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## A Novel One-pot Synthesized Organosiloxane: Synthesis and Conversion to Directly Thermo-crosslinked Polysiloxanes with Low Dielectric Constant and Excellent Thermostability

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**A novel organosiloxane containing thermally cross-linkable benzocyclobutene group was successfully synthesized through one-pot Grignard reaction procedure. The organosiloxane can be easily polymerized or copolymerized to form the oligomers which can be directly converted to cross-linked network structures with excellent thermostability and low dielectric constants, implying the organosiloxane has potential application in electrical and microelectronic industry.**

Polysiloxanes have been well investigated and widely used in many areas such as aerospace and aviation, microelectronics, pharmacy and cosmetics due to their high stability, excellent insulating properties and good biocompatibility.<sup>1-3</sup> Among various polysiloxanes, these possess reactive groups<sup>4-8</sup> in the main and/or side chains have attracted much attention because they are important precursors for the preparation of silicon-based rubbers, coatings and sealants. In the presence of the catalyst (platinum salts) or the initiators (peroxides),<sup>9</sup> the reactive groups can be converted to the cross-linked-networks, which usually endow polysiloxanes with high performance. In many cases, however, the residues of the catalysts or the initiators greatly influence the dielectric properties of the polysiloxanes. Therefore, directly thermo-crosslinkable organic siloxanes are required. So far, a series of candidate materials have been developed, whereas further investigation on the synthesis and application of the new organosiloxane is still desirable.<sup>1, 5, 9, 10</sup>

Previously, we reported the synthesis and properties of a new polysiloxane containing trifluorovinylether ( $-\text{OCF}=\text{CF}_2$ ) groups which was directly thermo-crosslinkable and the cross-linked networks showed high heat resistance and good dielectric properties.<sup>10</sup> This procedure<sup>10</sup> has been proved to be an efficient way to prepare high performance polysiloxanes. However, the monomer (organosiloxane containing  $-\text{OCF}=\text{CF}_2$  group) is difficultly prepared

in large scale for industrial utilization because its synthesis needs a multi-step reaction procedure.<sup>10</sup> Thus we devoted to develop novel directly thermo-crosslinkable organosiloxanes that can be easily obtained. It is noted that the compounds containing benzocyclobutene (BCB) moieties have high reactivity and they can polymerize to form poly(*o*-xylylene) without releasing volatiles.<sup>11-15</sup> Such characteristic of BCB group inspires us to develop new directly thermo-crosslinkable polysiloxanes. To further investigate the synthesis and properties of directly thermo-crosslinkable organosiloxanes, we designed and synthesized a novel organosiloxane (**m-Si-BCB**) substituted by benzocyclobutene group. After hydrolysis in acetic acid, **m-Si-BCB** converted to an oligomer (**p-Si-BCB**). At high temperature, **p-Si-BCB** was directly cross-linked to form a network structure, which showed excellent thermal stabilities, good mechanical and dielectric properties. This characteristic of **p-Si-BCB** implies that it could be used as the varnish for enameled wire, the cross-linking agents for high performance glass fiber and the matrix resin for the production of laminated composites utilized in the printed-circuit-board (PCB) industry. Besides, copolymerization of **m-Si-BCB** with a commercial organosiloxane without crosslinkable groups was also investigated. The results suggested that **m-Si-BCB** was an efficient cross-linking agent for various organosiloxanes. This contribution provides a new way for the preparation of high performance organic polysiloxanes, implying this route is of great industrial importance.

