benzene (1)

A round bottom flask was placed 1,2-dibromobenzene (19.4 g, 82 mmol) and dry THF (250 mL) under N_2 atmosphere. The flask was cooled to -78°C. While stirring, the *n*-BuLi (51.44 mL, 1.6 M *n*-hexane solution, 82 mmol) was added dropwise causing a lightening of the yellow color. After 1 hr stirring at -78°C, the mixture was allowed to room temperature and stirred for an additional 1 hr. After cooling to -78°C, chlorododecyldimethylsilane (21.6 g, 82 mmol) was added dropwise, and the system was allowed to slowly warm to room temperature and stirred for an additional 3 hrs. Most of solvent was evaporated under a reduced pressure. The resulting oily product was further purified by column chromatography on silica gel using hexane as an eluent. (yield: 30 %). ^{1}H-NMR ($CDCl_3$): δ 0.27 (s, 6H, $Si(CH_3)_2$, 0.77 (t, 2H, $SiCH_2$), 0.92 (t, 3H, $-CH_3$), 1.27 (m, 20H, $(CH_2)_{10}$), 7.21 and 7.49 (d, 4H, aromatic protons)

Synthesis of 2-(4,4,5,5-tetramethyl-2-isopropoxy dioxaborolanyl)-1,4-xylene (2)

A round bottom flask was placed 2-bromo-*p*-xylene (20 g, 0.11mol) and dry THF (200 mL) under N_2 atmosphere. While stirring, the *n*-BuLi (71 mL, 1.6 M n-hexane solution, 0.11mol) was added dropwise at –78°C. When dropping was finished, the mixture was stirred at the same temperature for 2 hrs. And then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24.2 g, 0.13 mol) was added dropwise to the solution at -78°C. The solution was allowed to slowly warm to room temperature and stirred for an additional 24 hrs. The reaction mixture was quenched by water and extracted with ether. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by evaporation under reduced pressure. The product was purified by chromatography on silica gel using hexane/ethyl acetate (9/1) as an eluent. (yield: 90 %). ^{1}H-NMR ($CDCl_3$, ppm): δ 7.6 (s, 1H), 7.15 (d, 1H), 7.1(d, 1H), 2.5 and 2.3 (s, 6H, $2CH_3$ on aromatic ring), 1.3 (s, 12H)

Synthesis of 1,4-dimethyl-2-(2-dimethyldodecyl silylphenyl)benzene (3)

To a stirred solution of compound (1) (9.98 g, 26 mmol) in DME was added $Pd(PPh_3)_4$ (0.45 g, 0.39 mmol) at room temperature under N_2 atmosphere. After 10 min at room temperature, compound (2) (9.06 g, 39 mmol) was added and followed by $NaHCO_3$ (1.0 M, 95 ml). And then, the mixture was refluxed for 5 hrs. The catalyst was filtered off, and the phases were separated. The water phase was extracted twice with ether. The resulting organic extracts were combined and washed twice with water, dried over anhydrous $MgSO_4$ and evaporated. The resulting oily product was purified by column chromatography on silica gel using hexane as an eluent. (yield : 56 %). ^{1}H-NMR ($CDCl_3$): δ 0.31 (s, 6H, $Si(CH_3)_2$, 0.77 (t, 2H, $SiCH_2$), 0.93 (t, 3H, $-CH_3$), 1.56 (m, 20H, $(CH_2)_{10}$), 2.28 and 2.4 (s, broad, 6H, $2CH_3$ on aromatic ring), 7.05-7.55 (m, 7H, aromatic protons)

Synthesis of 1,4-bis(bromomethyl)-2-(2-dimethyl dodecylsilylphenyl)benzene (4).

