

# Synthesis of Vinyl Substitute Poly(silphenylene-siloxane) via Silyl Hydride-dialkoxysilane Process

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**ABSTRACT:** The synthesis of vinyl-substituted silphenylene-siloxane polymer through  $B(C_6F_5)_3$  catalyzed polycondensation of 1,4-bis(dimethylsilyl)benzene and vinylmethyl-dimethoxysilane is described.  $^1H$ -NMR,  $^{29}Si$ -NMR, and UV spectroscopy indicate that the vinyl groups remain undamaged during the polycondensation reaction. No hydrosilylation side reaction is observed under the reaction conditions. The microstructure of the polymer is not perfectly alternating

with a randomization of 20%. The temperature for 5% mass loss is 430°C in inert atmosphere and 417°C in oxidative atmosphere with a residue of 56% at 700°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1007–1013, 2007

**Key words:** high temperature materials; elastomer; poly(silphenylene-siloxane)s; polycondensation; fire-retardant materials

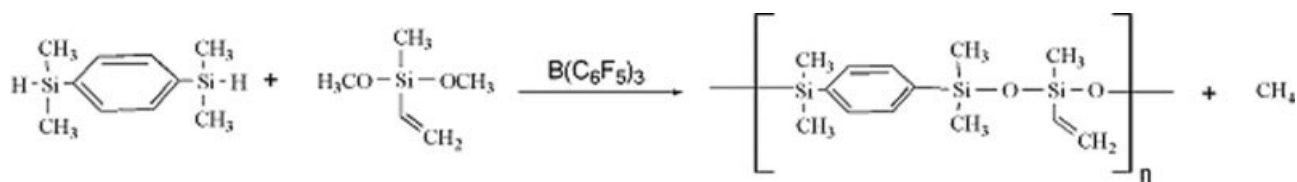
## INTRODUCTION

High-temperature polymers are used in many applications, such as insulators for microelectronic components, sealants for fuel tanks in high-speed aircraft, coatings on cookware, binders in brake systems, and structural components in space vehicles.<sup>1</sup> In conventional technologies, polymers containing halogens, nitrogen or phosphorous, such as fluorocarbon polymers, polyimide, polyphosphazenes,<sup>2</sup> and so on, are widely used as heat-resistant or fire-retardant polymers. However, the drawback of these materials in practical applications is the possible emission of toxic and corrosive gasses during combustion. Poly(silphenylene-siloxane) has long been known for their excellent ability to exhibit and retain superior mechanical properties over a broad temperature range. Poly(silphenylene-siloxane) is one kind of candidates for high-temperature polymers that do not generate hazardous gases during thermal decomposition. Polysilphenylene-siloxane is generally prepared by polycondensation of difunctional organosilanes or oligosiloxanes, such as dehydration of 1,4-bis(hydroxydimethylsilyl) benzene (BHSB) and 1,3-bis(hydroxydimethylsilyl)benzene,<sup>3</sup> condensation polymerization of BHSB and bis(dimethylamino)-,<sup>4–8</sup> bisureido-<sup>9,10</sup> or dichlorodialkylsilanes.<sup>6,11</sup> Dehydrogenative coupling of organohydrosilanes and organosilanols or other compounds with active hydrogen such as water is

particularly convenient due to its high selectivity and easy removal of the byproduct, hydrogen.<sup>12–19</sup> Unfortunately, this reaction requires relatively high concentration of precious catalysts (more than 0.1 mol %), and only moderate molecular weight copolymer have been obtained. Moreover, silanol self-condensation may accompany this process, leading to disruption of the desirable perfectly alternating architecture. Silyl hydrides/ $B(C_6F_5)_3$ , generally  $Ph_3SiH/B(C_6F_5)_3$  or  $Et_3SiH/B(C_6F_5)_3$  is a useful system in organic chemistry, particularly in the transformation of aldehydes, ketones, alcohol, carboxylic acids, and their derivatives into silyl ethers or hydrocarbons.<sup>20–29</sup>  $B(C_6F_5)_3$  catalyzed coupling reaction of silyl hydrides with alkoxysilanes was a newly developed methods to prepare linear polysiloxanes by Rubinsztajn and coworkers.<sup>30,31</sup> This reaction takes place at or below room temperature in the presence of very low levels of  $B(C_6F_5)_3$ . The rate of the reaction can be controlled by the rate of addition of reagents. The reaction is completed in 2–3 h, and high molecular weight (10–50 k) products are obtained.<sup>30</sup>

