

New Polymers Derived from 4-Vinylsilylbenzocyclobutene Monomer with Good Thermal Stability, Excellent Film-Forming Property, and Low-Dielectric Constant

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ABSTRACT: A series of benzocyclobutene (BCB) polymers derived from a new readily available monomer, 4-(1',1'-dimethyl-1'-vinyl) silylbenzocyclobutene (4-DMVSBCB), were conveniently prepared by radical and anionic polymerization. The homo- and co-polymerization results show that the reactivity of 4-DMVSBCB in anionic polymerization is relatively higher compared with radical polymerization. The molecular weight of 4-DMVSBCB polymers and content of 4-DMVSBCB can be controlled by anionic copolymerization. The introduction of rigid

and crosslinkable BCB building blocks in side chains and carbosilanes in molecule gives rise to insulating materials with good film-forming property, smooth and flat film surface, and low-dielectric constants of 2.41–2.45, as preserving good thermal stability. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 49: 381–391, 2011

KEYWORDS: anionic polymerization; benzocyclobutene; cross-linking; dielectric properties; vinylsilane

INTRODUCTION In contrast to conventional polysiloxanes and polysilanes, polymers derived from silicon-containing vinyl compounds, such as vinyltrialkoxysilanes [$\text{CH}_2=\text{CHSi}(\text{OR})_3$] and vinyltrialkylsilanes [$\text{CH}_2=\text{CHSiR}_3$], are of particular interest because of their silicon-containing side chain structure. There are many reports on polymerization reactions of vinylsilanes, including radical,^{1,2} anionic,³ and coordination anionic methods.^{1(b),4} Itoh et al.² studied the radical polymerization of vinylsilanes. In the case of $\text{CH}_2=\text{CHSiH}_3$, radicals were initiated from addition and hydrogen abstraction reaction, which gave rise to C—C and Si—C main chains, respectively, whereas for vinyltrimethylsilane only vinyl polymerization was conducted. Thompson^{1(a)} reported the copolymerization of vinylsilanes and other common vinyl monomers. The results indicate a very low-rate constant for self-propagation of vinylsilanes. Itoh et al.² also reported the anionic polymerization of vinylsilanes. In the anionic polymerization of $\text{CH}_2=\text{CHSiH}_3$, the addition reaction of an anion to the silyl group yields a pentacoordinated silicon anion, a hydrogen transfer reaction occurred and Si—C units were generated in main chains. This was explained by low-steric hindrance around the silicon and bond energy of the Si—H bond. In the case of vinyltrimethylsilane, the C=C

bond would be more easily attacked by the anion than the silicon because of the large steric hindrance around the silicon. Stanczyk and coworkers^{3(a)} reported the vinyl polymerization of $\text{CH}_2=\text{CHSiMe}_3$ and $\text{CH}_2=\text{CHSiMe}_2\text{Ph}$ (4-DMVSPH) by anionic approach, and the polymerization degree of 4-DMVSPH is relatively low. Oku et al.^{3(d,e)} reported that the polymerization of vinyltrimethylsilane ($\text{CH}_2=\text{CHSiMe}_3$) in the presence of *sec*-BuLi and *N,N,N,N*-tetramethylethylenediamine gave only vinyl polymerization product [$-\text{CH}_2\text{CH}_2(\text{SiMe}_3)-$] accompanied by the transfer reaction.

As noted above, much interest has been concentrated on the polymerization of present vinylsilanes. The work related to the modification of vinylsilane monomers remained rare, although this part of work is also very important. Incorporation of some special moieties would give rise to novel monomers and derived polymers with additional interesting properties which are worth investigating.⁵

Benzocyclobutene (BCB) constitutes the basis of a broad new family of polymer forming technologies that have been used to prepare various resins. BCB resins are generally prepared from BCB-bicapped monomer and polymer via intramolecular Diels-Alder reaction of *o*-quinodimethanes, which

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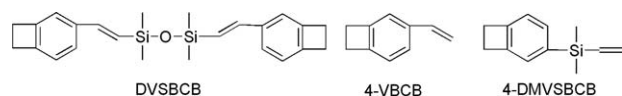


FIGURE 1 Chemical structures of DVSBCB, 4-VBCB, and 4-DMVBCB.

are formed upon thermolysis of cyclobutene.⁶ A typical BCB resin is the commercialized CYCLOTENE (trademark of the DOW Chemical Company), which is derived from bis(benzocyclobutenyl)divinyltetramethylsiloxane (DVSBCB) monomer (Fig. 1).⁷ Recently, polymers bearing BCB pendant groups have aroused much interest.^{8–11} Polymers from unique 4-vinyl substituted BCB (4-VBCB, Fig. 1) have been developed by Baskaran and coworkers,⁹ which have exhibited good processing property, thermal stability, and low-dielectric constant.^{9,10} Russell and coworkers^{11(a,c,e,g)} further developed a series of microstructure and nanostructure materials by using 4-vinyl BCB specie as an attractive building block and discovered that the intramolecular crosslinking via ring-opening reaction of BCB could lead to the formation of nanoparticles. However, the synthesis of 4-vinyl BCB monomer was relatively difficult in large scale,^{9,11(a)} thus limiting their application.

BCB resins generally have good thermal stability, chemical resistance, and low-dielectric constants and dissipation factors,⁷ which are commonly used as insulating materials. Another characteristic of BCB resins is that the crosslinking process does not need an added crosslinking agent and does not yield any small molecule, which makes BCB a very good candidate to develop high-performance materials.¹² A large number of experiments show that Si-containing BCB-dielectric materials exhibit improved performance such as the increase of thermal stability and the decrease of wettability.⁷ However, almost all BCB resins are difficult to process, and thus a prepolymer has to be prepared to provide enough viscosity before formation of film. In addition, most Si-containing BCB compounds are difficult to purify, resulting in limited applications.

As part of our continuous research on BCBs,¹³ we designed a new BCB monomer: 4-(1',1'-dimethyl-1'-vinyl)silylbenzocyclobutene (4-DMVBCB) (Fig. 1). This structure has some advantages. First, the structures of Si-containing vinyl and BCB can be integrated in this monomer with simple strategy. This monomer can be conveniently and efficiently synthesized by the Grignard crosscoupling reaction in high yield after simple a purification process. Second, the introduction of BCB structure in Si-containing vinyl compounds will give rise to polymers combining the advantages of BCB resins and Si-containing polymers. In addition, the resulted polyDMVBCBs have silylbenzocyclobutene side chain and polyethylene backbone, which exhibit better processing property and preserve almost all of the advantages of them in contrast to general BCB resins. Third, the polyDMVBCBs belong to polycarbosilanes family, which generally exhibits higher thermal stability^{3(a)} and lower dielectric constant compared

with polysiloxanes, as a result of lower polarization of Si—C bonds. In this work, we will present the detailed synthesis of 4-DMVBCB, the polymerization of 4-DMVBCB, the crosslinking process, and the properties of the polymers.

