

Synthesis and Properties of Poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole)

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ABSTRACT

Grignard metathesis (GRIM) polymerization of 1,1-diisopropyl-2,5-dibromo-3,4-diphenylsilole (**3**) was carried out to afford poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (**4**) containing fluorescent aromatic chromophore groups such as phenyl and silole in the polymer main chain. The prepared material is soluble in common organic solvents such as CHCl_3 and THF. FTIR spectrum of the polymer exhibits the characteristic C=C stretching frequency at 1622 cm^{-1} . In the THF solution, the prepared polymeric material shows strong maximum absorption peaks at 240 and 273 nm, a strong maximum excitation peak at 276 nm, and strong maximum fluorescence emission bands at 440 nm. TGA thermogram indicates that the polymer is stable up to 200°C with a weight loss of about 10% in nitrogen.

Key words : Absorption, Fluorescence, Grignard metathesis (GRIM) polymerization, Poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole), Polycarbosilane

Introduction

Organosilicon polymeric materials bearing π -conjugated groups have attracted considerable interest due to their potential applications [1,2]. Fluorescent organosilicon polymers have also been of great interest for the use in electroluminescence materials [3]. As the instances of polymeric materials, polysiloxanes containing fluorophores such as pyrene or carbazole in the polymer side chain were synthesized by hydrosilation reactions of poly(methylhydrosiloxane) with vinyl- or allyl-functionalized pyrene or carbazole in the presence of Pt catalyst [4].

Silacyclopentadienes, also called siloles, are a series of five-membered silacyclic dienes that contain π -electron system. π -Conjugated materials containing siloles have also received a great deal of attention for potential applications in the area of electronic, photoluminescence, and sensors [5,6]. End-capped silole dendrimers on an ethenyl-phenyl carbosilane periphery also exhibit green to greenish-blue fluorescence for potential electroluminescent materials [7]. However, synthesis of poly-

(1,1-diisopropyl-3,4-diphenyl-2,5-silole)s has not been reported yet [8].

We have reported the melt copolymerizations of 1,3-bis(diethylamino)tetramethyldisiloxane with several fluorescent aryl-diols to yield poly(arylcarbottetramethyldisiloxane)s that contain fluorescent aromatic chromophores in the main chain [9]. We have also reported the melt copolymerization of several bis(diethylamino)silane derivatives with 2,7-dihydroxyfluorene-9-one to yield poly[oxy(2,7-fluorene-9-onenylene)oxy(dio-rgnaosilylene)]s that contain fluorene-9-one as a fluorescent aromatic chromophore group in the main chain [10].

Very recently, we have also reported the melt copolymerization of 1,2-bis(diethylamino)tetramethyldisilane with several aryl-diols to afford poly[oxy(arylene)oxy(tetramethyldisilylene)]s containing fluorescent aromatic chromophore groups in the polymer main chain [11].

In general, aryl and heteroaryl conjugating polymers have usually been synthesized by through metal-catalyzed polycondensation reactions based on Yamamoto, Suzuki, or Stille coupling reactions including the Grignard metathesis (GRIM) me-

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thod [12,13]. In GRIM, Ni (II) complexes are used to polymerize functionalized Grignard monomers at room temperature, which has some advantages over previous procedures [14]. Very recently, to expand GRIM applicability, “turbo-Grignard” reagents (LiCl plus a Grignard reagent) were used for the synthesis of a variety of aryl and heteroaryl conjugated polymers [15]. The GRIM method can shorten polymerization times and lower reaction temperatures, facilitating the preparation of aryl and heteroaryl conjugating polymers [16].

With these results in mind, we have extended our study to the preparation and photoelectronic properties of fluorescent poly(carbosilane) materials containing an aromatic chromophore group of silole derivatives in the polymer main chain.

Here we report the synthesis of poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (**4**) via Grignard metathesis polymerization of 1,1-diisopropyl-2,5-dibromo-3,4-diphenylsilole (**3**) by utilizing a so-called “turbo-Grignard” reagent, i.e., LiCl plus a Grignard reagent. The material obtained was characterized by FTIR and ^1H , ^{13}C , and ^{29}Si NMR spectrophotometry in the solution state along with by elemental analysis. We have investigated the photoelectronic and thermal properties of the prepared polymer **4** using absorption, excitation, and fluorescence emission spectrophotometers in the solution state as well as thermogravimetric analysis (TGA).

