

# Synthesis and Properties of Copolymer Containing 1,1-Diethyl-3,4-diphenyl-2,5-silolene and Diphenylgermylene Groups

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## ABSTRACT

Polycarbogermosilane copolymer containing 1,1-diethyl-3,4-diphenyl-2,5-silolene and diphenylgermylene, such as poly[(1,1-diethyl-3,4-diphenyl-2,5-silolene)-*co*-(diphenylgermylene)], was prepared for its possible application to the energy storage material. The Fourier-transform infrared (FTIR) spectrum of the copolymer shows the characteristic diene stretching frequency at  $1596\text{ cm}^{-1}$ . The obtained material is highly soluble in common organic solvents such as tetrahydrofuran (THF) and chloroform. According to gel permeation chromatography (GPC) the average molecular weight of the polymer was determined as 659/629 ( $M_w/M_n$ ) with polydispersity of 1.04. The prepared material in tetrahydrofuran solvent shows strong absorption maximum peak at 259 nm along with shoulder band of 299 nm extending from 259 to 400 nm in the UV-visible absorption spectrum, strong excitation maximum peak at 287 nm, and strong emission maximum peak at 376 nm in the fluorescence emission spectrum. All the absorption, excitation, and emission spectra above mentioned are indicative of chromophores of phenyl and diene groups along the polymer backbone. Thermogravimetric analysis (TGA) shows that the copolymer is thermally stable up to  $200^\circ\text{C}$  with a weight loss of 7% only in nitrogen.

**Key words :** 2,5-Dibromo-1,1-diethyl-3,4-diphenylsilole, Copolymerization, Electronic properties, Poly[(1,1-diethyl-3,4-diphenyl-2,5-silolene)-*co*-(diphenylgermylene)], Thermal stability

## Introduction

Organosilicon copolymeric materials containing germylene group have received considerable attention due to their potentially useful applications [1-4]. Organosilicon polymers composed of fluorescent groups are also of great interest for application in electroluminescence as well as semiconductor materials [5,6].

Silacyclopenta-2,4-dienes called as siloles are a series of five-membered silacyclic dienes containing unique  $\pi$ -electron system of low-lying lowest unoccupied molecular orbital (LUMO) level, which are associated with  $\sigma^*$ - $\pi^*$  conjugation arising from the interaction between the  $\sigma^*$  orbital of two exocyclic  $\sigma$ -bond on the silicon atom and the  $\pi^*$  orbital of

butadiene group [7,8].  $\pi$ -Conjugated polymers containing siloles have also received much attention for potential optoelectronic, photoluminescence [9,10], and sensor applications [11]. End-capped silole dendrimers containing an ethenyl-phenyl-carbosilane skeleton exhibit green to greenish-blue fluorescence and have potential applications as electroluminescent materials [12]. However, syntheses of conjugated polycarbogermosilane containing 1,1-diethyl-3,4-diphenyl-2,5-silolene and diphenylgermylene along the polymer backbone such as poly[(1,1-diethyl-3,4-diphenyl-2,5-silolene)-*co*-(diphenylgermylene)] have not been reported so far [13]. Recently, stable persilyl-substituted free radical of heavy group 14 elements was reported as possible for its application to the energy storage system such as pseudocapacitors [14].

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Aryl- and heteroaryl-conjugated polymers are commonly prepared through metal-catalyzed polycondensation reactions using Yamamoto, Suzuki, or Stille coupling reactions [15,16], and the Grignard metathesis (GRIM) method [17]. In order to expand the use of GRIM, turbo-Grignard reagents of LiCl plus a Grignard reagent have been utilized for the synthesis of various aryl and heteroaryl conjugated polymers [18]. Recently, we reported the syntheses of poly(1,1-disubstituted-3,4-diphenyl-2,5-silole)s *via* GRIM polymerizations of 1,1-disubstituted-2,5-dibromo-3,4-diphenylsiloles using a turbo-Grignard reagent [19].

