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Acyclic Diene Metathesis (ADMET) Polymerization. Design and Synthesis of Unsaturated Poly(carbosiloxane)s

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ABSTRACT: The synthesis of unsaturated poly(carbosiloxane)s, a new class of siloxane polymers possessing a perfectly alternating siloxane and alkenylene main chain, is presented. 1,5-Bis(allyl)-1,1,3,3,5,5-hexamethyltrisiloxane (**4**), 1,3-bis(4-pentenyl)tetramethyldisiloxane (**6**), 1,4-bis(3-allyl-1,1,3,3-tetramethyldisiloxanyl)benzene (**8**), and telechelic α,ω-di-4-pentenylpoly(1,1,3,3-tetramethyldisiloxanylpentylene) (**10**) undergo acyclic diene metathesis (ADMET) polymerization catalyzed by $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (**1**). These polymerizations, which are performed under bulk conditions and at low temperatures, continuously release ethylene to give poly(1,1,3,3,5,5-hexamethyltrisiloxanyl-2-butenylene) (**5**), poly(1,1,3,3-tetramethyldisiloxanyl-4-octenylene) (**7**), poly(1,1,3,3-tetramethyldisiloxanyl-*p*-phenylene-1,1,3,3-tetramethyldisiloxanyl-2-butenylene) (**9**), and poly(1,1,3,3-tetramethyldisiloxanylpentylene-*co*-1,1,3,3-tetramethyldisiloxanyl-4-octenylene) (**11**), respectively. Bis(vinyl)tetramethyldisiloxane fails to homopolymerize under ADMET conditions, and bis(allyl)tetramethyldisiloxane (**2**) releases ethylene when catalyzed by **1** in the absence of solvent, to give, exclusively, the ring-closed product, 1,1,3,3-tetramethyldisiloxacyclohept-5-ene (**3**). Extending the methylene units or the siloxane linkage in the monomer results in facile ADMET polycondensation, in essentially quantitative conversions, affording well-defined, low-T_g, linear polymers with known vinylic end groups. The polymerizations are void of competing reactions except when back-biting reactions are favorable. Polymer **5** undergoes back-biting to generate the nine-membered cyclic silaoxalkene **13**, when active polymer is diluted or, to a lesser extent, when in the bulk. All monomers and polymers were characterized by infrared spectroscopy and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. Number average molecular weights were determined by gel permeation chromatography and quantitative ^{13}C NMR end group analysis when possible. Synthesis, characterization, thermal analysis, and the current scope of this polymerization are discussed.

Introduction

Acyclic diene metathesis (ADMET) polymerization represents a unique equilibrium condensation route to a variety of well-defined polyalkenylenes with known olefin end groups.[1-4] ADMET step polymerization is a reversible[5] diene condensation where the removal of a small molecule drives the equilibrium to a high molecular weight polymer (Figure 1), and is distinguished from the well-known and commercially practical ring-opening metathesis polymerization (ROMP),[6] which propagates by chain growth.

ADMET polymerizations are possible *only* if vinyl addition reactions are eliminated.[1a,b] This singularity of reaction type is accomplished when Lewis acid-free metathesis catalysts such as $[(CF_3)_2CH_3CO]_2(NAr)M{=}CHC(CH_3)_2Ph$ (Figure 1) are employed, where M = Mo[7] (**1**) or W[8] and Ar = 2,6-C_6H_3-*i*-Pr_2. These highly active Schrock alkylidenes have contributed great success to the chain growth, and in some cases living,[6b,g,7b] polymerization of various strained cyclic olefins.[6b-g] The molydenum alkylidene **1** has been shown to be more tolerant to polar functionality[3,6b,f,g,7b] than the tungsten analog. Recently, catalyst **1** has been used to synthesize cyclic ethers,[9a] amines,[9b] and lactams[9b] from dienes and has also demonstrated the ability to initiate the living cyclopolymerization of dipropargyl esters.[7d] ADMET polymerization offers a complementary use for these catalysts; and we have shown that when particular synthetic "rules" are obeyed, this chemistry is also compatible with many functionalities of importance to polymer chemistry.[2-4] A variety of main-chain functionalized unsaturated polymers are currently accessible from the metathesis condensation of acyclic dienes, including, most recently, ether-,[2] carbonyl-,[3] and organosilane-containing[4] polymers. This paper describes an expansion of the successful functionalities tolerated during ADMET polymerizations using $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (**1**) by now including the important siloxane functionality.

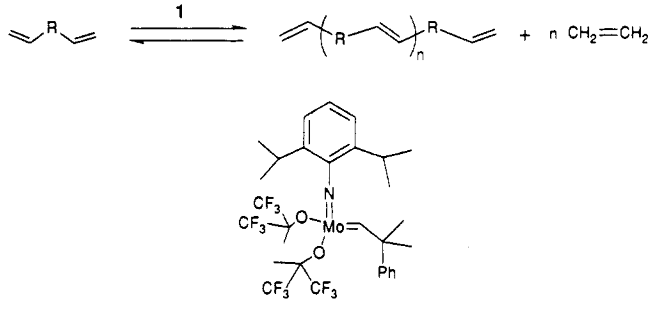

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Figure 1. Acyclic diene metathesis (ADMET) polymerization.

Considerable emphasis has been devoted to the synthesis of organofunctional siloxane polymers due to their unique combination of properties including low-temperature flexibility, hydrophobicity, thermal stability, and gas permeability.[10] These features have initiated much interest in the design of new hybrid systems where siloxane incorporation into the polymer main chain is used to tailor specific properties.[11,12] Block copolymers of poly(dimethylsiloxane) and a variety of polyolefins, polycarbonates, and poly(oxyalkylene)s, which, for example, find application as polymer blend compatibilizers, have been prepared.[12]

Polymers possessing regularly alternating carbon and siloxane linkages within the main chain are of particular interest, since the introduction of organic segments generally increases thermal stability and may improve mechanical properties of subsequent elastomers, without sacrificing advantageous siloxane properties.[13f,h] The synthesis of these poly(carbosiloxane) systems currently is confined to the poly(silarylene–siloxane)s,[13] typically

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prepared by the condensation of dichlorosilanes and bis(hydroxysilyl)benzenes, and to a limited number of saturated poly(carbosiloxane)s prepared by the ring-opening polymerization of cyclocarbosiloxanes.[14]

Here we report the monomer structural requirements for the successful ADMET polymerization of methyl-substituted carbosiloxadienes. Monomers which fail to polymerize (Figure 2) and those which undergo successful ADMET polycondensation (Figure 3) are presented and rationalized on the basis of our current understanding of this chemistry. To our knowledge, main-chain unsaturated poly(carbosiloxane)s were not known previously.

Experimental Section

General Information. ^{1}H 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* or benzene-d_6 was used as solvent, and all chemical shifts reported are internally referenced to tetramethylsilane. Heteronuclear gated and decoupled quantitative ^{13}C NMR spectra were run for 10–14 h with a pulse delay of 10–20 s. Number average molecular weights (M_n) were calculated from integration of the terminal vs internal olefin carbon signals when possible. 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. High-resolution mass spectroscopy (HRMS) data were obtained with a Finnigan 4500 gas chromatograph/mass spectrometer (EI or CI as indicated).

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

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 polybutadiene standards of known polydispersity: 110 000, 24 000, 2760, 982, and 439 whose M_w/M_n are at most 1.07.

Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) data were obtained from a Dupont 2000 thermal analysis system. DSC samples were analyzed with liquid nitrogen as coolant at a nitrogen flow rate of 25 mL/min. The pure polymer samples were annealed at 200 °C, quenched to −150 °C, and then cycled from −150 to 150 °C at successive decreasing scan rates ranging from 10 to 1 °C/min. TGA was performed under nitrogen and air with a flow rate of 50 mL/min with program heating from 50 to 700 °C at a rate of 10 °C/min.

The Lewis acid-free catalyst used in the polymerizations, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (**1**), was prepared by published methods.[7a] Catalyst **1**, like the tungsten analog, is extremely air and moisture sensitive and was handled under an inert and dry, or high-vacuum, atmosphere.