EXPERIMENTAL

Materials

4-Bromobenzocyclobutene (97%) was synthesized from BCB according to the method reported in literature.¹⁴ Chlorodimethylvinylsilane (97%) was purchased from Alfa Aesar Company. Tetrahydrofuran (THF) was distilled over sodium under nitrogen before use. Initiators (*n*-BuLi 2.5 M and *sec*-BuLi 1.3 M) solutions in hexane were purchased from Acros Chemicals. The preparation of 4-DMVSPH was described in Supporting Information.

Synthesis of Monomer 4-DMVBCB

Magnesium 0.95 g (0.040 mol) was added to a flask. A solution of 6.0 g (0.033 mol) 4-bromobenzocyclobutene in 20 mL of dry THF was added dropwise over a period of 2 h. The reaction mixture was heated to 40 °C and stirred continuously for 1 h, then cooled to room temperature. A solution of 4.3 g (0.036 mol) of vinyltrimethylchlorosilane in 15 mL of dry THF was added into the front reaction mixture over a period of 1 h at ambient temperature. The reaction mixture was heated to 40 °C, and stirring was continued for 2 h. Then the mixture was allowed to stand overnight and was poured into distilled water. The aqueous phase was extracted with diethyl ether (20 mL 3×). The organic layers were combined and dried over anhydrous sodium sulfate. After removal of the solvents by rotary evaporation, the liquid residue was fractionated at reduced pressure. The fraction boiling at 125 °C and 9 mmHg was collected and redistilled. The yield of product was 5.3 g (86%).

¹H NMR (400 MHz, CDCl₃) δ: 0.37 (s, 6H, —CH₃), 3.21 (d, 4H, *J* = 4.0, —CH₂CH₂), 5.78 (dd, 1H, *J* = 4.0, *J* = 19.2, —CH=CH₂), 6.07 (dd, 1H, —CH=CH₂, *J* = 4.0, 14.8), 6.31 (dd, 1H, —CH=CH₂, *J* = 14.8, 19.8), 7.10 (d, 1H, *J* = 7.60, ArH), 7.26 (s, 1H, ArH), 7.41 (d, 1H, *J* = 7.20, ArH). ¹³C NMR (100 MHz, CDCl₃) δ: —2.71 (Si(CH₃)₂), 29.77 (CH₂), 29.89 (CH₂), 121.94 (CH=CH₂), 127.58 (CH=CH₂), 132.12 (Ar—C), 132.55 (Ar—C), 136.41 (Ar—C), 138.38 (Ar—C), 145.60 (Ar—C), 147.13 (Ar—C). ²⁹Si NMR (CDCl₃) δ: —10.5 (Supporting Information Fig. S1). Infrared absorption (KBr plate, cm^{−1}): 2962.1 (s), 2931.9 (s), 1592.3 (w), 1460.0 (w), 1403.9 (vs), 1259.2 (s), 1095.4 (s), 1051.1 (s), 1011.3 (s), 952.7 (vs), 813.7 (s), 773.9 (vs), 710.9 (w), 690.0 (w), 615.5 (w) (Supporting Information Fig. S2). EI-MS (*m/z*, %): 188.1 (M⁺, 50), 173.2 (M⁺−15, 100) (Supporting Information Fig. S3).

Radical Homo- and Co-Polymerization of 4-DMVBCB

4-DMVBCB (0.20 g, 1.1 × 10^{−3} mol) in neat conditions or in toluene (1.0 mL) was added to an ampule equipped with a magnetic bar. The radical initiators (1–5 mol % in a very small amount of hexane) were injected into reactor by using a microinjector. Polymerization was stopped by addition a little of methanol (0.1 mL). The product was precipitated by

pouring into 20 mL methanol thrice. The radical copolymerization was performed in a similar way as described above. In a typical reaction, 2,2-azobis(isobutyronitrile) (AIBN) (0.0034 g, 2.1×10^{-5} mol) and 4-DMVSBCB (0.20 g, 1.1×10^{-3} mol) were mixed in toluene (1.0 mL) under the nitrogen atmosphere at room temperature. Subsequently, styrene (0.28 g, 2.7×10^{-3} mol) was added dropwise by funnel. The reaction was carried out under the nitrogen atmosphere. The polymerization was terminated with methanol (0.1 mL). The product was precipitated in methanol thrice and dried under vacuum at 40 °C for 24 h to give white powders.

Anionic Polymerization of 4-DMVSBCB

Anionic polymerizations were carried out using a high-vacuum break-seal technique. In a typical process, 4-DMVSBCB (1.5 g, 7.9×10^{-3} mol) was added to an ampule equipped with a magnetic bar and a sidearm break-seal containing initiator *n*-BuLi (2.5 M in hexane, 33 μ L). The reaction was initiated by breaking the glass membrane and mixing the initiators with monomer. The reaction mixture was stirred at room temperature for 24 h, and polymerization was stopped by addition of methanol (0.1 mL). The polymer was precipitated in 20 mL methanol thrice and dried under vacuum at 40 °C for 24 h to give white powders.

Synthesis of Monomer 4-DMVSPH

4-DMVSPH was prepared from vinyl dimethylchlorosilane and bromobenzene by the Grignard crosscoupling reaction. Magnesium 0.93 g (0.039 mol) was added a flask. A solution of 5.0 g (0.032 mol) bromobenzene in 20 mL dry THF was added dropwise over a period of 2 h at ambient temperature. The reaction mixture was heated to 40 °C, stirring was continued for 1 h; and then the mixture was cooled to room temperature. A solution of 4.0 g (0.033 mol) of vinyl dimethylchlorosilane in 15 mL of dry THF was added into the front reaction mixture over a period of 1 h at ambient temperature. The reaction mixture was heated 40 °C, and stirring was continued for 2 h. Then the mixture was allowed to stand overnight and poured into distilled water. The aqueous phase was extracted with ethylether (20 mL 3 \times) and the ether layer was separated. The ether layer was dried over anhydrous sodium sulfate. After removal of solvent, the liquid residue was fractionated at reduced pressure. The fraction boiling at 100 °C and 9 mmHg was collected and redistilled. The yield of product was 3.9 g (75%).

Anionic Copolymerization of 4-DMVSBCB with Other Vinyl Monomers

The anionic copolymerization was performed in a similar way as described above. In a typical reaction, 4-DMVSBCB (0.50 g, 2.7×10^{-3} mol) and 4-DMVSPH (0.60 g, 3.7×10^{-3} mol) was added to an ampule equipped with a magnetic bar and a sidearm break-seal containing initiator *n*-BuLi (2.5 M in hexane, 33 μ L). Two compounds were fully mixed before reaction. The reaction was initiated by breaking the glass membrane and mixing the initiator with the solution of monomer. The reaction mixture was stirred at room temperature for 24 h, and then the living polymerization was stopped by addition of methanol (0.1 mL). The polymer

was precipitated in 20 mL methanol thrice, and then it was centrifuged and dried under vacuum to give white powders.

