Synthesis, Thermal, and Dynamic Mechanical Properties of 1,3-Bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane-Containing Polydimethylsiloxanes

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ABSTRACT: New and effective approaches to the synthesis of 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane-containing polydimethylsiloxanes (**P1** and **P2**) were developed. **P1** was obtained by polycondensation of cyclodisilazane lithium salt and chloro-terminated polydimethylsiloxane. **P2** was produced by hydrosilylation of vinyl-terminated cyclodisilazane and hydrogen-terminated polydimethylsiloxane. The polycondensation completed quickly at room temperature, while the hydrosilylation was facile and did not require cumbersome air-sensitive operations. **P1** and **P2** were characterized by Fourier transform infrared, nuclear magnetic resonance, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis (TGA), and isothermal gravimetric analysis (IGA). TGA revealed the outstanding thermal properties of **P1** and **P2** with 5% weight loss temperatures (T_{d5}) higher than 450°C. IGA proved their better thermal stability at 450°C for 800 min, compared to polydimethyldiphenylsiloxane. Dynamic mechanical analysis showed that silicone rubbers made from cyclodisilazane-containing polydimethylsiloxanes could have a maximum tan δ value as high as 1.13 and had good prospects for damping material applications. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4231–4236, 2013

INTRODUCTION

Polysiloxanes, which possess excellent thermal properties, are among the best choices for applications whenever a polymer material is required to withstand an unusually wide range of temperatures and still maintain desired properties.[1] They embrace a unique combination of pronounced elasticity at unusually low temperatures and substantial thermal and thermo-oxidative stability at elevated temperatures.[1] Their glass transition temperatures (T_g) vary from −140 to −70°C, depending on the pendant groups attached to — $(Si—O)_n$— backbone, and their onset temperatures of degradation may reach to more than 300°C.[1] By contrast, most T_g of —C—C— polymers do not dive below −70°C, and degradation temperatures can hardly touch 200°C. Hence, polysiloxanes are widely used, sometimes irreplaceable, in extreme conditions, especially in aerospace and aviation industries.[1] But when it comes to damping properties, the loss factor of polysiloxanes-based silicone rubbers is only around 0.05–0.1, while conventional damping materials, such as butyl and urethane rubbers, are usually higher than 0.3. Methods to improve the damping properties of silicone rubbers include blending with organic or inorganic additives, copolymerizing or blending with other polymers, and so on.[2]

Studies on properties and practical applications of cyclodisilazanes had shown that dozens of these four-membered cyclic compounds possessed striking thermal stability.[3] No appreciable decomposition was observed even at 450°C for some cyclodisilazanes.[4,5] There were also a plenty of reports about possible applications of compounds with cyclodisilazane structures,[3] such as high-temperature liquid heat exchangers, lubricants, additives to lubricating oils, film-forming coatings, adhesion-improving coatings and reagents in leather, paper, mica, dye, and plastic industries; however, few literature reports about the effects of cyclic disilazane structures on thermal and dynamic mechanical properties of polysiloxanes have been published.

Our laboratory has successfully synthesized different cyclodisilazane-containing polydimethylsiloxanes by polycondensation of hydroxyl-terminated cyclodisilazanes and amino-terminated polydimethylsiloxanes[6,7]; and in this work, we are covering new
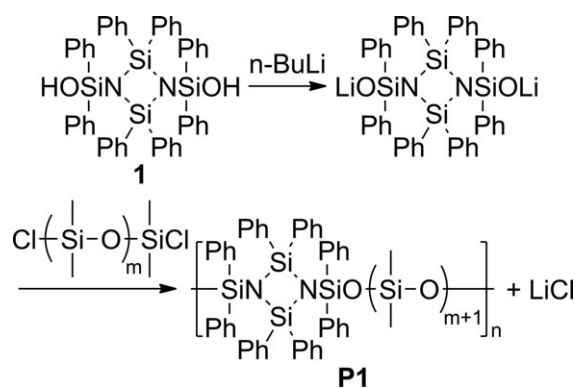
Scheme 1. Synthesis of **P1**.

synthetic approaches for 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane-containing polydimethylsiloxanes, their thermal properties, and the enhancement they bring to the dynamic mechanical properties of silicone rubber.