Volatile monomers were fractionally distilled from CaH_2 and degassed under high vacuum by several freeze–pump–thaw cycles. The monomers were than vacuum transferred to a potassium mirror (successively until no reaction was observed) and then directly into the reaction vessel or a storage flask. Bis(vinyl)tetramethyldisiloxane, allylchlorodimethylsilane, alkylmagnesium bromide, and 1,4-pentadiene were obtained from Aldrich. All dichloro-2*n*-methyl-*n*-siloxanes and 1,4-bis(dimethylhydroxysilyl)benzene were purchased from Petrarch Systems Inc. and used as received. Tetramethyldisiloxane and bis(divinyltetramethyldisiloxane)platinum(0) (Karstedt catalyst)[25] were obtained from Rhone-Poulenc Centre de Recherches St. Fons, France. All reaction solvents were dried by refluxing over sodium/potassium ketyl and distilled under inert gas.

1,3-Bis(allyl)-1,1,3,3-tetramethyldisiloxane (2). To a solution of allylmagnesium bromide (200 mL, 0.2 mol, 2.1 equiv), in diethyl ether (1.0 M), under argon at −78 °C was added a solution of 1,3-dichloro-1,1,3,3-tetramethyldisiloxane (18.47 g, 0.091 mol, 1 equiv) in diethyl ether (3.6 M), dropwise over a period of 1 h. An additional 10 mL of dry diethyl ether was added, and the mixture (0.39 M in chlorosilane after addition) was allowed to warm to room temperature, stir for 3.5 h, and then reflux for 10 h. The mixture was quenched with 100 mL of $NaHCO_3$ (saturated), extracted with diethyl ether, and dried over anhydrous Na_2SO_4, and the solvent was evaporated giving 15.9 g of the clear liquid **2** in 82% yield. Diene **2** was purified by distilling from CaH_2 (bp = 37–40 °C, 1.0 mmHg), degassing by several freeze–pump–thaw cycles, and stirring on a potassium mirror. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.08 (s, 12 H), 1.54 (d, 4 H, J = 8 Hz), 4.82 (m, 4 H), 5.79 (m, 2 H, J = 8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.11, 26.41, 113.31, 134.36. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 5.61. IR: ν 3090 (m, vinyl), 1635 (m, allyl Si), 1260 (s, sh, SiMe), 1065 (s, br, SiOSi) 825 cm^{-1}. Anal. Calcd for $C_{10}H_{22}OSi_2$ (found): C, 55.99 (55.98); H, 10.36 (10.39).

1,1,3,3-Tetramethyldisilaoxacyclohept-5-ene (3). To an evacuated flask containing **1** (20 mg, 2.6 × 10^{-5} mol, 1 equiv) was added, in vacuo, pure **2** (3.5 g, 0.02 mol, 600 equiv) at liquid N_2 temperature. The mixture was allowed to warm at room temperature, and upon homogeneity (ca. −20 °C) evolution of ethylene began and persisted, increasing in rapidity with temperature, for 40 min. The mixture was allowed to stir for an additional 2 h and then vacuum transferred, yielding the clear liquid (bp 60–61 °C (18 mmHg)), **3**, in 99% conversion. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.09 (s, 12 H), 1.53 (m, 4 H, $A_2XX'A'_2$), 5.62 (m, 2 H, $A_2XX'A'_2$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.14, 19.70, 124.13. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 8.62. IR: ν 3040 (m, cis), 1630 (allyl Si), 1260 (s, sh, SiMe), 1035 (s, br, cyclic SiOSi), 850, 810 cm^{-1}. HRMS (EI): *m/z* 186.0911; calcd for $C_8H_{18}OSi_2$, *m/z* 186.0896. Anal. Calcd for $C_8H_{18}OSi_2$ (found): C, 51.54 (51.44); H, 9.75 (9.77).

1,5-Bis(allyl)-1,1,3,3,5,5-hexamethyltrisiloxane (4). To a solution of allylmagnesium bromide (200 mL, 0.2 mol, 2.2 equiv) in diethyl ether (1.0 M) under argon at −5 °C was added a solution of 1,5-dichloro-1,1,3,3,5,5-hexamethyltrisiloxane (20.47 g, 0.09 mol, 1 equiv) in dry THF (3.0 M), dropwise over a period of 1 h. An additional 150 mL of dry THF was added, and the mixture (0.26 M in chlorosilane after addition) was allowed to warm to room temperature, stir for 2 h, and then reflux for 5 h. The mixture was quenched with 100 mL of aqueous $NaHCO_3$ (5 g/L), extracted with diethyl ether, and dried over anhydrous Na_2SO_4, and the solvent was evaporated giving 19.90 g of the oil, **4**, in 77% yield. Monomer **4** was purified by distilling from CaH_2 (bp = 42–43 °C, 5.0 mmHg), degassing by several freeze–pump–thaw cycles, and stirring on a potassium mirror. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.03 (s, 6 H), 0.09 (s, 12 H), 1.57 (d, 4 H, J = 8 Hz), 4.87 (m, 4 H), 5.79 (m, 2 H, J = 8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ −0.26, 1.25, 26.29, 113.34, 134.36. ^{29}Si NMR (40 MHz, $CDCl_3$): δ −20.72, 4.12. IR: ν 3095 (m, vinyl), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 825, 800 cm^{-1}. Anal. Calcd for $C_{12}H_{28}O_2Si_3$ (found): C, 49.93 (50.19); H, 9.80 (9.84).

1,3-Bis(4-pentenyl)-1,1,3,3-tetramethyldisiloxane (6). To a solution of 1,4-pentadiene (10.0 g, 0.147 mol, 2.5 equiv) and bis(divinyltetramethyldisiloxane)platinum(0) (1.488 mg of 10.6% solution in hexane, 10^{-5} equiv) at 10 °C, under N_2, was slowly added hexamethyldisiloxane (7.89 g, 0.059 mol, 1 equiv) over 40 min. An exotherm was produced, and intermittent cooling with an ice bath was required to keep the solution below 35 °C during the addition. The solution was allowed to stir at room temperature for 42 h under N_2 and then fractionally distilled (bp = 68 °C (1 mmHg)) giving the pure β isomer, **6**, in 17% isolated yield. GC indicated that the monomer was produced with 95% β regioselectivity prior to distillation. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.04 (s, 12 H), 0.52 (m, 4 H), 1.41 (m, 4 H), 2.06 (m, 4 H), 4.98 (m, 4 H, $=CH_2$), 5.80 (m, 2 H, $-CH=$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.38, 17.95, 22.83, 37.43, 114.40, 139.00. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 8.61. IR: ν 3090 (m, vinyl), 1643 (m, allyl Si), 1255 (s, sh, SiMe), 1060 (s, br, SiOSi), 845, 800 cm^{-1}. HRMS (CI): *m/z* 271.2091; calcd for $C_{14}H_{31}OSi_2$, *m/z* 271.1914.

1,4-Bis(3-allyl-1,1,3,3-tetramethyldisiloxanyl)benzene (8). To a solution of 1,4-bis(dimethylhydroxysilyl)benzene (9.45 g, 0.042 mol, 1 equiv) in 100 mL of dry THF (0.42 M) at 0 °C was added a solution of allylchlorodimethylsilane (12.36 g, 0.092 mol, 2.2 equiv) in 60 mL of dry THF (1.5 M) over a period of 1 h. The solution was allowed to stir at 0–5 °C for 1 h, 10 mL of pyridine was added whereupon a white solid formed, and the mixture was allowed to warm to room temperature. An additional 100 mL of THF was added and stirring continued for 12 h before refluxing for 7 h, cooling to room temperature, and filtering over neutral alumina. The residue was washed repeatedly with hexane, and the combined washings were removed from the filtrate in vacuo to give the crude oil in 92% yield. The crude product was dissolved in ether and extracted twice each with saturated Na_2CO_3 solution, brine, and water, then dried over $MgSO_4$, and evaporated to give **8** as a colorless solid in 61% isolated yield. Monomer **8** was purified by recrystallization from ethanol, mp = 55–60 °C. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 12 H), 0.34 (s, 12 H), 1.59 (d, 4 H, J = 7 Hz), 4.89 (m, 4 H), 5.79 (m, 2 H, J = 7 Hz), 7.56 (s, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.07, 0.89, 26.43, 113.47 (vinyl CH_2), 132.22 (vinyl CH), 134.22 (aromatic CH), 140.94 (ipso). ^{29}Si NMR (40 MHz, $CDCl_3$): δ −21.59, 5.61. IR: ν 3080 (m, vinyl), 3060 (m, aromatic), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 835, 800 (s) cm^{-1}. HRMS (CI): m/z 422.1940; calcd for $C_{20}H_{38}O_2Si_4$, m/z 422.1949. Anal. Calcd for $C_{20}H_{38}O_2Si_4$ (found): C, 56.80 (56.98); H, 9.08 (8.65).

