

## Synthesis and Characterization of Oligomers Composed of Alternating 2,5-Bis(ethynyldimethylsilylene)thienylene and Arylene Units

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The reactions of 2,5-bis(ethynyldimethylsilyl)thiophene (**1**) with aromatic dihalides (1,4-dibromobenzene, 4,4'-dibromobiphenyl, 9,10-dibromoanthracene, 2,5-dibromopyridine, 2,5-dibromothiophene, and 2,6-diiodo-4-nitroaniline) were carried out in the presence of a [(PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>]-CuI catalyst in refluxing triethylamine to give poly{[2,5-bis(ethynyldimethylsilylene)thienylene](arylene)} (**2-7**) with molecular weights of 2200-7400. The oligomers reveal characteristic absorption in the UV/visible region. The thermal behavior of **2-7** was examined by thermogravimetric analysis in an argon atmosphere.

**Key Words :** Aromatic dihalides, Dehydrohalogenation, 2,5-Bis(ethynyldimethylsilyl)thiophene, Poly{[2,5-bis(ethynyldimethylsilylene)thienylene](arylene)}, Thermogravimetric analysis

### Introduction

Organosilicon polymers in which silicon atoms are linked by organic groups with conjugated  $\pi$ -electron systems have been studied intensively over the last decade.<sup>1</sup> Such polymers could be widely used as functional materials<sup>2</sup> in the field of electronics and material science. Some organosilicon polymers containing silylene and diethynylencarylene unit might be readily prepared by using the palladium(II)-catalyzed coupling reaction of aromatic dihalides with acetylenic reagents reported by Sonogashira,<sup>3</sup> Cassar,<sup>4</sup> Dieck and Heck,<sup>5</sup> Havens,<sup>6</sup> and Trumbo *et al.*<sup>7</sup>

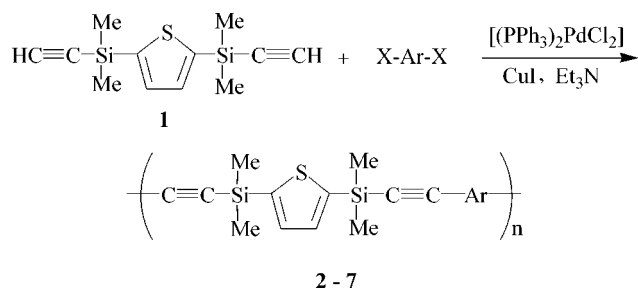
Here we describe the preparation and thermal behavior of a series of oligomers composed of a regular alternating arrangement of 2,5-bis(ethynyldimethylsilylene)thienylene unit and arylene unit as the  $\pi$ -electron system in the polymer backbone. This type of polymers with an organosilicon moiety and a  $\pi$ -electron system has received much attention with regard to their heat-resistant properties.<sup>8,9</sup> The oligomers **2-7** are obtained from 2,5-bis(ethynyldimethylsilyl)thiophene (**1**) and (hetero)aromatic dihalides [Ar = (hetero)aromatic group, X = Br or I] in the presence of a

catalytic amount of bis(triphenylphosphine)palladium(II) chloride and copper(I) iodide in refluxing triethylamine.

### Experimental Section

**General Procedures.** All reactions were carried out under an atmosphere of dry nitrogen. Triethylamine used as the solvent for polymerization was dried over KOH and distilled prior to use. The aromatic dihalides and the Pd catalyst used were purchased from Aldrich Chemical Company and used without further purification. GC analyses were performed using a Hewlett-Packard 5890 instrument on a HP-1 capillary column (cross-linked 5% methylphenylsilicone, 25 m). <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si NMR spectra were run on a Bruker Avance 400 spectrometer. Mass spectra were obtained by a Shimadzu model QP-1000A spectrometer. UV/visible and IR spectra were recorded on Shimadzu UV-2100 PC and Mattson Galaxy 7020A FT-IR spectrometers. Molecular weights of oligomers were determined by gel permeation chromatography (GPC) relative to polystyrene standards, using Shodex 804 and 803 as the column and using THF as the eluent. Thermogravimetric analyses were performed on a Rhotometric STA 1500 thermal analyzer. The temperature program for the thermogravimetric analysis was from room temperature to 1200 °C with a typical heating rate of 10 °C/min under argon flow rate of 40 mL/min. The thermolysis of the oligomer **3** were carried out in an alumina boat which was placed into an alumina tube (1 m, i.d. 3 cm) under an atmosphere of flowing argon (50 mL/min), using a temperature program of 10 °C/min for 1 h at the thermolysis temperature. Elemental analyses were performed by a FISON, EA 1106 elemental analyzer.