Materials and Methods

1. General procedures

All synthetic manipulations were carried out by standard vacuum-line Schlenk techniques under nitrogen or argon. All glassware was assembled and then flame-dried while being swept with argon before reaction. Chemicals were purchased from Aldrich Aldrich Chemicals Inc. and used as received. Tetrahydrofuran was distilled from sodium benzophenone ketyl before use [17].

^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy was performed on a Varian Mercury Plus 300 or a Bruker DRX Avance 400 MHz FT-NMR spectrometers using CDCl_3 as solvent. ^{29}Si nuclear magnetic resonance (NMR) spectroscopy was performed on Varian Unity INOVA 500 MHz FT-NMR spectrometer at the Daegu Center of the Korea Basic Science Institute using CDCl_3 as solvent. The chemical shifts are expressed in ppm relative to tetramethylsilane (TMS) as an internal standard or the residual proton signal of the solvent as standard. IR

spectra were recorded by a Shimadzu IR 430 spectrometer or a Bruker IFS-48 FT-IR spectrometer. Gel permeation chromatography (GPC) analyses were performed on a Waters 1525 pump and Breeze software system with a Waters Styragel HR 3 column and refractive index detector at 40°C . The eluent was THF at a flow rate of 1.0 mL/min. Calibration was done with a series of monodispersed polystyrene standards: M_p 580, 3250, 10100, and 28500 whose a M_w/M_n value is less than 1.2. UV-vis absorption spectra were obtained on a Hewlett Packard 8453 spectrophotometer. Excitation and fluorescence emission spectra were taken on a Spex Fluorolog-3-11 fluorescence spectrophotometer. Thermogravimetric analysis (TGA) of polymer samples was performed on a TGA-50 Shimadzu thermal analysis system. The temperature was increased at the heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C with nitrogen flow rate of 20 mL/min.

2. Synthesis of Diisopropyl-bis(phenylethynyl)silane (2)

A three-necked flask equipped with a thermometer, rubber septa and magnetic stir bar was charged with phenylacetylene (25.5 mL, 232 mmol) and THF (180 mL). The solution was cooled to -70°C in a dry ice/acetone bath. *n*-Butyllithium (2.5 M, 78.6 mL, 197 mmol) was added via syringe into the stirring solution under a stream of argon. The acetone/dry ice bath was replaced with an ice/water bath. When the reaction temperature reached approximately -5°C , dichloroisopropylsilane (16.7 mL, 92.8 mmol) was added dropwise via syringe. The solution was allowed to warm to room temperature with stirring. The reaction mixture was poured into aqueous ammonium chloride solution (200 mL). The organic phase was separated using a separatory funnel and an aqueous layer was extracted with diethylether. The combined organic layer was washed with water and brine, then was dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation and vacuum. A reddish yellow liquid as product (29.3 g, 99%) was obtained after volatile substances were removed under vacuum during an overnight. ^1H NMR (300 MHz, CDCl_3) δ 1.22-1.25 (m, 14H), 7.33-7.36 (m, 6H), 7.53-7.57 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 12.75, 17.95, 87.83, 107.35, 123.08, 128.39, 128.95, 132.39. ^{29}Si NMR (99.36 MHz, CDCl_3) δ -23.13 .

