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Acyclic Diene Metathesis Polymerization. Synthesis and Characterization of Unsaturated Poly[carbo(dimethyl)silanes]

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ABSTRACT: The first equilibrium polycondensation polymerization approach to unsaturated poly[carbo(dimethyl)silanes] is presented. Diallyldimethylsilane (I), 4,4,7,7-tetramethyl-4,7-disiladeca-1,9-diene (II), and 1,4-bis(allyldimethylsilyl)benzene (III) undergo acyclic diene (metathesis (ADMET) polymerization when catalyzed by highly active tungsten alkylidenes, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2R$, where R = CH_3 or Ph. These polymerizations, which are performed under bulk conditions, continuously release ethylene to give poly(1,1-dimethyl-1-silapent-3-ene) (VI), poly(1,1,4,4-tetramethyl-1,4-disilaoct-6-ene) (VII), and poly[1-(dimethylsilyl)-4-(1,1-dimethylsilapent-3-en-1-yl)phenylene] (VIII), respectively. Polymers VI and VII produce trace amounts of the cyclic dimer and monomer, respectively, at the end of the polymerizations. Dimethyldivinylsilane (IV) does not homopolymerize; however, it does copolymerize with 1,9-decadiene (V) to give poly(1,1-dimethyl-1-silapropene)-*co*-octenamer (IX). All vinylsilane linkages in the copolymer are isolated. All polymers were characterized by infrared spectroscopy and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. Average molecular weights were determined by gel permeation chromatography and end-group analysis. Synthesis, characterization, and the current scope of this polymerization are discussed.

Introduction

Acyclic diene metathesis (ADMET)[1-4] polymerization (Figure 1) has proven to be a viable synthetic route to high molecular weight unsaturated polymers[2] and copolymers,[3] including polymers possessing various functionalities.[4] In comparison with the well-known and very successful ring-opening metathesis polymerization (ROMP),[5] which propagates by chain growth, we have demonstrated that the polymerization of a broad range of acyclic dienes can be accomplished in an equilibrium step condensation fashion.[6]

The polymerization is facilitated by highly active tungsten alkylidene Schrock[7] metathesis catalysts of the type $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2R$, where R = CH_3 or Ph. In pursuing the scope of ADMET chemistry, an opportunity to construct unique and ordinarily difficult-to-prepare polymers and copolymers became evident. This paper describes the synthesis of silicon-containing polymers, inorganic materials that are of growing interest and importance.

In recent years, considerable emphasis has been given to the study of silicon-containing polymers due to their electronic, optical, and thermal properties and because they are precursors to ceramics.[8] In particular, the examination of linear poly(carbosilanes)—polymers containing silicon and carbon in the backbone—has, for the most part, been neglected due to synthesis difficulties.[9] Until now, the synthesis of these materials has been confined to coupling reactions,[10] thermal cyclopolymerizations,[11] and a variety of ring-opening polymerizations including anionic,[12] thermolytic,[9] and catalytic coordination[9] techniques, each with obvious limitations. ADMET polymerization avoids many of these limitations and may stimulate the expansion of this class of polymers.

Recently, Weber[12] and co-workers successfully demonstrated the anionic ring-opening polymerization of silacyclopent-3-enes to give the first high molecular weight poly(allylsilanes) with various substituents. Prior to this work, Sartori[13] reported the ring-opening metathesis polymerization of this monomer yielding low molecular weight products. Although these ring-opening methods find great importance throughout polymer chemistry, the requirement that strained cyclic monomers be used somewhat limits the choice of polymer structure and properties. The condensation polymerization of acyclic diallyl-containing dimethylsilanes via ADMET chemistry appears to offer a more general selection of polymer structure.

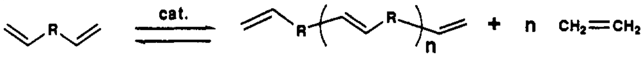

Figure 1. Acyclic diene metathesis (ADMET) polymerization.

As mentioned above, the anionic polymerization of 1,1-dimethyl-1-silacyclopent-3-ene to give polymer VI has been reported by Weber.[12a] Here we report a new synthesis of polymer VI (with a different average geometric configuration) and three new poly[carbo(dimethyl)silanes] by the ADMET polymerization of acyclic dimethylsiladienes (Figure 2).

Experimental Section

^1H NMR 200-MHz, ^{13}C NMR 50-MHz, and ^{29}Si NMR 40-MHz spectra were obtained with a Varian XL-Series NMR superconducting spectrometer system. Chloroform-*d* was used as solvent, and all chemical shifts reported are internally referenced to tetramethylsilane. Quantitative ^{13}C NMR spectra were run for 8–12 h with a pulse delay of 6–20 s. A heteronuclear gated decoupling pulse sequence with a pulse delay of 10 s was used to obtain ^{29}Si NMR spectra. Infrared analyses were performed on neat oils between NaCl plates using a Perkin-Elmer 2 infrared spectrophotometer. Mass spectroscopy data were obtained with a Finnigan 4500 gas chromatograph/mass spectrometer. Ethylene samples were collected from the reaction by condensation with liquid nitrogen, in a 100-mL evacuated flask equipped with a rotoflow high-vacuum stopcock and a Suba Seal septum. Samples were syringed directly from the pressurized flask. Other nonmonomer volatiles were condensed in the same manner and dissolved in chloroform and injected.

