

Effect of Flexible Units on the Properties of Silicon-containing Phenyleneethynylene Hybrid Oligomers^{*}

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Abstract New silicon-containing phenyleneethynylene hybrid oligomers **P2**, **P3**, and **P4** were synthesized *via* Sonogashira cross-coupling reactions of ethynyl-terminated silazane monomer *N,N'*-bis(4-ethynylphenyl)-1,1-diphenylsilazane (**M1**) and corresponding bis-(4-bromo-phenyl)-ended organosilicon unit containing monomers, respectively. These new oligomers were easily soluble in common solvents. The incorporation of flexible organosilicon units in the oligomers leads to blue-shift in both the UV-Vis absorption and fluorescence emission spectra similarly. The results of differential scanning calorimetry (DSC) indicate that the flexible units relieve the rigidity of oligomeric chain and provide favorable conformation for thermal cross-linking reactions. The oligomers show good thermal and thermal-oxidative stability from the thermogravimetric analysis (TGA), with their decomposition temperature at 10% weight loss ($T_{10\%}$) higher than 400 °C under both nitrogen and air atmosphere.

Keywords: Sonogashira cross-coupling; Organosilicon unit; Hybrid oligomers; Thermal properties.

INTRODUCTION

As one of the important inorganic-organic hybrid polymers, the molecules based on acetylene and silicon-containing unit have attracted great attention for their high potential application in the fields of organic electronics and aerospace, as optoelectronic functional materials^[1–5], ceramic precursors^[6, 7], and heat-resistant materials^[8–12].

In the past few years, we have focused our attention on the design and synthesis of new silicon-containing inorganic-organic hybrid polymers for optoelectric and high temperature resistant materials^[13–15]. On the basis of design and synthesis of a new ethynyl-terminated silylenediamine monomer, *N,N'*-bis(4-ethynylphenyl)-1,1-diphenylsilazane (**M1**), the new polymers containing Si-N bond, phenylene, and acetylene unit in main chain were synthesized using Sonogashira cross-coupling reaction of **M1** and diiodobenzene^[14]. These polymers show good thermal stability with their temperatures at 5% weight loss ($T_{5\%}$) higher than 394 °C, and char yield at 1000 °C are above 70% under nitrogen atmosphere. However, the very rigid main chain structure, which contributes to their good thermal stability, on the other hand, also results in their poor processability.

In this work, organosilicon unit containing compounds, bis-(4-bromo-phenyl)-dimethyl-silane (**M2**), 1,3-bis-(4-bromo-phenyl)-1,1,3,3-tetramethyl-disiloxane (**M3**), and 1,5-bis-(4-bromo-phenyl)-1,1,3,3,5,5-hexamethyl-trisiloxane (**M4**) were used as comonomers instead of diiodobenzene to react with **M1**, and the new phenylene-silazane-acetylene oligomers, **P2**, **P3** and **P4** were synthesized, respectively. We expected the

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incorporation of short length of silylene or siloxane units into the backbones of the oligomers could effectively improve their processability without scarification of thermal stability. The effects of the structural modification on the properties of oligomers were investigated. For comparison, oligomer **P1** was also synthesized by cross-coupling reactions between **M1** and 1,4-dibromobenzene.

EXPERIMENTAL

All reactions were carried out under nitrogen atmosphere unless otherwise noted. **M1** was prepared according to the method described in previous work^[14]. 1,4-dibromobenzene was purchased from Alfa Aesar. **M2**, **M3** and **M4** were prepared according to procedures described in the literature^[16]. Triethylamine (Et₃N) was distilled from calcium hydride before use. Tetrahydrofuran (THF) and toluene were freshly distilled over sodium/benzophenone. All other chemicals were purchased from Alfa Aesar or Acros and used as received. ¹H-NMR spectra were recorded on a Bruker AVANCE 400 spectrometer at frequency of 400 MHz in CDCl₃ with solvent signals allotted as internal standards. ²⁹Si-NMR spectra were recorded on a Bruker DMX 300 spectrometer at frequency of 60 MHz with TMS as external standard. Fourier transfer infrared spectra (FTIR) were recorded with a Bruker TENSOR-27 IR spectrometer in the range of 4000–400 cm⁻¹ using KBr discs. Differential scanning calorimetry (DSC) measurements were performed on an SII EXTRA 6200 DSC in flowing nitrogen at a heating rate of 10 K/min. Thermogravimetric analyses (TGA) were performed on an SII EXTRA 6300 TG/DTA at a heating rate of 10 K/min under nitrogen or air atmosphere. UV-Vis absorption and fluorescence spectra were measured at room temperature with a Shimadzu UV-1601PC spectrometer and a Hitachi F4500 spectrometer, respectively. Average molecular weights were estimated by gel permeation chromatography (GPC) analysis with polystyrene standard calibration using a WATERS 1515 isocratic HPLC pump and WATERS 2414 refractive index detector equipped with HR-4 column in THF.