A mixture of 1,4-dimethyl-2-(2-dimethyldodecyl silylphenyl)benzene (3) (10.4 g, 25.4 mmol), N-bromosuccinimide (9.95 g, 55.9 mmol), and benzoyl peroxide (12 mg, 0.05 mmol) in CCl_4 (200 mL) was heated to reflux for 3 hrs under N_2 atmosphere. A bright red solution with precipitated succinimide was produced. The warm reaction mixture was filtered under suction and washed with a little hot CCl_4. The combined organics were dried over anhydrous $MgSO_4$. After removing of the solvent, the residue was subjected to purification by chromatography on silica gel using hexane as an eluent. (yield : 40 %). ^{1}H-NMR ($CDCl_3$): δ 0.29 (s, 6H, $Si(CH_3)_2$, 0.79 (t, 2H, $SiCH_2$), 0.91 (t, 3H, $-CH_3$), 1.31 (m, 20H, $(CH_2)_{10}$), 4.1- 4.63 (m, 4H, $2-CH_2Br$), 7.29-7.62 (d, 7H, aromatic protons)

Synthesis of poly[2-(2-dimethyldodecylsilyl phenyl)-1,4-phenylenevinylene], (*o*-SiPhPPV)

To a 100 mL Schlenk flask, the monomer (4) (0.2 g, 0.35 mmol) and dry THF (20 mL) were placed and cooled in an ice bath under N_2 atmosphere. With stirring, the potassium *tert*-butoxide (2.13 mL, 1.0 M THF solution, 2.13 mmol) was added dropwise for 20 min. After about 2 min, the reaction mixture turned to yellow and cloudy, and then a bright yellowish green viscous solution was formed. The reaction mixture was stirred additionally for 3 hrs. The polymerization

solution was precipitated into 400 mL of MeOH with stirring. The crude polymer was Soxhlet extracted with MeOH. The resulting polymer was redissolved in chloroform and reprecipitated into MeOH. After filtration and drying under vacuum, a bright yellow polymer was obtained (0.07 g, 75%). The obtained polymer has the following ^{1}H-NMR spectral characteristics in $CDCl_3$: δ 0.30 (s, 6H, $Si(CH_3)_2$, 0.70 - 0.98 (m, 5H, $SiCH_2$ and $-CH_3$), 1.10 - 1.52 (m, 20H, $(CH_2)_{10}$), 7.10 - 7.80 (br, 9H, aromatic protons and vinylic protons); Anal. Calcd for $C_{28}H_{40}Si$ C 83.10, H 9.96. Found : C 82.90, H 9.86.

