

Synthesis, Characterization, and Thermal Properties of Alternate Copolymers Containing *N,N'*-Bis(diphenylsilyl)tetraphenylcyclodisilazane

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ABSTRACT: Hexamethyldisilazane was used as the starting material to synthesize *N,N'*-bis(hydroxydiphenylsilyl)-tetraphenylcyclodisilazane (BHPTPC). By condensation polymerization of BHPTPC with α,ω -bis(dialkylamino)dimethylsiloxane, a series of alternate copolymers containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane was synthesized. GPC studies show that the highest molecular weight was obtained at a ratio of 1.005 : 1 (BHPTPC: α,ω -bis(dimethylamino)dimethylsiloxane). Data of DSC indicate that the temperature of glass transition (T_g) and temperature of melting point (T_m) decreased with the increasing of dimethylsiloxane segments units. Three stages of degradation were found in

the thermogravimetric analysis curves. The activation energy of the copolymer (with $m = 2, 3,$ and 7) was calculated by using Flynn–Wall–Ozawa method. The activation energy of the copolymer with $m = 2, 3,$ and 7 at second stage is 214, 211, and 184 kJ/mol, respectively. Isothermal gravimetric analysis shows that for the same temperature and the same time, the weight loss of the alternate copolymer was greatly less than that of common polydimethylsiloxane. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 611–617, 2007

Key words: thermal properties; polysiloxanes; polycondensation; high temperature materials; activation energy

INTRODUCTION

Silicone rubbers have many excellent properties, such as good resistance to heat and cold, good hydrophobicity, good electroinsulating properties, etc. They have been widely used in many fields, such as aviation, aerospace, automobile industry, and medical field, to withstand very extreme conditions.^{1–3} The increasing need for thermally stable materials is constantly bringing demands for new polysiloxanes resisting even higher temperatures. The main reason for the degradation of high-temperature vulcanized silicon rubber in the inert atmosphere is adhered water and residual Si-bonded hydroxide group.^{3–5} Formation of small cyclosiloxanes leads to reduction in the thermal stability of polysiloxane.⁶ Preventing the main-chain ring-forming reaction is very necessary to improve the thermal stability of the high-temperature vulcanized silicon rubber. One method is using Si-bonded hydroxide group cleaners^{4,7–9}; another method is changing the main-chain structure by introducing bulky rigid groups, such as arylene,^{10–19} carborane,^{20–24} and cyclodisilazane groups.^{25–31} Our laboratory had reported the materials containing *N,N'*-bis(diphenylsilyl)tetrame-

thylcyclodisilazane (BPTMC), and these materials had very excellent thermal stability.^{8,31–34} However, the applications of these materials are limited by the synthesis of the monomers (BPTMC). In this study, the facile synthesized *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane (BPTPC) is employed instead of BPTMC to synthesize the high-temperature resistant polymers.

EXPERIMENTAL

Materials

Diphenyldichlorosilane, dimethyldichlorosilane, hexamethyldisilazane, diethylamine, and triethylamine were purchased from Beijing Chemical Works (Beijing, China) and fractional distilled before use. Solvents were purified by reported methods before use. Butyllithium (2.5 mol/L in hexane) was purchased from Acros Company, and was used as-received. Common polydimethylsiloxane with viscosity 300 cP was purchased from Beijing Chemical Works.

Synthesis of 1,3-dichloro-1,1,3,3-tetraphenyl-disilazane (1)

A mixture of Ph_2SiCl_2 (506 g, 2 mol) and hexamethyldisilazane (MM^{N} , 161 g, 1 mol) was stirred at 120°C to distill trimethylchlorosilane for over 24 h. After tri-

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methylchlorosilane was totally distilled out, the mixture was cooled to room temperature. The crude product was recrystallized from the mixed solvent of hexane and toluene to give 348 g (yield 77.24%) of pure **1** as white crystals. Melting point: 110.3–111.1°C.

¹H-NMR (CDCl₃), δ (ppm): 2.5 (s, 1H, NH), 7.2–7.6 [m, 20H, (C₆H₅)₄]. ²⁹Si-NMR(CDCl₃), δ (ppm): –8.25[s, NSi(C₆H₅)₂Cl]. Anal. calcd for C₂₄H₂₁Si₂NCl₂ (%): C, 63.99; H, 4.70; N, 3.11; Cl, 15.74. Found (%): C, 63.70; H, 4.56; N, 2.91; Cl, 15.49.