A Typical Procedure for the Synthesis of the Oligomers: Oligomer P1

A mixture of **M1** (622 mg, 1.5 mmol), 1,4-dibromobenzene (354 mg, 1.5 mmol), Pd(PPh₃)₂Cl₂ (41 mg, 0.06 mmol), CuI (23 mg, 0.12 mmol), PPh₃ (79 mg, 0.3 mmol) in a THF/Et₃N (30/30 mL) mixed solvent was stirred at 65 °C for 24 h. Then the mixture was filtered and concentrated under reduced pressure. After addition of 30 mL toluene, the mixture was washed with brine. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The concentrated solution was added dropwise into 120 mL of vigorously stirred *n*-hexane to form a yellow precipitation. After filtration, the solid was dried in vacuum to afford 590 mg of **P1** in 80% yield as a yellow powder. ¹H-NMR (400 MHz, CDCl₃): δ = 7.72–7.64 (m, 4H, Ar–H), 7.49–7.39 (m, 10H, Ar–H), 7.26–7.22 (m, 4H, Ar–H), 6.83–6.76 (m, 4H, Ar–H), 4.34 (bs, 2H, NH); ²⁹Si-NMR (60 MHz, acetone-d₆): δ = –31.4; FTIR (KBr, cm⁻¹): 3376 (N–H), 3042 (C–H, Ar), 2209 (C≡C), 1604, 1514, 1441, 1374, 1282 (C–N), 1182, 1116, 1069, 1011, 903, 830, 779, 741, 701, 642, 595.

Polymer P2

P2 was synthesized in the same manner as described for **P1** by the reaction of **M1** and **M2** in 83% yield as a yellow powder. ¹H-NMR (400 MHz, CDCl₃): δ = 7.72–7.65 (m, 4H, Ar–H), 7.49–7.34 (m, 14H, Ar–H), 7.26–7.22 (m, 4H, Ar–H), 6.82–6.76 (m, 4H, Ar–H), 4.33 (bs, 2H, NH), 0.53 (s, 6H, CH₃); ²⁹Si-NMR (60 MHz, acetone-d₆): δ = –8.2, –30.6. FTIR (KBr, cm⁻¹): 3377 (N–H), 3046 (C–H, Ar), 2955 (C–H, SiCH₃), 2208 (C≡C), 1604, 1511, 1443, 1374, 1281 (C–N), 1181, 1113, 1068, 1011, 903, 828, 776, 742, 699, 639, 577, 515.

Polymer P3

P3 was synthesized in the same manner as described for **P1** by the reaction of **M1** and **M3** in 46% yield as a reddish-brown powder. ¹H-NMR (400 MHz, CDCl₃): δ = 7.73–7.63 (m, 4H, Ar–H), 7.49–7.36 (m, 14H, Ar–H), 7.28–7.22 (m, 4H, Ar–H), 6.83–6.76 (m, 4H, Ar–H), 4.32 (bs, 2H, NH), 0.32 (s, 12H, CH₃); ²⁹Si-NMR (60 MHz, acetone-d₆): δ = –2.4, –32.1. FTIR (KBr, cm⁻¹): 3380 (N–H), 3047 (C–H, Ar), 2956 (C–H, SiCH₃), 2209 (C≡C), 1597, 1512, 1443, 1375, 1297 (C–N), 1258, 1181, 1111, 1064 (Si–O–Si), 1014, 904, 829, 792, 743, 700, 662, 580, 542.