1,4:1′,4′-Bis(1,1,3,3-tetramethyldisiloxanediyl)dibenzene (12). The byproduct **12** sublimed directly from the product mixture of **8** upon heating to 50 °C under high vacuum (ca. 10^{-6} mmHg). The crystals were washed with ethanol and vacuum dried to give 4% (wt.) isolated yield, mp = 208 °C (lit. 208 °C).[24] It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.39 (s, 12 H), 7.0 (s, 4 H, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.08, 132.15 (aromatic CH), 138.71 (ipso). HRMS (CI): m/z 416.1485; calcd for $C_{20}H_{32}O_2Si_4$, m/z 416.1480. The structure of **12** was determined by X-ray crystallography.[15]

α,ω-Di-4-pentenylpoly(1,1,3,3-tetramethyldisiloxanylpentylene) (10). The oligomer, **10**, was prepared simultaneously by the method described above for monomer **6** in 63% conversion. Telechelomer **10** was dissolved in hexane, chromatographed over silica gel, and then filtered under Ar through Celite. The solvent was removed in vacuo and dried under high vacuum for 12 h, giving the pure β isomer as a colorless oil. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.04 (s, 12 H), 0.52 (m, 4 H), 1.41 (m, 4 H), 2.06 (m, 4 H), 4.98 (m, 4 H, =CH_2), 5.80 (m, 2 H, –CH=). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.38, 17.95, 22.83, 37.43, 114.40, 139.00. A 200-MHz ^{13}C NMR attached proton test (APT) revealed no methyl or methine signals corresponding to the α isomer. ^{29}Si NMR (40 MHz, $CDCl_3$): δ 6.95, 7.12, 7.29, 8.61 (oligomeric homologs). IR: ν 3090 (m, vinyl), 1643 (m, allyl Si), 1255 (s, sh, SiMe), 1060 (s, br, SiOSi) 845, 800 cm^{-1}. Anal. Calcd (x = 3.4 by quantitative ^{13}C NMR end group analysis) for $C_{44.7}H_{107.0}O_{4.4}Si_{8.8}$ (found): C, 55.79 (55.89); H, 11.13 (11.01).

ADMET Polymerizations. The following general procedure was used to prepare polymers **5**, **7**, and **11** (see spectral data section below for the preparation of polymer **9**). Monomers (ca. 1–3 g, 500–800 equiv) were vacuum transferred or added under a dry, inert atmosphere to a previously evacuated and flame dried, high-vacuum valve equipped flask. The catalyst, $[(CF_3)_2CH_3CO]_2(NAr)Mo{=}CHC(CH_3)_2Ph$ (**1**) (Figure 1), was then added (10 mg, 1 equiv) directly, without solvent, under an inert atmosphere. The homogeneous, tan-colored mixtures were stirred at room temperature, and in most cases an immediate evolution of ethylene occurred accompanied by an increase in viscosity within 20 min. In some instances, the evolution of ethylene ceased and an additional aliquot (10 mg) of **1** was added to reinitiate polymerization. The reactions were then evacuated, and ethylene evolution persisted with stirring in the bulk at room temperature until viscosity reached a point as to hinder stirring. At this time the polymerizations were heated to 50–55 °C, and stirring resumed under full vacuum until magnetic agitation was no longer possible. Polymerizations were terminated by exposure to the atmosphere, and the viscous polymer reaction mixtures were dissolved in chloroform or THF and analyzed by NMR and GPC. Pure polymer samples were obtained by filtering over neutral alumina in methylene chloride, yielding transparent viscous oils. Reaction times range from 24 to 48 h, and conversions were essentially quantitative if negligible monomer was lost during evacuation. The polymers had the following spectral properties.

Poly(1,1,3,3,5,5-hexamethyltrisiloxanyl-2-butenylene) (5). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.40 (s), 0.93 (s), 1.49 (m), 5.24 (m, trans), 5.33 (m, cis). ^{13}C NMR (50 MHz, $CDCl_3$): δ −0.19, 1.24, 19.98 (cis allylic), 24.42 (trans allylic), 122.78 (cis), 124.12 (trans). ^{29}Si NMR (40 MHz, $CDCl_3$): δ −20.95, 4.63, 4.94. IR: ν 3010 (m), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 825, 800 cm^{-1}. Anal. Calcd for $C_{10}H_{24}O_2Si_3$ (found): C, 46.09 (45.91); H, 9.30 (9.32).

Poly(1,1,3,3-tetramethyldisiloxanyl-4-octenylene) (7). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.04 (s, 12 H), 0.50 (m, 4 H), 1.35 (m, 4 H), 1.99 (m, 4 H), 5.37 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.41, 18.02 (Si–CH_2), 18.23 (C–CH_2–C, cis), 23.51 (C–CH_2–C, trans), 30.94 (cis allylic), 36.31 (trans allylic), 129.93 (cis), 130.49 (trans). ^{29}Si NMR (40 MHz, $CDCl_3$): δ 7.17. IR: ν 3010 (m, shoulder), 1650 (w, allyl Si), 1255 (s, sh, SiMe), 1060 (s, br, SiOSi) 845, 800 cm^{-1}. Anal. Calcd for $C_{12}H_{26}OSi_2$ (found): C, 59.42 (58.88); H, 10.83 (10.68).

Poly(1,1,3,3-tetramethyldisiloxanyl-*p*-phenylene-1,1,3,3-tetramethyldisiloxanyl-2-butenylene) (9). Monomer **8** was dissolved in a minimum amount of dry deolefinated toluene under an inert atmosphere, and catalyst **1** was added as described above. The polymerization continued under the general conditions described above with the exception that care was taken not to evacuate the mixture to the point of precipitation. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.10 (s), 0.34 (s), 1.50 (d, internal allylic), 1.59 (d, terminal allylic), 4.89 (m, terminal CH_2), 5.24 (m, trans), 5.34 (m, cis), 5.79 (m, terminal CH), 7.56 (s, aromatic). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.11, 0.37, 0.97, 1.10, 1.58, 19.80 (trans allylic), 24.62 (cis allylic), 26.45 (terminal allylic), 113.52 (terminal CH_2), 122.90 (cis), 124.24 (trans), 132.30 (terminal CH), 134.23 (aromatic CH), 140.87 (ipso). ^{29}Si NMR (40 MHz, $CDCl_3$): δ −21.60, −2.40, −2.20, 1.29, 6.57, 8.61. IR: ν 3060 (s, aromatic), 1634 (m, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi) 830, 790 cm^{-1}. Anal. Calcd (n = 2.5 by ^{1}H NMR) for $C_{65}H_{122}O_7Si_{14}$ (found): C, 55.40 (56.98); H, 8.75 (8.65).

Poly(1,1,3,3-tetramethyldisiloxanylpentylene-*co*-1,1,3,3-tetramethyldisiloxanyl-4-octenylene) (11). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.03 (s, 32 H), 0.50 (m, 11 H), 1.41 (m, 16 H), 2.00 (m, 4 H), 5.37 (m, 2 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.41, 18.01, 18.32, 22.97, 23.49, 31.00 (cis allylic), 36.34 (trans allylic), 37.24, 130.00 (cis), 130.48 (trans). ^{29}Si NMR (40 MHz, $CDCl_3$): δ 7.10, 7.20. IR: ν 1650 (w, allyl Si), 1260 (s, sh, SiMe), 1060 (s, br, SiOSi), 845, 800 cm^{-1}. Anal. Calcd (x = 3.4 and n = 36 by quantitative ^{13}C NMR end group analysis) for $C_{1548}H_{3659}O_{159}Si_{319}$ (found): C, 55.01 (55.25); H, 10.94 (10.81).

