Cross-Linkable Carbosilane Polymers with Imbedded Disilacyclobutane Rings Derived by Acyclic Diene Metathesis Polymerization

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Received February 4, 2004; Revised Manuscript Received May 12, 2004

ABSTRACT: Cyclolinear carbosilane polymers with disilacyclobutane (DSCB) rings in the main-chain structure were prepared by means of acyclic diene metathesis (ADMET) polymerization of the corresponding 1,3-dibutenyl-1,3-disilacyclobutanes. The copolymerization of a monomer of this type with a noncyclic organosilane diene allowed for the incorporation of a varying number of DSCB rings into the polymer backbone. Subsequent hydrogenation of the double bonds with *p*-toluenesulfonhydrazide resulted in a saturated hydrocarbon structure in the main chain without affecting the DSCB ring. All of the resultant polymers are well-defined materials with DSCB rings incorporated into the backbone structure, as evidenced by NMR spectroscopy and GPC analyses. The thermal behavior of these polymers was characterized by DSC and TGA. DSC indicated low T_g s, and TGA evidenced high thermal stability in an inert atmosphere. In addition, large exothermic peaks were observed in the DSC, which indicated, along with the IR and solid-state ²⁹Si NMR spectra, that cross-linking occurs during heating to ca. 250 °C via opening of the imbedded DSCB rings. The swelling properties of the resultant, thermally stable, carbosilane network materials on exposure to various solvents were also examined.

Introduction

In the past few decades, cross-linkable polymers and polymer composites have found a high demand in such domains as interpenetrating polymer networks,¹ organic light-emitting materials,^{2,3} formation of thermally and chemically resistant coatings and bulk materials,⁴ and precursors to ceramic materials.⁵ Considerable effort has been expended in order to introduce reactive functionality into polymers, which will act as sites for cross-linking reactions. Such built-in cross-linkable functionality offers substantial advantages over alternative two-component mixtures or one-step formation of cross-linked, network solids. Chain growth and crosslinking reactions become independent of one another, either expanding the materials application ranges or improving the processability of thermally stable polymers. Cross-linking reactions are also separated from chain growth, providing complete control over the chemical structure of the primary polymer and network structures. In addition, the cross-linking agent is incorporated as a comonomer into the backbone of relatively high molecular weight polymers, allowing the cross-linking density to be directly related to the monomer composition. Polymers with vinyl,⁶ siloxane,⁷ silane,⁸ and phosphazene⁹ backbones are some examples of materials that have been synthesized with reactive cross-linkable functionalities at the ends or on a side chain.

High-temperature cross-linkable polymers and oligomers containing reactive functionalities such as acetylene,¹⁰ benzocyclobutene,¹¹ ethylene,¹² and epoxide¹³ have been widely investigated. In recent years, the thermally induced ring opening of pendant or end group monosilacyclobutane rings has also been suggested as a way to cross-link various kinds of polymers and oligomers.^{14,15} The idea comes from the fact that the four-membered silacyclobutane ring is susceptible to ring-opening polymerization (ROP) without any catalyst present.¹⁶ Residual catalysts in thermoset materials are

often hard to remove and can change their properties; they can also limit their potential application in such fields as microelectronics and medicine. The use of the disilacyclobutane (DSCB) ring as a means of thermosetting polymers, however, has not been previously reported. This is despite the fact that such rings are also known to undergo thermally induced ROP to produce polymers containing alternating silicon and carbon atoms in the backbone, which have unique properties such as good thermal and hydrolytic stability, low T_{gs} , owing to a high chain flexibility, as well as serving as high-yield precursors to SiC ceramics.^{17,18} Our recent efforts have been directed toward the synthesis of monomers that contain a reactive DSCB ring incorporated into the main chain of relatively high molecular weight, linear, carbosilane polymers and copolymers.¹⁹ Such cyclolinear carbosilane polymers offer the prospect of thermally induced cross-linking at moderate temperatures to afford elastomers and resins which possess the excellent thermal stability characteristics of the base carbosilane polymers.²⁰

Acyclic diene metathesis polymerization (ADMET), a relatively new route to olefin-containing organic polymers that emerged in the late 1980s,²¹ offers a potential approach to such cross-linkable, cyclolinear, carbosilane polymers. The polymerization is typically carried out on terminal diene monomers by using the highly selective Shrock²² or Grubbs²³ catalysts. The driving force for this metathesis reaction is the removal of ethylene, resulting in the formation of linear, olefin-containing, polymers. This reaction allows the polymerization of many different monomers with different functionality and produces regular, well-defined, condensation polymers with unique properties. Various silicon-containing polymers have been prepared in this manner by Wagener and coworkers during the past decade.²⁴ However, no studies have been reported involving diene monomers that contain a di- or monosilacyclobutane group, which can ring-open and subsequently cross-link on heating, to



Scheme 1. Two Synthetic Routes to Monomers 3a,b Route 1:

produce heat-resistant, thermosetting materials. The advantage of this cross-linking route is that the resultant network carbosilane materials could then be obtained without added catalyst or cross-linker and without evolution of volatiles. By controlling the cross-link density and the polymer functionality, the resulting materials could be used, for example, as thermally stable elastomers, coatings, matrix resins for advanced composites, and a source of SiC_x ceramic fibers, matrixes, or molded ceramic objects.