Synthesis of *N,N*-bis-(chloro-diphenyl-silanyl) tetraphenylcyclodisilazane (**2**)

Compound **1** (135 g, 0.3 mol) was dissolved in 600 mL toluene and to this solution was added the butyllithium (2.5 mol/L in hexane, 120 mL) in ice-water bath. The solution was warmed to room temperature and stirred for 4 h, after which hexane was removed. Stirring was continued at refluxing temperature for 12 h. The reaction mixture was filtered quickly and toluene was removed under reduced pressure. The crude product was recrystallized from the mixed solvent of toluene and hexane to give 185 g pure colorless crystal (yield 74.5%). Melting point: 256.4–257.0°C.

¹H-NMR (CDCl₃), δ (ppm): 6.8–7.6 [m, (C₆H₅)₈]. ²⁹Si-NMR(CDCl₃), δ (ppm): –12.36[s, NSi(C₆H₅)₂Cl], –13.60[s, NSi(C₆H₅)₂N]. Anal. calcd for C₄₈H₄₀Si₄N₂Cl₂ (%): C, 69.62; H, 4.87; N, 3.38; Cl, 8.56. Found (%): C, 69.61; H, 4.95; N, 3.46; Cl, 8.67.

Synthesis of *N,N*-bis-(hydroxy-diphenyl-silanyl) tetraphenylcyclodisilazane (**3**)

A suspension of compound **2** (124 g, 0.15 mol) in 200 mL ethyl ether was added dropwise to a mixture of ethyl ether (200 mL), distilled water (30 mL), and ammonia water (30 mL) in ice-water bath. After that the mixture was stirred at room temperature for 1 h. The precipitated crystals were filtered out and washed with hexane. The crude product was recrystallized from the mixed solvent of THF and hexane to give 89.32 g (yield 75.3%) of pure cyclodisilazane **3** as white crystals. Melting point: 222.7–223.6°C.

¹H-NMR (CDCl₃), δ (ppm): 2.05 (s, 2H, OH), 6.8–7.5 [m, 40H, (C₆H₅)₈]. ²⁹Si-NMR(CDCl₃), δ (ppm): –32.84 [s, NSi(C₆H₅)₂OH], –15.89[s, NSi(C₆H₅)₂N]. Anal. calcd for C₄₈H₄₂Si₄N₂O₂ (%): C, 72.87; H, 5.35; N, 3.54. Found (%): C, 72.89; H, 5.44; N, 3.29.

Synthesis of α,ω -dichlorodimethylsiloxane

In a 1000-mL flask, 20 mL water in 80 mL dioxane was added dropwise to the mixture of 242 mL Me₂SiCl₂ (2 mol) and 400 mL anhydrous ethyl ether. The mixed solution was refluxed for 2 h to remove the HCl. After removing the solvents, the remaining liquid was

fractionally distilled, and ClSiMe₂OSiMe₂Cl and Cl(SiMe₂O)₂SiMe₂Cl were obtained at their boiling points 138–140°C and 179–180°C (yield 32% and 28% respectively). The other α,ω -dichlorodimethylsiloxanes were synthesized in a similar way.

Synthesis of α,ω -bis(diethylamino) dimethylsiloxane

Et₂NSiMe₂OSiMe₂NEt₂ was prepared as follows. To the mixture of 250 mL Et₂NH and 450 mL petroleum ether, 102 g (0.5 mol) ClSiMe₂OSiMe₂Cl in 100 mL petroleum ether was added slowly. After the addition, the mixture was refluxed for 2 h. After removing the precipitate, the solvent was distilled out. The product, Et₂NSiMe₂OSiMe₂NEt₂, was fractionally distilled out at 75–78°C/1 mmHg (yield 74%). Other α,ω -bis(diethylamino)dimethylsiloxanes were prepared in a similar way.

Synthesis of α,ω -bis(dimethylamino) dimethylsiloxane

A solution of 220 g dimethylamine hydrochloride (2.70 mol) in 70 mL water was slowly added to 400 g anhydrous potassium hydroxide. The gaseous dimethylamine obtained was dried by anhydrous calcium oxide, and was then added to the mixture of 143 g of Cl(SiMe₂O)₆SiMe₂Cl (0.25 mol) in 500 mL petroleum ether. After the addition, the mixture was refluxed for 2 h. After removing the precipitate, the solvent was distilled out. About 119 g of the colorless product, Me₂N(SiMe₂O)₆SiMe₂NMe₂, was obtained (yield 81%).