EXPERIMENTAL

Materials

N-butyllithium (1.6M in n-hexane) was purchased from Acros Company without further purification. Polydimethyldiphenylsiloxane (PDMDPS, 9% —Ph$_2$SiO—, viscosity 5000 cP at 25°C) was manufactured by Shanghai Resin Factory Co., 1,3-bis(hydroxydiphenylsilanyl)-2,2,4,4-tetraphenylcyclodisilazane (**1**), 1,3-bis(3,3-dimethyl-1,1-diphenyl-3-vinyldisiloxanyl)-2,2,4,4-tetraphenylcyclodisilazane (**2**), α,ω-dichloropolydimethylsiloxanes, and α,ω-dihydrogenpolydimethylsiloxanes were synthesized according to our previous work.[7,8] Commercial precipitated silica (specific surface area, 200 m^2/g) was purchased from Nanchang Kehong Chemical Co. Other chemicals were supplied by Beijing Chemical Works, and tetrahydrofuran (THF) was dried by refluxing over sodium wire under nitrogen and distilled before use.

Polycondensation to Afford Cyclodisilazane-Containing Polydimethylsiloxanes

P1 was synthesized by polycondensation (Scheme 1). In a three-necked flask, 12.5 mL n-butyllithium (0.02 mol) was cooled with ice-water bath. About 7.90 g (0.01 mol) **1** was dissolved in THF and added to the flask through an addition funnel. White precipitates were formed immediately. Then the flask was warmed to room temperature. About 12.39 g (m = 15, 0.01 mol) α,ω-dichloropolydimethylsiloxane was injected into the flask, and most of the white precipitates vanished. After the reaction was complete, all solvents were removed under reduced pressure. Crude product was dissolved in toluene and then filtered. After toluene was removed under reduced pressure, the product was washed with ethanol three times and dried in a vacuum desiccator. The final product was a yellow transparent sticky liquid (14.33 g, yield 74%). ^{1}H-nuclear magnetic resonance (^{1}H–NMR; 400 MHz, CDCl$_3$, δ): 6.87–7.50 (C$_6$H$_5$), 0.03–0.10 [OSi(CH$_3$)$_2$OSi(CH$_3$)$_2$OSi(CH$_3$)$_2$O], −0.03 [Si(C$_6$H$_5$)$_2$OSi(CH$_3$)$_2$OSi(CH$_3$)$_2$OSi(CH$_3$)$_2$], −0.21 [Si(C$_6$H$_5$)$_2$OSi(CH$_3$)$_2$OSi(CH$_3$)$_2$], and −0.32 [Si(C$_6$H$_5$)$_2$OSi(CH$_3$)$_2$]. ^{13}C-nuclear magnetic resonance (^{13}C–NMR; 400 MHz, CDCl$_3$, δ): 126.9–136.2 (C$_6$H$_5$) and 1.1 (CH$_3$). ^{29}Si-nuclear magnetic resonance (^{29}Si-NMR;

300 MHz, CDCl$_3$, δ): −14.1 [NSi(C$_6$H$_5$)$_2$N], −22.4 [OSi(CH$_3$)$_2$O], and −36.2 [NSi(C$_6$H$_5$)$_2$O]. M_n = 1.02 × 10^4 g/mol and M_w/M_n = 1.53.

### Hydrosilylation to Afford Cyclodisilazane-Containing Polydimethylsiloxanes

P2 was synthesized by hydrosilylation (Scheme 2). In a three-necked flask, 9.58 g (0.01 mol) **2** and 11.70 g (m = 15, 0.01 mol) α,ω-dihydrogenpolydimethylsiloxane were dissolved in THF, and then a catalytic amount of H$_2$PtCl$_6$ was added. The flask was heated to 60°C for 30 min. After THF was removed under reduced pressure, the product was washed with ethanol three times and dried in a vacuum desiccator. The final product was a brown transparent sticky liquid (17.82 g, yield 84%). ^{1}H-NMR (400 MHz, CDCl$_3$, δ): 6.86–7.47 (C$_6$H$_5$), 0.42 (CH$_2$), 0.02–0.07 [OSi(CH$_3$)$_2$OSi(CH$_3$)$_2$OSi(CH$_3$)$_2$O], −0.05 [CH$_2$Si(CH$_3$)$_2$OSi(CH$_3$)$_2$], −0.13 [CH$_2$Si(CH$_3$)$_2$OSi(CH$_3$)$_2$], and −0.37 [Si(C$_6$H$_5$)$_2$OSi(CH$_3$)$_2$CH$_2$]. ^{13}C-NMR (400 MHz, CDCl$_3$, δ): 126.9–136.2 (C$_6$H$_5$), 9.4 (CH$_2$), 1.1 [OSi(CH$_3$)$_2$O], and −0.7 [CH$_2$Si(CH$_3$)$_2$O]. ^{29}Si-NMR (300 MHz, CDCl$_3$, δ): 10.1 [CH$_2$Si(CH$_3$)$_2$OSi(CH$_3$)$_2$], 8.4 [Si(C$_6$H$_5$)$_2$OSi(CH$_3$)$_2$CH$_2$], −13.8 [NSi(C$_6$H$_5$)$_2$N], −21.8 [OSi(CH$_3$)$_2$O], and −35.6 [NSi(C$_6$H$_5$)$_2$O]. M_n = 1.52 × 10^4 g/mol, M_w/M_n = 1.40.