**Preparation of 2,5-Bis(ethynyldimethylsilyl)thiophene (1).** In a three neck flask equipped with a condenser, dropping funnel and magnetic bar were placed 8.4 g (0.10



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mol) of thiophene and 29.1 g (0.25 mol) of N,N,N',N'-tetramethylethylenediamine (TMEDA) in 250 mL of anhydrous hexane at room temperature. A solution of butyllithium in hexanes (1.6 M, 156 mL, 0.25 mol) was placed in the dropping funnel and slowly added dropwise to the well stirred solution under nitrogen at room temperature.<sup>10</sup> After being stirred for an additional 5 h at room temperature, a solution of 23.7 g (0.25 mol) of chlorodimethylsilane in 55 mL of anhydrous hexane was added dropwise to the reaction mixture maintained at  $-78^{\circ}\text{C}$ . After addition was completed, the reaction mixture was stirred for 12 h at room temperature followed by filtration of the salts, then the organic layer was treated with water and dried over anhydrous magnesium sulfate. The volatile solvent was evaporated and the residue was distilled under reduced pressure to give 12.6 g (63.0 mmol, 63%) of 2,5-bis(dimethylsilyl)thiophene. The spectral properties of 2,5-bis(dimethylsilyl)thiophene are in agreement with those previously reported.<sup>11</sup> For the preparation of 2,5-bis(chlorodimethylsilyl)thiophene, in a 100 mL two neck flask fitted with a reflux condenser and a rubber septum was placed a mixture of 3.6 g (18.0 mmol) of 2,5-bis(dimethylsilyl)thiophene and about 6 mg of palladium dichloride in 70 mL of carbon tetrachloride. The mixture was heated to reflux for 3 h. After evaporation of the solvent, the residue was distilled under reduced pressure to afford 4.3 g (16 mmol, 89%) of 2,5-bis(chlorodimethylsilyl)thiophene. The spectral data of this product are identical with the previously reported values.<sup>11a,b</sup>

For the preparation of 2,5-bis(ethynyl)dimethylsilyl)thiophene **1**, a solution of 4.5 g (17 mmol) of 2,5-bis(chlorodimethylsilyl)thiophene in 10 mL THF was added dropwise to a solution of ethynylmagnesium bromide in THF (0.5 M, 90 mL, 45 mmol). After the addition was finished, the mixture was stirred for 12 h at  $30^{\circ}\text{C}$  followed by the filtration of the salts. The organic layer was treated with water and dried over anhydrous magnesium sulfate. The volatile solvent was evaporated and the residue was fractionally distilled under reduced pressure to give 2.9 g (11.7 mmol, 69%) of **1**. Compound **1**: b.p.  $104^{\circ}\text{C}$  (10 torr). IR:  $\nu(\text{HC}\equiv)$  3279,  $\nu(\text{C-H})$  2963,  $\nu(\text{C}\equiv\text{C})$  2037  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 243 nm ( $\epsilon = 13900$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.56 (s, 12H,  $\text{SiCH}_3$ ), 2.55 (s, 2H,  $\text{C}\equiv\text{CH}$ ), 7.53 (s, 2H, thiophene).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.42, 86.74, 96.09, 136.86, 142.43.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -26.73. MS  $m/z$  (rel. intensity): 248 ( $M^+$ , 19), 233 (100), 218 (1), 183 (1), 165 (2), 145 (1), 143 (2), 109 (11), 93 (12), 83 (39), 77 (5), 75 (8), 73 (7), 67 (13), 55 (28), 53 (50). Anal. calcd. for  $\text{C}_{12}\text{H}_{16}\text{SSi}_2$ : C, 58.00; H, 6.49. Found: C, 57.85; H, 6.58.

