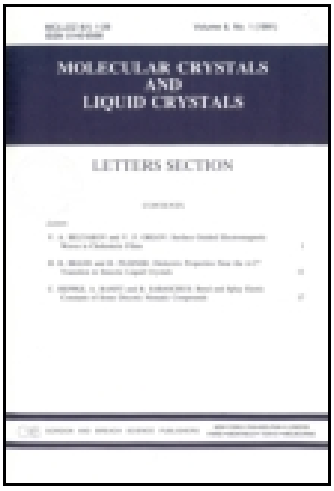

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Synthesis and Characterization of Poly(silole-pyridine)

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Published online: 17 Nov 2014.

To cite this article: Ye Rim Cheon, Yun-Ji Lee, Jeong Cheol Park, Jaeyoung Hwang, Sung-Chul Shin & Yun-Hi Kim (2014) Synthesis and Characterization of Poly(silole-pyridine), Molecular Crystals and Liquid Crystals, 599:1, 125-131, DOI: 10.1080/15421406.2014.935974

To link to this article: http://dx.doi.org/10.1080/15421406.2014.935974

Mol. Cryst. Liq. Cryst., Vol. 599: pp. 125–131, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.935974

Synthesis and Characterization of Poly(silole-pyridine)

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New poly(silole-pyridine) was designed and synthesized. Polymer was obtained by Yamamoto coupling reaction. The structure of obtained polymer was characterized by the spectroscopic methods such as FT-IR and ^{1}H-NMR. The resulting polymer was soluble in common organic solvents such as toluene, tetrahydrofurane, chloroform, chlorobenzene, etc. The obtained polymer showed good thermal stabilities, which was characterized by TGA and DSC.

Keywords Polymer organic light-emitting diode; pyridine; polysilole; energy transfer

Introduction

Organic light-emitting diodes (OLEDs) [1–8] have been profitably employed in small-sized flat panel display [9]. Polymer light-emitting diodes (PLEDs) [10–12] have also attracted considerable interest due to their applications in large-area flat panel displays [13] with high-efficiency. For the highly efficient PLED devices, charge injection and transport from both the anode and cathode should be balanced at the emitting layer to yield maximum exciton formation [14,15].

Silole-containg molecules have low LUMO energy level by a $\sigma^* \rightarrow \pi^*$ conjugation and increase their electron affinities [16–18] and have been used as electron-transporting [19,20] by the high electron mobility. Pyridine is very useful moiety in OLED and PLED, which was important factor in determining the electro-injection properties and OLED properties. To enhance the electron mobility of organic semiconductors, aza-aromatics such as phenanthroline, quinoline, pyridine and triazole have been incorporated into π-conjugated systems [21–25].

In this study, we designed the polymer which is composed of pyridine and silole unit as possessing high electron transport ability. We studied the physical, optical, electrochemical and thermal properties of new obtained polymer.

