

Synthesis and characterization of poly[(2-dimethylsilyl-2-cyclopentene-1,4-diyl) vinylene]

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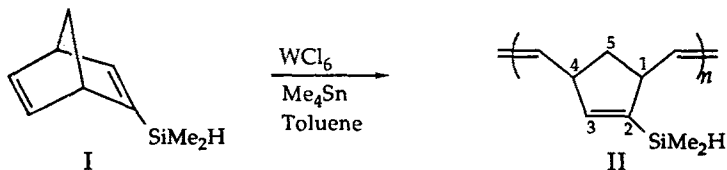
SUMMARY

Ring opening metathesis polymerization (ROMP) of 2-dimethylsilylbicyclo[2.2.1]hept-2,5-diene (I) cocatalyzed by tungsten hexachloride/tetramethyltin yields poly[(2-dimethylsilyl-2-cyclopentene-1,4-diyl) vinylene] (II). This is the first example of ROMP of a monomer which contains a reactive Si-H bond. ^1H , ^{13}C , ^{29}Si and IR spectroscopy were utilized to characterize II. The molecular weight distribution of II has been determined by gel permeation chromatography (GPC), its thermal stability by thermogravimetric analysis (TGA) and its glass transition temperature (T_g) by differential scanning calorimetry (DSC).

INTRODUCTION

Ring opening metathesis polymerization (ROMP) of cyclic olefins to yield unsaturated hydrocarbon polymers has been extensively studied.¹ Recently, ROMP of cyclic olefins substituted with a wide range of reactive functional groups, such as alcohol, boron, ether, ester, halide and nitrile to give the corresponding functionally substituted unsaturated hydrocarbon polymers, has attracted considerable interest.²⁻⁵ ROMP of monomers with a reactive Si-H bond has not been previously reported.

While there has been extensive work on polysiloxanes, much less work has been done on carbosilane polymers. Yajima's proposal that polycarbosilanes such as poly(methylene methylsilylene) are key intermediates in the thermal decomposition of polysilanes to form β -silicon carbide has increased interest in this area.^{6,7} Unsaturated polycarbosilanes containing Si-H bonds in the backbone appear to facilitate the formation of silicon carbide.^{8,9} This probably results from the ability of these polymers to undergo cross-linking via thermal hydrosilation. Cross-linking has been shown to be an essential requirement for the high yield conversion of linear preceramic polymers to ceramic materials.^{10,11} Also, polymers containing Si-H bonds can be cross-linked to form films or gels via hydrosilation using various catalysts. It is also interesting because polymers which contain vinyl silyl groups are capable of undergoing facile chemical modification or acting as polymeric coupling agents.¹²⁻¹⁴



Polymerization of 2-Dimethylsilylbicyclo[2.2.1]hepta-2,5-diene (I)

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EXPERIMENTAL

^1H and ^{13}C NMR spectra were obtained using a Bruker AM-250 MHz FT NMR spectrometer. ^{29}Si NMR spectra were obtained using a Bruker AM-270 MHz FT NMR spectrometer. ^{13}C NMR spectra were acquired with broad band proton decoupling. One percent solutions in chloroform-*d* were used to obtain all NMR spectra. ^1H and ^{13}C NMR spectra were internally referenced to chloroform. ^{29}Si NMR spectra were externally referenced to tetramethylsilane in chloroform-*d* and acquired using an inverse gated heteronuclear decoupling sequence (NONOE).¹⁵ IR spectra of neat films were recorded on a Perkin-Elmer PE-281 spectrometer on NaCl plates.

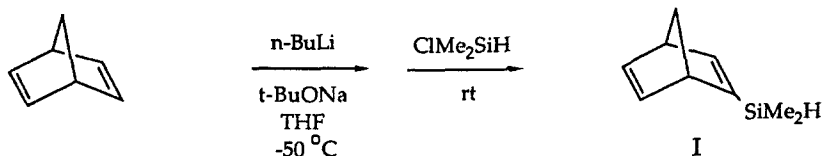
GPC analysis of the polymer molecular weight distribution was performed on a Waters system comprised of a U6K injector, a 510 pump, a R401 differential refractometer and an 820 Maxima Control system. A Waters 7.8 mm x 30 cm, 10 μm , cross-linked polystyrene gel column was used. HPLC grade THF at a flow rate of 0.6 mL/min was used as the elution solvent. Retention times were calibrated against monodisperse polystyrene standards of molecular weight 612,000, 114,200, 47,500, 18,700 and 5,120 having M_w/M_n of less than 1.09.