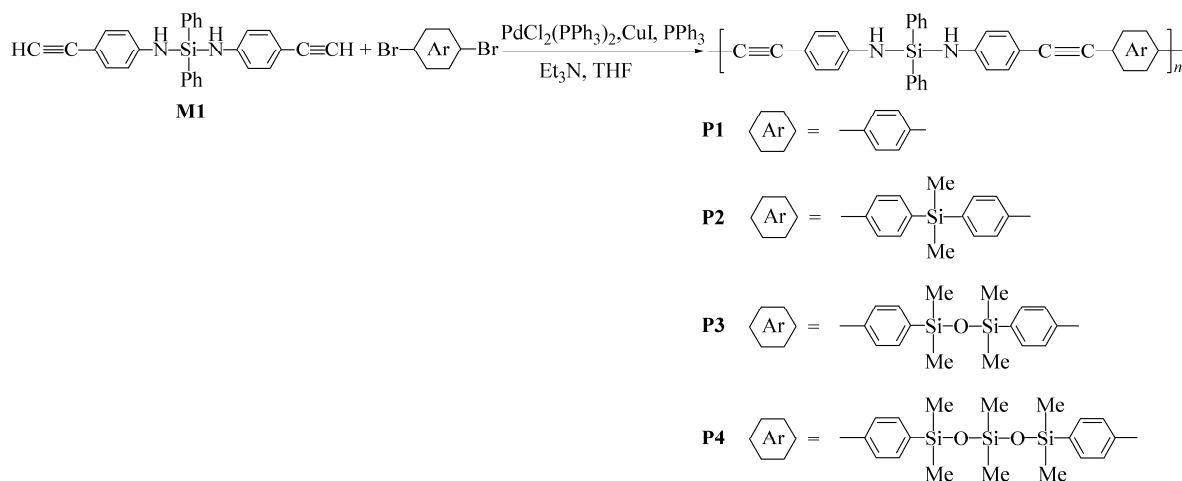
Polymer P4

P4 was synthesized in the same manner as described for **P1** by the reaction of **M1** and **M4** in 38% yield as a reddish-brown powder. $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 7.72\text{--}7.63$ (m, 4H, Ar—H), 7.48–7.34 (m, 14H, Ar—H), 7.28–7.22 (m, 4H, Ar—H), 6.82–6.76 (m, 4H, Ar—H), 4.32 (bs, 2H, NH), 0.30 (m, 12H, CH_3), 0.04 (m, 6H, CH_3); $^{29}\text{Si-NMR}$ (60 MHz, acetone- d_6): $\delta = -3.3, -19.3, -31.0$. FTIR (KBr, cm^{-1}): 3380 (N—H), 3046 (C—H, Ar), 2957 (C—H, SiCH_3), 2208 ($\text{C}\equiv\text{C}$), 1603, 1512, 1443, 1374, 1338, 1297 (C—N), 1258, 1181, 1112, 1043 (Si—O—Si), 904, 830, 797, 742, 700, 640, 571, 542.

RESULTS AND DISCUSSION

Synthesis and Characterization

The Sonogashira cross-coupling reaction between **M1** and 1,4-dibromobenzene or different silicon-containing bromophenyl-ended monomers **M2–M4** were carried out to afford oligomers **P1**, **P2**, **P3** and **P4**, as shown in Scheme 1. The coupling reactions proceeded well using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, PPh_3 , and CuI as co-catalysts in a mixed solvent of THF/ Et_3N . The solubility of the oligomers in several common organic solvents was tested at room temperature (Table 1). **P1** can be easily soluble in moderate to strong polar solvents such as THF and DMF, but it is only slightly soluble in toluene, CHCl_3 , and acetone due to its rigid chain structure. However, **P2**, **P3**, and **P4** are easily soluble in all used solvents. This fact suggests introduction of silylene, disiloxane, or trisiloxane units into the main chain of the oligomers increases the flexibility of the molecules and obviously improves their solubility in organic solvents. The molecular weights of the hybrid oligomers were determined by GPC measurements using polystyrene standards. The weight average molecular weights (M_w) of **P1–P4** are 2.4×10^3 , 2.8×10^3 , 3.3×10^3 , and 3.7×10^3 , with their polydispersity distribution indices (PDI) 1.74, 1.84, 1.92, and 1.79, respectively. All oligomers show relatively low average molecular weights, and the degree of polymerization ranged from 3 to 5. The fact is consistent with the results of previous work on synthesis of phenylene-silazane-acetylene polymers by Sonogashira cross-coupling reaction^[14]. All efforts tried to increase the molecular weight, including extending reaction time, increasing reaction temperature, and changing catalytic systems were failed. The facts suggest that the use of **M1** as a monomer is favor of formation of oligomers under the adopted reaction conditions.