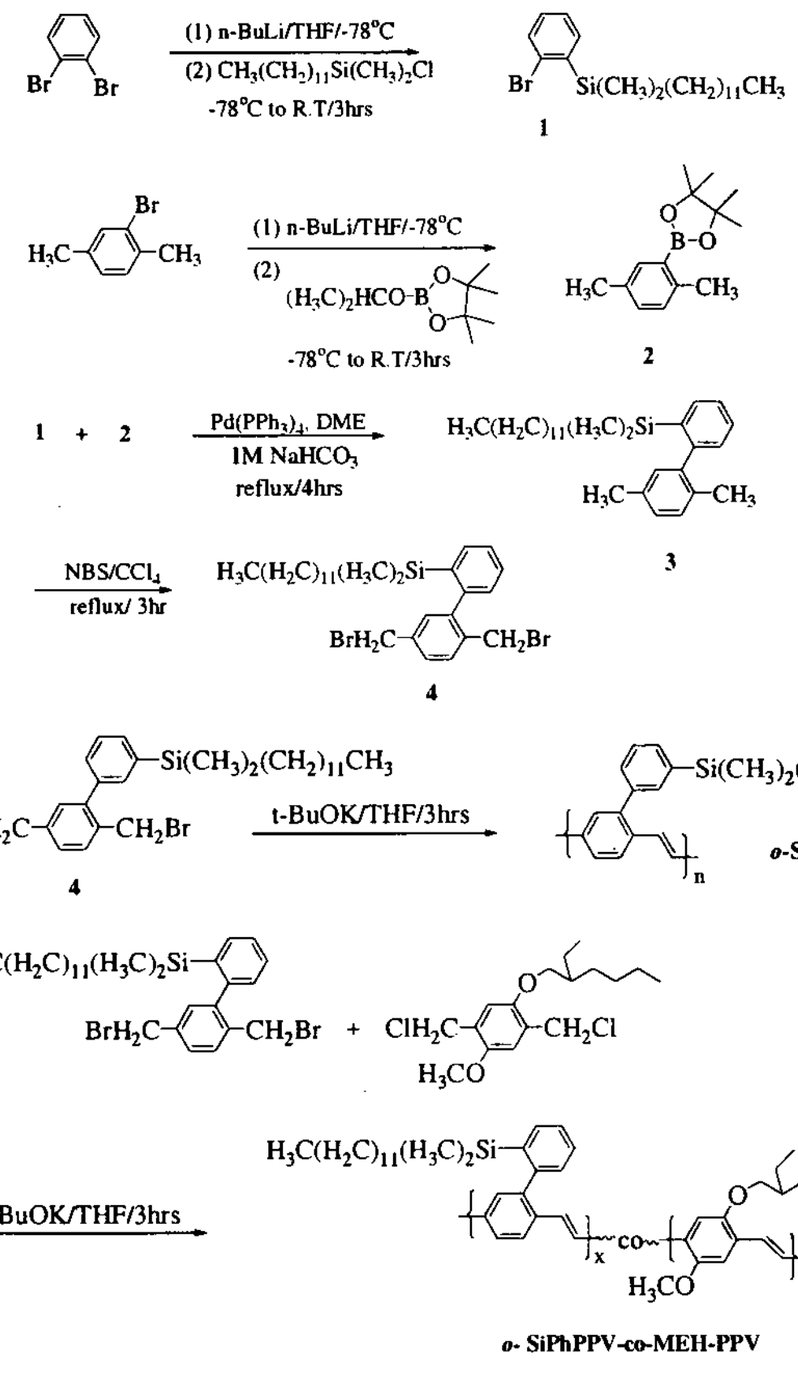
Synthesis of poly[2-(2-dimethyldodecylsilylphenyl)-1,4-phenylenevinylene-co-2-methoxy-5-(2-ethyl hexyloxy)-1,4-phenylenevinylene], (*o*-SiPhPPV-co-MEH-PPV)

A solution of 3.6 mL of potassium *tert*-butoxide (1.0 M THF solution, 3.6 mmol) was slowly added over 1 hr using a syringe pump to a stirred solution of monomer (0.102 g, 0.18 mmol) and 1,4-bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxy benzene (0.140 g, 0.42 mmol) in 20 mL of dry THF that was cooled to –5°C. The reaction mixture gradually increased its viscosity with orange-red fluorescence and was stirred for 3 hrs. The polymerization solution was precipitated into 600 mL of MeOH and the crude polymer was Soxhlet extracted with MeOH to remove the impurities and oligomers. The resulting polymer was redissolved in chloroform and reprecipitated into MeOH. After filtration and drying under vacuum, bright red fibrous polymer, o-SiPhPPV-co-MEH-PPV (50:50 mol %) was obtained. (yield: 50%) ^{1}H-NMR ($CDCl_3$) δ . 0.28 (s, 6H, $Si(CH_3)_2$), 0.70 - 0.91 (m, 11H, $SiCH_2$ and $-CH_3$ x 3), 1.10 - 1.60 (m, 31H, methylene and methine protons), 3.8 - 4.2 (m, 5H, $-OCH_2$ and $-OCH_3$), 7.10 - 7.60 (br, 13H, aromatic protons and vinylic protons).