Thermal stability of the polymer was determined by TGA. A Perkin-Elmer TGS-2 with nitrogen flow rate of 40 cm^3/min was used. The temperature profile used was: 50 $^\circ\text{C}$ for 10 min, then the temperature was increased at a rate of 4 $^\circ\text{C}/\text{min}$ to 750 $^\circ\text{C}$. The glass transition temperature (T_g) was determined using a Perkin-Elmer DSC-7 differential scanning spectrometer. The temperature profile began at -100 $^\circ\text{C}$ and increased at a rate of 20 $^\circ\text{C}/\text{min}$ to 150 $^\circ\text{C}$.

Toluene was distilled from sodium benzophenone ketyl immediately prior to use. Tungsten hexachloride and tetramethyltin were used as received from Aldrich. All reactions were carried out under a nitrogen atmosphere in flame dried glassware.

2-Dimethylsilylbicyclo[2.2.1]hepta-2,5-diene (I)

2-Sodiobicyclo[2.2.1]hepta-2,5-diene was prepared using Schlosser's method.¹⁶ Quenching of the metalated intermediate with dimethylchlorosilane gave I. It had the following spectral properties: ^1H NMR δ : 7.09(d, 1H, $J = 2.9$ Hz), 6.68(dq, 2H, $J = 5.1$ and 3.2 Hz), 4.11(septet, 1H, $J = 3.7$ Hz), 3.70(m, 1H), 3.63(m, 1H), 1.90(tq, 1H, $J = 5.9$ and 1.5 Hz), 0.12(d, 3H, $J = 3.7$ Hz), 0.10(d, 3H, $J = 3.7$ Hz). ^{13}C NMR δ : 155.29, 152.87, 143.13, 142.33, 74.21, 53.67, 52.09, -4.84, -4.92. ^{29}Si NMR δ : -25.0. IR ν : 3060, 2980, 2880, 2130, 1580, 1550, 1460, 1430, 1310, 1260, 1240, 1220, 1200, 1170, 1100, 1025, 1010, 940, 890, 850, 840, 820, 770, 750, 700, 660, 620 cm^{-1} .



Synthesis of 2-Dimethylsilylbicyclo[2.2.1]hepta-2,5-diene (I)

ROMP of 2-Dimethylsilylbicyclo[2.2.1]hepta-2,5-diene (I)

The reaction was carried out in a dry 25 mL round bottom flask which contained a Teflon-covered magnetic stirring bar and was sealed with a rubber septum. The WCl_6 (11.0 mg) was weighed into a round bottom flask in a Vacuum Atmospheres dry box. Toluene (5.0 mL) and 8 μL of Me_4Sn were added by syringe. Initially, the solution is a deep burgundy or red-black color. The mixture was stirred for approximately 3 min, before addition of I (180 mg) via syringe. Almost instantly, the solution changed to a yellow-gold color and its viscosity increased. Within 1 h, the mixture had completely gelled. The reaction was allowed to stand for 4 h at room temperature, prior to quenching by addition of methanol (10 mL). The solvents were removed by evaporation under reduced pressure. The residue was dissolved in CHCl_3 and filtered to remove insoluble material. Most of the solvent was removed by evaporation under reduced pressure. The polymer was then precipitated by addition of methanol. A pale yellow solid (95 mg, 53%) was recovered. It had the following properties: ^1H NMR δ : 5.92-5.82(br.m, 1H), 5.34-5.17(br.m, 2H), 4.04(br.s, 1H), 3.71-3.67(br.s, 1H), 3.26(br.s, 1H), 2.29(br.s, 1H), 1.26-1.20(br.s, 1H), 0.06(br.s, 6H). ^{13}C NMR δ : 146.5, 145.5, 133.8, 132.9, 53.6, 50.7, 48.0, 45.9, 40.5, 40.1, -3.8, -3.9, -4.0, -4.1. ^{29}Si NMR δ : -25.9, -25.95, -26.0. IR ν : 3040, 2980, 2400, 2130, 1700, 1590, 1530, 1430, 1260, 1230, 1050, 980, 940, 900, 880, 840, 778, 770, 760 and 680 cm^{-1} . GPC: $M_w/M_n = 20,400/11,700$. $T_g = 71$ $^\circ\text{C}$.

RESULTS AND DISCUSSION

The ^1H NMR spectra of I, Figure 1, is similar to that of 2-trimethylsilylbicyclo[2.2.1]hepta-2,5-diene.¹⁷ The major differences are a result of the replacement of a methyl group on silicon by a proton. This gives rise to diastereotopic methyl groups on silicon.