Preparation of Silicone Rubbers

About 100 phr (parts per hundred parts of rubber by mass) PDMDPS was vulcanized by 3 phr tetraethylorthosilicate (TEOS) to give rubber sample **R1**. Similarly, 100 phr **P1** (m = 15) and 3 phr TEOS were made into rubber sample **R2**. About 40 phr **P1** (m = 15) was blended with 100 phr PDMDPS on a three-roll mill. About 25 phr of silica was added to 100 phr of the preblended polymers and then followed by 3 phr TEOS. The final blend was vulcanized at room temperature for 2 weeks to give rubber sample **R3**. Samples **R4**, **R5**, and **R6** were made in the same way as R3, except that the m value of **P1** was 10, and the PDMDPS/**P1** ratios were 100/40, 100/20, and 100/60, respectively.

Measurements

Fourier transform infrared (FTIR) spectroscopy was recorded with a Bruker TENSOR-27 IR spectrometer. ^{1}H and ^{13}C-nuclear magnetic resonance (NMR) spectra were acquired on a 400 MHz Avance 400 spectrometer and ^{29}Si-NMR on a 300 MHz Bruker DMX 300 spectrometer, using chloroform (CDCl$_3$) as solvent and tetramethylsilane as external reference. Nonpolar
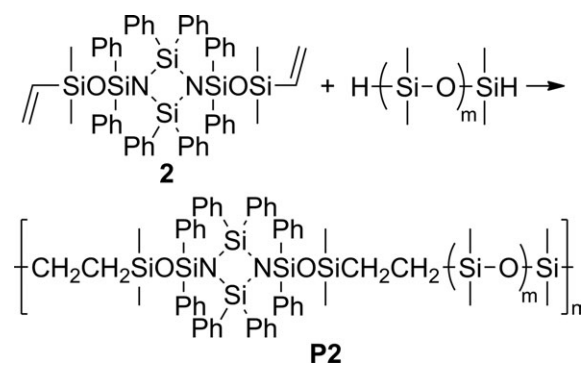
Scheme 2. Synthesis of **P2**.
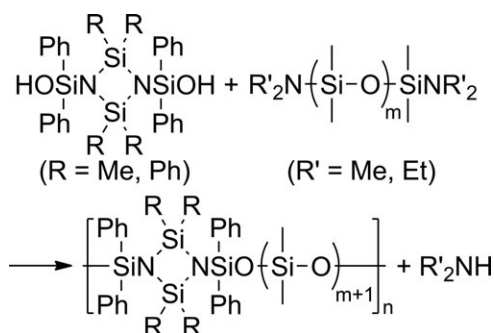
Scheme 3. Synthesis of cyclodisilazane-containing polydimethylsiloxanes.

Figure 2. ^{13}C-NMR spectra of P1 and P2.

paramagnetic relaxation agent for ^{29}Si-NMR was chromium acetylacetonate. Molecular weight and molecular weight distribution were determined by gel permeation chromatography at room temperature using Waters 515 HPLC pump, Waters 2410 refractive-index detector, and Waters Styragel columns (HT4). Flow rate of toluene eluent was 1.0 mL/min. Monodispersive polystyrene samples were used for molecular weight calibration. Differential scanning calorimetry (DSC) data were collected by a SII Extra 6200 Differential Scanning Calorimeter from −140 to −20°C at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) and isothermal gravimetric analysis (IGA) were carried out on a PerkinElmer Pyris Thermogravimetric Analyzer under 200 mL/min nitrogen flow and the IGA was carried out at 450°C for 800 min at a rate of 10°C/min, and the IGA parameter was 450°C 800 min. Dynamic mechanical properties of column samples with 10 mm in diameter and 10 mm in height were evaluated on a Perkin Elmer 7e Dynamic Mechanical Spectroscopy in compression mode from −130 to 130°C at a heating rate of 5°C/min with a fixed frequency of 1 Hz.

