Synthesis and Characterization of Alternate Copolymers Constructed by 1,3-Bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane Units with Oligo-dimethylsiloxane Segments

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ABSTRACT: 1,3-Dichloro-1,1,3,3-tetraphenyldisilazane (DCTPS) with 71.6% yield was synthesized by the reaction of hexaphenylcyclotrisilazane (HPCT) with Ph_2SiCl_2 catalyzed by dibutyltin dilaurate. A ring-closure reaction of DCTPS was carried out with BuLi in xylene–hexane mixture solvent; 1,3-bis(chlorodiphenylsilyl)-2,2,4,4-tetraphenyl-cyclodisilazane (BcPTPC) with 73.2% yield was obtained. Hydrolysis of BcPTPC in ether–triethylamine solvent resulted in 71.9% yield of 1,3-bis(diphenylhydroxysilyl)-2,2,4,4-tetraphenylcyclodisilazane (B_HPTPC). By condensation polymerization of B_HPTPC with α,ω-bis(diethylamino)-oligo-dimethylsiloxane, a kind of alternate copolymer constructed by 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane units with oligo-dimethylsiloxane segments [P(BPTPC-*alt*-ODMS)] was synthesized. BcPTPC, B_HPTPC as well as P(BPTPC-*alt*-ODMS) were characterized by ^{29}Si-NMR spectra, FT-IR spectra, and elemental analysis. DGA study shows that P(BPTPC-*alt*-ODMS)s are thermally stable. The thermal decomposition onsets of P(BPTPC-*alt*-ODMS)s are all above 520°C. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1484–1490, 2005

Key words: polysiloxanes; heteroatom-containing polymer; high temperature materials; polycondensation; synthesis

INTRODUCTION

Silicone rubber such as polydimethylsiloxane (PDMS) is widely used in many fields due to its excellent properties such as weather resistance, low and high temperature resistance, and electric insulation. Although it has high temperature stability, the most common PDMS was used just at temperatures below 300°C. But when PDMS was used at further high temperature, the Si–O linkage in the main chains was apt to be attacked by the terminal silanol groups, resulting in cyclic dimethylsiloxane oligomers, and the properties of the polymer became deteriorated.[1,2] To enhance the heat stability, scientists introduced some rigid chain segments, such as $-SiMe_2-CB_{10}H_{10}C-SiMe_2-$[3] as well as the substituted cyclodisilazane units[4,5] into the main chains of normal PDMS. The heat-resistant property was highly improved. Xie et al.[4,5] synthesized polysiloxanes having 1,3-bis(dimethylsilyl)-2,2,4,4- tetramethylcyclodisilazane (BMTMC) and 1,3-bis(diphenylsilyl)-2,2,4,4-tetramethyl-cyclodisilazane (BPTMC) units in the main chains. The
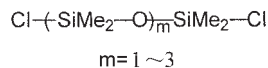
thermal decomposition onsets of these polysiloxanes are 150–200°C higher than that of the most common PDMS. In this article, we synthesized polydimethylsiloxanes having 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenyl- cyclodisilazane (BPTPC) units in the main chains, e.g., a kind of alternate copolymer constructed by 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane units with oligo-dimethylsiloxane segments [P(BPTPC-*alt*-ODMS)] and characterized the structure by ^{29}Si-NMR and FT-IR spectra. The heat resistant property of these polymers was studied by DGA and DSC spectroscopy.
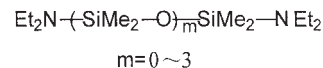
EXPERIMENTAL

Materials

n-Hexane, xylene, and tetrahydrofuran (THF) were purchased as chemical reagents and were refluxed with metal sodium before use. *n*-Butyllithium was prepared from *n*-butyl chloride reacted with lithium plate under N_2 atmosphere in hexane; a 1.37 mol/L hexane solution was obtained. Hexaphenylcyclotrisilazane (HPCT) was synthesized as described by Larsson and Bjellerup;[6] m.p.: 213–214°C.

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Cl—$($SiMe$_2$—O$)_{\overline{m}}$SiMe$_2$—Cl

m = 1 ~ 3

Structure 1

Et$_2$N—$($SiMe$_2$—O$)_{\overline{m}}$SiMe$_2$—NEt$_2$

m = 0 ~ 3

Structure 2

1,3-Dichloro-1,1,3,3-tetraphenyldisilazane (DCTPS)

In a 250-mL three-neck flask 30 g (0.051mol) HPCT was reacted with 45 mL (0.22 mol) Ph$_2$SiCl$_2$ in the presence of 0.5 g dibutyltin dilaurate at 150–170°C for 15 h. The reaction mixture gradually became homogeneous. After cooling, white crystals formed. The crude product was filtrated and recrystallized by toluene–hexane mixture solvent. 49.1 g 1,3-dichloro-1,1,3,3-tetraphenyldisilazane was obtained (71.6% yield); mp: 115–117°C.