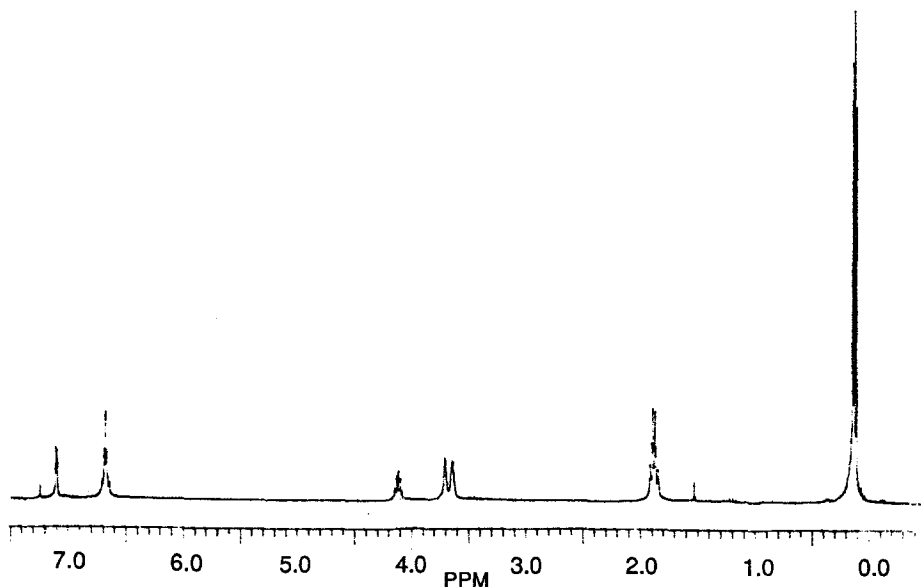


Figure 1. ^1H spectra of 2-dimethylsilylbicyclo[2.2.1]hepta-2,5-diene (I).

As expected, ROMP of I proceeds regioselectively with opening of the disubstituted carbon-carbon double bond in preference to the dimethylsilyl substituted carbon-carbon double bond. Tungsten hexachloride based catalyst systems have not been observed to catalyze ring opening of trisubstituted double bonds in cyclic compounds.¹

ROMP of I yields a polymers whose ¹H, ¹³C and ²⁹Si NMR spectra are similar to those of poly[(2-trimethylsilyl-2-cyclopentene-1,4-diyl) vinylene].¹⁷ The differences of the microstructures are due to the stereochemistry of the vinylene units bonded at C1 and C4. These can be *cis,cis*; *cis,trans*; *trans,cis* and *trans,trans* (Figure 2).

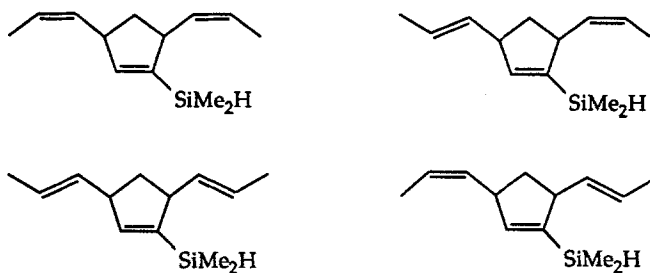


Figure 2. Polymer (II) microstructure.

Four groups of resonances (45.9, 48.0, 50.7, and 53.6 ppm) assigned to methine carbons are observed in the ¹³C NMR (Figure 3). Following Rooney,¹⁸ the chemical assignments of II are assumed to be *cis* C1 45.9 ppm, *trans* C1 48.0 ppm, *cis* C4 50.7 ppm and *trans* C4 53.6. The differences in chemical shift are due to the stereochemistry of the adjacent vinylene group and distance to the dimethylsilyl group. Further splitting is undoubtedly due to the orientation (*head to head*, *head to tail*, *tail to head* or *tail to tail*) of adjacent 2-dimethyl-