RESULTS AND DISCUSSION

Synthesis of Cyclodisilazane-Containing Polydimethylsiloxanes

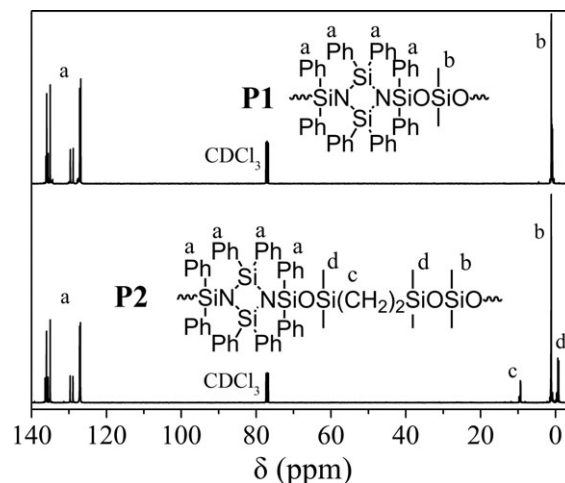Our laboratory has developed a synthesis route to obtain cyclodisilazane-containing polydimethylsiloxanes by polycondensation of hydroxyl-terminated cyclodisilazanes and amino-terminated polydimethylsiloxanes (Scheme 3).[6,7] However, this route required high temperature (>100°C) and long reaction time (>3 h), because the Si—OH of cyclodisilazane lacked reactivity. Instead of using 1 directly, we turned 1 into a lithium salt, which was extremely reactive to react with chloro-terminated polydimethylsiloxane at room temperature (Scheme 1). As soon as the white THF suspension of lithium salt came into contact with α,ω-dichloropolydimethylsiloxane, the suspension turned into a clear solution, indicating the rapid completion of the reaction.

Although both condensation reactions shown in Schemes 1 and 3 could give desired cyclodisilazane-containing polydimethylsiloxanes, they involved handling air-sensitive reactants that could be easily contaminated. To make matters worse, such contamination would generate acid or base that could further destroy cyclodisilazanes[9,10] and thus severely affect the molar ratio of cyclodisilazane to polydimethylsiloxane, resulting in low-molecular weight product. To eliminate the undesirability, we resorted to hydrosilylation, because this reaction (Scheme 2) involved neither air-sensitive reactant nor non-neutral substance and
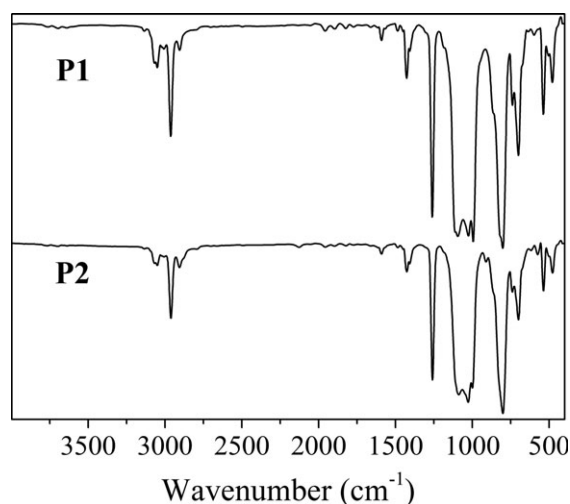
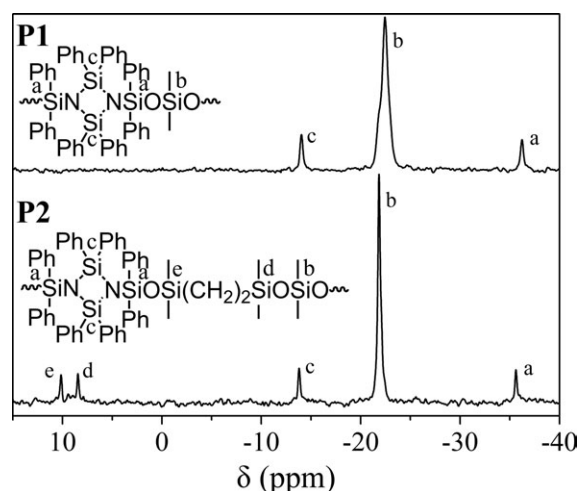