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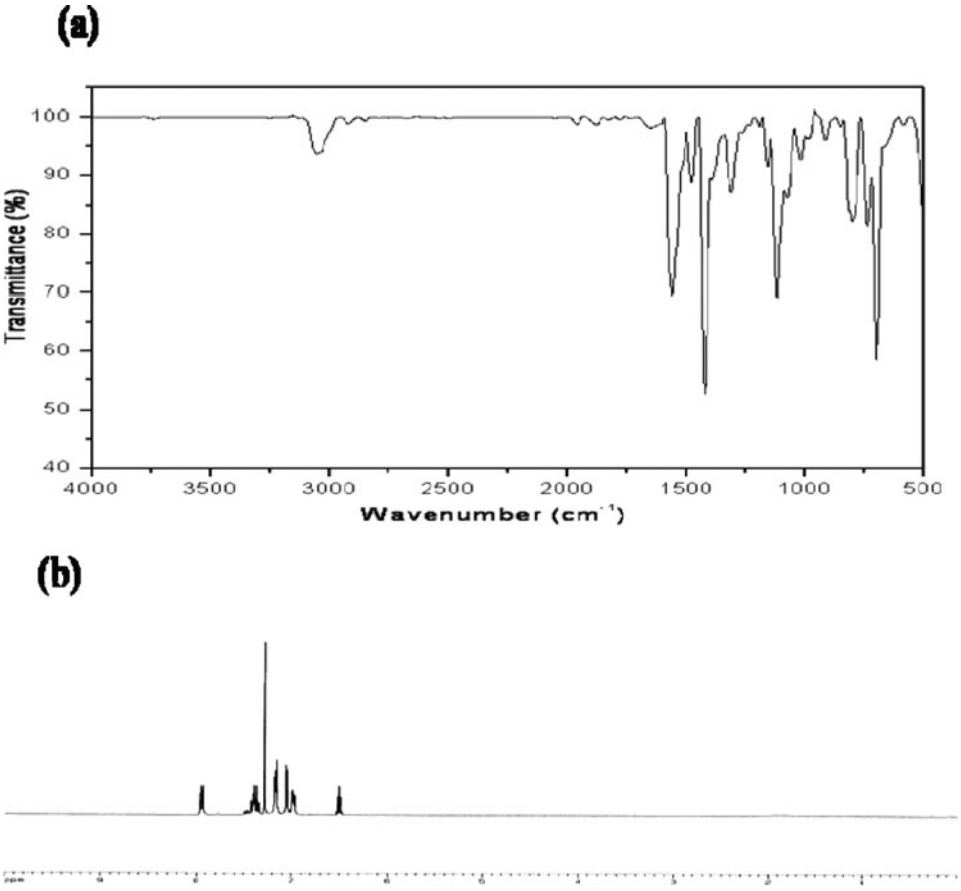


Figure 1. The spectrum of polymer (a) FT-IR, (b) ^{1}H-NMR.

Experimental

Synthesis

Synthesis of bis(phenylacetyl)diphenylsilane. n-Butyllithium (2.5 M in hexane, 70.8 mL, 0.761 mol) was slowly added to phenyl acetylene (13.9 g, 0.136 mol) in anhydrous tetrahydrofuran (THF) (200 mL) at −78°C. After 1 h stirring at room temperature, diphenyl dichlorosilane (15 g, 0.059 mol) was slowly dropped into the mixture at −78°C and stirred at room temperature. After 12 h, the reaction was terminated by the addition of ice water and extracted with ethyl acetate (EA). The crude product was purified by column chromatography and re-crystallization with hexane/EA: 20/1 as eluent. Yield: 13 g (57%). m.p: 174°C. FT-IR (KBr) (cm^{-1}): 3069-3000 (aromatic C−H), 1487, 1441, 1426 (aromatic C = C), 2148 (C=C), 1112 (Si−C); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) $\delta = 7.89 \sim 7.92$ (dd, 4H), $7.60 \sim 7.74$ (dd, 4H), $7.35 \sim 7.51$ (m, 6H), $7.09 \sim 7.28$ (m, 6H). Anal. Calcd. for $C_{28}H_{20}Si$: C, 87.45; H, 5.24. Found: C, 86.85; H, 5.30.

2,5-Di(bromopyridyl)-1,1-diph-enyl-3,4-diphenylsilole was synthesized in the second step. Lithium (0.032 g, 0.004 mol) and naphthalene (4.2 g, 0.032 mol) in THF (50 mL) were stirred for 6 h. Bis(phenylacetyl)diphenylsilane (3 g, 0.007 mol) in THF was dropped to the mixture at −78°C. After 1 h stirring at room temperature, 1 M $ZnCl_2$ was slowly added to

Table 1. The thermal, optical and electrochemical properties of the polymer

	M_n	M_w	PDI	T_g (°C)	$T_{5\%}$ (°C)	UV (nm) film	PL (nm) film	HOMO (eV)	LUMO (eV)	E_{onset}^{red} (V)
Poylmer	5,300	5,800	1.09	92	292	400	511	–	−3.0	−1.40

the mixture at 0°C and stirred for further an hour. 2,6-Dibromopyridine (3.8 g, 0.016 mol) and $PdCl_2(PPh_3)_2$ was added and the result solution was refluxed for 16 h at 85 ∼ 90°C. Once the reaction was completed, the crude product was worked up with water. The product was extracted with EA. The crude product was purified by column chromatography with