We previously published the synthesis of polycarbosilanes conjugated with diacetylene and aromatic groups of thiophene or phenylene simultaneously present in the polymer backbone using *n*-butyllithium [20] as well as their molecular energy dynamics using ultrafast fluorescence spectroscopy [21]. Very recently, we reported the synthesis, photoelectronic, and electrochemical properties of poly[(1,1-dihexyl-3,4-diphenyl-2,5-silole)-*co*-(disubstitutedsilylene)]s *via* copolymerizations of 1,1-dihexyl-2,5-dibromo-3,4-diphenylsilole with dichlorodisubstitutedsilanes [22].

We focused on the synthesis of fluorescent poly (carboger-mosilane) material containing aromatic chromophores such as 1,1-diethyl-3,4-diphenyl-2,5-silolene and diphenylgermylene in the polymer main chain. Now, we report synthesis of new conjugated polycarboger-mosilane material of poly[(1,1-diethyl-3,4-diphenyl-2,5-silolene)-*co*-(diphenylgermylene)] (**6**) *via* copolymerization of 2,5-dibromo-1,1-diethyl-3,4-diphenyl-2,5-silolene (**3**) with dichlorodiphenylgermane (**5**) using *n*-butyllithium. The obtained copolymer was characterized using  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  nuclear magnetic resonance (NMR) as well as FTIR spectroscopies in the solution state. We investigated the photoelectronic and thermal properties of the prepared polymer **6** using absorption, excitation, and fluorescence emission spectrophotometry in solution state as well as TGA.

## Materials and Methods

### 1. General procedures

All glassware was assembled and then dried with flame while being swept with argon before reaction. All synthetic manipulations were carried out by standard vacuum-line Schlenk techniques under argon. All chemicals were purchased from Sigma-Aldrich Korea Co. and used as received. Tetrahy-

drofuran was distilled from sodium benzophenone ketyl prior to use, using the standard literature [23].  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectra were obtained on a Bruker DRX Avance 400 MHz FT-NMR spectrometer using deuteriochloroform ( $\text{CDCl}_3$ ) as solvent.  $^{29}\text{Si}$  nuclear magnetic resonance spectroscopy was performed using Varian Unity INOVA 500 MHz FT-NMR spectrometer using  $\text{CDCl}_3$  as solvent. The chemical shifts are expressed in ppm relative to the residual proton signal of the solvent as standard or tetramethylsilane (TMS) as an internal standard. FTIR spectra were recorded using a Bruker IFS-48 FT-IR spectrometer or a Shimadzu IR 430 spectrometer. Gel permeation chromatography analyses were performed at 40°C, using a Waters 1525 pump, a Waters Styragel HR 3 column, and refractive index detector with Breeze software system. THF was used as the eluent at a flow rate of 1.0 mL/min. Calibration was made with a series of monodispersed polystyrene standards:  $M_p$  580, 3250, 10,100, and 28,500 of which  $M_w/M_n$  values were less than 1.2. UV-vis absorption spectra were recorded using a Hewlett Packard 8453 spectrophotometer. Excitation and fluorescence emission spectra were obtained using a Spex Fluorolog-3-11 fluorescence spectrophotometer. Thermogravimetric analysis of polymer sample was carried out using a TGA-50 Shimadzu thermal analysis system. The temperature was increased at the heating rate of 10°C/min from room temperature to 900°C with nitrogen flow rate of 20 mL/min.

### 2. Synthesis of diethylbis(phenylethynyl)silane (**2**)

A three-necked flask equipped with a magnetic stirring bar, thermometer, and rubber septa was charged with phenylacetylene (25.5 mL, 232 mmol) and THF (200 mL). The solution was cooled to  $-78^\circ\text{C}$  in a dry ice/acetone bath. *n*-Butyllithium (2.5 M, 78.8 mL, 197 mmol) was added to the stirred solution, using a syringe, under a stream of argon. The acetone/dry ice bath was replaced with an ice/water bath. When the temperature of reaction mixture approached approximately  $-5^\circ\text{C}$ , dichlorodiethylsilane (**1**) (13.9 mL, 92.8 mmol) was added dropwise by using a syringe. The reaction solution was allowed to warm up to room temperature with stirring. The reaction mixture was then poured into aqueous ammonium chloride solution (200 mL). The organic phase was separated by using a separating funnel and the aqueous layer was extracted with 50 mL of diethyl ether. The combined organic layer was washed with water and brine several times, dried over anhydrous magnesium sulfate, filtered, and concentrated by rotary evap-

