2818 *Macromolecules* **1997,** *30,* 2818−2824

Ethene and Propene Copolymers Containing Silsesquioxane Side Groups

Akira Tsuchida,[‡] Carsten Bolln,[†] Friedrich G. Sernetz,[†]
Holger Frey,*,[†] and Rolf Mülhaupt[†]

Institut für Makromolekulare Chemie und Freiburger Materialforschungszentrum (FMF) der Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Strasse 21/31, D-79104 Freiburg, Germany, and Department of Applied Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan

Received June 11, 1996; Revised Manuscript Received February 28, 1997[⊗]

ABSTRACT: The novel monovinyl-functional silsesquioxane cage 1-(9-decenyl)-3,5,7,9,11,13,15-heptaethylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane has been prepared and copolymerized with ethene and propene. The monovinyl-functional spherosiloxane was obtained from the octahydridosilsesquioxane $(HSiO_{3/2})_8$ via hydrosilation with dibrominated decadiene, followed by reaction of the nonreacted SiH groups with ethene, debromination, and chromatographic separation. Homopolymerization and copolymerization with ethene and propene was performed using different methylalumoxane-activated metallocene catalysts. Depending on catalyst structure comonomer incorporation between 17 and 25 wt % was achieved. High molar mass copolymers were obtained containing pendant octasiloxane cubes. Characterization by ^{13}C, ^{1}H, and ^{29}Si NMR spectroscopy confirmed that the catalyst did not modify the Si−O−Si framework. Incorporation up to 25 wt % (1.2 mol %) of the spherosiloxane-based monomer accounted for a decrease of the melting temperature by 18 K with respect to polyethene. As demonstrated by means of thermal gravimetric analysis, thermostability under air was improved in the polyethene copolymer in comparison to polyethene.

Introduction

Spherosiloxanes, inorganic cage molecules consisting of a silicon−oxygen-based framework, continue to fascinate both inorganic chemists and materials scientists. These compounds belong to the class of silsesquioxanes, which are generally characterized by the composition $(RSiO_{3/2})_n$, in which R is an organic group or hydrogen. Silsesquioxanes are interesting building units for organic−inorganic hybrid materials, in which the incorporated inorganic segment is expected to contribute to unusual properties, such as thermal stability and abrasion resistance. Silsesquioxanes have also been considered as molecular silicate units and possess analogies with structures found in zeolites.[1,2]

The cube-shaped molecule 1,3,5,7,9,11,13,15-octahydridopentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**1**), referred to as H_8T_8, is well characterized and available in reasonable yields via the synthetic route described by Agaskar et al.[3] Various substitution methods[4−8] for H_8T_8 have been developed. Hydrosilation of H_8T_8 can be conveniently employed to prepare substituted derivatives with different degrees of functionalization. Highly cross-linked thermosets[9,10] as well as linear polymers with main chain silsesquioxane units[11−13] or silsesquioxane side groups[11,14,15] have been synthesized. Brown and Vogt discovered incompletely condensed silanols and demonstrated that the trisilanols can be corner-capped with silanes.[18] This elegant route to mono- and difunctional T_8 units was further developed by Feher et al.[16,17] and also described by Lichtenhan et al.[11,14,15,19−20] In these works, after controlled hydrolysis of cyclopentyl-, cyclohexyl-, or cycloheptyltrichlorosilane, a T_8 precursor compound with exactly one missing corner with the composition $(cy)_7Si_7O_9(OH)_3$ was obtained. Subsequently, this trisilanol was mono- or difunctionalized by "corner-capping" with a trichlorosilane bearing the desired functional moiety. However, in this case the silsesquioxane unit is substituted by large organic groups.

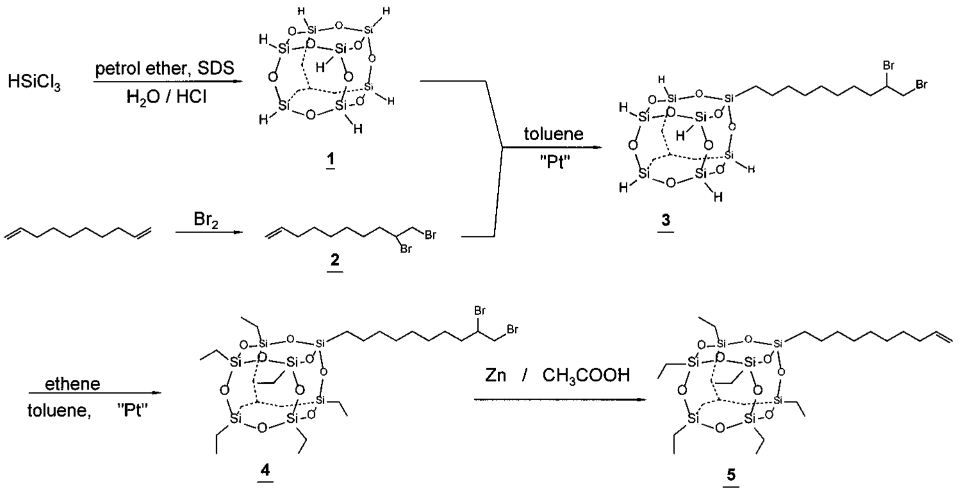
Our interest is centered on metallocene-catalyzed polymerization of 1-alkenes as well as copolymerization of 1-alkenes with ethene and propene. Consisting of only one type of catalytically active center, metallocene catalysts, in contrast to conventional Ziegler−Natta catalysts, are able to produce copolymers with narrow molar mass distribution and uniform comonomer distribution.[21−23] A well-known type of copolymer is linear low-density polyethene (LLDPE).[24] In order to modify the properties of LLDPE, it is of interest to copolymerize 1-alkenes with functional groups.[25] Different approaches have been used recently to employ functionalized monomers in the copolymerization of α-olefins.[26−30] There are no reports concerning LLDPE or other olefin copolymers with pendant silsesquioxane cubes.

The objective of this research was the preparation of monovinyl-functional spherosiloxanes as new class of comonomers useful in transition-metal catalyzed olefin copolymerizations. Attachment of T_8 substituted with alkyl groups as small as possible to a polymer chain appeared interesting to us. In this paper we describe the synthesis and copolymerization of 1-(9-decenyl)-3,5,7,9,11,13,15-heptaethylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]-octasiloxane (**5**, Scheme 1) with ethene and propene, using methylalumoxane (MAO) activated metallocenes zirconocene dichloride (Cp_2ZrCl_2) (**6a**), dimethylsilylenebis(indenyl)zirconocene dichloride ($Me_2Si(C_9H_6)ZrCl_2$) (**6b**), and dimethylsilylene(tetramethylcyclopentadienyl)-(*N-tert*-butyl)titanium dichloride ($Me_2Si(Me_4Cp)$(N-t-Bu)$TiCl_2$) (**6c**). These catalyst systems are well-known to produce homo- and copolymers of ethene or propene with higher α-olefins.[31−34] The copolymers were characterized with respect to comonomer incorporation of T_8 (^{1}H, ^{13}C, ^{29}Si NMR spectroscopy, IR), molar mass (GPC) and thermal properties (DTA, DSC, TGA).