Incorporation vinyl group into the poly(silphenylene-siloxane) molecular demonstrates greatly improved thermal stability with low  $T_g$ s when compared with the corresponding methyl derivatives.<sup>5,8,32</sup> Furthermore, vinyl substituted poly(silphenylene-siloxane) can easily be crosslinked. The crosslinking density may be controlled over a broad range, depending on the ratio of the crosslinker to the vinyl groups. Thus, high-temperature materials can be obtained with properties controlled by the extent of crosslinking, ranging from a slightly crosslinked elastomer to a

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Scheme 1  $B(C_6F_5)_3$  catalyzed polycondensation of 1 and 4.

highly crosslinked resin structure. Thus, vinyl substituted polysilphenylenesiloxanes are described to be good candidates of high-temperature elastomers. Vinyl substituted silphenylene siloxane copolymers had been synthesized using the disilanol-diaminosilane and disilanol-dichlorosilane polycondensation methods,<sup>5,6,8,32,33</sup> but have not been synthesized through silyl hydride-dialkoxysilane polycondensation process yet (Scheme 1). Although  $B(C_6F_5)_3$  is also used to catalyze the hydrosilation of alkenes<sup>22</sup> and activate vinylic C—H to form vinylborane products,<sup>34</sup> the aim of this work is to disclose whether the vinyl substituted silphenylene siloxane copolymers can be synthesized through the newly developed silyl hydride-dialkoxysilane process while the vinyl group remain undamaged.

## EXPERIMENTAL

### Materials and instrumentation

#### Materials

Tetrahydrofuran (THF) and toluene were refluxed upon sodium sand to blue with benzophenone as indicator and then distilled; others reagents were used as received. 1,4-dibromobenzene (2), 98%, purchased from LongShen Fine Chemical Co. (Yangcheng City, China). Dimethylchlorosilane (3) and  $B(C_6F_5)_3$  were purchased from Fluka. Vinylmethyldimethoxysilane (4) was purchased from Aldrich (Milwaukee, WI).

#### Instrumentation

Mass spectrogram was acquired on GCMS-QP2010 (Shimadzu Co., Japan). Infrared spectrum was acquired on EQUINOX 55 (Bruker Co., Germany). UV spectroscopy was acquired on 760 CRT double-beam spectrophotometer (Shanghai, China).  $^1H$ -NMR and  $^{29}Si$ -NMR were recorded on an INOVA 500 NMR spectrometer (Varian Co., Palo Alto, CA) at 400 ( $^1H$ ), 99.3 MHz ( $^{29}Si$ ), respectively, with  $CDCl_3$  as solvent. TG curves were acquired on NETZSCH TG 209 (Netzsch Co., Germany) at a heating rate of  $10^\circ C/min$ , both the nitrogen and the air flow were 20 mL/min.

### Preparation of 1,4-bis(dimethylsilyl)benzene

To a 500-mL four-neck flask equipped with thermometer,  $N_2$  inlet, stir bar, condenser (the outlet was con-

nected to a dry tube filled with calcium chloride), drop funnel, was added 15.5 g magnesium powder and 100 mL THF. The flask was heated to  $60^\circ C$ . 50 g of 2 was dissolved in 100 mL THF, and it was added to the flask dropwise via drop funnel under ultrasonic condition and the atmosphere of dry  $N_2$ . The reaction started after several minutes of addition of the THF solution of 2. The start of reaction was indicated by a rapid exotherm and boil of the mixture.

*Caution:* when the THF solution of 2 is added to the flask under ultrasonic, an induction period is observed, and the reaction does not start after addition of the first few drops. The reaction may start suddenly after a significant amount of 2 is added with very high exotherm and violent boil of the mixture. In that situation it is preferable to turn off the ultrasonic and stop adding the solution of 2. Turn on the ultrasonic again and restart the addition after several minutes' boil of the mixture and the reaction will run smoothly this time. It is important to run experiments on a small scale and in a large enough flask so that significant volume is available for expansion of the reaction mixture.