oration under vacuum. Yellowish liquid of product **2** (27.2 g, 99.0%) were obtained by removal of solvents under high vacuum [7].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.91 (q,  $J=8$  Hz,  $2\text{CH}_2\text{CH}_3$ , 4H), 1.21 (t,  $J=8$  Hz,  $2\text{CH}_2\text{CH}_3$ , 6H), 7.31-7.36 (m,  $2\text{C}_6\text{H}_5$ , 6H), 7.53-7.57 (m,  $2\text{C}_6\text{H}_5$ , 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.78, 7.52, 89.03, 106.89, 122.95, 128.37, 128.97, 132.33.  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{CDCl}_3$ ,  $\delta$ ):  $-30.71$ . IR (neat)  $\nu_{\text{max}}$ : 3060, 2950, 2870, 2156 ( $\nu_{\text{C}=\text{C}}$ ), 1592, 1488, 829, 686  $\text{cm}^{-1}$ .

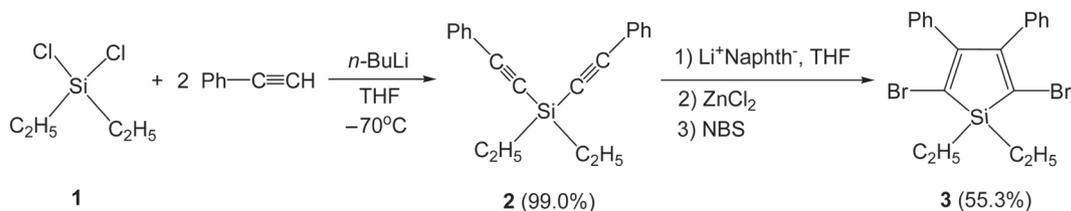
### 3. Synthesis of 2,5-dibromo-1,1-diethyl-3,4-diphenylsilole (**3**)

A three-necked flask equipped with a rubber septa, and magnetic stirring bar, and thermometer was charged with lithium (0.53 g, 75.6 mmol), naphthalene (10.1 g, 79.0 mmol) and THF (50 mL) under an atmosphere of argon. The reaction mixture solution was stirred overnight at room temperature to dissolve the lithium. A solution of **2** (6.73 g, 16.8 mmol) in THF (120 mL) was added dropwise, by using a cannula, to the lithium naphthalenide over 25 min. Once the addition was finished, the solution was cooled to  $-10^\circ\text{C}$  by using an acetone bath with a small amount of dry ice. A solution of anhydrous  $\text{ZnCl}_2$  (11.45 g, 84.0 mmol) in THF (70 mL) was added to the naphthalenide/silane mixture, by using a cannula, over 20 min. The acetone/dry ice bath was removed and the resulting mixture solution was allowed to warm up to room temperature. A three-necked, foil-wrapped, round-bottomed flask equipped with a stirring bar, rubber septa, and thermometer was charged with NBS (7.45 g, 41.9 mmol) and THF under an atmosphere of argon. The resulting mixture solution was cooled to  $-70^\circ\text{C}$  by using a dry ice/acetone bath. The room-temperature silane solution was added to the cold NBS solution by using a cannula, ensuring that the internal temperature did not exceed  $-50^\circ\text{C}$ . After the addition was finished, the resulting mixture solution was stirred for a further 30 min at  $-70^\circ\text{C}$ . The reaction mixture solution was poured into aqueous ammonium chloride solution (200 mL). The organic phase was separated by using a separating funnel and the aqueous layer was extracted with diethyl ether several times. The combined organic layer was washed with aqueous sodium thiosulfate solution, water, and brine several times, dried over anhydrous magnesium sulfate, filtered, and concentrated by using rotary evaporation. The crude naphthalene-silole mixture product was sublimed under vacuum at  $35^\circ\text{C}$ . The residual material after the sublimation was redissolved in hot hexane, followed by cool-