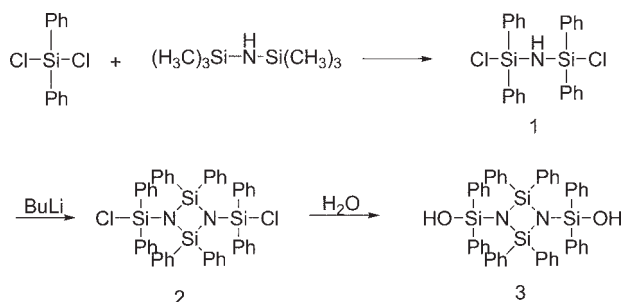
Synthesis of alternate copolymers

About 3.19 g of BHPTPC(4.04 mmol) and 1.70 g of Et₂N(SiMe₂O)₃SiMe₂NEt₂ (4 mmol) were dissolved in 50 mL toluene. The mixture was stirred at 90°C in nitrogen atmosphere for over 24 h, until no Et₂NH was detected. The polymer was precipitated in ethanol, filtered, and dried in a vacuum oven to give 3.52 g of product (yield 76%). The other alternate copolymers were all synthesized in a similar way.

Measurements

The chemical structures and compositions of the monomers and copolymers were studied by a 300 MHz Bruker DMX-300 NMR spectrometer. Tetramethylsilane was used as the external reference and CDCl₃ was the solvent.

The molecular weight and molecular weight distribution were determined by gel permeation chromatography (Waters 515 HPLC) at room temperature. The eluent was toluene and the flow rate was 0.35 mL/min. The molecular weights and the molecular weight



Scheme 1

distributions were calculated against polystyrene standards.

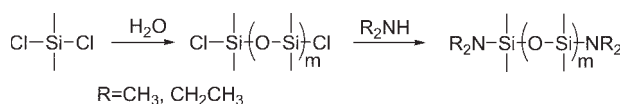
The thermal properties were determined by differential scanning calorimetry with a Mettler Toledo DSC822^e instrument. Specimens were heated from -100°C to 200°C at a constant rate of $10^{\circ}\text{C}/\text{min}$. All the measurements were conducted under a high-purity nitrogen gas atmosphere. Thermogravimetric analyses (TGA) of the polymer were carried out on a Perkin-Elmer Pyris 1 TGA Thermogravimetric Analyser. The studies were done in nitrogen atmosphere at a flow rate of $60\text{ mL}/\text{min}$. The weight of the sample used was from 5 to 10 mg, and was heated from 50°C to 800°C .

The melting points were measured with WRS-1A Digital Melting Point Apparatus. Elemental analyses were performed by Center for Physicochemical Analysis and Measurement, Institute of Chemistry, Chinese Academy of Sciences, Beijing.

RESULTS AND DISCUSSION

1,3-Dichloro-1,1,3,3-tetraphenyldisilazane (DCTPS) was used as the starting material to synthesize *N,N'*-bis(chlorodiphenylsilyl)tetraphenylcyclodisilazane (BCPTPC) as described in Scheme 1. DCTPS was synthesized by the reaction of hexamethyldisilazane with Ph_2SiCl_2 . The reaction was carried out in a moderate temperature (about 120°C), and the yield of DCTPS was about 78%. The method we used is much simpler and more effective than those that were reported. In the literature, the DCTPS was synthesized by the reaction of octamethylcyclotetrasilazane (D_4^N) or hexamethylcyclotrisilazane (D_3^N) with excess diphenyldichlorosilane, and the reaction was carried out at a high temperature, at least 180°C , and the yield was no more than 70%.^{35,36}

BCPTPC was synthesized by a ring-closure reaction of DCTPS, illustrated in Scheme 1, as described by Breed and Wiley.³⁷ In the literature, the solvent was