When addition of the THF solution of 2 was completed, the reaction mixture was stirred for another 1 h under ultrasonic at  $60^\circ C$ , then the ultrasonic was turned off and the mixture was chilled to  $5^\circ C$  with ice water bath. THF (50 mL) and 43 g of 3 was added to the mixture dropwise via drop funnel. When it was completed, the mixture was heated to  $60^\circ C$  and stirred for another 1 h to complete the reaction. The slurry was washed with petroleum ether and filtered. The filtrate was washed with water and dried with anhydrous sodium sulfate. The disilane 1 was obtained by vacuum distillation at  $130$ – $134^\circ C$  (under 1.3 kPa). Spectroscopic data for disilane 1 are as follows. IR: 835 (m), 872 (versus), 889(s), 1136 (s), 1250 (s), 2120 (versus), 2960 (m)  $cm^{-1}$ . Mass spectrum:  $m/z$  (relative intensity): 194 ( $M^+$ , 11), 179 (16), 139 (5), 135 (100), 121 (6), 117 (3), 105 (7), 93 (1), 73 (3), 59 (5), 43 (5).  $nd^{20} = 1.5017$ .

### Polymerization

A dry 50-mL three-neck flask equipped with magnetic stirrer, condenser (the outlet was connected to a dry tube filled with calcium chloride), thermometer, and rubber septum seal was evacuated and then filled back with nitrogen. The flask was charged with 10 mL

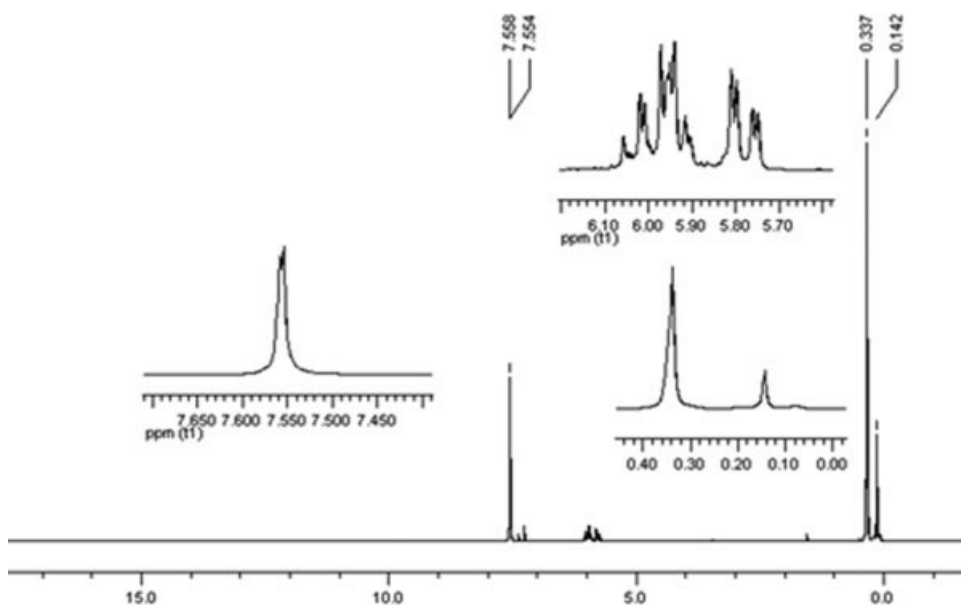


Figure 1  $^1\text{H-NMR}$  spectra of Copoly (tetramethyl-*p*-silphenylene-vinylmethylsiloxane).

of toluene, 1.40 g (7 mmol) of **1**, and 4.0 mg ( $7.4 \times 10^{-3}$  mmol) of  $\text{B}(\text{C}_6\text{F}_5)_3$ . The flask was heated to  $30^\circ\text{C}$ , and 0.90 g of **4** (7 mmol) was added dropwise via a glass syringe over a period of 2 h. The start of the condensation reaction was indicated by an exotherm and release of a gaseous byproduct.