3a-b

a: R=Me

b: R=Ph

(Cis/Trans)

Results and Discussion

Monomer Syntheses. 1,3-Diene-1,3-disilacyclobutane monomers were prepared by using two approaches. Approach 1 (Scheme 1) is analogous to that employed for the synthesis of 1,1,3,3-tetramethyl-1,3-disilacyclobutane,²⁵ roughly comprising the synthetic steps employed by Auner for the synthesis of other substituted 1,3-disilacyclobutanes.²⁶ The syntheses were carried out

first by nucleophilic substitution of a dichlorosilane (1a,b) with a Grignard reagent to form an olefinsubstituted monochlorosilane, followed, after purification, by reaction with magnesium to carry out the ring closure reaction, thereby producing the olefin-substituted 1,3-disilacyclobutane four-membered ring. Approach 2 (Scheme 1) is the synthetic route developed in this laboratory,²⁷ which first employs an isopropoxy group to facilitate the formation of the DSCB ring in the "reverse Grignard" ring closure reaction. This isopropoxy intermediate was then converted to a more reactive dichloro-substituted DSCB. In the last step the diene-substituted DSCB was obtained by coupling with butenylmagnesium bromide. Both of the two methods provide similar overall yields of about 40%. However, although approach 2 contains more steps, this approach was preferred due to the relative ease in carrying out the ring closure reaction, which is difficult to initiate in the case of the first approach. These monomers were obtained as liquids which contained two isomers (the ratio of trans and cis was about 1:1 for the R = Memonomers and 6:4 for the R = Ph monomers) as confirmed by ¹H, ¹³C, and ²⁹Si NMR and GC.

Homopolymer Syntheses. The unsaturated homopolymers 4a,b were prepared by acyclic diene metathesis (ADMET) polymerization of the corresponding 1.3-dibutenyl-1.3-disilacyclobutane monomer. as shown in Scheme 2. It has already been reported that dienes readily undergo ADMET polymerization in the presence of the Shrock or Grubbs catalyst systems.^{22,23} In this study, the Grubbs second-generation catalyst was employed.²³ After polymerization and purification, the polymers were obtained as clear, colorless viscous materials, which were readily soluble in common solvents such as hexane. THF, chloroform, and toluene. The polymerization reaction proceeded cleanly with almost complete conversion and with very little residual, unreacted monomers remaining.



Scheme 2. Synthetic Routes to Cyclolinear Carbosilane Polymers



Figure 1. ¹H NMR spectra of monomer **3a** (A), polymer **4a** (B), and the reduced polymer **5a** (C).

In the ¹H NMR spectrum, the terminal olefinic protons are clearly observed for the monomers but completely disappear in the spectra of the polymers. The resultant spectra indicated the occurrence of a condensation polymerization, but not a ring-opening polymerization, and also showed that relatively high molecular weight polymers are formed. The ¹H NMR peaks assigned to the disilacyclobutane methylene protons were still observed in the same chemical shift range as the monomer, except for signal broadening (Figure 1). This indicates that the disilacyclobutane ring, which is very sensitive to ring opening with various catalysts,²⁸ survives the ADMET polymerization.

The silicon atoms of the disilacyclobutane ring in the polymer are clearly observed as doublets in the ²⁹Si NMR spectra (Figure 2), suggesting that the cis and trans isomers still exist in the ADMET polymer. The internal olefinic carbons in the polymer are also easily distinguished as trans and cis by ¹³C NMR spectroscopy, with the cis-olefinic carbons appearing at 131.46 ppm and the trans carbons appearing at 131.65 ppm (for polymer 4a).²⁴ Thus, this is a very unusual linear polymer with both the rings and olefins in the main chain having trans and cis structures. The GPC analysis of these polymers showed $M_{\rm n}$ values of 1.4 \times 10⁴ (polymer **4a**) and 1.1×10^4 (polymer **4b**). The polydispersities were 1.9 and 2.1, respectively, which fit well with the step-growth mechanism of the ADMET polymerization and provide further evidence that significant cross-linking did not occur during polymerization.

Copolymer Syntheses. As shown in Scheme 2, the monomer **3a** was copolymerized with the noncyclic organosilane 1,2-bis(butenyldimethylsilyl)ethane **3c** to



Figure 2. ²⁹Si NMR spectra of monomer **3a** (A), polymer **4a** (B), and the reduced polymer **5a** (C).

dilute the disilacyclobutane ring on the main chain and to determine the copolymerization efficiency. Polymerization conditions were similar to the homopolymerization of the monomer **3a**. Fortunately, these conditions were suitable for obtaining relatively high molecular weight copolymers. Gel permeation chromatography (GPC) in chloroform relative to narrow polystyrene standards showed only one relatively sharp peak, which indicates that homopolymer mixtures are not produced. The incorporation of the disilacyclobutane rings into the polymer chains is confirmed by ¹H, ¹³C, and ²⁹Si NMR spectra. In the ¹H NMR spectra, a sharp peak was observed at $\delta = 0.24$ ppm characteristic of the CH₃ group attached to the disilacyclobutane ring. The ratio of this resonance with respect to the resonance at $\delta =$ 0.42 ppm characteristic of the SiCH₂CH₂Si grouping proved to be a reliable check of the copolymer composition, which showed that the incorporation of disilacyclobutane units matched the expected values fairly well. Finally, neither the ¹H, ¹³C, nor the ²⁹Si NMR spectra revealed any indication of chain microstructure ordering in the copolymers, which we assume to be random copolymers that are formed with no preferential reactivity between the different monomers.

The initially obtained ADMET polymers and copolymers were saturated by hydrogenation using the method developed by Hahn,²⁹ which does not require the use of high-pressure H₂. This method uses an in-situ generated hydrogenating agent, diimide, obtained from toluenesulfonhydrazide by heating. To prevent the ring opening of the disilacyclobutanes in the polymer at this stage, the reaction temperature was decreased to 100–110 °C instead of the refluxing conditions originally reported.²⁹ Again, ¹H NMR spectroscopy indicated that the disilacyclobutane rings survived this reduction reaction (Figure 1), and ²⁹Si NMR indicated that the rings still had trans and cis structures in a 1:1 ratio. These reactions provided apparently 100% hydrogenation as evidenced

Table 1. Physical Properties of the Reduced Carbosilane Polymers and Copolymers



Figure 3. Representative DSC scan (polymer **5a**) and (inset) a plot of the enthalpy of the reaction vs comonomer content. All DSC data were recorded using a heating rate of 10 °C/ min.

by the complete disappearance of the olefin peaks in the ¹H NMR spectra (Figure 1). After reduction, GPC analyses showed that the molecular weights of the polymers had increased very slightly, which indicated there was no chain degradation during this process (Table 1).

