Synthesis and characterization of poly(silphenylenesiloxane)s containing functional side groups, a study to high-temperature elastomer

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Abstract

Poly(silphenylenesiloxane)s containing hydride or vinyl functional side groups were successfully synthesized by deaminative polycondensation of bis(aminosilane)s having the functional groups with monomeric or polymeric bis(silanol). The bis(silanol) prepolymer was prepared by palladium-catalyzed dehydrocoupling polymerization of 1,4-bis(dimethylsilyl)benzene with water. \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{29}Si NMR revealed that the polymers have exactly alternating structure of the starting component units. The poly(silphenylenesiloxane)s containing functional side groups have low \textit{T}_g\textsubscript{s} ranging from 23 to 48°C, and exhibit good thermal stability in both nitrogen and air atmosphere. For example, the most thermally stable polymer 3b-\textit{alt}, having vinyl side groups on half silicon atoms, has \textit{T}_g at –33°C which is 11°C lower than that of the all-methyl substituted PTMPS, and shows the highest degradation temperature at 498°C in nitrogen and 521°C in air. The TGA residues at 800°C are 67% in nitrogen and 54% in air. Isothermal studies revealed 3b-\textit{alt} only lost 2.5% weight after 5h at 400°C in nitrogen.

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1. Introduction

Modern technologies, especially in the technological areas of advanced aerospace and electrical devices, have continuous demands on development of high-temperature elastomeric materials. In some applications under extreme environmental conditions, the elastomers are required to exhibit thermal stability up to several hundred degree, and simultaneously to maintain flexibility to temperatures much lower than ambience. Polysiloxane is a kind of good candidate as high-temperature elastomer because of flexible and heat-resistant Si–O–Si backbone, which is also the origin of good dielectric and surface properties, and so on [1–3]. Thus, polysiloxanes have become one of the most important industrial products.

Silarylene–siloxane polymers, derivatives of polysiloxanes by partially replacing –O– by arylene groups, show better mechanical property than polysiloxane, and have attracted much interest as high-temperature elastomers for many years [2–5]. Corriu [6] investigated thermal reactions of the silphenylene siloxane polymers (Scheme 1, \(x \gg 1\)) at high temperature, and elucidated that the main course of degradation is the intermolecular exchanges of Si–O bonds leading to rearrangement to random copolymer, followed by intramolecular exchanges of Si–O bonds to depolymerization. Incorporation of rigid aromatic units into the siloxane backbone generally interrupts the siloxane redistribution reaction at high temperature, and improves both mechanical and thermal properties without simultaneous loss of other good features of polysiloxane.

Silphenylene–siloxane polymers, synthesized from 1,4-bis(hydroxydimethylsilyl)benzene (BHSB) and difunctional silane or siloxane, were intensively reported as materials possessing thermal stability and satisfying low temperature elasticity. One of the attractive aspects of these copolymers is the easiness of introducing variety of functional substituents (\(R_1, R_2\) in Scheme 1), such as vinyl, phenyl, hydrido, fluoroalkyl, etc. into the silane or siloxane unit [7–10]. These functional side groups were found to significantly affect the thermal properties of polymers. Among them, vinyl group was found superior to others for...
enhancing the thermal stability perhaps due to the thermal cross-linking reaction of the vinyl functions, and thus, vinyl substituted silphenylene siloxane copolymers are described to be good candidates of high-temperature elastomers [11,12].

Merker reported polycondensation of BHSB to give poly[(oxydimethylsilylene)(1,4-phenylene)(dimethylsilylene)] (Scheme 1, x = 0) [13], commonly called as poly(tetramethyl-p-silphenylenesiloxane) (PTMPS). This PTMPS contains the maximum number of rigid phenylene groups and the shortest disiloxane segments in the polymer backbone. It should be more reluctant to undergo siloxane rearrangement and would possess high thermal stability. However, PTMPS is not good as high-temperature elastomer because it is crystalline and would exhibit elasticity only at elevated temperatures [14,15]. Thus, for the application as high-temperature elastomers, proper chemical modification of the structure of PTMPS should be made to gain non-crystallinity and low temperature elasticity. For instance, poly(tetramethyl-silphenylenesiloxane) shows elastomeric behavior at low temperature when the p-phenylene units in the backbone are totally or partially replaced by m-phenylenes [16–18]. Keller and Homrighausen reported silphenylenesiloxane–diacetylene copolymers, having the Vulcanizable diacetylene moiety in the backbone, as high-temperature elastomers [19].