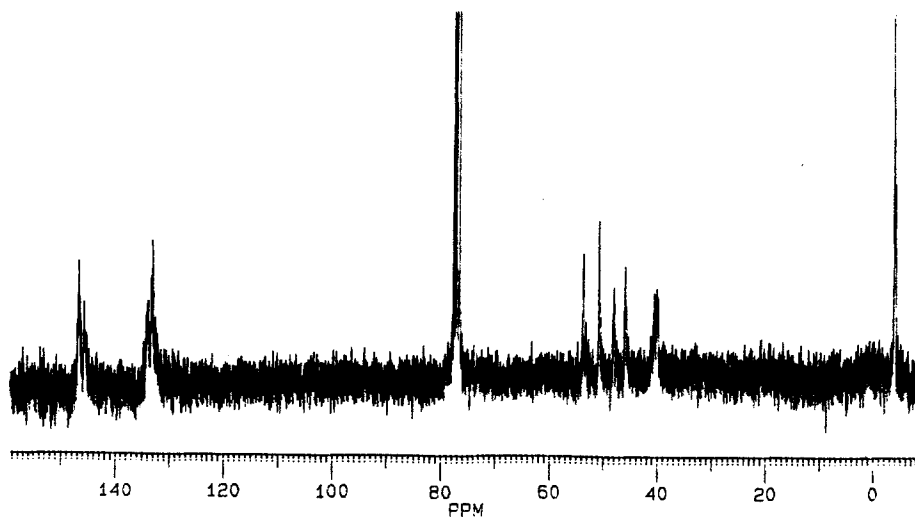


Figure 3. ¹³C spectra of poly[(2-dimethylsilyl-2-cyclopentene-1,4-diyl) vinylene].

silylcyclopent-2-ene groups as well as other factors. The ^1H NMR shows two different signals for the methine hydrogens (3.69 and 3.26 ppm) (Figure 4). It is assumed that the dimethylsilyl group causes the signal for the proximate methine hydrogen to be shifted upfield.

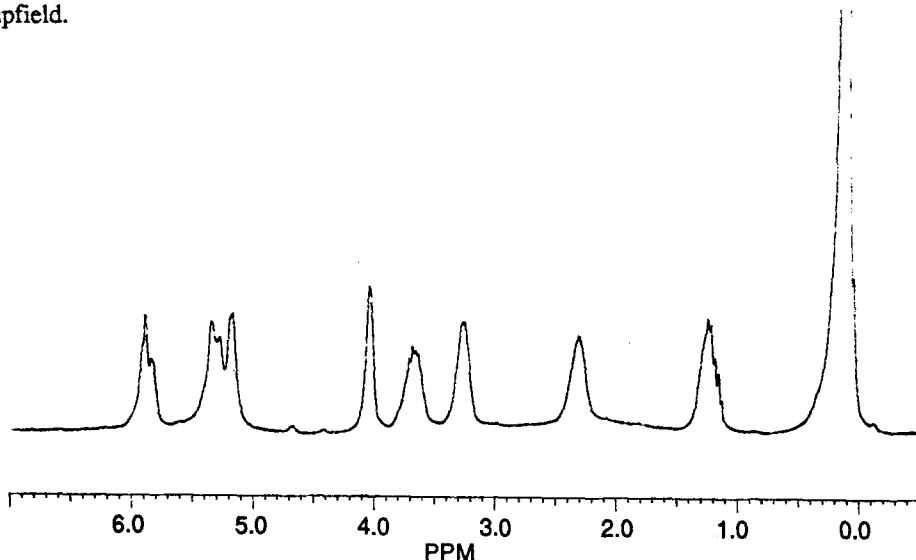


Figure 4. ^1H spectra of poly[(2-dimethylsilyl-2-cyclopentene-1,4-diyl) vinylene].

Unlike poly[(2-trimethylsilyl-2-cyclopentene-1,4-diyl) vinylene], both *cis* and *trans* C5 peaks, (40.5 and 40.0 ppm), are resolved in the ^{13}C NMR spectra of II.¹⁷ The methylene hydrogens in the ^1H NMR (2.30 and 1.34 ppm) are of equal intensity. The *syn* orientation of the vinylene groups bonded to C1 and C4 of the cyclopentene ring create two distinct

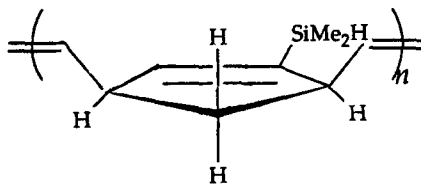


Figure 5. Orientation of methylene hydrogens in II.

environments for the methylene hydrogens (Figure 5). A broad singlet at 0.12 ppm is assigned to the dimethylsilyl group. Peak broadening prevents splitting corresponding to the diastereotopic nature of the two methyl groups from being observed. Multiple signals for this group are seen in both the ^{13}C and ^{29}Si NMR (Figures 3 and 6). The degree of splitting

indicates that the dimethylsilyl group is sensitive to the effects of the proximate vinylene group as well as the, *head to head*, *head to tail*, *tail to head* or *tail to tail* orientation of the adjacent 2-dimethylsilylcyclopent-2-ene groups.