^{1}H-NMR (δ, CDCl$_3$): 7.20–7.40, 7.59–7.62 (m, 20H of 4 –C$_6$H$_5$), 2.50 (s, 1H of –NH–). ^{29}Si-NMR (δ, CDCl$_3$): –14.57 (s, –SiPh$_2$Cl). Elem. anal. calcd for C$_{24}$H$_{21}$Cl$_2$NSi$_2$: C, 64.00%; H, 4.67%; N, 3.11%; Cl, 15.78%. Found: C, 63.29%; H, 4.56%; N, 2.97%; Cl, 15.03%.

1,3-Bis(chlorodiphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (BcPTPC)

In a three-neck flask, 18.0 g (0.04mol) DCTPS was dissolved in 150 mL xylene. At room temperature, 30 mL 1.37 mol/L (0.041 mol) BuLi was dropped in 2.5 h and was stirred 2 h and then refluxed for 4 h. The solvents were removed by rotatory evaporation, and white crystals were obtained. The crude product was recrystallized with toluene–heptane mixture solvent: 11.72 g BcPTPC was obtained (73.2% yield); mp: 258–260°C.

m/e: 827(M + 1), detected by field desorption (FD) mass spectrum. Elem. anal. calcd for C$_{48}$H$_{40}$Cl$_2$N$_2$Si$_4$: C, 69.84%; H, 4.84%. N, 3.38%; Cl, 8.58%. Found: C, 69.40%; H, 4.85%; N, 3.06%; Cl, 8.50%.

1,3-Bis(diphenylhydroxysilyl)-2,2,4,4-tetraphenylcyclodisilazane (B$_H$PTPC)

In a 1,000-mL flask, 18.2 g (0.022 mol) BcPTPC was dissolved in an ether–triethylamine mixture solvent. Under stirring, 0.79 mL (0.044 mol) water in 80 mL triethylamine was dropped over 5 ~ 6 h into the mixture solution at 2 ~ 3°C. The hydrolysis reaction continued for an additional 30 min. The mixture then was dried by 10 g anhydrous sodium sulfate. After filtration, the solvents in the filtrate were removed by rotatory evaporation under reduced pressure. The crude product obtained was recrystalized by an ether–hexane mixture solvent; 10.8 g B$_H$PTPC was obtained (71.9% yield); mp: 158 ~ 160°C.

^{1}H-NMR (δ, CDCl$_3$): 6.93 ~ 7.00, 7.13 ~ 7.28, 7.38 ~ 7.40, 7.48 ~ 7.52 (m, 40H of 8 –C$_6$H$_5$), 2.04 (s, 2H of 2 –OH). Elem. anal. calcd for C$_{48}$H$_{42}$N$_2$O$_2$Si$_4$: C, 72.91%; H, 5.32%; N, 3.54%. Found: C, 72.95%; H, 5.35%; N, 3.55%.

α,ω-Dichloro-oligo-dimethylsiloxane[7]

In a 2,000-mL three-neck flask, 500 mL (4.15 mol) Me$_2$SiCl$_2$ and 500 mL anhydrous ether was added and stirred mechanically under room temperature. 37.5 mL (2.09 mol) water in 39 mL dioxane was added over 3 to 4 h. After the addition, the mixture solution was refluxed 2 h to remove the HCl formed. Solvents were removed by distillation. The remained liquid was fractionally distilled and different α,ω-dichloro-oligo-dimethylsiloxane components were obtained. The structure of the components is shown as Structure **1**; their boiling point and the yield are compiled in Table I.

α,ω-Bis(diethylamino)-oligo-dimethylsiloxane

Et$_2$NSiMe$_2$NEt$_2$ was prepared as follows. In a 1,000-mL three-neck flask, 227 mL (2.2 mol) Et$_2$NH and 450 mL petroleum ether were added and stirred at 1 ~ 3°C. 60 mL (0.5 mol) Me$_2$SiCl$_2$ in 150 mL petroleum ether was slowly added over 3 ~ 4 h. The mixture was stirred for 30 min and then refluxed for 2 h. After cooling, the solvent was removed by distillation. The crude Et$_2$NSiMe$_2$NEt$_2$ was distilled and

TABLE I
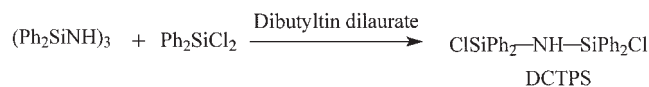**The Components of α,ω-Dichloro-oligo-dimethylsiloxane Obtained**

m	Boiling point (°C)	Yield (%)
1	135 ~ 136	27.5
2	182 ~ 184	29.8
3	220 ~ 222	27.9