3. Synthesis of 2,5-Dibromo-1,1-diisopropyl-3,4-diphenylsilole (3)

A three-necked flask equipped with a thermometer, rubber

septa and magnetic stir bar was charged with lithium (0.53 g, 75.6 mmol), naphthalene (10.12 g, 79.0 mmol) and THF (50 mL) under a stream of argon. The reaction mixture was left to stir at room temperature for 3 hrs to dissolve the lithium. The solution of diisopropylbis(phenylethynyl)silane (**2**) (5.25 g, 16.8 mmol) in THF (120 mL) was added to the lithium naphthalenide dropwise over 20 min via cannula. Once the addition was complete, the solution was cooled to -10°C using an acetone bath with a small amount of dry ice. The solution of anhydrous ZnCl_2 (11.45 g, 84.0 mmol) in 70 mL of THF was added to the naphthalenide/silane mixture via cannula over 20 min. The acetone/dry ice bath was removed and the resulting solution was allowed to warm to room temperature. Meanwhile a three-necked, foil-wrapped, round-bottomed flask equipped with a thermometer, stir bar and rubber septa was charged with *N*-bromosuccinimide (7.45 g, 41.9 mmol) and THF under argon atmosphere. The resulting solution was cooled to -70°C using a dry ice/acetone bath. The silane solution was added into the cold NBS solution via cannula such that internal temperature did not exceed -50°C . After the addition was complete the resulting mixture was stirred for a further 30 min at -70°C . The reaction mixture was poured into aqueous ammonium chloride solution (200 mL). The organic phase was separated using a separatory funnel and an aqueous layer was extracted with ethylether. The combined organic layer was washed with aqueous sodium thiosulfate solution, water and brine, then was dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evaporation. The crude product of naphthalene-silole mixture was sublimed under vacuum at 35°C . The residual material from sublimation was dissolved in hot hexane followed by cooling in a freezer. A pale brownish crystalline solid **3** as product (2.40 g, 30%) was obtained by vacuum filtration. ^1H NMR (300 MHz, CDCl_3) δ 1.27 (d, $J=6.9$ Hz, 12H), 1.46-1.58 (m, 2H), 6.92-6.96 (m, 4H), 7.14-7.27 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 10.05, 17.41, 120.03, 127.57, 127.78, 129.19, 137.55, 158.14. ^{29}Si NMR (99.36 MHz, CDCl_3) δ 7.46.

4. Synthesis of Poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (**4**)

1) Preparation of *i*-PrMgCl.LiCl.

A three-necked flask was charged with *i*-PrMgCl in THF (2 M, 2.10 mL, 4.20 mmol) and 5 mL of anhydrous THF. Lithium chloride (0.18 g, 4.2 mmol) was added to the reaction flask under nitrogen. The reaction mixture was stirred for 8 hrs at room temperature.

2) Poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (**4**)

A solution of 2,5-dibromo-1,1-diisopropyl-3,4-diphenylsilole (**3**) (2.00 g, 4.20 mmol) in 5 mL of anhydrous THF was added under nitrogen to the previously prepared solution of *i*-PrMgCl.LiCl (4.20 mmol). The reaction mixture was stirred at room temperature for 17 hrs. $\text{Ni}(\text{dppp})\text{Cl}_2$ (0.018 g, 0.034 mmol) was added to the reaction mixture dissolved in 10 mL anhydrous THF. The polymerization was allowed to proceed for 48 hrs at room temperature followed by quenching of the reaction mixture with methanol. The precipitated polymer was separated and dried under reduced pressure. A pale yellow powder **4** as product, (0.54 g, 41%), was obtained. ^1H NMR (300 MHz, CDCl_3) δ 1.12-1.54 (m, 14H), 6.92-7.24 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3) δ 10.07, 10.56, 17.41, 18.01, 18.30, 120.04, 124.63-129.36 (m), 137.56-140.98 (m), 156.87-163.11 (m). ^{29}Si NMR (99.36 MHz, CDCl_3) δ 7.03. IR (KBr disk): ν 3068, 2941, 2863 ($\nu_{\text{C-H}}$), 1622 ($\nu_{\text{C=C}}$), 1459, 1079, 698, 578 (cm^{-1}). GPC (THF) $M_w=658$, $M_n=610$, PDI=1.08.

The excitation and fluorescence emission spectra in THF solution as well as TGA thermogram for polymer **4** are described in Results and Discussion.