[†] Albert-Ludwigs-Universität Freiburg.
[‡] Gifu University.
[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S0024-9297(96)00846-7 CCC: $14.00

Scheme 1. Synthesis of Monomer 5



Experimental Section

Materials. Triethoxysilane (Wacker), trichlorosilane (Aldrich), anhydrous ferric chloride, sodium dodecyl sulfate, calcium carbonate, potassium chloride, decadiene, powdered zinc, and bromine (all reagents obtained from Fluka), acetone and hydrochloric acid (Riedel-De-Haen), and trichloromethane and dichloromethane (Roth) were obtained in p.a. quality and used without further purification. Toluene (Roth) was extracted with concentrated sulfuric acid to remove thiophene and purified by distillation. Toluene employed for polymerization and hydrosilation reactions was purified by passing it through a column with acidic Al_2O_3, and it was distilled over $LiAlH_4$ and refluxed over Na/K alloy, from which it was freshly distilled prior to use. Cyclohexane was dried over CaH_2. For synthesis of H_8T_8 petroleum ether (technical grade), and for precipitation of the polymers methanol (technical grade) were used without purification. For column chromatography silica gel (Merck 60, 230−400 mesh) was employed. A solution of hexachloroplatinic acid (1 wt % Pt in diglyme) was used for hydrosilation reactions. Methylalumoxane (MAO) was provided by Witco GmbH as 10 wt.-% solution in toluene. Cp_2ZrCl_2 was obtained from Aldrich. Propene (polymerization grade) was supplied by BASF AG, ethene was supplied by GHC Gerling, Holz & Co. Handels GmbH.

Methods. ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker ARX 300 spectrometer operating at 300 MHz for ^1H, 75.4 MHz for ^{13}C and 59.6 MHz for ^{29}Si, using TMS as internal standard in $CDCl_3$ at ambient temperature. $C_2D_2Cl_4$ was used as solvent at 100 °C for the copolymer with ethene. IR spectra were measured with a Perkin-Elmer 1330 IR spectrometer. GC spectra were recorded with a GC 6000 Vega Series 2 controlled by an ICU 600 (Carlo Erba Instruments) using the following heating rates: start 60 °C, 20 °C/min to 100 °C (holding 1 min), and 20 °C/min to 300 °C (holding 5 min). Molar masses and molar mass distributions were determined by gel permeation chromatography (GPC). Homopolymer and propene copolymer were analyzed by a combination of 10^5, 10^3, and 100 nm PL columns (Polymer Laboratories), using toluene as solvent at ambient temperature. Molar masses are referenced to narrow polystyrene standards. The ethene copolymer was analyzed with a combination of AT-800P, AT-80 M/S 3x, and AT-807 S 1x (Shodex GPC columns), using 1,2,4-trichlorobenzene as solvent at 140 °C. Molar masses are referenced to narrow and broad polypropene. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-4 thermal analyzer at heating rates 9, 16, and 25 °C/min. Melting temperatures were obtained by extrapolation vs the square root of the heating rate to heating rate 0 as a reliable standard method for comparison of melting points. Thermogravimetric (TGA) investigations and differential thermo analysis (DTA) data were recorded on a Netzsch simultaneous thermo analysis (STA) 409 controlled by a Netzsch TASC 412/2 unit. Nitrogen- and air-atmosphere (flow: 150 cm^3/min) with a heating rate of 5 K/min were employed.

Synthesis of 1-(9-Decenyl)-3,5,7,9,11,13,15-heptaethylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane. The synthetic route to **5** is shown in Scheme 1. Homo- and copolymerization with ethene and propene are shown in Scheme 2. Unless noted otherwise, all manipulations were carried out under dry argon atmosphere.

Preparation of 1,3,5,7,9,11,13,15-Octahydridopentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (1). A 80 g (0.49 mol) sample of anhydrous $FeCl_3$, 40 mL of HCl_{conc} (37 wt % in water), 3 g (10 mmol) of sodium dodecyl sulfate, and 1500 mL of petroleum ether were stirred vigorously for 30 min using a magnetic stirrer. Under vigorous stirring, a solution of 80 mL (107.3 g, 0.79 mol) of $HSiCl_3$ in 800 mL of petroleum ether was added dropwise to the flask in the course of 10 h. After additional stirring for 30 min, the petroleum ether layer was separated, dried, and neutralized with Na_2CO_3 and $CaCl_2$. Subsequent to filtration, the petroleum ether was reduced to a residual volume of 200 mL. After 30 min the precipitated crystals were collected and thoroughly washed with petroleum ether (2.5 mL × 4): yield 7.81 g (18.6%). ^1H NMR ($CDCl_3$): δ 4.23 ppm (s, Si−H). ^{29}Si NMR ($CDCl_3$): δ −84.70 ppm. MS(EI): *m/z* 424 (100%) [M^+].

Preparation of 9,10-Dibromo-1-decene (**2**). Under ambient conditions 27.9 g (175 mmol) of bromine in 10 mL of $CHCl_3$ was added to a solution of 24.2 g (175 mmol) of decadiene in 25 mL of $CHCl_3$. After evaporation of the solvent, the residue was distilled twice under reduced pressure: bp 90 °$C_{0.1\ mbar}$; yield 16.1 g (31%). ^1H NMR ($CDCl_3$): δ 1.21−2.23 (m, $-CH_2-$, 12 H), 3.54−3.91 (m, CH_2Br, 2 H), 4.06−4.24 (m, CHBr, 1 H), 4.84−5.07 (m, $C{=}CH_2$, 2 H), 5.70−5.91 (m, C=CH−C, 1 H).

Preparation of 1-(9,10-Dibromodecanyl)-3,5,7,9,11,13,-15-heptahydridopentacyclo[9.5.1. 1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**3**). A 10.4 g (24.5 mmol) sample of **1** and 7.62 g (25.6 mmol) of **2** were dissolved in 400 mL of dry cyclohexane. Then 50 μL of platinum catalyst solution were added and the solution was refluxed for 72 h. Every 24 h, 50 μL of Pt catalyst was added to continue the reaction. The reaction was terminated after disappearance of the signals for the terminal vinyl protons in ^1H NMR spectrum. After the reaction was cooled to room temperature, 4.1 g (9.7 mmol) of unreacted H_8T_8 was collected by filtration of the cyclohexane solution. Subsequent to evaporation of the solvent, from the residual viscous oil another portion of 1.2 g (2.8 mmol) unreacted H_8T_8 could be isolated. The crude product was used without further purification. ^1H NMR ($CDCl_3$): δ 0.70 (q, Si−CH_2, 2H), 1.21−2.23 (m, CH_2), 3.62 and 3.84 (m, CH_2Br, 2 H), 4.17 (m, CHBr, 1 H), 4.2−4.3 ppm (m, SiH, 7H). IR (KBr): 2930, 2880 (ν_{H-C-H}), 2270 (ν_{Si-H}), 1433, 1375, 1255 (ν_{Si-C}), 1120 (ν_{Si-O}), 965, 875, 840, 785, 715, 645, 570, 460, 390 cm^{-1} (ν_{Si-O}).