Gel permeation chromatography (GPC) data were collected using a Waters Associates liquid chromatograph apparatus equipped with a U6K injector and refractive index detector. Two phenomenex 7.8 mm × 30 cm Phenogel 5 consecutive linear gel columns were used, a 500 Å followed by a 1000 Å type. The eluting solvent was HPLC-grade THF at a flow rate of 1.0 mL/min. Retention times were calibrated against the following polystyrene standards of known polydispersity: 110 000, 39 000, 7820, 4000, and 1152 whose M_w/M_n are, at most, 1.06.

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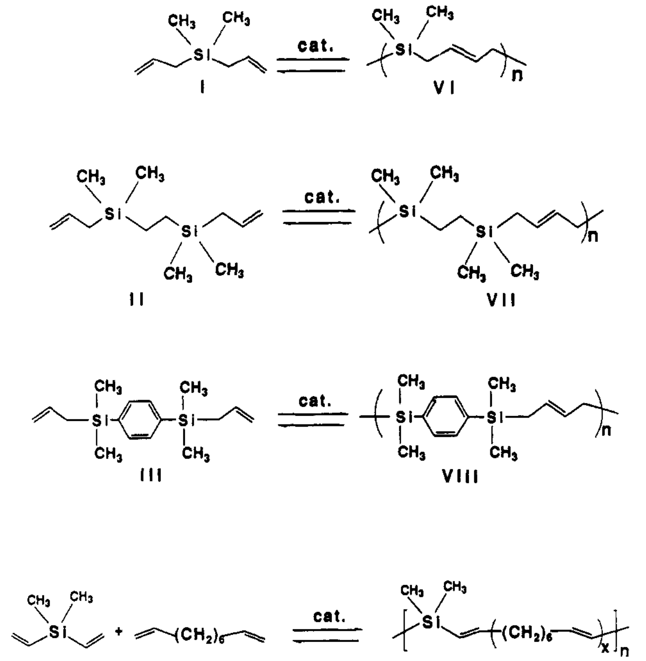


Figure 2. Poly[carbo(dimethyl)silanes] produced by acyclic diene metathesis (ADMET) polymerization.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data were obtained with a Perkin-Elmer 7 Series thermal analysis system. DSC samples were analyzed with liquid nitrogen as coolant and a helium flow rate of 25 mL/min. The homopolymer samples were cycled from −100 to 40 °C at successive decreasing scan rates ranging from 20 to 5 °C/min. The copolymer was cycled from −100 to +80 °C at decreasing scan rates ranging from 20 to 1 °C/min. TGA samples were performed under nitrogen and air with a flow rate of 50 mL/min with program heating from 50 to 600 °C at a rate of 10 °C/min.

Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

The Lewis acid free catalysts used in the polymerizations, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2R$, where R = CH_3 (neopentyl) and Ph (neophyl), were prepared by published methods.[14] The catalyst was dissolved in pentane, syringed into a high-vacuum Rotoflow valve equipped break-seal ampules, evaporated, sealed in vacuo, and stored dry and dark in a freezer.

All monomers were fractionally distilled from CaH_2, degassed under high vacuum by several freeze–thaw cycles, then vacuum transferred to a potassium or sodium mirror successively until no reaction was observed, and then vacuum transferred directly into the reaction flask or break-seal ampule. On occasion, treatment with catalyst for purification was necessary. Diallyldimethylsilane (I; Aldrich), dimethyldivinylsilane (IV; Petrarch), and 1,9-decadiene (V; Aldrich) were purchased and purified in this manner.

All polymerizations were conducted in a flame-dried custom ADMET apparatus[15] equipped with a dry ice/isopropyl alcohol condenser and an ethylene collection flask separated by a high-vacuum Rotoflow valve under a vacuum of 10^{-6} mmHg.

4,4,7,7-Tetramethyl-4,7-disiladeca-1,9-diene (II) was prepared by the slow addition of allylmagnesium chloride (1 M in diethyl ether) (2.1 equiv) over 30 min to a THF solution (1.1 M after addition) of 1,1,4,4-tetramethyl-1,4-dichlorodisilaethylene (Petrarch; 1 equiv) followed by strong reflux for 14 h. The reaction was quenched with aqueous $NaHCO_3$ (5 g/L), extracted with diethyl ether, dried, and fractionally distilled from CaH_2 at 60 °C (3.5 mmHg) to give the clear liquid product in 82% yield. The monomer was stirred on a potassium mirror, vacuum transferred to a break-seal ampule, and sealed. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ −0.19 (s, 12 H), 0.20 (d, 4 H), 1.34 (d, 4 H), 4.64 (m, 4 H), 5.56 (sept, 2 H, J = 7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.29, 6.72, 22.73, 112.58, 135.15. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 3.05. Anal. Calcd for $C_{12}H_{26}Si_2$ (found): C, 63.61 (63.36); H, 11.59 (11.63).