Solution Preparation of 1,1,3,3,5,5-Hexamethyltrisilaoxacyclonon-7-ene (13). The active polymer **5** reaction mixture (0.1 g, 570 repeat unit equiv) was diluted with benzene-d_6 (1 mL) in a Rotoflow-equipped NMR tube at room temperature. After 5 min the ^{1}H NMR spectra revealed that 36 mol % of **13** (99% cis) had formed. See bulk preparation of **13** for spectral data (below).

Bulk Preparation of 1,1,3,3,5,5-Hexamethyltrisilaoxacyclonon-7-ene (13). The active polymer **5** reaction mixture was partially stirred and heated to 50 °C under high vacuum (ca. 10^{-6} mmHg), whereupon cyclic **13** slowly distilled, immediately upon cooling an attached condenser to −78 °C. The geometric isomers of **13** were collected at −197 °C to give 7 mol % of **13** (80% cis) isolated in 5 h. It had the following spectral properties. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.01 (s, 6 H), 0.09 (s, 12 H), 1.52 (m, 4 H, $A_2XX'A'_2$), 5.27 (m, 2 H, $A_2XX'A'_2$, trans), 5.41 (m, 2 H, $A_2XX'A'_2$, cis). ^{13}C NMR (50 MHz, $CDCl_3$): δ 0.73 (cis Me), 0.86 (trans Me), 0.95 (cis Me), 1.30 (transMe), 20.04 (cis allylic), 24.07 (trans allylic), 122.50 (cis), 123.60 (trans). ^{29}Si NMR (40 MHz, $CDCl_3$): δ −21.60, 2.24. IR: ν 3020 (m), 1640 (allyl Si), 1260 (s, sh, SiMe), 1050 (s, br, cyclic SiOSi), 840, 800 cm^{-1}. HRMS (EI): m/z 260.1083 (cis), 260.1091 (trans); calcd for $C_{10}H_{24}O_2Si_3$, m/z 260.1084. Anal. Calcd for $C_{10}H_{24}O_2Si_3$ (found): C, 46.09 (46.07); H, 9.30 (9.25).

Results and Discussion

Monomer Structure/Reactivity Relationships. Acyclic diene monomers containing functional groups which

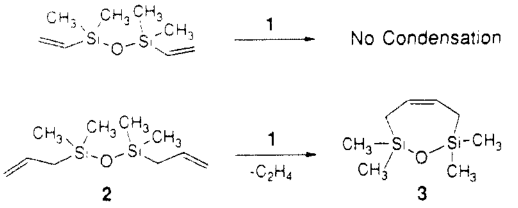

Figure 2. Carbosiloxadienes which fail to homopolymerize via ADMET.

are Lewis bases have shown resistance to metathesis condensation unless the functionality is sufficiently separated from the reactive olefin by methylene spacers.[2,3] This "negative neighboring group effect" is attributed to electronic influences affecting inactive catalysis and is one of two types of monomer structural restraints observed in ADMET chemistry. The second type is steric in nature and is prevalent with dienes containing alkyl substitution at the allylic position. Steric groups provide a barrier to the formation of a productive catalytic intermediate and also must be separated from the reactive olefin if successful ADMET condensation polymerization is to occur.[4]

It is now clear that these structural and functional group monomer restraints need not be a disadvantage since subtle structural changes can produce desired effects on monomer reactivity. For example, we have shown previously that monomers disubstituted at the allylic position, such as divinyldimethylsilane, do not homometathesize when treated with the tungsten analog of catalyst 1 (Figure 1) yet undergo selective cross-metathesis condensation with a nonsubstituted acyclic diene, yielding copolymers containing isolated units of the discriminating monomer.[4] These results, which support previous observations by Schrock and co-workers,[8a] suggest that steric crowding between substituents on the intermediate α,β-disubstituted tungstacyclobutane (required for productive metathesis to occur) causes the homometathesis failure. Similar, yet somewhat undefined, resistance to vinyltrimethylsilane metathesis using classical tungsten-based catalyst systems like $WCl_6(OR)_2/EtAlCl_2$ was reported as early as 1979.[17] Apparently, the silylalkylidene, $[W]=CHSiMe_3$, was initially produced in this classical system yet was completely unreactive to further metathesis. Thus far, the only α-substituted acyclic olefins which we have shown to undergo successful ADMET homopolymerization with Schrock alkylidenes are those in which the substituted allylic atom is sp^2 or contained within a cyclic structure.[18] These observations are valid only for the tungsten-based catalyst, and subtle differences have been revealed recently for the molybdenum catalyst, 1.[7a,19]

The possibility that a less crowded Si–O environment (vs that of $Si-CH_2$) would permit productive homometathesis prompted us to attempt the polymerization of divinyltetramethyldisiloxane (Figure 2). Recent work by Marciniec and co-workers[20] demonstrated that monovinylsilanes containing alkoxy substituents underwent successful metathesis condensation, in less than quantitative conversions, when catalyzed by $RuCl_3(H_2O)_n$ or $RuCl_2(PPh_3)_3$. These results ensured access to functionalized silicon-containing small molecules; and this present study was undertaken to expand the analogy to include ADMET chemistry.

Commercially available divinyltetramethyldisiloxane (Figure 2) was found to be completely resistant to productive metathesis when treated with either the molybdenum catlayst, 1, or the tungsten analog. Pure starting material was recovered, upon repeated attempts, in each case. For the tungsten-catalyzed case, the most likely cause for productive metathesis inhibition is that the α-dimethyl substitution, in divinyldisiloxane, sufficiently prevents productive cleavage of the required α,β-disubstituted metallacycle due to steric restraints. Whereas the reason for metathesis failure using catalyst 1 arises, presumably, from the previously reported[7a] instability of molybdacycles (vs tungstacyclobutanes) formed from the reaction of catalyst 1 with vinylsilanes such as $CH_2=CHSiMe_3$ and not due to electronic interferences attributed to the β-oxygen. In fact, other β-oxo monomers, such as diallyl ethers, have been shown to undergo homometathesis with catalyst 1, which is sound evidence for this presumption.[9,21]

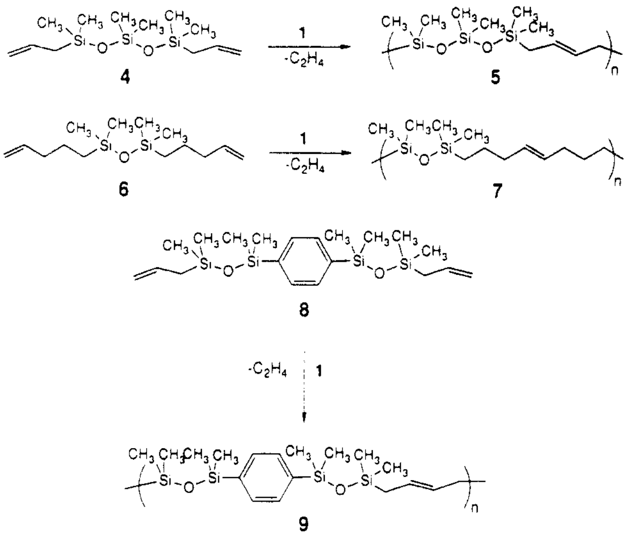

Figure 3. Polymerization of carbosiloxadienes via acyclic diene metathesis (ADMET) condensation.

This result directed us to the successful strategy of separating the preventative functional group or sterically hindering methyl group from the olefin with methylene spacers. In fact, one methylene spacer is sufficient, such that neat bis(allyl)tetramethyldisiloxane (**2**) (Figure 2) metathesizes readily upon catalytic treatment with **1** giving, exclusively, the seven-membered cyclic product, **3**, in essentially quantitative conversion. Evolution of ethylene was observed below 0 °C and was complete within 40 min as the reaction mixture was allowed to warm to room temperature. This rapid and exclusive cyclization, in the absence of solvent, indicates that monomer **2** prefers to adopt the conformation predicted by the *gem*-dimethyl or Thorpe–Ingold effect[22]—placing the olefins in close proximity. Cyclic compound **3** has been prepared previously by Weyenberg et al.,[23] through a different route, and the compound's refractive index and boiling point were reported.