Preparation of 1-(9,10-Dibromodecanyl)-3,5,7,9,11,13,-15-heptaethylpentacyclo[9.5.1.1^{3,9}. 1^{5,15}.1^{7,13}]octasiloxane (**4**). The viscous reaction product from the previous step containing **3** was transferred to a 250 mL two-necked flask

Scheme 2. Oligomerization of 5 and Copolymerization of 5 with Ethene and Propene

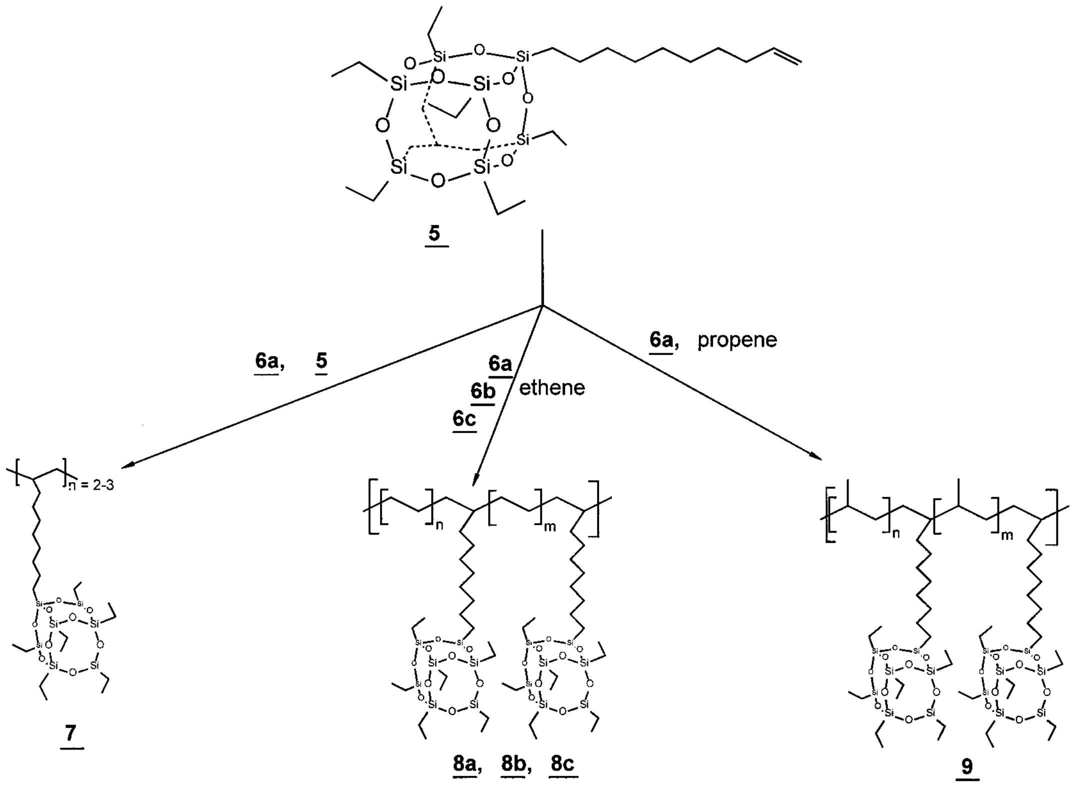


Table 1. Copolymerization of Decenyl-Functionalized Silsesquioxane (5) with Ethene and Propene Using Methylalumoxane-Activated Metallocene Catalysts[a]

run[a]	**5** concn (mol/L)	ethene pressure (bar)	propene pressure (bar)	t (h)	yield (g)	catalyst activity[b]	comonomer in the copolymer mol %	comonomer in the copolymer wt %	T_g (°C)	T_m (°C)	ΔH (J/g)	M_w	M_w/M_n
1	0.021			12	0.2	19	100	100				1500	
2	0.053		0.8	12	9.7	637	1.1	17.0	−40			3300	1.5
3	0.016	0.8		0.25	1.1	6750	0.7	17.2		125.0	n.d.	203000	6.4
4	0.006	0.8		0.08	0.8	17800	0.9	19.6		123.5	101	318000	3.3
5	0.016	0.8		2	1.1	834	1.2	24.5		115.0	77	234000	1.9

[a] Catalysts: runs 1−3, zirconocene dichloride (Cp_2ZrCl_2)/MAO; run 4, dimethylsilylenebis(indenyl)zirconocene dichloride ($Me_2Si(C_9H_6)ZrCl_2$)/MAO; run 5, dimethylsilylene(tetramethylcyclopentadienyl)(*N*-*tert*-butyl)titanium dichloride ($Me_2Si(Me_4Cp)(N\text{-}t\text{-}Bu)TiCl_2$)/MAO. Polymerization conditions: [cat] = 100 μmol/L, Al:Zr or Ti = 1000, total volume = 50 mL, ambient temperature. [b] Activity in [kg polymer/mol Ti·h·mol/L].

and dried in vacuo. Then 100 mL of dry toluene and 50 μL of Pt catalyst solution were added. The solution was refluxed under stirring and saturated with a continuous flow of ethene. Another 50 μL of Pt catalyst solution was added after 24 h to continue the reaction. The disappearance of the Si−H bond (ν = 2250 cm^{-1}) was confirmed by IR spectroscopy. After removal of the solvent, the remaining product solidified during cooling. The crude product still contained isomerized **2** which was removed by washing with hot methanol (20 mL × 5) and decantation after cooling. Finally the solid product was dried in vacuo. No further purification was carried out. ^1H NMR ($CDCl_3$) beside other peaks: δ 0.60 (q, Si−CH_2, 16H), 0.98 (t, CH_3, 21 H), 1.20−2.24 (m, CH_2), 3.62 and 3.84 (m, CH_2Br, 2 H), 4.17 ppm (m, CHBr, 1 H). IR (KBr): 2960, 2920, 2880, 2860, (ν_{H-C-H}), 1460 (ν_{CH_3}), 1430, 1255 and 1230 (ν_{Si-C}),, 1120 (ν_{Si-O}), 1010, 965, 880, 800, 760, 695, 645 (ν_{C-Br}), 550, 465, 390 cm^{-1} (ν_{Si-O}).