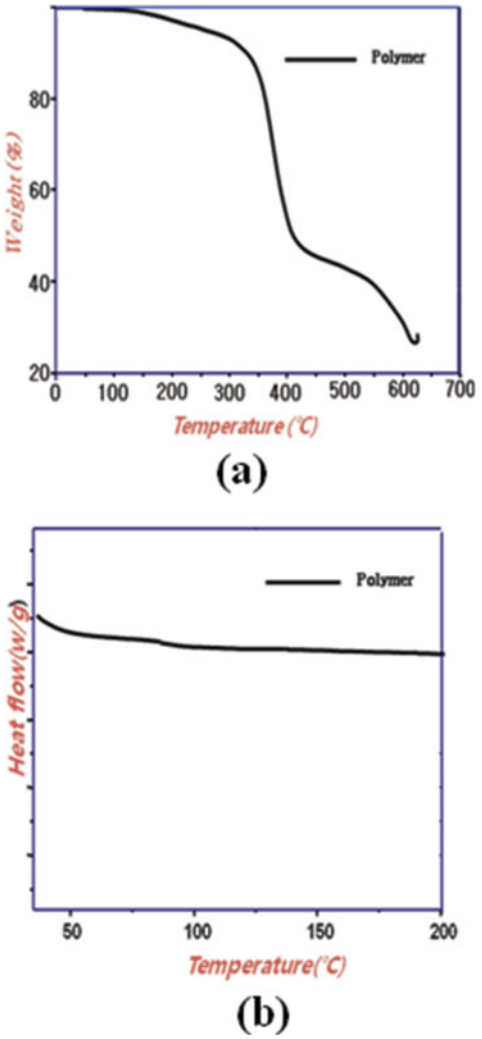


Figure 2. The thermal properties of polymer (a) TGA and (b) DSC curve.

Table 2. Solubility of polymer

Solvent	n-Hexane	Methanol	Ethyl acetate	DMF	Methylene chloride	Chloroform	Toluene	THF	Chlorobenzene
Poylmer	−	−	++	−+	++	++	++	++	++

++: soluble, −+: partially soluble, −: insoluble.

hexane/EA: 20/1 as eluent and re-crystallization with methylene chloride (MC) and hexane. Yield: 2 g (36%). m.p: 244 ∼ 255°C. FT-IR (KBr) (cm^{-1}): 3046 (aromatic C−H), 1465, 1427 (aromatic C=C), 1566 (C=N), 1116 (Si−C), 1023 (C−Br); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) $\delta = 7.9$ (d, 4H), 7.3 ∼ 7.45 (m, 6H), 7.12 ∼ 7.2 (t, 6H), 7.09 ∼ 6.9 (m, 8H), 6.35 ∼ 6.45 (m, 2H). Anal. Calcd. for $C_{38}H_{26}Br_2N_2Si$: C, 65.34; H, 3.75; N, 4.01. Found: C, 55.14; H, 3.85, N, 4.26.

Bis(1,5-cyclooctadiene) nickel(0) ($Ni(COD)_2$) (0.70 g, 2.541 mmol), dipyridyl (0.40 g, 2.562 mmol), 1,5-cyclooctadiene (0.3 g, 2.771 mmol) in anhydrous DMF (10 mL) and toluene (10 mL) was refluxed for 30 min at 80°C. 2,5-Di(bromopyridinyl)-1,1-diphenyl-3,4-diphenyl silole (1 g, 1.453 mmol) was added to the mixture and refluxed for further 72 h at 80°C. Bromobenzene was injected into the reaction mixture and the reaction was stirred for 24 h. The crude mixture was worked up with HCl/acetone/methanol : 1/1/1 (v/v). After precipitation from methanol, the desired polymer was obtained. We can get poly(2,5-dipyridyl-1,1-diphenyl-3,4-diphenylsilole). Yield: 0.3 g (37%). FT-IR (KBr) (cm^{-1}): 3046 (aromatic C−H), 1413 (aromatic C=C), 1560 (C=N), 1112 (Si−C); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) $\delta = 7.9$ (d, 6H), 7.34 ∼ 7.42 (m, 6H), 7.14 ∼ 7.19 (t, 6H), 7.05 ∼ 6.96 (m, 8H), 6.48 ∼ 6.51 (m, 2H).