Figure 1. IR spectra of P1 and P2.
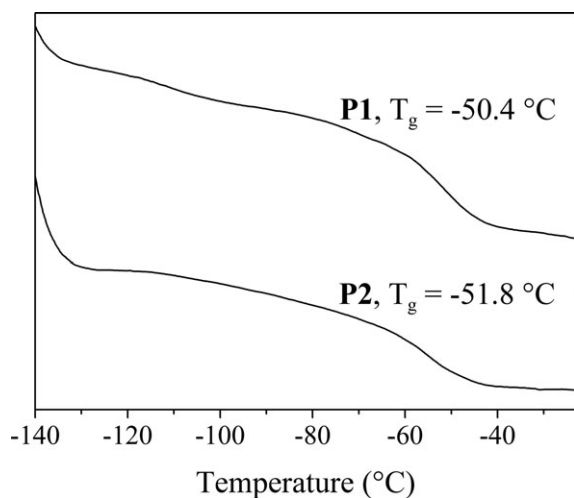

Figure 3. ^{29}Si-NMR spectra of P1 and P2.

Figure 4. DSC curves of **P1** and **P2** (10°C/min, in N$_2$).

Table I. TGA Data of P1, P2 and PDMDPS (10°C/min, in N$_2$)

	T_{d5} (°C)[a]	T_{dmax} (°C)[b]	wt % (800°C)[c]
P1	480	561	60.3
P2	464	525	26.1
PDMDPS	401	440	1.2

[a]Temperature at 5% weight loss, [b]Temperature at the maximum weight-loss rate, [c]Weight percentage at 800°C.

Thermal Analysis of Polysiloxanes

Thermal properties under nitrogen atmosphere were investigated by DSC, TGA, and IGA. Figure 4 showed the DSC curves of **P1** ($m = 15$) and **P2** ($m = 15$). Each of the curves had only one single glass transition. The Si—C segments in polymer backbone made only tiny difference between the T_g of **P1** and **P2**, which were -50.4 and -51.8°C, respectively. Generally speaking, when the molecular weight of a polymer is high enough (usually with M_n bigger than 10^5 g/mol), its T_g does not change as the molecular weight varies.[11] Although our previous work had demonstrated that the T_g of **P1** declined as the value of m grew from 0 to 6,[7] one should notice that all the M_n of polymer samples were no more than 7×10^4 g/mol; therefore, **P1** or **P2** with different m could have similar T_g. That means if a sample had greater m value and also higher molecular weight than another, these two samples may have similar T_g.

TGA curves of **P1** and **P2** were shown in Figure 5 and compared to PDMDPS that was a commonly used thermal-stable polysiloxane. Degradation temperatures at 5% weight loss (T_{d5}), decomposition temperatures at the maximum weight-loss rate (T_{dmax}), and weight percentages at 800°C were listed in Table I. There was no noticeable weight loss below 350°C for all the three polysiloxanes, but as temperature rose, the advantages of **P1** and **P2** over PDMDPS became glaringly apparent. T_{d5} of **P1** and **P2** was 480 and 464°C, respectively, overtaking PDMDPS by more than 60°C. The T_{dmax} of **P1** and **P2** was as high as 561 and 525°C, respectively, and PDMDPS was left behind with T_{dmax} no more than 450°C. The introduction of 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane structure into the —(Si—O)$_n$— backbone also tremendously increased the weight

therefore could control the molar ratio of reactants more easily. Furthermore, unlike condensation polymerization, hydrosilylation released no small molecule and, as a result, took fewer steps to purify the product and led to higher yield. Consequently, the molecular weight and yield of hydrosilylation were higher than that of polycondensation.