With the above results clear, we focused our efforts on preventing cyclization. This was easily accomplished by either extending the disiloxane linkage of monomer **2** to the trisiloxane (see monomer **4**) or by extending the propenyl appendage within the monomer (see monomer **6**), as shown in Figure 3. We find that monomers **4** and **6** polymerize readily via ADMET condensation, when catalyzed by **1**, and give polymers **5** and **7** cleanly at low temperatures. Furthermore, arylene monomer **8** and α,ω-diene telechelomer **10** polymerize to polymers **9** and **11**, respectively, and demonstrate the generality of this polymerization method as applied to the siloxane functionality.

As previously mentioned, we recently reported the condensation polymerization of various carbosiladienes[4] catalyzed by the tungsten analog of catalyst 1, $[(CF_3)_2$-

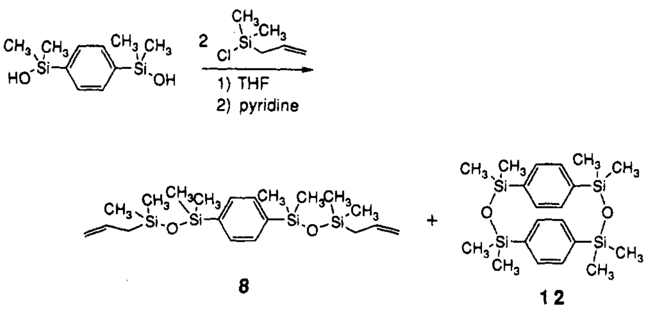

Figure 4. Synthesis of monomer 8 and cyclic byproduct 12.

$CH_3CO]_2(NAr)W{=}CHC(CH_3)_2Ph$.[8] Although this present study initially employed the molybdenum alkylidene (1) (Figure 1) which is used here throughout, the tungsten catalyst was later shown to be tolerant to carbotrisiloxadiene 4 as well. Monomer 4 exhibits no resistance to ADMET polycondensation when catalyzed by the tungsten alkylidene and has been reported elsewhere.[16]

Carbosiloxane Monomer Synthesis. Monomers 2 and 4 were prepared, in good yield, by treatment of the corresponding dichlorosiloxane with allylmagnesium bromide, a reaction which is typical of the well-known Grignard chemistry associated with carbosilanes.[24]

The synthesis of monomer 6 and α,ω-diene telechelomer 10 (Figure 9) was accomplished by the hydrosilation of 1,4-pentadiene with tetramethyldisiloxane catalyzed by tris(divinyltetramethyldisiloxane)diplatinum(0) (Karstedt's catalyst).[25] Hydrosilation polymerization, first reported by Curry,[26a,b] has become a popular route to novel silicon polymers, as well as telechelic polymers,[26c–f] and has stimulated considerable efforts in unique applications for metal catalysis in general.[26] In particular, Karstedt's platinum(0) olefin complex, which has received recent attention concerning its true structure,[25b,c] provided a clean and convenient route to the β-adduct isomer of telechelic diene 10. Both monomers 6 (β isomer separated by distillation) and 10 were easily isolated and required minimal purification. ^{13}C NMR attached proton test (APT) spectroscopy was used to confirm that the pure β-adduct isomer of monomers 6 and 10 had been obtained.

Monomer 8 was prepared by the condensation of allylchlorodimethylsilane with the corresponding bis(hydroxysilyl)benzene (Figure 4). Pyridine was used to avoid the acid-catalyzed silanol polymerization for which this reagent is typically used.[13] No oligomerization was observed; however 4% (wt.) of the crystalline cyclic condensation product, 12, was isolated. Byproduct 12 was formed from an intermolecular siloxane interchange reaction of diene 8, producing bis(allyl)-1,1,3,3-tetramethyldisiloxane which was also isolated from the reaction mixture. This mechanism was confirmed by subsequent experiments where neat 1,4-bis(pentamethyldisiloxanyl)benzene underwent thermal interchange giving 12 and hexamethyldisiloxane. The cyclic byproduct 12 is a monomer for ring-opening polymerization to poly(disiloxanylphenylene) and has been previously sought.[27]

Monomer 8, as well as telechelomer 10, have not been previously reported in the literature.

Carbosiloxane Monomer Polymerization. Acyclic diene metathesis (ADMET) polymerization is an equilibrium step propagation condensation type polymerization, where the production and removal of ethylene (when terminal olefins are used) drives the reaction. As described previously,[1c,d,2–4] ADMET polymerizations are performed under step (bulk) conditions and high vacuum with a typical monomer to catalyst ratio of (500–1000):1. ADMET polymer chemistry is void of side reactions and only pure alkene condensate is produced. Cyclic products are sparingly present in some cases, due to slow back-biting reactions, as typical for some condensation polymerizations.

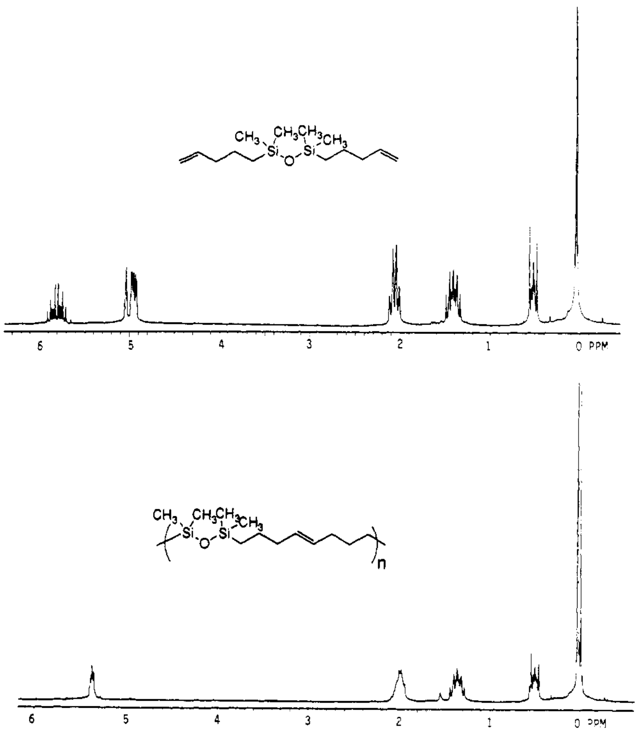

Figure 5. 200-MHz ^1H NMR spectra of monomer 6 (top) and resulting polymer 7.

Figure 5 displays the ^1H NMR spectra for monomer 6 and the reaction mixture of its resulting high molecular weight polymer 7. No terminal olefin signals are visible in the ^1H NMR as well as the quantitative ^{13}C NMR spectra of polymer 7. Residues of decomposed catalyst 1 are the only impurities in polymer 7 and are too low in concentration to be observed in the ^1H and ^{13}C NMR spectra at 200 and 50 MHz, respectively. The multiplet at 5.39 ppm for polymer 7 represents the internal vinylic protons from which the trans and cis isomers are indistinguishable. However, the cis and trans vinylic carbon signals are easily resolved in the ^{13}C NMR spectrum (see Experimental Section).

In some cases, the factor limiting the degree of polymerization for ADMET chemistry is the thermal stability of the catalyst. Although the molybdaneophylidene, 1 ($ArN(RO)_2Mo{=}CHCMe_2Ph$), has been observed in solution at temperatures approaching 85 °C, it is technically a catalytic precursor. Upon initial reaction with a terminal olefin, the highly reactive molybdamethylidene ($ArN(RO)_2Mo{=}CH_2$) is generated and remains the only recyclable catalytic species throughout the polymerization, when vinyl monomers are used.[1c] The methylidene complex is less stable than its precursor, 1, and can decompose at lower temperatures. These temperatures are below the melt temperatures of many polymers, and the solid-state intervenes as the polymer begins to grow. This retards the high conversions required for step-growth polymer chemistry. However, as in the case for the unsaturated poly(carbosilane)s,[4] polymers 5, 7, and 11 remain viscous oils at room temperature, thereby allowing for reasonably high molecular weight polymers to form at low temperature. Table I contains some of the physical data for the unsaturated poly(carbosiloxane)s.