When addition of **4** was complete, the reaction mixture was stirred for two additional hours at  $30^\circ\text{C}$  to complete the polymerization, then the reaction mixture was poured into 100 mL of methanol. Solvent was decanted from the precipitated polymer, and the residue was dissolved in methylene chloride. The polymer solution was filtered through anhydrous

$\text{CaSO}_4$ , solvent was removed under vacuum, and the polymer was dried on the vacuum line to yield of 1.73g (75%) of colorless viscous liquid. GPC analysis indicated  $M_w = 8688$ , and  $M_w/M_n = 1.71$ .

## RESULTS AND DISCUSSION

### Synthesis of vinyl substituted poly(silphenylene-siloxane)

Vinyl substituted silphenylene siloxane polymers have been synthesized previously using the chlorosilane,<sup>6</sup> ureidosilane,<sup>9,10,35</sup> and diaminosilane<sup>5,6,8,33</sup> routs. The chlorosilane-silanol condensation reaction will generate HCl that can catalyze the self-condensa-

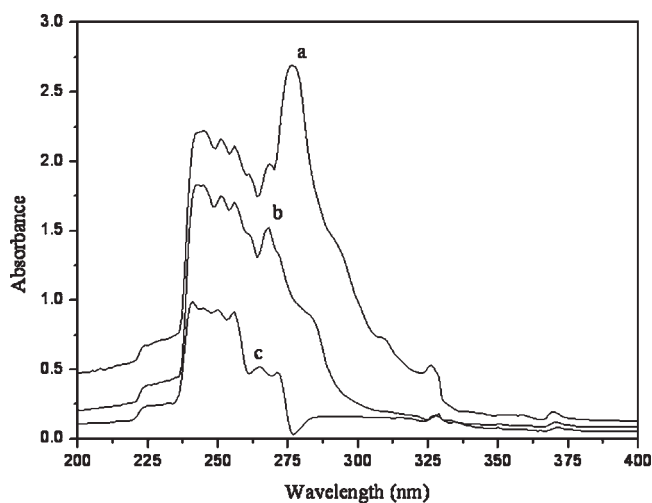
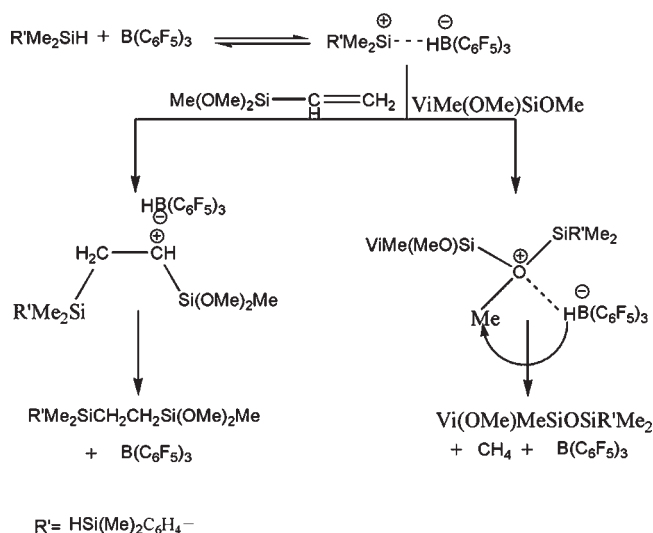


Figure 2 UV absorbance of Copoly (tetramethyl-*p*-silphenylene-vinylmethylsiloxane). (a) A mixture of **1** and **4** dissolved in  $\text{CH}_2\text{Cl}_2$ ; (b) 0.101g polymer dissolved in 2 mL  $\text{CH}_2\text{Cl}_2$ ; (c) **4** dissolved in  $\text{CH}_2\text{Cl}_2$ , with solvent  $\text{CH}_2\text{Cl}_2$  as blank.



Scheme 2  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyzed competition reaction of hydrosilation of vinyl group and dehydrocarbon reaction.