Structures of **P1** and **P2** were confirmed by FTIR and NMR. In the IR spectra (Figure 1), the C—H vibrations of the phenyl groups appeared at 3050, 2960, and 2906 cm^{-1}. The C—H vibrations of the methyl group appeared at 1591 cm^{-1} and also at 2960 cm^{-1}, which overlapped the phenyl groups. Two sharp and strong peaks at 1260 and 801 cm^{-1} were typical of Si—Me. A medium peak at 1427 cm^{-1}, a strong peak at 701 cm^{-1}, and three weak peaks at 1957, 1895, and 1823 cm^{-1} were attributed to the Si—Ph. The broad and strong Si—O peaks at 1093–1026 cm^{-1} overlapped the Si—N peak at 995 cm^{-1}. The differences between **P1** and **P2** were not clear in IR spectra, but could be easily identified in NMR spectra. About 0.42 ppm in ^{1}H-NMR, -0.7 and 9.4 ppm in ^{13}C-NMR (Figure 2), and 8.4 and 10.1 ppm in ^{29}Si-NMR (Figure 3), all denoted the presence of Si—CH$_2$ in **P2**.
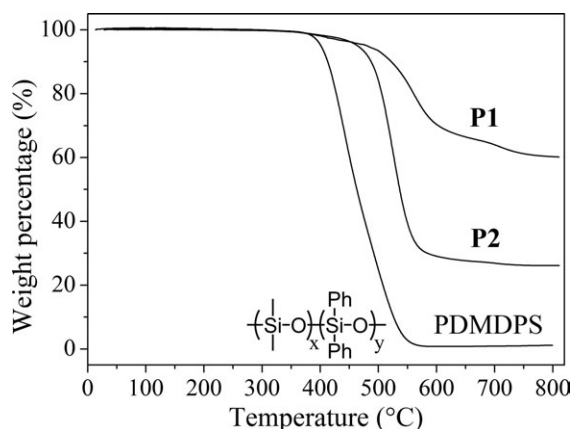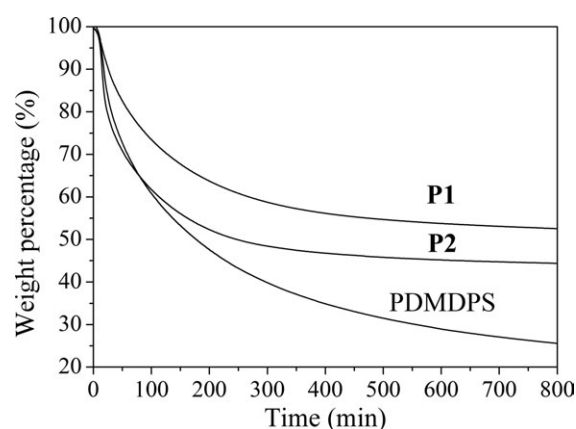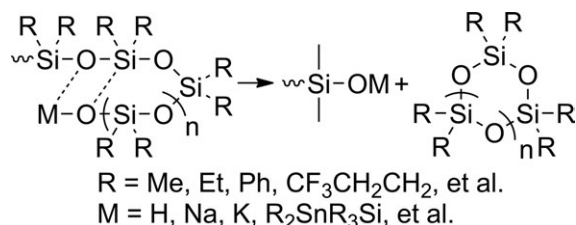

Figure 5. TGA curves of **P1**, **P2**, and PDMDPS (10°C/min, in N$_2$).

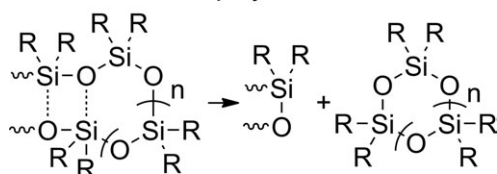**Figure 6.** IGA curves of **P1**, **P2**, and PDMDPS (450°C, in N$_2$).

Scheme 4. Unzipping mechanism.

retentions at 800°C: PDMDPS had almost no char left (only 1.2%), while **P1** still had 60.3% and **P2** 26.1%.
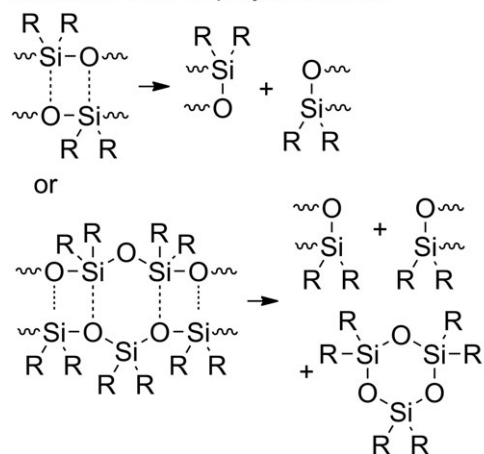
IGA is another important method to characterize the thermal stability of polysiloxanes. The lesser weight loss of a polysiloxane at a given period of time and a certain temperature, the more stable it is. IGA results of **P1**, **P2**, and PDMDPS at 450°C for 800 min were shown in Figure 6. In general, PDMDPS degraded faster than **P1** and **P2**. After 800 min of heating, the weight retention of PDMDPS was 25.6%, whereas **P1** was 52.5% and **P2** 44.4%.