Results and Discussion

1. Synthesis of monomer and polymer

2,5-Dibromo-1,1-diisopropyl-3,4-diphenylsilole (**3**) as monomer was prepared by two step reactions as shown in Scheme 1. In the first step, dichlorodiisopropylsilane (**1**) as starting material was reacted with phenylethynyllithium, which was prepared by reaction of phenylacetylene with *n*-butyllithium in THF at -70°C , to yield diisopropylbis(phenylethynyl)silane (**2**) quantitatively. In the second step, the intramolecular reductive cyclization of **2** was carried out by the treatments of 4 mol of lithium naphthalenide followed by anhydrous ZnCl_2 and *N*-bromosuccinimide, finally afforded the monomer **3** [5].

The monomer **3** was characterized using NMR spectrometer. As shown in Fig. 1, the ^1H NMR spectrum of **3** exhibits clearly doublet and multiplet resonances at 1.27 and 1.54 ppm, respectively, attributed to the protons of isopropyl group bonded to silicon [18,19]. In the ^{13}C NMR spectrum of **3**, two carbon peaks of the isopropyl group bonded to the silicon are observed at 10.05 and 17.41 ppm [18,19]. In the ^{29}Si NMR spectrum of **3**, the single silicon resonance is observed at 7.46 ppm [20]. The intramolecular reductive cyclization reaction of diisopro-

pylbis(phenylthynyl)silane **2** was completed under this reaction condition to yield 2,5-dibromo-1,1-diisopropyl-3,4-diphenylsilole **3**.

To apply Grignard metathesis (GRIM) polymerization, a so-called “turbo-Grignard” reagent, i.e., LiCl plus a Grignard reagent [14], is used for the synthesis of poly(2,5-silole)s. A Ni(II) complex such as [1,3-bis(diphenylphosphine)propane]dichloronickel(II) (Ni(dppp)Cl₂) is also used to polymerize functionalized Grignard monomer at room temperature [14]. The addition of lithium chloride to a Grignard reagent dissociates the polymeric aggregates formed in solution to produce a very reactive complex [*i*-PrMgCl₂⁻Li⁺].

A solution of 2,5-dibromosilole **3** as monomer in THF was added to *i*-PrMgCl.LiCl and stirred for 17 hrs at room temperature to result in magnesium halogen exchange reaction as shown

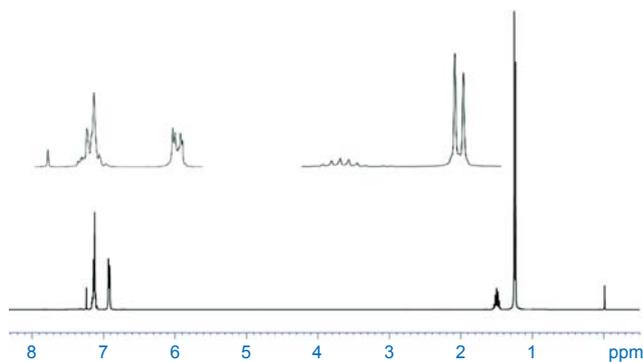
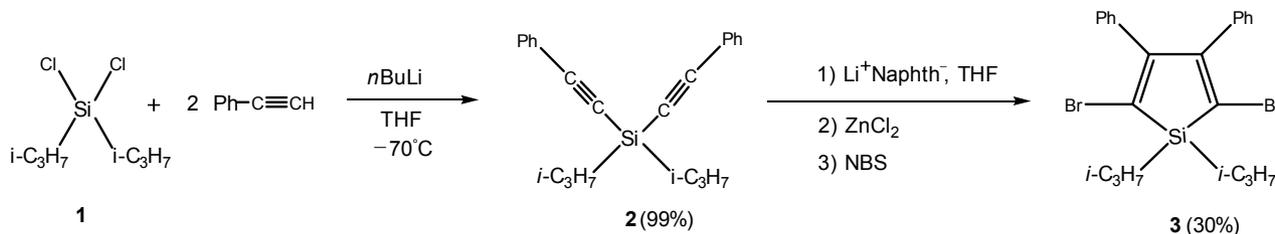


Fig. 1. ¹H NMR spectrum of the monomer **3** in CDCl₃.