Thermal Properties. The thermal behavior of the hydrogenated polymers was examined by DSC. In the thermogram of homopolymer 5a (Figure 3), a glass transition was observed at around -65 °C, along with a large exotherm, which starts at about 210 °C and concludes at approximately 300 °C (with a maximum at 250 °C). In the thermogram of polymer **5b**, in which phenyl replaces methyl as the other DSCB substituent, a glass transition temperature was observed at -5 °C along with a somewhat sharper strong exotherm between 220 and 290 °C. Interestingly, the starting temperature for this ring-opening reaction is significantly higher than that which has been reported for other small disilacyclobutane compounds like 1,1,3,3tetramethyl-1,3-disilacyclobutane (170 °C) or 1,1,3,3tetraphenyl-1,3-disilacyclobutane (180 °C).³⁰

For all of the other hydrogenated polymers (5c-e), a glass transition was also observed between -60 and -70°C (see Table 1), and this transition temperature was nearly invariant with copolymer stoichiometry. The T_{g} was reversible during the second scan, provided that temperatures did not exceed 150 °C for an extended period of time. At higher temperatures, for copolymers 5c and 5d, an irreversible exothermic transition was also observed in the range 200-300 °C, which presumably corresponds to the opening of the DSCB rings. The starting temperature for this reaction is, again, higher than that which has been reported for other small DSCB compounds. This ca. 40 °C difference in the starting temperature of this curing exotherm from that of the small DSCB may relate to the relatively lower mobility of the reactive DSCB groups in the polymer chain and the need to move them into the proper relative position to undergo the cross-linking reaction. The enthalpy (ΔH) for this ring-opening reaction, obtained from the integrated area under the exothermic peak, is directly



Figure 4. TGA thermograms of carbosilane polymers **5a–5e** heated to 1000 °C under a nitrogen atmosphere at 20 °C/min.

proportional to the molar content of the DSCB monomer **3a** in the polymer (see inset, Figure 3). The resultant cross-linked materials are insoluble in both polar and nonpolar solvents, while a similarly heat-treated polymer containing no DSCB rings (polymer **5e**) undergoes no changes in NMR spectra and remains soluble in solvents such as THF, hexane, or chloroform. Thus, these experiments indicated that the cross-linking reaction resulted from the opening of the DSCB ring.

Thermal gravimetric analysis (TGA) was used to determine the thermal stability and the char yield for both the original polymers and the hydrogenated polymers. As mentioned before, the thermal stabilities of the original olefin-containing polymers were relatively low.³¹ Both the unsaturated homopolymers and copolymers started to lose weight (5%) between 150 and 300 °C. In contrast, thermogravimetric analysis results for the saturated polymer **5a** (Figure 4) showed that no weight loss occurs before 470 °C on heating in an inert atmosphere, even in the region where cross-linking occurred, as was observed by DSC. For the polymer **5b**, an even higher onset temperature for weight loss of 480 °C was observed. In both cases, a significant char yield of solid residue (presumably SiC_x) is obtained on pyrolysis (25% for polymer 5a and 55% for polymer 5b by 1000 °C). Thus, the result of this thermosetting ROP process is a three-dimensional cured network that resists thermal decomposition to high temperatures and yields a substantial solid residue even after heating to 1000 °C. Since cross-linking generally enhances thermal stability, this should also be reflected in the decomposition temperatures of the copolymers, the temperature at which 5% weight loss occurs, as determined by TGA. As shown in Figure 4, the TGA results clearly demonstrated the difference in thermal stability among these materials. In the comparison of thermal stability among polymers 5a and 5c-5e, the thermal stability and char yield increase with an increase in the concentration of DSCB rings in the main chain.

Curing Studies. The thermally induced ring-opening polymerization of the DSCB rings in these polymers resulted in distinct changes in the infrared spectrum. Mixtures of the un-cross-linked and cross-linked forms of polymer **5a** were prepared in Nujol and were used for IR analysis. The IR spectra showed that the intensity of the sharp peak at 930 cm⁻¹, which was assigned to the wagging mode of the CH₂ on the DSCB rings, decreased gradually as the curing reaction proceeded and that a broad peak is formed at 1050 cm⁻¹, which is assigned to the stretching mode for the bridging CH₂ group in the SiCH₂Si open-chain structure (Figure 5).^{27,32,33}



Figure 5. IR spectra of polymer **5a** in Nujol: (A) uncured, (B) cured at 220 °C for 2 h, (C) cured at 240 °C for 4 h, and (D) cured at 280 °C for 8 h.



Figure 6. ²⁹Si NMR spectra of cured polymer **5a**: (A) uncured, (B) cured at 220 $^{\circ}$ C for 2 h, (C) cured at 240 $^{\circ}$ C for 4 h, and (D) cured at 280 $^{\circ}$ C for 8 h.

In an effort to better understand the cross-linking chemistry of the polymers, solid-state NMR spectra were taken for non-, partially, and fully cross-linked polymer 5a. There were no notable changes in peak positions in the ¹³C SS-NMR spectra during the cross-linking process. Using ²⁹Si SS-NMR under magic angle spinning (MAS), it was found that nearly all of the DSCB rings undergo ring opening after heating to 280 °C for 8 h under an inert atmosphere (Figure 6). This is monitored by the loss of a peak at 4.7 ppm (assigned to Si in the strained DSCB ring) and the growth of a peak at 2.3 ppm (assigned to Si in the linear -SiCH₂- unit) in the ²⁹Si NMR spectrum of the polymer.³⁴ Comparison of the line widths of the two peaks shows the silicon atoms in the cross-linked polymer are more restricted to motion than in the original polymer, as would be expected for a cross-linked polymer. These IR and NMR studies show clearly that the cross-linking mechanism involves the ring opening of the DSCB rings in the polymers and that this process occurs without side reactions to yield the corresponding three-dimensional, cured, carbosilane network structures.