3. Results and Discussion

The synthetic procedure for monomer and its corresponding polymers are depicted in Scheme I. All synthetic steps for the monomer are facile and can be easily controlled. In order to improve the processability and amorphous morphology of the present polymers, dodecyldimethylsilyl group was introduced into the *ortho*-positions of the phenyl side group. Compound 3 was synthesized using a Pd $(PPh_3)_4$-mediated carbon-carbon coupling reaction.

Scheme I



The monomer was finally obtained using the bromination of compound 3 and the overall yield of the monomer was about 40 %. Polymerization of the monomer, 4 was performed with an excess of potassium *tert*-butoxide in cooled THF in an ice water bath under N_2 atmosphere. In order to increase the molecular weight and to improve the device performance, copolymerization was carried out with various initial monomer concentration of bis(chloromethyl)-2-(2-ethylhexyloxy)-5-methoxy benzene according to the similar method for the synthesis of *o*-SiPhPPV. The weight average molecular weights (M_w) and polydispersities of the *o*-SiPhPPV, *o*-SiPhPPV-co-MEH-PPV and MEH-PPV for comparison were in the range of 8.0–80.0 x 10^4 and 2.67-7.80, respectively. The resulting EL polymers were completely soluble in common organic solvents, such as chloroform, chlorobenzene, toluene, THF, xylene, etc., ad easily spin-coated onto the ITO coated glass substrate. The structure and thermal stability of the *o*-SiPhPPV, *o*-SiPhPPV-co-MEH-PPV and MEH-PPV were identified by ^{1}H-NMR, UV-

visible spectroscopy and TGA thermogram. The compositions of *o*-SiPhPPV-co-MEHPPV are about 70:30, 50:50, and 30:70 mol % with *o*-SiPhPPV and MEH-PPV units. The TGA thermograms of the *o*-SiPhPPV and *o*-SiPhPPV-co-MEH-PPV revealed a high thermal stability of up to 355-410°C. The high thermal stability of the *o*-SiPhPPV and *o*-SiPhPPV-co-MEH-PPV prevents the deformation of the polymer morphology and degradation of the polymeric emitting layer by applied electric fields of the LED. Figure 1 shows optical absorption spectra of the *o*-SiPhPPV, *o*-SiPhPPV–co-MEH-PPV and MEH-PPV thin films.

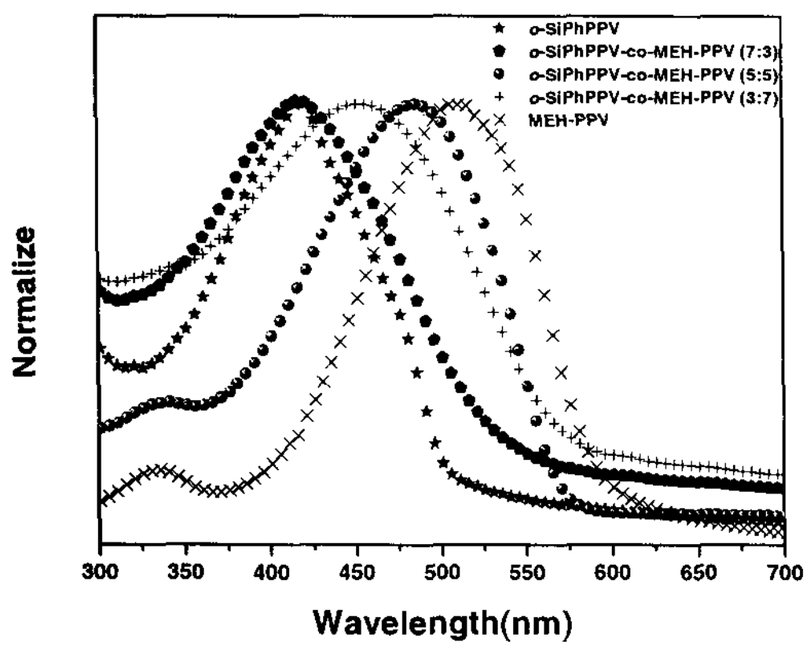


Figure 1. UV-visible absorption spectra of *o*-SiPhPPV, *o*-SiPhPPV-co-MEH-PPV, and MEH-PPV in thin film.