TABLE II
Boiling Point and the Yield of α,ω-Bis(diethylamino)-oligo-dimethylsiloxane

m	Bp (°C/Pa)	Yield (%)	A_{N-Me}/A_{Si-Me}[a]	
			Calculated	Found
0	196~198/1.01 ×10^5	59.7	2.00	1.97
1	92~94/666.5	65.5	1.00	0.99
2	120~122/1999.5	71.4	0.67	0.68
3	147~149/2399.4	75.9	0.50	0.48

[a] A_{N-Me}/A_{Si-Me} is the area ratio of the methyl group in N–CH$_2$CH_3 to that in Si–CH_3 in the ^{1}H-NMR spectra.

$$(Ph_2SiNH)_3 \ + \ Ph_2SiCl_2 \xrightarrow{\text{Dibutyltin dilaurate}} \underset{\text{DCTPS}}{ClSiPh_2\text{—}NH\text{—}SiPh_2Cl}$$

Scheme 1

$$Cl\text{—}SiPh_2\text{—}N\underset{\underset{Ph_2}{Si}}{\overset{\overset{Ph_2}{Si}}{\diamond}}N\text{—}SiPh_2\text{—}Cl \ + \ H_2O \xrightarrow[\text{Et}_3\text{N}]{\text{Et}_2\text{O}} HO\text{—}SiPh_2\text{—}N\underset{\underset{Ph_2}{Si}}{\overset{\overset{Ph_2}{Si}}{\diamond}}N\text{—}SiPh_2\text{—}OH$$

B$_H$PTPC
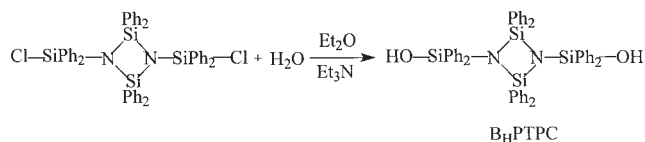
Scheme 3

collected at 196 ~ 198°C. 60 g of Et$_2$NSiMe$_2$NEt$_2$ was obtained (59.7% yield).

Other α,ω-bis(diethylamino)-oligo-dimethylsiloxane (shown as Structure **2**) was prepared in a similar way as that of Et$_2$NSiMe$_2$NEt$_2$. Their structures were characterized by ^{1}H-NMR spectra. The boiling point and the yield are compiled in Table II.

Alternate copolymers constructed by 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenyl-cyclodisilazane units with oligo-dimethylsiloxane segments[8]

In a 100-mL three-neck flask, 1.17g (0.0033 mol) Et$_2$N–(SiMe$_2$–O)$_2$–SiMe$_2$–NEt$_2$, 2.63 g (0.0033 mol) B$_H$PTPC, and 20 mL xylene were added and stirred over 90 ~ 95°C oil bath under N$_2$ atmosphere. The reaction was maintained over 16 h until no Et$_2$NH was detected. The mixture was precipitated in hexane, filtered, and dried in a vacuum oven. 2.87 g P(BPTPC-*alt*-ODMS) (*m* = 2) was obtained (86.4% yield).

Determination methods

^{1}H-NMR and ^{29}Si-NMR spectra were recorded on a Unity 200 MHz nuclear resonance spectrometer. DCCl$_3$ was used as solvent. In ^{29}Si-NMR spectra, bis (trimethylsilyl) ether was used as external labeling compound, whose chemical shift is at 6.97 ppm in ^{29}Si-NMR spectrum using tetramethylsilane as the labeling compound.[9] The FD mass spectrum was taken on a Finnigan MAT 90 spectroscope.

The molecular weight and its distribution of the polymers were detected on a PL-GPC210 gel permeation chromatograph (GPC) equipped with two 30-cm PL gel Mixed-B columns (particle size10 μm, porosity 10^3–10^6 Å) and a refractive index detector. Tetrahydrofuran was used as the mobile phase with a flow rate of 1 mL/min and polystyrene was used as standard.
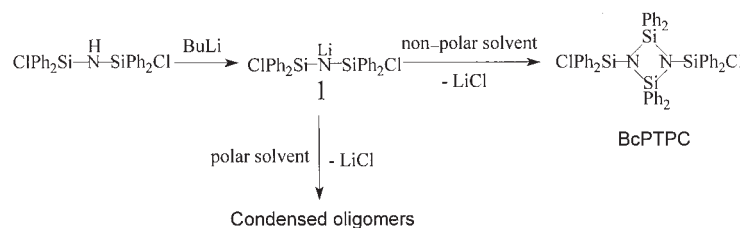
The thermogravimetric analysis (TGA) was recorded on a PE TGA7 thermal analysis system under N$_2$ atmosphere. The sample weight was about 3.5 mg and the temperature range was from room temperature to 900°C with the heating rate at 20°C/min. The glass transition temperature (T_g) was recorded on a DSC7 analyzer under N$_2$ atmosphere. The sample weight was about 15.0 mg and the temperature range was from 50 to 400°C with the heating rate at 20°C/min. The polymer samples prepared as described above were used directly in TGA and DSC analysis.