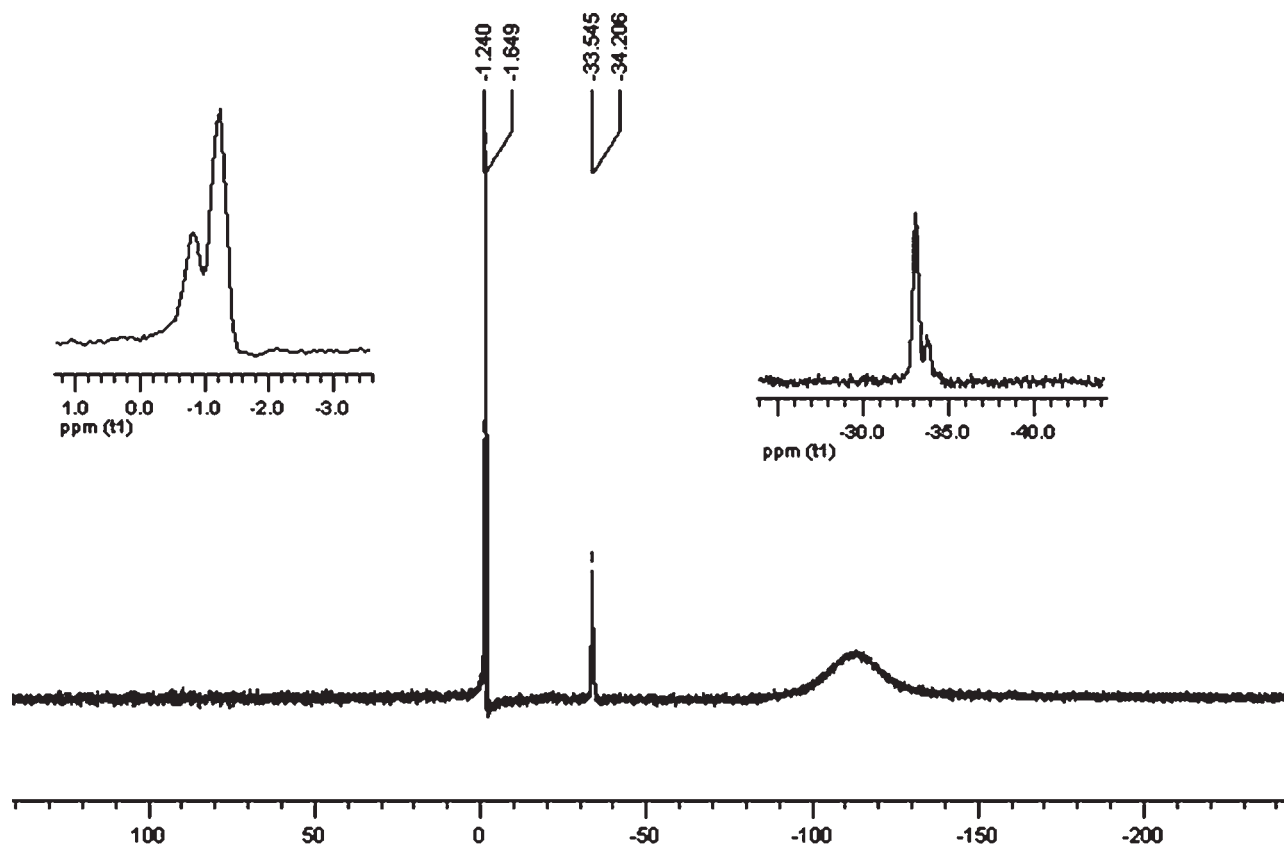


Figure 3  $^{29}\text{Si}$ -NMR spectra of Copoly (tetramethyl-*p*-silphenylene-vinylmethylsiloxane).

tion of the silanol monomer, thus preventing the formation of exactly alternating polymer structures. Although the ureidosilane and the diaminosilane approach can produce alternating polymers with high molecular weight, broad molecular weight distributions are common (in Zhu's investigation,<sup>8</sup> the PDI was 4.4). The reaction time of the ureidosilane-silanol reaction is extremely long, and the reaction temperature is extremely low. The diaminosilane-silanol process needs to reflux in toluene at 110°C, which may lead to a small amount of crosslinking side reaction of the vinyl group, the high vinyl substituted polymer synthesized through this process even can not be completely dissolved in THF.<sup>33</sup>

Poly(tetramethyl-*p*-silphenylene-vinylmethyl)siloxanes were synthesized through silyl hydride-dimethoxysilane process in this investigation. The reaction was easily carried out at room or slightly higher temperature catalyzed by very low level of  $\text{B}(\text{C}_6\text{F}_5)_3$  (0.1 mol % or  $6.2 \times 10^{-4}$  mol/L) with clean  $\text{CH}_4$  as the only byproduct. Reducing the amount of  $\text{B}(\text{C}_6\text{F}_5)_3$  to 0.05%, the reaction also proceeded successfully but took much longer time to complete. The reduced viscosity of the reaction mixture increased slowly when the reaction temperature was elevated to 45°C, indicated that higher temperature will slow down the polymerization reaction rate.