### Synthesis of the monomer and oligomer and formation of the cross-linked structure

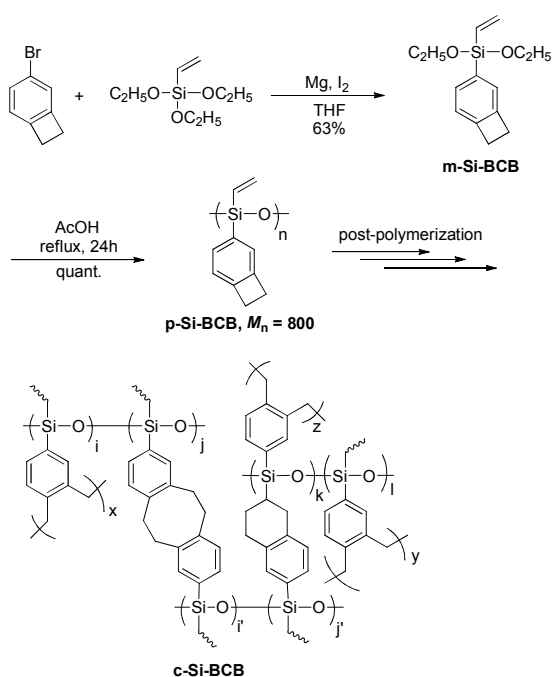
The new organosiloxane (**m-Si-BCB**) was easily prepared in a one-pot route via Grignard reaction, as shown in Scheme 1. Traditionally, such monomer was prepared by a two-step procedure. E.g., the aromatic halogen hydrocarbons reacted with magnesium to form Grignard agents, which were then added to the organosiloxanes to obtain the target products. In our case, the monomer was prepared through a one-pot route. Thus, bromobenzocyclobutene was directly added dropwise to a mixture of an organosiloxane, Mg and THF. Because the formed Grignard agent (benzocyclobutenemagnesium bromide) directly reacted with the

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organosiloxane, the dimerization of the Grignard agent can be efficiently restrained.

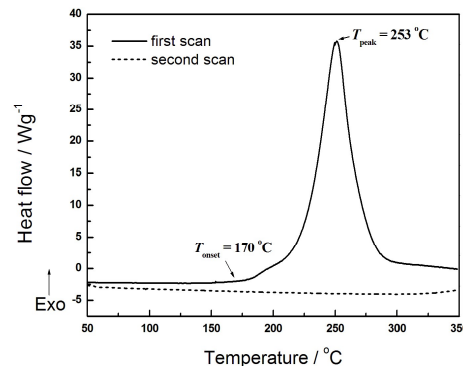
After hydrolysis in acetic acid,<sup>10, 16</sup> **m-Si-BCB** converted to a polysiloxane (**p-Si-BCB**) as a colorless viscous liquid with near quantitative yield. GPC determination showed that **p-Si-BCB** had a number-average molecular weight ( $M_n$ ) of about 800. According to the  $M_n$ , the number of the repeating unit of **p-Si-BCB** is estimated at about 5. The molecular weight was also confirmed by matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), as shown in Supplementary Information (Fig. S1), which was closely consistent with that detected by GPC. **p-Si-BCB** showed good solubility in common organic solvents such as THF, chloroform, toluene and acetone, suggesting its good processability.



**Scheme 1** Procedures for the synthesis of the new organosiloxane (**m-Si-BCB**), organic polysiloxane (**p-Si-BCB**) and cross-linked structure (**c-Si-BCB**).

Since the ring-opening reaction of benzocyclobutene groups can be taken at appropriate temperature, as depicted in Scheme 1. The crosslinking behavior of **p-Si-BCB** was characterized by DSC (Fig. 1). **p-Si-BCB** shows an onset curing temperature of about 170 °C and a peak temperature of about 250 °C. Moreover, the onset curing temperature is much lower than that of some benzocyclobutene-functionalized monomers or polymers.<sup>17-20</sup> This phenomenon may be attributed to a fact that the ethylene groups attached to the Si atom easily reacted with the opening-ring product of the benzocyclobutene groups (e.g., *o*-quinodimethane intermediate) to form a Diels-Alder adduct. According to the DSC result, **p-Si-BCB** was treated at 170 °C for 1 h, 250 °C for 3 h and 300 °C for 2 h to form a cross-linked network, which was insoluble in common