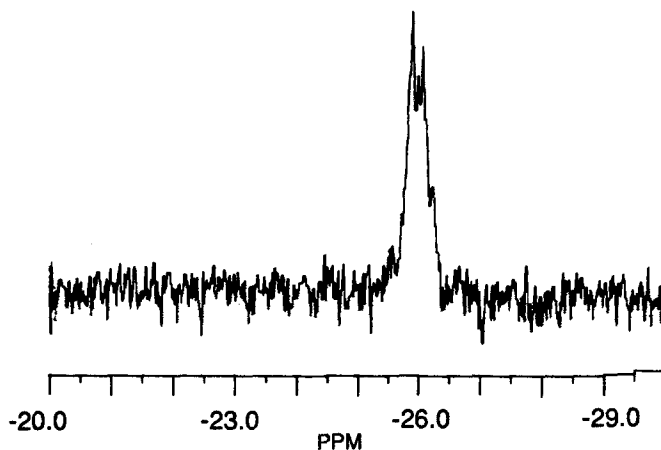


Figure 6. ^{29}Si spectra of poly[(2-dimethylsilyl-2-cyclopentene-1,4-diyl) vinylene].

There are two sets of vinyl carbons. The *cis* and *trans*-vinylene carbons are assumed to be at (133.8 and 132.1 ppm). The vinyl carbons of the 2-dimethylsilylcyclopent-2-ene ring are at (146.5 and 145.5 ppm). Two broad resonances for the vinyl hydrogens are observed in the ^1H NMR (5.92-5.82 and 5.34-5.14 ppm, 1:2). The low field multiplet is assigned to the C3-hydrogen of the cyclopentene ring.

The GPC analysis of the polymer molecular weight distribution was performed using HPLC grade THF. II was only partly soluble in THF. Higher molecular weight II is expected to be less soluble than low molecular weight fractions. This may account for the low M_w/M_n found for II.

The thermal stability of II has been determined by TGA. II slowly loses five percent of its initial weight between 50 and 350 °C. Between 350 and 550 °C more rapid decomposition occurs. Thirty-eight percent of the initial weight remains at 550 °C. Above 700 °C there is a black residue accounting for 20% of the initial weight (Figure 7). The TGA of II is similar to that of III.

Acknowledgments: This work was supported by the Air Force Office of Scientific Research and the Office of Naval Research.

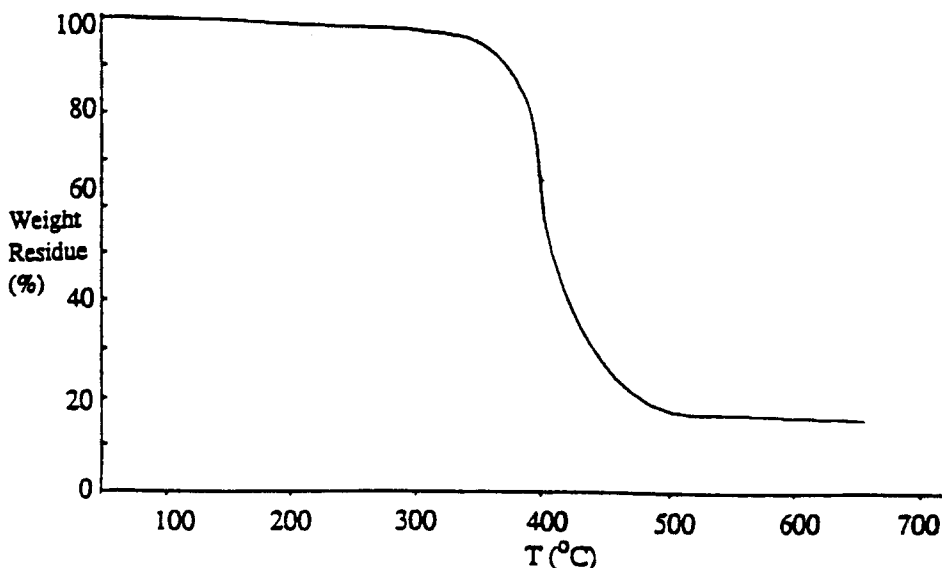


Figure 7. Residue weight of II versus temperature.

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