1,4-Bis(allyldimethylsilyl)benzene (III) was prepared by the in situ Grignard reaction of 1,4-dibromobenzene (1.0 equiv) with magnesium powder (2.2 equiv) and allylchlorodimethylsilane (2.0 equiv) in refluxing THF. 1,4-Dibromobenzene was stirred at room temperature in THF with Mg powder (1.1 equiv) and catalytic iodine with periodic heating with a heat gun for 5 h. The solution was then added via cannula to allylchlorodimethylsilane (0.7 M in THF) (2.0 equiv) and allowed to stir at room temperature for 18 h, after which another addition of Mg powder (1.1 equiv) (0.3 M in THF) was added and the mixture was allowed to reflux for 51 h. The reaction was quenched with aqueous $NaHCO_3$ (5 g/L), extracted with diethyl ether, dried, and distilled at 90–100 °C (10^{-6} mmHg) to give the clear liquid product in 37% yield. The monomer was stirred over a sodium mirror, vacuum transferred to a break-seal ampule, and sealed. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ 0.18 (s, 12 H), 1.61 (d, 4 H), 4.86 (m, 4 H), 5.80 (sept, 2 H, J = 7 Hz), 7.54 (s, 4 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ −3.54, 23.58, 113.43, 132.84, 132.88, 139.99. ^{29}Si NMR (40 MHz, $CDCl_3$): δ −4.77. Anal. Calcd for $C_{16}H_{26}Si_2$ (found): C, 69.98 (69.98); H, 9.56 (9.58).

Poly(1,1-dimethyl-1-silapent-3-ene) (VI). To a flame-dried custom ADMET apparatus equipped with stir bar and under a vacuum of 10^{-6} mmHg was added via break-seal techniques 20 mg (1 equiv) of the catalyst (neopentyl) and 5 mL (1000 equiv) of diallyldimethylsilane at room temperature. The solution was slowly heated to 45 °C at which time began a rapid evolution of ethylene. Ethylene was collected and an increase in viscosity was noted within 30 min. When viscosity increased to a point as to hinder stirring, the temperature was increased to 50 °C and stirring continued for 74 h under full vacuum. During this time, solid white volatiles were collected and upon analysis were shown to be the cyclic dimer (X). After exposure to atmosphere, the reaction contents were dissolved in CCl_4 and washed with methanol to give 85% yield of an opaque viscous polymer. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ −0.04 (s, 6 H), 1.41 (d, 4 H), 5.20 (trans, t, br), 5.28 (cis, t, br, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ −3.41 (cis), −3.86 (trans), 16.26 (cis allylic), 20.99 (trans allylic), 123.03 (cis), 124.31 (trans). ^{29}Si NMR (40 MHz, $CDCl_3$): δ 0.756 (trans), 1.512 (cis). IR: ν 1637 (s, C=C), 1630 (w, allyl Si), 1260 (st, br, SiMe), 1150 cm^{-1}. Anal. Calcd for $C_6H_{12}Si$ (found): C, 64.18 (64.26); H, 10.80 (10.81).

Poly(1,1,4,4-tetramethyl-1,4-disilaoct-6-ene) (VII) was prepared by a procedure similar to that described for VI above in 79% yield after purification. The monomer was treated with catalyst (neophyl) as purification and vacuum transferred to a break-seal ampule. Upon second contact with catalyst (neophyl), the mixture immediately began to froth rapidly with the evolution of ethylene. Viscosity quickly increased, and heating was required for consistent stirring. After 21 h, trace liquid volatiles were collected and upon analysis were shown to be the cyclic monomer (XI). Stirring was continued for 72 h at 50 °C under full vacuum. The polymer was dissolved in CCl_4 and precipitated in methanol. Due to its viscous oily nature, centrifugation was necessary to isolate the polymer. The clear viscous polymer was dried under high vacuum. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ −0.06 (trans), −0.04 (cis, s, 12 H), 0.39 (d, 4 H), 1.41 (d, 4 H), 5.03 (trans), 5.42 (cis, t, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ −4.10 (trans), −3.88 (cis), 7.04, 16.07 (cis allylic), 20.87 (trans allylic), 123.17 (cis), 124.39 (trans). ^{29}Si NMR (40 MHz, $CDCl_3$): δ 3.181 (trans), 3.966 (cis). IR: ν 1637 (s, C=C), 1260 (st, br, SiMe), 1150 cm^{-1}. Anal. Calcd for $C_{10}H_{22}Si_2$ (found): C, 60.50 (60.31); H, 11.19 (11.18).