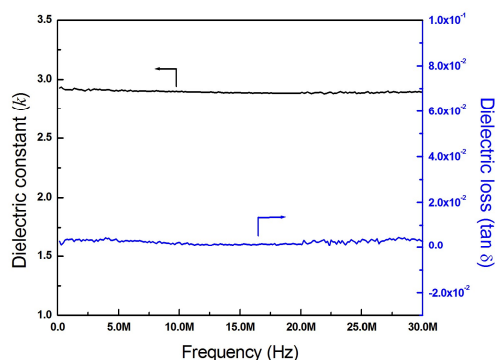
organic solvents, even in NMP with strong polarity, implying the cross-linked **c-Si-BCB** processes good solvent resistance. FT-IR spectroscopy (ESI, Fig. S7) showed the characteristic absorption of cyclobutene at about 1400 cm<sup>-1</sup> disappeared in **c-Si-BCB**, indicating that the oligomer (**p-Si-BCB**) was fully cured.



**Fig. 1** DSC traces of **p-Si-BCB** at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>.

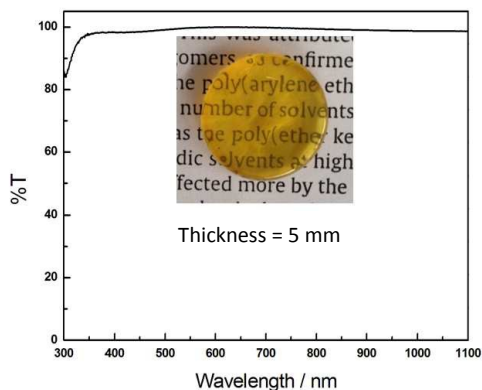
### Properties of the cross-linked **c-Si-BCB**

As benzocyclobutene resins are often used as dielectric materials, the dielectric constant of **c-Si-BCB** was investigated. **p-Si-BCB** (about 1.05 g) was added into a flat bottomed glass tube (with a diameter of 8 mm) filled with argon. The tube was maintained at 170 °C for 1 h, 210 °C for 2 h, 250 °C for 3 h and 300 °C for 2 h, respectively. A completely cured sample was thus obtained for the measurement of dielectric properties. Fig. 2 illustrates the dielectric properties of the cured sample, it can be seen obviously that cured **c-Si-BCB** shows an average  $k$  values of about 2.9 with dissipation factors ( $\tan \delta$ ) of less than  $3 \times 10^{-3}$  in a range of frequencies from 40 Hz to 30 MHz, which is comparable to most of previously reported benzocyclobutene resins.



**Fig. 2** Dielectric constants ( $k$ ) and dissipation factors ( $\tan \delta$ ) of the crosslinked **c-Si-BCB** sample depending on the frequencies.

The cross-linked sample was highly transparent and it showed transmittances of higher than 98% in a range of wavelengths from 1100 nm to 400 nm, as shown in Fig. 3.



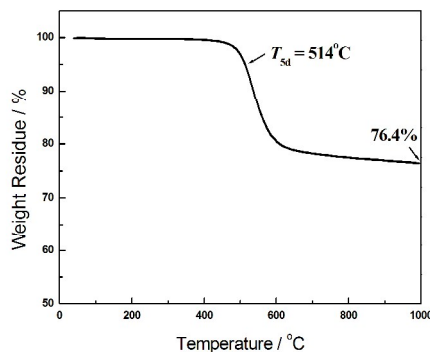
**Fig. 3** UV-vis-NIR spectrum of the cross-linked **c-Si-BCB**. The insert is an image that shows the sample sheet of **c-Si-BCB** on a page of an article, indicating good transparency of **c-Si-BCB**.

The polymer films for mechanical tests were formed on the silicon wafers (heavily doped single crystal silicon with a resistivity of  $3.5 \times 10^{-3} \Omega\text{-cm}$ ) by spin-coating a solution of **p-Si-BCB** in toluene (300 mg/mL). The wafers were quickly placed on a hot-plate under argon which was preheated to 300 °C. After being maintained at 300 °C for about 1 minute, the wafers were placed into the quartz tube furnace under  $\text{N}_2$  and heated at 250 °C for 3 h and 300 °C for 2 h respectively to afford fully cross-linked **c-Si-BCB** films. Mechanical properties of **c-Si-BCB** films were measured on a nanoindenter system and the results were shown in Table 1. As summarized in Table 1, the **c-Si-BCB** films show an average hardness of 1.29 GPa and a Young's modulus of about 9.58 GPa. Such high hardness and Young's modulus may be attributed to that the high cross-linking density of the cross-linked sample.