Number average molecular weights were determined directly, when possible, by quantitative ^{13}C NMR end

Table I
Poly(carbosiloxane)s Prepared via Acyclic Diene Metathesis

polymer	M_n GPC[a]	M_n NMR	M_w/M_n[d]	% trans[b]	DSC T_g[e]	TGA[f] N_2 (air)
5	15 000		1.7	65	−97	398 (284)
7	32 000		1.7	79	−93	427 (282)
9	1 400	1 400[b]	1.2	40		
11	38 200	29 000[c]	1.7	75	−90	435 (287)

[a] GPC M_n relative to polybutadiene. [b] Measured by quantitative ^{13}C NMR end group analysis. [c] Measured by ^{1}H NMR end group analysis. [d] Reaction mixture. [e] Temperature (°C) upon heating at 5 °C/min. [f] Temperature (°C) at which 10% weight loss occurs.

group analysis. This technique has been a reliable asset to ADMET polymer characterization since polymers produced by this chemistry possess monomodal molecular weight distributions of linear chains terminated with known olefin end groups. Quantitative ^{13}C NMR was also essential for accurate determination of the geometric isomer ratio for these unsaturated polymers. In most cases, the cis and trans proton signals were unresolved in the ^{1}H NMR spectra. Relative number average molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) using polybutadiene standards. These standards, when applied to the polymers presented here (Table I), gave a much better correlation with the exact M_n determined by quantitative ^{13}C NMR than did the more common polystyrene calibration standards.

For polymers **5** and **7**, the molecular weights were high enough so that the concentration of terminal carbons fell below the limit of detection for NMR end group analysis. Although the highest molecular weight was obtained from the polymerization of telechelomer **10** to polymer **11**, the degree of polymerization, as calculated by end group analysis, reached only 36 before the viscosity of the reaction mixture prevented magnetic agitation, at which time the reaction was terminated. However, the degrees of polymerization achieved in polymers **5** and **7** are estimated to be much greater (ca. 100). The molecular weight distributions for ADMET polymerizations typically approach 2, as predicted for step polymerizations, and high average trans content polymers are normally produced due to trans metathesis, or interchange, reactions which occur throughout the polymerization.

Polymer **9** possesses the lowest number average molecular weight for the series and, likewise, the lowest average trans content (Table I). The low molecular weight of **9** is most likely due to poisoning of the catalyst by some impurity which eluded repeated purification attempts. Ethylene evolution was observed upon treatment of monomer **8** with catalyst **1** yet stopped after several minutes, and attempts to reinitiate with subsequent additions of **1** failed. The fact that monomer **8** is a solid within the temperature range of polymerization, and thus required solution techniques, may also have been a factor which limited the molecular weight.

Formation of Cyclics Due to Back-Biting Reactions. Cyclizations which occur during ADMET polymerizations are the result of slow back-biting reactions when a cyclic product is favored. Cyclic byproducts have been observed in the case of poly(carbosilane)s,[4] albeit in trace quantities, and were only detected at the very end of the polymerizations. These results were confirmed concurrently by other researchers using catalyst 1.[28] Under these conditions, the molar concentration of condensable terminal olefin becomes negligible and the evolution of ethylene is no longer observed, suggesting a "resting state" equilibrium has been reached after condensation has ended.

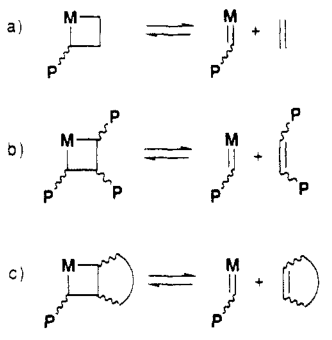

Figure 6. Postcondensation resting state equilibria for an unsaturated polymer, P, containing catalyst, M = Mo(N-2,6-C_6H_3-i-Pr_2)[$OCMe(CF_3)_2$]$_2$.

The favored postcondensation resting intermediate of the catalyst is not known for the polymerization of these siloxane monomers. Postcondensation resting state equilibria composed of various substituted molybdacycle and alkylidene species are perhaps stabilized through coordination of a nearby siloxane oxygen, as has previously been shown for catalyst **1** in the presence of more basic carbonyl-[3a,7e] and amine-containing[9b] olefins. Despite the true identity of the favored postcondensation intermediate, under these conditions a finite quantity of metal alkylidene must be formed on the chain ends if back-biting is to occur (Figure 6).

Figure 6 illustrates three possible equilibria which are present at the resting state, after ADMET condensation has ceased. Equilibrium a represents the reaction of a terminal alkylidene with any remaining ethylene, while equilibria b and c represent degenerate and cyclic-forming reactions, respectively. If the terminal alkylidene should choose to add to the nearest internal olefin within the chain on which it is attached (which should be kinetically favored vs more distant double bonds), then a trisubstituted intermediate metallacycle would form and, upon nondegenerate cleavage, produce a cyclic containing a single repeat unit (Figure 6c). Therefore, back-biting begins (when possible) after the more favored condensation chemistry ends and the resting state is reached. This implies that the cyclic products formed from the poly(carbosilane)s discussed earlier could have been generated in greater quantities, time permitting, since that system had achieved its resting state.

Similarly, the trisiloxane polymer **5** also undergoes back-biting to give the nine-membered cyclic product, **13** (Figure 7). Unlike those poly(carbosilane)s which back-bite, cyclic **13** was not first observed during the bulk homopolymerization of monomer **4** but was discovered during a solution copolymerization of oligomers of **5** with another diene monomer which we have communicated elsewhere.[16] Before this observation, only oligomers of **5** had been obtained due to synthetic difficulties, and cyclic **13** was not detected during the bulk oligomerization of **4**. These observations are consistent with the above poly(carbosilane) results, in that cyclics observed from ADMET polymers result from back-biting reactions and are not present when condensation is a catalytic option.

Once high molecular weight polymer **5** was obtained and its postcondensation resting state established, we found that the reaction mixture did contain 7 mol % of the cyclic carbosiloxane **13**. Further, this nine-membered cyclic could be generated and removed under high vacuum if the final reaction mixture (after the condensation of ethylene was no longer observed) of polymer **5** was

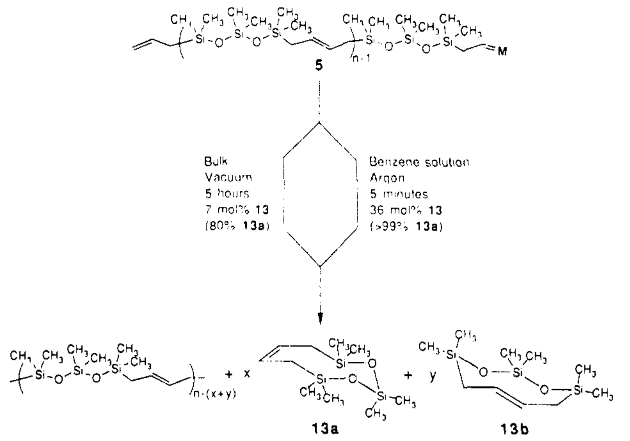

Figure 7. Preparation of cis and trans cyclic compound 13 via back-biting reactions from polymer 5, where M = Mo(N-2,6-C_6H_3-i-Pr_2)[$OCMe(CF_3)_2$]$_2$.

equipped with an efficient condenser. Under these conditions, cyclic 13 was slowly distilled so that 7 mol % was isolated in 5 h, and the relative concentration (7 mol %) of cyclic 13 remaining in the reaction mixture was unchanged. This implies that a slow ring/chain equilibrium had been established under these conditions which removal of 13 slowly advanced.

These results complement those reported for classical metathesis systems, recently summarized by Ivin.[29] At the resting state equilibria (Figure 6), after ADMET condensation has stopped, the kinetics of the system (polymer 5 containing catalyst) presumably obey those controlling any depolymerizable polyalkenylene containing an active metathesis catalyst (Figure 7). Here, reversible ring-opening metathesis polymerization (ROMP) can take place, and the rate of the forward reaction is given by

$$R_p = (k_p[M] - k_d)[P]$$

where k_p and k_d are the rate constants for polymerization by ROMP and depolymerization by back-biting, respectively, and where [M] and [P] are the respective concentrations of monomer and polymer.[29] Therefore, cyclic 13 is a slow kinetic product, and the rate of intramolecular back-biting (Figure 6c) is limited by competing intermolecular degenerate equilibria (Figure 6b). The situation changes, and cyclic 13 is nonexistent, if an appreciable concentration of condensable terminal olefin is present where the thermodynamics of condensation polymerization is predominant, as in the case during the oligomerization of monomer 4. Back-biting is not observed, nor expected, during the polymerization of monomers 6 and 10 to polymers 7 and 11, respectively, simply due to the unfavored formation of extremely large cyclic molecules.