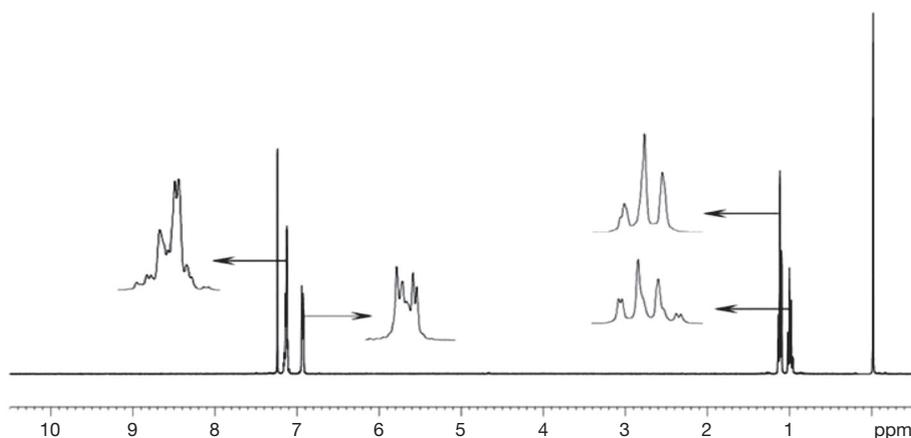
ing in a freezer. A white powder product **3** (4.16 g, 55.3%) were obtained by vacuum filtration [8].  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 1.03 (q,  $J=7.5$  Hz,  $2\text{CH}_2\text{CH}_3$ , 4H), 1.15 (t,  $J=7.5$  Hz,  $2\text{CH}_2\text{CH}_3$ , 6H), 6.94-6.98 (m,  $2\text{C}_6\text{H}_5$ , 4H), 7.14-7.18 (m,  $2\text{C}_6\text{H}_5$ , 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 1.74, 6.75, 121.06, 127.62, 127.76, 129.22, 137.36, 157.54.  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.52. IR (neat)  $\nu_{\text{max}}$ : 3054, 2954, 2873, 1554 ( $\nu_{\text{C}=\text{C}}$ ), 1461, 1377, 1060, 766, 697  $\text{cm}^{-1}$ . UV-vis (THF)  $\lambda_{\text{max}}$  nm ( $\epsilon$   $\text{cm}^{-1}\text{M}^{-1}$ ): 260 ( $1.19 \times 10^4$ ).

### 4. Synthesis of poly [(1,1-diethyl-3,4-diphenyl-2,5-silolene)-co-(diphenylgermylene)] (**6**)

A flame dried 100 mL three-neck round bottom flask equipped with a Teflon covered magnetic stirring bar, a pressure equalizing addition funnel, and reflux condenser was cooled to  $-78^\circ\text{C}$  using a dry ice/acetone bath under argon atmosphere and then *n*-BuLi (2.5 M/hexane, 1.96 mL, 4.90 mmol) and THF (10 mL) were added. Monomer **3** (1.00 g, 2.23 mmol) and THF (10 mL) were placed in the addition funnel. This solution was slowly added to the flask with well stirring. The reaction mixture solution was allowed to stir at  $-78^\circ\text{C}$  for 2 h, and then warm to room temperature. The reaction mixture was again cooled to  $-78^\circ\text{C}$  and  $(\text{C}_6\text{H}_5)_2\text{GeCl}_2$  (**5**) (0.49 mL, 2.23 mmol) was added with well stirring at  $-78^\circ\text{C}$  for 2 h. The reaction mixture solution was allowed to warm up to room temperature with stirring overnight. The crude product was precipitated by the addition of methanol and 10% aqueous HCl (20-30 mL) and isolated by decantation. The crude polymer was redissolved in THF (40-50 mL), washed with 10% aqueous HCl, deionized water, and concentrated at reduced pressure. The polymer was reprecipitated by addition of methanol (50-100 mL) and dried under reduced pressure. Polymer **6**, 1.10 g, 95.7% was obtained as a viscous brownish-black liquid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 0.42-1.10 (m,  $2\text{C}_2\text{H}_5$ , 10H), 6.88-7.96 (m,  $4\text{C}_6\text{H}_5$ , 20H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.75, 6.92, 6.99, 7.17, 7.28, 8.18, 8.48, 8.55, 127.17, 127.63, 128.20, 128.71, 129.14, 129.82, 130.47, 131.15, 133.19, 134.47, 143.75, 155.10.  $^{29}\text{Si}$  NMR (99.36 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 6.76, 7.18, 8.64. IR (KBr disk)  $\tilde{\nu}_{\text{max}}$ : 3053, 2956, 2874, 1596 ( $\nu_{\text{C}=\text{C}}$ ), 1433, 1378, 734, 693  $\text{cm}^{-1}$ . UV-vis (THF)  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{cm}^{-1}\text{M}^{-1}$ ): 259 ( $7.16 \times 10^2$ ), 299 ( $4.67 \times 10^2$ ). GPC (THF)  $M_w = 659$ ,  $M_n = 629$ , PDI = 1.04. The excitation and fluorescence emission spectra in THF solution and TGA thermogram for **6** are described in the Results and Discussion.