The molecular weight distribution ( $M_w/M_n$ ) of polymers synthesized through silyl hydride-dimethoxysilane process, which was 1.71 in this investigation, was much lower than the molecular weight distribution of analogue polymers synthesized through diaminosilane-silanol process, which was 4.4 in Zhu's investigation.<sup>8</sup>

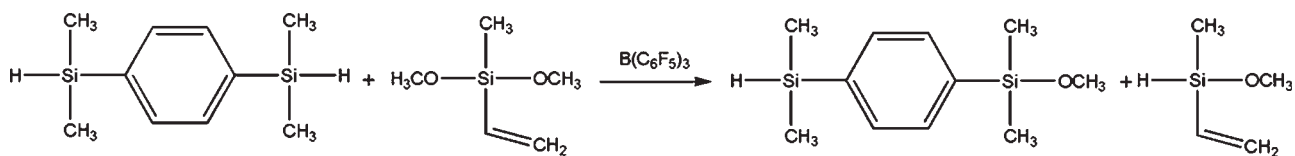
### $^1\text{H}$ -NMR

The  $^1\text{H}$ -NMR assignments and chemical shifts of characteristic absorption peaks of silarylene-siloxane

TABLE I  
Chemical Shift Assignment of Copoly(tetramethyl-*p*-silphenylene-vinylmethylsiloxane) From  $^{29}\text{Si}$  NMR Spectra  
 $-\text{Me}_2\text{SiArSi}^1\text{Me}_2-\text{O}-\text{Me}_2\text{Si}^1\text{ArSiMe}_2\text{O}-$   
 $-\text{Me}_2\text{SiArSi}^2\text{Me}_2-\text{OSi}^3\text{MeVi}-\text{OMe}_2\text{Si}^2\text{ArSiMe}_2\text{O}-$   
 $-\text{Me}_2\text{SiArSi}^2\text{Me}_2-\text{OSi}^4\text{MeVi}-\text{OSi}^4$   
 $\text{MeVi}-\text{OMe}_2\text{Si}^2\text{ArSiMe}_2\text{O}-$

Assignment	Chemical shifts <sup>a</sup>
$\text{Si}^1$	-1.240
$\text{Si}^2$	-1.649
$\text{Si}^3$	-33.545
$\text{Si}^4$	-34.206

<sup>a</sup> Chemical shifts (ppm) from TMS.



**Scheme 3** The exchange of hydrogen and alkoxy group catalyzed by  $\text{B}(\text{C}_6\text{F}_5)_3$ .

polymers have been reported by Dvornic and Lenz,<sup>9</sup> Lai,<sup>11</sup> and Dvornic and Lenz.<sup>35</sup> The peaks centered at 7.55 ppm are assigned to silphenylene and the peaks centered at 5.90 ppm to vinyl proton (Fig. 1). Methyl proton of  $-(\text{CH}_3)_2\text{Si Ar Si}(\text{CH}_3)_3\text{O}-$  and  $-\text{CH}_3\text{Si}(\text{Vi})\text{O}-$  show absorption at 0.337 and 0.142 ppm, respectively. The integrated intensity of the peak at 0.142 ppm is equal to the intensity of the multiplets centered at 5.9 ppm. The  $^1\text{H-NMR}$  spectra distinctly indicates that vinyl group tolerant of this reaction condition. UV study of the polymer also confirms this conclusion (Fig. 2). The prepared polymer shows remarkable absorbance between 242 and 256 nm, which are characteristic UV absorbance peaks of vinyl groups in vinylmethyldimethoxysilane.

