Synthesis of Silylene−Alkylene−Silylene−Vinylene Polymers via Catalytic Silylative Coupling (SC) Polycondensation

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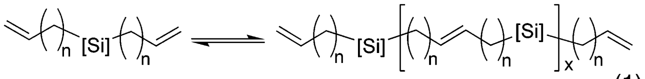
ABSTRACT: α,ω-Bis(vinyldimethylsilyl)alkanes (**1**−**4**) of the general formula $CH_2{=}CH(CH_3)_2Si(CH_2)_n(CH_3)_2SiCH{=}CH_2$ (where $n = 1-4$) undergo effective silylative coupling (SC) polycondensation, if catalyzed by $[RuCl_2(PPh_3)_3]$ (**II**) or $[RuHCl(CO)(PPh_3)_3]$ (**III**), giving linear polymers (**5**−**8**) ($M_w = 7300-8500$) containing a mixture of *trans*-1,2- and *gem*-fragments, but in the presence of $[\{RuCl_2(CO)_3\}_2]$ (**I**) as a catalyst, highly stereoselective *trans*-tactic linear polymers are isolated (**9**−**12**) ($M_w = 6200-9200$). The products of both new processes cannot be synthesized via ADMET polymerization or ring-closing metathesis (RCM).

Introduction

Acyclic diene metathesis (ADMET) polymerization represents a versatile route toward the synthesis of linear well-defined unsaturated polymers.[1] The reaction developed by Wagener et al. occurs in the presence of highly active tungsten and molybdenum metathesis catalysts such as Schrock's alkylidenes, e.g., $[\{(CF_3)_2MeCO)\}_2(ArN){-}M{=}CH(t\text{-}Bu)]$, where M = Mo and W[2] and Grubbs' ruthenium catalyst−$[RuCl_2({=}CHPh)(PCy_3)_2]$[3]. ADMET polymerization of silicon-containing dienes such as dialkenylsilanes and -siloxanes (except vinyl derivatives), furnishes a variety of unsaturated homopolymers including carbosilane and carbosiloxane[4] units (eq 1):



(1)

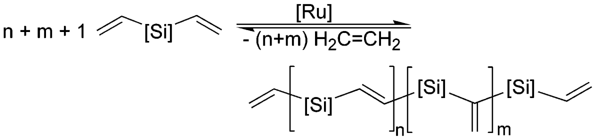
where $[Si] = -Si(CH_3)_2$, $-(CH_3)_2Si{-}O{-}Si(CH_3)_2-$.

Finkel'shtein et al. reported that ADMET reaction of di(allyl,butenyl)silanes and silacyclobutanes and siloxanes as well as diallyltetramethyldisiloxane proceeded effectively in the presence of heterogeneous catalyst $[Re_2O_7/Al_2O_3 + SnR_4(PbR_4)]$, giving predominantly a mixture containing both cyclic and linear products.[5]

Unfortunately, vinyl derivatives of organosilicon compounds, which are of fundamental industrial importance, are completely inert to productive homometathesis presumably due to steric hindrance of silyl groups stimulating nonproductive cleavage of disilylmetallacyclobutane.[6] This supposition is based on an analogy to inactivity of metallacarbenes in self-metathesis of vinyl substituted silicon compounds.

Very recent reports on ADMET oligomerization of tetravinylsilane and divinyldisubstituted silanes in the presence of $[Re_2O_7/Al_2O_3/SnBu_4]$ indicate a formation of oligomers identified by the GPC methods, with very low yields[7] (~10−15%). Actually, no yields of isolated products have been given in these reports.

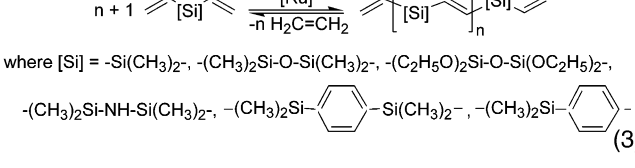
Contrary to the inactivity of metallacarbenes in ADMET polymerization, divinyldiorganosilicon compounds in the presence of ruthenium complexes containing or generating Ru−H and Ru−Si bond, undergo intermolecular polycondensation under the optimum conditions yielding linear unsaturated polymers according to the following scheme (eq 2):[8]



(2)

where $[Si] = -Si(CH_3)_2-$,[8a] $-(CH_3)_2Si{-}O{-}Si(CH_3)_2-$,[8b] $-(CH_3)_2Si{-}NH{-}Si(CH_3)_2-$[8c] and catalysts are as follows: $[RuCl_2(PPh_3)_3]$, 130 °C, 120 h, $M_w = 1510$, $M_w/M_n = 1.19$, DP = 17;[8a] $[RuCl_2(PPh_3)_3]$, 130 °C, 72 h, $M_w = 1815$, $M_w/M_n = 1.16$, DP = 10;[8b] $[RuHCl(CO)(PPh_3)_3]$, 130 °C, 1 week, $M_w = 2385$, $M_w/M_n = 1.21$, DP = 15.[8c]

Previous reports have shown that less active ruthenium complexes, i.e., $[\{RuCl_2(CO)_3\}_2]$ (**I**), catalyze the polycondensation of divinyl substituted silanes,[8a] siloxanes,[8b] and silazanes[8c] as well as bis(silyl)benzene[8d] (while $[RuH(OAc)(CO)(PPh_3)_2]$ catalyzes the reaction of silylstyrene[8e]) to give stereoregular *trans*-tactic linear polymers according to the following scheme (eq 3):



(3)

The condensation (silylative coupling) of monovinyl substituted silicon compounds proceeds through cleavage of the =C−Si bond of the vinyl substituted silicon compound and the activation of the =C−H bond of the second vinylsilane molecule according to the following equation, eq 4:[11]