Preparation of 1-(9-Decenyl)-3,5,7,9,11,13,15-heptaethylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**5**). The complete portion of **4** from the previous step was transferred into a 100 mL two-necked flask and 3.0 g (45.9 mmol) of powdered zinc and 40 mL of acetic acid were added. The reaction mixture was refluxed for 4 h. Acetic acid was removed under reduced pressure and the residue was washed with acetone and successively with dichloromethane. A yield of 6.8 g of crude product obtained after drying was purified by column chromatography, using petroleum ether:toluene (20:1) as eluant. By collection of all fractions with a R_f value of 0.45 (silicagel-TLC; monitoring with iodine chamber), **5** was obtained as a white solid: mp 67.5 °C; yield 3.9 g (43% based on H_8T_8). ^1H NMR ($CDCl_3$): δ 0.59 (q, Si−CH_2, 16H), 0.98 (t, CH_3, 21 H), 1.21−1.47 (m, CH_2, 12 H), 1.95−2.09 (q, =CH−CH_2, 2 H), 4.88−5.02 (m, C=CH_2, 2 H), 5.70−5.88 ppm (m, C=C*H*−C, 1 H). ^{13}C NMR ($CDCl_3$): δ 4.08 (Si−CH_2−CH_3), 6.51 (Si−CH_2−CH_3), 11.89 (Si−CH_2−), 22.78 (CH_2), 29.0 (CH_2), 29.18 (CH_2), 29.24 (CH_2), 29.39 (CH_2), 32.58 (CH_2), 33.86 (CH_2), 114.10 (CH_2=CH−), 139.20 ppm (=CH−). ^{29}Si NMR ($CDCl_3$): δ −65.68 (Si−Et, 3 Si), −65.79 (Si−Et, 4 Si), −66.29 ppm (Si−Dec, 1 Si). IR (KBr): 3070 ($\nu_{C=C-H}$), 2960, 2920, 2880, 2850, 2740 (ν_{H-C-H}), 1640 ($\nu_{C=C}$), 1460 (ν_{CH_3}), 1410, 1250, 1230, (ν_{Si-C}), 1120 (ν_{Si-O}), 1015, 960, 800, 755, 695, 535, 465, 390 cm^{-1} (ν_{Si-O}). Anal. Calcd for $C_{24}H_{54}Si_8O_{12}$: C, 37.99; H, 7.18. Found: C, 40.02; H, 7.62.

Polymerization. Experimental details for all polymerizations are summarized in Table 1. Homo- and copolymerizations were carried out in a 100 mL Schlenk flask, which was filled with **5**, toluene, and part of the methylalumoxane (MAO). Subsequently, argon was removed by evacuation and the reaction mixture saturated with either ethene or propene, respectively, which was then kept under a constant flow. The catalyst (**6a**, **6b**, or **6c**) was dissolved in 10 wt % MAO toluene solution and then injected into the reactor for an in situ start of the copolymerization. The following polymerization conditions were used: [catalyst] = 100 μmol/L, Al:Zr or Ti = 1000, *P*(ethene) = *P*(propene) = 0.8 bar, *T* = 25 °C. The further procedure after termination of the polymerization is described in the following.

Homopolymer 7 (Run 1). The toluene solution was poured into 500 mL of acidic methanol to dissolve the catalyst system. The white precipitate formed was collected by filtration. The filter cake was washed with hot methanol (40 mL × 4) and dried under reduced pressure. After drying, the methanol-soluble part was 60 mg, still containing some oligomer **7**, while the methanol-insoluble part was 240 mg, still containing a trace of monomer **5**. Yield: 240 mg (30%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.57 (q, $\mathrm{Si{-}C\mathit{H}_2{-}CH_3}$, 28H), 0.97 (t, $\mathrm{CH_3}$, 42 H), 1.18−1.46 (m, $\mathrm{CH_2}$, 32 H), 1.97 (q, $\mathrm{{=}C(C\mathit{H}_2)_2}$, 4 H), 4.66 ppm (s, $\mathrm{{=}C\mathit{H}_2}$, 2 H). IR (KBr): 3065 ($\nu_{\mathrm{C{=}C{-}H}}$), 2955, 2915, 2850, 2740 ($\nu_{\mathrm{H{-}C{-}H}}$), 1640 ($\nu_{\mathrm{C{=}C}}$), 1465 ($\nu_{\mathrm{CH_3}}$), 1410, 1250, 1230 ($\nu_{\mathrm{Si{-}C}}$), 1120 ($\nu_{\mathrm{Si{-}O}}$), 1015, 960, 800, 760, 698, 535, 465, 390 cm^{-1} ($\nu_{\mathrm{Si{-}O}}$). Anal. Calcd for $\mathrm{C_{24}H_{54}Si_8O_{12}}$: C, 37.99; H, 7.18. Found: C, 39.98; H, 7.37.

Copolymers 8a−c (Runs 3−5). Immediately after the copolymerization was started in an analogous manner as in the case of **7**, the reaction mixture became turbid and the viscosity increased. After 15 min the toluene solution was poured into 250 mL of diethyl ether containing 50 mL of methanol and hydrochloric acid. After filtration, the white product was dried to constant weight in vacuo. Removal of remaining traces of monomer **5** in the product was achieved by Soxhlet extraction with cyclohexane for 36 h; yield 1.08 g. ^{1}H NMR ($\mathrm{C_2D_2Cl_4}$, 373 K): δ 0.58 (q, $\mathrm{Si{-}C\mathit{H}_2{-}CH_3}$, 14H), 0.95 (t, $\mathrm{Si{-}CH_2{-}C\mathit{H}_3}$, 21H), 1.25 (s, PE-chain, 507 H, and $\mathrm{CH_2}$-spacer of **5**, 16 H). ^{13}C NMR ($\mathrm{C_2D_2Cl_4}$, 373 K): δ 4.10 ($\mathrm{Si{-}\mathit{C}H_2{-}CH_3}$), 6.16 ($\mathrm{Si{-}CH_2{-}\mathit{C}H_3}$), 12.01 ($\mathrm{Si{-}\mathit{C}H_2{-}R}$, C^1 of spacer), 18.58 (polymer chain endgroup), 22.8 ($\mathrm{Si{-}CH_2{-}\mathit{C}H_2{-}R}$, C^2 of spacer), 27.0 ($\mathrm{R_2CH{-}CH_2\mathit{C}H_2{-}}$), 29.65, 30.17 (PE-chain and C^4−C^7 of spacer), 31.88 (polymer chain endgroup) 32.50 (C^3 of spacer), 34.29 ($\mathrm{R_2CH{-}\mathit{C}H_2}$), 38,00 ($\mathrm{PE{-}R\mathit{C}H{-}PE}$), 40.71 ppm (polymer chain endgroup). IR (KBr): 2960, 2850 ($\nu_{\mathrm{H{-}C{-}H}}$), 1468 ($\nu_{\mathrm{CH_3}}$), 1412, 1370, 1255, 1230 ($\nu_{\mathrm{Si{-}C}}$), 1115 ($\nu_{\mathrm{Si{-}O}}$), 1015, 760, 718, 700, 540, 470, 390 cm^{-1} ($\nu_{\mathrm{Si{-}O}}$). Anal. Calcd for PE: C, 85.63; H, 14.37. Found: C, 78.09; H, 13.49.