In this research, we were dedicated in the study of PTMPS derivatives from viewpoints of side group modification of –(CH₃)₂Si–Ph–Si(CH₃)₂–O– (TMPS) unit by hydride and vinyl group, in order to improve the thermal stability and simultaneously decrease the crystallinity of the polymer.

2. Experimental

2.1. Measurements

NMR (¹H, 500 MHz; ¹³C, 125 MHz; ²⁹Si, 99 MHz) spectra were obtained in CDCl₃ on a Varian 500 MHz spectrometer model Unity INOVA. Chemical shifts are reported in ppm relative to CHCl₃ (δ 7.26, ¹H), CDCl₃ (δ 77.0, ¹³C), and tetramethylsilane (δ 0.00, ²⁹Si). IR spectra were recorded using KBr pellets on a JASCO VALOR-III spectrophotometer. Size exclusion chromatography (SEC) analysis was performed on a JASCO HPLC Gulliver 900 with the combination of Shodex KF-801 (exclusion limit: polystyrene, 1.5 x 10⁴ Da) and KF-802 (exclusion limit: polystyrene, 5.0 x 10⁵ Da), or KF-803L (exclusion limit: polystyrene, 7.0 x 10⁵ Da) and KF-804 (exclusion limit: polystyrene, 4.0 x 10⁵ Da) columns using tetrahydrofuran (THF) as an eluent (flow rate, 1 ml/min). The differential scanning calorimetric (DSC) analysis was performed on a Seiko DSC6200 instrument at a heating rate of 5.0 °C/min under nitrogen flow. The thermogravimetric analysis (TGA) was performed on a Seiko Instruments TGA/DTA 220 with a heating rate of 5.0 °C/min under nitrogen flow or in air.

2.2. Materials

1,4-Bis(hydroxydimethylsilyl)benzene (BHSB) and 1,4-bis(dimethylchlorosilyl)benzene (BCSB) were obtained from Shin-Etsu Chemical. BHSB was recrystallized from a mixture of hexane and THF (1.5 ratio by volume) before use. Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct [Pd₂(dba)₃·CHCl₃] was purchased from Sigma–Aldrich. 1,4-Bis(dimethylsilyle)benzene (BSB) and poly(tetramethyl-p-silphenylenesiloxane) (PTMPS) were prepared according to the literatures [13,20–21]. Hexane, THF, benzene and toluene were distilled from sodium prior to use.

2.3. Synthesis of monomers and prepolymer

2.3.1. 1,4-Bis(methylchlorosilyl)benzene (1a) and 1,4-bis(methylvinylchlorosilyl)benzene (1b)

To the mixture of methyldichlorosilane or methylvinyl dichlorosilane (0.60 mol) and magnesium turning (8.0 g, 0.33 mol) in THF (100 ml), p-dibromobenzene (35.4 g, 0.15 mol, in 60 ml THF) was slowly added, and stirred at room temperature for 8 h in preparing 1a, and at 70 °C for 20 h for 1b under argon atmosphere. The yellowish crude product, obtained from the hexane extract, was purified by fractional distillation to give the pure product as colorless liquid.

In giving NMR data, protons of vinyl group are indicated as follows.

\[
\text{Si} \quad \text{H}_a \quad \text{H}_b \quad \text{H}_c
\]
2.3.2. 1,4-Bis(methylidylenamino)silyle (2a), 1,4-bis(methylidylenamino)silyle (2b) and 1,4-bis(dimethylidylenamino)silyle (2c)

1a, 1b and BCSB were converted to 2a, 2b and 2c by reacting with diethylanine (four-fold excess) in dry hexane. The pale yellow crude product was purified by fractional distillation to give pure product as colorless liquid.