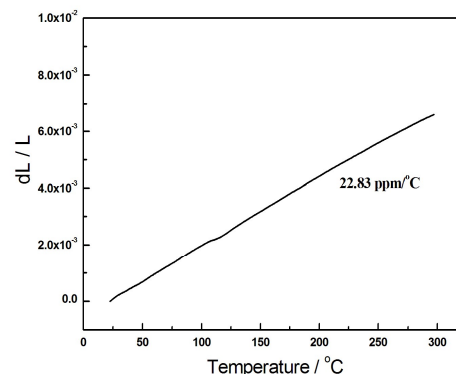
**Table 1** Detailed data for the hardness and Young's modulus of **c-Si-BCB** films

Test	1	2	3	4	5	6	7	Mean
Hardness (GPa)	1.28	1.30	1.24	1.25	1.35	1.28	1.31	1.29
Young's modulus (GPa)	9.51	9.59	9.46	9.42	9.76	9.67	9.62	9.58

The thermal stability of **c-Si-BCB** was evaluated by TGA (Fig. 4) and TMA (Fig. 5). **c-Si-BCB** exhibits a 5 wt% loss temperature of 514 °C and a weight residue of 76.4% at 1000 °C. Besides, TMA results indicate that **c-Si-BCB** shows an average linear CTE of about 22.83 ppm/°C in a range of temperatures from 20 to 300 °C, which is much lower than the most of previously reported organic siloxanes. The cross-linked structure can hinder the stretches of polymer chains when being heated, which makes the cured polysiloxane retain the dimensional stability under high temperature. This implies that **p-Si-BCB** is a suitable precursor for the preparation of the materials utilized at high temperature.



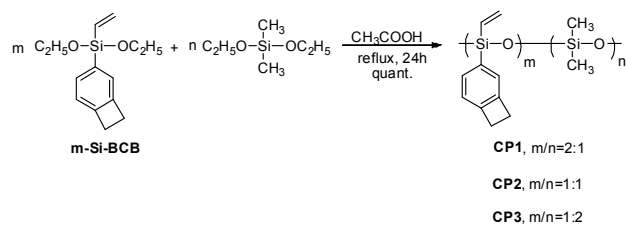
**Fig. 4** TGA curve of **c-Si-BCB** at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in  $\text{N}_2$ .



**Fig. 5** TMA curves of the cross-linked **c-Si-BCB** sample.

## Further applications for preparing high performance organosiloxanes

On the basis of the good properties of **c-Si-BCB**, **m-Si-BCB** is very suitable to use as a cross-linker for the organosiloxanes which can not be directly thermo-cured. For this purpose, a commercial diethoxydimethylsilane was chosen, and the co-polymerizations were investigated, as shown in Scheme 2.



**Scheme 2** Copolymerization reactions of **m-Si-BCB** and diethoxydimethylsilane (the ratio between *m* and *n* is molar ratio).

The copolymers (**CP1**, **CP2** and **CP3**) showed molecular weights of less than 1,100, suggesting that the copolymers are suitable as coating, as well as the matrix resin for the production of laminated

composites. After being heated at high temperature, the copolymers converted to cross-linked network structures. The thermostability and mechanical properties of the cured copolymers were evaluated by TGA, TMA and nanoindenter system, respectively. The results are listed in Table 2. As shown in Table 2, the thermostability and hardness of the cured copolymers are strongly dependent on the content of **m-Si-BCB**. With the increasing of the content of benzocyclobutene units, the  $T_{5d}$  and hardness of cured polymer increased and their CTE decreased. Among the three cured copolymer, cured **CP1** showed the highest  $T_{5d}$  of 517 °C, the highest hardness of 0.814 GPa and lowest CTE of 47.52 ppm/°C, which are prior to these of the commercial epoxy resins.<sup>21</sup> These results imply that introducing **m-Si-BCB** to the organosilanes can greatly improve the heat-resistance and hardness of the organosilanes.