RESULTS AND DISCUSSION

Synthesis of 1,3-dichloro-1,1,3,3-tetraphenyldisilazane

1,3-Dichloro-1,1,3,3-tetraphenyldisilazane was used as starting material to synthesize BcPTPC. In the literature, DCTPS was synthesized by the reaction of octamethylcyclotetrasilazane with Ph$_2$SiCl$_2$, in which the yield of DCTPS is very low, just 20%. Another method using hexaphenylcyclotrisilazane reacted with Ph$_2$SiCl$_2$ is also inefficient, the yield of DCTPS was less than 20%, even at high reaction temperatures up to 300°C.[10] In this article, we conducted the reaction of HPCT with Ph$_2$SiCl$_2$ in the presence of dibutyltin dilaurate and found that the dibutyltin dilaurate is an effective catalyst. The yield of DCTPS in this catalyzed reaction is high, nearly 71.6%. The reaction is described in Scheme 1.

DCTPS obtained in this reaction was characterized by ^{1}H-NMR and ^{29}Si-NMR spectra. In the ^{1}H-NMR spectrum, the multiple peaks at 7.20 ~ 7.40 ppm and 7.59 ~ 7.62ppm correspond to the hydrogen in –C$_6$H$_5$; a broad peak at 2.50 ppm corresponds to the hydrogen of –NH–. In the ^{29}Si-NMR spectrum, a peak at –14.57
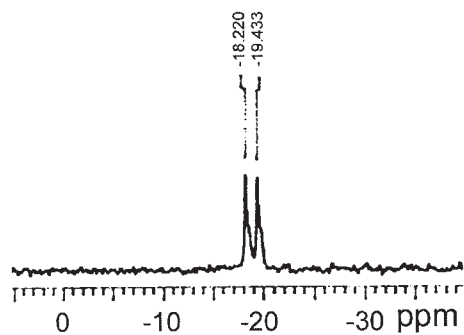
$$\underset{}{ClPh_2Si\text{—}\overset{H}{N}\text{—}SiPh_2Cl} \xrightarrow{\text{BuLi}} \underset{\mathbf{1}}{ClPh_2Si\text{—}\overset{Li}{N}\text{—}SiPh_2Cl} \xrightarrow[\text{- LiCl}]{\text{non–polar solvent}} ClPh_2Si\text{—}N\underset{\underset{Ph_2}{Si}}{\overset{\overset{Ph_2}{Si}}{\diamond}}N\text{—}SiPh_2Cl$$

BcPTPC

polar solvent | - LiCl

↓

Condensed oligomers

Scheme 2

Figure 1 ^{29}Si-NMR spectrum of BcPTPC.

Figure 3 ^{29}Si-NMR spectrum of B_HPTPC.

ppm is correspondent to the Si atom in –SiPh$_2$Cl. The DCTPS was also verified by the elemental analysis.

Synthesis of BcPTPC and B$_H$PTPC

BcPTPC was synthesized by a ring-closure reaction of DCTPS through dehydrochlorination with BuLi similarly as described by Breed and Wiley.[11] In this reaction, the yield of BcPTPC was highly influenced by the polarity of the solvents used. In nonpolar solvents such as the xylene–hexane mixture solvent, the ring-closure reaction of DCTPS can smoothly take place, and the yield of BcPTPC is high, nearly 73.2%. In this system, the suitable ring-closure reaction temperature is from −65 to 25°C. If the ring-closure reaction was carried out in polar solvent such as THF, the main products would be condensed oligomers of DCTPS,[12] even though the ring-closure temperature is below −65°C. The ring-closure reaction was described as Scheme 2.

In the ring-closure reaction, DCTPS first reacted with BuLi, turned to its lithium salt **1**. The reactivity of the lithium salt **1** was highly influenced by the polarity of the solvents used. When the nonpolar solvent, e.g., xylene–hexane mixture solvent was used, the lithium
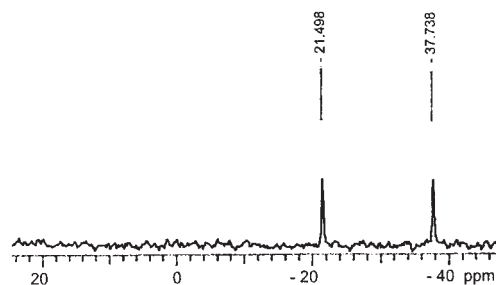
salt **1** was in its compact ion-pair state. It is stable and less reactive, so the intramolecular ring-closure reaction took place more smoothly and BcPTPC was formed with high yield. When the polar solvent, e.g., THF was used, the lithium salt **1** was in its loose ion-pair state or free ion state. Its reactivity is high, so the intermolecular condensation reaction took place and the condensed oligomers were formed.