Scheme 1 Synthesis of oligomers **P1–P4**

The stability of **M1**, **P1**, **P2**, **P3**, and **P4** was also examined. After being stored under ambient condition for three months, their $^1\text{H-NMR}$ spectra were examined and compared with those of as synthesized samples. Figure 1 shows $^1\text{H-NMR}$ spectra of **M1**, **M1'**, **P2**, and **P2'**, where **M1** and **P2** are new synthesized samples, while **M1'** and **P2'** are their 3-month stored counterparts, respectively. Compared with that of **M1**, new peaks at

$\delta = 7.81, 6.65, 4.10$ and 2.84 are observed in the spectrum of **M1'**, which are from the partial hydrolysis of Si—N bonds. However, oligomer **P2** is very stable and no variation is observed in the spectrum of **P2'**. The same results were also observed for the other oligomers, indicating that strong steric effects of bulky phenyl groups surrounding each Si—N bond prevent it from being attacked by water.

Table 1. Solubility of oligomers at room temperature

Samples	Toluene	CHCl ₃	THF	Acetone	DMF
P1	+ ^a	+	+++ ^b	+	+++
P2	+++	+++	+++	+++	+++
P3	+++	+++	+++	+++	+++
P4	+++	+++	+++	+++	+++

^a + Slightly soluble;

^b +++ Freely soluble

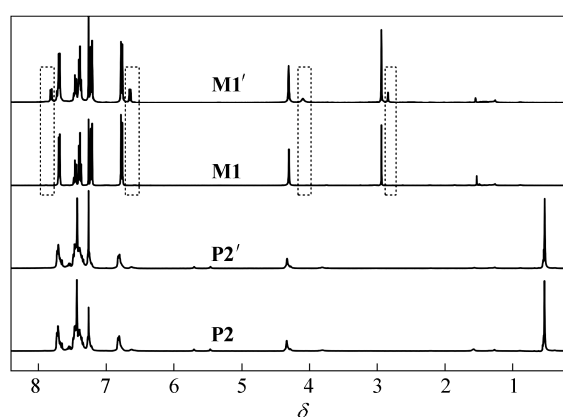


Fig. 1 ¹H-NMR spectra of **M1**, **P2**, and **M1'**, **P2'**

Photophysical Properties

Usually the poly(phenyleneethynylene) materials have the fluorescent behaviors^[17, 18], the photophysical properties of the oligomers were investigated by UV-Vis and fluorescence analyses in acetonitrile solutions. The samples were excited at their longest absorption maxima in the fluorescence measurement. The UV-Vis absorption and fluorescence emission spectra of oligomers **P1–P4** are shown in Fig. 2. Although the long distance conjugation is interrupted by the Si—N unit, oligomer **P1** containing Ph—C≡C—Ph—C≡C—Ph segments exhibits strong absorption and emission, with its absorption maximum at 330 nm and emission