**Table 2** Properties of the copolymerized polysiloxanes prepared by different molar ratios

Entry	$M_n^a$	$T_{5d}^{b,e}$ (°C)	$R_w^{b,e}$ (%)	CTE <sup>c,e</sup> (ppm/°C)	Hardness <sup>d,e</sup> (GPa)	Young's Modulus <sup>d,e</sup> (GPa)
<b>CP1</b>	873	517	76.3	47.52	0.814	6.97
<b>CP2</b>	1,088	507	72.7	74.57	0.606	7.42
<b>CP3</b>	1,098	490	61.7	102.72	0.474	6.76

<sup>a</sup>The number average molecular weight, measured at room temperature by GPC. <sup>b</sup>The 5 wt% loss temperature ( $T_{5d}$ ) and weight residual ( $R_w$ ) measured by TGA at a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub>. <sup>c</sup>Average linear coefficient of thermal expansion depicted by TMA in a range of temperature from 20 °C to 300 °C. <sup>d</sup>Mechanical properties of the cross-linked polymer films on silicon wafers. <sup>e</sup>Measured from cured copolymers.

## Conclusions

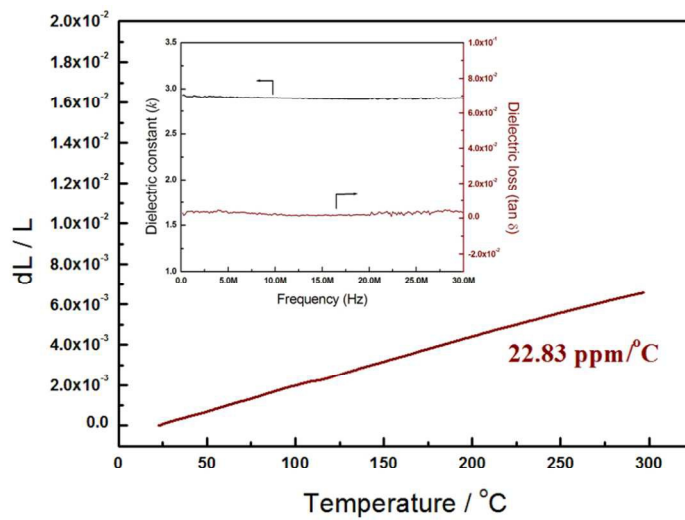
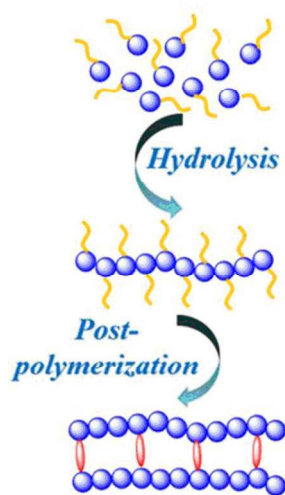
A novel organosiloxane containing thermo-crosslinkable benzocyclobutene group was successfully prepared by using the one-pot Grignard reaction procedure. Such organosiloxane can be easily polymerized to form an oligomer in an acid media. After being heated at high temperature, the oligomer directly converted to a cross-linked network structure, which showed excellent thermostability, low dielectric constant and good mechanical properties. These data indicate that the thermo-crosslinkable organosiloxane could be used as the crosslinking agents for high-performance glass fiber, the matrix resin for the production of laminated composites utilized in the printed-circuit-board (PCB) industry, as well as the varnish for enameled wire. Furthermore, the copolymerization of the organosiloxane with a commercial "inert" organosiloxane indicated that the reactive organosiloxane was an efficient crosslinkable agent for the commercial organosiloxane. Hence, this contribution develops a new way to cure organosiloxanes, in which the cross-linking of the organosiloxanes occurs by only heating, suggesting this route is of great industrial importance.

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*Cross-linked Polysiloxanes with Excellent Thermostability and Low Dielectric Constant*

315x175mm (96 x 96 DPI)