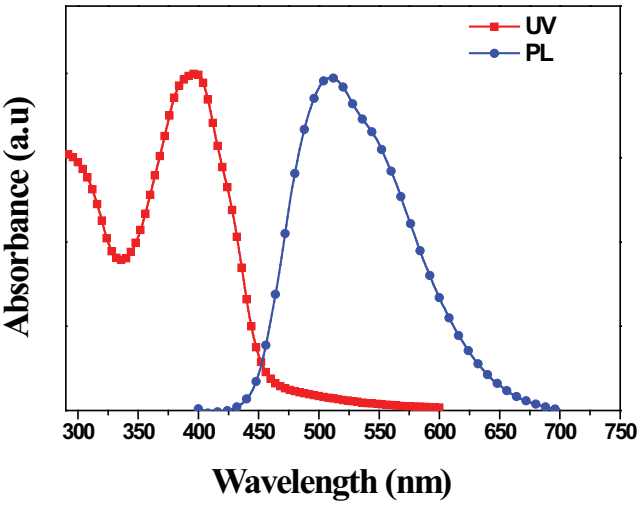
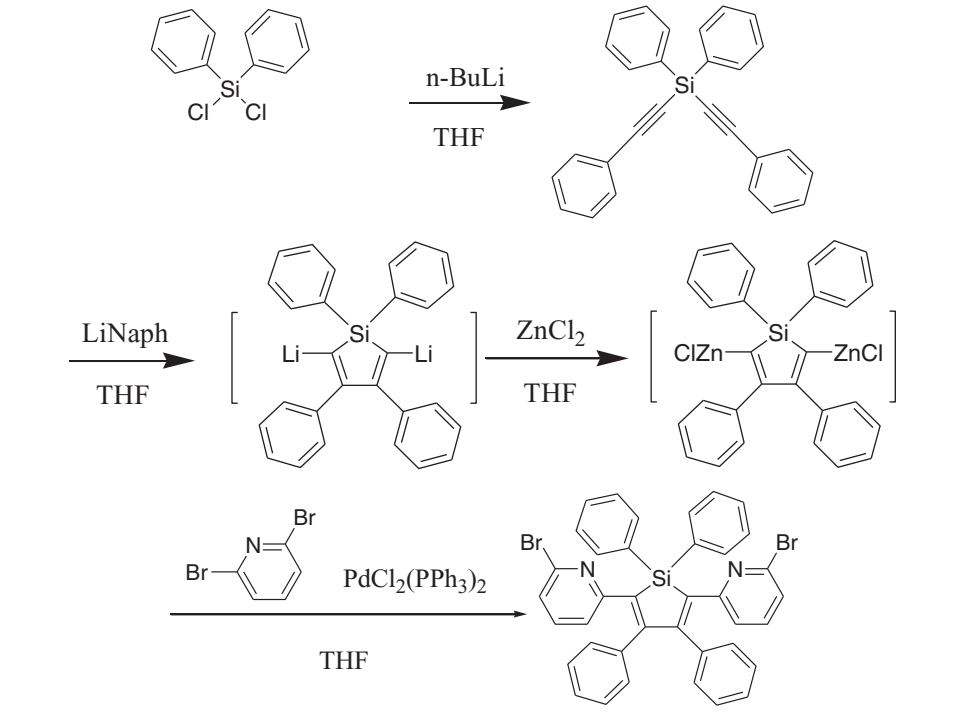
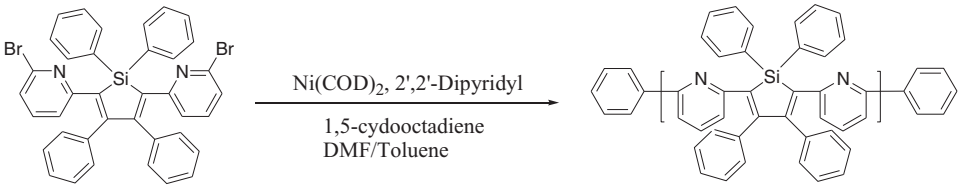


Figure 3. The optical properties of copolymer (a) UV-visible spectra in film, (b) PL spectra in film.