Pre-Crosslinking of Poly(4-DMVSBCB)s

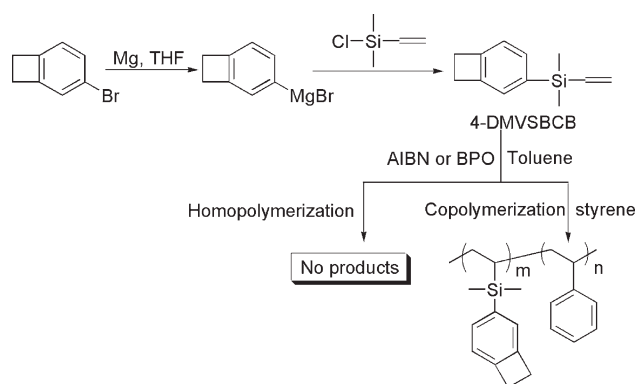
In a dry and clean reactor, the linear polymer (100 mg) was dissolved in 1 mL of mesitylene and was refluxed for 10 h under the nitrogen atmosphere at 160–170 °C. A transparent polymer solution with relatively high viscosity was obtained.

Formation of Polymer Films and Curing Reaction

Polymer films were fabricated from pre-crosslinked polymers by spin-coating method (KW-4A Spin Processor, 2000 rpm), using silicon wafer as the substrate and mesitylene as solvent. The residue solvent was allowed to evaporate under vacuum at 140 °C. The film was cured at 200 °C for 8 h under the nitrogen atmosphere to produce highly crosslinked materials.

Testing Methods

Fourier transform infrared (FTIR) measurements at 400–4000 cm^{-1} were conducted on a Nicolet FTIR 5700 spectrophotometer at room temperature and the sample films were prepared by casting solution on KBr plates. On-line infrared spectra were recorded on a Nicolet FIT-IR 6700 at a heating rate of 5 °C/min. ^1H and ^{29}Si NMR spectra (NMR) were obtained with a Bruker Avance-400 using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. ^{13}C NMR spectra were obtained with a Bruker Avance-600 using deuterated chloroform as the solvent and tetramethylsilane as the internal reference. The Mass spectra (MS) and pyrolysis-GC-MS spectra were obtained on a 3900 GC-Saturn 2100 Gas-Mass spectrometer, using electron ionization as the ion source and CDS5150 as the pyrolysis device. The molecular weight and polydispersity index were measured by size exclusion chromatography (SEC) equipped with a refractive index detector (Optilab rEX) and a Dawn Heleos light scattering detector. Gel permeation chromatography (GPC) was performed in THF using gel columns (5 μm , 10^5 nominal pore diameter and 5 μm , 10^4 nominal pore diameter; Mz-Gel SDplus) and a flow rate of 1 mL/min. Typically, 20 μL of polymer was injected. Differential scanning calorimetry (DSC) was performed on powdered samples using a TA Q200 differential scanning calorimeter at a heating rate of 10 °C/min under a nitrogen atmosphere. Thermal analysis was conducted in nitrogen or air atmosphere from 20 °C to the desired temperature using SDT-2960 TG-DSC thermogravimetric (TG) analyzer. The atomic force microscopy (AFM) images were obtained by means of a Digital Instruments Dimension 3100 microscope working in tapping mode. The samples were prepared by spin-coating from mesitylene solution. The thicknesses were measured by white light interferometer in which the refractive index of polymer is determined by that of polystyrene. Dielectric constants were measured using a Novocontrol dielectric analyzer on thin films which were spin-coated on a silicone wafer from the polymer solution in Mesitylene. Copper electrodes were magnetron sputtered on the surface and back of the film. Dielectric constants of poly(4-DMVSBCB) were obtained in the frequency range (5–20 MHz), in which the sample films



SCHEME 1 Radical polymerization of 4-DMVSBCB.

were prepared with a thickness of 0.15 mm and a diameter of 4 cm. Polymer thicknesses were measured on an AMBAOS XT-200 Surface Profilometer.

RESULTS AND DISCUSSION

Monomer Synthesis

As described above, the main purpose of the structure design of DMVSBCB monomer was to synthesize a new silicon-containing BCB polymer that is equivalent or superior to traditional polymers by an economic route. The characteristic feature of our methodology to the development of organic low-*k* materials is that the polymerization of DMVSBCB yields polyethylene side chains with pendant Si and BCB containing groups. Our interest in developing this novel monomer was also based on the ease of synthesis and the convenient radical and anionic polymerization of this monomer. The synthetic route for DMVSBCB, which was the

Grignard crosscoupling reaction of vinyl dimethylchlorosilane and 4-bromobenzocyclobutene, was outlined in Scheme 1.

The structure of DMVSBCB was analyzed on the basis of EI-MS as well as IR, ^1H NMR, and ^{13}C NMR spectroscopy. The IR spectrum showed the characteristic adsorption corresponding to the cyclobutene ring bending at 1460 cm^{-1} , the dimethylsilyl Si—C stretching at 1403 and 1260 cm^{-1} , and the vinyl C—H rocking at 953 cm^{-1} . In the ^1H NMR spectrum, signals assignable to cyclobutene (3.2 ppm), dimethylsilyl (0.4 ppm), and vinyl (5.8, 6.1, and 6.3 ppm) moieties were observed.

Polymer Synthesis

Polymerization of vinylsilanes was generally radical and anionic polymerization. One important factor affecting the polymerization behavior is the properties of substituted groups on silicon atom. It was reported that an isomerization mechanism occurred on radical and anionic polymerization of vinylhydrosilanes, leading to branched structures of polycarbosilane type, that is, with silicon-carbon bonds in the main chain.¹⁵ In comparison, the polymerization of vinyltrialkylsilanes and vinyltrialkoxysilanes was only vinyl polymerization. Additionally, the replacement of alkyl groups with aromatic groups, having electron-withdrawing effect, would lead to some changes of monomer reactivity. The introduction of BCB group in vinylsilane might lead to different reactivity from previous reported vinylsilanes. Herein, we will present detailed study of radical and anionic polymerization of 4-DMVSBCB, respectively.

Radical Polymerization

In radical polymerization process, AIBN or benzoylperoxide (BPO) were used as radical initiators. The reaction results are shown in Table 1. No homo-polymer was detected, which is consistent with this fact that the effective homo-polymerization of most of vinyltrialkylsilanes and vinylphenylsilanes

TABLE 1 Polymerization and Copolymerization of 4-DMVSBCB

Products	Initiator (10^{-2} mmol)	4-DMVSBCB (mmol)	Comonomer (mmol)	Temperature ($^{\circ}\text{C}$)	Time (h)	Content ^a of	
						4-DMVSBCB (mol %)	Yield ^b (%)
RH-1	AIBN, 8.64	4.28		60–65	60		
RH-2	BPO, 5.08	2.64		75–80	60		
RC-1	AIBN, 6.35	2.65	St, ^c 2.69	60	48	5.3	45
RC-2	AIBN, 8.34	3.19	St, 1.61	60	48	7.3	36
RC-3	AIBN, 8.74	4.26	St, 1.06	60	48	9.5	29
RC-4	AIBN, 7.92	2.68	4-BrSt, ^d 2.58	60	48	13	48
RC-5	BPO, 7.38	3.19	St, 1.73	75	36		38
RC-6	BPO, 8.68	2.16	MMA, ^e 2.21	75	36		
RC-7	BPO, 11.46	3.22	VA, ^f 3.16	75	36		

^a Contents of 4-DMVSBCB were calculated from the ratio of the integrated areas of each corresponding ^1H NMR peak.