2a: Bp: 85 °C/12 Pa. Yield: 70 %. 1H, δ: 7.56 (s, 4H, –C6H4–), 4.83 (q, J = 3.3 Hz, 2H, SiH2). 2.89 (q, J = 6.9 Hz, 8H, NCH2CH3), 1.02 (t, J = 6.9 Hz, 12H, N–CH2CH3), 0.40 (d, J = 3.3 Hz, 6H, –Si–C6H4–). 13C, δ: 139.6, 133.4 (–C6H4–), 41.0, 15.5 (NCH2CH3), −3.23 (SiCH3).

2b: Bp: 105 °C/10 Pa. Yield: 73 %. 1H, δ: 7.53 (s, 4H, –C6H4–), 6.30 (dd, Jab = 14.7 and Jca = 20.2 Hz, 2H, H2), 6.06 (dd, Jcb = 4.2 and Jab = 14.7 Hz, 2H, H3), 5.75 (dd, Jbc = 4.2 and Jab = 20.2 Hz, 2H, H2), 2.87 (q, J = 7.0 Hz, 8H, NCH2CH3), 0.99 (t, J = 7.0 Hz, 12H, NCH2CH3), 0.38 (s, 6H, SiCH3). 13C, δ: 139.2, 133.6 (–C6H4–), 137.7, 133.8 (–CH2–), 40.1, 15.6 (NCH2CH3), −3.13 (SiCH3).

2c: Bp: 105 °C/12 Pa. Yield: 82 %. 1H, δ: 7.54 (s, –C6H4–), 2.87 (q, J = 7.0 Hz, 8H, NCH2CH3), 1.01 (t, J = 7.0 Hz, 12H, NCH2CH3), 0.32 (s, 12H, SiCH3). 13C, δ: 141.1, 133.0 (–C6H4–), 40.1, 15.7 (NCH2CH3), −1.37 (SiCH3).

2.3.3. Prepolymer 4

To a 30 ml Schlenk flask were added Pd2(dba)3·CHCl3 (31.0 mg, 30 μmol) and THF (15 ml). In argon atmosphere, distilled water (0.612 g, 34.0 mmol) was added slowly by a syringe at room temperature. Vigorous hydrogen gas evolution occurred and ceased. After stirring for 5 h, the reaction was exposed to air and stirred for another 3 h to destroy the catalyst. Then the catalyst was removed by filtration through a short Florisil column using chloroform as eluent. Fractional precipitation was carried out by adding poor solvent methanol to the saturated toluene solution of the polymeric product to obtain three fractions of different molecular weight. The second fraction was used as prepolymer 4.

Prepolymer 4: Yield: 34 %. Mn = 2840, Mn/Mw = 1.03. FTIR (cm⁻¹): 3345 (vw, Si–O–H), 3047, 2975 (m, C–H), 1139, 1075 (s, Si–O–Si). 1H, δ: 7.54 (s, 4H, –C6H4–), 0.33 (s, 6H, SiCH3). 13C, δ: 140.7, 132.1 (–C6H4–), 0.90 (SiCH3). 29Si, δ: −1.23 (–O(SiMe2)2– in chain), −1.48 (minor, –(Me2)Si–Ph–Si(Me2)2OH), −2.53 (minor, terminal –(Me2)Si–Ph–Si(Me2)2OH).