**Scheme 1.** Synthesis of Monomer.



**Fig. 1.**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$ .

## Results and Discussion

### 1. Synthesis of monomer

As shown in Scheme 1, 2,5-dibromo-1,1-diethyl-3,4-diphenylsilole (**3**) as a monomer was synthesized by a two-step reaction reported previously [6,7,17]. In the first step, dichlorodiethylsilane (**1**) was treated with phenylethynyllithium, which was synthesized *in situ* by a reaction of phenylacetylene with *n*-butyllithium in THF at  $-70^\circ\text{C}$ , to afford diethylbis(phenylethynyl)silane (**2**). In the second step, intramolecular reductive cyclization of **2** was carried out by the treatment of 4 mol of lithium naphthalenide followed by anhydrous  $\text{ZnCl}_2$  and *N*-bromosuccinimide (NBS), to yield compound **3** in moderate yield [7,8,19].

**3** was characterized using various spectroscopic methods, such as  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopies in the solution state. As shown in Fig. 1, the  $^1\text{H}$  NMR spectrum of **3** exhibits resonances at 1.03–1.15 and 6.94–7.18 ppm, attributed to ethyl and phenyl groups of **3**, respectively [24,25]. In the  $^{13}\text{C}$  NMR spectrum of **3**, two carbon peaks from the ethyl group bonded to the silicon is observed at 1.74 and 6.75 ppm [24,25]. In the  $^{29}\text{Si}$  NMR spectrum of **3**, the silicon resonance is observed at

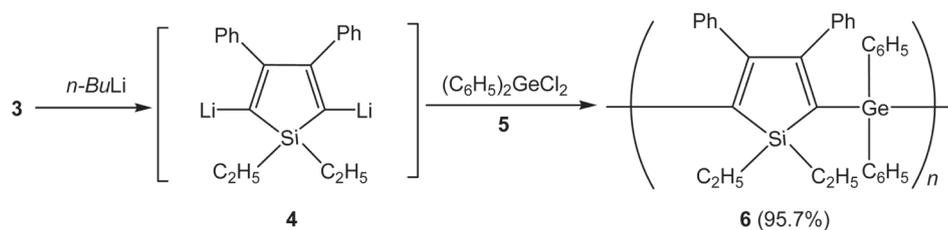
8.52 ppm. The intramolecular reductive cyclization reaction of **2** was completed under this reaction condition to yield the monomer **3**.

We examined the absorption spectrum of **3** in THF solution. The maximum absorption band for **3** is observed at 260 nm, with a molar absorptivity of  $1.19 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ . The strong absorption band in the ultraviolet-visible (UV-vis) spectrum of **3** may result from chromophores such as phenyl and diene groups in the 3,4-diphenylsilole monomer [6].