$\text{B}(\text{C}_6\text{F}_5)_3$  is also an efficient catalyst of the aryl-containing hydrosilation of alkenes with high yields.<sup>22</sup> In the reaction of BDSB and vinylmethyldimethoxysilane, the Si—H bond is first activated by reversible formation of a  $\text{SiH-B}(\text{C}_6\text{F}_5)_3$  complex (Scheme 2), and then the incipient silylium species may form carbenium borate complex via addition silylium species across a double bond (Scheme 2),<sup>22</sup> or coordinate methoxy group of vinylmethyldimethoxysilane to yield an intermediate oxonium ion, which is subsequently reduced by hydride transfer from  $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$  to form polysiloxane.<sup>31</sup> In our investigation, the  $^1\text{H-NMR}$  and UV spectra of the polymer clearly indicate that no side hydrosilation reaction was observed, and the vinyl group remained undamaged during the reaction, which allow us in preparing vinyl substitute poly(silphenylene-siloxane), i.e., crosslinkable poly(silphenylene-siloxane), through this new efficient silyl hydride-dialkoxysilane process. The hydrosilation of olefins need relative high level of  $\text{B}(\text{C}_6\text{F}_5)_3$ , 5 mol %, which is much more higher than the level of  $\text{B}(\text{C}_6\text{F}_5)_3$  in the silyl hydride-dialkoxysilane couple reaction, which is only 0.1 mol % ( $6.2 \times 10^{-4}$  mol/L). At such a low level of  $\text{B}(\text{C}_6\text{F}_5)_3$ , the silylium species will merely coordinate the more basic function group, i.e., methoxy, to produce polysiloxanes.

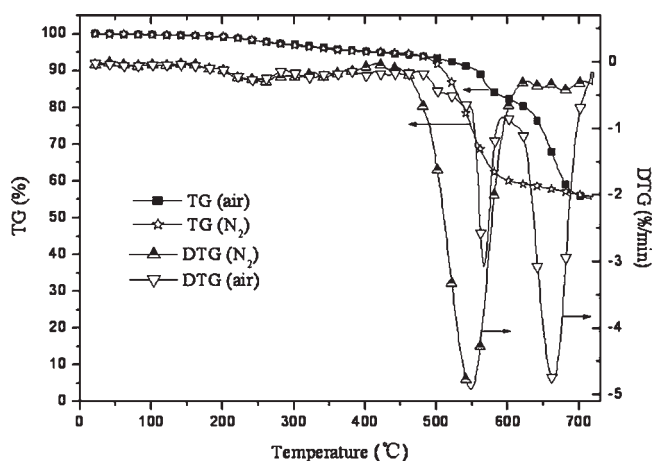
### $^{29}\text{Si-NMR}$

$^{29}\text{Si-NMR}$  can provide detailed information about the structure of the polysiloxanes. The  $^{29}\text{Si}$  chemical shifts of the prepared polymer show four absorption peaks (Fig. 3) indicates that the structure of the polymer is

not perfectly alternate. The absorption peaks in  $^{29}\text{Si-NMR}$  are readily assigned and are listed in Table I. The chemical shifts are similar to those observed by Babu and Newmark.<sup>6</sup> The randomization calculated from the integrated intensities of peaks at  $-33.545$  and  $-34.206$  ppm is 20%, much smaller than the randomization observed in the analogous polymer prepared via polycondensation of 1,4-Bis(hydroxydimethylsilyl)benzene (BHSB) and dichloromethylvinylsilane, but much greater than the randomization observed in the analogous polymer prepared via polycondensation of BHSB and bis(dimethylamino)methylvinylsilane. The randomization of the polymer prepared via these two processes was 50 and 4%, respectively.<sup>6</sup> The formation of observed nonalternating structure may explain as the exchange of hydrogen and alkoxy group (Scheme 3). This phenomenon is common in the  $\text{B}(\text{C}_6\text{F}_5)_3$  catalyzed reaction of silyl hydride and alkoxysilane.<sup>30,31</sup>

### TG analysis

The TG curves obtained in nitrogen and air atmosphere for the polymer are shown in Figure 4, while the characteristic mass loss data is presented in Table II. It can be seen that a single-step process occurred while degradation in nitrogen and a multi-step process was involved in air. Similar behavior has been observed previously.<sup>33,36</sup> a residue of about 56% was obtained at 700°C both in nitrogen and in air. The TG curves show that the onset of major thermal degrada-