Absorption maximum of the *o*-SiPhPPV is shown at about 420 nm. The maximum absorption spectra of the *o*-SiPhPPV–co-MEH-PPV are more red-shifted than that of o-SiPhPPV. This is due to the introduction of MEH-PPV segment and the extension of the effective conjugation length in copolymers. Figure 2 shows the emission spectra of the *o*-SiPhPPV, *o*-SiPhPPV-co-MEH-PPV, and MEH-PPV thin films under excitation at the absorption maximum wavelength of corresponding polymer. The emission maximum of the *o*-SiPhPPV showed two peaks at about 500 and 530 nm with a shoulder at about 570 nm. As the increasing the MEH-PPV content, the emission peaks of the *o*-SiPhPPV-co-MEH-PPV were red-shifted from 500 and 530 nm to 588 nm. The maximum peaks of the *o*-SiPhPPV-co-MEH-PPV are similar to that of MEH-PPV thin film.

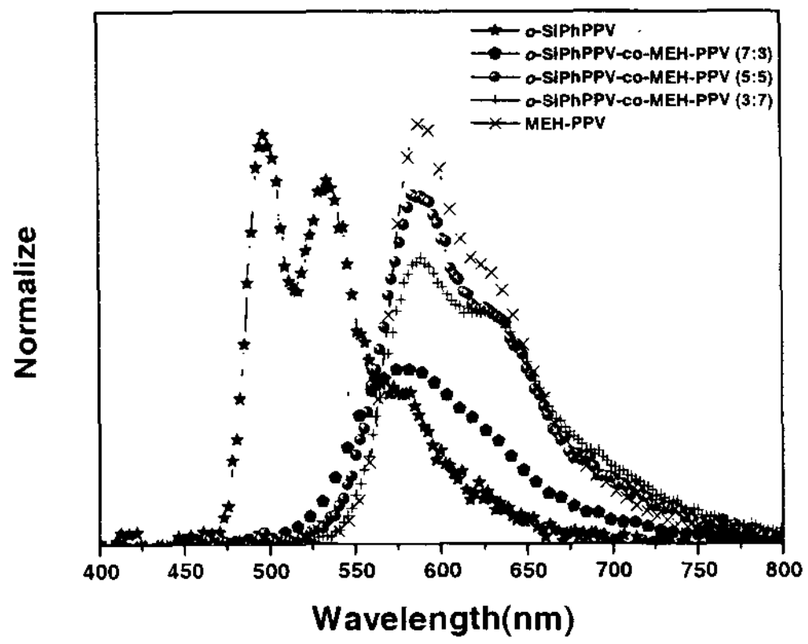


Figure 2. Photoluminescence spectra of *o*-SiPhPPV, *o*-SiPhPPV-co-MEH-PPV, and MEH-PPV in thin film.

The tuning of emission maximum is due to the efficient energy transfer via intramolecular chain interaction in thin film state. The EL spectra were essentially identical to the PL spectra of the resulting EL polymers. The turn-on voltage of the *o*-SiPhPPV is approximately 4.0 V. However, the turn-on voltages of the *o*-SiPhPPV-co-MEH-PPV were observed 1.8–4.0 V, which trend to follow that of MEH-PPV. The current densities of *o*-SiPhPPV and *o*-SiPhPPV-co-MEH-PPV increase exponentially with the increasing forward bias voltage. The luminance intensity of the *o*-SiPhPPV and *o*-SiPhPPV-co-MEH-PPV exponentially increased with an increased voltage. It is expected that the luminance power efficiency of the *o*-SiPhPPV-co-MEH-PPV is higher than that of *o*-SiPhPPV or MEH-PPV.

4. References

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