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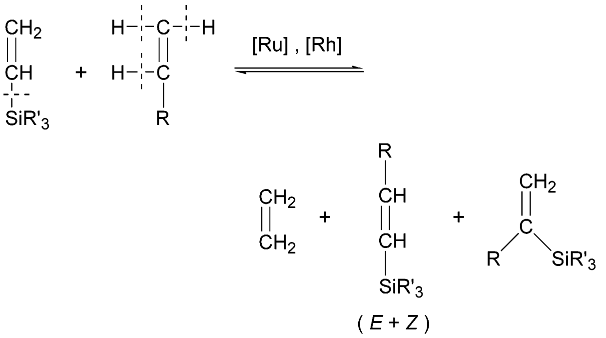
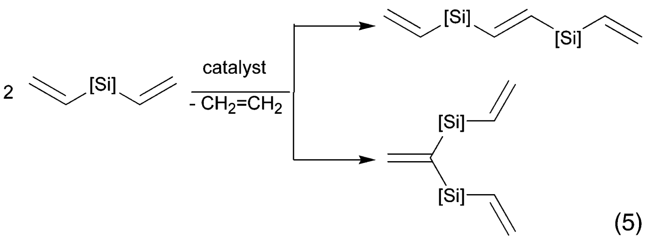


(4)

The evidences for the nonmetallacarbene mechanism of monovinylsilane transformation has been reported[12a−c] previously, but it can be generalized for dimerization of divinyl substituted silicon compounds[12d] (see eq 5)



(5)

leading subsequently to competitive linear oligomerization and ring-closing silylative coupling.[12d,e]

In the presence of $[\{RuCl_2(CO)_3\}_2]$, 1,2-*trans*-dimer is exclusively yielded, whereas $[\{RhX(cod)\}_2]$, $X = \mu$-Cl or μ-$OSiMe_3$ catalyze preferably a formation of 1,1-product, and ruthenium-phosphine complexes $[RuCl_2(PPh_3)_3]$ (**II**) and $[RuHCl(CO)(PPh_3)_3]$ (**III**) furnish both dimeric products.[9a]

The aim of this paper is to use this new synthetic route to prepare linear polycarbosilanes via polycondensation of divinyl substituted carbosilanes.

Experimental Section

General Considerations. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Gemini series NMR superconducting spectrometer system or a Varian 300 XL, in C_6D_6 as a solvent. ^1H NMR and ^{13}C NMR spectra were referenced to residual signals from C_6D_6.

Infrared spectra (KBr plates) were recorded using an FT-IR Brücker IFS-113v.

The mass spectra of all products were determined by GC−MS analysis on a Varian 3300 gas chromatograph equipped with a DB-1, 30 m capillary column and a Finigan Mat 800 ion trap detector. GC analyses were carried out on a Varian 3300 gas chromatograph.

GPC data were collected using a Gilson HPLC system with a 2 × 250 × 10 mm Jordi-Gel DVB column, 500 and 100 Å, and polysiloxane standards (analysis conditions: mobile phase, THF; flow rate, 1.2 mL/min.; temperature, ambient; injection volume, 20 μL).

Differential scanning calorimetric (DSC) data was obtained with a Perkin-Elmer 7 series thermal analysis system. DSC samples (5−10 mg) were analyzed with ice as coolant and under the nitrogen flow rate of 25 mL/min. All samples were predried at 40−50 °C under reduced pressure (<0.1 mmHg) for at last 24 h. The instrument was calibrated for peak onset temperature transition and peak area, using indium as a standard. Samples were scanned at the heating/cooling rate of 5 °C/min. The DSC samples were analyzed over the temperature range −120 to +150 °C with data collection during the second cycle. TGA data were recorded on a CHNS analyzer model 1108 Carlo Erba, TGA model 2950 TA Instruments equipped with a model 2000 data analysis software program. All analyses were performed under a nitrogen atmosphere.

Materials. Organosilicon chemicals allyldimethylchlorosilane, chlorodimethylsilane, vinyl(chloromethyl)dimethylsilane and 1,2-bis(chlorodimethylsilyl)ethane were received from ABCR, vinyldimethylchlorosilane and 1,4-dibromobutane from Fluka, and $[\{RuCl_2(CO)_3\}_2]$ (**I**) was purchased from Strem and used without further purification. Other complexes were synthesized by standard procedures: $[RuCl_2(PPh_3)_3]$ (**II**),[13] $[RuCl(SiMe_3)(CO)(PPh_3)_2]$,[12a] and $[RuHCl(CO)(PPh_3)_3]$ (**III**).[14] THF prior to use was dried over sodium and benzophenone and stored under argon and freshly distilled before use. 1,2-Bis(chlorodimethylsilyl)ethane and 1,3-bis(chlorodimethylsilyl)propane synthesized by hydrosilylation were dried over CaH_2 for 12 h under argon and distilled before use. Vinylmagnesium bromide was synthesized via a well-known procedure.

Synthesis and Characterization of α,ω-Bis(vinyldimethylsilyl)alkanes (1—4). To obtain bis(vinyldimethylsilyl)methane (**1**), vinyl(chloromethyl)dimethylsilane in THF was added to a suspension of Mg turnings in THF, and vinylchlorodimethylsilane in THF was subsequently added dropwise over a period of 3 h. The mixture was allowed to warm to room temperature and stirred under reflux for 12 h; subsequently, it was extracted three times with NH_4Cl in water and dried over $MgSO_4$. The combined organic extracts were filtered off and evaporated under reduced pressure. The product was than placed over CaH_2, stirred overnight, and distilled under reduced pressure after filtration of CaH_2. 1,4-Bis(vinyldimethylsilyl)butane (**4**) was prepared from vinylchlorodimethylsilane and 1,4-dibromobutane in THF according to the same procedure. 1,2-Bis(vinyldimethylsilyl)ethane (**2**) and 1,3-bis(vinyldimethylsilyl)propane (**3**) were prepared by the reaction of 1,2-bis(chlorodimethylsilyl)ethane (and 1,2-bis(chlorodimethylsilyl)propane, respectively) with vinylmagnesium bromide in dry THF.