Copolymer 9 (Run 2). 2-Propanol (10 mL) was added to the toluene solution to terminate the reaction. After solvent removal, the viscous residue was dissolved in 200 mL of petroleum ether and washed with dilute hydrochloric acidic (20 mL × 3). After removal of petroleum ether under reduced pressure, 10.2 g of a viscous liquid was obtained. In order to separate remaining monomer **5** from the copolymer, 40 mL of acetone was added to the product. The mixture was heated briefly. After cooling to room temperature, the acetone-soluble part was separated from the insoluble part by centrifugation. This procedure was repeated twice. After solvent removal and drying, the acetone-insoluble fraction (**9a**) yielded 4.27 g of a turbid, viscous reaction product. The acetone-soluble part (**9b**) consisted of 5.40 g of a clear viscous liquid. ^{1}H NMR of **9a** ($\mathrm{CDCl_3}$): δ 0.59 (q, $\mathrm{Si{-}C\mathit{H}_2{-}}$, 3.1 H), 0.81 (m, $\mathrm{CH(C\mathit{H}_3)}$ in PP, 54 H), 0.97 (t, $\mathrm{Si{-}CH_2{-}C\mathit{H}_3}$, 3.1 H), 1.13 ($\mathrm{CH_2}$ in PP, 38 H), 1.24 ($\mathrm{CH_2}$ in spacer, 3.5 H), 1.58 (m, CH, 19 H), 1.67 (s, $\mathrm{{=}C{-}CH_3}$, 3H), 1.9−2.08 (m, $\mathrm{{=}C{-}CH_2{-}}$, 2H), 4.63 (s) and 4.71 (s) ppm ($\mathrm{{=}CH_2}$, 2H). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 4.06 ($\mathrm{Si{-}\mathit{C}H_2CH_3}$), 6.51 ($\mathrm{Si{-}CH_2{-}\mathit{C}H_3}$), 11.9 ($\mathrm{Si{-}\mathit{C}H_2{-}R}$), 14.4 ($\mathrm{CH_3}$ of propyl end-group), 18.9−21.4 ($\mathrm{CH_3}$ in PP), 22.23 ($\mathrm{{=}C(CH_3){-}\mathit{C}H_2{-}}$), 22.77 ($\mathrm{Si{-}CH_2{-}\mathit{C}H_2{-}R}$), 26.9−27.8 (CH in PP), 27.86 (CH at propyl end-group), 29.3−29.9 (C^3 - C^7 in spacer), 35.29 ($\mathrm{PP{-}\mathit{C}H(CH_2R){-}PP}$), 40.47 ($\mathrm{PP\text{-}CH(\mathit{C}H_2R)\text{-}PP}$), 43.7−57.4 ($\mathrm{CH_2}$ in PP), 111.28 ($\mathrm{{=}CH_2}$ of PP end group), 144.78 ppm ($\mathrm{{=}CH(CH_3)}$ of PP end-group). ^{29}Si NMR ($\mathrm{CDCl_3}$): δ −65.49 (Si-Et, 3 Si), −65.60 (Si−Et, 4 Si), 66.07 (Si−Dec, 1 Si). IR (neat): 3060 ($\nu_{\mathrm{C{=}C{-}H}}$), 2910, 2875, 2845, 2725 ($\nu_{\mathrm{H{-}C{-}H}}$), 1650 ($\nu_{\mathrm{C{=}C}}$), 1460 ($\nu_{\mathrm{CH_3}}$), 1415, 1378 1255 1230 ($\nu_{\mathrm{Si{-}C}}$), 1115 ($\nu_{\mathrm{Si{-}O}}$), 1015, 972, 988, 810, 760, 700, 540, 470, 390 cm^{-1} ($\nu_{\mathrm{Si{-}O}}$). Anal. Calcd for PP: C, 85.63; H, 14.37. Found: C, 77.86; H, 11.75.

Results and Discussion

Monomer Synthesis. The synthesis of the monofunctionalized monomer **5** was achieved via five steps as shown in Scheme 1. The cubic hydridospherosiloxane 1,3,5,7,9,11,13,15-octahydridopentacyclo-[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**1**) (O_h-$\mathrm{H_8Si_8O_{12}}$ or $\mathrm{H_8T_8}$) was prepared according to the method of Agaskar and Desu by controlled hydrolysis of $\mathrm{HSiCl_3}$.[3,35] We were able to obtain pure $\mathrm{H_8T_8}$ in good yields (18%) via a slightly modified procedure, using petroleum ether instead of the solvent mixture of toluene, methanol, and hexane isomers described by Agaskar.[3] It should be mentioned that partial solvent removal permitted us to isolate $\mathrm{H_8T_8}$ by fractionation crystallization and enabled us to separate it from a mixture containing $\mathrm{H_8T_8}$ and $\mathrm{H_{10}T_{10}}$.

In order to protect one double bond, decadiene was partially brominated to yield 9,10-dibromo-1-decene (**2**). Subsequently, **2** was hydrosilated with $\mathrm{H_8T_8}$ to obtain 1-(9,10-dibromodecyl)-3,5,7,9,11,13,15-heptahydridopentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**3**) in a similar manner as reported before.[36] The disappearance of the terminal vinyl protons of **2** was confirmed by monitoring the reaction with ^{1}H NMR spectroscopy. Unfortunately, during this reaction step, isomerization of approximately 50% of the terminal vinyl bonds (12.8 mmol) of **2** to internal double bonds was always observed as a side reaction of hydrosilation. The isomerized double bond could clearly be distinguished from the terminal vinyl group of **2** in the ^{1}H NMR spectrum (5.4 ppm). On the other hand, 51% of $\mathrm{H_8T_8}$ were recovered after the reaction, thus the actual molar ratio of $\mathrm{H_8T_8}$:**2** was 1:1.02. It should be noted, that although isomerization of double bonds as a side reaction of hydrosilation is well-known, 50% isomerization was unexpectedly high. $\mathrm{H_8T_8}$ seemed to promote the isomerization reaction. This result was observed by us in other $\mathrm{H_8T_8}$-substitution reactions too.[37]

The product of the third step was successively used for the synthesis of 1-(9,10-dibromodecyl)-3,5,7,9,11,13,-15-heptaethylpentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]octasiloxane (**4**) without purification, because isomerized **2** was no longer reactive to the Si−H bond. In the fourth step all remaining Si−H bonds of the hydridospherosiloxane were concerted to $\mathrm{Si{-}C_2H_5}$ by hydrosilation with ethene in order to eliminate reactive SiH groups, which impede separation of the monofunctional $\mathrm{T_8}$ derivative by chromatography. Furthermore, nonalkylated $\mathrm{T_8}$ was expected to interact with the metallocene catalyst employed for the ensuing copolymerization. After completion of the ethylation, which was monitored by following the disappearance of the SiH vibration in IR, isomerized **2** was separated and subsequently **4** debrominated with Zn/$\mathrm{CH_3COOH}$ to obtain monomer **5.** After chromatography, **5** was obtained in 43% yield with respect to $\mathrm{H_8T_8}$ used.