**Polymerization of 1 with 1,4-Dibromobenzene.** A mixture of 0.25 g (1.0 mmol) of **1**, 0.24 g (1.0 mmol) of 1,4-dibromobenzene, 2.0 mg ( $2.8 \times 10^{-3}$  mmol) of bis(triphenylphosphine)palladium(II) chloride, 8.6 mg ( $4.5 \times 10^{-2}$  mmol) of cuprous iodide and 20 mg ( $7.6 \times 10^{-2}$  mmol) of triphenylphosphine in 12 mL of triethylamine was stirred at  $89^{\circ}\text{C}$  for 16 h. The reaction mixture was filtered, and after evaporation of the solvent, the residue was taken up in THF. Addition of pentane to the solution precipitated the oligomer.

The oligomer was purified with repeated precipitation from THF by addition of pentane and dried under reduced pressure to give 0.15 g of poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene[1,4-phenylene]} (**2**) (46% yield, light brown solid). The oligomer is soluble in common organic solvents such as THF, chloroform and toluene. Compound **2**:  $M_w = 7400$ ,  $M_n = 4200$  ( $M_w/M_n = 1.76$ ). IR:  $\nu(\text{C}\equiv\text{C})$  2160  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 284 nm (33000), 298 nm (31500).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.61 (s, 12H,  $\text{SiCH}_3$ ), 7.48 (s, 4H, phenylene ring protons), 7.56 (s, 2H, thienylene ring protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.47, 94.10, 106.24, 123.27, 132.06, 136.75, 143.09.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ): -26.46. Anal. calcd. for  $(\text{C}_{18}\text{H}_{18}\text{SSi}_2)_n$ : C, 67.02; H, 5.62. Found: C, 64.94; H, 5.34.

**Polymerization of 1 with 4,4'-Dibromobiphenyl.** A mixture of 0.27 g (1.1 mmol) of **1**, 0.31 g (1.0 mmol) of 4,4'-dibromobiphenyl, 14 mg ( $2.0 \times 10^{-2}$  mmol) of bis(triphenylphosphine)palladium(II) chloride and 5.7 mg ( $3.0 \times 10^{-2}$  mmol) of cuprous iodide in 12 mL of triethylamine was stirred at  $89^{\circ}\text{C}$  for 16 h. On completion of the reaction, 0.35 g of poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene[4,4'-biphenylene]} (**3**) was isolated in a similar manner as described in the preceding experiment (83%, brown solid). Compound **3**:  $M_w = 3000$ ,  $M_n = 2100$  ( $M_w/M_n = 1.43$ ). IR:  $\nu(\text{C}\equiv\text{C})$  2158  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 300 nm ( $\epsilon = 29500$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.59 (s, 12H,  $\text{SiCH}_3$ ), 7.44-7.60 (m, 10H, thienylene and biphenylene ring protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.49, 92.67, 106.58, 126.89, 128.69, 132.73, 136.64, 140.56, 143.26.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -26.46. Anal. calcd. for  $(\text{C}_{24}\text{H}_{22}\text{SSi}_2)_n$ : C, 72.30; H, 5.56. Found: C, 69.28; H, 5.40.

**Polymerization of 1 with 9,10-Dibromoanthracene.** A mixture of 0.27 g (1.1 mmol) of **1**, 0.34 g (1 mmol) of 9,10-dibromoanthracene, 14 mg ( $2.0 \times 10^{-2}$  mmol) of bis(triphenylphosphine)palladium(II) chloride and 5.7 mg ( $3.0 \times 10^{-2}$  mmol) of cuprous iodide in 12 mL of triethylamine was stirred at  $89^{\circ}\text{C}$  for 16 h. On completion of the reaction, 0.35 g of poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene[9,10-anthrylene]} (**4**) was isolated in a similar manner (78% yield, brick red solid). Compound **4**:  $M_w = 3000$ ,  $M_n = 2100$  ( $M_w/M_n = 1.43$ ). IR:  $\nu(\text{C}\equiv\text{C})$  2131  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 274 nm ( $\epsilon = 35200$ ), 400 nm ( $\epsilon = 10200$ ), 418 nm ( $\epsilon = 21100$ ), 443 nm ( $\epsilon = 25600$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.78 (s, 12H,  $\text{SiCH}_3$ ), 7.40-7.80 (m, 6H, thienylene and anthrylene protons), 8.43-8.75 (m, 4H, anthrylene protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.80, 103.39, 105.56, 127.18, 127.53, 128.36, 132.51, 136.85, 143.44.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -26.17. Anal. calcd. for  $(\text{C}_{26}\text{H}_{22}\text{SSi}_2)_n$ : C, 73.88; H, 5.25. Found: C, 71.15; H, 5.32.