Characterization of 1—4. 1. Bp: 53 °C/1.1 mmHg. Yield: 90%. ^1H NMR (C_6D_6, δ (ppm)): −0.12 (s, 2H, $-SiCH_2Si-$), 0.12 (s, 12H, $-SiCH_3$), 5.5−6.2 (m, 6H, $-SiCH{=}CH_2$). ^{13}C NMR (C_6D_6, δ (ppm)): −0.06 ($-SiCH_3$), 1.77 ($-SiCH_2Si-$), 130.84 ($-CH{=}CH_2$), 141.19 ($-CH{=}CH_2$). Anal. Calcd for $C_9H_{20}Si_2$: C, 58.70; H, 10.87. Found: C, 58.72; H, 10.86.

2. Bp: 100 °C/1.2 mmHg. Yield: 85%. ^1H NMR (C_6D_6, δ (ppm)): 0.03 (s, 12H, $-SiCH_3$), 0.45 (s, 4H, $-SiCH_2CH_2Si-$), 5.5−6.3 (m, 6H, $-SiCH{=}CH_2$). ^{13}C NMR (C_6D_6, δ (ppm)): −3.35 ($-SiCH_3$), 8.21 ($-SiCH_2CH_2Si-$), 132.36 ($-CH{=}CH_2$), 139.47 ($-CH{=}CH_2$). Anal. Calcd for $C_{10}H_{22}Si_2$: C, 60.52; H, 11.17. Found: C, 59.80; H, 11.10.

3. Bp: 126 °C/1.2 mmHg. Yield: 83%. ^1H NMR (C_6D_6, δ (ppm)): 0.04 (s, 12H, $-SiCH_3$), 0.5−0.7 (m, 4H, $-CH_2-C-C$), 1.2−1.5 (m, 2H, $-C-CH_2-C-$), 5.5−6.3 (m, 6H, $-CH{=}CH_2$). ^{13}C NMR (C_6D_6, δ (ppm)): −3.96 ($-SiCH_3$), 18.27 ($-CH_2CH_2CH_2-$), 20.02 ($-CH_2CH_2CH_2-$), 131.84 ($-CH{=}CH_2$) 139.79 ($-CH{=}CH_2$). Anal. Calcd for $C_{11}H_{24}Si_2$: C, 62.18; H, 11.38. Found: C, 62.63; H, 11.41.

4. Bp: 150 °C/1.2 mmHg. Yield: 90%. ^1H NMR (C_6D_6, δ (ppm)): 0.03 (s, 12H, $-SiCH_3$), 0.4−0.7 (m, 4H, $-CH_2C-C-$), 1.2−1.5 (m, 4H, $-C-CH_2-C-$), 5.5−6.3 (m, 6H, $-CH{=}CH_2$). ^{13}C NMR (C_6D_6, δ (ppm)): −2.75 ($-SiCH_3$), 15.85 ($-CH_2CH_2CH_2CH_2-$), 28.54 ($-CH_2CH_2CH_2CH_2-$), 132.05 ($-CH{=}CH_2$), 139.90 ($-CH{=}CH_2$). Anal. Calcd for $C_{12}H_{26}Si_2$: C, 63.63; H, 11.57. Found: C, 63.60; H, 11.51.

General Procedure for Silylative Coupling (SC) Polycondensation. The monomer was degassed and distilled from CaH_2 prior to polycondensation, which was carried out in the bulk. In a typical reaction 1.5 mL of a monomer (**1** (6.5 mmol), **2** (6.4 mmol), **3** (5.8 mmol), or **4** (5.5 mmol)) was combined with the catalyst and placed in a 10 mL flask equipped with a magnetic stirring bar and refluxed. The typically used monomer-to-catalyst ratio was 100:1. The catalyst $[RuHCl(CO)(PPh_3)_3]$ (**III**) was used to prepare polymers **5** and **6** and $[RuCl_2(PPh_3)_3]$ (**II**) for polymers **7** and **8**, and the catalyst $[\{RuCl_2(CO)_3\}_2]$ (**I**) was added to synthesize polymers **9**−**12**.

The reaction mixture was stirred in an oil bath at 90 °C until its viscosity increased and a slow to moderate bubbling of ethylene was observed. After 10 days, the reactions were terminated. The polymers were filtered off on $\mathrm{SiO_2}$ using hexane as an eluent and subsequently dissolved in methylene chloride, precipitated in dry $\mathrm{CH_3OH}$, and dried in an evaporator until constant weight.

Characterization of 5—12. 5. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.20−0.22 (m, $-\mathrm{SiC}H_2-$), 0.29 (m, $-\mathrm{SiC}H_3$), 6.86−6.91 (m, $-\mathrm{C}H{=}\mathrm{C}H-$), 6.40−6.42 ($-\mathrm{C{=}C}H_2$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): 1.34−1.55 (m, $-\mathrm{Si}C\mathrm{H_3}$), 3.44 ($-\mathrm{Si}C\mathrm{H_2}-$), 140.02 ($-C{=}C\mathrm{H_2}$), 152.50 ($-C\mathrm{H}{=}C\mathrm{H_2}$), 154.18 ($-C{=}\mathrm{CH_2}$). GPC: $M_w = 8500$; PDI = 1.45; $y + z = 53$. TGA: 10% weight loss at 465 °C. DSC: $T_g = -65$ °C. Anal. Calcd for $\mathrm{C_7H_{16}Si_2}$: C, 53.85; H, 10.26. Found: C, 53.14; H, 10.18.

6. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.00−0.41 (m, $-\mathrm{SiC}H_3$), 0.53−0.55 (m, $-\mathrm{SiC}H_2-$ in terminal group), 0.60−0.65 (m, $-\mathrm{SiC}H_2-$ in chain), 5.66−5.78 (m, $-\mathrm{CH{=}C}H_2$), 6.13−6.28 (m, $-\mathrm{C}H{=}\mathrm{CH_2}$), 6.40−6.42 ($-\mathrm{C{=}C}H_2$), 6.86−6.90 (m, $-\mathrm{C}H{=}\mathrm{C}H-$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): −3.76 to +1.58 (m, $-\mathrm{Si}C\mathrm{H_3}$), 7.27−7.95 ($-\mathrm{Si}C\mathrm{H_2}-$ in terminal group), 8.54−10.74 ($-\mathrm{Si}C\mathrm{H_2}-$ in chain), 31.02 ($-\mathrm{Si}C\mathrm{H_2}-$ in chain), 131.65 ($-\mathrm{CH}{=}C\mathrm{H_2}$), 138.91 ($-C\mathrm{H{=}CH_2}$), 141.65 ($-\mathrm{C}{=}C\mathrm{H_2}$), 150.88 ($-C\mathrm{H}{=}C\mathrm{H}-$), 156.18 ($-C{=}\mathrm{CH_2}$). GPC: $M_w = 7300$; PDI = 1.40; $y + z = 42$. TGA: 10% weight loss at 468 °C. DSC: $T_g = -67$ °C. Anal.: Calcd for $\mathrm{C_8H_{18}Si_2}$: C, 56.47; H, 10.59. Found: C, 56.11; H, 10.29.

7. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.00−0.29 (m, $-\mathrm{SiC}H_3$), 0.62−0.76 (m, $-\mathrm{SiC}H_2-$), 1.42−1.55, 1.88−2.13 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$), 6.28−6.30 ($-\mathrm{C{=}C}H_2$), 6.92−7.01 (m, $-\mathrm{C}H{=}\mathrm{C}H-$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): −3.16 to +1.48 (m, $-\mathrm{Si}C\mathrm{H_3}$), 18.03−18.12 (m, $-\mathrm{Si}C\mathrm{H_2}-$ in terminal group), 18.77−18.81 (m, $-\mathrm{SiC}H_2-$ in chain), 20.18−20.22 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$ in terminal group), 23.33−23.35 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$ in chain), 139.41 ($-\mathrm{C}{=}C\mathrm{H_2}$), 149.71 ($-C\mathrm{H}{=}C\mathrm{H}-$), 153.73 ($-C{=}\mathrm{CH_2}$). GPC: $M_w = 7600$; PDI = 1.42; $y + z = 40$. TGA: 10% weight loss at 475 °C. DSC: $T_g = -65$ °C. Anal. Calcd ($\mathrm{C_9H_{20}Si_2}$): C, 58.70; H, 10.87. Found: C, 58.12; H, 10.29.

8. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.00−0.24 (m, $-\mathrm{SiC}H_3$), 0.51−0.63 (m, $-\mathrm{SiC}H_2-$ in terminal group), 0.92−0.94 (m, $-\mathrm{SiC}H_2-$ in chain), 1.30−1.40 (m, $-\mathrm{C-C}H_2\mathrm{-C}$ in terminal group), 1.42−1.53 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$ in chain), 6.58 ($-\mathrm{C{=}C}H_2$), 6.93−7.00 (m, $-\mathrm{C}H{=}\mathrm{C}H-$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): −3.10 to +1.08 (m, $-\mathrm{Si}C\mathrm{H_3}$), 14.21−14.24 (m, $-\mathrm{Si}C\mathrm{H_2}-$ in terminal group), 15.41−15.47 (m, $-\mathrm{SiC}H_2-$ in chain), 27.38−27.50 ($-\mathrm{C}-C\mathrm{H_2-C}$ in terminal group), 28.26−28.31 (m, $-\mathrm{C-C}H_2\mathrm{-C}$ in chain), 142.65 ($-\mathrm{C}{=}C\mathrm{H_2}$), 150.85 (m, $-C\mathrm{H}{=}C\mathrm{H}-$), 158.16 ($-C{=}\mathrm{CH_2}$). GPC: $M_w = 8400$; PDI = 1.45; $y + z = 42$. TGA: 10% weight loss at 487 °C. DSC: $T_g = -68$ °C. Anal. Calcd for $\mathrm{C_{10}H_{22}Si_2}$: C, 60.61; H, 11.11. Found: C, 59.18; H, 10.95.

9. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.19−0.22 (m, $-\mathrm{SiC}H_2-$), 6.89 ($-\mathrm{C}H{=}\mathrm{C}H-$), 0.27−0.30 (m, $-\mathrm{SiC}H_3$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): 3.49 (m, $-\mathrm{Si}C\mathrm{H_3}$), 10.13−10.55 (m, $-\mathrm{Si}C\mathrm{H_2}-$), 151.53 (m, $-C\mathrm{H}{=}C\mathrm{H}-$). GPC: $M_w = 9500$; PDI = 1.35; $x = 61$. TGA: 10% weight loss at 465 °C. DSC: $T_g = -54$ °C. Anal. Calcd for $\mathrm{C_7H_{16}Si_2}$: C, 53.85; H, 10.26. Found: C, 53.90; H, 10.01.

10. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.00−0.21 (m, $-\mathrm{SiC}H_3$) 0.54−0.60 (m, $-\mathrm{SiC}H_2-$), 5.67−5.79 (m, $-\mathrm{CH{=}C}H_2$), 6.14−6.29 (m, $-\mathrm{C}H{=}\mathrm{CH_2}$), 6.74−6.84 (m, $-\mathrm{C}H{=}\mathrm{C}H-$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): −3.80 to +1.42 (m, $-\mathrm{Si}C\mathrm{H_3}$), 7.28, 10.28−10.86 (m, $-\mathrm{Si}C\mathrm{H_2}-$), 131.95 ($-\mathrm{CH}{=}C\mathrm{H_2}$), 139.03 ($-C\mathrm{H{=}CH_2}$), 150.89 (-$C\mathrm{H}{=}C\mathrm{H}-$). GPC: $M_w = 6200$; PDI = 1.18; $x = 35$. TGA: 10% weight loss at 468 °C. DSC: $T_g = -54$ °C. Anal. Calcd for $\mathrm{C_8H_{18}Si_2}$: C, 56.47; H, 10.59. Found: C, 55.79; H, 10.21.

11. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.00−0.27 (m, $-\mathrm{SiC}H_3$), 0.65−0.69 (m, $-\mathrm{SiC}H_2-$ in terminal group), 0.70−0.79 (m, $-\mathrm{SiC}H_2-$ in chain), 1.41−1.58 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$ in terminal group), 1.59−1.61 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$ in chain), 5.66−5.76 (m, $-\mathrm{CH{=}C}H_2$), 6.14−6.84 (m, $-\mathrm{C}H{=}\mathrm{CH_2}$), 6.84−6.86 (m, $-\mathrm{C}H{=}\mathrm{C}H-$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): −2.72 to +1.83 (m, $-\mathrm{Si}C\mathrm{H_3}$), 18.74 ($-\mathrm{Si}C\mathrm{H_2}$ in terminal group), 19.18 (m, $-\mathrm{Si}C\mathrm{H_2}-$ in chain), 20.62 ($-\mathrm{C}-C\mathrm{H_2-C}-$ in terminal group), 23.76 ($-\mathrm{C}-C\mathrm{H_2-C}-$ in chain), 132.07 ($-\mathrm{CH}{=}C\mathrm{H_2}$), 138.82 ($-C\mathrm{H{=}CH_2}$), 151.34 ($-C\mathrm{H}{=}C\mathrm{H}-$). GPC: $M_w = 7600$; PDI = 1.21; $x = 40$. TGA: 10% weight loss at 471 °C. DSC: $T_g = -58$ °C. Anal. Calcd for $\mathrm{C_9H_{20}Si_2}$: C, 58.70; H, 10.87. Found: C, 59.14; H, 11.47.

Table 1. Effect of Catalyst on the Conversion of Bis(vinyldimethylsilyl)methane (1) and Selectivity of Products[a]

catalyst	silane convn (%)	selectivity: dimers (%) linear	cyclic	trimers (%)	others (%)
$\mathrm{[RuCl(SiMe_3)(CO)(PPh_3)_2]}$	85	39	2	18	41
$\mathrm{[RuHCl(CO)(PPh_3)_3]}$	89	35	3	20	42
$\mathrm{[RuCl_2(PPh_3)_3]}$	88	38	3	19	40
$\mathrm{[\{RuCl_2(CO)_3\}_2]}$	81	40	2	20	38

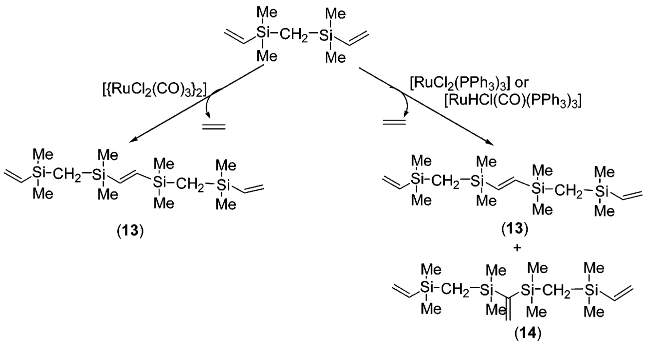
[a] Reaction conditions: molar ratio monomer:catalyst = 100:1; temperature: 130 °C; time = 24 h; glass ampules.

Table 2. Effect of the Time on the Conversion of Bis(vinyldimethylsilyl)methane (1) in the Presence of $\mathrm{[RuHCl(CO)(PPh_3)_3]}$[a]

time (h)	silane convn (%)	selectivity: dimers [%] linear 1,2-	linear 1,1-	cyclic	trimers (%)	others (%)
1	5	6	94	0	0	0
2	5	20	80	0	0	0
3	8	39	61	0	0	0
5	10	43	55	2	0	0
10	16	44	45	3	8	0
20	37	35	32	2	15	16
25	58	27	33	0	15	22

[a] Reaction conditions: molar ratio monomer:catalyst = 100:1; temperature = 110 °C; glass ampules.