Monomer **5** was characterized by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy as well as IR-spectroscopy and elemental analysis. The signal pattern observed in the ^{29}Si NMR spectrum (Figure 1, top) is in agreement with the general pattern for hetero-1:7-substituted spheric $\mathrm{T_8}$ derivatives ($\mathrm{R_7R'Si_8O_{12}}$), described by Marsmann[38] recently. Three signals with signal ratio 1:3:4 evidence monosubstitution. Silicon **a** (66.29 ppm) bearing the decenyl group (1 Si), the silicon atoms **b** (−65.68 ppm) in the neighborhood of the former (3 Si), and the silicon atoms which occupy the face-diagonal (**c**) and the body-diagonal (**d**) corners to silicon **a**. The signals for **c** and **d** can not be distinguished in the ^{29}Si NMR spectrum; they appear as one signal (−65.79 ppm). The ^{13}C NMR spectrum (Figure 1, middle) shows large signals for the seven ethyl groups (4.08 and 6.51 ppm) as well as

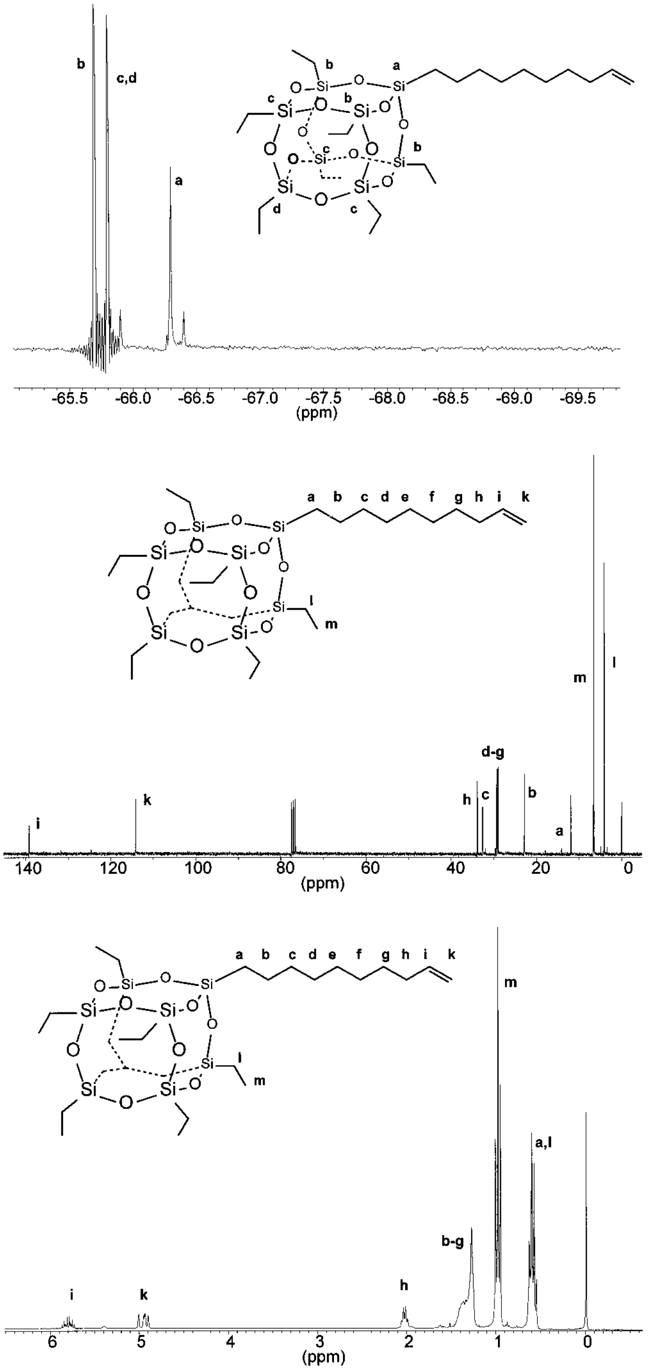


Figure 1. ^{29}Si NMR spectrum (top), ^{13}C NMR spectrum (middle), and ^{1}H NMR spectrum (bottom) spectra of monomer **5**.

signals for the terminal vinyl bond (114.1 and 139.2 ppm) and eight signals for the $(CH_2)_8$ spacer of the decenyl group (11.89–33.86 ppm). The ^{1}H NMR spectrum (Figure 1, bottom) supplements characterization of **5**.

Polymerizations. Polymerizations as shown in Scheme 2 were carried out under dry argon atmosphere, using Schlenk flasks. Different MAO-activated metallocene catalysts were used as explained in Table 1. Reaction times and other conditions employed are summarized in Table 1. The further procedure concerning workup of the resulting copolymers was different in each case. Homopolymerization as well as copolymerization experiments with ethene and propene, respectively, have been performed.

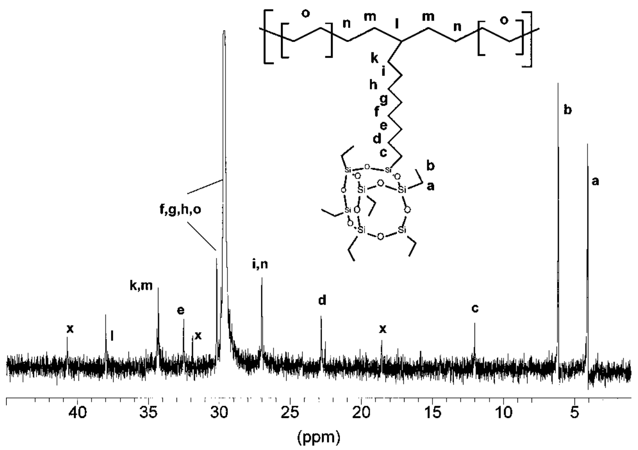


Figure 2. ^{13}C NMR spectrum of copolymer **8b**, poly(ethene-*co*-**5**).

Table 2. Calculation of the Number of 5 Units per Polymer Chain for Poly(ethene-*co*-5)s from Runs 3–5

run	M_n	**5** content (mol %)	no. of comonomer **5** units per polymer chain
3	32 000	0.7	1.2
4	96 000	0.9	3.6
5	123 000	1.2	4.3

Homopolymerization of **5** yielded oligomers with an average degree of polymerization of 2–3, as clearly derived from the ratio of terminal vinyl protons and ethyl protons in the ^{1}H NMR spectrum. Copolymerizations of **5** with ethene (Table 1, runs 3–5) and propene (Table 1, run 2) clearly led to incorporation of **5** into the polyethene and polypropene chains, respectively, reaching up to 24.5 wt % **5** incorporated into poly(ethene-*co*-**5**). Calculation of the number of **5** units per polymer chain (Table 2) revealed an average of four comonomeric units per copolymer chain in runs 4 and 5. This confirms predominately incorporation of **5** into the polymer chain with respect to possible chain termination by **5**.