**Polymerization of 1 with 2,5-Dibromopyridine.** A mixture of 0.27 g (1.1 mmol) of **1**, 0.24 g (1.0 mmol) of 2,5-dibromopyridine, 14 mg ( $2.0 \times 10^{-2}$  mmol) of bis(triphenylphosphine)palladium(II) chloride and 5.7 mg ( $3.0 \times 10^{-2}$  mmol) of cuprous iodide in 12 mL of triethylamine was stirred at  $89^{\circ}\text{C}$  for 16 h. On completion of the reaction, 0.18 g of poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene[2,5-pyridylene]} (**5**) was isolated in a similar manner (52%

yield, dark brown solid). Compound **5**:  $M_w = 2200$ ,  $M_n = 800$  ( $M_w/M_n = 2.75$ ). IR:  $\nu$  (C≡C) 2162  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 305 nm ( $\epsilon = 17200$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.57 (br. s, 12H, SiCH<sub>3</sub>), 7.36–7.55 (m, 3H, pyridylene and thienylene protons), 7.60–7.79 (m, 1H, pyridylene proton), 8.66 (s, 1H, pyridylene proton).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -0.01, 0.10, 94.60, 97.86, 102.66, 104.62, 119.47, 126.79, 126.87, 136.69, 136.74, 136.83, 136.87, 138.95, 139.00, 141.62, 142.25, 142.30, 142.48, 142.52, 152.75.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -25.96, -26.08. Anal. calcd. for  $(\text{C}_{17}\text{H}_{17}\text{NSSi}_2)_n$ : C, 63.10; H, 5.30; N, 4.33. Found: C, 61.57; H, 5.17; N, 3.85.

**Polymerization of 1 with 2,5-Dibromothiophene.** A mixture of 0.27 g (1.1 mmol) of **1**, 0.24 g (1 mmol) of 2,5-dibromothiophene, 14 mg ( $2.0 \times 10^{-2}$  mmol) of bis(triphenylphosphine)palladium(II) chloride and 5.7 mg ( $3.0 \times 10^{-2}$  mmol) of cuprous iodide in 12 mL of triethylamine was stirred at 89 °C for 16 h. On completion of the reaction, 0.23 g of poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene} (2,5-thienylene) (**6**) was isolated in the same manner (66% yield, dark brown solid). Compound **6**:  $M_w = 5000$ ,  $M_n = 1300$  ( $M_w/M_n = 3.85$ ). IR:  $\nu$  (C≡C) 2149  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 254 nm ( $\epsilon = 10600$ ), 320 nm ( $\epsilon = 13100$ ), 335 nm ( $\epsilon = 13300$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.55 (s, 12H, SiCH<sub>3</sub>), 7.09 (s, 2H, thienylene protons), 7.49 (s, 2H, thienylene protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.32, 97.66, 98.60, 124.66, 130.03, 136.86, 142.78.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -26.21. Anal. calcd. for  $(\text{C}_{16}\text{H}_{16}\text{S}_2\text{Si}_2)_n$ : C, 58.48; H, 4.91. Found: C, 56.80; H, 4.85.