Poly[1-(dimethylsilyl)-4-(1,1-dimethylsilapent-3-en-1-yl)phenylene] (VIII) was prepared similarly as above except the catalyst (neophyl) (1 equiv) was washed down the inside of the ADMET flask with toluene, which was then removed in vacuo. Monomer III (500 equiv) was added via break-seal techniques and, upon contact with catalyst, vigorous release of ethylene occurred. An increase in viscosity was noted after 30 min. The polymer was allowed to stir at 50 °C for 23 h until no further ethylene was produced and then was exposed to the atmosphere. The opaque, viscous polymer was dissolved, washed, and isolated as before in 74% yield. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ 0.25 (m, 12 H), 1.65 (m, 4 H), 4.69

(m, terminal CH=), 5.33 (m, 2 H), 5.57 (sept, terminal =CH_2), 7.50 (m, 4 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ −3.25, 16.85 (cis allylic), 21.75 (trans allylic), 23.41 (terminal allylic), 113.23 (terminal =CH_2), 123.37 (cis), 124.58 (trans), 132.86, 132.90, 139.85 (terminal CH=). ^{29}Si NMR (40 MHz, $CDCl_3$): δ −2.515, −1.279. IR: ν 1637 (s), 1630 (s, allyl Si), 1420 (s, SiPh), 1250 (st), 1135 (s, st, SiArSi) cm^{-1}. Anal. Calcd for $C_{14}H_{22}Si_2$ (found): C, 68.52 (67.61); H, 9.11 (8.43).

Poly(1,1-dimethyl-1-silapropene)-*co*-octenamer (IX) was prepared by stirring, under the conditions described above, dimethyldivinylsilane (0.05 mol, 2000 equiv) with the catalyst (neophyl) (1 equiv) for 3 h at 40 °C and then at room temperature for 111 h. 1,9-Decadiene (0.05 mol, 2000 equiv) was then added, and viscosity increased within 30 min. The mixture was stirred at 50 °C for 5 days. The white powderous copolymer was washed and precipitated from methanol in 77% yield. It had the following spectral properties. ^1H NMR (200 MHz, $CDCl_3$): δ 0.04–0.28 (five SiMe signals, sh), 1.30 (s, br), 1.98 (s, br), 5.38 (m, br). Integration gives a 1:21:10:5 respective ratio (approximately 6 mol % dimethyldivinylsilane silane repeat unit). ^{13}C NMR (50 MHz, $CDCl_3$): δ −2.83, −2.35, −1.44, −0.979, 0.354 (SiMe), 27.19 (cis internal octenamer allylic), 29.06, 29.64, 32.60 (trans internal octenamer allylic), 33.70 (terminal octenamer allylic), 36.75 (vinylsilane allylic), 114.12 (terminal octenamer =CH_2), 126.42, 127.35, 128.10, 128.29, 128.66 (terminal divinylsilane CH=), 129.81 (cis internal octenamer), 130.29 (trans internal octenamer), 131.27 (cis terminal vinylsilane =CH_2), 131.62 (trans terminal vinylsilane =CH_2), 139.20 (terminal octenamer CH=), 147.77, 148.19, 148.75, 149.42, 149.82, 150.41 (internal vinylsilane). Quantitative ^{13}C NMR integration also gave approximately 6 mol % dimethyldivinylsilane silane repeat unit. IR: ν 1600 (s, sh), 1640 (m), 1490 (s), 1260 (s, sh, SiMe) cm^{-1}.

Results and Discussion

We have begun to formulate the synthesis rules governing the metathesis of acyclic dienes using Schrock catalyst. Concurrent work in our laboratory[4,16] is revealing some of the subtle requirements necessary for successful acyclic diene metathesis polymerization, in addition to delineating the emerging mechanistic challenges therein. We have found, as did Schrock[17] in previous work, that monomers with functional groups such as ethers and esters[18] are very sensitive with respect to their position in the monomer. For example, divinyl and diallyl ethers are completely inert to productive homometathesis; yet when a two-carbon (or greater) spacer is placed between the terminal olefin and the functional group, polymerization occurs readily.[19] Further, we have found that the position of hydrocarbon substituents on the diene backbone also can influence reactivity and that 1,1-disubstituted olefins completely reject polymerization by ADMET chemistry.[16]

These rules for ADMET polymerization were reinforced during our initial polycarbosilane synthetic efforts reported herein. We began this study by attempting, repeatedly, the homopolymerizations of dimethyldivinylsilane and diphenyldivinylsilane with no success. The results confirm the research of Schrock et al.[7,20] concerning the metathesis of vinyltrimethylsilane, which concluded that vinyltrimethylsilane reacts with $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH\text{-}t\text{-}Bu)$ to form the noncatalytic metathesis products, neohexene, and the trimethylsilylalkylidene. This alkylidene, in the presence of excess vinyltrimethylsilane, gives the isolable bis(trimethylsilyl)tungstacyclobutane adduct in equilibrium with vinyltrimethylsilane. According to Schrock,[20] the productive metathesis product, 1,2-bis(trimethylsilyl)ethylene, is never formed, and we have confirmed this observation with our analogous system. These results directed us to a successful strategy of separating the preventative functional group or a sterically hindering methyl group from the metal center with carbon atom spacers. Upon doing this, we find that the diallylsilane monomers exhibit no resistance to productive metathesis and afford polymers VI–VIII cleanly at low temperatures.