BcPTPC obtained was characterized by ^{29}Si-NMR spectrum, FT-IR spectrum, and field desorption mass spectroscopy. Figure 1 is the ^{29}Si-NMR spectrum of BcPTPC. In the ^{29}Si-NMR spectrum, the peak at −18.22 ppm corresponds to the Si in =N–SiPh$_2$Cl; the peak at −19.43 ppm is correspondent to the Si of =N–SiPh$_2$–N= in the Si$_2$N$_2$ ring. Figure 2 is the FT-IR spectrum of BcPTPC. There are two characteristic peaks in the FT-IR spectrum, the one at 1006.4 cm^{-1} corresponds to the Si–N asymmetric stretching vibration outside the particular Si$_2$N$_2$ ring in BcPTPC; the other peak at 818.4 cm^{-1} corresponds to the Si–N asymmetric stretching vibration in the Si$_2$N$_2$ ring.

In the FD spectrum, the M + 1 peak of BcPTPC emerged at m/e 827. BcPTPC was also verified by elemental analysis.

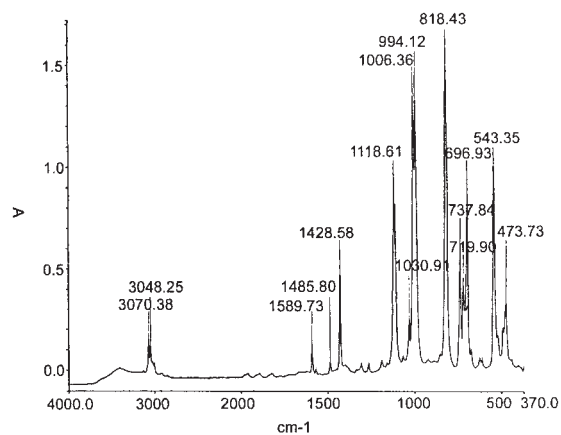BcPTPC was hydrolyzed by water at 2 ~ 3°C in the ether–triethylamine mixture solvent. B$_H$PTPC with
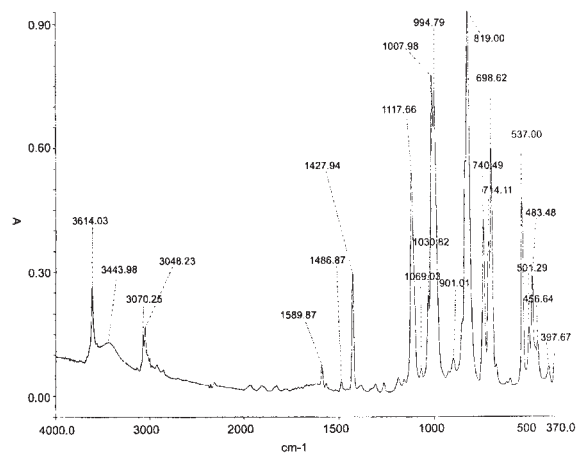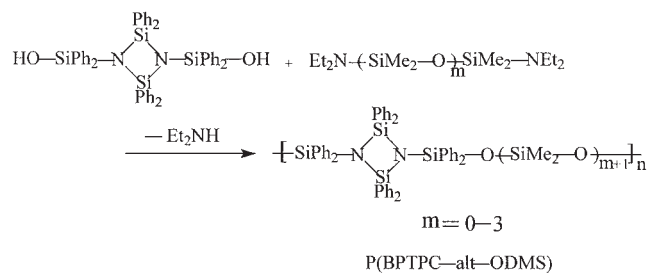

Figure 2 FT-IR spectrum of BcPTPC.

Figure 4 FT-IR spectrum of B$_H$PTPC.

Scheme 4

71.9% yield was obtained and its structure was verified by ^{1}H-NMR spectrum, ^{29}Si-NMR spectrum, FT-IR spectrum, and elemental analysis. The hydrolyzing reaction of BcPTPC is described in Scheme 3.

In the ^{29}Si-NMR spectrum of B_HPTPC (Figure 3), the peak at –21.50 ppm corresponds to the Si of $=N–SiPh_2–N=$ in the Si_2N_2 ring; the other peak at –37.74 ppm corresponds to the Si of $=N–SiPh_2OH$ outside of the Si_2N_2 ring.

In the FT-IR spectrum of B_HPTPC (Figure 4), the characteristic peak at 1008.0 cm^{-1} is correspondent to the asymmetric stretching vibration of Si–N outside the particular Si_2N_2 ring; the other characteristic peak at 819.0 cm^{-1} is correspondent to the asymmetric stretching vibration of Si–N in the Si_2N_2 ring. It was shown that, during the hydrolysis of BcPTPC, the Si_2N_2 ring remains unchanged.

α,ω-Dichloro-oligo-dimethylsiloxane and α,ω-bis(diethylamino)-oligo- dimethylsiloxane

α,ω-Dichloro-oligo-dimethylsiloxane components were synthesized by controlled hydrolysis of Me_2SiCl_2 in ether solution. The purified components were obtained by fractional distillation. The boiling point and the yield of each component are compiled in Table I. The general formula of α,ω-dichloro-oligo-dimethylsiloxane is described as Structure **1**.