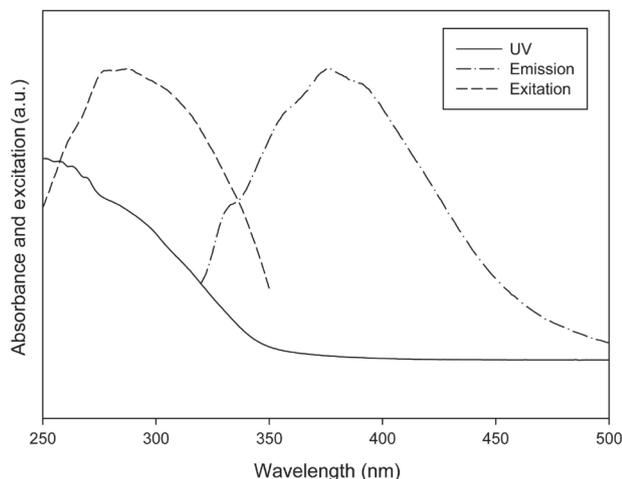
### 2. Synthesis of polymer

The synthetic scheme for polycarbgermosilane copolymer containing 1,1-diethyl-3,4-diphenyl-2,5-silolene and diphenylgermylene along main chain is outlined in Scheme 2, which is similar to the copolymerization reactions of 1,4-bis(4-chlorophenyl or 5-chlorothiophenyl)-buta-1,3-diyne using *n*-butyllithium as reported previously [21].

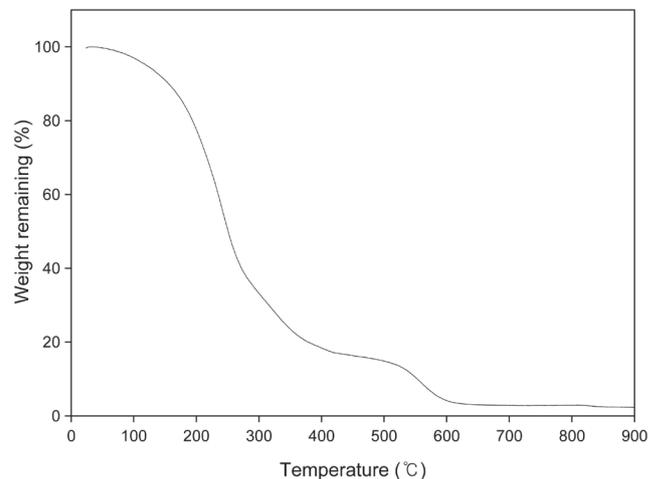
**3** was treated with *n*-butyllithium at  $-78^\circ\text{C}$  to give the dilithiated intermediate (**4**) of 1,1-diethyl-3,4-diphenylsilolene, followed by copolymerization of **4** with  $(\text{C}_6\text{H}_5)_2\text{GeCl}_2$  (**5**) *in situ* was performed to yield polycarbgermosilane copolymer such as poly[(1,1-diethyl-3,4-diphenyl-2,5-silolene)-*co*-



**Scheme 2.** Synthesis of Polymer.



**Fig. 2.** Absorbance (solid line,  $\lambda_{\text{max}} = 259, 299$  nm), excitation (dashed line,  $\lambda_{\text{ex,max}} = 287$  nm,  $\lambda_{\text{det}} = 376$  nm), and fluorescence emission (dot-and-dash line,  $\lambda_{\text{em,max}} = 376$  nm,  $\lambda_{\text{ex}} = 287$  nm) spectra of **6** in THF solution.



**Fig. 3.** TGA thermogram of **6** in nitrogen.

(diphenylgermylene)] (**6**).

The prepared polymeric material **6** is obtained in good yield as a brownish-black viscous liquid, and is soluble in general organic solvents such as  $\text{CHCl}_3$  and THF. The observed molecular weight of **6** was 659/629 ( $M_w/M_n$ ) with polydispersity of 1.04, indicating that **6** is oligomeric. This phenomenon may be explained by the intrinsic-low reactivities of the functionalities at the 2,5-position of the silole monomers [10] and severe steric congestion [26].