^b The yield was obtained from the weight of precipitated material. The real yield would be higher because portions of oligomers were difficult to precipitate from methanol.

^c Styrene.

^d 4-BromoStyrene.

^e Methyl methacrylate.

^f Vinyl acetate.

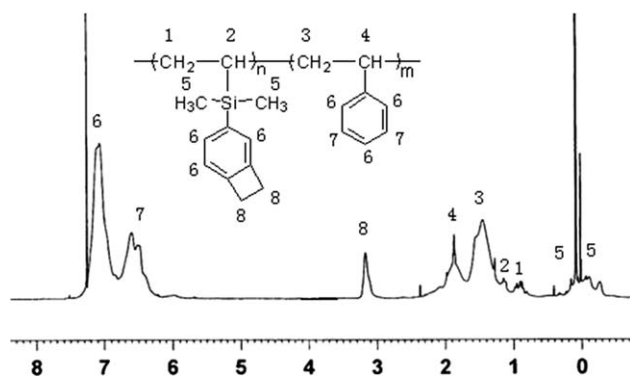


FIGURE 2 ^1H NMR spectrum of poly(4-DMVSBCB-*r*-St) from radical polymerization.

has not been reported until now. The qualitative explanation is that the silane groups have electron-donating effect, thereby reducing the stability of resulted radicals.

In contrast to homo-polymerization, radical copolymerization of vinylsilanes with styrene (Scheme 1) was successfully carried out. Colorless polymers of molecular weight (M_n) 7500–9800 g/mol were obtained in a low yield. This copolymer was soluble in toluene, THF, chloroform, pentane, and ethyl acetate, but insoluble in methanol and acetonitrile.

The results of IR, ^{13}C , and ^1H NMR analysis (See Supporting Information Figs. S4 and S5 and Fig. 2) for the copolymer **RC-3** indicate that the copolymer contains dimethylsilyl $\text{Si}(\text{CH}_3)_2$, BCB, and benzene moieties. The results of the copolymerization are shown in Table 1. The use of AIBN or BPO has no obvious effect on polymerization (**RC-2** and **RC-5**). The increase of 4-DMVSBCB feed ratio slightly reduces the yield of polymers but improves the incorporated ratio of 4-DMVSBCB in polymers (**RC-1** to **RC-3**), although the percentages of 4-DMVSBCB in the polymers are still lower than 10 mol %. The copolymerization of 4-BrSt/4-DMVSBCB gives rise to higher 4-DMVSBCB incorporated percentage (ca. 13%). Similar copolymerization behavior was reported in the case of $\text{CH}_2=\text{CHSiH}_3$,² in which copolymers with high molecular weight were obtained. However, the percentage of vinylsilanes in most of copolymers was also lower than 30%. An unfavorable equilibrium for generating active radicals exists in the copolymerization and thus makes obtainment of the copolymers with relatively high-vinylsilane contents unlikely in this condition. The vinyl compound such as vinyl acetate (VA) and MMA, and so forth, which generate radicals with relatively low reactivity and is difficult to attack by the relatively electron rich nonpolar olefin,¹⁶ shows the failure copolymerization. However, it was reported that the free radical copolymerization of acrylates with simple alkenes, also electron rich nonpolar compounds, in the presence of Lewis or Brønsted acids can lead to both a significant increase in the polymerization rate and the incorporation of alkenes.¹⁶

Anionic Polymerization

Anionic polymerization approach was commonly used for the polymerization of vinylsilanes. The results of our experi-

ments are shown in Table 2. Anionic homo-polymerization of 4-DMVSBCB were carried out using *n*-BuLi and *sec*-BuLi as initiators. Colorless solid polymers having molecular weight (M_n) of 9800–26,000 g/mol were obtained in high yield (up to 94.5%). The molecular weight polydispersity index of most polymers is in the range of 1.6–1.8 and only one single peak can be observed from GPC curves. The polymer molecular weight can be controlled by adjusting the amount of initiators (**AH-1** to **AH-3**). Moreover, the use of solvent causes a large decrease in product yield. The signals at 1.12–1.47 ppm and 0.58–0.88 ppm in the ^1H NMR spectrum [Fig. 3(a)] would be assigned to CH and CH_2 in polyethylene main chain, respectively, indicating that the vinyl polymerization products [$-\text{CH}_2\text{CHSiMe}_2\text{BCB}-$] were obtained. The two wide resonances at 22–26 ppm and 31–38 ppm in the ^{13}C NMR spectrum [Fig. 3(b)] show that the main chain of poly(4-DMVSBCB) is mainly head-to-tail arrangement but does not possess stereoregularity. The NMR spectrum does not reveal any resonances, characteristic for partly rearranged poly(vinylsilane)s. The addition between vinylsilane and organolithiums easily occurred due to the low-activation energy and high reactivity toward carbolithiation.¹⁷ In comparison, the barrier for the deprotonation of the methyl groups next to silicon is considerably higher for BuLi, thus explaining why 4-DMVSBCB undergoes carbolithiation rather than deprotonation when reacted with alkyllithiums.

The anionic polymerization of 4-DMVSBCB can be described in Scheme 2. Structural studies have shown that $d\pi$ - $p\pi$ interactions in the vinyl-silicon bond give resonance contributions to the vinyl-silicon bond, which should provide the polarization of the vinyl group necessary for anionic polymerization. Brooks et al.¹⁸ has reported that RLi adds to vinylsilanes so as to produce a secondary lithium compound. In another paper, it was described that silicon atom has α -stabilizing effect to a metalated carbon atom which is caused by a polarization of the electron density and also an electrostatic bond reinforcement.^{17(b)} Both literatures support that addition of alkyllithium to 4-DMVSBCB mainly gives rise to a secondary lithium compound. Additionally, the BCB group on silicon atom can provide silicon atom with enhanced positive charge and α -stabilizing effect due to the electron-

TABLE 2 Results of the Anionic Homo-Polymerization

Name	Initiator I	$[\text{I}]/[\text{M}]^a$	M_n^b	M_w/M_n	Yield ^c (%)
AH-1	<i>n</i> -BuLi	1.9×10^{-3}	13,900	1.62	92
AH-2	<i>n</i> -BuLi	1.2×10^{-3}	14,500	1.71	89
AH-3	<i>n</i> -BuLi	9.4×10^{-4}	22,400	1.77	93
AH-4^d	<i>n</i> -BuLi	5.7×10^{-4}	–	–	27
AC^e	<i>n</i> -BuLi	1.0×10^{-3}	21,900	1.45	91

^a Concentration of monomers.