Scheme 1. Synthetic Route to *trans*-1,2- (13) and 1,1-Isomers (14) of Bis(vinyldimethylsilyl)methane (1) Dimerization



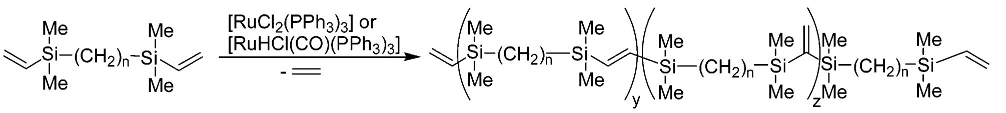
12. ^{1}H NMR ($\mathrm{C_6D_6}$, δ (ppm)): 0.00−0.17 (m, $-\mathrm{SiC}H_3$), 0.53−0.62 (m, $-\mathrm{SiC}H_2-$ in terminal group), 0.90−0.92 (m, $-\mathrm{SiC}H_2-$ in chain), 1.31−1.36 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$ in terminal group), 1.38−1.46 (m, $-\mathrm{C-C}H_2\mathrm{-C}-$ in chain), 5.64−5.73 (m, $-\mathrm{CH{=}C}H_2$), 6.11−6.23 (m, $-\mathrm{C}H{=}\mathrm{CH_2}$), 6.91−6.98 (m, $-\mathrm{C}H{=}\mathrm{C}H-$). ^{13}C NMR ($\mathrm{C_6D_6}$, δ (ppm)): −3.01 to +0.87 (m, $-\mathrm{Si}C\mathrm{H_3}$), 14.58 ($-\mathrm{Si}C\mathrm{H_2}-$ in terminal group), 15.57−15.71 (m, $-\mathrm{Si}C\mathrm{H_2}-$ in chain), 27.85 ($-\mathrm{C}-C\mathrm{H_2-C}-$ in terminal group), 28.22−28.25 (m, $-\mathrm{C}-C\mathrm{H_2-C}-$ in chain), 131.62 (m, $-\mathrm{CH}{=}C\mathrm{H_2}$), 139.40 (m, $-C\mathrm{H{=}CH_2}$), 150.83 (m, $-C\mathrm{H}{=}C\mathrm{H}-$). GPC: $M_w = 9200$; PDI = 1.25; $x = 45$. TGA: 10% weight loss at 490 °C. DSC: $T_g = -62$ °C. Anal. Calcd for $\mathrm{C_{10}H_{22}Si_2}$: C, 60.61; H, 11.11. Found: C, 60.26; H, 10.49.

Results and Discussion

To find the optimum conditions for an effective and selective polycondensation, catalytic screenings were made in the presence of various ruthenium complexes that initially contain or generate in situ Ru−H and Ru−Si bonds, using the model process of bis(vinyldimethylsilyl)methane (**1**). Silane conversion and the yields of dimers, trimers and higher oligomers were measured using GC−MS and GPC methods. The results are compiled in Table 1.

Conversion of monomer **1** and distribution of products in time of polycondensation catalyzed by [RuHCl(CO)-

Scheme 2. General Scheme of Silylative Coupling (SC) Polycondensation of Divinyl-Substituted Carbosilanes in the Presence of Catalyst (II) and/or (III)



	n	y + z
(**5**)	1	53
(**6**)	2	42
(**7**)	3	40
(**8**)	4	42

Table 3. Polycarbosilanes Prepared via Silylative Coupling (SC) Polycondensation

polymer	yield (%)	M_w[a]	M_n[a]	PDI[b]	DSC T_g[c] (°C)	TGA/N_2[d] (°C)
5	83	8500	5860	1.45	−65	465
6	75	7300	5210	1.40	−67	468
7	79	7600	5350	1.42	−65	475
8	84	8400	5790	1.45	−68	487

[a] GPC M_w and M_n relative to polysiloxane. [b] Reaction mixture. [c] Temperature (°C) upon heating at 5 °C/min. [d] Temperature (°C) at which 10% weight loss occurs.

$(PPh_3)_3$] (**III**) performed under mild conditions (110 °C) in glass ampules are presented in Table 2.

The ^{1}H NMR and DEPT methods used could distinguish between *trans*-1,2- (**13**) and 1,1-isomers (**14**) of dimers observed in the first step of the reaction. If the reaction is catalyzed by [{$RuCl_2(CO)_3$}$_2$], *trans*-1,2-isomer (**13**) is yielded exclusively, but in the presence of ruthenium−phosphine catalyst (see Scheme 1), a mixture of **13** and **14** is found. A distribution of products **13** and **14** is confirmed by GC methods.

Synthesis and Characterization of Poly[bis(vinyldimethylcarbosilane)s]. α,ω-Bis(vinyldimethylsilyl)alkanes (**1**−**4**) in the presence of either [$RuCl_2(PPh_3)_3$] (**II**) or [$RuHCl(CO)(PPh_3)_3$] (**III**) undergo silylative coupling (SC) polycondensation to yield polymers **5**−**8** according to the Scheme 2. The polymer chemistry is clean with no side products being evident except pure ethylene and trace amounts of cyclic products. The molecular weight distribution of SC polycondensation is typically ∼2 as expected of step polymerization. The narrower distribution of polymers **5**−**8** is due to the loss of some low molecular weight fractions on purification (Table 3).

The thermal stability and extent of decomposition of polymers **5**−**8** is given in Table 3.

Thermal data for these polymers agree with literature values for similar products.[15]

The ^{13}C NMR and DEPT spectra of polymer **6** are given in Figure 1 and evidence the presence of both isomeric products (1,2- and 1,1-) in the polymer.

Figure 1 displays the quantitative ^{13}C NMR spectrum of the reaction mixture of polymer **6** containing 1,2- and 1,1-ethylene species. The carbon signals at 131.65 and 138.91 ppm represent the terminal vinylic groups in polymer. The signal at 156.18 ppm, characteristic of the SC polycondensation mechanism, comes from the quaternary carbon atom, and it is representative for all polymers **5**−**8**. The carbon signal at 150.88 ppm corresponds to the internal vinyl group. DEPT spectrum analysis has confirmed the presence of 1,1-disilyl isomers.