**Figure 4** TG and DTG curves for Copoly (tetramethyl-*p*-silphenylene-Vinylmethyldimethoxysilane).

**TABLE II**  
The TG Data of Copoly(tetramethyl-*p*-silphenylene-vinylmethylsiloxane) Obtained in Nitrogen and Air Atmosphere

Atmosphere	Temperature for mass loss (°C)		Temperature for maximal rate of mass loss (°C)	Residue at 700°C (%)
	5%	40%		
Nitrogen	430	603	548	56.3
Air	417	679	567, 664	56.0

**TABLE III**  
Thermal Performance of Copoly(tetramethyl-*p*-silphenylene-vinylmethylsiloxane) Synthesized Through Different Routs

Work	Methods	$M_w \times 10^{-3}$ (PDI)	$T_g$ (°C)	$T_d$ onset <sup>a</sup> (°C)	$T_d$ <sup>b</sup> (°C)	Residue
Lauter et al. <sup>33</sup>	Diaminosilane-silanol	Not completely dissolve in THF	-63	- <sup>c</sup>	~560 <sup>d</sup> (air) ~560 <sup>d</sup> (N <sub>2</sub> )	~56% <sup>d</sup> (air) ~62% <sup>d</sup> (N <sub>2</sub> )
Zhu et al. <sup>8</sup>	Diaminosilane-silanol	477 (4.4)	-63	431 (air) 547 (N <sub>2</sub> )	- <sup>c</sup>	- <sup>c</sup>
Babu and Newmark <sup>6</sup>	Diaminosilane-silanol Dichlorosilane-silanol	10-30 (- <sup>c</sup> )	-62 -65	- <sup>c</sup>	- <sup>c</sup>	- <sup>c</sup>
This work	Silyl hydride-dimethoxysilane	8.7 (1.71)	-60.5	417 (air) 430 (N <sub>2</sub> )	510 (air) 560 (N <sub>2</sub> )	56% (air) 56% (N <sub>2</sub> )

<sup>a</sup> General 5% weight loss temperature.

<sup>b</sup> The onset of major thermal degradation of the polymer evidenced by an abrupt change of slope.

<sup>c</sup> Not presented by the author. The heat rate of the TG analysis of Lauter's and Zhu's work was 15°C/min, but it is 10°C/min in this work.

<sup>d</sup> Estimated from the TG curves.

tion of the polymer evidenced by an abrupt change of slope is about 510°C in Nitrogen and about 560°C in oxidative atmosphere. The temperature of onset of degradation ( $T_d$ , general 5% weight loss temperature) of the polymer was 430°C in nitrogen and 417°C in air. The polymer prepared through the silyl hydride-dialkoxysilane process has similar thermal performance to the polymer synthesized via dichlorosilane-silanol or diaminosilane-silanol routs. The results of different works are listed in Table III. The  $T_d$  of the similar polymer synthesized via diaminosilane-silanol process with very high  $M_w$  of  $477 \times 10^3$  g/mol was 431°C in air, which is slightly higher than the  $T_d$  of the polymer of this investigation, and 547°C in nitrogen atmosphere, which is much higher than the  $T_d$  of the polymer of this investigation.<sup>8</sup> The higher  $T_d$  in nitrogen may ascribe to the high molecular weight with less end group and very slight crosslinked structure.<sup>33</sup>

## CONCLUSIONS

Polysilphenylene-siloxane containing vinyl functional side groups was successfully synthesized through the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyzed polycondensation of 1,4-bis(dimethylsilyl)benzene and Vinylmethyl dimethoxysilane. <sup>1</sup>H-NMR, <sup>29</sup>Si-NMR, and UV spectra indicate that the vinyl groups remain undamaged during the polycondensation reaction. The microstructure of the polymer is not perfectly alternate, a randomization of 20% has been observed due to the exchange of the hydrogen

atom and methoxy group catalyzed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. The temperature for 5% mass loss of the materials is 430.2°C while degradation in nitrogen and 417.4°C in air with a high residue of about 56% at 700°C.

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