^b Number-average molecular weight (M_n) from GPC/LS.

^c The yield was obtained from the weight of precipitated polymers.

^d The polymerization was conducted in toluene.

^e Random copolymer, poly((4-DMVSBCB)_n(4-DMVSPh)_m), $n:m = 2:3$; GPC was performed in DMF using gel columns (shodex OHPak SB-803HQ and SB-804HQ) and a flow rate of 0.5 mL/min.

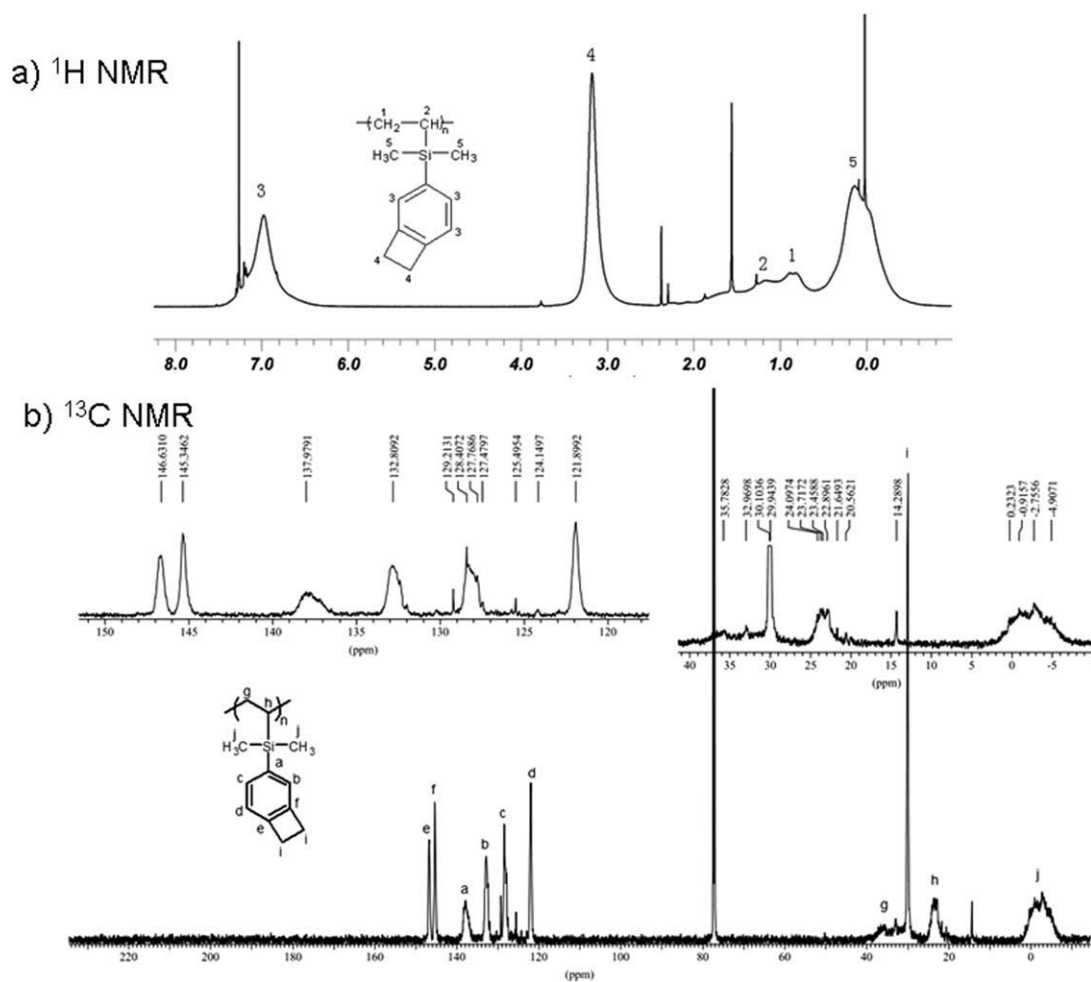
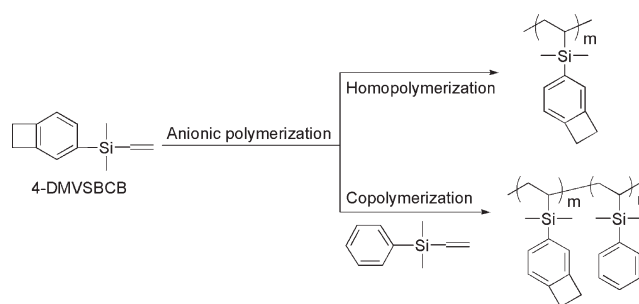


FIGURE 3 ^1H and ^{13}C NMR spectrum of poly(4-DMVSB CB) from anionic polymerization.

withdrawing property of BCB group. Therefore, relatively high yield and degree of polymerization was attainable for the polymerization of 4-DMVSB CB.

The content of 4-DMVSB VB was low in copolymer of styrene/4-DMVSB CB. To increase the incorporation of vinylsilane, the 4-DMVSP h probably with similar reactivity to 4-DMVSB CB was used as co-monomer. ^1H NMR analysis (See Fig. 4) shows that copolymerization of 4-DMVSB CB/DMVSP h occurred. The GPC results showed that only one single peak, indicating the homo-polymerization of 4-DMVSB CB or

DMVSP h was absent. The 4-DMVSB CB/4-DMVSP h ratio in copolymers AC was almost consistent with the feed ratios, and thus the random copolymerization seems reasonable in



SCHEME 2 Anionic polymerization of 4-DMVSB CB.