α,ω-Bis(diethylamino)-oligo-dimethylsiloxane with different m from 0 to 3 was prepared by aminolysis of Me_2SiCl_2 and α,ω-dichloro-oligo-dimethylsiloxane ($m = 1 \sim 3$) with Et_2NH in petroleum ether solution at ice bath temperature. Each α,ω-bis(diethylamino)-oligo-

dimethylsiloxane was purified by distillation and the yield as well as the boiling point are compiled in Table II. The general structure of α,ω-bis(diethylamino)-oligo-dimethylsiloxane was described as Structure **2**. The structure was also characterized by ^{1}H-NMR spectra. Table II shows that the area ratio of $N–CH_2CH_3$ methyl hydrogen to Si–CH_3 hydrogen in the ^{1}H-NMR spectra is the same as that calculated from Structure **2**.

Synthesis of P(BPTPC-*alt*-ODMS)

Condensation polymerization of B_HPTPC with α,ω-bis(diethylamino)-oligo-dimethylsiloxane was carried out in xylene at 90–100°C. A kind of alternate copolymer constructed by 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane units with oligo-dimethylsiloxane segments was obtained. The condensation polymerization was described in Scheme 4.

B_HPTPC is insoluble in xylene. When $m = 0$, e.g., $Et_2NSiMe_2NEt_2$ was reacted with B_HPTPC, the B_HPTPC solid at first gradually dissolved in the solution and the system became homogeneous. As the reaction continued, precipitation occurred. After the precipitate was filtered and dried, about 32.4% of P(BPTPC-*alt*-ODMS) with $m = 0$ was obtained. It is insoluble in toluene, xylene, THF, and chloroform and in N,N-dimethylformamide, perhaps due to the high stiffness of the main chains. Its molecular weight and distribution (M_w/M_n) could not be determined by the GPC method. Table III also shows its elemental analysis, which is almost the same as that calculated from the formula of P(BPTPC-*alt*-ODMS) with $m = 0$. This means that the precipitate is the P(BPTPC-*alt*-ODMS) with $m = 0$. When α,ω-bis(diethylamino)-oligo-dimethylsiloxane with $m = 1$ was condensed with B_HPTPC, the precipitation just occurred at the late stage of the reaction, P(BPTPC-*alt*-ODMS) ($m = 1$) with $M_n = 1.57 \times 10^4$ and $M_w/Mn = 2.18$ was obtained. It is insoluble in xylene, but soluble in THF. Perhaps the precipitation obstructed the end functional groups of the formed polymer chains from further polymerization, therefore M_n is not too high. When α,ω-bis(diethylamino)-oligo-dimethylsiloxane with $m = 2$ and 3 was condensed with B_HPTPC, the

TABLE III
Synthesis and Characterization of P(BPTPC-alt-ODMS)s

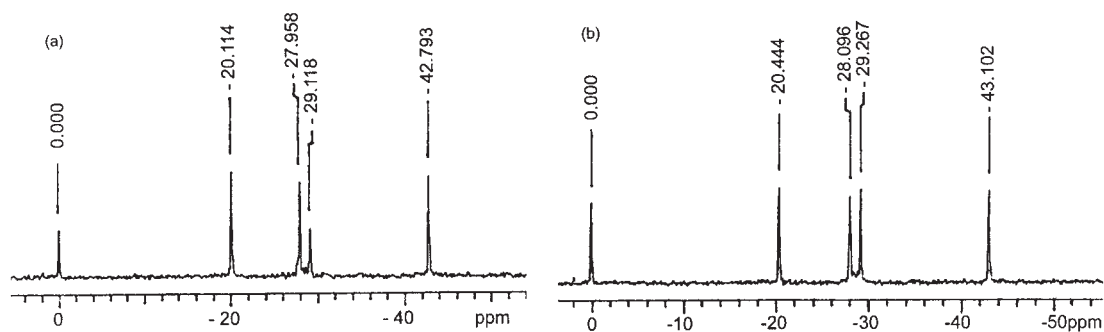| | | | | Element analysis (%) | | | | | |
| | | | | Calculated | | | Found | | |
m	Yield (%)	M_n ($\times 10^{-4}$)	M_w/M_n	C	H	N	C	H	N
0	32.4	Insoluble	—	70.92	5.44	3.31	70.91	5.82	3.39
1	64.1	1.57	2.18	67.83	5.65	3.04	67.67	5.68	2.64
2	86.4	3.74	2.17	65.19	5.84	2.82	65.28	5.81	2.67
3	83.1	3.28	2.59	61.92	5.99	2.62	61.15	6.07	2.28

Figure 5 ^{29}Si-NMR spectra of P(BPTPC-*alt*-ODMS) with $m = 2$ (a) and $m = 3$ (b).

reaction mixture gradually turned homogeneous and no precipitation occurred. After precipitation with hexane, P(BPTPC-*alt*-ODMS) with $m = 2$ and 3 were obtained. Their M_n were 3.74×10^4 and 3.28×10^4; M_w/M_n were 2.17 and 2.59, respectively. P(BPTPC-*alt*-ODMS) with $m = 1 \sim 3$ were also verified by elemental analysis. It was shown that the found values of C, H, and N are almost the same as that calculated from the formula P(BPTPC-*alt*-ODMS) with $m = 1 \sim 3$.