We characterized copolymer **6** using various spectroscopic methods such as by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  NMR spectroscopies in the solution state and FTIR spectroscopy. The FTIR spectrum of **6** show characteristic  $\text{C}=\text{C}$  stretching frequencies at  $1596\text{ cm}^{-1}$ , suggesting that the conjugated diene groups were kept intact during polymerization reaction [27]. The  $^{29}\text{Si}$  NMR spectrum of **6** in  $\text{CDCl}_3$  solution shows major resonance peaks at 6.76, 7.18, and 8.64 ppm, mainly due to the repeating unit composed of 3,4-diphenylsilolene and germylene, indicating that the silicon atoms in the polymer main chain has the structural

environments composed of 1,1-diethyl-3,4-diphenylsilolene and diphenylgermylene groups in the form of oligomeric low molecular weight, suggesting structures consistent with the backbone shown in Scheme 2 [28].

### 3. Properties of polymer

We examined the absorption, excitation, and fluorescence emission spectra of **6** in THF solution as shown in Fig. 2.

The maximum absorption bands  $\lambda_{\text{max}}$  for **6** was observed at 259 nm along with shoulder band of 299 nm with molar absorptivities of  $7.16 \times 10^4$  and  $4.67 \times 10^2\text{ cm}^{-1}\text{ M}^{-1}$ , respectively, which the band extends from 259 to 400 nm. The strong absorption band in the UV-vis spectra of **6** is attributed to chromophores of phenyl and diene groups along the polymer backbone [5]. A comparison of the absorption band of copolymer **6** with that of the monomer **3** in THF solution shows that the copolymer **6** exhibits the broad maximum absorption band to 400 nm, probably because of strong intermolecular interactions along the polymer backbone.

The excitation spectrum for **6** at a detection wavelength of 376 nm shows a strong excitation peak at  $\lambda_{\text{ex,max}}$  of 287 nm, as

shown in Fig. 2 as a dashed line. The strong excitation band in the excitation spectra of **6** is attributed to the phenyl and diene groups through the polymer backbone [5].

The fluorescence emission spectrum of **6** at an excitation wavelength of 287 nm in THF solution has a strong emission peak at  $\lambda_{em,max}$  of 376 nm, as shown in Fig. 2 as a dot-and-dash line. The strong emission band in the fluorescence spectrum of the polymer is ascribed to fluorophores of phenyl and diene groups along the polymer backbone [5]. The fluorescence emission FWHM (full width at half maximum) value of **6** is observed at 96 nm. The excitation and fluorescence emission spectra of the polymer implies that **6** has chromophores containing phenyl and diene groups through the polymer main chains [5].

The thermal stability of **6** in a nitrogen atmosphere was examined using TGA, with a heating rate of 10°C/min and the result is shown in Fig. 3. Copolymer **6** is stable up to 200°C, with only 7% loss of the initial weights in nitrogen. Copolymer **6** rapidly lost weight on heating above 200°C. Rapid weight losses of 80% of the initial weights occurred between 200 and 400°C. Additionally, weight losses of 8% of the initial weights occurred between 500 and 600°C. When polymer **6** was heated to 900°C, the polymers lost 98% of their initial weights, and char yields of about 2% was observed.

## Conclusion

We have successfully synthesized a new conjugated polycarbogermosilane contained with 1,1-diethyl-3,4-diphenylsilolene and diphenylgermylene groups in the polymer main chain such as poly[(1,1-diethyl-3,4-diphenyl-2,5-silolene)-*co*-(diphenylgermylene)] (**6**) *via* copolymerization of 1,1-diethyl-2,5-dibromo-3,4-diphenyl-2,5-silolene (**3**) with diphenyldichlorogermane (**5**) using *n*-butyllithium. The prepared material is soluble in common organic solvents such as CHCl<sub>3</sub> and THF. The polymer was characterized in solution state, using various spectroscopic methods. The FTIR spectrum of the polymeric material shows characteristic diene stretching frequency at 1596 cm<sup>-1</sup>. In THF solution, the material has strong maximum absorption bands at 259 nm along with shoulder band of 299 nm extending from 259 to 400 nm and strong maximum fluorescence emission band at 376 nm. All the absorption, excitation, and emission spectra indicate that the prepared material contains chromophores of phenyl and diene groups in the polymer main chains. TGA shows that the polymer is

thermally stable up to 200°C with a weight loss of 7% in nitrogen.

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