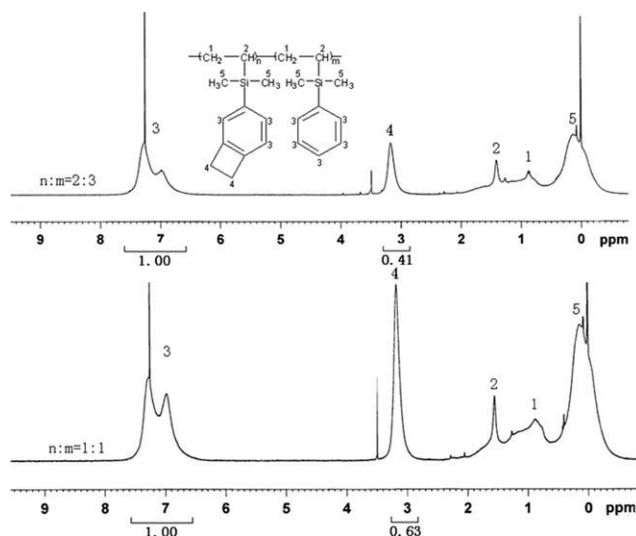
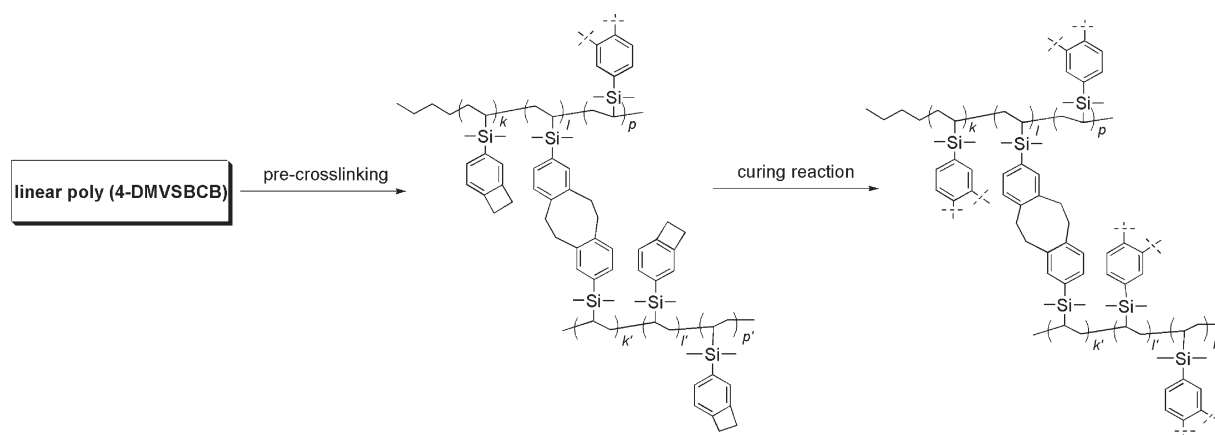


FIGURE 4 ^1H NMR spectrum of poly(4-DMVSB CB-*r*-4-DMVSP h).



SCHEME 3 Pre-crosslinking and curing of linear poly(4-DMVSBCB).

this case. It provides an important approach for incorporating a certain amount of BCB units and adjusting the content of 4-DMVSBCB in resulted copolymer.

Curing Process

A problem encountered in the coating process for the polymer with low molecular weight is its low viscosity, which presented difficulties in obtaining quality coatings, particularly at high temperatures. One solution to this might be to use polymer with higher molecular weight. In the film-forming process of CYCLOTENE, the approach was to use prepolymerization for spin-coating. However, the degree of prepolymerization was difficult to control because gel formation occurred immediately when gel point was achieved, attributed to the existence of carbon double bonds with relatively high reactivity. Thus, our purpose of using poly(4-DMVSBCB) was to control the viscosity and molecular weight for film forming. Linear poly(4-DMVSBCB) can form film directly, in addition, the molecular weight of the linear polymer can be further increased by pre-crosslinking, in which the reaction rate is slow, and thus the molecular weight and viscosity of polymer were controllable. The curing of pre-crosslinked polymer film under temperature as high as 220 °C will give rise to highly crosslinked polymer. The reaction route is

shown in Scheme 3, in which we attribute the crosslinking reaction of polymer to the formation of dibenzocyclooctadiene as generally described in previous reports.^{9,11(a)} The pre-crosslinking process of linear poly(4-DMVSBCB), with end group of *n*-butane, M_n of 20,150 and M_w/M_n of 2.015, was monitored by ¹H NMR, on-line FTIR, and DSC measurements. ¹H NMR measurements were used to monitor the pre-crosslinking process in 10 wt % solution state, whereas on-line FTIR and DSC measurements were used to monitor the process in solid state.

Table 3 shows the change of conversion ratios of BCB with different pre-crosslinking time which was obtained by ¹H NMR integration analysis (See Supporting Information Fig. S10). Although the conversion ratio achieved about 32%, no obvious gels formed. The pre-crosslinked polymer **3** with moderate BCB conversion ratio of about 23% and good processing property was used to investigate the film formation, curing, and electrical properties.

DSC analysis is shown in Figure 5. T_g of linear polymer is about 75 °C. The ring-opening of BCB was found to take

TABLE 3 Conversion Ratio of BCB with Time in the Pre-Crosslinking Process

Pre-Crosslinked Polymers	Reaction Time (h)	Peak Integrated Area Ratio (r) ^a	Conversion Ratio of BCB ^b (%)
1	7	1.18	11
2	8	1.12	16
3	10	1.03	23
4	12	0.91	32

^a The ratios of pre-crosslinked poly(4-DMVSBCB)s were calculated from the peak area of cyclobutene hydrogen to that of phenyl hydrogen in ¹H NMR spectra. The ratio of linear poly(4-DMVSBCB)s (r') was 1.33 theoretically.

^b BCB represents the cyclobutene. The conversion ratios of BCB were calculated from $(r' - r)/r'$.

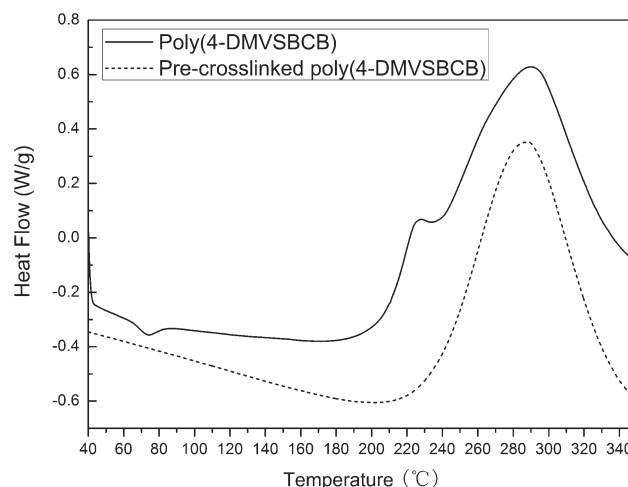


FIGURE 5 DSC spectra of linear and pre-crosslinked poly(4-DMVSBCB)s.