The structure of P(BPTPC-*alt*-ODMS)s was also characterized by ^{29}Si-NMR spectra and FT-IR spectra. Figures 5(a) and (b) show ^{29}Si-NMR spectra of P(BPTPC-*alt*-ODMS) with $m = 2$ and 3, respectively. In Figure 5(a), the peak at –20.1 ppm corresponds to the Si atoms of =N–SiPh$_2$–N= in the 1,3-bis(diphenyl-silyl)-2,2,4,4-tetraphenylcyclodisilazne (BPTPC) units in P(BPTPC-*alt*-ODMS); the peak at −42.8ppm corresponds to = N–SiPh$_2$–O– in BPTPC; peaks at –27.9 and –29.1 ppm correspond to the (a) Si atoms and (b) Si atom in the Structure **3**. The intensity of the peak at –20.1, − 42.8, and −27.9 ppm is almost the same, but is nearly two times that at –29.1 ppm. This shows evidence of P(BPTPC-*alt*-ODMS) with $m = 2$. In Figure 5(b), the peaks appear at a little more negative location, perhaps due to the different environments of Si atoms in P(BPTPC-*alt*-ODMS) with $m = 3$ from that with $m = 2$. In Figure 5(b), the intensity of different peaks is almost the same, including the peaks at –28.1 and –29.3 ppm, which correspond to Si (a) and Si (b), respectively, in Structure **4**.

Figure 6 is the FT-IR spectrum of P(BPTPC-*alt*-ODMS) with $m = 3$. In the FT-IR spectrum, the peak at
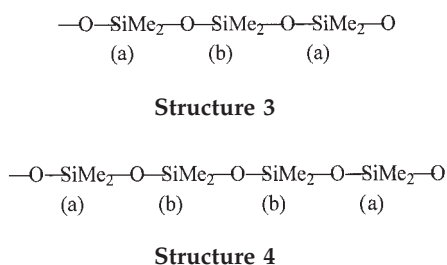
989.8 cm^{-1} corresponds to the asymmetric stretching vibration of Si–N outside the particular Si$_2$N$_2$ ring in BPTPC units, which has 16.6 cm^{-1} red shift compared with that of BcPTPC and 18.2 cm^{-1} red shift compared with that of B$_H$PTPC. Another peak at 825.1 cm^{-1} is correspondent to the asymmetric stretching vibration of Si–N in the Si$_2$N$_2$ ring of BPTPC units, which has 6.7 and 6.1 cm^{-1} blue shift compared with BcPTPC and B$_H$PTPC, respectively. In the P(BPTPC-*alt*-ODMS), the BPTPC units were connected with the oligo-dimethyl-siloxane (ODMS) segments, which are different from the Cl groups in BcPTPC and OH groups in B$_H$PTPC. Meanwhile, Si–O linkage is much stronger than Si–N and O is more electronegative than N and the ODMS segments weakened the Si–N linkage outside Si$_2$N$_2$ ring in the BPTPC units, resulting the remarkable red shift of the Si–N stretching vibration. The Si–N linkage in the Si$_2$N$_2$ ring was less influenced. The environment of the Si–N linkage in the Si$_2$N$_2$ ring in P(BPTPC-*alt*-ODMS) is different to some extent from that in BcPTPC and B$_H$PTPC. The flexibility of the ODMS segments was perhaps beneficial to the strengthening of the Si–N bond in the Si$_2$N$_2$ ring, so that about 6.7 or 6.1 cm^{-1} blue shift of the stretching vibration of that Si–N bond occurred in the FT-IR spectrum of

—O—SiMe$_2$—O—SiMe$_2$—O—SiMe$_2$—O
   (a)   (b)   (a)

Structure 3

—O—SiMe$_2$—O—SiMe$_2$—O—SiMe$_2$—O—SiMe$_2$—O
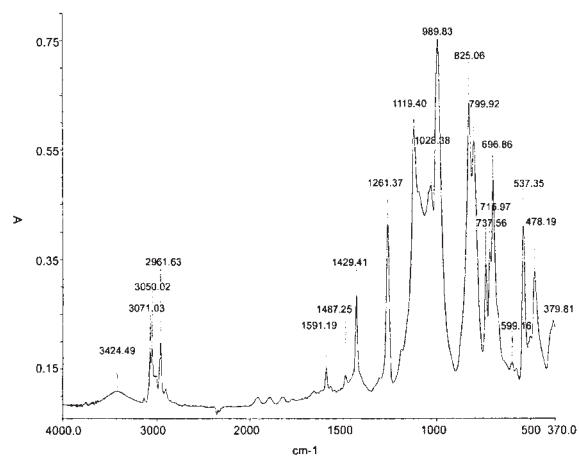   (a)   (b)   (b)   (a)