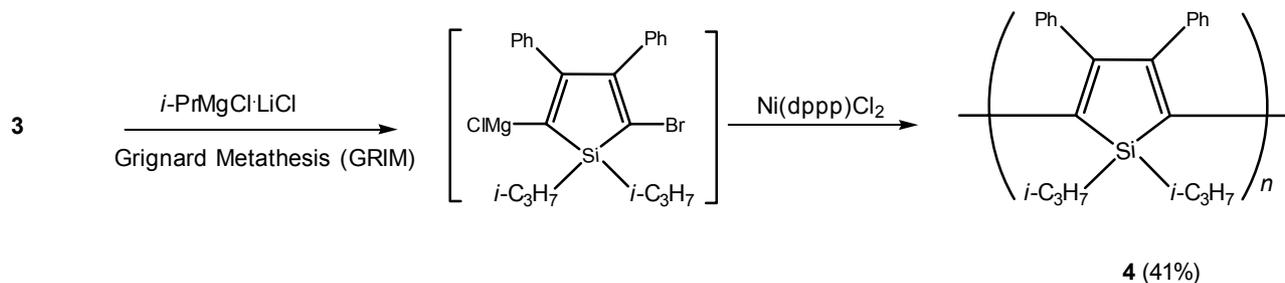
in Scheme 2. Then polymerization was allowed to proceed for 48 hr by addition of Ni(dppp)Cl₂ to the reaction mixture. A redish yellow powder poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) (**4**) was obtained.

The prepared poly(2,5-silole) **4** is soluble in common organic solvents such as CHCl₃ and THF. We determined molecular weight of the polymer **4** using gel permeation chromatography (GPC) in THF as an eluent. The observed weight average molecular weights (*M_w*) of material **4** was 658 with the polydispersity of 1.08, indicating that the obtained material **4** is oligomeric. This phenomenon seems to be explained by considering the steric bulkiness of 1,1-diisopropyl-3,4-diphenylsilole **3** used as monomer.

We characterized the polymer **4** by using several spectroscopic methods such as NMR and IR spectrometers. FTIR spectrum of the polymer **4** shows the characteristic C=C stretching frequency at 1622 cm⁻¹, suggesting that C=C bonds conjugated with alkene double bond are newly formed during the copolymerizations [21]. In CDCl₃ solution, ¹H NMR of **4** shows a broad multiplet peak at 1.12-1.54 ppm and a broad multiplet peak at 6.92-7.24 ppm due to isopropyl and phenyl groups, respectively [18,19]. The ²⁹Si NMR spectrum of the polymer **4** shows that the major singlet resonance peak appears at 7.03 ppm [20], indicating that the silicon atoms in the polymer main chain have the structural environment of silole groups, and suggesting structures consistent with the backbone shown in Scheme 2.



Scheme 1.



Scheme 2.

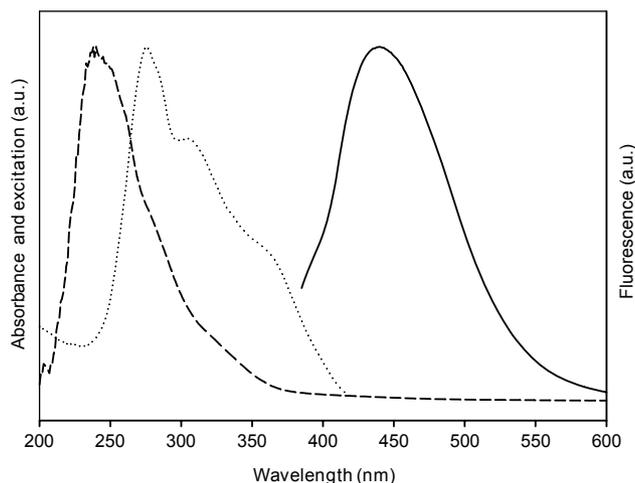


Fig. 2. Absorbance (dashed line, $\lambda_{\text{max}}=240, 273$ nm), excitation (dotted line, $\lambda_{\text{det}}=440$ nm) and fluorescence (solid line, $\lambda_{\text{ex}}=276$ nm) spectra of the polymer **4** in the THF solution.