It should be noted that these synthesis rules do not necessarily reflect limitations and need not be disadvantageous. Well-defined differences in monomer reactivity toward acyclic diene metathesis (ADMET) polymerization provide a unique opportunity for polymer structural design.

Monomer Synthesis. The synthesis of monomer II (Figure 2) was accomplished using the successful Grignard chemistry associated with carbosilanes.[21] Although various substituted monoallylsilanes are known, the diallyl monomers II and III had not been reported in the literature until now. The synthesis of III was accomplished by the in situ Grignard reaction of aryl and silyl halides. Magnesium powder was used rather than magnesium turnings to accelerate the reaction, since previous reports indicated both long reaction times (20–50 h) for just monosilylated benzenes and poor yields for disilylated pyridine analogues.[22] Also, tetrahydrofuran was used as solvent rather than the more common, but very toxic, hexamethylphosphorus triamide (HMPT). The extended reaction time in the presence of activated magnesium and the method of addition may have compensated for the decrease in solvent assistance and the lowered reflux temperature from that of HMPT. The product, monomer III, was extremely stable and withstood heating to 90–100 °C on a sodium mirror.

Polymerization. As distinguished from ROMP chemistry, acyclic diene metathesis (ADMET) polymerization is an equilibrium step propagation condensation type polymerization, where the production and removal of ethylene (when using terminal olefins) drive the reaction. As previously described,[1-4] ADMET polymerizations are performed under step (bulk) conditions, under high vacuum, and with a typical monomer to catalyst ratio of 1000:1. The polymer chemistry is very clean, with no side products being evident except pure ethylene and trace amounts of cyclic products when formation of the cyclics is favorable. The molecular weight distributions in ADMET polymerizations typically approach 2, as expected of step polymerizations. The narrower distribution of polymers VII and VIII is due to loss of some low molecular weight fractions during purification (Table I).

In some cases, the factor limiting the degree of polymerization for ADMET chemistry is the thermal stability of the catalyst. Since Schrock's catalyst decomposes in the range 65–75 °C, which is below the melt temperature of many polymers, the solid state intervenes when ADMET polymer begins to grow. This change of state can retard the high conversions required for step-growth polymer chemistry. However, because poly(carbosilanes) VI and VII are viscous oils at low temperature, we have been able to obtain reasonably high molecular weight polymers. Figure 3 displays proton and carbon NMR spectra for polymer VII. Other results from the polymerizations are compiled in Table I.

Polymer VI differs from the mostly cis polymer reported by Weber[12a] since it contains an unprecedented high average trans content (81%), as measured by ^1H and ^{13}C NMR. This observation is typical of ADMET chemistry and seems to be retained here, except when π-bonding carbons are adjacent to a silicon atom (Table I). The average geometric configuration for the vinylsilane linkages in copolymer IX has not yet been determined. Thermal data for polymer VI (Table I) concur with literature values (T_g = −64 °C, TGA rapid weight loss at 330 °C).[12e]

Table I
Poly(carbosilanes) Prepared via Acyclic Diene Metathesis

polymer	reaction time[a]	M_n[b] GPC	M_n[b] NMR	M_w/M_n[c]	% trans	T_g[d]	TGA[e]
VI	74	12 000		1.94	81	−67	330
VII	92	50 000		1.10	73	−59	440,[h] 230[i]
VIII	23	1 500	1300	1.34	47	−46	
IX	5 days	7 800	6400	2.10	75[f]	[g]	

[a] In hours. [b] GPC M_n relative to polystyrene. NMR M_n measured by quantitative ^{13}C NMR end-group analysis (integration of terminal olefins). [c] After precipitation in methanol. [d] In degrees Celsius. [e] Temeprature (°C) at which 10% weight loss occurs. [f] Octenamer units. [g] T_m = 43 °C, T_{recr} = 30 °C (Figure 12). [h] In nitrogen. [i] In air.