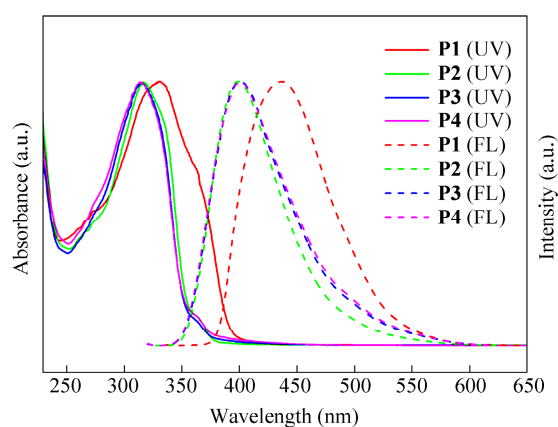


Fig. 2 UV absorption and fluorescence emission spectra of oligomers **P1–P4**

maximum at 438 nm. However, after introduction of silylene, disiloxane, or trisiloxane units into the oligomer backbone, both absorption and emission maxima shift to shorter wavelengths. Oligomers **P2–P3** exhibit almost identical absorption and emission spectra with their absorption and emission maxima at 316 and 400 nm, respectively. The $\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}$ segments in **P1** are efficiently conjugated, while in **P2–P4**, the conjugation is interrupted by the incorporated silylene, disiloxane, or trisiloxane groups, and the short $\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}$ units cannot form effective conjugation.

Thermal Properties

The thermal properties of the oligomers were primarily evaluated by DSC analysis under nitrogen atmosphere at a heating rate of 10 K/min. The DSC thermograms for the oligomers **P1–P4** are shown in Fig. 3, and the exothermic peak temperatures (T_p) and exothermic enthalpies (ΔH) of the oligomers are summarized in Table 2. All the oligomers exhibit similar DSC traces. The melting or glass transition points were not observed, and all samples show only broad exothermic peaks in the range of 120 °C to 250 °C. The exothermic peaks are attributed to thermal cross-linking reactions of the ethynyl groups including the cyclotrimerization, addition reaction and so on of those polymerization^[19–24]. After the thermal cross-linking reaction, the oligomers were transferred into stable cured polymers. As the important parameter which can value cross-linking reaction, the T_p of the synthesized hybrid oligomers are below 190 °C, which are lower than those of silarylene-ethynylene polymers (238–385 °C)^[15, 16] and **M1** (234 °C)^[14]. This may be due to the distinctive backbone structure and solid-state polymerization of acetylenes^[25]. The secondary amines ($-\text{NH}-$) in the polymer main chain are electron-donating groups, which can activate phenyleneethynylenes *via* inductive effect. On the other hand, there are no melting points before the thermal cross-linking reaction of the oligomers. The reaction is a solid-state polymerization of ethynylenes, which may occur easily at low temperatures in an ordered crystalline-like phase^[26]. Therefore, the lower exothermic temperature of cross-linking reactions for the synthesized oligomers is reasonable. As shown in Table 2, from **P1** to **P4**, the exothermal peaks for oligomers shift to lower temperatures gradually, with their exothermic enthalpies decrease as well. The oligomer **P1** shows the highest T_p because it has more rigid main chain structure, which limits the cross-linking reaction of ethynylenes. For **P2**, **P3** and **P4**, the flexible units relieve the rigidity of molecular main chain and provide favorable conformation for the reactions. Moreover, the length of flexible units in the main chain extends from **P2** to **P4**, the proportion of flexible structures in the oligomers gradually increases. The flexible units improve the movement of chain segment of oligomers, thus, the cross-linking reaction is possible at lower temperatures in solid-state circumstance. Also, along with the enlarged proportion of flexible units in these similar structure and molecular weight oligomers, the content of the ethynylene groups may decrease. The cooperative effects of above facts lead to the decrease in T_p from 182 °C to 162 °C, and a reduction of the exothermic enthalpies from 127 J/g to 113 J/g, respectively.

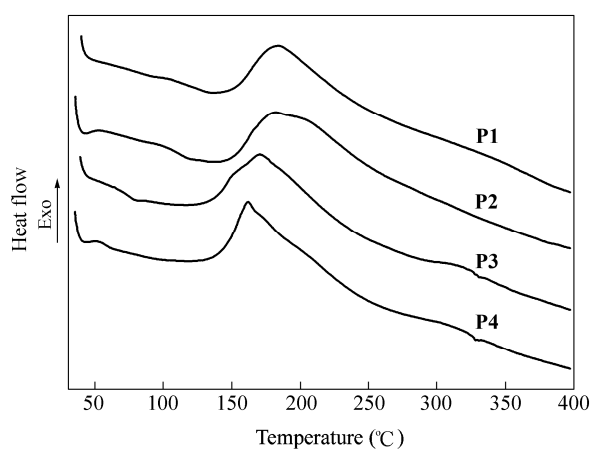
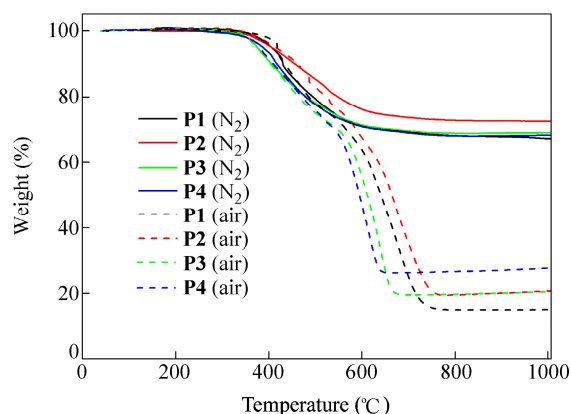