The catalyst productivity was hardly affected. Evidently, the ethyl groups shield T_8 sufficiently to prevent coordination reactions with catalyst and cocatalyst. In the case of poly(ethene-*co*-**5**) the ^{13}C NMR spectrum (Figure 2) shows that isolated T_8-units were incorporated, as expected for random copolymers containing 0.7–1.2 mol % **5**. Due to the different conditions used for the NMR spectra of **5** and the copolymer **8** ($C_2D_2Cl_4$ as solvent and higher temperature, 100 °C) the peaks are shifted slightly in comparison to the spectrum of **5**. The signals at 12.01 ppm (C^1 in spacer), 22.80 ppm (C^2 in spacer), and 32.47 ppm (C^3 in spacer) and for a part of the $(CH_2)_x$ spacer are unchanged after polymerization, similar to the peaks for the ethyl group at 4.10 and 6.16 ppm. The latter are substantially larger than the resonances of the decenyl carbons, as also observed in the spectrum of **5**. A part of the $(CH_2)_x$ spacer of **5** leads to signals in the same region of the spectrum as the polyethene chain at about 29.7 ppm. The vinyl resonances of **5** at 114.1 and 139.2 ppm as well as the signals due to the CH_2 unit adjacent to the vinyl group at 33.86 ppm disappeared. New peaks at 27.0 ($R_2CH-CH_2-CH_2$), 34.29 ($R_2CH_2-CH_2$), and 38.0 ppm (R_3CH) appear, due to the spacer attachment of **5** to the PE chain. Additional peaks at 18.64, 31.9, and 40.7 ppm might be a result of chain termination after the insertion of comonomer **5**. The content of **5** incorporated in

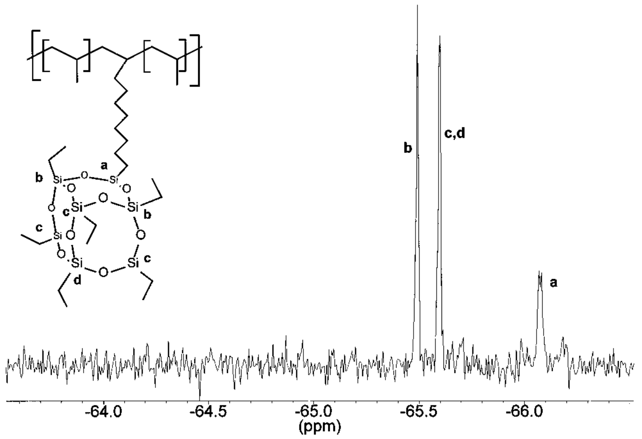


Figure 3. ^{29}Si NMR spectrum of copolymer **9**, poly(propene-*co*-**5**).

the copolymers was determined by ^{1}H NMR spectroscopy and elemental analysis showing that up to 24.5 mol % **5** were incorporated using **6c**/MAO. This catalyst is known for its high degree of incorporation of α-olefins.[34b]

The ^{29}Si NMR spectrum of the polypropene copolymer **9** (Figure 3) evidences that no rearrangement reaction of T_8 due to the Lewis acidic catalyst components took place. The catalyst employed led to atactic low molar mass oligopropene, which was obtained as a viscous liquid. The molar mass of **9** (poly(propene-*co*-**5**)) according to ^{1}H NMR spectroscopy was determined to be $M_n = 1000$; GPC analysis shows a low molar mass of $M_w = 2200$ with $M_w/M_n = 1.5$. Similar molar masses are commonly observed for copolymerizations of propene with 1-octene in the presence of Cp_2ZrCl_2, giving soluble polymers of low molar mass.[30]

Thermal Properties of the Copolymers. Poly(ethene-*co*-**5**) (**8**) resembles linear low density polyethene (LLDPE) in appearance, but its melting point (determined by DSC and DTA) is 7 K lower (125 °C) than the melting point of pure PE (132 °C). This is due to the structural irregularities, which are caused by the incorporated spherosiloxane-bearing monomer. The variation of the melting point may appear small; however, only 0.7 mol % of **5** was incorporated, leading to one pendant spherosiloxane every 140 monomer units in the copolymer chain. Poly(propene-*co*-**5**) (**9**) is a viscous liquid, with a T_g at -40 °C.

Copolymer **8** and **9** have been investigated with respect to their thermostability, **8** under nitrogen- and air-atmosphere (Figure 4) and **9** only under air atmosphere (Figure 5), using TGA. The thermostability was compared to that of pure PE and oligopropene, respectively.

Polyethene and poly(ethene-*co*-**5**) (**8**) show no difference in thermostability under N_2 (Figure 4, top), but under air the thermostability of **8** is superior (Figure 4, bottom). The TGA curve under air is shifted to higher temperatures. The weight increase observed at 220 °C under air is most probably due to elimination of ethyl groups and reaction of Si with oxygen. Similar effects were observed for T_8 substituted with 8 *n*-alkyl groups, such as *n*-octyl or *n*-decyl units, which were employed as model compounds.[39] Above 220 °C, the T_8 units are irreversibly linked, and the resulting material clearly shows an improved thermostability. Also copolymer **9** shows a slight increase of weight and a higher thermostability in air (Figure 5).

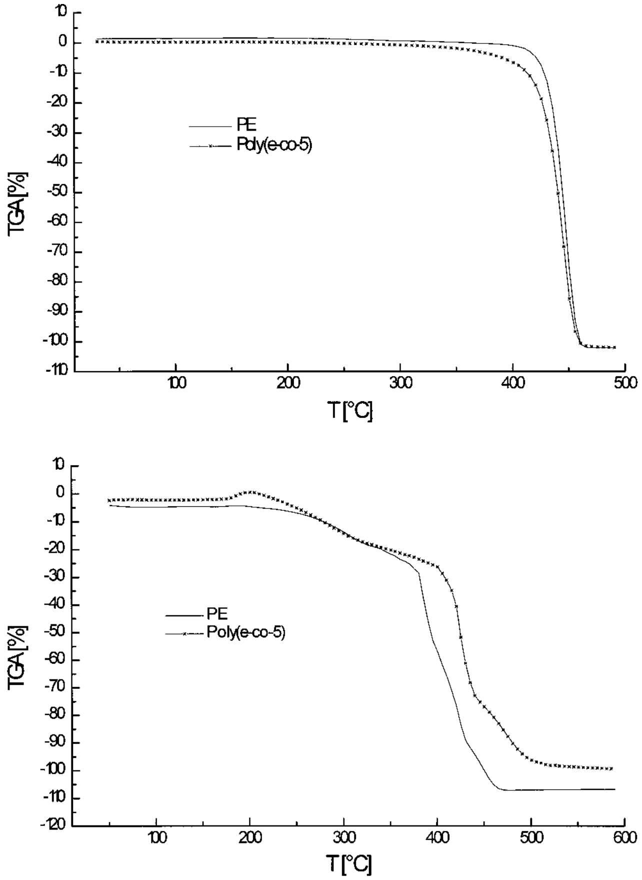


Figure 4. TGA-trace of PE and copolymer **8a** under N_2 atmosphere (top) and under air atmosphere (bottom).