Scheme 2

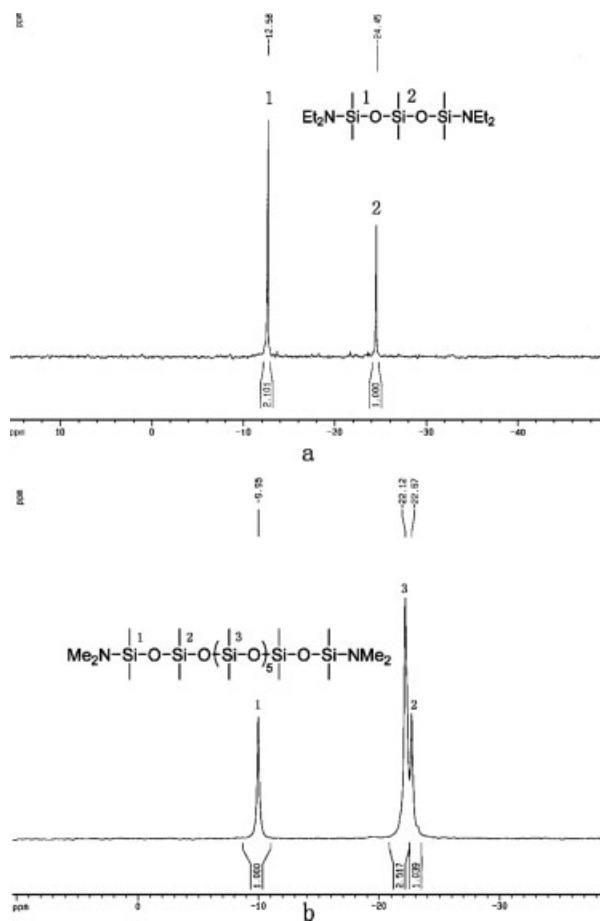
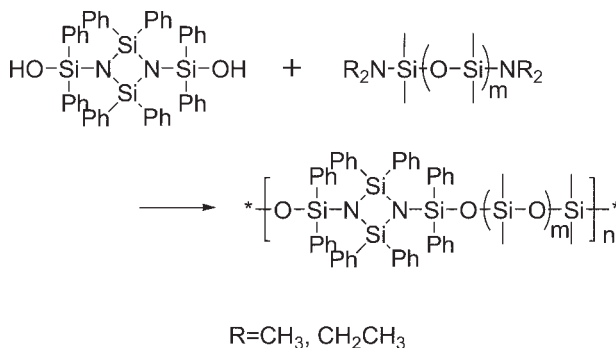


Figure 1 ^{29}Si -NMR spectra of (a) $\text{Et}_2\text{NSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{NEt}_2$ and (b) $\text{Me}_2\text{NSiMe}_2(\text{OSiMe}_2)_7\text{OSiMe}_2\text{NMe}_2$.

xylene, and the reaction temperature was about 140°C . In our study, toluene was chosen as the solvent, and the temperature of the ring-closure reaction was 120°C ; even then, the yield of BCPTPC did not change very much. The product was characterized by ^{29}Si -NMR, ^1H -NMR, and elemental analysis. In the ^1H -NMR spectra, the multiple peaks at 6.8–7.6 ppm correspond to the hydrogen in $-\text{C}_6\text{H}_5$. In the ^{29}Si -NMR spectra, the single peak at -12.36 ppm corresponds to the exocyclic silicon atoms, and the single peak at -13.60 ppm corresponds to the endocyclic silicon atoms.



Scheme 3

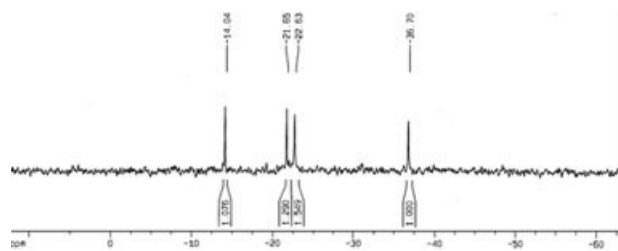


Figure 2 ^{29}Si -NMR spectrum of the alternate copolymer with $m = 3$.

By adding dropwise a suspension of BCPTPC in ethyl ether to a mixture of ammonia water and ethyl ether, N,N' -bis(hydroxydiphenylsilyl)tetraphenylcyclodisilazane (BHPTPC), the hydrolysis product of BCPTPC, was obtained. The chemical shifts of the exocyclic and endocyclic silicon atoms changed to -32.84 and -15.89 ppm, respectively.

α,ω -Dichlorodimethylsiloxane components were synthesized by the partial hydrolysis of Me_2SiCl_2 in ether solution, as described in Scheme 2. The products with different m values were fractional distilled out. α,ω -Bis(dialkylamino)dimethylsiloxanes were synthesized by the aminolysis of α,ω -dichlorodimethylsiloxane with Et_2NH or Me_2NH in petroleum ether solution. Me_2NH was obtained by the reaction of dimethylamine hydrochloride and potassium hydroxide. The products were characterized by ^{29}Si -NMR, ^1H -NMR, and elemental analysis. Figure 1 shows the NMR spectra of $\text{Et}_2\text{NSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{NEt}_2$ and $\text{Me}_2\text{NSiMe}_2(\text{OSiMe}_2)_7\text{OSiMe}_2\text{NMe}_2$. In $\text{Et}_2\text{NSiMe}_2\text{OSiMe}_2\text{OSiMe}_2\text{NEt}_2$, the shift of the silicon atoms attached to the nitrogen atoms is -12.58 ppm, and the shift of the middle silicon atom is -24.45 ppm [Fig. 1(a)]. In $\text{Me}_2\text{NSiMe}_2(\text{OSiMe}_2)_7\text{OSiMe}_2\text{NMe}_2$, the chemical shifts of the silicon atoms adjacent to the dimethylamino group is -9.95 ppm, and the shift of the next silicon atoms is -22.67 ppm. The left silicon atoms have the same shift in the ^{29}Si -NMR spectrum, -22.12 ppm [Fig. 1(b)].