**Polymerization of 1 with 2,6-Diiodo-4-nitroaniline.** A mixture of 0.27 g (1.1 mmol) of **1**, 0.39 g (1.0 mmol) of 2,6-diiodo-4-nitroaniline, 14 mg ( $2.0 \times 10^{-2}$  mmol) of bis(triphenylphosphine)palladium(II) chloride and 5.7 mg ( $3.0 \times 10^{-2}$  mmol) of cuprous iodide in 12 mL of triethylamine was stirred at 89 °C for 16 h. On completion of the reaction, 0.31 g of poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene}[2,6-(4-nitroanilylene)] (**7**) was isolated in the same manner (77% yield, brick red solid). Compound **7**:  $M_w = 2200$ ,  $M_n = 1100$  ( $M_w/M_n = 2.0$ ). IR:  $\nu$  (C≡C) 2147  $\text{cm}^{-1}$ . UV:  $\lambda_{\text{max}}$  ( $\text{CHCl}_3$ ) 284 nm ( $\epsilon = 19500$ ), 364 nm ( $\epsilon = 12100$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.59 (s, 12H, SiCH<sub>3</sub>), 5.54 (s, 2H, NH<sub>2</sub>), 7.50 (s, 2H, thienylene protons), 8.19 (s, 2H, phenylene protons).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.29, 100.28, 103.46, 106.47, 129.05, 136.90, 137.62, 142.60, 154.28.  $^{29}\text{Si}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -25.72. Anal. calcd. for  $(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{SSi}_2)_n$ : C, 56.51; H, 4.74; N, 7.32. Found: C, 55.31; H, 4.36; N, 6.94.

## Results and Discussion

In 1975, Sonogashira,<sup>3</sup> Cassar,<sup>4</sup> Heck *et al.*<sup>5</sup> reported independently that monosubstituted acetylenes are easily converted into disubstituted acetylenes by the palladium(II)-catalyzed reaction with aryl halides in a basic amine. Linear polymers of alternating ethynylene and arylene units were synthesized by a cross-coupling reaction utilizing the same catalyst.<sup>6,7</sup> Corriu *et al.*<sup>12</sup> reported that the preparation of diphenylsilylene polymers containing diethynylenearylene unit in the presence of a Pd(II)-CuI catalyst. West<sup>13</sup> and



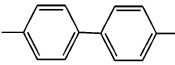
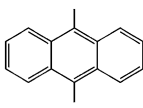
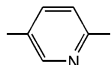
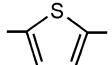
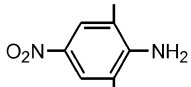
Ishikawa *et al.*<sup>14</sup> reported that alternating organosilicon copolymers consisting of disilanylene and ethynylene units are prepared by the different methods. The preparation of disilanylene polymers containing ethynylenearylene unit in the polymer backbone was reported by West.<sup>15</sup> The first synthesis of polymer bearing disilanylene and ethynylene-pyridylene units in the conjugated backbone has been reported by Ishikawa and Kunal.<sup>16</sup> Recently organosilicon polymers with silole (=silacyclopentadiene) skeleton have been extensively studied as the new  $\pi$ -electron system with unusual optical properties.<sup>12a,17</sup>

We are concerned with the synthesis and properties of organosilicon oligomers consisting of a 2,5-bis(ethynyl)dimethylsilylene)thienylene unit and an arylene unit as the  $\pi$ -electron system in the oligomer backbone. The oligomers were prepared from the reaction of 2,5-bis(ethynyl)dimethylsilylene)thiophene (**1**) and (hetero)aromatic dihalides in a refluxing triethylamine solution in the presence of a mixture of catalysts composed of bis(triphenylphosphine)palladium (II) chloride and copper(I) iodide. The reaction was completed after about 16 h which was monitored by the disappearance of acetylenic bands in the IR spectrum of **1** at 2037  $\text{cm}^{-1}$ .