The conclusion that the competing intermolecular equilibrium (Figure 6b) is the limiting factor for the production of cyclic 13 in the bulk is best supported by the observation that 13 is produced much faster and to a greater extent in solution (Figure 7). In an NMR experiment, active polymer 5 was diluted with benzene-d_6 and 36 mol % of cyclic compound 13 was generated within 5 min. If simple mobility of the alkylidene-terminated chain end was the limiting rate factor for the production of cyclic 13, then upon dilution, all equilibria would increase by the same factor and the observed enhanced cyclization (vs cyclization in the bulk) would not have been expected.

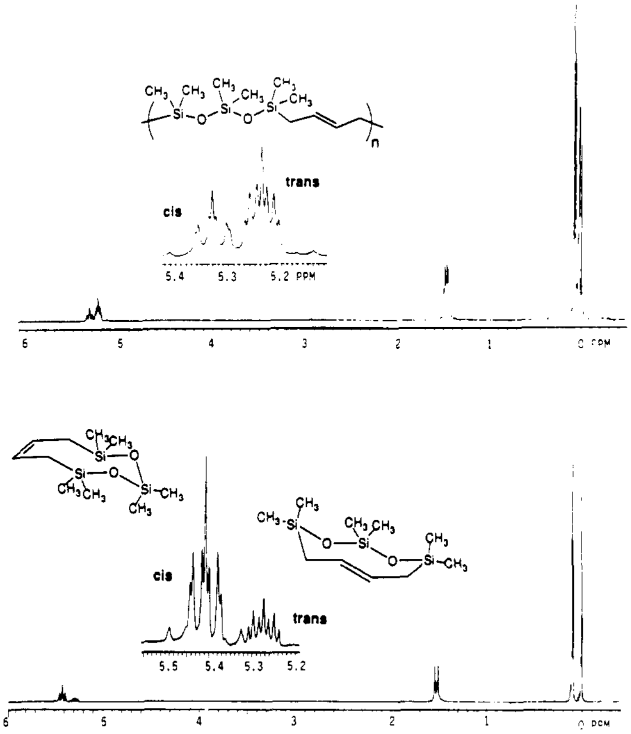

Figure 8. 200-MHz ^{1}H NMR spectra of polymer 5 (top) and cyclic compound 13.

The quantity of cyclic 13, generated from the dilution of polymer 5, did not significantly change over a period of several days at room temperature and may indicate that an equilibrium between linear and cyclic oligomers had been established as predicted by the equation above. The rate of back-biting, or cyclization, should become negligible when [M] ([13] in this case) becomes sufficient for competing ring-opening reactions to occur. However, it is unlikely that cyclic 13 is a ROMP monomer, under these conditions, simply because it is produced by back-biting. If cyclic 13 is polymerizable by ROMP, then its ceiling temperature should exist below 25 °C, under these conditions. Similar processes have been observed where diallyl ether bulk oligomerization,[21] and diallylsilane solution polymerization,[28] when catalyst 1 was used, established an equilibrium with monomer cyclization. Furthermore, as mentioned earlier, Grubbs and Fu[9] have shown, very recently, that various diene–ethers and diene–amines will selectively cyclize in solution when catalyzed by 1.

Interestingly, the bulk isolation of 13 gave an 80% to 20% cis to trans mixture, while during the solution production of 13, the trans isomer (13b) (Figure 7) was not present in concentrations sufficient to integrate by ^{1}H NMR. It seems reasonable that 13b is produced in solution yet is readily isomerized by polymer-terminated alkylidenes to the presumably more thermodynamically stable cis isomer (13a).[30] In the bulk, and especially under conditions where 13a and 13b are being continuously removed, the opportunity for trans to cis metathesis mediated isomerization is greatly diminished.

Figure 8 depicts the ^{1}H NMR spectra for polymer 5 and the mixture of cis and trans isomers of 13 collected from the bulk reaction mixture of 5. The two (top and bottom) expanded regions represent the internal vinylic protons for polymer 5 and cyclic compound 13a,b, respectively. These signals illustrate the subtle downfield chemical shift that ring strain induces on the vinylic (as well as the allylic) protons of 13 as compared to the corresponding proton signals in 5. Although not legible in Figure 8, it is clear that the cis and trans isomers of polymer 5 and cyclic 13 also impose different environments on both the non-equivalent methyl substituents in that the trans-affected methyl protons are slightly shifted upfield from those

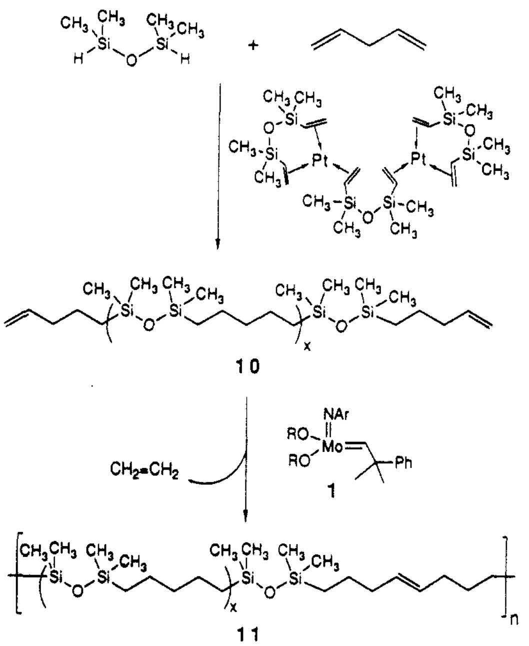

Figure 9. Synthesis of α,ω-diene telechelomer **10** and resulting polymer **11**.

affected by the cis isomer. This effect is also obvious when the methyl substituent signals in the ^{13}C NMR spectra are compared for the two. No other significant differences are observed in the ^{13}C NMR or ^{29}Si NMR spectra between **5** and **13** (see Experimental Section for chemical shifts). The Si atom shift similarities, however, are expected since Si atoms contained in large siloxane rings, e.g., the cyclic tri- and tetrasiloxanes, D$_3$ (−20 ppm) and D$_4$ (−22 ppm), respectively, possess nearly the same chemical shifts as for the Si atoms in the D units observed for linear poly(dimethylsiloxane).[31]

Polymerization of the α,ω-Telechelic Diene (10). The polymerization of α,ω-telechelic diene macromonomer **10** to polymer **11** is the first example of an oligodiene applied to ADMET polymerizations. Figure 9 displays the synthetic scheme used to prepare polymer **11** from commerical materials and Karstedt's catalyst.[25] As mentioned earlier, the true structure of Karstedt's catalyst has been recently determined and is shown in Figure 9.[25b] The hydrosilation oligomerization technique was found to be a convenient method of preparing macromonomer **10** and could provide access to a variety of oligomeric dienes containing main-chain silicon functionalization.[26] Telechelomer **10** was well defined and contained an average degree of polymerization of 3.4 by quantitative ^{13}C NMR spectroscopy which corresponds to $M_n = 960$. These data agree well with results obtained from elemental analysis. According to gel permeation chromatography (GPC) analysis (relative to polybutadiene standards), a number average molecular weight of 550 ($M_w/M_n = 1.3$) was measured for telechelomer **10** compared to a $M_n = 920$ ($M_w/M_n = 1.2$) obtained when poly(dimethylsiloxane) standards were used.[32]

Telechelic diene **10** is an ideal monomer for ADMET polymerization since it is a nonvolatile quick flowing liquid. This feature allows for the use of continuous high vacuum at these polymerization temperatures which permits efficient removal of ethylene. Figure 10 illustrates the increase in molecular weight from telechelomer **10** to polymer **11** by GPC. Individual oligomers are partially resolved in the lower chromatogram representing telechelomer **10** yet are averaged as ADMET condensation ensues (upper trace), giving a more Gaussian molecular weight distribution approaching 2 for high molecular weight polymer **11**.