The condensation polymerization of BHPTPC with α,ω -bis(dialkylamino)dimethylsiloxane was carried out in toluene at 90 – 100°C . A series of alternate copolymers containing BPTPC were obtained. The condensa-

TABLE I
The Molecular Weight in the Condensation Copolymerization with Different Ratios of BHPTPC and α,ω -Bis(diethylamino)dimethylsiloxane

Ratio of the reactants	M_n	M_w	Polydispersity	Yield (%)
1	11,400	41,500	3.64	74
1.0056	16,400	59,200	3.61	79
1.0075	17,600	52,000	2.94	80
1.01	22,000	55,500	2.52	76
1.0138	13,300	42,800	3.22	78
1.015	20,300	62,600	3.08	72

TABLE II
The Molecular Weight in the Condensation Copolymerization with Different Ratios of BHPTPC and α,ω -Bis(dimethylamino)dimethylsiloxane

Ratio of the reactants	M_n	M_w	Polydispersity	Yield (%)
1	37,370	952,00	2.55	83
1.0024	47,600	104,700	2.20	87
1.005	66,200	115,700	1.75	82
1.0075	47,700	94,400	1.98	89
1.01	35,570	82,000	2.31	80

tion polymerization is described in Scheme 3. Nitrogen was used to bubble out the byproduct, dialkylamine, to accelerate the polymerization. The copolymers were characterized by ^{29}Si -NMR, ^1H -NMR, and GPC methods. Figure 2 illustrates the ^{29}Si -NMR spectrum of alternate copolymer with $m = 3$. The chemical shifts of the endocyclic and exocyclic silicon atoms changed to -14.0 and -36.7 ppm respectively. The four silicon atoms in dimethylsiloxane unit had two equal peaks at -21.6 and -22.6 ppm, owing to the little different chemical environments.

The main reasons that restrict the applications of the polysilazanes are the molecular weight of the polysilazanes and the hydrolytic stability of the silicon-nitrogen compounds. The structure of BPTPC provides excellent hydrolytic stability. It is important to get high-molecular-weight copolymers.

It is well known that the molecular weight of the condensation polymerization is very sensitive to the ratio of the two reactants. A series of condensation polymerizations were carried out with different ratios of the reactants. In the condensation polymerizations of BHPTPC and α,ω -bis(diethylamino)dimethylsiloxane, the ratios of reactants (BHPTPC/ α,ω -bis(diethylamino)dimethylsiloxane) was changed from 1 to 1.015. The molecular weight of these copolymers was shown

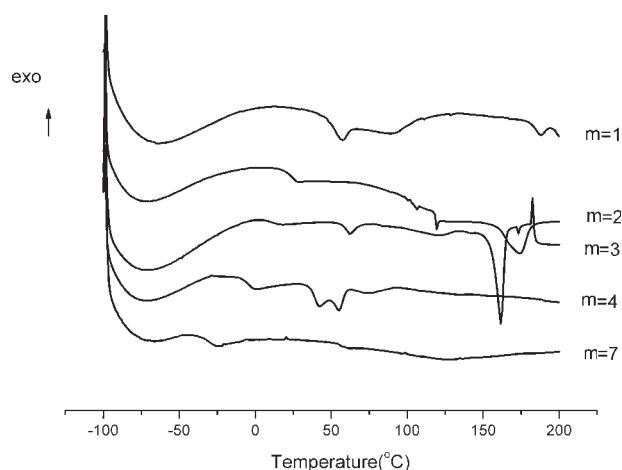


Figure 3 The DSC curves of the alternate copolymers with different m .