A swelling test was carried out for some of the crosslinked polymers according to the method described in ref 35. Thin films of the cyclolinear carbosilane polymer **5a** and the copolymers **5c** and **5d** were partially cured in a glass vial in nitrogen at a temperature of 200 °C

Table 2. Surface Area Changes of Cured Specimens in Different Solvents after Swelling for 48 h (Measured at 25 °C, after Curing for 8 h at 280 °C under Nitrogen)

-				-
area changes (%) in medium cured polymers	hexane	chloroform	acetone	ethyl alcohol
5a	0	0	0	0
5c	24	6	0	0
5 d	150	110	14	9

for 2 h. The films were then removed from the glass vial and cut into thin strips. The strips were then heated to a temperature of 280 °C for 8 h in nitrogen to complete the curing process. The cured polymers (**5a**, **5c**, **5d**) were insoluble in all of the common solvents, except the homopolymer 5e which, lacking the imbedded carbosilane rings, could not be cured under the same conditions. The completely cured polymer samples were placed in different solvents at room temperature to test their solubility and swelling characteristics. Cured homopolymer 5a shows no observable swelling over 48 h in all the solvents, while the copolymers 5c and 5d all swell to a certain degree. The surface area of the cured copolymer strips increases with the swelling time up to 48 h, while no change was detected in the thickness of these samples. For the cured polymer 5d, after swelling for 48 h, the area of the polymer strips increases by 9–150%, as shown in Table 2. These results also show that the lower the content of the DSCB moiety in its backbone, the more the polymer swells after crosslinking. The results also show that the polymers swell more in nonpolar solvents than in polar solvents.

Before curing, the polymers are transparent, very viscous materials. Cured films of the polymers **5a** and **5c** were hard and brittle, while a cured film of the 10:1 copolymer **5d** was a transparent, flexible, material with rubberlike properties. Samples obtained by curing the polymer **5a** in glass tubes, sealed at one end and heated to 280 °C for 8 h, were easily removed from the tubes on cooling, owing to shrinkage occurring after cross-linking. The density was changed from 0.92 to 0.94 g/cm³, corresponding to a reduction in volume of 2.1%. A detailed study of the mechanical properties of these materials is currently in progress.

Experimental Section

Materials. All manipulations involving air- and/or moisturesensitive materials were performed under a nitrogen atmosphere with glovebox and conventional Schlenk line techniques. All ether and hydrocarbon solvents were distilled before use from their purple sodium/benzophenone solutions. All the chemicals were purchased from Aldrich Chemical Co. 4-Bromo-1-butene (97%), magnesium (99%), methylmagnesium bromide (3.0 M solution in diethyl ether), 1,2-bis(chlorodimethylsilyl)ethane (96%), tripropylamine (99%), *p*-toluenesulfonylhydrazide (97%), and the Grubbs second-generation catalyst were all used as received without further purification. Chloromethyldichloromethylsilane, chloromethyldichlorophenylsilane, and 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane were prepared according to the literature methods and purified by distillation.^{25,26}

Instrumentation. All of the solution NMR spectra were obtained on Varian Unity-300 or Unity-500 MHz spectrometers. ¹H and ¹³C spectra were referenced to the solvent peaks, and ²⁹Si spectra were referenced to TMS. Infrared spectra were taken with a Perkin-Elmer Paragon 1000 spectrometer. The molecular weight of the polymers was measured on a Waters GPC system equipped with a refractive index detector and three Styragel columns packed with 5 μ m particles (HR1: effective molecular weight 100–5000; HR3: effective molecular weight 500–30 000; HR4: effective molecular weight 5000–

500 000) using THF as eluent at a flow rate of 1.0 mL/min. Molecular weights were reported relative to polystyrene standards. DSC measurements were obtained on a TA 2920 instrument. The transition temperatures were determined by using a heating rate of 10 °C/min after an initial heating/ cooling cycle to 100 °C. TGA studies were carried out using a Mettler-Toledo thermogravimetric analyzer at a rate of 20 °C/ min under a flowing nitrogen atmosphere. All of the solid-state NMR spectra were acquired on a Chemagnetics Infinity 360 MHz spectrometer. ²⁹Si spectra were externally referenced to TMS using tetrakis(trimethylsilyl)silane and acquired under single-pulse conditions with decoupling during acquisition and magic angle spinning (MAS); the 29 Si pulse width was 4.5 μ s for a $\pi/2$ pulse, and the optimal relaxation delay was 60 s. ¹³C spectra were externally referenced to TMS using hexamethylbenzene and acquired under the same conditions as the ²⁹Si spectra.

1. Preparation of Butenylchloromethylmethylchlorosilane (2a). Compound **2a** was prepared by a two-step reaction process. The first step of the preparation of the Grignard reagent between 4-bromo-1-butene and magnesium turnings was carried out in a 250 mL three-necked, roundbottomed flask with stirring bar, addition funnel, and reflux condenser. The flask was charged with 6.0 g (0.25 mol) of magnesium turnings in 10 mL of dried THF. 4-Bromo-1-butene (27.0 g, 0.2 mol) dissolved in 50 mL of dry THF was added slowly within 1 h by means of an addition funnel. A heating gun was used to warm the flask to initiate the reaction. After the reaction mixture was stirred at 45 °C for 2 h, the reaction was stopped, and the remaining magnesium was removed and weighed to determine the conversion (97%).