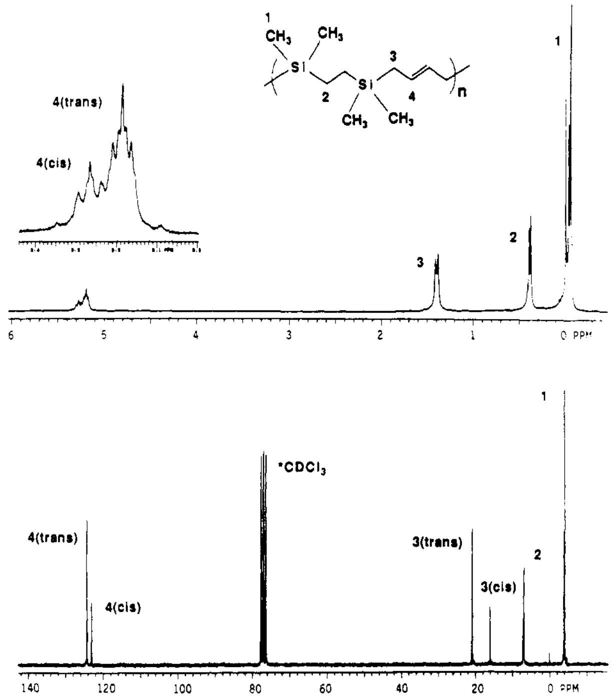
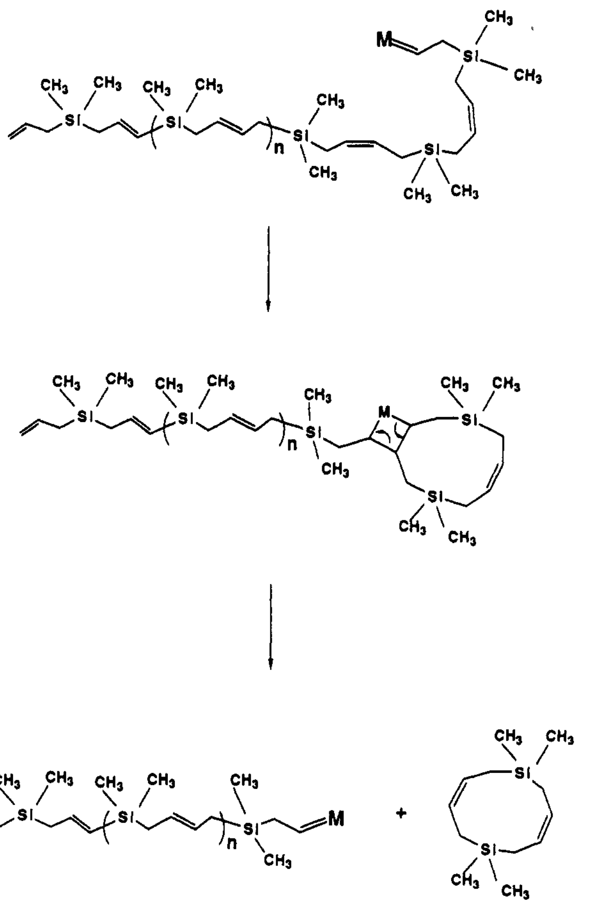


Figure 3. 200-MHz ^1H and 50-MHz ^{13}C NMR spectra of 81% trans polymer VII.

The polymerization of diallyldimethylsilane to polymer VI produces trace (<0.01 mol %) amounts of the cyclic dimer, 1,1,6,6-tetramethyl-1,6-disilacyclodeca-3,8-diene (X). We believe that the formation of the 10-membered ring is due to a kinetically slow back-biting reaction (Figure 4) since no dimer is collected until near the end of polymerization when intrachain metathesis is undoubtedly occurring. Further, a favorable cyclic dimerization early in the reaction would have precluded polymer formation. It is interesting to note that the ^{13}C NMR spectrum is nearly identical to that of the all-cis polymer reported by Weber.[12a]

Polymer VII, in Figure 3, was produced in the highest molecular weight for the polymerizations examined (M_n = 50 000, GPC relative to polystyrene; Table I). The extended reaction time and maintained catalyst activity are presumably responsible for the higher molecular weight of polymer VII versus that of VI, VIII, and copolymer IX (Table I). The polymerization of monomer II to form polymer VII also results in the formation (<0.1 mol %) of a cyclic byproduct. In this case, polymer VII can form the liquid eight-membered cyclic compound, 1,1,4,4-tetramethyl-1,4-disilacyclooct-6-ene (XI) (Figure 5). As was the case for the reaction of diallyldimethylsilane (I), condensation of the cyclic compound XI was not observed until the end of the reaction, after the viscosity of the mixture seemed to reach a maximum; therefore, we believe polymer is forming the cyclic product, and initial cyclization of monomer is not favorable.



X

Figure 4. Proposed mechanism for formation of cyclic dimer X from polymer VI. M = $W(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$.

Polymers VIII and IX, unlike polymers VI and VII, are low enough in molecular weight to display visible end groups in the NMR spectrum, and thus they permit number-average molecular weight determination by end-group analysis (Table I). The fact that ADMET polymers possess vinyl end groups has been a convenient asset in the determination of the molecular weights for these polymers. We show good correlation (below M_n = 20 000) in number-average molecular weights, as determined by gel permeation chromatography, end-group analysis, and vapor pressure osmometry.[3] This is unequivocal data for the presence of vinyl end groups in ADMET polymers.