It had been widely accepted that pure thermal degradation of polysiloxanes involves intramolecular or intermolecular reactions, which occurs readily because of the pronounced polarity of the Si—O bond and flexibility of the $—(Si—O)_n—$ segments.[1] Mechanisms, such as the unzipping mechanism (Scheme 4) and the random scission mechanism (Scheme 5),[12–14] had been proposed to explain different types of degradation. But when rigid and bulky groups were incorporated into the flexible $—(Si—O)_n—$ backbone, they would severely retard the movement and internal rotation of a macromolecule and also repelled the macromolecules from each other. As a result, the unzipping and random scissions could be greatly reduced. Therefore, **P1** and **P2**, which had rigid

Table II. The Polymer Contents of Silicone Rubbers

	The m value of P1	Amount of P1 (phr)	Amount of PDMDPS (phr)
R1	N/A	0	100
R2	15	100	0
R3	15	40	100
R4	10	40	100
R5	10	20	100
R6	10	60	100

and bulky cyclodisilazane structure in their main chains, showed better thermal stability than PDMDPS. The difference between **P1** and **P2** stemmed from the presence of C—C in **P2**, because C—C bond was much easier to cleavage than Si—O bond.

Dynamic Mechanical Properties of Silicone Rubbers

Damping capability of a polymer material is largely related to its viscoelastic behavior at glass transition region where the material changes from glassy state to rubbery state as the temperature rises. During the transition, chain segments, not the entire molecular chain, tend to vibrate in response to external force, but the conformation changes of molecular chains cannot catch up with the imposed force, resulting in internal friction and energy dissipation.[15] The stronger the internal friction, the better damping properties a polymer material possesses.

Dynamic mechanical analysis (DMA) is most commonly used to determine damping properties, which directly collect the data of storage modulus (E'), loss modulus (E''), and loss factor (tan δ, the ratio of E' to E''). Near the glass transition region, E' decreases by about three orders of magnitude, while E'' and tan δ go through maxima.

Silicone rubbers were prepared using different mass ratios of PDMDPS and **P1** (Table II). **R1** and **R2** were made from PDMPDS and **P1**, respectively, without adding silica. **R3**, **R4**, **R5**, and **R6** consisted of both PDMDPS and **P1** and were blended with 25 phr silica to make the rubber samples more similar to end-use products.
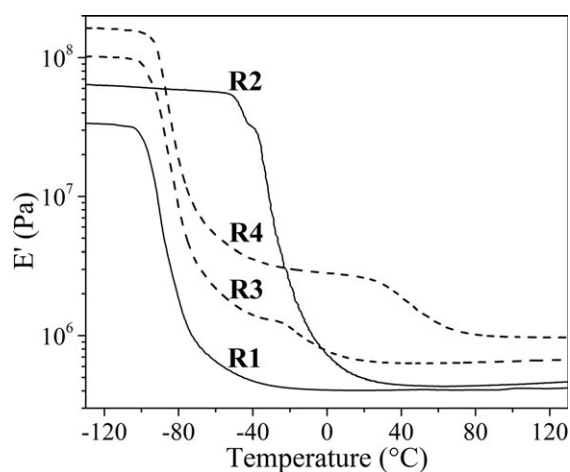

Scheme 5. Random scission mechanism.

Figure 7. E'—T curves of **R1**, **R2**, **R3**, and **R4** (5°C/min, 1 Hz).

Figure 7 showed the temperature dependence of E'. The storage modulus curves of **R1** and **R2** displayed only one transition near their T_g. The cyclodisilazane structure caused **R2** to have much larger E' than **R1**, especially below $-40°C$. **R3** and **R4** both had two transitions near the T_g of their component polymers. Because of the reinforcement effect of silica, the E' of **R3** and **R4** was higher than that of **R1** and **R2**. And more cyclodisilazane structure in the polymer backbone of **R4** made the E' of **R4** greater than **R3**.