A 1 L three-necked, round-bottomed flask was charged with 24.5 g (0.15 mol) of chloromethyldichloromethylsilane and 150 mL of THF. Freshly made butenylmagnesium bromide (0.15 mol) was added under vigorous stirring within 1 h. The exothermic reaction that occurred resulted in the formation of solid magnesium bromide as a byproduct. The reaction was stirred at 60 °C for 8 h. After the reaction mixture was cooled to room temperature, 200 mL of dried hexane was added to precipitate the magnesium salt. Then the liquid was transferred to another 1 L flask by using a Teflon cannula. Two 100 mL portions of THF were used to extract the product from the salts. All of the collected liquid was combined for distillation. The solvents were stripped off by atmospheric pressure distillation. Vacuum distillation of the residue gave 21.2 g (0.13 mol) of product collected at 40-44°C/0.5 mmHg. Yield: 77.3%. ¹H NMR (CDCl₃): δ 0.24 (s, 3H, SiCH₃), 0.85 (t, J = 7.2 Hz, 2H, SiCH₂CH₂CH), 2.12 (m, 2H, SiCH₂CH₂CH), 3.70 (s, 2H, CH₂Cl), 5.03 (d, 2H, CH₂CHCH₂), 5.81 (m, 1H, CH₂CHCH₂). ¹³C NMR (CDCl₃): δ -4.95 (SiCH₃), 12.68 (SiCH₂CH₂), 28.75 (SiCH₂CH₂CH), 37.25 (SiCH₂Cl), 116.80 (CH₂CHCH₂), 140.72 (CH2CHCH2). 29Si NMR (CDCl3): 8 23.41.

2. Preparation of Butenylchloromethylphenylchlorosilane (2b). 2b was prepared in an analogous manner to the synthesis of 2a described in the preceding section by using chloromethylphenyldichlorosilane as starting material. The boiling point and final yield of 2b were 100°C/0.5 mmHg and 76.3%. ¹H NMR (CDCl₃): δ 1.40 (t, J = 7.4 Hz, 2H, SiCH₂-CH₂), 2.28 (m, 2H, SiCH₂CH₂), 3.20 (s, 2H, CH₂Cl), 5.05 (d, 2H, CH₂CHCH₂), 5.9 (m, 1H, CH₂CHCH₂), 7.40-7.74 (m, 5H, C₆H₅). ¹³C NMR (CDCl₃): δ 13.46 (SiCH₂CH₂), 26.72 (SiCH₂CH₂-CH), 28.99 (SiCH₂Cl), 114.33 (CH₂CHCH₂), 128.45, 131.32, 133.85, 134.16 (SiC₆H₅), 139.74 (CH₂CHCH₂). ²⁹Si NMR (CDCl₃): δ 11.97.

3. Preparation of 1,3-Dibutenyl-1,3-dimethyl-1,3-disilacyclobutene (3a). Monomer **3a** was prepared by two procedures. Procedure a: Following the "reverse addition" procedure described by Kriner, a 500 mL three-necked, roundbottomed flask was equipped with stirring bar, addition funnel, and reflux condenser. Then 22.0 g (0.12 mol) of butenylchloromethylmethylchlorosilane in 50 mL of dry THF was added to bring the silane concentration to about 30%. 0.5 g of magnesium powder was added to the solution, and the coupling reaction was initiated by using a heating gun. Subsequently, 4.8 g (0.2 mol) of magnesium was added in portions during the course of 1 h, while cooling occasionally with a cold water bath to maintain the reaction temperature between 40 and 50 °C. After refluxing for another several hours, the reaction mixture was cooled to room temperature. 50 mL of dry hexane was added to precipitate the magnesium salt from the THF solution. All of the combined liquid (THF/ hexane/product) was transferred to another flask via a cannula. After removal of the solvents under atmospheric pressure with a N₂ stream, the residue was collected and purified by fractional distillation one or two times using a packed column. The final yield was 6.6 g (49%).

Procedure b: 2.34 g (12.6 mmol) of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane mixed with 50 mL of THF was charged in a three-necked 250 mL flask equipped with a reflux condenser. Butenylmagnesium bromide (37.5 mmol; as prepared in part 3) was added via a syringe over 1 h. The reaction mixture was continuously stirred with a magnetic stir bar. Some magnesium salts formed during addition of the 3-butenylmagnesium bromide. The resulting mixture was further refluxed for 2 days, and then the solution was cooled to room temperature. The excess Grignard reagent was destroyed by adding 40 mL of saturated aqueous ammonium chloride solution. The solution formed two phases with the excess magnesium dissolving in the acidic aqueous layer. The organic phase was separated and dried overnight by using anhydrous sodium sulfate. The solvent was removed by atmospheric distillation, and a final distillation under reduced pressure using a packed column gave 2.31 g (10.3 mmol) of pure product (mixture of trans and cis isomers). The final yield of **3a** was 81.7%. ¹H NMR (CDCl₃): δ –0.10–0.11 (quintet, 4H, SiCH₂-Si), 0.24 (s, 6H, SiCH₃), 0.78 (t, 4H, SiCH₂CH₂), 2.16 (m, 4H, SiCH₂CH₂), 4.91-5.07 (m, 4H, CH₂CHCH₂), 5.91 (m, 2H, CH₂C*H*CH₂). ¹³C NMR (CDCl₃): δ 0.71, 0.86 (Si*C*H₃), 0.89, 0.95 (SiCH₂Si), 17.67, 17.77 (SiCH₂CH₂), 27.99, 28.04 (SiCH₂CH₂), 113.18, 113.20 (CH₂CH*C*H₂), 141.53, 141.57 (CH₂*C*HCH₂). ²⁹Si NMR (CDCl₃): δ 4.97, 5.04. IR (neat, cm⁻¹): 3076, 2954, 2908, 1639, 1428, 1408, 1340, 1248, 991, 936, 906, 824, 779, 693.