The low molecular weight of polymer VIII (Table I) most likely is due to decomposition of the catalyst by some impurity. Figure 6 compares the ^1H NMR spectra of the olefinic regions of monomer III with that of polymer VIII, illustrating the formation of internal unsaturation and the decreased intensities for the vinyl end-group signals. The low volatility of monomer III used to make polymer VIII is ideal for the ADMET technique in that it allows for the use of continuous high vacuum at these polym-

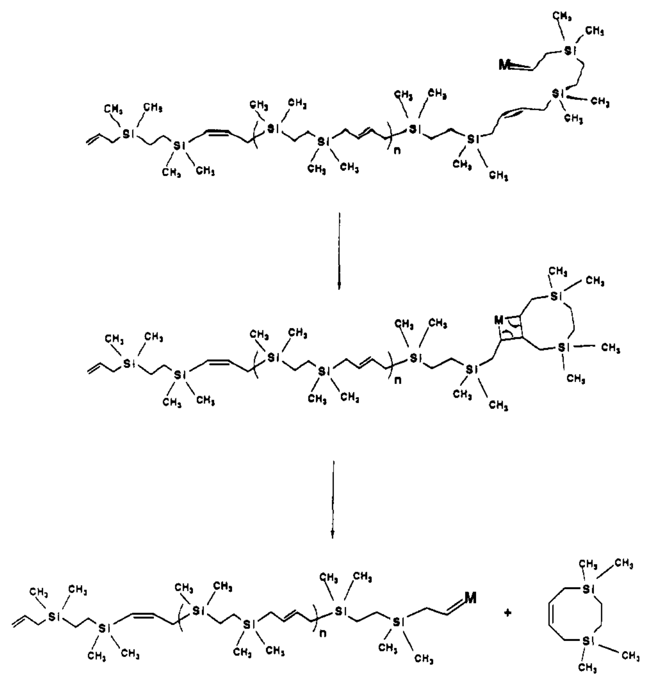


Figure 5. Proposed mechanism for formation of cyclic compound XI from polymer VII. $M = W(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$.

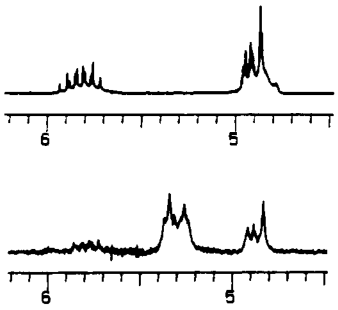


Figure 6. 200-MHz ^1H NMR spectra of the olefinic region for (a) monomer III and (b) polymer VIII.

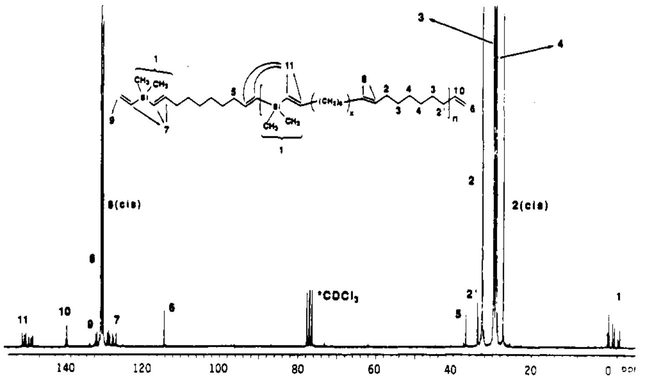


Figure 7. Quantitative 50-MHz ^{13}C NMR spectra of copolymer IX.

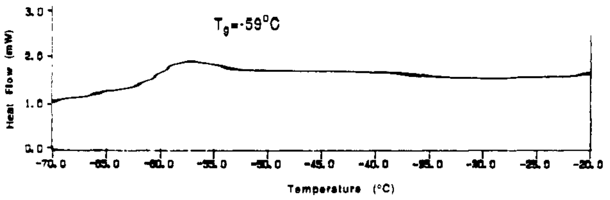


Figure 8. Differential scanning calorimetry of polymer VII: scan rate 10 °C min^{-1}.

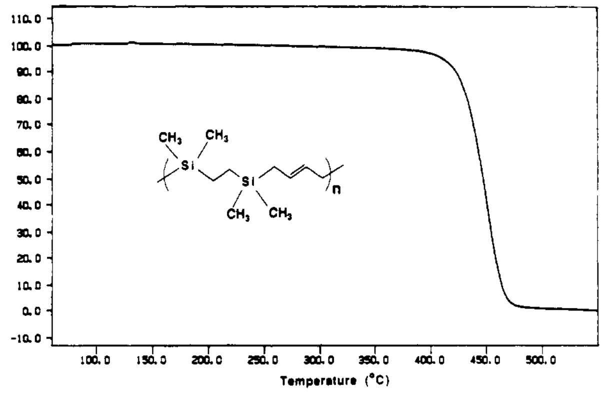


Figure 9. Thermogravimetric analysis of polymer VII in nitrogen: scan rate 10 °C min^{-1}.

erization temperatures.