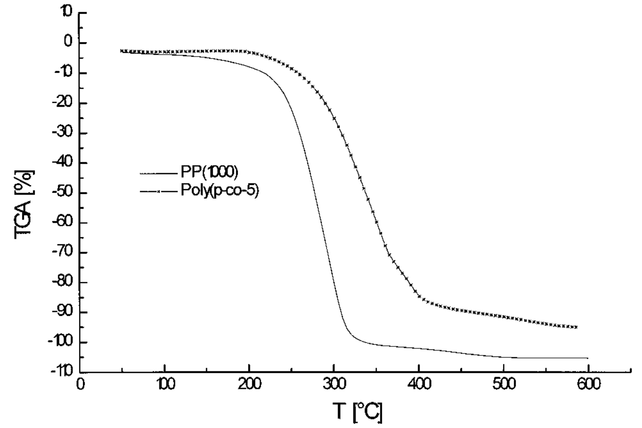


Figure 5. TGA-trace of PP and copolymer **9** under air atmosphere.

Conclusion

1-(9-Decenyl)-3,5,7,9,11,13,15-heptaethylpentacyclo-[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]octasiloxane (**5**) has been prepared via a five-step synthesis. H_8T_8 could be synthesized in a slightly simplified procedure according to the method of Agaskar. The yield of **5** with respect to H_8T_8 employed was 43%. Monomer **5** was incorporated into copolymers with ethene (**8a**–**c**) and propene (**9**) via metallocene catalysis, yielding the first example of copolymers with polyolefin main chain and silsesquioxane cages as side groups. ^{13}C NMR spectroscopy of poly(ethene-*co*-**5**) shows covalent incorporation of **5** into the copolymer with comonomer contents up to 24.5 mol %. ^{29}Si NMR spectroscopy confirms that **5** inserted without rearrangement of the cubic silsesquioxane part of **5** in spite of the Lewis acidic catalyst employed.

Thermal investigations of the copolymers showed that an increase of thermostability could be achieved.

The novel copolymers poly(ethene-*co*-**5**) and poly(propene-*co*-**5**) are interesting materials with respect to the effect of T_8 as a structural irregularity on the crystallization and morphology of polypropene and polyethene. Using *ansa*-metallocene catalysts, it was possible to improve molar masses and comonomer incorporation with respect to the unbridged catalyst Cp_2ZrCl_2/MAO.

Acknowledgment. F.G.S. is grateful for a fellowship by the Studienstiftung des deutschen Volkes and financial support by the BASF AG. A.T. as well as C.B. acknowledges support by the Graduiertenkolleg of the SFB 60. We also want to thank Wacker Chemie for providing triethoxysilane.

References and Notes

(1) Bärtsch, M.; Bornhauser, P.; Calzaferri, G.; Imhof, R. *J. Phys. Chem.* **1994**, *98*, 2817−2831.
(2) Feher, F. J.; Tajima, T. L. *J. Am. Chem. Soc.* ***1994***, *116*, 2145−2146.
(3) Agaskar, P. A. *Inorg. Chem.* **1991**, *30*, 2707−2708.
(4) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262−8264.
(5) Bürgy, H.; Calzaferri, G. *Helv. Chim. Acta* **1990**, *73*, 698−699.
(6) Agaskar, P.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554.
(7) Herren, D.; Bürgy, H.; Calzaferri, G. *Helv. Chim. Acta* **1991**, *74*, 24−26.
(8) Gentle, T.; Bassindale, A. R. *J. Inorg. Organomet. Polym.* **1995**, *5*, 281.
(9) Weidner, R.; Zeller, N.; Deubzer, B.; Frey, V. U.S. Pat. 5,047,492, 1991.
(10) Sellinger, A.; Laine, R. M. *Macromolecules* **1996**, *29*, 2327−2330.
(11) (a) Shockey, E.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36* (2), 525−526. (b) Haddad, T. S.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (1), 708−709.
(12) Mantz, R. A.; Jones, P. F.; Chaffee, K. P.; Lichtenhan, J. D.; Gilman, J. W.; Ismail, I. M. K.; Burmeister, M. J. *Chem. Mater.* **1996**, *8*, 1250−1259.
(13) Lichtenhan, J. D.; Mantz, R. A.; Jones, P. J.; Carr, M. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (1), 523−524.
(14) Haddad, T. S.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (1), 511−512.
(15) Lichtenhan, J. D.; Otonari, Y. A.; Carr, M. J. *Macromolecules* **1995**, *28*, 8435−8437.
(16) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741−1748.
(17) Feher, F. J.; Budzichowski, T. A.; Rahimian, K.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3859−3866.
(18) Brown, J. F.; Vogt,L. H. *J. Am. Chem. Soc.*, **1965**, *87*, 4313.
(19) (a) Shockey, E.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35* (1), 525−526. (b) Shockey, E.; Bolf, A. G.; Lichtenhan, J. D. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36* (1), 515−516.
(20) Lichtenhan, J. D. *Comments Inorg. Chem.* **1995**, *17*, 115−130.
(21) Chien, J. C. W.; He, D. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 1585.
(22) Kaminsky, W.; Noll, H. *Polym. Bull.* **1993**, *31*, 175.
(23) Herfert, N.; Montag, P.; Fink, G. *Makromol. Chem.*, **1993**, *194*, 3167.
(24) Tait, P. J. T.; Berry, I. G. *Comprehensive Polymer Science*; Eastwood, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 4, p 575.
(25) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem.* **1995**, *107*, 1255.
(26) Kesti, M. R.; Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1992**, *114*, 9679.
(27) Chung, T. C.; Rhubright, D.; Jiang, G. J. *Macromolecules* **1993**, *26*, 3467.
(28) Ramakrishnan, S.; Berluche, E.; Chung.T. C. *Macromolecules* **1990**, *23*, 378.
(29) Aaltonen, P.; Löfgren, B. *Macromolecules* **1995**, *28*, 5353.
(30) Mülhaupt, R.; Duschek, T.; Rieger, B. *Macromol. Symp.* **1991**, *48/49*, 317.
(31) Koivumäki, J. *Polym. Bull.* ***1996***, *36*, 7.
(32) Schneider, M. J.; Mülhaupt, R. *J. Mol. Catal. AQ*: *Chem.* **1995**, *101*, 11. (b) Sernetz, F. G.; Mülhaupt, R.; Waymouth, R. M. *Macromol. Chem. Phys.* **1996**, *197*, 1071.
(33) Fischer, D.; Mülhaupt, R. *J. Organomet. Chem.* **1991**, *417*, C7−C11.
(34) (a) Kolthammer, B. W. S.; Mangold, D. J.; Gifford, D. R. *J. Polym. Sci., Polym. Chem.*, **1992**, *30*, 1017. (b) Story. B. A.; Knight, G. W. Presented at MetCon'93, Houston, TX, 1993.
(35) Nyman, M. D.; Desu, S. B.; Peng, C. H. *Chem. Mater.* **1993**, *5*, 1636−1640.
(36) Calzaferri, G.; Herren, D.; Imhof, R. *Helv. Chim. Acta* **1991**, *74*, 1278−1280.
(37) Bolln, C. Unpublished results.
(38) Hendan, B. J.; Marsmann, H. C. *J. Organomet. Chem.* **1994**, 33−38.
(39) Bolln, C.; Tsuchida, A.; Frey, H.; Mülhaupt, R. *Chem. Mater.*, in press.

MA960846G