4. Preparation of 1,3-Dibutenyl-1,3-diphenyl-1,3-disilacyclobutene (3b). 3b was prepared in an analogous manner to the synthesis of **3a** described in the preceding section from butenylchloromethylphenylchlorosilane. Purification by column chromatography gave the product as a mixture of trans and cis isomers. Yield: 51.2%. ¹H NMR (CDCl₃) (both trans and cis isomers): δ 0.56–0.66 (m, 4H, SiCH₂Si), 1.01–1.22 (m, 4H, SiCH₂CH₂), 2.10–2.26 (m, 4H, SiCH₂CH₂), 5.01–5.15 (m, 4H, CH₂CHCH₂), 5.80–6.05 (m, 2H, CH₂CHCH₂), 7.37–7.74 (m, 10H, C₆H₅). ¹³C NMR (CDCl₃): δ –0.83, –0.75 (SiCH₂Si), 16.81, 16.87 (SiCH₂CH₂), 27.80, 27.98 (SiCH₂CH₂), 113.28, 113.45 (CH₂CHCH₂), 127.95, 127.97, 129.31, 129.43, 133.84, 138.47, 138.77 (SiC₆H₅), 141.09, 141.17 (CH₂CHCH₂). ²⁹Si NMR (CDCl₃): δ 0.82, 1.01. IR (neat, cm⁻¹): 3066, 2973, 2910, 1638, 1426, 1347, 1111, 992, 936, 908, 759, 732, 698, 626.

5. Preparation of 1,2-Bis(butenyldimethylsilyl)ethane (3c). 30 g (0.14 mol) of 1,2-bis(chlorodimethylsilyl)ethane was mixed with 150 mL of THF in a two-necked 500 mL flask equipped with a reflux condenser. 0.30 mol of 3-butenylmagnesium bromide (as prepared in section 3) was added slowly via a syringe over 2 h. Some magnesium salts formed during addition of the butenylmagnesium bromide. The resulting mixture was further refluxed for 1 day, and then the solution was cooled to room temperature. 100 mL of hydrochloric acid (1 M) solution was added very slowly to destroy any excess Grignard reagents and dissolve the magnesium salts. The solution formed two layers. The organic phase was separated and dried by anhydrous sodium sulfate for several hours. The solvent was removed by atmospheric distillation, and the final yield of **3c** was 83.2%; bp 67°C/0.9 mmHg. ¹H NMR (CDCl₃): δ -0.02 (s, 12H, SiCH₃), 0.40 (s, 4H, SiCH₂CH₂Si), 0.62 (t, 4H, SiCH₂CH₂CH), 2.04 (m, 4H, SiCH₂CH₂CH), 4.87-5.04 (m, 4H, CH₂CHCH₂), 5.88 (m, 2H, CH₂CHCH₂). ¹³C NMR (CDCl₃): δ -3.68 (SiCH₃), 7.39 (SiCH₂CH₂Si), 14.06 (SiCH₂CH₂CH), 28.28 (SiCH₂CH₂CH), 112.83 (CH₂CHCH₂), 142.08 (CH₂CHCH₂). ²⁹Si NMR (CDCl₃): δ 4.34. IR (neat, cm⁻¹): 3076, 2952, 2904, 1640, 1411, 1247, 1133, 1055, 992, 905, 829, 778.

General Polymerization Procedures. In a glovebox under an inert N₂ atmosphere, the dry monomer or mixture of monomers and the second-generation Grubbs catalyst (1 wt %) were added to a round-bottom flask. The mixture was stirred at room temperature in the glovebox until a clear solution resulted, which indicated that the catalyst was completely dissolved in the monomer. The flask was then removed from the glovebox, and the contents were stirred under vacuum on a Schlenk line and heated in an oil bath to 40 °C. After 1 day the reaction mixture was again taken into the glovebox, and an additional aliquot of catalyst was added. The mixture was then stirred at 65 °C until the evolution of ethylene was no longer visible and the stir bar did not stir. The reaction was terminated by exposure to air. The resultant polymer was dissolved in toluene or THF, treated with activated carbon, passed through silica gel column, twice precipitated by pouring into methanol, and then vacuum-dried. Yields for these polymerization reactions were all above 85% with some loss in yield attributed to polymer lost in the workup. The polymers obtained as colorless or light yellow, very viscous materials. Polymers **4a**–**e** were synthesized by this method and characterized by standard methods including ¹H, ¹³C, and ²⁹Si NMR, IR, and GPC.

Polymer 4a. ¹H NMR (CDCl₃): δ -0.01-0.08 (m, 4H, SiCH₂Si), 0.23 (s, 6H, SiCH₃), 0.77 (br, 4H, SiCH₂CH₂), 2.08 (br, 4H, SiCH₂CH₂), 5.49 (br, 2H, CH₂CHCHCH₂). ¹³C NMR (CDCl₃): δ 0.83 (SiCH₃), 0.99 (SiCH₂Si), 18.54, 18.62 (SiCH₂-CH₂), 26.75 (SiCH₂CH₂), 131.46 (CH₂CHCHCH₂, cis-olefin), 131.65 (CH₂CHCHCH₂, trans-olefin). ²⁹Si NMR (CDCl₃): δ 4.78, 4.85. IR (neat, cm⁻¹): 3008, 2952, 2912, 2850, 1655, 1612, 1442, 1405, 1342, 1247, 1152, 965, 931, 822, 688.

Polymer 4b. ¹H NMR (CDCl₃): δ 0.47–0.49 (br, 4H, SiC*H*₂-Si), 0.81–0.95 (br, 4H, SiC*H*₂CH₂), 1.86–2.06 (br, 4H, SiCH₂C*H*₂CH), 5.19–5.42 (br, 2H, CH₂C*H*CH₂), 7.19–7.56 (br, 5H, SiC₆*H*₅). ¹³C NMR (CDCl₃): δ –0.93 (Si*C*H₂Si), 17.46 (Si*C*H₂CH₂CH), 26.47 (SiCH₂*C*H₂CH), 131.36 (CH₂*C*H*C*HCH₂), 127.90, 128.03, 129.25, 133.83, 135.22 (Si*C*₆H₅). ²⁹Si NMR (CDCl₃): δ 0.40, 0.56. IR (neat, cm⁻¹): 3066, 3007, 2911, 2840, 1647, 1588, 1427, 1347, 1301, 1260, 1111, 966, 935, 761, 732, 699, 608.