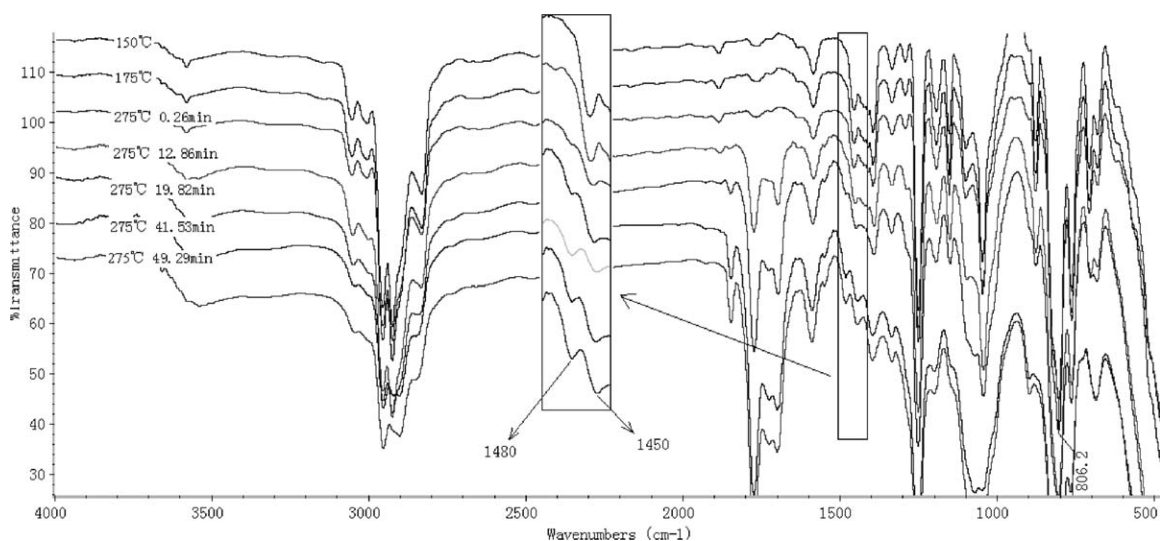


FIGURE 6 On-line infrared spectra of pre-crosslinked poly(4-DMVSBCB)s.

place at temperature above 180 °C, which might be due to the increased steric hindrance accompanied with crosslinking of polymer. Additionally, one can see that the ring opening reaction of BCB displays two stages, 180 °C to 250 °C and 250 °C to above 350 °C. The ring-opening reaction rate of BCB in the second stage is relatively slower also due to the steric hindrance. The transition point may be the gel point, where polymer network forms, density of polymer dramatically increases and thus polymer cannot be melted even under high temperature. On the other hand, no glass transition temperature and only one stage of ring opening were observed from the DSC curve of pre-crosslinked poly(4-DMVSBCB). These results show that network structure with higher rigidity was formed during pre-crosslinking process.

The ring-opening reaction mechanism of small molecule BCB is well known. It was reported that the BCB group could undergo thermal ring opening to generate diradicals.^{11(a),19} However, the ring-opening reaction of BCB attached to polymer may be different for larger steric hindrance. Here, on-line infrared analysis (See Fig. 6) was used to monitor the structure transformation during ring-opening reaction in polymer. C—H rocking mode and ring bending of the strained cyclobutene ring at 1194 and 1456 cm^{-1} , respectively, and C—H stretching of cyclobutene decreased in intensity during curing process, indicating the opening of BCB rings by thermal activation. Concomitant to the disappearance of the BCB is the appearance of ring bending modes associated with the tetrahydronaphthalene structure being formed in the reaction (1498 cm^{-1}). The spectra do not reveal any signal of C=C, indicating that the highly unstable *o*-quinodimethane rapidly reacted to yield ring-opened product via aromatization.²⁰ Moreover, characteristic adsorption bonds of carbonyl at about 1780 cm^{-1} occurred, indicating oxidation of cyclobutene moieties. The oxidation may occur primarily at the tetrahydronaphthalene group formed during the Diels-Alder

reaction of BCB.⁷ Therefore, the curing of poly(4-DMVSBCB) must be carried out in the absence of oxygen, particularly at elevated temperatures.

Polymer Characterization

The flatness of film significantly affects the electrical property of film, especially for high-frequency microelectronic requiring high accuracy. The flatness of the film with thickness of about 90 nm was characterized by AFM (See Fig. 7). The films obtained from pre-crosslinked polymer **3** are very flat and smooth in the range of 1000 nm \times 1000 nm area. It was observed that the maximum height difference is only 1 nm. The curing of film giving highly crosslinked polymer resulted in slight increase in roughness, indicating the enhanced fluctuation of surface polymer layer. This shows that the curing accompanied with increased thermal energy certainly causes the stronger chain motion and oxidation reaction within the surface polymer. The fluctuation eventually led to the formation of thickening domains which could be clearly identified within the mother phase in AFM height images. However, this slight increase in roughness does not affect the use properties of films.

The thermal properties of highly crosslinked poly(4-DMVSBCB), cured in nitrogen, were characterized by the thermogravimetric analysis (TGA) (See Figs. 8 and 9) under air and nitrogen, respectively. TGA under air shows a slight increase of weight at 230–318 °C, indicating the oxidation of poly(4-DMVSBCB). The initial decomposition temperature (T_0) and 5 wt % weight loss temperature ($T_{5\%}$) is about 318 and 400 °C, respectively. The residue weight is around 25.0 wt %. The derivative weight loss with respect to temperature shows three steps of decomposition. The first decomposition was observed at 318–425 °C, the second at 425–485 °C ($T_{\text{max}} = 438.8$ °C) and the third at a higher temperature of 485–600 °C ($T_{\text{max}} = 523.8$ °C). The first weight loss is also observed in the decomposition of CYCLOTENE

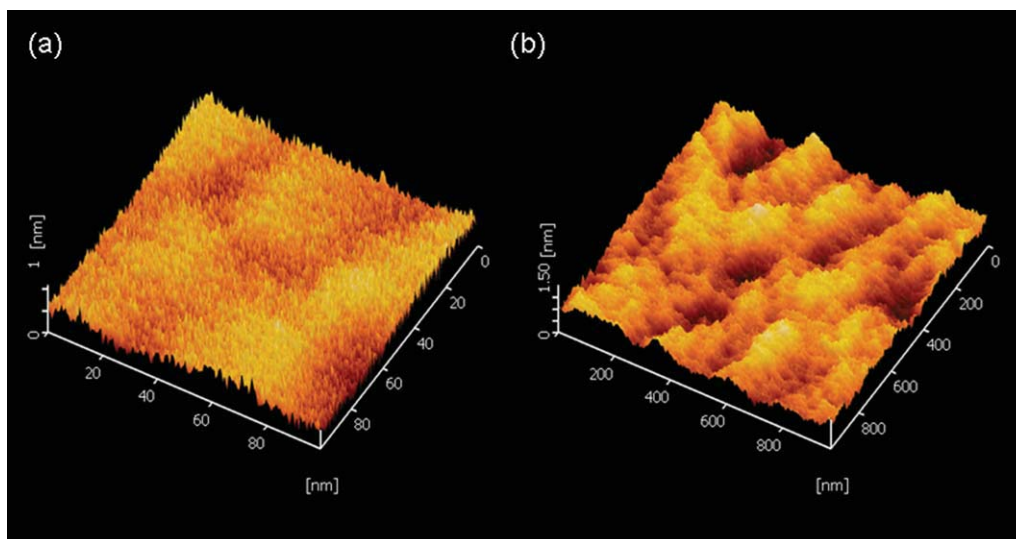


FIGURE 7 AFM spectra of pre-crosslinked and highly crosslinked poly(4-DMVSBCB) film.

and poly(4-VBCB), which is possibly due to the decomposition of some oxidized moieties. The second weight loss process is a result of the thermal decomposition of crosslinked polymer formed in curing process under nitrogen. The third composition was attributed to the poly(4-DMVSBCB) further crosslinked via oxidation reaction. They were supported by the fact that when the TGA experiments were performed under nitrogen, the increase in weight was not observed, and the homo-polymer underwent decomposition at higher temperature and in a single step at 380–548 °C ($T_{\max} = 460$ °C). Moreover, T_0 , $T_{5\%}$, and the residue weight in nitrogen is about 380 °C, 428 °C, and 20%, respectively.