Structure 4

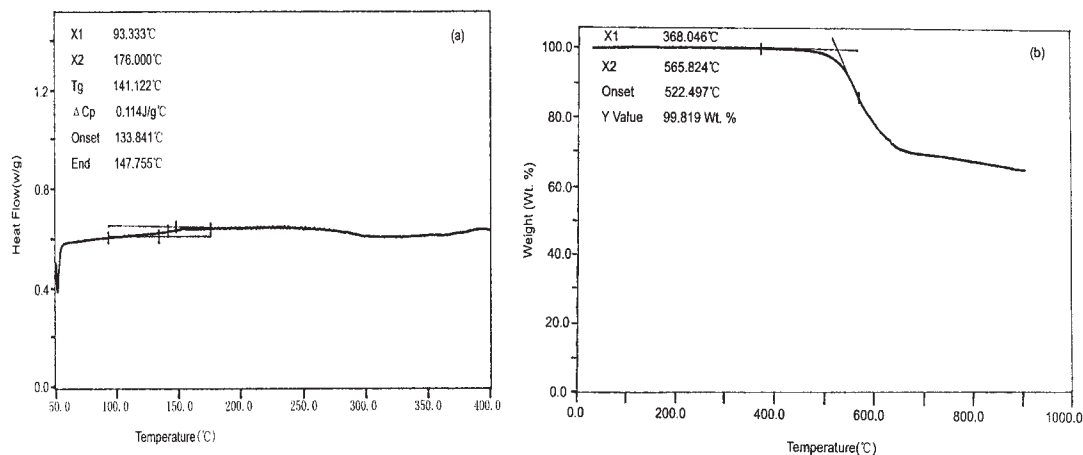**Figure 6** FT-IR spectrum of P(BPTPC-*alt*-ODMS) with $m = 3$.

Figure 7 DSC spectrum (a) and TGA spectrum (b) of P(BPTPC-*alt*-ODMS) with $m = 3$. Temperature rate: 20°C/min.

TABLE IV
Thermal Properties of P(BPTPC-alt-ODMS)s

m	M_n $(\times 10^{-4})$	M_w/M_n	Thermal decomposition onset (°C)	Thermal decomposition activation energy (KJ/mol)[a]	T_g (°C)
0	Insoluble	—	546.9	276.6	221.4
1	1.57	2.18	524.6	279.1	146.1
2	3.74	2.17	526.4	278.1	124.3
3	3.28	2.59	522.5	214.1	141.1

[a] Thermal decomposition activation energy of polydimethylsiloxane is 152 KJ/mol.

P(BPTPC-*alt*-ODMS) compared with that of BcPTPC or B_HPTPC.

Figures 7(a) and (b) are the DSC spectrum and TGA spectrum of P(BPTPC-*alt*-ODMS) with $m = 3$. From the spectra, it was found that the T_g of P(BPTPC-*alt*-ODMS) with $m = 3$ is 141.1°C; its thermal decomposition onset is 522.5°C. Other T_g and thermal decomposition onset data of P(BPTPC-*alt*-ODMS)s with m from 0 to 2 were compiled in Table IV. From Table IV, it was found that the thermal decomposition onset of P(BPTPC-*alt*-ODMS)s are all above 520°C; the T_gs are above 124°C. It was also found that the thermal decomposition activation energy of P(BPTPC-*alt*-ODMS)s are much higher than that of PDMS. The thermal decomposition activation energy of P(BPTPC-*alt*-ODMS)s are from 214.1 to 279.1 KJ/mol, nevertheless, that of PDMS is just 152 KJ/mol. The thermal stability of P(BPTPC-*alt*-ODMS)s is much higher than the normal polydimethylsiloxane.

CONCLUSIONS

1. By the reaction of HPCT with Ph_2SiCl_2 at 150–170°C catalyzed by dibutyltin dilaurate, DCTPS was synthesized with 71.6% yield.
2. BcPTPC was synthesized by a ring-closure reaction from DCTPS through dehydrochlorination

with BuLi in xylene–hexane mixture solvent. The yield of BcPTPC is 73.2%. Hydrolysis of BcPTPC in ether–triethylamine mixture solvent resulted in 71.9% yield of B_HPTPC.

3. P(BPTPC-*alt*-ODMS) with $m = 0 \sim 3$ was synthesized by condensation polymerization of B_HPTPC with α,ω-bis(diethylamino)-oligo-dimethylsiloxane. P(BPTPC-*alt*-ODMS)s is thermally stable. The thermal decomposition onsets of P(BPTPC-*alt*-ODMS)s are all above 520°C.

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