TABLE III
DSC Data of Alternate Copolymers with Different m Values

m	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)
1	49.3	187.8	–
2	18.65	119.4	174.4
3	2.4	62.2	161.2
4	–7.4	42.3	54.8
7	–37.6	–	–

in Table I. The highest molecular weight is 22,000 (1.01 : 1), and the smallest molecular weight is 11,400 (1 : 1). This result was not satisfactory. To improve the molecular weight, α,ω -bis(dimethylamino)dimethylsiloxane was synthesized as the reactant. The result of the condensation polymerization was shown in Table II. The molecular weight of the copolymers was much higher than that in the condensation polymerization of BHPTPC and α,ω -bis(diethylamino)dimethylsiloxane, and the molecular weight even reached 66,200 (1.005 : 1). The reason of the difference of this two condensation polymerizations is the bulky effect of phenyl groups and ethyl groups. The smaller dimethylamino group is easier to react with the SiOH group in BHPTPC. This results in the higher molecular weight, narrower polydispersity, and higher yield in the products of condensation polymerization.

The thermal behavior of the alternate copolymers was studied using DSC. The samples were quenched to -100°C and reheated at rate of $10^\circ\text{C}/\text{min}$ under N_2 purge. The results are shown in Figure 3. The glass transition and endothermal melting of crystalline formation were detected. The DSC traces obtained were sensitive to the length of the dimethylsiloxane unit. Two endothermal peaks were detected, when m equals

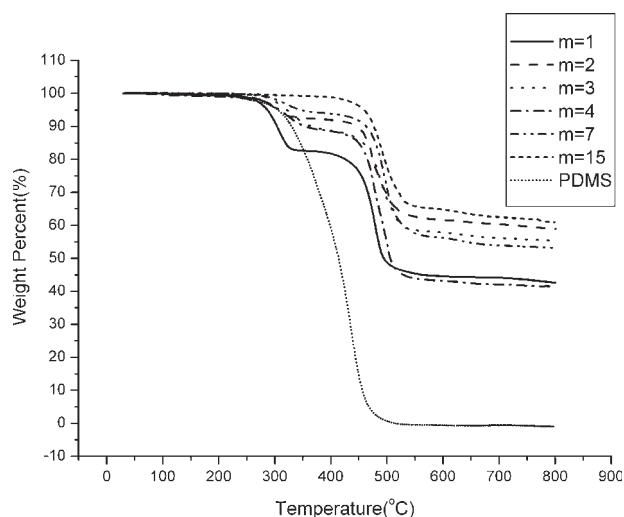


Figure 4 The TG curves of the alternate copolymers with different m .

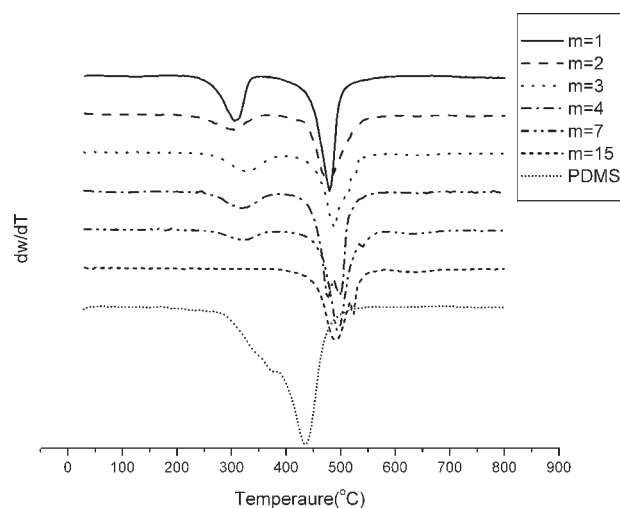


Figure 5 The DTG curves of the alternate copolymers with different m .

2, 3, and 4. However, when m equals 7, only one glass-transition temperature was detected. The glass-transition temperature (T_g) and melting point temperature (T_m) of the polymers are shown in Table III. A decreasing trend of T_g and T_m upon increasing the dimethylsiloxane units was observed. This may be attributed to a restriction in chain mobility caused by the steric effect and chemical interaction of the N,N' -bis(diphenylsilyl)tetraphenylcyclodisilazane groups in main chain.