The rapid decomposition may be attributed to polyethylene backbone, which is generally seen in the TGA of vinyl polymer, for example, poly(4-VBCB). The mass evolution for poly(4-DMVSBCB) was measured during isothermal exposure at 350 °C (See Supporting Information Fig. S11). The equilibrium rate of mass loss for this sample was 0.95 wt %/h,

which shows that poly(4-DMVSBCB) can be applied in some interconnect fabrication processes which are implemented at temperature as high as 350 °C.

A detailed study of thermal decomposition behavior of highly crosslinked poly(4-DMVSBCB) is conducted by pyrolysis-GCMS. Pyrolysis results of 350 °C are shown in Figure 10. The MS of peak 1 at m/e 72 shows a fragmentation pattern consistent with a pentane chain, which is evidenced of the structure of poly(4-DMVSBCB) obtained by anionic polymerization (Scheme 3). Analysis of the peaks 2–5 can provide detailed information of decomposition mechanism and cross-linking structure. For example, the structures 2 and 3 indicate the cleavage of dibenzocyclooctadiene and Si–C bonds; the structures 3–5 prove the dibenzocyclooctadiene structure in the crosslinked poly(4-DMVSBCB) and indicate the cleavage of Si–C bond linking backbone and side chain during thermal decomposition. Pyrolysis results at 400 °C is shown in Supporting Information Table 2S.

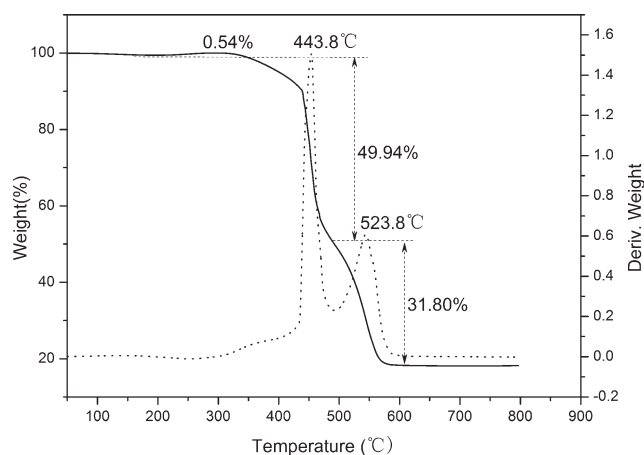


FIGURE 8 TGA spectrum of highly crosslinked poly(4-DMVSBCB) under nitrogen atmosphere.

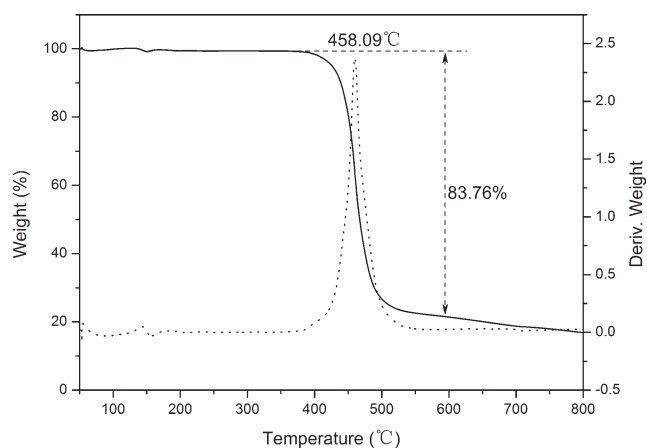


FIGURE 9 TGA spectrum of highly crosslinked poly(4-DMVSBCB) under oxygen atmosphere.

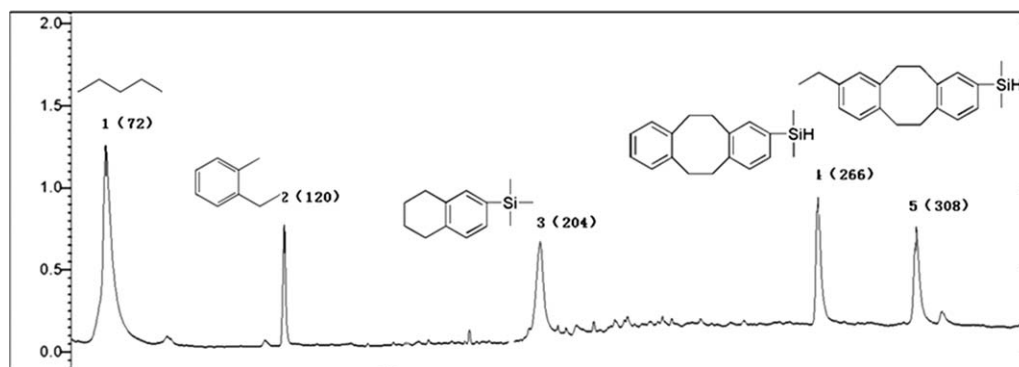


FIGURE 10 Pyrolysis results of highly crosslinked poly(4-DMVSBCB) at 350 °C.

The dielectric constant, ϵ values for pre-crosslinked polymer **3** are in the range 2.41–2.45 from 5 MHz to 20 MHz, which are lower than that of most matrix materials. To our surprise, the measured ϵ values for highly crosslinked (4-DMVSBCB) are only about 1.5. The highly crosslinking structure of the polymer which will lead to extremely rigid free volumes may be responsible for the ultra low ϵ value.²¹ Moreover, the orientation polarization in the polymer which has significant contribution to the dielectric constant at low frequency (<1 MHz)²² may exist. Further work including characterization at low frequency to get detail information is underway in our laboratory.

CONCLUSIONS

A novel monomer 4-(1',1'-dimethyl-1'-vinyl) silylbzocyclobutene was designed and prepared by simple Grignard cross-coupling reaction. The homo- and co-polymerization of monomer was conducted using radical and anionic methods. The content of 4-DMSBCB in copolymer formed by 4-DMVSBCB/4-DMVSph copolymerization can be controlled by using different feed ratio. Smooth and flat film with thickness 90 nm was obtained by spin-coating technique, and further curing only slightly decreased flatness. The crosslinking of poly(4-DMSBCB) was accomplished by the ring-opening reaction of BCB. The T_d of poly(4-DMVSBCB) is 380 °C and the thermal decomposition rate for poly(4-DMVSBCB) at 350 °C was 0.95 wt %/h. Pyrolysis-GC-MS results demonstrate the dibenzocyclooctadiene structure formed with crosslinking of BCB moieties and the cleavage of Si–C and dibenzocyclooctadiene with thermal decomposition. The dielectric constants of poly(4-DMVSBCB) are only about 2.45, which are lower than most matrix dielectric materials.

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