Polymer 4c. ¹H NMR (CDCl₃): δ -0.015 (SiC*H*₂Si and SiC*H*₃, overlapped), 0.24 (SiC*H*₃), 0.42 (SiC*H*₂C*H*₂Si), 0.58–0.64 (SiC*H*₂CH₂), 0.77 (SiCH₂CH₂), 1.99–2.03 (SiCH₂C*H*₂CH), 5.33–5.47 (CH₂C*H*C*H*CH₂). ¹³C NMR (CDCl₃): δ -3.51 (SiC*H*₃), 0.85 (SiC*H*₂C, H), 18.55, 18.63 (SiC*H*₂C*H*₂Si), 14.94, 15.44 (SiC*H*₂C*H*₂CH), 131.61–131.83 (multiple signals, CH=CH). ²⁹Si NMR (CDCl₃): δ 4.20, 4.78, 4.85. IR (neat, cm⁻¹): 2951, 2902, 1696, 1441, 1407, 1246, 1131, 1053, 935, 903, 829, 779, 713, 688.

Polymer 4d. ¹H NMR (CDCl₃): δ -0.015 (SiC*H*₂Si and SiC*H*₃, overlapped), 0.24 (SiC*H*₃), 0.42 (SiC*H*₂C*H*₂Si), 0.58–0.64 (SiC*H*₂CH₂), 1.99–2.03 (SiCH₂C*H*₂CH), 5.33–5.47 (CH₂C*H* C*H*CH₂). ¹³C NMR (CDCl₃): δ -3.51 (SiC*H*₃), 1.01 (SiC*H*₂Si), 7.49 (SiC*H*₂C*H*₂Si), 14.94, 15.44 (SiC*H*₂C*H*₂C*H*), 21.62, 27.04 (SiC*H*₂C*H*₂C*H*), 131.61–131.83 (multiple signals, CH=CH). ²⁹Si NMR (CDCl₃): δ 4.20. IR (neat, cm⁻¹): 2951, 2902, 1696, 1441, 1407, 1246, 1131, 1053, 935, 903, 829, 779, 713, 688.

Polymer 4e. ¹H NMR (CDCl₃): δ –0.04 (12H, SiC*H*₃), 0.38 (4H, SiC*H*₂C*H*₂Si), 0.59 (4H, SiC*H*₂CH₂CH), 2.01 (4H, SiC*H*₂-*CH*₂CH), 5.35, 5.44 (2H, SiC*H*₂C*H*₂C*H*). ¹³C NMR (CDCl₃): δ –3.56 (Si*C*H₃), 7.48 (Si*C*H₂C*H*₂Si), 14.94 (Si*C*H₂CH₂CH), 27.02 (SiC*H*₂*C*H), 131.85 (CH₂C*H*₂*C*H). ²⁹Si NMR (CDCl₃): δ 4.19. IR (neat, cm⁻¹): 2952, 2903, 1725, 1407, 1249, 1175, 1132, 1054, 967, 836, 719, 689.

General Hydrogenation Procedure for the Polymers. For preparation of the corresponding saturated hydrocarbon polymers, in a typical experiment, 0.2 g (1 mmol) of the ADMET polymer **4a** mixed with 20 mL of xylene was added to a two-necked round-bottom flask with a reflux condenser. 0.29 g (2 mmol) of tripropylamine (TPA) and 0.37 g (2 mmol) of *p*-toluenesulfonhydrazide (TSH) were added to this flask, and the mixture was heated at 100 °C in an oil bath for 4 h under nitrogen. After cooling to room temperature, an additional equivalent of TPA and TSH was added to the mixture. The temperature was increased to 110 °C for another 4 h. After removing the solid precipitate, the entire liquid mixture was added to methanol, and the product was recovered by decantation and dried in a vacuum. Yields typically ranged from 80 to 90% with the lost yield attributed to polymer not recovered from the precipitation. Polymers **5a**–**e** were synthesized by this method and characterized by standard methods including ¹H NMR, ¹³C NMR, ²⁹Si NMR, IR, and GPC.

Polymer 5a. ¹H NMR (CDCl₃): δ –0.03 (m, 4H, SiC*H*₂Si), 0.22 (s, 6H, SiC*H*₃), 0.69 (br, 4H, SiC*H*₂CH₂), 1.37 (br, 8H, SiCH₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂Si). ¹³C NMR (CDCl₃): δ 0.79, 0.83 (Si*C*H₃), 0.91 (SiC*H*₂Si), 18.69, 18.74 (SiC*H*₂C*H*₂C*H*₂), 23.85, 23.87 (SiCH₂C*H*₂C*H*₂), 33.26 (SiCH₂C*H*₂C*H*₂). ²⁹Si NMR (CDCl₃): δ 4.33, 4.38. IR (neat, cm⁻¹): 2952, 2918, 2851, 1459, 1406, 1340, 1247, 930, 894, 858, 823, 778.

Polymer 5b. ¹H NMR (CDCl₃): δ 0.57 (br, 4H, SiC*H*₂Si), 1.01 (br, 4H, SiC*H*₂CH₂), 1.35 (br, 8H, SiCH₂C*H*₂C*H*₂), 7.37– 7.67 (br, 10H, SiC₆*H*₅). ¹³C NMR (CDCl₃): δ –1.08 (Si*C*H₂Si), 17.67 (Si*C*H₂CH₂CH₂), 23.83 (SiCH₂*C*H₂CH₂), 33.05 (SiCH₂-CH₂*C*H₂), 127.89, 129.23, 133.79, 139.74 (Si*C*₆H₅). ²⁹Si NMR (CDCl₃): δ –0.01, 0.21. IR (neat, cm⁻¹): 3065, 2919, 2851, 1648, 1484, 1458, 1426, 1348, 1186, 1110, 997, 934, 909, 763, 732, 699, 610.