2.4. Polymerization

2.4.1. Copolymerization to give alternating structure

To a 30 ml two-necked flask equipped with a magnetic stirring bar and a water condenser were added BHSB or hydroxy terminated silphenyleneoxosilane prepolymer 4 and anhydrous toluene (or benzene for 3a and 5a). When heated to 110 °C (80 °C for 3a and 5a), bis(aminosilane) 2 equivalent to 90 molar% BHSB or prepolymer 4, was added to the flask by a syringe. After stirring for 4 h, the leftover 10% bis(aminosilane) was added in two or three portions with a time interval of 1 h. The reaction mixture was finally precipitated in methanol twice from toluene (or benzene) to give the product polymer.

Polymer 3a: FTIR (cm⁻¹): 3050, 2959 (m, C–H), 2132 (s, Si–H), 1139, 1064 (vs, Si–O–Si). 1H, δ: 7.57, 7.54 (ss, 8H, –C6H4–), 5.14 (q, J = 3.0 Hz, 2H, SiH2), 0.41 (d, J = 3.0 Hz, 6H, HSiCH3), 0.34 (s, 12H, Si(CH3)2). 13C, δ: 140.6, 139.3, 132.8, 132.4 (–C6H4–), 0.46, 0.38 (Si(CH3)2), −0.49 (HSiCH3). 29Si, δ: 0.84, −13.80.

Polymer 3b-alt: FTIR (cm⁻¹): 3051, 2988, 2957 (m, C–H), 1594, 959 (w, C=C), 1138, 1067 (s, Si–O–Si). 1H, δ: 7.57 (s, 8H, –C6H4–), 6.27 (dd, Jab = 14.8 and Jaw = 20.1 Hz, 2H, H2), 6.04 (dd, Jab = 4.1 and Jaw = 14.8 Hz, 2H, H3), 5.79 (dd, Jab = 4.1 and Jaw = 20.1 Hz, 2H, H4), 0.39 (s, 6H, –=CHSiCH3), 0.33 (s, 12H, Si(CH3)2). 13C, δ: 140.8, 139.3, 132.9, 132.3 (–C6H4–), 137.5, 133.8 (–CH=CH2), 0.78 (Si(CH3)2), −1.13 (=CHSiCH3). 29Si, δ: −0.40, −12.76.

Polymer 5a: FTIR (cm⁻¹): 3049, 2957 (m, –CH3), 2129 (w, Si–H), 1138, 1073 (s, Si–O–Si). 1H, δ: 7.57, 7.54 (ss, –C6H4–), 5.12–5.15 (q, SiH2), 0.40–0.42 (d, HSiCH3), 0.32 (s, Si(CH3)2). 13C, δ: 141.0, 132.8, 132.3 (–C6H4–), 0.76 (Si(CH3)2), −0.47 (HSiCH3). 29Si, δ: 0.86, −1.26, −13.82.

Polymer 5b: FTIR (cm⁻¹): 3048, 2956 (m, C–H), 1623 (vw, C=C), 1138, 1073 (s, Si–O–Si). 1H, δ: 7.55 (s, –C6H4–), 6.24 (dd, H2), 6.04, 5.80 (2dd, H6 and H5), 0.38 (s, –=CHSiCH3), 0.33 (s, Si(CH3)2). 13C, δ: 140.9, 139.3, 132.9, 132.3 (–C6H4–), 137.5, 133.8 (–CH=CH2), 0.76 (Si(CH3)2), −1.13 (=CHSi–CH3). 29Si, δ: −0.33, −1.17, −12.71.

2.4.2. Copolymerization of 2b and 2c with water to give statistical structure

To the toluene solution of equimolar amounts of 2b and 2c, water [1:1 mole to the total bis(aminosilane)] was added within 8 h at 110 °C. After refluxing for another 20 h, random copolymer 3b-ran was obtained by precipitation in methanol.

Polymer 3b-ran: 1H, δ: 7.54 (s, –C6H4–), 6.23 (dd, H2), 6.04, 5.79 (2dd, H6 and H5), 0.41, 0.39 (ss, –=CHSi–CH3), 0.33, 0.32 (ss, Si(CH3)2). 13C, δ: 140.8, 140.6, 139.3, 139.1, 132.8, 132.3 (–C6H4–), 137.4, 137.3, 133.9, 133.7 (–CH=CH2), 0.93, 0.89 (Si(CH3)2), −0.96, −0.99 (=CHSiCH3). 29Si, δ: −0.38, −1.25, −12.01, −12.76.