The thermal degradation of alternate copolymer with different m was contrasted at a heating rate of $1^\circ\text{C}/\text{min}$. The TGA curves are shown in Figure 4, and DTG curves in Figure 5. There are three stages in the course of thermal degradation of the alternate copolymer. There is no significant weight loss below 250°C , and the first stage occurred at the temperature range of $250\text{--}400^\circ\text{C}$. TGA curves indicate that in this stage, the weight loss varies with different m . The weight loss of the first stage is about 18% for $m = 1$, 4.4% for $m = 7$, and 1.2% for $m = 15$. The weight loss decreased with m increasing. The second stage occurs in the temperature range of $400\text{--}600^\circ\text{C}$. In this stage, the weight loss is from 30% to 47%. The third stage occurs above 600°C . There is about 2–4% weight loss in this stage. In DTG curves, there are two obvious regions at about 300°C and 490°C except $m = 15$, which has only one main region at about 500°C . The results are listed in

TABLE IV
The Temperatures of the Peaks in DTG Curves (°C) with Different m Values

	$m = 1$	$m = 2$	$m = 3$	$m = 4$	$m = 7$	$m = 15$
1	305.2	304.4	327.3	299.4	319.9	
2	479.3	475.0	488.2	477.2	493.5	493.3
3				500.9		523.9

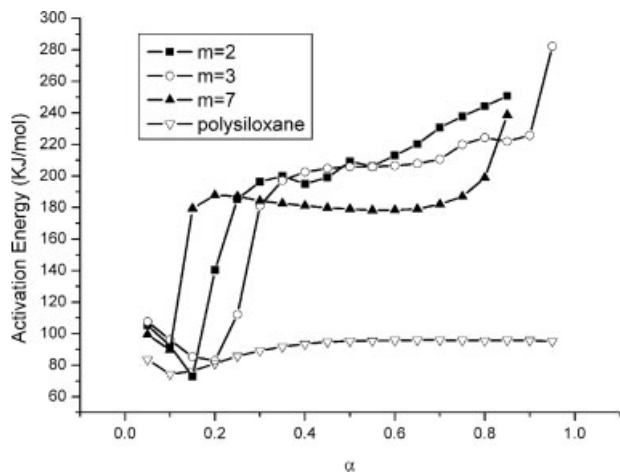


Figure 6 Activation energies of the alternate copolymer with $n = 2, 3, 7$ and the polysiloxane obtained by Flynn–Wall–Ozawa method.

Table IV. These results were different from those reported in the literature.^{32,38,39} The probable reason for the weight loss at the first stage was the volatilization of the small molecules, which was hard to be separated from the alternate copolymers because of the similar structure.

Determination of activation energy (E)

TGA has been used widely to estimate the kinetic parameters of degradation processes, such as activation energies. Kinetic data obtained from TGA are very useful to help us understand the thermal degradation processes and mechanism. In this article, the TG data of the alternate copolymer have been taken under a steady flow of nitrogen at different heating rates (1, 5, 10, and 15°C/min) to evaluate the activation energy. The most widely used Flynn–Wall–Ozawa method

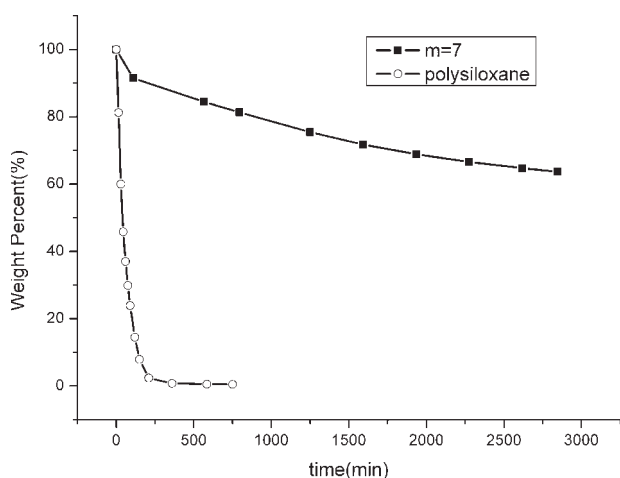


Figure 7 IGA curves of alternate copolymer with $m = 7$ and common polydimethylsiloxane at 400°C in N_2 .

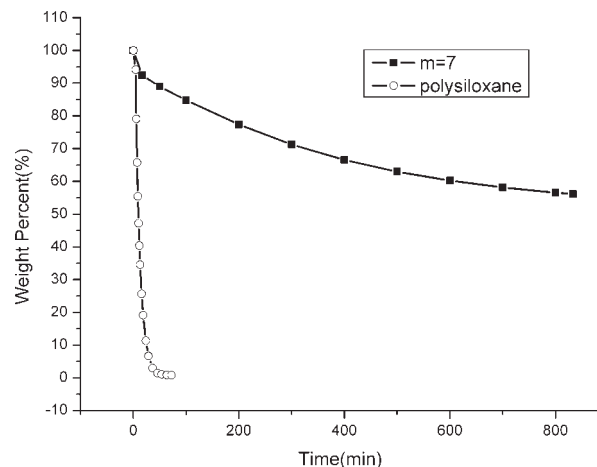
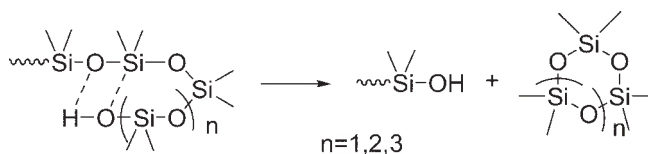


Figure 8 IGA curves of alternate copolymer with $n = 7$ and common polydimethylsiloxane at 450°C in N_2 .