DSC was used to determinate the glass transition temperature (T_g) of the high molecular weight polymers **5**−**8** (Table 3). The polymers were characterized as having low glass transition temperatures, as expected for flexible systems incorporating the carbosilane linkage. For all polymers these transitions were reproducible. Melting transitions were not observed for the polymers below 200 °C.

The results of the thermogravimetric analysis of polymers **5**−**8** have shown their thermal stability. In the 50−400 °C range there is no change in the polymers mass.

The almost total weight loss observed for all polymers **5**−**8**, in nitrogen at about 500 °C, indicates a possibility of a few decomposition pathways fully consistent with the SC polycondensation mechanism. The less-defined unsaturated silicon polymers formed in various reactions such as thermal cross-linking, often reveal irregular structure, which enhances their thermal stability.[4d]

Synthesis of *trans*-Tactic Poly[(silylene—alkylene—silylene—vinylene)s]. Similarly to the previously reported silylative coupling polycondensation of divinyltetramethyldisilazane,[8c] the polycondensation of **1**−**4** in the presence of [{$RuCl_2(CO)_3$}$_2$] (**I**) occurs to give *trans*-tactic polymers **9**−**12** with a high stereoselectivity of 94−96% according to Scheme 3.

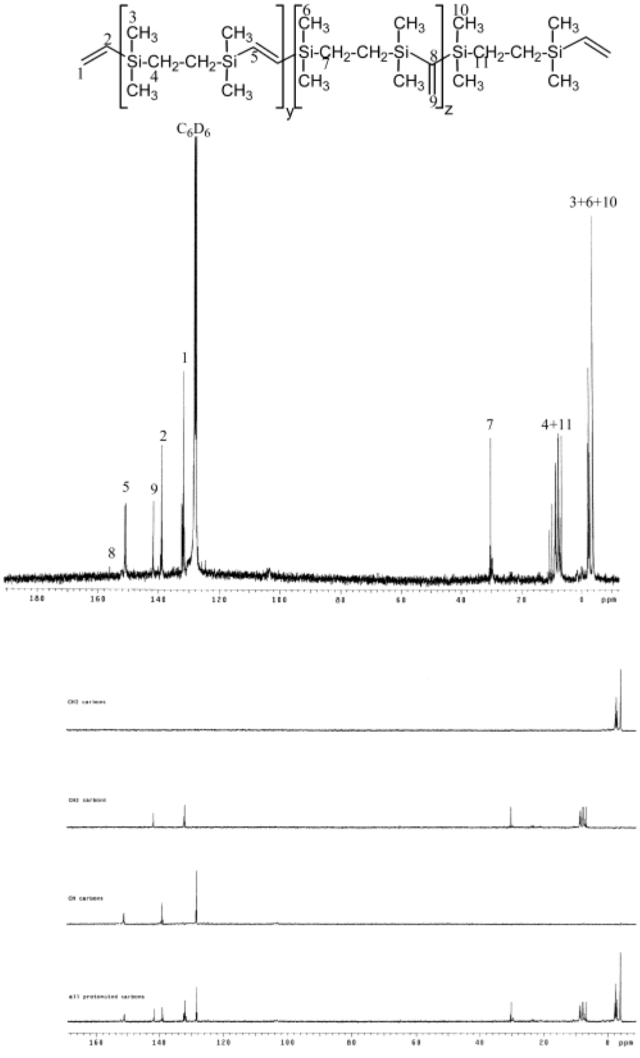
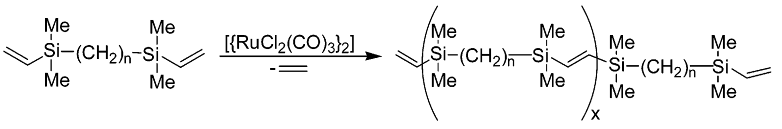


Figure 1. ^{13}C NMR and DEPT spectra of polymer **6**.

Scheme 3. General Scheme of Silylative Coupling (SC) Polycondensation of Divinyl-Substituted Carbosilanes in the Presence of Catalyst (I)



	n	x
(**9**)	1	53
(**10**)	2	42
(**11**)	3	40
(**12**)	4	42

Table 4. Polycarbosilanes Prepared via Silylative Coupling (SC) Polycondensation

polymer	yield (%)	M_w[a]	M_n[a]	PDI[b]	% trans	DSC T_g[c] (°C)	TGA/N_2[d] (°C)
9	78	9500	7040	1.35	95	−54	465
10	77	6200	5250	1.18	96	−54	468
11	77	7600	6280	1.21	94	−58	471
12	81	9200	7360	1.25	96	−62	490

[a] GPC M_w i M_n relative to polysiloxane. [b] Reaction mixture. [c] Temperature (°C) upon heating at 5 °C/min. [d] Temperature (°C) at which 10% weight loss occurs.