Polymer 5c. ¹H NMR (CDCl₃): δ –0.04 (16H, SiC*H*₂Si and SiC*H*₃, overlapped), 0.22 (6H, SiC*H*₃), 0.38 (4H, SiC*H*₂C*H*₂Si), 0.51 (4H, SiC*H*₂CH₂), 0.69 (4H, SiC*H*₂CH₂), 1.32–1.37 (16H, SiCH₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂Si), ¹³C NMR (CDCl₃): δ –3.58 (Si*C*H₃), 0.84 (Si*C*H₃), 0.93 (Si*C*H₂Si), 7.49 (Si*C*H₂*C*H₂Si), 15.02 (Si*C*H₂CH₂, 18.72, 18.78 (Si*C*H₂CH₂), 23.89, 24.12 (SiCH₂*C*H₂), 33.28, 33.70 (SiCH₂CH₂*C*H₂). ²⁹Si NMR (CDCl₃): δ 3.89 (*Si*CH₂CH₂S*i*), 4.33, 4.37 (*Si*CH₂*Sf*). IR (neat, cm⁻¹): 2952, 2919, 2872, 1460, 1407, 1340, 1246, 1186, 1132, 1053, 934, 908, 827, 779, 736, 689, 663.

Polymer 5d. ¹H NMR (CDCl₃): $\delta -0.05 -0.05$ (SiC*H*₂Si and SiC*H*₃, overlapped), 0.22 (SiC*H*₃), 0.38 (SiC*H*₂C*H*₂Si), 0.50-0.53 (SiC*H*₂CH₂), 0.69 (SiC*H*₂CH₂), 1.32 (SiCH₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂C*H*₂Si), ¹³C NMR (CDCl₃): $\delta -3.59$ (Si*C*H₃), 0.83 (Si*C*H₃), 0.92 (Si*C*H₂Si), 7.51 (Si*C*H₂*C*H₂Si), 15.04 (Si*C*H₂CH₂C*H*₂, 18.79 (Si*C*H₂CH₂), 23.85, 24.13 (SiCH₂*C*H₂), 33.70 (SiCH₂CH₂C*H*₂). ²⁹Si NMR (CDCl₃): $\delta 3.87$. IR (neat, cm⁻¹): 2950, 2918, 2851, 1460, 1407, 1186, 1131, 1053, 933, 830, 778, 712, 690.

Polymer 5e. ¹H NMR (CDCl₃): $\delta -0.04$ (12H, SiC*H*₃), 0.38 (4H, SiC*H*₂C*H*₂Si), 0.50 (4H, SiC*H*₂C*H*₂C*H*₂), 1.31 (8H, SiC*H*₂C*H*₂C*H*₂). ¹³C NMR (CDCl₃): $\delta -3.617$ (SiC*H*₃), 7.50 (SiC*H*₂C*H*₂Si), 15.02 (SiC*H*₂C*H*₂C*H*₂), 24.12 (SiC*H*₂C*H*₂C*H*₂), 33.69 (SiC*H*₂C*H*₂C*H*₂). ²⁹Si NMR (CDCl₃): δ 3.87. IR (neat, cm⁻¹): 2951, 2919, 2791, 1459, 1408, 1246, 1187, 1132, 1053, 831, 714.

Swelling. Based on a previously described procedure,³⁵ swelling studies for the cured polymers were carried out in the following manner: ca. 0.5 g samples of the polymers were partially cured in a glass vial under nitrogen at a temperature of 200 °C for 2 h. The partially cured polymers were then removed from the glass vial as intact films and cut into strips with dimensions of ca. $0.1 \times 5 \times 10 \text{ mm}^3$. The resultant polymer samples were then heated to a temperature of 280 °C under nitrogen for 8 h to complete the cure process. After curing, the samples were immersed in the indicated solvents, and the change in the area of the films was measured.

Conclusions

A series of novel cyclolinear polymers with 1,3disilacyclobutane (DSCB) rings imbedded into the mainchain structure were obtained by using ADMET polymerization. These olefin-containing, cyclolinear, carbosilane polymers were then hydrogenated with *p*-toluenesulfonhydrazide to produce a saturated hydrocarbon structure in the main chain without affecting the imbedded DSCB rings. NMR spectroscopy and GPC analyses showed that all of the resultant, relatively high molecular weight polymers have well-defined, regular structures consisting of DSCB rings [-SiMe(CH₂)₂SiMe-] linked by linear hydrocarbon or carbosilane chains. DSC studies of these

polymers indicated a glass transition at low temperatures $(-70 \rightarrow -60 \text{ °C} \text{ for the methyl-substituted poly-})$ mers and -5 °C for the phenyl-substituted polymer) followed, on first heating, by a strong exotherm centered at ca. 250 °C. IR and solid-state NMR spectra, along with the change in physical form, showed that the second transition at 250 °C corresponds to the thermally induced ring opening of the DSCB rings, resulting in a transparent, cross-linked, solid material having the shape of the container with little overall shrinkage. TGA of the reduced form of the homopolymer under N₂ showed no weight loss until 470-480 °C with char yields of 25% (polymer 5a) and 55% (polymer 5b) after pyrolysis to 1000 °C.

Acknowledgment. Financial support from the Chemistry Division of the National Science Foundation through Grant CHE-0109643 is gratefully acknowledged. The authors also acknowledge the 2001 Mettler-Toledo Thermal Analysis Educational Grant in honor of Professor Edith Turi, which made possible the purchase of the TGA instrument that was used in this work.

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MA049760A