Fig. 3 DSC traces of oligomers **P1–P4** in nitrogen atmosphere at a heating rate of 10 K/min

Table 2. DSC and TGA data of oligomers **P1–P4** at a heating rate of 10 K/min

Samples	DSC		TGA in N ₂		TGA in air	
	T_p (°C)	$-\Delta H$ (J/g)	$T_{10\%}$ (°C)	Char yield (%, 1000 °C)	$T_{10\%}$ (°C)	Char yield (%, 1000 °C)
P1	184	130	427	67.2	434	15.2
P2	182	127	457	72.5	464	20.8
P3	170	120	407	69.0	404	20.6
P4	162	113	422	68.2	410	27.7

The thermal degradation behaviors of the oligomers were studied by TGA analysis at a heating rate of 10 K/min under nitrogen or air atmosphere. The TGA traces of **P1–P4** are shown in Fig. 4, and the detailed data are summarized in Table 2. Their TG curves demonstrated similar thermal stability. In comparison with **P1**, the new oligomers **P2**, **P3** and **P4** retain good thermal stabilities after introduction of new silylene, disiloxane and trisiloxane units into the backbone. Under nitrogen atmosphere, the hybrid oligomers show high decomposition temperatures and char yields, and their decomposition temperatures at 10% weight loss ($T_{10\%}$) are above 405 °C. The most of weight loss occurred in the range of 400 °C to 650 °C due to the the thermal degradation of the cured polymer which had cross-linking structures formed by ethynylene groups during heating process. There is no obvious weight change for all samples after 750 °C, and the char yield at 1000 °C are all above 67%, the flexible units provide less effect in the thermal behaviors. Oligomer **P2** exhibits the best thermal property (even better than **P1**), suggests its potential application as high temperature resistant resin and precursor for Si-based ceramic. Under air atmosphere, the $T_{10\%}$ of **P1–P4** are 433, 464, 404, and 410 °C, respectively, with their char yield at 1000 °C lower than 28%. It is noteworthy that the $T_{10\%}$ of the oligomers under air are comparative to those of them under nitrogen, which indicates their good thermal-oxidative stability. Among all samples, **P2** also exhibits the highest decomposition temperature $T_{10\%}$ under air. The highest thermal and oxidative stability of **P2** may be attributed to the synergistic effect of proportional silylene and ethynylene in the molecular structure^[20, 27]. Siloxane units in the oligomers weaken slightly the oxidative stability of polymers in air.

**Fig. 4** TGA traces of oligomers **P1–P4** in nitrogen or air at a heating rate of 10 K/min

CONCLUSIONS

New Si–N bond containing hybrid oligomers **P2**, **P3**, and **P4** were synthesized *via* Sonogashira cross-coupling reactions of *N,N'*-bis(4-ethynylphenyl)-1,1-diphenylsilazane (**M1**) with three silicon-containing (silylene, disiloxane and trisiloxane units) bromophenyl-ended monomers. These oligomers show improved solubility in common organic solvents than the oligomer **P1** obtained from the reaction of **M1** and 1,4-dibromobenzene, due to introduction of flexible silylene, disiloxane or trisiloxane units. The new oligomers retain good thermal properties. **P2** show the best thermal and thermal-oxidative stability, which may be attributed to the synergistic effect of proportional silylene and ethynylene in the molecular structure.

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