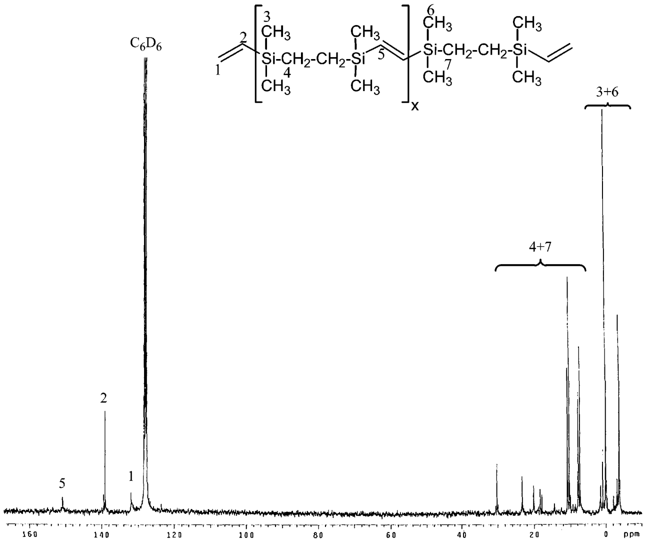


Figure 2. ^{13}C NMR spectrum of polymer **10**.

The polydispersity index and glass transition temperatures are given in Table 4.

Figure 2 displays the ^{13}C NMR spectrum of polymer **10**.

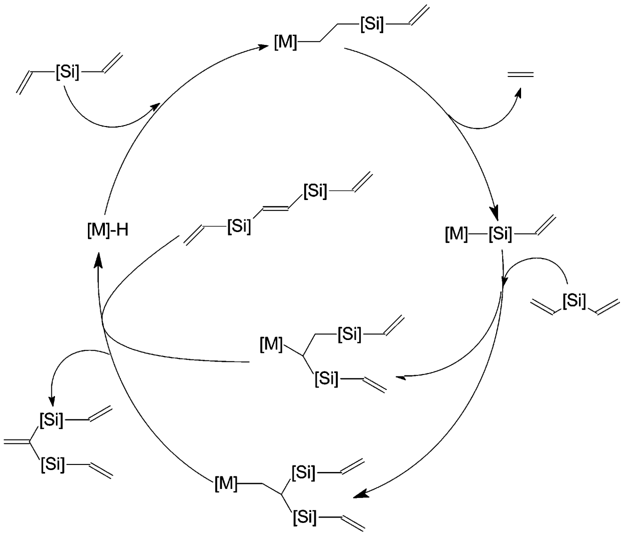
The average content of the *trans*-ethylene linkages contained in the carbosilane repeat units is constant and, as proved by the results ^1H NMR and ^{13}C NMR spectroscopies, the polymer contains only one geometric isomer identified as the *E*-isomer. The signal at 151.34 ppm (in the ^{13}C NMR spectrum) corresponds to the 1,2-*trans* isomer. The quaternary carbon atom is not observed in the ^1H NMR and ^{13}C NMR spectra.

For the polymers with a high content of *trans*-isomer, no melting transition was observed.

The results of the thermal gravimetric analysis of the nitrogen-exposed product (**10**) indicated a much greater loss in thermal stability of this polymer starting from 380 °C. Polymer **12** decomposes as expected in high temperatures. Nearly 10% of the material remains at temperatures exceeding 500 °C.

Mechanistic Implications. The mechanistic pathways of silylative coupling of monovinylsilanes are well-established,[11] and exemplary schemes for condensation of divinyl-substituted silicon compounds has been given earlier for divinyldimethylsilane,[8a] divinyltetramethyldisiloxane,[8b] and divinyltetramethyldisilazane[8c] as well as 1,4-bis(vinyldimethylsilyl)benzene[8d] and 4-(dimethylvinylsilyl)styrene.[8e] A condensation (dimerization) of vinyl-substituted carbosilanes is summarized in Scheme 4.

Scheme 4. Catalysis of the Dimerization of Divinyl-Substituted Carbosilanes in the Presence of [{$RuCl_2(CO)_3$}$_2$] (I) and [$RuHCl(CO)(PPh_3)_3$] (III)



[Si] = $-(CH_3)_2Si-(CH_2)_n-Si(CH_3)_2-$,

n = 1 - 4

The mechanism of catalysis involves the insertion of the vinyl-silicon dienes into the M−H and M-Si bonds, followed by β-Si and β-H elimination to yield ethene and two isomeric *trans*- and *gem*-bis(vinylsilyl)ethenes, respectively. If the process is catalyzed by [{$RuCl_2(CO)_3$}$_2$] (**I**), *trans*-$CH_2{=}CH[Si]CH{=}CH[Si]CH{=}CH_2$ is exclusively formed. Under the optimum conditions, the well-defined *trans*-tactic silylene−alkylene−silylene−vinylene polymers **9**−**12** can be effectively formed. When the reaction is catalyzed by ruthenium phosphine complexes, e.g., [$RuHCl(CO)(PPh_3)_3$] (**III**), the following cross-coupling polycondensation of both dimeric compounds gives linear polymers of **5**−**8**.

Conclusions

In the presence of ruthenium complexes as the catalysts α,ω-bis(vinyldimethylsilyl)alkanes (**1**−**4**) of the general formula $CH_2{=}CH(CH_3)_2Si(CH_2)_nSi(CH_3)_2CH{=}CH_2$ ($n = 1-4$) undergo silylative coupling (SC) polycondensation, giving linear polymers:

•If ruthenium−phosphine complexes, e.g., [$RuCl_2(PPh_3)_3$] (**II**) or [$RuHCl(CO)(PPh_3)_3$] (**III**) are used, the polycarbosilanes contain *trans*-1,2- and *gem*-1,1- fragments.

•If [{$RuCl_2(CO)_3$}$_2$] (**I**) is used, then highly stereoselective *trans*-tactic polymers **9**−**12** are yielded.

Because of steric hindrance of silyl groups in vinylsilanes, the linear products **5**−**8** and **9**−**12** cannot be synthesized via ADMET polymerization; this catalytic process opens a new synthetic route to silylene–alkylene–silylene–vinylene polymers of prospective importance as new materials of special application.

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