It is clear that dimethyldivinylsilane is completely inert to productive homopolymerization by metathesis, and so it came as a complete surprise when copolymers containing this monomer could be made by ADMET techniques. While dimethyldivinylsilane does copolymerize with 1,9-decadiene, albeit to a low percent of the polymer and with obviously less reactivity than 1,9-decadiene, there is no evidence of consecutive vinylsilane linkages. The vinylsilane repeat units are isolated. Figure 7 shows the ^{13}C NMR of copolymer IX. The terminal vinylsilane signals were determined by the ^{13}C NMR attached proton test (APT) technique, which distinguishes between methyl, methylene, and methine carbons. The fact that dimethyldivinylsilane copolymerizes with a linear alkyl monomer may suggest that nonproductive cleavage of the bis(trimethylsilyl)tungstacyclobutane arises from steric factors rather than orbital overlap stabilization or other electronic considerations dominant in $W{=}CHSi(CH_3)_3$.

Copolymer IX was prepared by adding 1,9-decadiene (V) to a mixture of Schrock's catalyst and dimethyldivinylsilane (IV) under polymerization conditions. Our intentions of forming a copolymer were based on the assumption that an equilibrium had been established, as Schrock had found with vinyltrimethylsilane,[20] between dimethyldivinylsilane and the vinylsilylalkylidene, $W{=}CHSi(CH_3)_3$. If this were the case, then the productive metathesis reaction containing dimethyldivinylsilane would have the best chance of occurring, before the homopolymerization of 1,9-decadiene ensued.

The glass transition temperatures, reported in Table I, for polymers VI–VIII were reproducible (to within 2 °C) and independent of heating rate. Figure 8 illustrates a typical glass transition temperature for polymers VI–VIII. Melting transitions were not observed for these high trans content polymers. The previously reported pure cis[12d] analogue to polymer VI apparently gives a melting transition at 25 °C.

The thermal gravimetric analysis data for polymer VII are depicted in Figure 9, where rapid weight loss does not occur until >400 °C under nitrogen. The notable thermal stability of polymer VII is clearly evident in that 0% weight loss was found at 350 °C in nitrogen. Polymer VII decomposes as expected much more rapidly in air, where rapid weight loss begins at 230 °C (see Table I). Also, when the polymer is heated in air, nearly 10% of the material remains at temperatures exceeding 600 °C.

No glass transition temperature above −100 °C was observed for copolymer IX. Introducing a vinylsilane unit into the backbone of the polymer decreases the melting temperature of the homopolymer, from 52 °C, for 77% trans polyoctenamer,[15] to 43 °C, for copolymer IX (Figure 10). Recrystallization occurs at essentially the same tem-

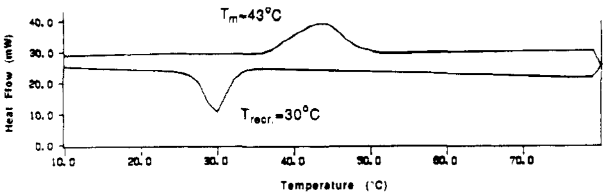


Figure 10. Differential scanning calorimetry of copolymer IX: scan rate 10 °C min^{-1}.

perature as that of the homopolymer, 30 °C vs 32 °C respectively.

Conclusions

Acyclic diene metathesis (ADMET) polymerization offers a new route to poly[carbo(dimethyl)silanes]. The use of highly active, Lewis acid free Schrock tungsten alkylidene catalysts facilitates a clean polymerization path, affording new poly[carbo(dimethyl)silanes] with known vinyl end groups. In some cases, trace amounts of small cyclic oligomers are isolated when back-biting reactions are favorable. The fact that dimethyldivinylsilane copolymerizes with 1,9-decadiene supports a steric argument for why the monomer does not homopolymerize by metathesis.

ADMET polymerization is providing access to a wide variety of polymers and copolymers from a variety of functionalized monomers, now including diallyl-containing silanes. Further, the inertness of particular chemical structures such as the vinylsilanes to homometathesis can be used to regulate polymer structure and properties. Questions pertaining to the mechanism and rules governing silane ADMET polymerizations are being pursued.

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Registry No. I (homopolymer), 88004-42-6; II, 55392-17-1; II (homopolymer), 136115-95-2; III, 136115-96-3; III (homopolymer), 136115-97-4; (IV)(V) (copolymer), 136115-98-5; X, 136115-99-6; XI, 136116-00-2; $ClSiMe_2(CH_2)_2SiMe_2Cl$, 13528-93-3; $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_3$, 101249-40-5; $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CHC(CH_3)_2Ph$, 136070-71-8; allylmagnesium chloride, 2622-05-1; 1,4-dibromobenzene, 106-37-6; allylchlorodimethylsilane, 4028-23-3.