3. Results and discussion

3.1. Synthesis and characterization

Silphenylene–siloxane polymer have been generally synthesized by homocondensation reaction of phenylene
disilanol or heterocondensation of disilanol with suitable difunctional silane or siloxane, in which the functionality was usually designed as chloro-, acetoxy-, amino-, or ureido- [22,23] groups. When considering the preparation of monomer and removal of byproducts with ease, the silanol–aminosilane condensation polymerization is the best choice for its high efficiency.

The synthesis of monomers for silanol–aminosilane polycondensation is shown in Scheme 2. Since only one Si–Cl group of the starting dichlorosilanes is desired to be consumed in the Grignard reaction, and the products in both steps are moisture sensitive, excess dichlorosilanes were used in the first step, and all procedures were performed under argon atmosphere. When preparing 1a, the reaction was controlled to proceed at around room temperature within a relatively short reaction time in order to minimize the unexpected disproportionation reaction of the silane derivatives, which is often observed in such reactions involving silanes containing at least one hydrido substituent [24–26]. By using slightly excessive amount of water in the palladium-catalyzed dehydrocoupling polymerization of BSB with water [18,20,21], and followed with careful fractional precipitation, the prepolymer 4 with hydroxy terminal and narrow polydispersity ($M_n = 2840$, $PD = 1.03$) was obtained.

Preparation of 3a was carried out in refluxing benzene which was a little milder than that of 3b-alt in refluxing toluene, because the silicon hydride in polymer 3a has a risk of decomposition and cross-linking in basic amine solution at higher temperature.

The exactly alternating structure of $-(\text{CH}_3)_2\text{Si}–\text{Ph}–\Si(\text{CH}_3)_2–\text{O}–$ (TMPS) unit and functional group substituted $-(R)\text{Si}–\text{Ph}–\text{Si}(\text{CH}_3)_2–\text{O}–$ (RMPS, $R = \text{H}$ or Vi) unit was confirmed by NMR. $^1\text{H}$ and $^{13}\text{C}$ NMR of polymer 3a and 3b-alt are very simple and show only well assignable signals to each specific hydrogen and carbon as described in experimental section. The integration is also well agreed with the expected polymer structures. As expected, $^{29}\text{Si}$ NMR of 3a shows only two sharp singlets at $-13.73$ and $0.86$ ppm due to the two kinds of backbone silicon atoms, methylhydridosilylene and dimethylsilylene.

$^{29}\text{Si}$ NMR of 3b-alt also presents two sharp singlets at $-12.76$ and $0.40$ ppm corresponding to methylvinylsilylene and dimethylsilylene, respectively, without detecting any other signals. The simplicity of these NMR spectra, especially $^{29}\text{Si}$ NMR spectra, suggested that the polymer 3a and 3b-alt have exactly alternating structures of TMPS and RMPS units.

The most persuadable proof for alternating structure of 3b-alt was given by the comparison with the random copolymer 3b-ran. The 3b-ran was synthesized by hydrolysis and in situ deaminative polycondensation of 2b and 2c (scheme 3). Although this synthetic approach is not commonly used and only gave a polymeric product with
Table 1
Molecular characteristics of poly(silphenylenesiloxane)

| Polymer no. | Yield a (%) | Molecular weight b | PDI | $T_c^c$ (°C) |
|-------------|-------------|--------------------|-----|-------------|
| 3a          | 90          | 69.3               | 23.3| 2.97        | 38           |
| 3b-alt      | 88          | 31.3               | 10.7| 2.92        | 33           |
| 5a          | 85          | 39.5               | 17.8| 2.21        | 23           |
| 5b          | 92          | 39.8               | 21.7| 1.83        | 24           |
| 3b-ran      | 68          | 4.7                | 3.6 | 1.3         | 40           |
| PTMPS       | 95          | 20.1               | 13.2| 1.52        | 22           |

a Isolated yield after reprecipitation in MeOH.
b Determined by SEC related to polystyrene standard.
c By DSC.

molecular weight about 4000 Da (Table 1), it is still satisfying to give 3b-ran. 