(a)



(b)

Scheme 1.

Measurements

^{1}H nuclear magnetic resonance (NMR) spectra were recorded using DRX 300 MHz Bruker spectrometer and chemical shifts in spectra were reported in parts per million (ppm) units with tetramethylsilane as internal standard. Infrared (IR) studies of the samples were carried out using a Genesis II FT-IR spectrometer. A Jeol JMS-700 mass spectrometer was used to obtain the mass spectra of the samples. Thermogravimetric analysis (TGA) was performed under nitrogen using a TA instrument 2025 thermogravimetric analyzer. The sample was heated from 50°C to 800°C with a heating rate of 10°C/min. Differential scanning calorimeter (DSC) studies were carried out under nitrogen using a TA instrument 2100 differential scanning calorimeter. The sample was heated from 30°C to 300°C with a heating rate of 10°C/min. UV-visible absorption and photoluminescence (PL) studies at room temperature were carried out using Perkin Elmer LAMBDA-900 UV/VIS/NIR

spectrometer and LS-50B lumininescence spectrophotometer. Cyclic voltammogram (CV) of the sample was recorded using a Epsilon E3 at room temperature in a 0.1 M solution of tetrabutylammonium perchlorate (Bu_4NClO_4) in acetonitrile under nitrogen environment at a scan rate of 50 mV/s. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (waters high-pressure GPC assembly Model M515 pump, u-Styragel columns of HR4, HR4E, HR5E, with 500 and 100 Å, refractive index detectors, solvent THF).

Results and Discussion

The synthetic scheme of polymer was prepared as depicted in scheme 1. Polymer was obtained by Yamamoto coupling reaction using ($Ni(COD)_2$). The obtained polymer was purified by precipitation using methanol. The structure of polymer was confirmed by FT-IR and ^{1}H-NMR (Fig. 1). The FT-IR spectrum of the polymer indicated that the chemical structure. C-Br peak (1023 cm^{-1}) of 2,5-di(bromopyridyl)-1,1-diph-enyl-3,4-diphenylsilole was not founded in this spectrum. The structure was confirmed by the proton peak at 7.9∼6.28 ppm in ^{1}H-NMR. Gel permeation chromatography (GPC) analysis determined the weight average molecular weight (M_W) to be 5,800 with a polydispersity index (PDI) of around 1.09, against polystyrene standards. The molecular weights and polydispersity indexes of the polymer was summarized in Table 1. The polymer showed good solubility in common organic solvents, such as methylene chloride, tetrahydrofuran, chloroform, toluene and chlorobenzene (Table 2).

The thermal properties of the polymer were evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The 5% weight loss of the polymer was observed at 292°C. From the DSC data of the polymer the glass transition temperature (T_g) was observed at 92°C (Fig. 2).

The UV-visible absorption and photoluminescence spectra of the polymer in film state are shown in Fig. 3. The UV-visible absorption was indicated at 400 nm in film and the PL absorption was indicated at 511 nm, at film. The electrochemical behaviors of these polymers were investigated by cyclic voltammetry (CV). They were summarized in Table 1. LUMO energy level was −3.0 eV. The polymer shows low LUMO energy level because of electron-withdrawing property of silole moiety and pyridine. [26, 27] The polymer OLED will be characterized by using obtained polymer as emitting layer as well as electron transporting layer.

Conclusions

The new polymer composed of silole and pyridine was synthesized by Yamamoto coupling reaction. The LUMO level of polymer was very low because of introduction of non-copolanar silole unit and pyridine unit, which are good electron transporting.

Funding

This research was supported by Industrial Strategic Technology Development Program (10045269) by MOTIE/KEIT.

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