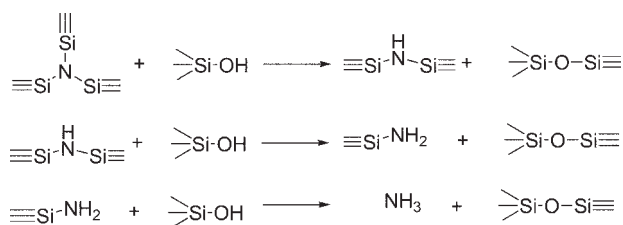
was used to analyze the TG data of the copolymer, because it was independent of any thermal degradation mechanism. Flynn–Wall–Ozawa method, which is an integral method, is based on eq. (1) and requires several thermograms at different heating rates.

$$C = \log\left(\frac{AE}{R}\right) - \log \beta - 0.4567 \frac{E}{RT} \quad (1)$$

where A , the pre-exponential factor, is assumed to be independent of temperature, E is the activation energy, T is the absolute temperature, R is the gas constant, β is constant heating rate dT/dt , and C is the function of the conversion. The values of activation energy can therefore be obtained from a plot of $\log \beta$ against $1/T$ for a fixed degree of conversion, since the slope of such a line is given by $0.4567E/R$. In this case, the activation energies of the alternate copolymer with $m = 2, 3, 7$ and the common polysiloxane were calculated. The activation energies calculated are shown in Figure 6. At the first stage the mean activation energy of the three copolymers is 90, 97, and 95 kJ/mol, respectively. However, the activation energy of the alternate copolymers differs in the second stage. The mean activation energy of the copolymers with $m = 2, 3$ is similar; 214 and 211 kJ/mol, respectively. The activation energy of this stage in the copolymer with $m = 7$ is much smaller; only 183 kJ/mol. The activation energy of the polysiloxane is 91 kJ/mol in contrast. The activation energy



Scheme 4



Scheme 5

of degradation process was increased by introducing BPTPC groups into polysiloxane, and this improved the thermal stability of the materials.

The isothermal gravimetric analysis (IGA) is an important method to characterize thermal stability of polysiloxane. At a given temperature, the lesser the weight loss, the better thermal stability the polysiloxane has. As shown in Figures 7 and 8, the weight loss of alternate copolymer with $m = 7$ and common polydimethylsiloxane were contrasted at 400°C and 450°C. Figures 7 and 8 indicate that the alternate copolymer has much better thermal stability than the common polydimethylsiloxane. At 400°C for 100 min, the polydimethylsiloxane almost degraded completely (14 wt % remained); while 91 wt % of the alternate copolymer still remained. Even after 3000 min, the remaining of the copolymer was still above 60 wt %; while the time for which the common polydimethylsiloxane remained 60 wt % was only 30 min. At 450°C, the common polydimethylsiloxane remained only 1 wt % after 50 min, while the copolymer still had 88.9 wt % left.

The most important reason for weight loss of silicon rubber at high temperature in nitrogen is that the residue SiOH or the adsorptive water in polysiloxane can result in main-chain degradation by forming small cyclosiloxanes³¹ (Scheme 4). Silicon-nitrogen compound can react with SiOH and water to form the Si—O—Si bonds (Scheme 5). Through eliminating the SiOH and water in the silicon rubber, the main-chain degradation is decreased, and then the thermal stability is improved.

CONCLUSIONS

The alternate copolymers containing BPTPC were synthesized from hexamethyltrisilazane successfully. By changing the ratio of the reactants, alternate copolymer with a M_n of 66,200 was obtained. The thermal properties of the copolymers were studied by DSC, TGA, and IGA methods. T_g and T_m are revealed in DSC curves, and decrease as the length of the oligodimethylsiloxane unit is increasing. The activation energies of the copolymer were calculated using the Flynn–Wall–Ozawa method. IGA studies reveal that the thermal stability of

the alternate copolymer with $m = 7$ is much better than the common polydimethylsiloxane.

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