$^1$H,$^{13}$C and $^{29}$Si NMR of 3b-ran were not as simple as 3b-alt though they have the same composition. $^{29}$Si NMR shows two sets of signals at $-0.38$, $-1.25$, and $-12.01$ ppm (Fig. 1). Referring to the spectrum of 3b-alt, the signals at $-0.38$ and $-12.76$ ppm are reasonably assigned to the dimethylsilylene and methylvinylsilylene in the disiloxane linkages of the alternating cross diad units in 3b-ran. The signals at $-1.25$ and $-12.01$ ppm are obviously generated by the dimethylsilylene and methylvinylsilylene in their homo diad units in the random building blocks. The representative differences from 3b-alt in $^1$H NMR can be observed at the region of methyl signals. As shown in Fig. 2, the signals of both methyl protons in TMPS and in RMPS are separated to two overlapped peaks in the spectrum of 3b-ran unlike the only two single peaks in the spectrum of 3b-alt. The peaks at 0.39 and 0.33 ppm, which are the same with 3b-alt, are attributed to the $x$- and $y$-methyls in the cross-condensed disiloxane linkages of the alternating diad units, and the other two signals at 0.41 and 0.32 ppm are to the $w$- and $z$-methyls in the homo-condensed units (see w, x, y, z-methyl in Scheme 3). On the contrary the signals of aromatic and vinylic protons did not show significant changes.

![Fig. 1. $^{29}$Si NMR spectra of poly(silphenylenesiloxane)s.](image)

Polymerization of prepolymer 4 with monomer 2a and 2b led smoothly to give polymer 5a and 5b, which have another alternating structure of chain segment $-[(CH_3)_2Si-Ph-Si(CH_3)_2-O]_n-$ and RMPS unit. The functional units, RMPS, are very well dispersed in the polymer chain. This defined structure was also proved by NMR. $^{29}$Si NMR of both 5a and 5b show one major peak of $-Me_2Si-$ (at $-1.26$ ppm for 5a and $-1.17$ ppm for 5b) and two minor peaks corresponding to $-MeRSi-$ (at $-13.82$ ppm for 5a and $-12.71$ ppm for 5b) and $-Me_2Si-$ (at 0.86 ppm for 5a and $-0.33$ ppm for 5b) which is adjacent to $-MeRSi-$ (Fig. 1).

3.2. Thermal properties

Thermal properties of the polymers investigated by DSC are summarized in Table 1. All polymers have glass transition temperatures ($T_g$) ranging from $-20$ to $-40$ °C, which are relatively lower than ambient temperature. The maintained flexibility of these polymers at low temperature may meet the requirement for the flexibility of long-range use as high-temperature elastomer. Polymers 3a and 3b-alt are gum like materials at room temperature, and the former having a lower $T_g$ is a transparent material while the latter looks opaque. Both of them are amorphous without observation of any crystallinity by DSC scans. It indicates that introducing hydride and vinyl side groups to form an alternating structure has made the crystallinity disappear and given the polymers elasticity at low temperature. Polymers 5a and 5b are white sponge powder after precipitation in methanol. DSC measurement revealed that the $T_g$s of them are about 10 °C higher than 3a and 3b-alt and partial crystallization occurred at 11 °C for 5a and 23 °C for 5b. The $T_g$s and $T_c$s are very similar to that of PTMPS ($T_g = -22$ °C, $T_c = 15$ °C).