2. Properties of polymer

Absorption, excitation, and fluorescence emission spectra of the polymer in THF solution were inspected. An absorption spectrum of the polymer **4** in THF is shown in Fig. 2 as a dashed line. The maximum absorption bands for **4** are observed at 240 and 273 nm with the molar absorptivities of 3.80×10^3 and $1.78 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$, respectively, and the bands extend from 240 to 430 nm. These strong absorption bands in the UV-vis spectra of **4** may be attributed to the aryl groups conjugated along the polymer backbone [3].

The excitation spectrum for **4** at the detection wavelength of 440 nm shows a strong excitation peak at the $\lambda_{\text{ex, max}}$ of 276 nm. An excitation spectrum of the polymer **4** in THF solution is shown in Fig. 2 as a dotted line. This strong excitation bands in the excitation spectrum of the polymer **4** may be attributed to the aryl groups conjugated along the polymer backbone [3].

The fluorescence emission spectrum for **4** at the excitation wavelength of 276 nm in THF solution reveals a strong emission peak at the $\lambda_{\text{em, max}}$ of 440 nm. A typical fluorescence spectrum of the polymer **4** in the THF solution is shown in Fig. 2 as a solid line. This strong emission band in the fluorescence spectrum of the polymer may be ascribed to the fluorophore of aryl groups conjugated along the polymer backbone [3]. Both excitation and fluorescence emission spectra of the polymers imply that the polycarbosilane **4** has chromophores containing the aryl functional groups conjugated along the polymer main chains [3]. Ultrafast time-resolved kinetic study may be required in order to further investigate the electronic conjugation pro-

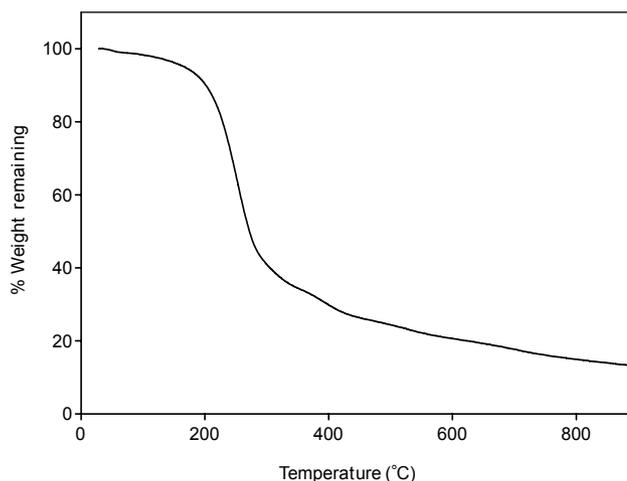


Fig. 3. TGA thermogram of the polymer **4** in nitrogen.

erties of the prepared materials.

The thermal stability of poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) **4** in a nitrogen atmosphere was evaluated by thermogravimetric analysis (TGA) with a heating rate of $10^\circ\text{C}/\text{min}$ (Fig. 3). Polymer **4** is stable up to 200°C with only 10% weight loss of the initial weight in nitrogen. Weight loss of polymer **4** occurs rapidly upon heating above 200°C . Rapid weight loss of 70% of the initial weight occurs between 200 and 600°C . Additionally, weight loss of 8% of the initial weight occurs between 600 and 900°C . When **4** is heated up to 900°C , 88% of the initial weight of the polymer is lost, and about 12% of char yield is observed.

Conclusion

We have successfully prepared poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) **4** by Grignard metathesis (GRIM) polymerization of 2,5-dibromo-1,1-diisopropyl-3,4-diphenylsilole **3**. The prepared material is soluble in common organic solvents such as CHCl_3 and THF. The polymer was characterized by using several spectroscopic methods in the solution states. In particular, FTIR spectrum of the polymeric material shows that the characteristic conjugated $\text{C}=\text{C}$ stretching frequency appears at 1622 cm^{-1} . The material in the THF solution shows strong maximum absorption bands at 240 and 273 nm, strong maximum excitation peaks at 276 nm, and strong maximum emission band at 440 nm. All the absorption, excitation, and emission spectra suggest that the obtained poly(1,1-diisopropyl-3,4-diphenyl-2,5-silole) contains the aromatic chromophore groups

conjugated in the polymer main chain. According to TGA the polymer is stable up to 200°C with a weight loss of 10% in nitrogen.

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