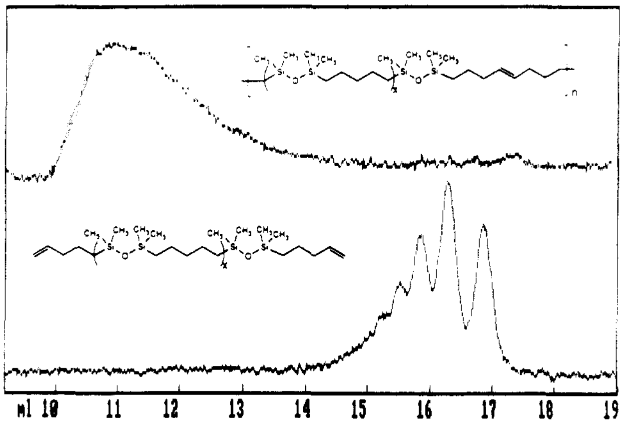

Figure 10. Gel permeation chromatography of α,ω-diene telechelomer **10** and resulting polymer **11**.

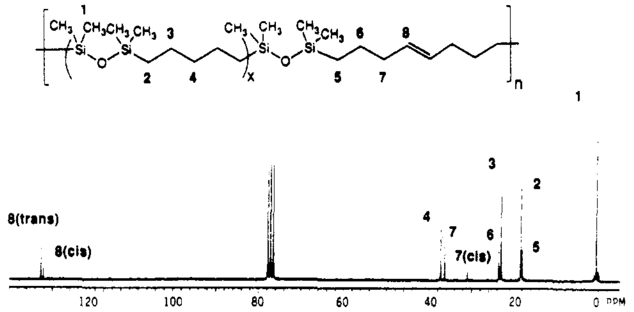

Figure 11. Quantitative 50-MHz ^{13}C NMR spectra of polymer **11**.

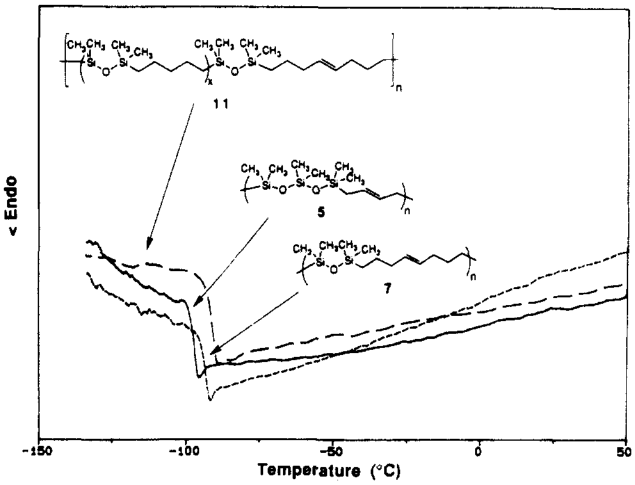

Figure 12. Differential scanning calorimetry (DSC) of polymers **5**, **7**, and **11**: scan rate 10 °C/min.

Figure 11 displays the quantitative 50-MHz ^{13}C NMR spectrum for the reaction mixture of polymer **11**. Every nonequivalent carbon in this macromolecule is easily identified, and the spectrum exemplifies the absolutely clean mechanism by which ADMET polymerization proceeds.

Thermal Properties. Differential scanning calorimetry (DSC) was used to determine the glass transition temperatures (T_g) for the high molecular weight polymers: **5**, **7**, and **11** (Table I). Low glass transition temperatures were observed for the polymers, as expected for very flexible systems incorporating the siloxane linkage.[10] Figure 12 contains the DSC thermograms for polymers **5**, **7**, and **11**, indicating glass transition endo-

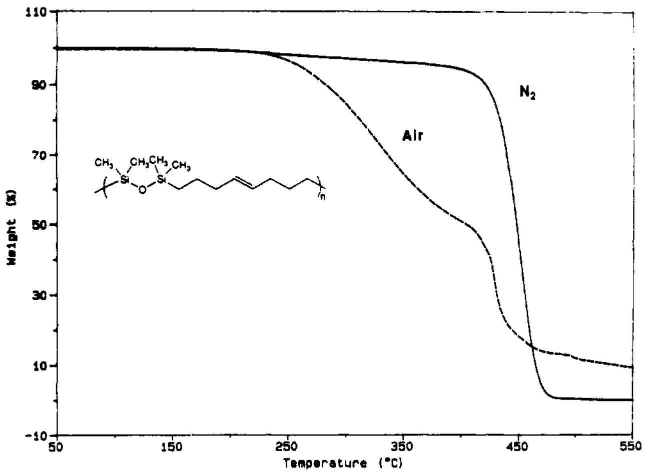

Figure 13. Thermogravimetric analysis (TGA) of polymer **7** in N_2 and air: scan rate 10 °C/min.

therms ranging from −97 to −90 °C. These transitions were reproducible, with little deviation, upon cycling at differing scan rates from 10 to 1 °C/min. Melting transitions were not observed for these high trans content polymers below 200 °C.

Thermal gravimetric analysis (TGA) was used to measure the thermal stability and extent of thermal decomposition for polymers **5**, **7**, and **11** (Table I) in nitrogen and in air environments. Figure 13 gives a typical TGA thermogram, in both mediums, for polymers **5**, **7**, and **11**. All three polymers retained nearly 100% of their original mass while approaching 400 °C with rapid weight loss ensuing to 0% weight in nitrogen. Thermal decomposition in air occurred much more rapidly, as expected, and typically ca. 10% weight remained at temperatures exceeding 700 °C (Figure 13).

The complete elimination of weight, for all three polymers, in nitrogen, over a temperature range of about 50 °C (5 min) perhaps indicates that few decomposition pathways are occurring. ADMET polymerizations are strictly confined to one repeat unit forming mechanism, thereby prohibiting structural irregularities such as branching or cross-linking. Irregular structures typically exhibit steps in the TGA curve and are frequently observed for less-defined unsaturated silicon polymers due to various reactions such as thermal cross-linking where formation of a three-dimensional network enhances thermal stability.[33]

Preliminary efforts to identify the thermal decomposition products of these poly(carbosiloxane)s have revealed that cyclic products are generated, as expected. In particular, the thermal decomposition of polymer **5** in nitrogen produces cyclic compound **13**, along with other unidentified products. Cyclotrisilaoxalkene **13** was detected by GC/MS analysis of the decomposition products from polymer **5** and was identified by comparison with mass spectral data from an authentic sample of **13** obtained from the earlier discussed metathesis reactions. The production of cyclic **13** can be rationalized on the basis of the ease in which other siloxane polymers redistribute to form cyclosiloxanes upon thermolysis.[13f,h]

Conclusions

Acyclic diene metathesis (ADMET) polymerization now provides access to a new class of polymers which we define as unsaturated poly(carbosiloxane)s. The use of a highly active molybdenum alkylidene catalyst facilitates a clean polymerization path to well-defined linear polymers with low glass transition temperatures and good thermal stability. Monomer structural designs have been developed which exceed limitations found with divinyltetramethyldisiloxane and obviate the exclusive monomer cyclization exhibited by bis(allyl)tetramethyldisiloxane. By extension of the methylene units or the siloxane linkage within the monomer, ADMET polymerization occurs readily while continuously releasing pure ethylene.

In some cases, back-biting reactions produce cyclic byproducts when active polymer is diluted or, to a lesser extent, when in the bulk. Back-biting occurs only after the concentration of terminal olefin is negligible and the system has reached a postcondensation resting state, where terminal alkylidene/metallacycle equilibria exist.

The hydrosilation reaction provides a convenient route to a well-defined α,ω-diene containing carbosiloxane telechelomer which ADMET polymerizes cleanly to a high molecular weight.

This new class of functionalized siloxane polymers provides perfectly alternating sites of unsaturation which may be of use in forming well-defined modified systems, such as graft copolymers and cross-linked elastomers. Investigations leading to other carbosiloxane polymers compatible with ADMET techniques are currently under way.

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