Figure 8 was the temperature dependence of tan δ. Both **R1** and **R2** had only one sharp tan δ peak. The peak of **R1** was 0.95 at $-87.6°C$ and that of **R2** was 1.13 at $-29°C$. As mentioned earlier, the damping capacity of a polymer material has close relationship with glass transition, the glass transition depends on molecular structure, and rigid bulky groups generally increase the T_g,[11] and so the introduction of cyclodisilazane structure into the —$(Si—O)_n$— backbone definitely makes the tan δ peak of **R2** appear at a higher temperature than that of **R1**. When PDMDPS and **P1** were used together to produce **R3**, the two tan δ peaks still emerged at the same temperature ranges as PDMDPS and **P1** were used separately. This was because when the T_g of two different polymers was too far away from each other, like PDMDPS and **P1** in this case, their tan δ peaks usually did not merge. In terms of **R4**, the m value of **P1** was 10, which was smaller than that of **R3** ($m = 15$). A smaller m value was equivalent to more cyclodisilazane in polymer backbone and led to higher T_g, thus causing **R4** to have a tan δ peak at a higher temperature than that of **R3**.

Figure 9 showed the influence of PDMDPS/**P1** ratios on tan δ–T curves. With increasing amount of **P1**, the tan δ peak near the T_g of PSMDPS sank, while the peak near the T_g of **P1** rose.

From the DMA results, we could speculate that if appropriate amounts of cyclodisilazane-containing polydimethylsiloxanes with different T_g were applied to produce silicone rubbers, it would probably have a broad tan δ peak over a wide temperature range.

CONCLUSIONS

1,3-Bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane-containing polydimethylsiloxanes were successfully synthesized by polycon-
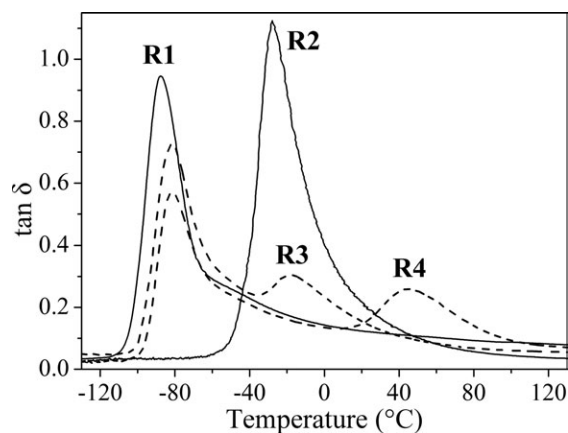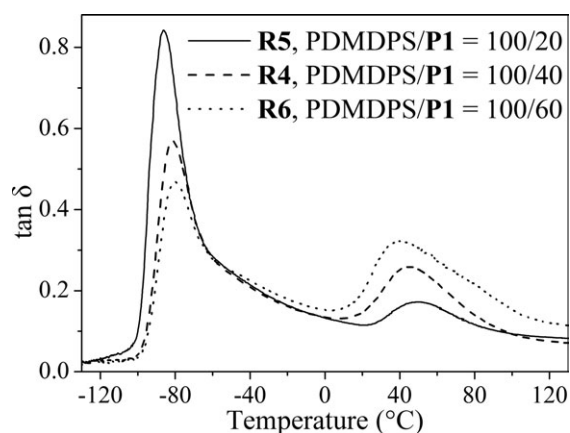

Figure 9. Influence of PDMDPS/**P1** ratios on tan δ–T curves.

densation and hydrosilylation. Polycondensation could rapidly generate **P1** under mild conditions, while hydrosilylation could easily afford **P2** with simple operation. IR, ^{1}H, ^{13}C, and ^{29}Si-NMR verified their structures. DSC determined their T_g. TGA unveiled their extraordinary thermal stability with T_{d5} above $450°C$ and good char yields at $800°C$. IGA at $450°C$ for 800 min also confirmed their advantages over conventional polysiloxane. DMA indicated that proper types and amounts of cyclodisilazane-containing polydimethylsiloxanes could produce silicone rubbers with tan δ peaks located at different temperature ranges and thus had potential damping applications.

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Figure 8. Tan δ–T curves of **R1**, **R2**, **R3**, and **R4** (5°C/min, 1 Hz).