A mixture of 1 equivalent of **1** and 1,4-dibromobenzene in the presence of a  $(\text{PPh}_3)_2\text{PdCl}_2\text{-CuI}$  catalyst was heated in triethylamine. Poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene}(1,4-phenylene) (**2**) with a molecular weight of 7400 was produced after several reprecipitation in pentane. Similar reactions of **1** with (hetero)aromatic dihalides under the same conditions gave products corresponding to poly{[2,5-bis(ethynyl)dimethylsilylene]thienylene}(arylene) (**3-7**) with molecular weights of 2200–5000 in moderate yields. Oligomers **2-7** are brown or brick-red coloured solids and are soluble in common organic solvents such as tetrahydrofuran, chloroform and toluene. The structures of oligomers **2-7** were identified by spectroscopic methods. The stretching frequency of carbon-carbon triple bond in IR spectra of oligomers **2-7** appears as a strong peak between at 2131 and 2162  $\text{cm}^{-1}$ . The C≡C bond stretching absorption of the anthracene containing oligomer **4** occurs at 2131  $\text{cm}^{-1}$  as Corriu has observed in the case of the polymer containing tetraphenylsilole<sup>12a</sup> or diphenylsilylene<sup>12b</sup> in the backbone. This is probably due to some degree of conjugation between the arylene and ethynylene unit for **4**. The oligomers **2-7** exhibit strong UV absorption band at 254–443 nm in chloroform solution, which are lower in energy than the monomer **1**.<sup>18</sup> The UV absorption bands and the extinction coefficients per {[2,5-bis(ethynyl)dimethylsilylene]thienylene}(arylene) unit of oligomers **2-7** are given in Table I.

The  $^1\text{H}$  NMR spectra of oligomers **2-7** obtained show one signal due to dimethylsilyl group at  $\delta$  0.61, 0.59, 0.78, 0.57, 0.55, and 0.59 ppm, respectively. The signals for the aromatic protons in the oligomer **2** are both singlet, due to phenylene and thienylene unit at  $\delta$  7.48 and 7.56 ppm, respectively. The  $^{13}\text{C}$  NMR signals for both the ethynylene carbons,  $C_\alpha$  and  $C_\beta$ , of the oligomers are more deshielded relative to those for the monomer **1**. The signal for the  $C_\alpha$  of

**Table 1.** Properties of Monomer **1** and Oligomers **2-7**

Compound	-Ar-	IR $\nu(\text{C}=\text{C})$ ( $\text{cm}^{-1}$ )	UV $\lambda_{\text{max}}$ , nm ( $\epsilon/\text{repeated unit}$ )	NMR (ppm)			$M_w$ ( $M_w/M_n$ )	Color <sup>a</sup>	
				<sup>13</sup> C <sup>c</sup>	<sup>1</sup> H	<sup>29</sup> Si			
				C $_{\alpha}$	C $_{\beta}$	SiMe			
<b>1</b>		2037	243(13900)	87.64	96.09	0.56	-26.73		
<b>2</b>		2160	284(33000) 298(31500)	94.10	106.24	0.61	-26.46	7400(1.76)	light brown
<b>3</b>		2158	300(29500)	92.67	106.58	0.59	-26.46	3000(1.43)	brown
<b>4</b>		2131	274(35200) 400(10200) 418(21100) 443(25600)	103.39	105.56	0.78	-26.17	3000(1.43)	brick red
<b>5</b>		2162	305(17200)	94.60 97.86	102.66 104.62	0.57	-25.96 -26.08	2200(2.75)	dark brown
<b>6</b>		2149	254(10600) 320(13100) 335(13000)	97.66	98.60	0.55	-26.21	5000(3.85)	dark brown
<b>7</b>		2147	284(19500) 364(12100)	100.28	103.46	0.59	-25.72	2200(2.00)	brick red

<sup>c</sup>Si-C $_{\alpha}$ =C $_{\beta}$ -Ar. <sup>a</sup>physical state: solid.