TGA curves of polymers under nitrogen atmosphere and in air at a heating rate of 5 °C/min are shown in Figs. 3 and 4. It can be seen that a single-step process occurred while degradation in nitrogen and a multi-step process was
involved in air. It is apparent that thermal degradation mechanism of the polymer in nitrogen is quite different from that of in air. A summary of the TGA results in nitrogen is given in Table 2. Each polymer has an onset degradation temperature above 400 °C and an end temperature of major degradation higher than 600 °C, except for polymer 3a. Compared to PTMPS, there is a dramatic increase of the residue yield for both SiH-substituted polymer 3a and vinyl-substituted 3b-alt and 3b-ran, even for 5b just containing a very low percentage of vinyl content. 3b-ran shows the almost same degradation stage with 3b-alt, but its weight loss at the end is 6% more than 3b-alt. This slight decrease of thermal stability of 3b-ran may be caused by its random structure and relative low molecular weight. It can be seen that introducing SiH functions made the polymer 3a produce the highest residue yield, although it showed a lower initial temperature of degradation. Meanwhile, incorporating vinyl functional units into the polymer chain have obviously increased both the thermal degradation temperature and the residue yield. Polymer 3b-alt, having the highest vinyl content (50% silicon atoms substituted with vinyl), shows the highest thermal stability.

Fig. 4 and Table 3 present the TGA results in air. It is clear that the major weight loss step of the functionalized polymers moved to higher temperatures compared to PTMPS. All polymers containing functional side groups show the temperature of 50% weight loss well above 600 °C, and final residues higher than that of PTMPS. Consistent with the result in nitrogen, polymers containing higher content of functional side groups (3a and 3b-alt) have higher stability than that of 5a and 5b, and alternating 3b-alt is also more thermally stable than 3b-ran having random structure. After undergoing a complicate multi-step degradation process, the residue of every polymer is white hard solid, which looks quite different from the black residue of degradation in nitrogen. As a common phenomenon of polysiloxane, the white residue is considered to be silica formed from the thermo-oxidative degradation in air, but the black one in nitrogen is still unsure in detail [9]. At this time, the degradation mechanism and detailed processes are beyond the discussion in this report.

Isothermal TGA was performed by keeping sample at 400 °C for about 5 h. 3b-ran was not investigated in this analysis. Figs. 5 and 6 show the curves of isothermal weight losses in nitrogen and air, respectively. Agreeing with the TGA results, polymer containing Si–H or vinyl side groups is stable and has less mass loss than PTMPS under such conditions. Polymer 3b-alt shows the lowest weight loss (2.5%) in nitrogen and 3a shows the lowest value (7.9%) in air, while PTMPS loses the highest 35% weight in nitrogen and 31% weight in air after 5 h at 400 °C. Although giving low weight losses during thermal degradation, 3a containing
The much Si–H content seemly prefer degrading from a lower temperature comparing to other samples. Polymer 3b-alt remarkably shows not only the highest degradation temperature, but also high residue yield. Thus, polymer 3b-alt containing the highest vinyl content was proved to be the most thermally stable by dynamic and isothermal TGA.

4. Conclusion

Poly(silphenylenesiloxane)s containing hydride or vinyl functional side groups were successfully synthesized through the deaminative polycondensation of hydride or vinyl substituted 1,4-bis(aminosilyl)benzene with 1,4-bis(hydroxydimethylsilyl)benzene (BHSB) and hydroxy terminated silphenylenesiloxane prepolymer 4. Except for the random copolymer 3b-ran, they all have exactly alternating structures and show low Tgs ranging from −23 to −40°C. Introducing hydride and vinyl substituents remarkably improves the thermal stability of the polymer. Polymer 3b-alt with high vinyl content is the most thermally stable proved by both dynamic and isothermal TGA. 3b-alt shows the highest degradation temperature at 498°C in nitrogen and 521°C in air. The TGA residues at 800°C are 67% in nitrogen and 54% in air, which are much higher than PTMPS. Isothermal studies revealed 3b-alt only lost 2.5% weight in nitrogen and 12.0% in air after 5h at 400°C. All polymers are considered having potential for using as high-temperature elastomers.

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