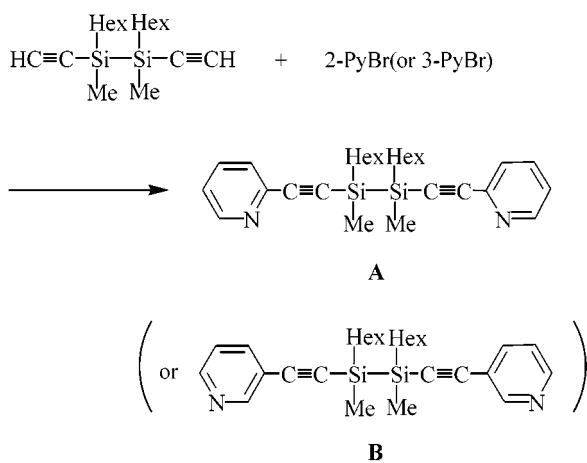
ethynylene unit of the oligomer **4** appears farther downfield with respect to those for the other oligomers, because there may be some electron delocalization in **4**.<sup>12a</sup> In the particular case of oligomer **5** containing 2,5-pyridylene unit, two C $_{\alpha}$  ( $\delta$  94.60 and 97.86 ppm) and two C $_{\beta}$  ( $\delta$  102.66 and 104.62 ppm) are observed, due to each ethynyl-pyridine linkage being in either the 2- or 5-pyridine position. Previously Corriu and co-workers also observed the multiple resonances for ethynylene carbons of the 2,5-pyridylene polymers containing a tetraphenylsilo<sup>12a</sup> or diphenylsilylene unit.<sup>12d</sup>

Recently, Ishikawa *et al.*<sup>16</sup> have clearly interpreted the multiple resonances for the ethynylene carbons in the <sup>13</sup>C NMR spectra of poly[(2,5-diethynylpyridylene)disilanyl]ene from the examination of <sup>13</sup>C NMR spectra of 1,2-bis(2-

pyridylethynyl)- and 1,2-bis(3-pyridylethynyl)-1,2-dihexyl-1,2-dimethyldisilane (**A** and **B**) as model compounds.

The <sup>29</sup>Si NMR spectrum of the monomer **1** shows a single resonance at  $\delta$ -26.73 ppm and those of the oligomers (**2-4**, **6-7**) reveal also a single resonance and that of oligomer **5** reveals two resonances at -25.96 and -26.08 ppm. These results suggest that the oligomers have the regular alternating structure of 2,5-bis(ethynylenedimethylsilylene)-thienylene and arylene units.

The thermal behavior of oligomers **2-7** was examined by thermogravimetric analysis (TGA) in argon atmosphere. TGA analyses were run from 25 °C to 1200 °C. The oligomers were stable until about 220 °C without any weight loss and took place decomposition at higher temperature. It was shown that the oligomers was decomposed in two steps. The first step in case of oligomer **3** was rapid weight loss at about 250-500 °C and the second was continuous weight loss starting at 700 °C. The weight remaining at 1200 °C was found to be 22%, 57%, 55%, 28%, 42%, and about 20% of the initial weight for **2-7**, respectively. The cross-linking process<sup>19</sup> during the thermolysis of **3**, a selection of the oligomers, was monitored by the changes in the IR spectra at different temperatures (200, 300, and 400 °C). When the sample is heated above 200 °C, the characteristic absorption band of acetylene group at 2158  $\text{cm}^{-1}$  has disappeared and one new absorption peak corresponding to the carbon-carbon double bond appeared at 1602  $\text{cm}^{-1}$ . The combustion analysis for the oligomers **2-7** shows lower carbon content than theoretical values.<sup>9a,12c,16,20</sup> This would be due to the formation of carbon containing ceramics, such as  $\beta$ -SiC



during the analysis. In fact, the IR spectrum of the ash obtained from combustion of oligomer **3** at 1000 °C, the same temperature as used for elemental analysis, shows a strong absorption at 1089 cm<sup>-1</sup> due to  $\nu_{\text{Si-C}}$  with a weak shoulder around 1200 cm<sup>-1</sup> due to  $\nu_{\text{Si-C}}$  as Kunai have observed in the case of the organosilicon polymers with a diethynylanthracene unit in the backbone.<sup>20</sup>

In conclusion, we have prepared oligomers **2-7** with molecular weights of 2200-7400 having a 2,5-bis(ethynyl-enedimethylsilylene)thienylene system linked by an arylene in the backbone, by dehydrohalogenation of 2,5-bis(ethynyl-dimethylsilyl)thiophene (**1**) and (hetero)aromatic dihalides in the presence of a (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>-CuI catalyst. Thermal behaviors of oligomers were also examined.

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